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HOMOGENEOUS METAL-CATALYSIS IN ORGANIC PHOTOCHEMISTRY†

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†Dedicated to Jay K. Kochi.

1. INTRODUCTION

Transition metal homogeneous catalysis of organic photochemistry is a rapidly growing new field.[1,2] Present interest in the subject grew out of at least four venerable areas: (1) the inorganic photochemistry of silver which remains the foundation of most photographic processes;[3] (2) biological solar energy conversion (photosynthesis) which is based on photoreactions involving light absorption by chlorophylls (macrocyclic complexes of magnesium), and catalytic roles for ferredoxin (an iron complex), plastocyanin (a copper containing protein), and cytochromes (macrocyclic complexes of iron);[4] (3) homogeneous transition metal catalysis of *thermal* organic transformations including reactions of major industrial importance, particularly in the areas of polymers and petrochemistry; and (4) organic photochemistry which provides a vast array of synthetically valuable transformations not readily achievable via ground state processes.

Economic pressures arising from limited supplies of natural resources have spurred a vigorous search for low-silver or silver-free photoimaging processes.[3,5] Light sensitive transition metal complexes are also under intensive scrutiny with regard to solar energy conversion and storage.[1d,6] The marriage of organic photochemistry and transition metals has spawned detailed investigation of the unique photochemistry of organometallic compounds.[7] The primary focus of the present review concerns the novel catalyzed chemistry of *organic* substrates which results from interactions with transition metals and light in homogeneous solution. Photoreactions promoted by heterogeneous catalysts and metal promoted photopolymerization are not included. The review is organized primarily in terms of the types of organic transformations involved and secondarily according to mechanistic characteristics or the identity of the transition metals involved.

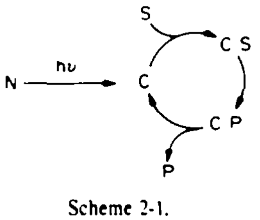
2. MECHANISMS OF CATALYSIS

Interactions of transition metal, organic substrate, and light leading to chemical modification of the substrate can be divided into two operationally unique categories. One category, for which we suggest the term *photogenerated catalysis*, is defined as light induced generation of a *ground state* catalyst C from a catalytically inactive precursor, the nominal catalyst N (eq 2.1). We prefer the term "photogenerated catalysis" rather than the less descriptive term *photocatalysis*[8] for such a process. Furthermore, the term photocatalysis is commonly used in a broader sense to denote any metal catalyzed photochemical process. The photogenerated catalyst (C) promotes transformation of substrate S into product P in a subsequent *thermal* process (eq 2-2).

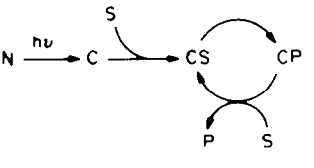
$$N \xrightarrow{h\nu} C \qquad (2\text{-}1)$$

$$S \xrightarrow{C} P \qquad (2\text{-}2)$$

Generally, catalysis in the ground state requires coordinative interaction between catalyst and substrate. The catalyst-substrate complex (C · S), often a transient intermediate and sometimes only a transition-state, transforms thermally into a catalyst-product complex (C · P). The product may then be released to regenerate C (scheme 2-1) or may be displaced by S to generate C · S directly (scheme 2-2). Since the catalyst generated by the action of a single photon might promote transformation of many substrate molecules into product, photogenerated catalysis may be catalytic in photons. The quantum yield of product, Φ or Φ_p (moles of P/moles of photons) may be greater than 1. Phenomenologically such reactions often exhibit an induction period (Fig. 2-1), during which the catalyst is being photogenerated, and catalysis may continue after termination of irradiation. An induction period and "post-photochemical"[1e] reaction are unique characteristics of photogenerated catalytic processes. However, while the post-photochemical reaction may continue at the same rate as observed during irradiation (Fig. 2-1: curve a), if the catalyst is consumed in a thermal side reaction, the post-photochemical rate will



Scheme 2-1.



Scheme 2-2.

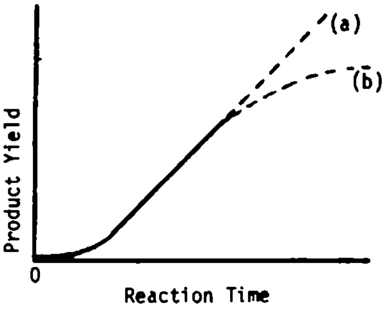


Fig. 2-1. Photogenerated catalysis during (——) and after (---) irradiation.

gradually fall (Fig. 2-1: curve b). The observation of an induction period, a post-photochemical reaction, or $\Phi_p > 1$ are presumptive evidence for the operation of a purely thermal catalytic cycle. It is important to recognize that photogenerated catalysis is not necessarily catalytic in photons. The quantum yield may also be less than or equal to one. Thus, for example, interactions of a thermally active catalyst C with a substrate S might regenerate the nominal catalyst N (eqn 2-3). Each cycle of catalysis may require photolytic regeneration of C.

$$N \xrightarrow{h\nu} C \tag{2-1}$$

$$C + S \longrightarrow P + N \tag{2-3}$$

We will refer to this subcategory as *stoichiometric photogenerated catalysis*. Such a process must be distinguished from *photosensitization* in which an *excited state* N^* of the nominal catalyst promotes transformation of the substrate S into product P with concomitant regeneration of ground state N (eqns 2-4 and 2-5).

$$N \xrightarrow{h\nu} N^* \tag{2-4}$$

$$N^* + S \longrightarrow P + N \tag{2-5}$$

Light induced generation of an initiator of a thermal chain reaction is related to photogenerated catalysis. Thus, the initiator I generated photochemically from the nominal initiator N (eqn 2-6) may promote transformation of many molecules of substrate in the subsequent thermal chain reaction such as a polymerization (eqns 2-7 and 2-8).

$$N \xrightarrow{h\nu} I \tag{2-6}$$

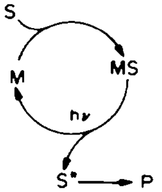
$$I + S \longrightarrow P_1 \tag{2-7}$$

$$P_n + S \longrightarrow P_{n+1} \tag{2-8}$$

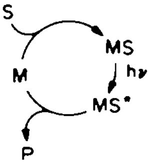
It is noteworthy that the role of a transition metal has not been specified in any of the examples of photogenerated catalysis presented above. One possibility is that a transition metal may be contained in the nominal catalyst N. However, other roles are also possible. For example, a photochemical reaction which generates a catalyst from an *organic* catalyst precursor may *itself* require a transition metal catalyst M (eqn 2-9).

$$N \xrightarrow{h\nu/M} C \tag{2-9}$$

While eqn 2-9 may represent a step in a photogenerated catalytic process, it also is an example of the second category of homogeneous transition metal catalysis of organic photoreactions. We will adopt the term *catalyzed photolysis* for processes in which a transition metal catalyst M promotes photoexcitation of a substrate S, transformation of an excited state S* of the substrate, or transformation of a photogenerated ground state intermediate I.[9] For example, photoexcitation of S may require coordination with M and lead via S* (scheme 2-3) or MS* (scheme 2-4) to product (eqns 2-10 to 2-13).



Scheme 2-3.



Scheme 2-4.

$$M + S \rightleftarrows MS \tag{2-10}$$

$$MS \xrightarrow{h\nu} MS^* \text{ or } S^* + M \tag{2-11}$$

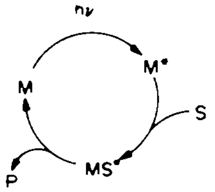
$$MS^* \longrightarrow P \tag{2-12}$$

$$S^* \longrightarrow P \tag{2-13}$$

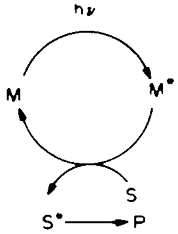
Alternatively, MS* (scheme 2-5; exciplex formation) or S* (scheme 2-6; energy transfer) may be generated in a reaction between photoexcited catalyst M* and ground state substrate (eqns 2-14 and 2-15) with subsequent generation of product P (eqn 2-12 or 2-13). The process of scheme 2-6 belongs to the subcategory known as sensitized photoreactions.

$$M \xrightarrow{h\nu} M^* \tag{2-14}$$

$$M^* + S \rightarrow MS^* \text{ or } S^* + M \tag{2-15}$$



Scheme 2-5.



Scheme 2-6.

Catalysis by M may also occur subsequent to photoexcitation of S (eqn 2-16) either directly (scheme 2-7 and eqn 2-17) or via an intermediate I (scheme 2-8 and eqns 2-18–2-20). For example, the product (P_t) obtained thermally without the involvement of the metal catalyst (M) may differ from that (P_c) obtained under the influence of M. The processes of schemes 2-5 and 2-7 depend on reactions of exciplexes, excited state complexes formed only between an excited state of one molecule and the ground state of another.

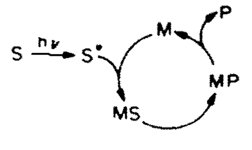
$$S \xrightarrow{h\nu} S^* \tag{2-16}$$

$$S^* \xrightarrow{M} P \tag{2-17}$$

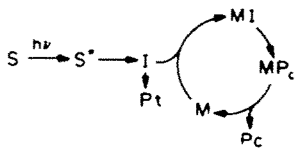
$$S^* \longrightarrow I \tag{2-18}$$

$$I \longrightarrow P_t \qquad (2\text{-}19)$$

$$I \xrightarrow{M} P_c \qquad (2\text{-}20)$$



Scheme 2-7



Scheme 2-8.

Since the photochemical step does not generate the catalyst and may even be an essential component of the catalytic cycle, the catalyzed photolysis (schemes 2-3–2-8) stops immediately when irradiation ceases (Fig. 2-2). While it is catalytic with respect to the metal, the catalyzed photolysis is *not catalytic* in photons and the quantum yield never exceeds unity.

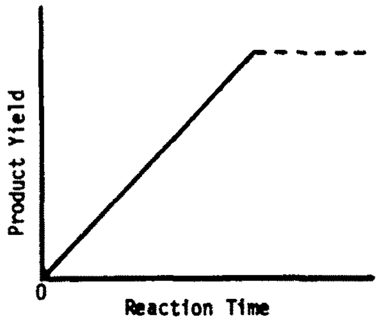


Fig. 2-2. Catalyzed photolysis during (——) and after (- - - -) irradiation.

Another concept, *photoassistance*, was proposed which is defined as "a situation where the reaction requires binding the substrate to the metal and the reaction is not catalytic in photons."[8] Catalyzed photolyses might be photoassisted reactions but not, for example, if a transition metal complex acts as a sensitizer without binding of the substrate to the metal.

In summary it is also noteworthy that there are three possible categories of light absorbing species in photoreactions of organic substrates in the presence of a metal catalyst. These are M, S, or MS. Photogenerated catalysis involves only ground states of the catalyst and substrate in the catalytic step which is thermally spontaneous (exoergic). In a catalyzed photolysis, on the other hand, either the catalyst, substrate, or both are in an excited state during the catalytic step. The overall process may result in a contrathermodynamic (endoergic) chemical change or "chemical photosynthesis."[10] The catalytic system absorbs light and converts it into chemical energy. Such a process may be of value for storage of solar light energy since "the reaction driven could be the photoproduction of a fuel or other high energy chemical."[10] Furthermore, some homogeneous transition metal catalyzed reactions may involve simultaneous photogenerated catalysis and catalyzed photolysis. Such a process may allow storage of both solar heat and light energy.

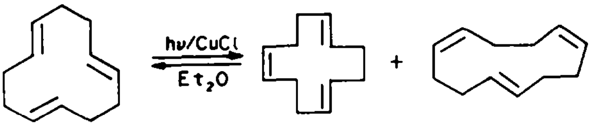
3. GEOMETRIC ISOMERIZATION OF ALKENES

(a) *Copper salts*

Many transition metal catalysts are known to promote cis-trans photoisomerization of isolated carbon–carbon double bonds (eqn 3-1). Especially interesting transformations were achieved with copper(I)

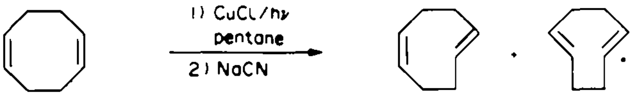
(3-1)

salts owing to their ability to form thermally stable adducts of thermodynamically disfavored trans isomers of certain cyclic alkenes. Cis-trans photoisomerization of isolated alkenes catalyzed by cuprous chloride was first described for 1,5,9-cyclododecatrienes.[11] Cuprous bromide and cupric chloride are also effective catalysts.[12]



Ref 12

Irradiation of cis,cis-1,5-cyclooctadiene in the presence of one equivalent of copper(I) chloride in pentane suspension generates insoluble copper(I) complexes of cis,trans- and trans,trans-1,5-cyclooctadienes besides other products from the diene (section 5b).[13] The thermally sensitive trans-isomers are released from the copper complexes upon reaction with sodium cyanide. A practical synthesis of trans-cyclooctene from the cis isomer exploits copper catalyzed photoisomerization.[14]



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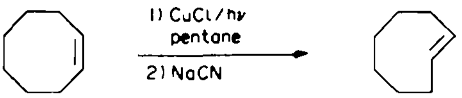
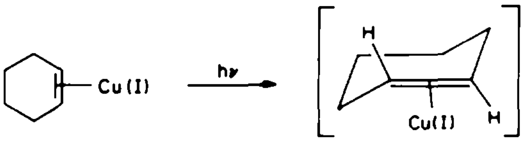
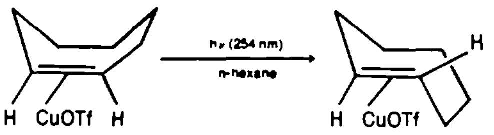


Ref 14

We suggested the possible involvement of trans-cyclohexene in copper(I) catalyzed photocycloadditions of cis-cyclohexene.[15] Although there is no direct evidence to support this hypothesis, it provides a plausible explanation for many novel photoreactions of cyclohexene which are catalyzed by copper(I) (sections 5c and 5d). On the other hand, a thermally stable copper(I) trifluoromethanesulfonate (triflate) complex 2 of trans-cycloheptene was prepared recently by irradiation of a hexane solution of η^2-cis-cycloheptene copper(I) triflate complex 1.[16] The UV spectrum of 2 is bathochromically shifted with respect to that of 1. The difference in the C=C stretching vibration frequencies in the Raman spectra of 1 and 2 indicate a relatively weaker double bond in 2. The ^{1}H NMR spectrum of 2 (Fig. 3-1) clearly shows two distinct resonances for the nonequivalent geminal hydrogens of the allylic methylene groups of 2. Displacement of the alkene ligand from 2, even at − 20°, does not afford trans-cycloheptene. Rather trans-cis isomerization of the free trans-cycloheptene occurs and only cis-cycloheptene is isolated.[16]



Ref 15



1 2

Ref 16

^{1}H NMR δ(=CH—)	5.51 ppm	4.55 ppm
Raman ν(C=C)	1545 cm^{-1}	1514 cm^{-1}
UV λ(max)	230 nm (log ε = 3.7) 260 nm (log ε = 3.3)	236 nm (log ε = 3.9) 288 nm (log ε = 3.2)

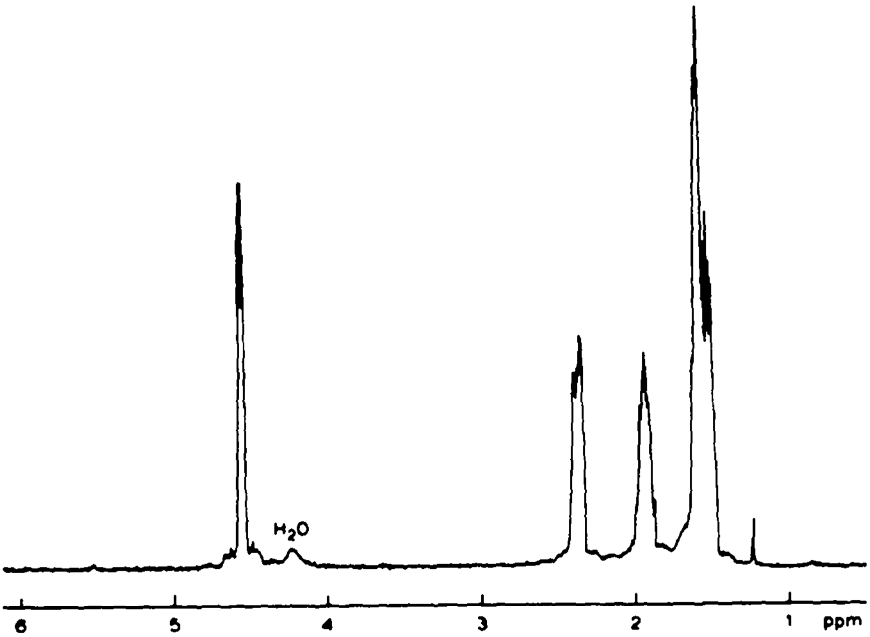
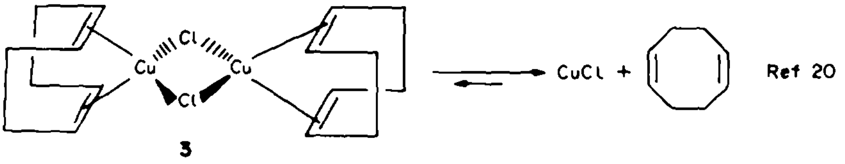


Fig. 3-1. ^{1}H NMR spectrum of 2 (in $CDCl_3$, 300 MHz).[16]

Copper(I) triflate catalyzed photoreactions of alkenes involve light absorption by preformed alkene-copper(I) complexes which exchange rapidly with free alkene.[17] Since CuOTf-alkene complexes generally show two strong UV absorption bands, one at 230–241 nm (ϵ_{max} 2500–3900) and one at 260–288 nm (ϵ_{max} 1500–3300),[16,17] while the free nonconjugated alkenes are nearly transparent in this region, UV light is absorbed by the complexed alkene. Direct absorption of light by free 1,5-cyclooctadiene, considered a possible alternative mode of photoexcitation,[13] was recently shown not to be operative in CuCl-catalyzed photorearrangements of this alkene.[18] Thus, CuCl forms a well characterized bridged dimeric complex 3 with 1,5-cyclooctadiene.[19] Although the complex dissociates readily,[20] nevertheless, sufficient alkene remains coordinated as a CuCl complex which is sufficiently soluble in pentane to absorb the vast majority of incident light.[18]



3

(b) *Metal carbonyls*

Carbonyl complexes of molybdenum, tungsten, rhenium, iron, ruthenium, and osmium catalyze cis-trans isomerization of olefins. Some of these catalysts also promote allylic 1,3-hydrogen migration in alkenes which possess allylic hydrogen. For such alkenes allyl-metal hydrides may be intermediates common to both types of isomerization and these will be considered in a subsequent section. One generalization seems valid for most $M_n(CO)_m$ catalyzed photoreactions of alkenes. Thus, the initial photochemical event is generation of a coordinatively unsaturated metal complex which interacts with alkene to form a metal-alkene complex. For example, photodissociation of carbon monoxide is known to lead to photosubstitution by alkene (eqns 3-2–3-4).[21] Often the resulting metal-alkene complex is the actual catalyst of alkene isomerization which might occur thermally or may require further photoactivation. Formation of (stilbene)$W(CO)_5$ upon photolysis of $W(CO)_6$ in the presence of stilbene is indicated by spectral changes during the photolysis (Fig. 3-2). Trans→cis isomerization is presumed to involve (stilbene)$W(CO)_5$ as the actual catalyst (vide infra). Similarly, 366 nm irradiation of trans-1,2-dideuterioethylene in the presence of $W(CO)_6$ initially generates (ethylene)$W(CO)_5$ as revealed by IR spectral changes.[23]

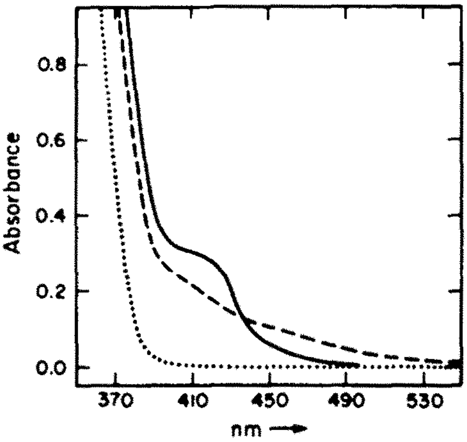


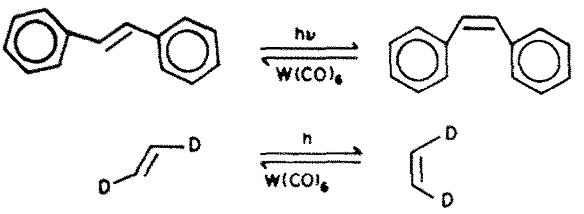
Fig. 3-2. Initial UV-VIS spectral changes upon 366 nm irradiation of $W(CO)_6$ (....) in the presence of cis-stilbene (----) and trans-stilbene (——).[23]

$$M(CO)_n \xrightarrow{h\nu} M(CO)_n^* \tag{3-2}$$

$$M(CO)_n^* \longrightarrow M(CO)_{n-1} + CO \tag{3-3}$$

$$M(CO)_{n-1} + \text{alkene} \longrightarrow (\text{alkene})\ M(CO)_{n-1} \tag{3-4}$$

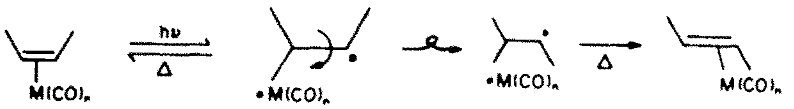
For alkenes which do not possess allylic hydrogens, cis-trans isomerization via allyl metal hydrides is precluded. Nevertheless, metal carbonyl catalyzed cis-trans isomerizations are known for such alkenes. Both $W(CO)_6$ and $Mo(CO)_6$ catalyze cis-trans isomerization of stilbene[22] and 1,2-dideuterioethylene.[23] A



Ref 22

Ref 23

mechanism proposed for such reactions involves a photoinduced $\eta^2 \rightarrow \eta^1$ rearrangement of a metal–alkene complex which generates an intermediate diradical with a metal–carbon σ bond and free rotation about the former alkenic bond (eqn 3-5). It was suggested that formation of the diradical intermediate



(3-5)

may be viewed as a reaction of an electronically excited C_{4v} $M(CO)_5$ with an alkene.[23] This excited state should have some reactivity properties in common with ground-state $Co(CN)_5^{3-}$ for which radical-like reactions such as addition to alkenes are known.[24] Alkene isomerization by reversible addition of free radicals is well known.[25]

For the highly conjugated alkene, stilbene, a possible alternative mechanism for isomerization involves generation of a ligand-localized (intraligand, stilbene-like) excited state by internal conversion from an initially populated metal-centered excited state (ligand field or metal-to-ligand charge transfer) presumably to the stilbene triplet state which lies below the energetic position of the first absorption in the complexes (Fig. 3-3).[26] The intermediacy of a stilbene-like electronic excited state in this isomerization is revealed by the production of cis-stilbene from trans-stilbene (Fig. 3-4) which constitutes

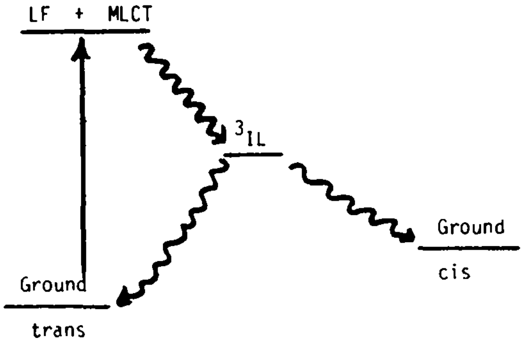


Fig. 3-3. State diagram for [W(CO)$_5$(stilbene)].[26]

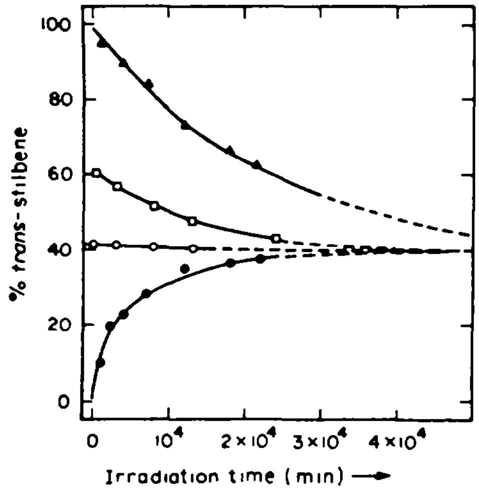
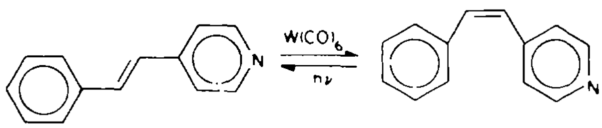


Fig. 3-4. W(CO)$_6$ photoassisted stilbene interconversion with different initial trans/cis stilbene ratios. Total stilbene concentration is ≈ 0.05M, irradiation is at 366 nm, temperature is 25° and W(CO)$_6$ concentration is $\approx 10^{-3}$M.[21]

movement away from the thermodynamic ratio of the two isomers. A similar mechanistic alternative is *not* available for isolated (nonconjugated) alkenes since the lowest intraligand excited state is well above the lowest electronic excited state of the complex.[23]

Irradiation of trans-2-styrylpyridine or trans-4-styrylpyridine at 436 nm in the presence of W(CO)$_6$ as catalyst results in trans-cis isomerization. These reactions occur by a multiphoton catalyzed photolysis



Ref 2

involving reactions (3-6–3-9).[2] The intermediate styrylpyridine (stpy) complexes were isolated and shown

$$\mathrm{W(CO)_6} \xrightarrow{h\nu} \mathrm{W(CO)_5} + \mathrm{CO} \tag{3-6}$$

$$\mathrm{W(CO)_5} + \text{(trans-alkene)} \longrightarrow \text{(trans-alkene)}\mathrm{W(CO)_5} \tag{3-7}$$

$$\text{(trans-alkene)}\mathrm{W(CO)_5} \xrightarrow{h\nu} \text{(cis-alkene)}\mathrm{W(CO)_5} \tag{3-8}$$

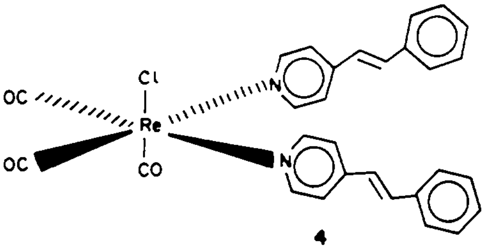
$$\text{(cis-alkene)}\mathrm{W(CO)_5} \xrightarrow{h\nu} \mathrm{W(CO)_5} + \text{cis-alkene} \tag{3-9}$$

to involve tungsten-pyridine N-coordination.[27] Photodissociation of the pyridine ligand (eqn 3-9) is rate determining.[2] Also, the tungsten-monoalkene complex (4-stpy) $W(CO)_5$ reacts according to (3-10) and (3-11) to give a bis-alkene complex $(4\text{-stpy})_2W(CO)_4$ which is photoinert at 436 nm. Photoisomerization of the stpy ligands in the bisalkene complex does occur at 313 nm.[28]

$$(\text{stpy})W(CO)_5 \xrightarrow{h\nu} (\text{stpy})W(CO)_4 + CO \tag{3-10}$$

$$(\text{stpy})W(CO)_4 + \text{stpy} \longrightarrow (\text{stpy})_2W(CO)_4 \tag{3-11}$$

In contrast, $ReCl(CO)_5$ reacts *thermally* with trans-4-styrylpyridine (t-4-stpy) to produce a bisalkene complex **4**.[29] The t-4-stpy ligands in **4** undergo trans→cis isomerization upon UV irradiation (eqns 3-12 and 3-13), but photosubstitution of the stpy ligands in these complexes is very inefficient.



4

$$ClRe(CO)_3(\text{t-stpy})_2 \xrightarrow{h\nu} ClRe(CO)_3(\text{c-stpy})(\text{t-stpy}) \tag{3-12}$$

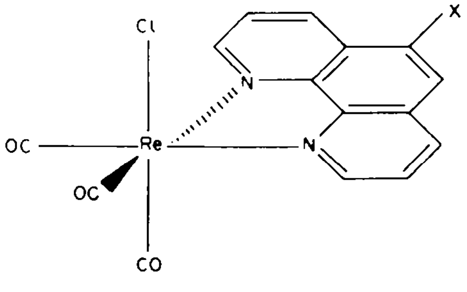
$$ClRe(CO)_3(\text{c-stpy})(\text{t-stpy}) \xrightarrow{h\nu} ClRe(CO)_3(\text{c-stpy})_2 \tag{3-13}$$

$$ClRe(CO)_3(\text{c-stpy})(\text{t-stpy}) + \text{t-stpy} \overset{\Delta}{\rightleftharpoons} ClRe(CO)_3(\text{t-stpy})_2 + \text{c-stpy} \tag{3-14}$$

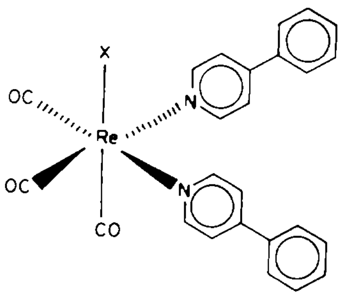
$$ClRe(CO)_3(\text{c-stpy})_2 + \text{t-stpy} \overset{\Delta}{\rightleftharpoons} ClRe(CO)_3(\text{c-stpy})(\text{t-stpy}) + \text{c-stpy} \tag{3-15}$$

At 25° thermal substitution reactivity of these complexes is insignificant. However, a catalyzed photolytic trans to cis isomerization according to (3-12)–(3-15) can be achieved at 56° where the thermal substitution lability of the stpy is markedly increased.[29] Interestingly, the trans-cis photoisomerization which occurs upon irradiation of **4** does not involve direct coordination of the C=C bond with rhenium.

Not all metal carbonyl promoted photoreactions of alkenes involve initial photodissociation of a carbonyl ligand. Intermolecular analogues of photoisomerizations of **4** are known. Thus, trans-stilbene quenches the luminescence of rhenium carbonyl complexes such as **5**[30] and **6**.[31] The resulting triplet excitation of trans-stilbene leads to trans→cis isomerization with $\phi = 0.52–0.65$.[30,31] With **5** as sensitizer



5



6

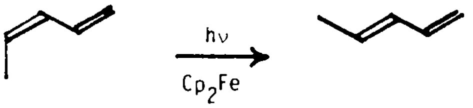
the photostationary state (PSS) is composed of almost pure cis-stilbene, whereas with **6** the PSS is 2 : 1 cis to trans (Table 3-1).[7d] These results demonstrate an important feature of transition metal complex sensitizers: the possibility of the fine tuning the excited state energy so that it is higher than the triplet state of the trans isomer (50 Kcal/mole for stilbene) but lower than the triplet state of the cis isomer (~ 57 Kcal/mol for stilbene). The complexes **5** only photoexcite trans-stilbene whereas the complexes **6** also excite the cis isomer and thus also sensitize the cis→trans isomerization, yielding a less cis-rich photostationary state (PSS).[7d]

Table 3-1[7d]. Sensitized trans→cis-stilbene isomerization

Sensitizer	$\Phi_{t\to c}$	PSS (% cis)
5, $X=CH_3$	0.62	>97
5, x=Cl	0.65	>97
5, x=Br	0.52	>97
6, x=Cl	0.58	66
6, x=Br	0.60	66
6, x=I	0.62	66
Benzophenone	0.60	60

(c) *Ferrocene*

Ferrocene sensitizes cis→trans isomerization of cis-piperylene. Observations interpreted as evidence for a ground state coordination of the diene with the iron complex[32] were not confirmed in later studies.[33]



Ref 32

A marked effect of solvent on the ratio of initial rates was demonstrated for cis→trans and trans→cis isomerization 0.4 in trans-1,2-dimethylcyclohexane and 0.8 in benzene solution.[33] In dimethylcyclohexane solution, ferrocene is considered to act as a low energy triplet sensitizer as pictured in Fig. 3-5, while in benzene solution it acts as a high-energy triplet sensitizer.[32,33]

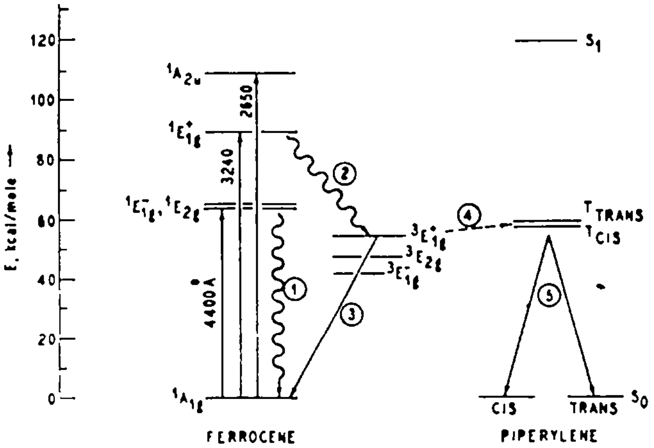
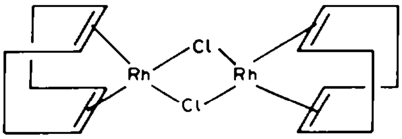


Fig. 3-5. Mechanistic scheme for energy transfer from excited ferrocene to piperlyene: (1) relaxation of ferrocene singlet state, (2) ferrocene intersystem crossing, (3) possible ferrocene phosphorescence, (4) triplet-triplet energy transfer, (5) relaxation of piperlyene triplet state to cis- and trans-piperylenes.[33]

4. ALLYLIC [1.3] HYDROGEN SHIFT

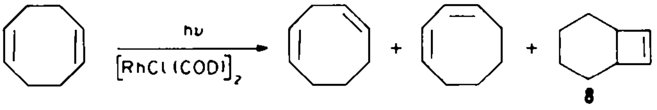
(a) *Rhodium(I) chloride*

Rhodium(I) chloride and 1,5-cyclooctadiene (COD) form a bridged dimeric complex $[RhCl(COD)]_2$ with structure **7**.[34] This complex catalyzes isomerization of 1,5-COD to 1,4-COD, 1,3-COD and bicy-



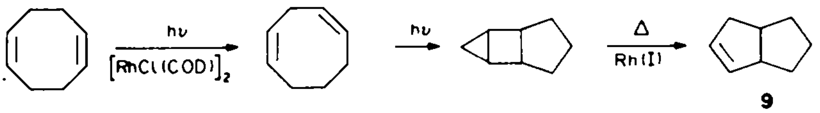
7

clo[4.2.0]oct-7-ene 8 upon irradiation with a medium pressure mercury are (~254 nm).[35] Formation of 8 probably involves direct photolysis of 1,3-cyclooctadiene. Further investigation of these rhodium



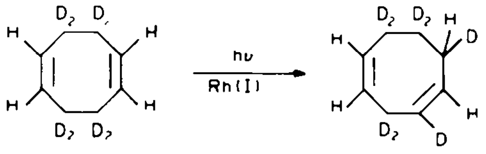
Ref 35

catalyzed photorearrangements uncovered the additional formation of cyclooctene and bicyclo[3.3.0]oct-2-ene 9.[36] Formation of 9 probably involves the intermediacy of 1,4-COD and tricyclo[5.1.0.$0^{2,6}$]octane since direct photolysis of 1,4-COD affords the tricyclooctane[37] and the latter rearranges to 9 in the dark under catalysis by $[RhCl(COD)]_2$.[36] The exclusive primary photoproduct in the rhodium(I) catalyzed



Ref 36

rearrangement of 1,5-COD is 1,4-COD which is formed by an irreversible intramolecular [1.3] hydrogen shift. Thus, 10 affords 11 exclusively; recovered 10 shows no scrambling of the deuterium label, and rearrangement of a 1:1 mixture of 1,5-COD and 10 shows no crossover, e.g. to produce 1,4-COD-d_1.[36]

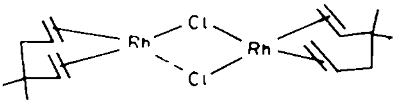


10 11

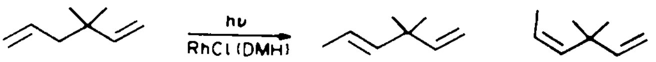
Ref 36

The other major photoproducts from rhodium(I) catalyzed photorearrangement of 1,5-COD arise from further rearrangement of 1,4-COD. Formation of 1,3-COD undoubtedly involves rhodium(I) assisted allylic [1.3] hydrogen shift and not a direct rearrangement of 1,5-COD via the multiple σ-bond reorganization postulated earlier.[35]

Rhodium(I) chloride and 3,3-dimethyl-1,5-hexadiene (DMH) form a 1:1 complex[36] which probably has a bridged dimeric structure 12 analogous to the 1,5-COD complex 7. This complex catalyzes photorearrangement of 3,3-dimethyl-1,5-hexadiene into 18% cis-3,3-dimethyl-1,4-hexadiene and 82% of trans-3,3-dimethyl-1,5-hexadiene but 12 does not catalyze cis→trans interconversion of these products.[36] If it is assumed that direct

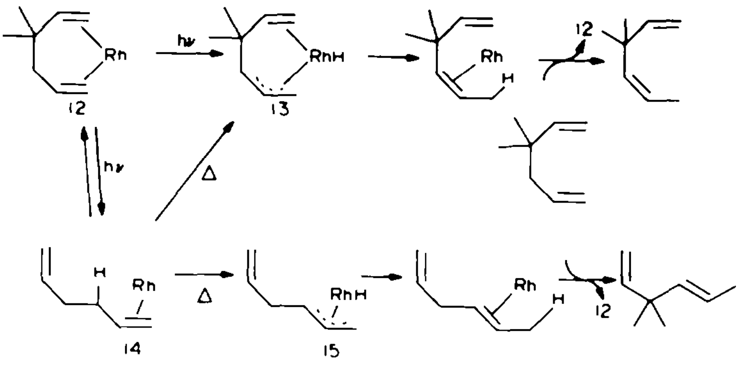


12

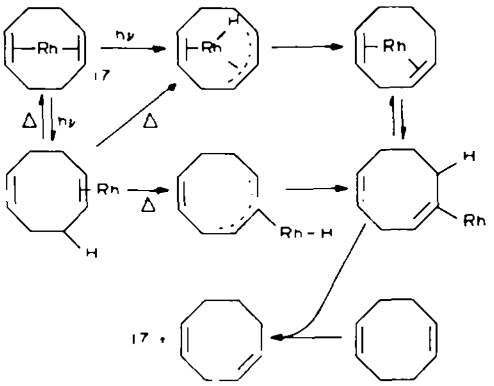


Ref 36

insertion of rhodium(I) into an allylic C–H bond can only produce a cisoid allylrhodium hydride intermediate 13, then reductive elimination is expected to produce cis-3,3-dimethyl-1,4-hexadiene exclusively. Since, on the contrary, the trans isomer not only is formed but is even the major product, direct photoinduced oxidative addition of an allylic C–H bond cannot account for the catalyzed photorearrangement. An attractive alternative mechanism (scheme 4-1) involves photodissociation of one of the alkene ligands to produce a monoalkene-rhodium(I) complex **14**. The resulting increase in the coordinative unsaturation of rhodium(I) enhances the proclivity of this d^8 metal atom toward oxidative addition in a subsequent reaction to produce either cisoid **13** or transoid **15** allylrhodium(III) hydride intermediates. These lead to cis- or trans-3,3-dimethyl-1,4-hexadiene respectively. A similar process (Scheme 4-2) accounts for rhodium(I) catalyzed photorearrangement of 1,5-COD to 1,4-COD. A kinetic deuterium isotope effect $K_H/K_D = 1.55 \pm 0.03$ observed for rearrangement of **10** suggests that oxidative addition of an allylic C–H bond occurs in a rate determining competition with reformation of the diene-rhodium complex **17**. Apparently the coordinatively unsaturated monoalkene intermediates do not readily generate new coordinatively unsaturated complexes by ligand exchange with free alkene since catalysis only occurs *during* irradiation. Thus, rhodium(I) promotes allylic[1.3]hydrogen shift by *stoichiometric photogenerated catalysis.*



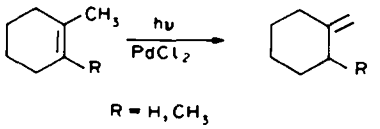
Scheme 4-1.



Scheme 4-2.

(b) *Palladium chloride*

Contrathermodynamic[38] allylic [1.3] hydrogen shifts occur with 1-methyl or 1,2-dimethylcyclohexene in the presence of palladium(II) chloride upon irradiation with Vycor filtered UV light from a medium pressure mercury vapor lamp.[39] Similar photorearrangements occur with 1-methylcyclohexenes upon irradiation in aromatic hydrocarbon solutions,[40] or in ether solution with toluene as a triplet sensitizer.[39]



Ref 39

The UV spectrum of cyclohexene exhibits weak end absorption in the region 210–250 nm associated with a $S_0 \rightarrow T_1$ transition.[41] In the presence of palladium(II) chloride, the UV spectra of 1-methylcyclohexene and 1,2-dimethylcyclohexene (Fig. 4-1) show intensified absorption in this region.[39] This intensification may arise from the large spin-orbit coupling factor of the palladium atom which is presumed to be associated with the alkene. It is assumed, therefore, that the reactive species may be a π,π^* triplet alkene in the alkene-palladium(II) chloride system.[39]

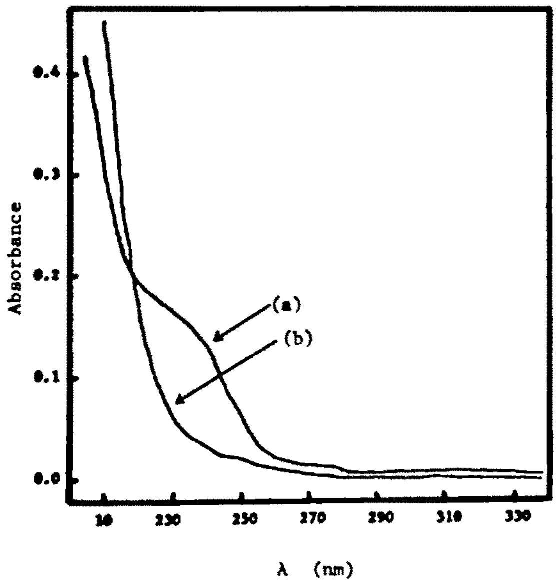
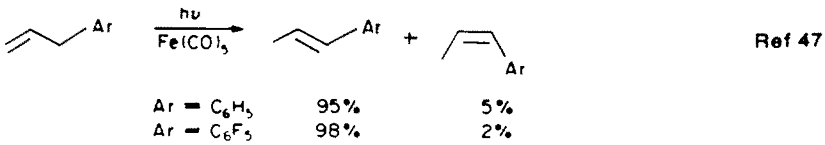


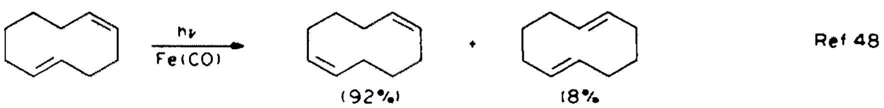
Fig. 4-1. The UV spectra of (a) 1,2-dimethylcyclohexene-PdCl$_2$ in diethyl ether and (b) 1,2-dimethylcyclohexene in diethyl ether.[39]

(c) *Metal carbonyls*

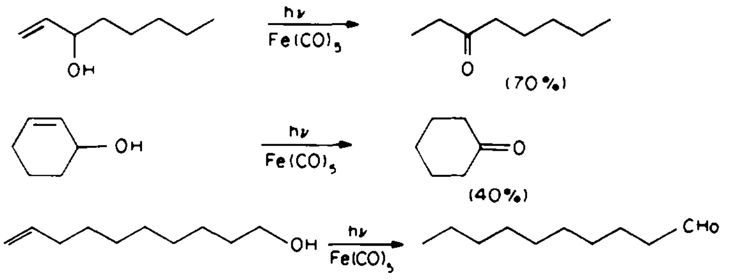
Carbonyl complexes of molybdenum, tungsten, iron, ruthenium, osmium, and cobalt catalyze allylic [1.3] hydrogen migration in alkenes. With UV irradiation Fe(CO)$_5$, Fe(CO)$_9$, or Fe$_3$(CO)$_{12}$ catalyze multiple hydrogen shifts in 1-undecene,[42–44] 1-octene,[43,45] 1-pentene,[46] or 4-octene[45] to eventually produce complex *thermodynamic equilibrium* isomeric mixtures in near quantitative yields. Similar rearrangements of allylbenzenes afford mainly E-propenylarenes.[47]



A poignant example of the synthetic utility of such mild photoinduced isomerizations is provided by reactions of cis,trans-cyclodecadiene. This diene readily rearranges thermally to cis-1,2-divinylcyclohexene. Therefore, an allylic hydrogen shift cannot be achieved *thermally* in the presence of Fe(CO)$_5$. However, UV irradiation of the diene at 60° in the presence of Fe(CO)$_5$ generates isomeric 1,6-dienes cleanly.[48]



The synthetic utility of thermally mild photoinduced isomerizations is further exemplified in the reactions of unsaturated alcohols. Irradiation of unsaturated alsohols in the presence of Fe(CO)$_5$ generates saturated aldehydes or ketones.[49] Yields of aldehydes or cyclic ketones are substantially lower under conditions of thermal (124°) catalyst activation owing to product instability. Thus, heating



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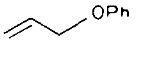
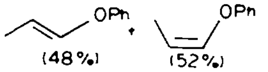
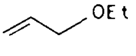
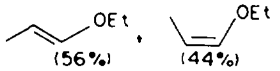
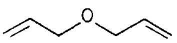
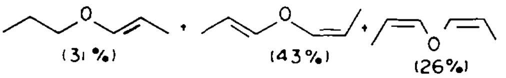
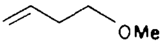
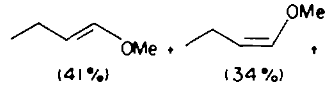
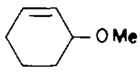
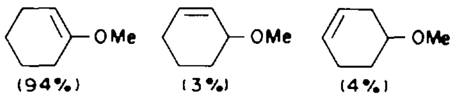
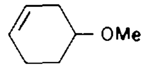
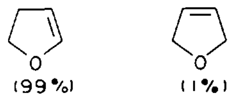
cis-3-hexen-1-ol with Fe(CO)$_5$ affords only 8% yield of hexanal together with a 29% yield of aldol condensation dimer.

Similar photoinduced rearrangements of unsaturated ethers in the presence of Fe(CO)$_5$ afford mainly vinyl ethers (Table 4-1) at room temperature under neutral conditions.[47,50,51]

Table 4-1. Photoinduced Fe(CO)$_5$ catalyzed isomerization of unsaturated ethers

Starting ether	Products (yield)[a]	Ref
		47
		47
		47
	 + MeCH=CHCH OMe (25%)	47
MeO(CH$_2$)$_3$CH=CH$_2$	MeOCH=CH(CH$_2$)$_2$CH$_3$ + MeOCH$_2$CH=CHEt + MeO(CH$_2$)$_2$CH=CHCH$_3$ (85%) (5%) (9%)	50
		50
	(95%) (2%) (3%)	50
		51

[a]Relative yields are indicated; absolute yields are nearly quantitative.

Evidence of suggesting the formation of an iron-alkene π-complex intermediate was obtained by periodic ^{1}H nmr monitoring of the reaction mixture during photoinduced isomerization of allyl phenyl ether.[51] The NMR spectrum of an irradiated solution of allyl phenyl ether containing pentacarbonyliron shows additional signals at δ 4.0 (allylic CH$_2$), 3.4 (alkenic CH), and 2.4 (vinylic CH$_2$) ppm, whose intensity is a function of the concentration of the catalyst. The corresponding signals from allyl phenyl ether are at δ 4.3, 6.0 and 5.2 ppm. Thus the alkelenic protons have undergone a large chemical shift, suggesting that they have become co-ordinated to the metal. NMR monitoring of the reaction mixture reveals that the π-complex generated initially disappears when all the starting material has been consumed (see Fig. 4-2).

Isomerization of N-allylamides to the corresponding N-prop-2-enyl amides occurs cleanly and in high yields upon UV irradiation in methanol solution in the presence of 5 mol% Fe(CO)$_5$ (Table 4-2).[52] Under the same conditions, N-allylsulfonamides afford N-propylidenesulfonamides, whereas isomerization stops at the initially formed N-prop-2-enylsulfonamide if the reaction is conducted in benzene solution (Table 4-2).[53]

Triruthenium dodecacarbonyl is nearly as effective as Fe$_3$(CO)$_{12}$ while Os$_3$(CO)$_{12}$ is virtually inactive

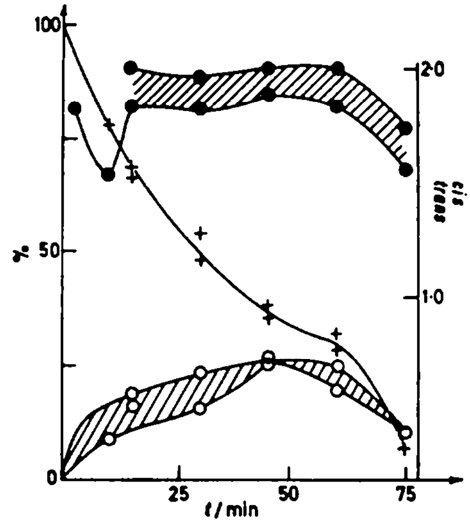
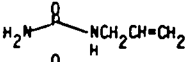
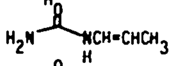
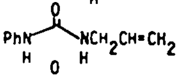
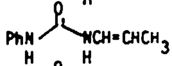
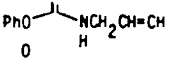
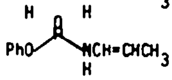


Fig. 4-2. Photochemical isomerization with pentacarbonyliron: ●, phenyl cis and trans-propenyl ether; O, π-complex; +, allyl phenyl ether.[51]

Table 4-2. Photoinduced $Fe(CO)_5$ catalyzed isomerization of N-allylamides and N-allylsulfonamides

Starting amide	Reaction Solvent	Products[a]	Ref
$AcNHCH_2CH{=}CH_2$	MeOH	$AcNHCH{=}CHCH_3$	52
$CF_3C(O)NHCH_2CH{=}CH_2$	MeOH	$CF_3C(O)NHCH{=}CHCH_3$	52
	MeOH		52
	MeOH		52
	MeOH		52
$PhS(O)_2NHCH_2CH{=}CH_2$	PhH	$PhS(O)_2NHCH{=}CHCH_3$	53
$MeS(O)_2NHCH_2CH{=}CH_2$	MeOH	$MeS(O)_2N{=}CH{-}CH_2CH_3$	53
$PhS(O)_2N(CH_3)CH_2CH{=}CH_2$	PhH	$PhS(O)_2N(CH_3)CH{=}CH_2CH_3$	53

[a]Mixtures of cis and trans isomers.

for pentene isomerization with 355 nm light.[46] With intense (700 Watt) mercury vapor lamp irradiation, $Os_2(CO)_9$ and $Co_2(CO)_8$ show slight activity for catalyzing isomerization of 1-undecene.[44] In all cases, similar catalyzed allylic [1.3] hydrogen shifts are promoted thermally by the above mentioned metal carbonyls albeit at often much higher temperatures.[42,50,54]

Definitive evidence for the operation of photogenerated catalysis in isomerizations involving $Fe(CO)_5$, $Fe_3(CO)_{12}$, or $Ru_3(CO)_{12}$ as nominal catalysts is provided by measurements of quantum yields, defined here to be the number of alkene molecules reacted per photon incident on the sample. Quantum yields vary with reaction conditions such as wavelength of the light employed. The influence of alkene concentration on Φ for isomerization with $Fe(CO)_5$ as catalyst precursor is presented in Table 4-3. For isomerization of 1-pentene, observed quantum yields are Φ-1.1–429 with $Fe(CO)_5$, $\Phi = 26$–41 with $Fe_3(CO)_{12}$, and $\Phi = 5$–34 with $Ru_3(CO)_{12}$ as catalyst precursor.[46,55]

Multiple hydrogen shifts must be induced upon interaction of a single molecule of 1-octene with the active catalyst generated by irradiation of $Fe_3(CO)_{12}$ with filtered (> 440 nm) tungsten light since the

Table 4-3. Observed quantum yields for $Fe(CO)_5$ photocatalyzed 1-pentene isomerization[55d]

(1-Pentene),M	$\Phi \pm 10\%$[a]
0.04	1.1
0.1	1.5
0.5	14.5
2.0	67.8
5.0	215
9.14(neat)	429

[a] Quantum yield for formation at 20° of *cis* + *trans*-2-pentene using 366 nm light at ~1.4 x 10^{-7} einstein/min in benzene with $Fe(CO)_5$ at 0.011 M. The quantum yield reported here is limiting quantum yield after induction period (*vide infra*).

composition of the initial product mixture closely resembles that expected at thermodynamic equilibrium.[45] Thus, intramolecular hydrogen shift can be more rapid than intermolecular transfer of the active catalyst. On the other hand, with $Fe(CO)_5$ as catalyst precursor, isomerizations of 1-octene or 1-undecene initially generate somewhat greater quantities of 2- and 3-isomers than found at thermodynamic equilibrium.[44]

That photodissociation of a carbonyl ligand (e.g. eqn 4-1) is involved in photogeneration of the active catalyst is indicated by the influence of added CO. The catalytic efficiencies of $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, and $Os_2(CO)_9$ are all strongly decreased under an atmosphere of CO compared to an argon atmosphere.[44] Also, with $Fe(CO)_5$ as catalyst precursor for rearrangements of 1-undecene[43] or cis-5-undecene,[44] there exists an optimum concentration of $Fe(CO)_5$ above or below which catalytic efficiency decreases (Table 4-4). These effects were explained in terms of the trapping of an $Fe(CO)_4$ intermediate by CO (eqn 4-2) or $Fe(CO)_5$ (eqn 4-3) which prevents formation of a catalytically important $Fe(CO)_4$-alkene complex intermediate (eqn 4-4).[44] Rapid thermal rearrangement of these $Fe(CO)_4$-alkene complexes (eqn 4-5) and alkene ligand exchange (eqn 4-6) was originally suggested to account for alkene isomerization.[44] Alternative mechanisms involving addition elimination reactions of an iron hydride (e.g.

Table 4-4. Dependence of catalytic efficiency for undecene photoisomerization on $[Fe(CO)_5]$[43,44]

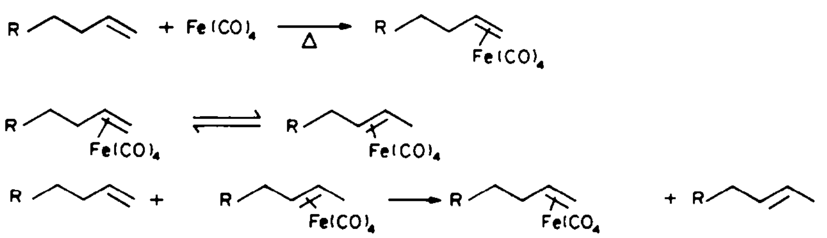
Mol % $Fe(CO)_5$[a]	Mol % 1-undecene after 0.5 hr	Mol % 5-undecene after 1.0 hr
initial	97.5	> 98.5
55	87.0	94.5
50	83.5	92.6
25	68.6	87.6
10	9.4	66.2
5.0	-	88.5
1.0	15.8	92.9
0.1	18.2	-

[a] In neat olefin as solvent.

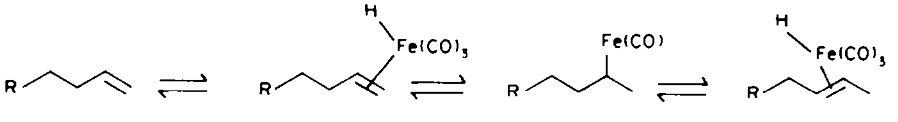
$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4 + CO \tag{4-1}$$

$$CO + Fe(CO)_4 \xrightarrow[\Delta]{} Fe(CO)_5 \tag{4-2}$$

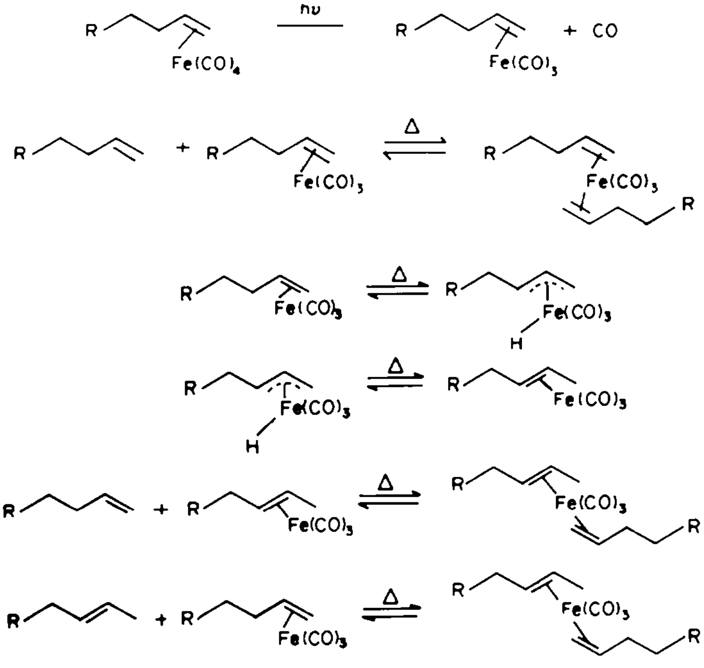
$$Fe(CO)_5 + Fe(CO)_4 \xrightarrow[\Delta]{} Fe_2(CO)_9 \tag{4-3}$$


(4-4)
(4-5)
(4-6)

eqn 4-7)[7a] were ruled out by the absence of intermolecular tritium exchange in rearrangements of allylically tritiated 1-octene in admixure with 1-hexene.[56]


(4-7)

However, since reaction 4-6 is expected to be too slow to account for the catalysis observed, the requirement of a second photodissociation (eqn 4-8) was suggested.[2,55d] Catalysis of allylic hydrogen shift might then proceed according to eqns (4-9)-(4-13). Such a scheme is supported by observation of a


(4-8)
(4-9)
(4-10)
(4-11)
(4-12)
(4-13)

small but measurable induction period (a few seconds) for 1-alkene disappearance and 2-alkene appearance suggesting that the active catalyst is not formed directly from $Fe(CO)_5$ by a one-quantum process.[55d,57] Similar induction periods are observed for isomerization of cis- or trans-2-pentene (Fig. 4-3).[55d] However, the actual catalyst of alkene isomerization here may be a carbonyl-bridged diiron species as has been suggested for photoinduced alkene isomerization with iron carbonyl trifluorophosphine complexes (see section 4d). In fact there is no *direct* evidence that either a diiron species or $(alkene)_2Fe(CO)_3$ are generated in these reactions or that they are precursors of thermally active catalyst of alkene isomerization.

As mentioned above, carbonyl complexes of molybdenum and tungsten catalyze [1.3]-hydrogen migration as well as cis-trans isomerization of alkenes possessing allylic hydrogen (Table 4-5).[23,58] These reactions are all characterized by an induction period, followed by a period of fast conversion, and finally a slow approach to a thermodynamic equilibrium mixture as exemplified in Fig. 4-4 for isomerization of 1-pentene. The induction period indicates that the actual isomerization catalyst is generated from $W(CO)_6$ which is thermally inactive. However, after irradiation a catalyzed *thermal* isomerization (photogenerated catalysis) can be observed as well as *photochemical* isomerization

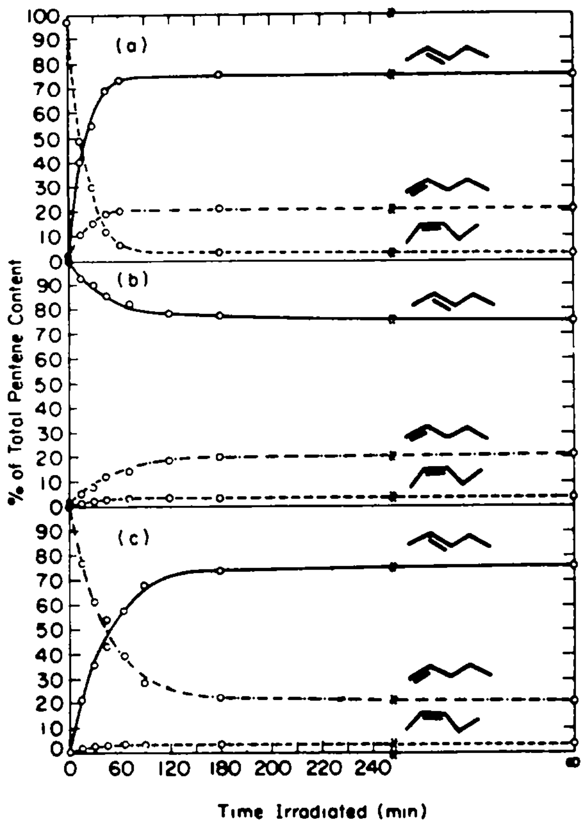


Fig. 4-3. (a) Plot of 1-pentene (---) disappearance and cis(-·-·) and trans-2-pentene (—) formation (b) plot of trans-2-pentene (—) disappearance and cis-2-pentene (-·-·) and 1-pentene (---) formation; and (c) plot of cis-2-pentene (-·-·) disappearance and trans-2-pentene (—) and 1-pentene (---) formation as a function of near-ultraviolet irradiation time of 0.1M alkene, 0.011M $Fe(CO)_5$ degassed benzene solutions at 20°.[554]

Table 4-5. $Mo(CO)_6$ and $W(CO)_6$ catalyzed alkene isomerizations[23]

Starting Olefin	Catalyst	Initial Product(s)
trans-2-Pentene	$W(CO)_6$	*cis*-2-Pentene, 1-pentene
cis-2-Pentene	$W(CO)_6$	*trans*-2-Pentene, 1-pentene
1-Pentene	$\left.\begin{matrix}W(CO)_6\\Mo(CO)_6\end{matrix}\right\}$	*cis*-2-Pentene, *trans*-2-pentene
1-Hexene	$W(CO)_6$	*cis*-2-Hexene(small), *trans*-2-hexene
cis-3-Hexene	$W(CO)_5$	*trans*-2-Hexene, *trans*-3-hexene, *cis*-2-hexene
trans-3-Hexene	$W(CO)_6$	*trans*-2-Hexene, *cis*-2-hexene, *cis*-3-hexene
1,4-Pentadiene	$W(CO)_6$	*trans*-1,3-Pentadiene, *cis*-1,3-pentadiene
cis-1,4-Hexadiene	$W(CO)_6$	*trans*,*trans*-2,4-Hexadiene, *cis*,*trans*-2,4-hexadiene, *cis*,*cis*-2,4-hexadiene
trans-1,4-Hexadiene	$W(CO)_6$	*trans*,*trans*-2,4-Hexadiene, *cis*,*trans*-2,4-hexadiene, *cis*,*cis*-2,4-hexadiene
trans-1,3-Pentadiene	$W(CO)_6$	*cis*-1,3-Pentadiene
cis-1,3-Pentadiene	$\left.\begin{matrix}W(CO)_6\\Mo(CO)_6\end{matrix}\right\}$	*trans*-1,3-Pentadiene
trans,*trans*-2,4-Hexadiene	$W(CO)_6$	*cis*,*cis*-2,4-Hexadiene, *trans*,*cis*-2,4-hexadiene
cis,*trans*-2,4-Hexadiene	$W(CO)_6$	*trans*,*trans*-2,4-Hexadiene, *cis*,*cis*-2,4-hexadiene
cis,*cis*-2,4-Hexadiene	$W(CO)_6$	*cis*,*trans*-2,4-Hexadiene, *trans*,*trans*-2,4-hexadiene

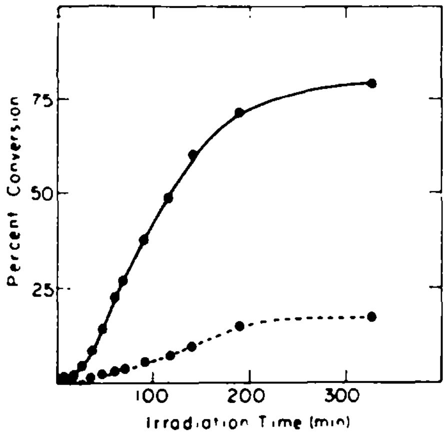
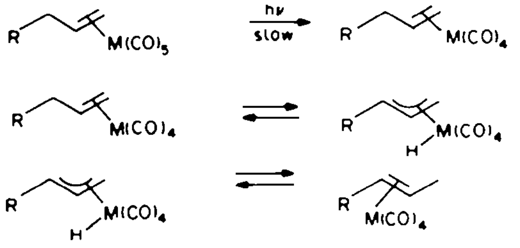


Fig. 4-4. W(CO)$_6$ photoassisted conversion of 1-pentene to cis-2-pentene (—) and trans-2-pentene (---) at ≈ 10^{-3}M W(CO)$_6$, 5×10^{-2}M 1-pentene in degassed isooctane solutions carried out at 366 nm irradiation and 25°.[23]

(catalyzed photolysis) as evidenced by different relative rates of production of cis- and trans-2-pentene during the periods of irradiation and the subsequent dark reaction periods. In every case, IR spectral changes provide presumptive evidence for initial generation of (alkene)M(CO)$_5$ which competes with M(CO)$_6$ for incident light and eventually is transformed into (alkene)M(CO)$_4$.[23] Reactions analogous to eqns (4-1), (4-2), (4-4), (4-8) and (4-9) can account for these transformations. Coordinatively unsaturated tetracarbonyl monoalkene complexes are favoured as key intermediates which would be generated initially by slow photodissociation of a carbonyl ligand from a pentacarbonylmonoolefin complex (eqn 4-14).[23] After isomerization via allylmetal hydrides (eqns 4-15 and 4-16), the initial tetracarbonyl

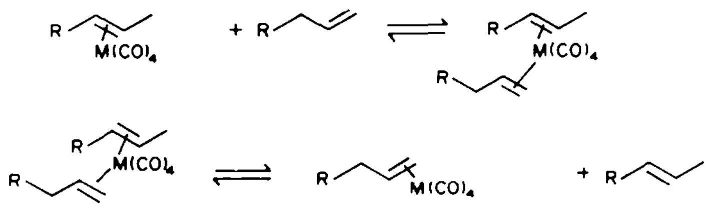


4-14

4-15

4-16

monoolefin complex could be regenerated via a tetracarbonyl bisolefin intermediate (eqns 4-17 and 4-18).



4-17

4-18

It is not clear which of these reactions is rate determining in the thermal and photochemical components of the isomerization. It is also not known whether the π-allyl metal hydride intermediates of eqn (4-15) are configurationally labile or if a different intermediate must be invoked to account for cis→trans isomerization (e.g. see eqn 3-5). Finally, overall quantum yields are low (10^{-2}–10^{-1}) for Mo(CO)$_6$ or W(CO)$_6$ catalyzed photoisomerizations[23] compared with iron or ruthenium carbonyl catalyzed isomerization which remains the synthetic method of choice for allylic [1.3] hydrogen shift.

(d) *Metal phosphine carbonyls*

Iron carbonyl complexes derived by replacement of one or two carbonyl ligands of Fe(CO)$_5$ with triphenylphosphine ligands are photoactive catalyst precursors for isomerization of 1-pentene (Table

4-6).[59] As for $Fe(CO)_5$, quantum yields exceed unity for the phosphine catalyst precursors, demonstrating a catalyst photogeneration mechanism. Notably, quantum yields and ratios of trans to cis-2-pentene products differ for each catalyst precursor implying that the catalytically active species formed retains the triarylphosphine ligand(s). The conclusion that the Fe-P bonds are photoinert relative to the Fe-CO bonds, receives further support from infrared spectroscopic studies on the photoreactions of $Fe(CO)_4PPh_3$ and $Fe(CO)_5$ in the presence of 1-pentene or $P(OMe)_3$ which show that CO and not PPh_3 ligands undergo photoinduced substitution. This fact allows anchoring of the catalyst to a polymer-anchored phosphine (PAPh)-PPh_2 (see Table 4-6).[59]

Table 4-6. Photocatalyzed Isomerization of 1-pentene[a,59]

catalyst precursor	% CNVRSN (Irrdn time, min)	obsd ϕ[b]	*trans*/*cis*[c]
$Fe(CO)_5$	6.2 (2)	117	2.92
	11.9 (4)	112	2.93
	31.5 (15)	96	3.29
$Fe(CO)_4PPh_3$	7.8 (5)	71	1.11
	12.7 (10)	58	1.20
	16.3 (15)	50	1.32
	19.8 (21)	43	1.43
	36.2 (60)	28	2.12
$Fe(CO)_3(PPh_3)_2$	8.6 (15)	12	0.56
	11.2 (30)	7.7	0.57
	18.4 (60)	7.7	0.58
$[(PAPh)\text{-}PPh_2]_{5-n}Fe(CO)_n$	3.9 (30)	6.0	0.71
	6.4 (60)	4.8	0.80
	10.6 (120)	4.0	1.10
	33.8 (720)	2.2	1.76

[a] All reactions were carried out in hermetically sealed, degassed ampules at 25°; [b] ϕ is the number of 1-pentene molecules isomerized per photon incident on the sample. [c] Ratio of *trans*-2- and *cis*-2-pentene products.[59]

Similarly, iron carbonyl-trifluorophosphine complexes $Fe(PF_3)_x(CO)_{5-x}$ are photoactive catalyst precursors for isomerization of 1-penetne to cis- and trans-2-pentene.[60] The reactions exhibit many features in common with the photoinduced $Fe(CO)_5$ catalyzed isomerizations including quantum yields exceeding unity, an induction period, a final thermodynamic equilibrium product mixture which is the same for all of the complexes $x = 1-4$, and an optimum concentration for the catalyst precursor above or below which catalytic effectiveness is decreased. This last feature implies that a coordinatively unsaturated active catalyst complex can be trapped by excess catalyst precursors to form *inactive aggregates*. Catalytic effectiveness decreases with increasing phosphine substitution (Fig. 4-5). $Fe(PF_3)_5$ does not

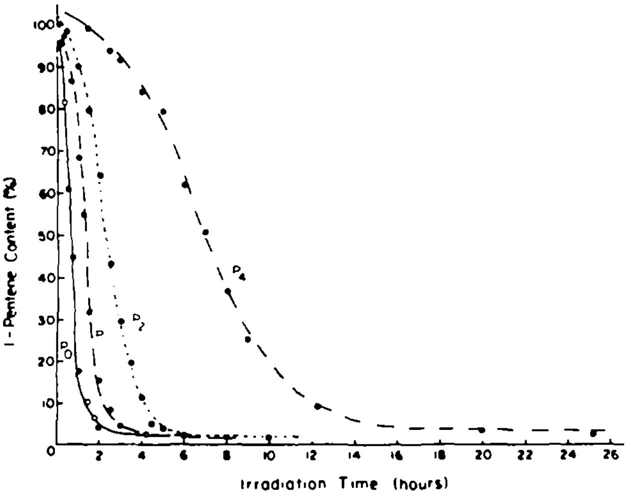


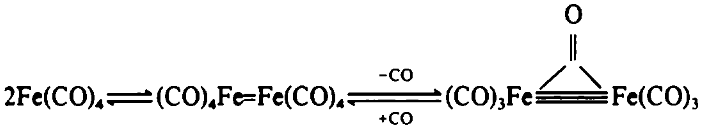
Fig. 4-5. Comparison of the extent of reaction as a function of irradiation time using various iron compounds as catalyst precursors: $Fe(CO)_5$ (open circles); $Fe(CO)_4PF_3$ (half-filled circles); $Fe(CO)_3$-$(PF_3)_2$ (filled circles); $Fe(PF_3)_4CO$ (circles and dots).[60]

produce an active catalyst although the PF_3 ligands are photolabile in this complex.[61] They are also photolabile in (1-pentene)$Fe(PF_3)_4$. A similar dichotomy is found between $H_2Fe(PF_3)_3CO$ and $H_2Fe(PF_3)_4$ (Table 4-7).[60] Thus, the CO ligands may play a greater role than being photosubstitutable ligands in photoinduced catalytic reactions of iron carbonyl complexes. It was suggested that the ability of CO, but not PF_3, to act as a bridging ligand for metal atoms could account for the effect of a CO ligand if the catalytically active complex is necessarily a bridged diiron species.[60] Indeed, $Fe(CO)_4$ is known to form a labile, multiply bonded, carbonyl-bridged dimer **16**.[62]

Table 4-7. Comparison of the photochemical reactivity for the isomerization of 1-pentene[a,60]

Compound	% 1-pentene remaining	Compound	% 1-pentene remaining
$Fe(PF_3)_4CO$	4.6	$H_2Fe(PF_3)_3CO$	16.6
$Fe(PF_3)_5$	98.5	$H_2Fe(PF_3)_4$	99.2

[a] Samples irradiated simultaneously at ambient temperature for 10.0 h by using unfiltered medium-pressure mercury light.



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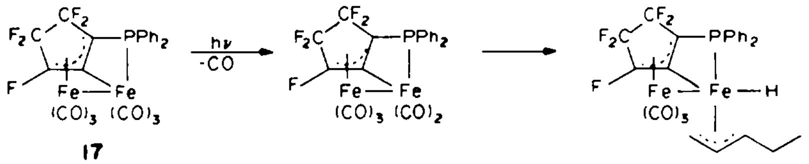
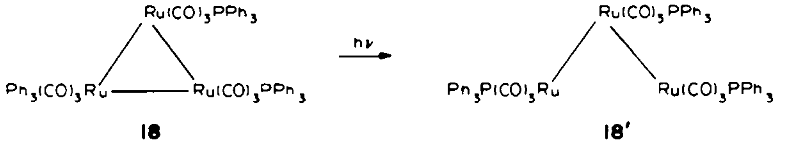
The diiron cluster complex **17** is also a catalyst precursor for photoinduced isomerization of 1-pentene.[60c] The primary photoreaction of **17** was shown to be dissociation of a carbonyl group cis to the phosphine ligand. Coordination with pentene and further loss of carbonyl ligands could produce a η^3-allyl hydride intermediate analogous to that suggested for $Fe(CO)_5$ (eqn 4-10) but dissociation of all three CO groups would be required to avoid 7-coordinate iron. Alternatively, it was noted that catalysis of photoinduced isomerization by **17** might involve both iron atoms.[60c]



With $Ru(CO)_4PPh_3$ and $Ru_3(CO)_9(PPh_3)_3$ as nominal catalysts, quantum yields as high as 3.1 and 1.9 respectively were observed for isomerization of 1-Pentene.[55c] Although $Ru(CO)_9(PPh_3)_3$ is formally a trimer of $Ru(CO)_3(PPh_3)$, and $Ru(CO)_4PPh_3$ yields $Ru(CO)_3(PPh_3)$ by photodissociation of CO, it appears that the actual isomerization catalysts generated from $Ru(CO)_4(PPh_3)$ and $Ru_3(CO)_9(PPh_3)_3$ by UV irradiation are not identical. Thus, isomerizations of 1-pentene produce different *initial* ratios of cis and trans-2-pentene products with $Ru(CO)_4(PPh_3)$ or $Ru_3(CO)_9(PPh_3)_3$ as nominal catalysts (Table 4-8).[55c] The *initial* ratio of the 2-pentenes with the cluster catalyst precursors appears to be independent of the excitation wavelength. For the mononuclear precursor, the actual catalyst is undoubtedly $Ru(CO)_3(PPh_3)$. With $Ru_3(CO)_9(PPh_3)_3$ (**18**) as catalyst precursor, the actual catalyst appears to be polynuclear. Thus, photoactivation may correspond to ring opening of the triangulo cluster **18** to a coordinatively unsaturated acylic complex **18'** rather than dissociation to mononuclear $Ru(CO)_3(Ph_3P)$ fragments.



18 **18'**

Table 4-8. Photocatalyzed 1-pentene isomerization [55c]

catalyst precursor	irrdn, λ(nm)	% convn	*trans/cis*
$Ru(CO)_4PPh_3$	355	5.7	2.3
		14.9	2.0
$Ru_3(CO)_9(PPh_3)_3$	355	5.3	4.3
		10.0	3.4
	436	6.7	3.0
		13.7	2.9
	550	6.9	3.3
		12.0	3.5
$Ru_3(CO)_{12}$	355	7.7	5.7
		13.8	6.2
	436	8.4	5.5
		14.6	7.0

In the presence of a hydride source, e.g. Et_3SiH, the binuclear cobalt phosphine carbonyl complexes $Co_2(CO)_6(P(nBu)_3)_2$, $Co_2(CO)_6(P(OPh)_3)_2$, and $Fe(\eta^5\text{-}C_5H_5)(CO)_2Co(CO)_3(P(OPh)_3)_3$ are photochemically active catalyst precursors for 1-pentene isomerization.[63] In each case the catalytically active intermediate is believed to be a cobalt hydride probably arising by photoinduced metal–metal bond homolysis (eqn 4-19, $L = P(nBu)_3$ or $P(OPh)_3$). Subsequent thermal reactions generate the thermally active isomerization catalyst $HCo(CO)_3L$, possibly according to eqns (4-20)–(4-22). Nonphotochemically prepared $[HCo(CO)_3P(OPh)_3]$ is a similarly thermally active isomerization catalyst. Its activity is enhanced (factor of ~3) by near-UV irradiation. Similarly, the activity of $RhHCO(PPh_3)_3$ and $IrClCO(PPh_3)_2$ as thermal alkene isomerization catalyst is enhanced by UV irradiation.[64b] Possibly these photochemical effects arise from photodissociative generation of catalytically active coordinatively unsaturated intermediates. Alternatively, a photoinduced concerted suprafacial [1.3] sigmatropic shift of a hydrogen atom in the alkene may be facilitated by complexation with a transition metal owing to orbital symmetry differences between free alkene and alkene complex.[64,65]

$$>\!M\text{–}Co(CO)_3L \xrightarrow{h\nu} >\!M\cdot + Co(CO)_3L \tag{4-19}$$

$$Co(CO)_3L \xrightleftharpoons{\Delta} Co(CO)_2L + CO \tag{4-20}$$

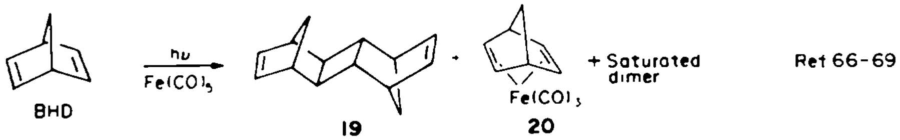
$$Co(CO)_2L + HSiEt_3 \xrightarrow{\Delta} Co(CO)_2(H)(SiEt_3)L \tag{4-21}$$

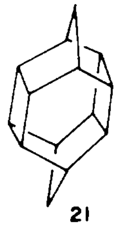
$$Co(CO)_2(H)(SiEt_3)L + Co(CO)_3L \xrightarrow{\Delta} HCo(CO)_3L + Co(CO)_2(SiEt_3)L \tag{4-22}$$

5. CYCLOADDITIONS OF ALKENES

(a) *Bicyclo*[2.2.1]*hepta*-2,5-*diene*

Photoinduced iron, chromium and nickel carbonyl catalyzed reactions of bicyclo[2.2.1]hepta-2,5-diene (BHD) exemplify three different relationships with their thermally induced counterparts. UV irradiation of BHD in the presence of $Fe(CO)_5$ affords dimer **19**, complex **20**, and a saturated dimer which may have structure **21** or **22**.[66–69] Irradiation of **20** with BHD does *not* yield the saturated dimer,[67] but it is formed from BHD with $Fe_2(CO)_9$ as catalyst at room temperature *in the dark* and presumably $Fe_2(CO)_9$ is the actual catalyst in photoinduced dimerizations with $Fe(CO)_5$ as the nominal catalyst.[68] Thus, the ability of light to induce this reaction with $Fe(CO)_5$ may merely arise from the earliest reported

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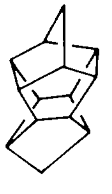
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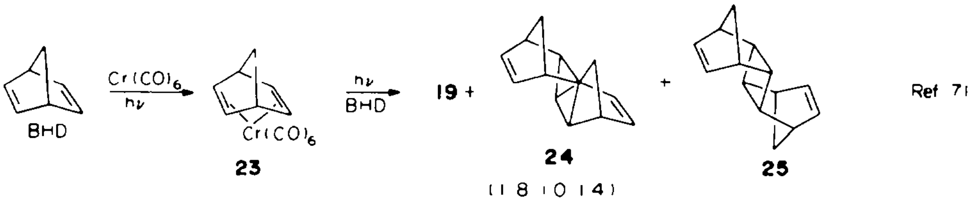
photoreaction of a metal carbonyl, photogeneration of the more active $Fe_2(CO)_9$ according to eqns (5-1) and (5-2).[70]

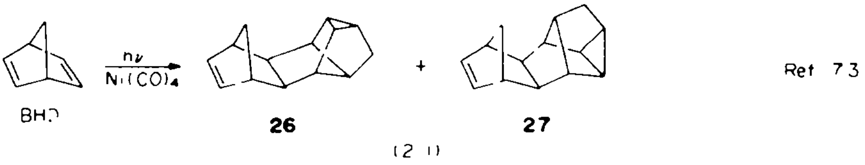
$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4 + CO \tag{5-1}$$

$$Fe(CO)_5 + Fe(CO)_4 \xrightarrow{\Delta} Fe_2(CO)_9 \tag{5-2}$$

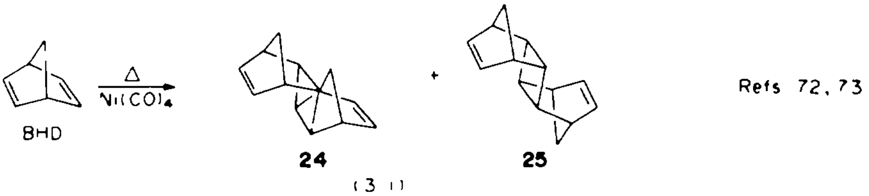
UV irradiation of BHD in the presence of $Cr(CO)_6$ affords complex **23** as well as three dimers, **19**, **24** and **25**.[71] In contrast with the iron complex **20**, irradiation of the chromium complex **23** with BHD affords **19**, **24**, and **25** in the same ratio obtained with $Cr(CO)_6$. Furthermore neither $Cr(CO)_6$ nor **23** catalyzes thermal dimerization of BHD.[71] η^6-Benzene-$Cr(CO)_3$ also is a photoactive catalyst precursor for BHD dimerization. It also produces the complex **23** during UV irradiations in BHD.[72]



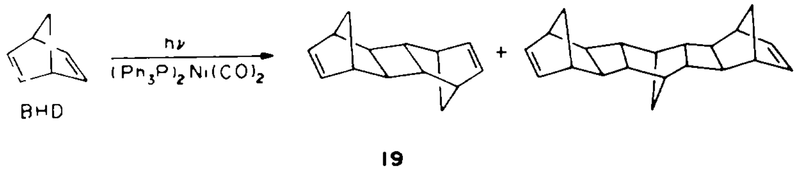
UV irradiation of BHD in the presence of $Ni(CO)_4$ generates $2\pi + 2\pi + 2\pi$ cycloadducts **26** and **27**.



$Ni(CO)_4$ is also a *thermally* active catalyst for BHD dimerization. But, remarkably, different products, **24** and **25**, are obtained in the $Ni(CO)_4$ catalyzed thermal dimerization than in the photoinduced reaction.[72,73]



Also remarkably, replacement of two carbonyl groups in $Ni(CO)_4$ by triphenylphosphine ligands gives a photoactive catalyst which promotes formation of yet another dimer as well as a trimer from BHD.[72] Similarly, replacement of two carbonyl groups of $Fe(CO)_5$ by 1,4-diphenylbutadiene gives a photoactive



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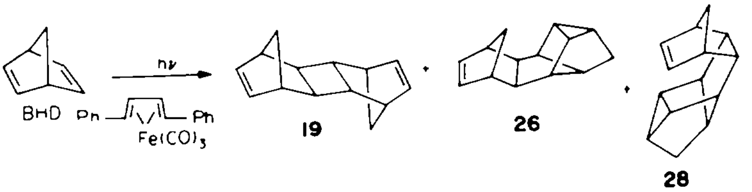
catalyst which promotes different dimerizations to give **26** and **28**, besides the formation of **19** which is found with the pentacarbonyl complex as catalyst precursor.[72] A cobalt complex, $Ph_3PCo(CO)_2NO$, is also a photoactive catalyst which selectively affords **19** from BHD.[72]



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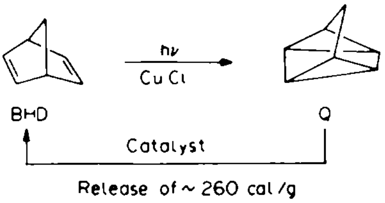
In striking contrast with the above mentioned catalyzed photoreactions of BHD, copper(I) catalysts selectively promote intramolecular $2\pi + 2\pi$ photocycloaddition to give quadricyclane (Q).[74] The reaction is remarkably *insensitive* to the presence and identity of ligands on Cu(I).[75–80] Since Q reversion of BHD,



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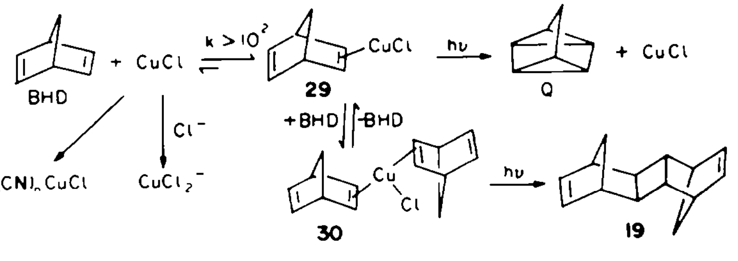
which is negligibly slow at room temperature, can be effected with appropriate transition metal catalysts with concomitant release of ~260 cal/g, BHD-Q interconversions are being considered for use as solar energy storage systems.[1d,75–80]

With CuCl as catalyst spectral studies of CuCl-BHD solutions[75,76] and X-ray crystal structural studies[81] indicate that CuCl is virtually exclusively present as an exo monodentate π-complex, probably with 1 : 1 stoichiometry as **29**. Although BHD and CuCl are essentially transparent, **29** absorbs strongly between 250 nm and 320 nm leading to photoproduction of Q and release of the CuCl catalyst (Scheme 5-1). Since the formation constant for **29** is $> 10^2$, all of the CuCl is coordinated with BHD, and the



Scheme 5-1.

quantum yield for Q production does not depend on the concentration of BHD ($\Phi = 0.34 \pm 0.06$ for 0.10 to 9.86M).[76] However, formation of a UV spectrally indistinguishable 1 : 2 π-complex **30** cannot be ruled out.[17] Both acetonitrile and chloride ions, which coordinate strongly with Cu(I)[82,83] displacing alkene ligands, inhibit Q production.[75,76] Small quantum yields of dimer **19** ($\Phi_{19} \sim 0.04\Phi_Q$) are formed only at high BHD concentrations which would favor generation of **30**. Analogy with photodimerization of bicyclo[2.2.1]hept-2-ene (section 5c) suggests that the 2 : 1 complex is required for CuCl catalyzed photodimerization of BHD to **19**. Catalytic factors (mol of Q formed per mol of CuCl initially present) of at least 394 have been measured for CuCl catalyzed BHD photocycloaddition producing Q.[76]

The UV spectrum of a 2×10^{-3}M CuCl–0.1M bicyclo[2.21]hepta-2,5-diene (BHD) solution in ethanol exhibits an intense band at 248 nm and a shoulder at about 300 nm (Fig. 5-1).[75a] These are probably charge-transfer transitions between Cu(I) and BHD within a π-complex. Although the directions of charge transfer associated with these absorptions are not known, it was noted that "the practical consequences in terms of the bonding changes within the alkene are similar in either case" (Fig. 5-2).[75a] Thus, transfer of a 3d electron from Cu(I) to the lowest unoccupied π molecular orbital, Ψ_3, on bicycloheptadiene weakens the bonding between C_2–C_3 and C_5–C_6 while enhancing that between C_2–C_6 and C_3–C_5. Electron transfer in the opposite sense, from the highest occupied π molecular orbital, Ψ_2, on bicycloheptadiene to the metal, produces a qualitatively similar effect on the bonding. The electronically excited complex may then partition between relaxation pathways that lead to BHD and Q.

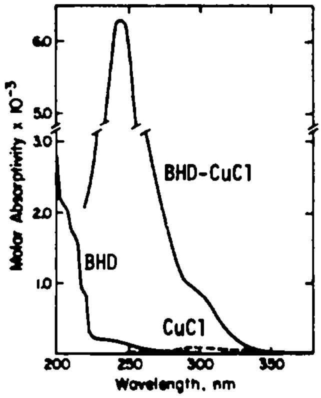


Fig. 5-1. Ultraviolet absorption spectrum of BHD, CuCl, and BHD + CuCl in ethanol solution.[75a]

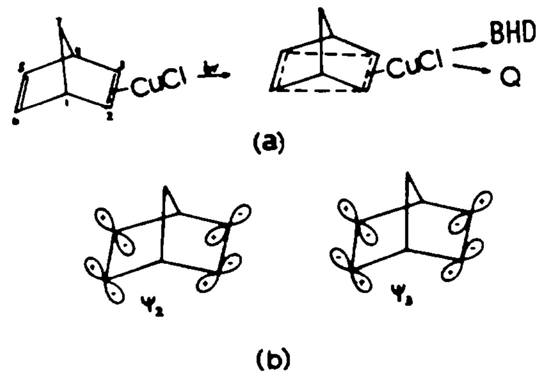
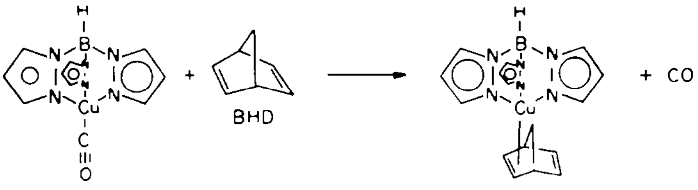


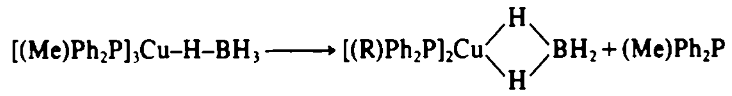
Fig. 5-2. (a) Proposed mechanism of the CuCl-catalyzed photoisomerization of bicycloheptadiene (BHD) to quadricyclene (Q). (b) Representation of the highest filled (Ψ_2) and lowest unfilled (Ψ_3) π molecular orbitals on BHD.

A mechanism, similar to scheme 5-1, involving ground state Cu-BHD π-complexation is probably operative with Cu[HB(PZ)$_3$]CO (31) as nominal catalyst for BHD to Q interconversion.[1d] UV spectral studies reveal that BHD replaces the CO ligand in 31 to afford the complex 32 which is photoactive for Q production (Φ = 0.2).[79]



31 32

Selective intramolecular photocycloaddition of BHD to give Q is not limited to Cu(I) photoassisted processes. Another category of catalyzed photochemical process, photosensitization, has also been observed to yield Q with certain Cu(I) complex catalysts. Thus, while Ph_3P or $(Me)Ph_2P$ weakly sensitize the BHD to Q rearrangement, complexes of these ligands with $CuBH_4$ are efficient sensitizers of this intramolecular photocycloaddition (Table 5-1). In solution, the triphosphine complex **33** loses one phosphine ligand to give **34** which is analogous to **35**. But the quantum yield is unaffected by added



$$[(Me)Ph_2P]_3Cu{-}H{-}BH_3 \longrightarrow [(R)Ph_2P]_2Cu(\mu\text{-}H)_2BH_2 + (Me)Ph_2P$$

33 **34**, R = Me; **35**, R = Ph

Ph_3P suggesting that BHD does not form a π-complex with **35** by displacing a phosphine ligand. IR spectral studies also failed to detect formation of a ground state complex of **34**. Also, the quantum yield with **35** is independent of light intensity over a fivefold range ruling out a multiphoton mechanism involving photogeneration of a transient Cu–BHD complex which produces Q by further photoexcitation. The quantum yields listed in Table 5-1 show linear correlations between $1/\Phi_{sen}$ vs 1/[BHD], a Stern–Volmer type relationship typical of sensitized photoreactions as in eqns (5-3)–(5-5). Limiting sensitization yields of $\Phi_{sen} = 0.54$ and 0.76 were measured with Cu(I) complexes **33** and **35** respectively as sensitizers.[78]

Table 5-1. Quantum yields for the sensitized conversion of BHD to Q upon 313 nm irradiation[78]

Sensitizer	[BHD],M	Φ_{sen} [a,b]
PPh_3	0.1	<0.01
PPh_2Me	0.1	<0.04
$Cu(PPh_3)_2BH_4$	0.055	0.13 ± 0.01 (4 values)
$Cu(PPh_3)_2BH_4$	0.07	0.20 ± 0.03 (6 values)
$Cu(PPh_3)_2BH_4$	0.1	0.23 ± 0.05 (11 values)
$Cu(PPh_3)_2BH_4$ [c]	0.1	0.22 (1 value)
$Cu(PPh_3)_2RH_4$ [d]	0.1	0.17 (1 value)
$Cu(PPh_2Me)_3BH_4$	0.1	0.32 ± 0.05 (10 values)
$Cu(PPh_2Me)_3BH_4$	0.32	0.45 ± 0.03 (4 values)
$Cu(PPh_2Me)_3BH_4$	0.5	0.48 ± 0.03 (9 values)

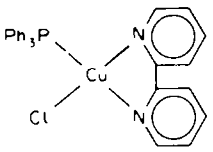
[a] Values of Φ_{sen} were determined at short (≤3 h) irradiation times. [b] Where quoted, error limits represent standard deviation of the mean. [c] Sample contained 9.6×10^{-4}M PPh_3. [d] Intensity of incident light was 4.8 times less than in other runs.

$$\underset{\textbf{35}}{(Ph_3P)_2CuBH_4} \xrightarrow{h\nu} [(Ph_3P)_2CuBH_4]^* \tag{5-3}$$

$$[(Ph_3P)_2CuBH_4]^* \xrightarrow{\Delta} (Ph_3P)_2CuBH_4 \tag{5-4}$$

$$[(Ph_3P)_2CuBH_4]^* + BHD \longrightarrow (Ph_3P)_2CuBH_4 + Q \tag{5-5}$$

Since the majority of solar light energy has wavelength longer than 350 nm, it is desirable to develop sensitizers which are effective for BHD to Q rearrangement with longer wavelength light. The complexes **36–39** sensitize the BHD to Q photorearrangement.[80] However, with 366 nm light the highest quantum yield, observed with **35**, was only $\Phi = 0.011$. An iridium bipyridyl (bipy) complex, $Ir(bipy)_3{\cdot}H_2O^{+3}$, was reported to be an efficient ($\Phi = 0.7$) sentizer of the BHD to Q rearrangement with 366 nm light.[1d]



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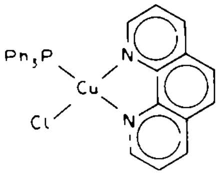

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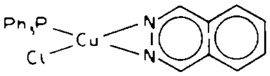

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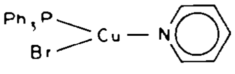
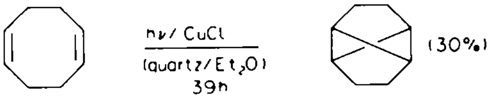


39

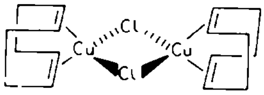
(b) *Cycloocta-1,5-diene*

Intramolecular photocycloaddition of cis,cis-1,5-cyclooctadiene (cc-COD) (37) to produce tricyclo[3.3.0.0^{2,6}]octane (38) was the first reported Cu(I) catalyzed organic photoreaction.[84] Although 37 was known to form a complex of structure 3,[19] it was concluded on the basis of UV spectral studies that uncomplexed diene is the major light absorbing species in saturated solutions of CuCl in ether and 4×10^{-3}M diene 37.[84] This erroneous assumption (vide infra) led to the suggestion that CuCl catalyzes the photorearrangement of 37 by interacting with photoexcited diene according to eqns (5-3) and (5-4).



37 **38**

Ref 84



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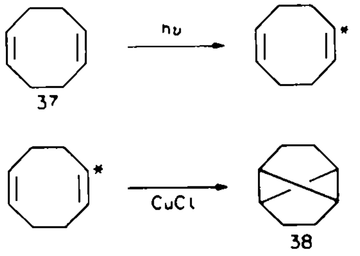
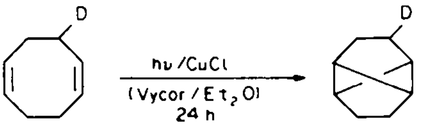


(5-3)

(5-4)

Photorearrangement of the allylically monodeuterated 37 upon irradiation with *Vycor filtered* UV-light (>240 nm) in the presence of CuCl is accompanied by loss of deuterium.[85] The amount of deuterium loss is in accord with theory for a cyclization process involving initial random abstraction of an allylic hydrogen atom (scheme 5-2).



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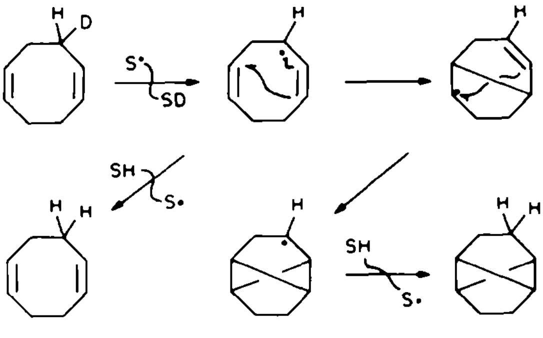
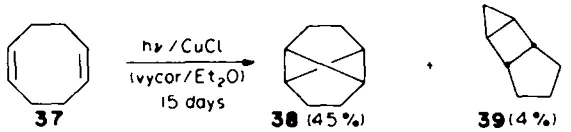
d_0,%	d_1,%	d_2,%		d_0,%	d_1,%	d_2,%	
2.3	96.7	1.0		13.4	86.1	0.5	
(6.7	92.4	0.9)	recovered	(14.4	84.7	0.9)	theory

An isomeric cyclobutane 39 was discovered later as a minor product from 37 upon irradiation with *Vycor filtered* UV-light.[86] The intervention of an allylic radical 40 may account for the 37→39



Scheme 5-2.



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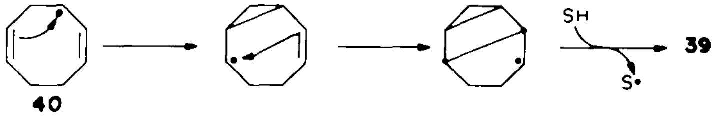
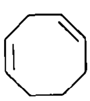
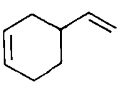
conversion. However, with shorter wavelength UV light (not Vycor filtered), the 37→38 rearrangement does not involve the allylic radical 40 since no deuterium is lost upon photorearrangement of

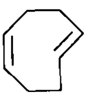


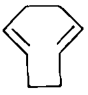
perdeuterated 37. Irradiation of 37-d_{12} in a quartz vessel in the presence of CuCl produces 38-d_{12} and no 38-d_{11}.[87] The allylic radical mechanism requires the formation of 38-d_{11} exclusively assuming hydrogen atom abstraction only from the ether solvent (see scheme 5-2).

UV irradiation of a pentane suspension of the diene-CuCl complex 3 produces 41–44 in addition to 38


41 (5%)


42 (7%)


43 (17%)

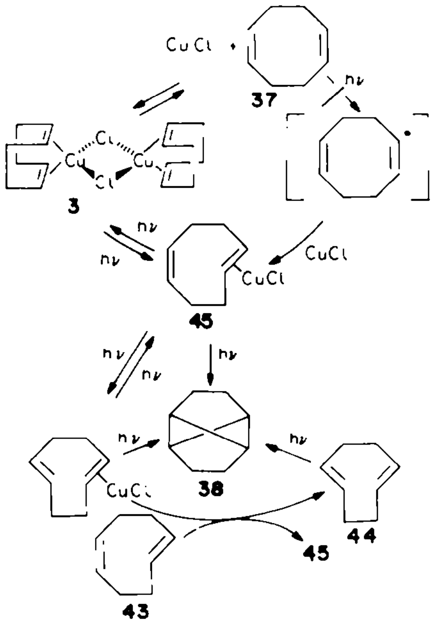

44 (1%)

(43%).[88] Importantly, the strained trans = 1,5-COD isomers 43 and 44 are strongly coordinated with CuCl, and are only isolable after decomposition of their CuCl complexes by reaction with NaCN.[88]

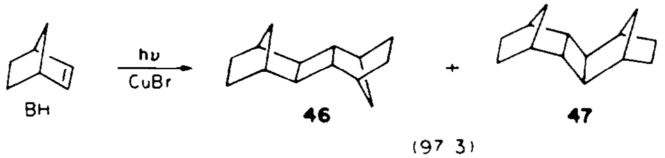
A multiphoton process was postulated for the CuCl catalyzed generation of cyclobutane 38 involving initial cis→trans isomerization of c,c-COD (37) to a CuCl complex 45 of the cis,trans isomer 43.[88] Recent studies[18] confirm that 45 is a primary photoproduct while cyclobutane 38 is formed from 45 only in one or more secondary photoreactions. Thus, the initial rate of formation of 45 is rapid relative to that for formation of 38 which exhibits a definite induction period.[18,88] UV spectral studies demonstrate that a complex of stoichiometry $(CuCl)_x \cdot (cc\text{-}COD)_2$, presumably of structure 3, is the primary light absorbing species in ether solutions of cc-COD saturated with CuCl and in the solution phase of pentane suspensions of 3.[18] Scheme 5-3 summarizes available information on the CuCl-catalyzed production of cyclobutane 38 from cc-COD. Direct photoexcitation of cc-COD does *not* contribute significantly to the catalyzed photoprocess. Although each of the routes shown (scheme 5-3) for the 45 to 38 conversion was independently confirmed, their relative importance remains uncertain.[88]

(c) *Cyclic monoenes*

Metal catalyzed photocycloaddition of a monoene was first observed with bicyclo[2.2.1]hept-2-ene (BH).[89] Irradiation of BH in the presence of CuCl or CuBr affords dimers 46 and 47 (97:3) in 38%



Scheme 5-3.



isolated yield.[74,89] Coordinative copper-alkene interaction is indicated by an intense UV absorption band at 239 nm in solutions containing BH and CuBr, but no significant absorption for BH or CuBr separately (Fig. 5-3). Also, a 1 : 1 BH–Cu complex was isolated. Noteworthily, irradiation of an ether solution of this complex alone did *not* produce any dimer although the complex catalyzes dimerization of excess BH.[74]

The dependence of the quantum yield for photodimerization, Φ, on the concentration of bicycloheptene, [BH], was measured over [BH] = 2.9–7.9M. Assuming the formation of only a single light absorbing complex between CuBr and BH, and on the basis of an approximately linear relationship between $1/\Phi$ and $1/[\mathrm{BH}]^2$, the mechanism presented in eqns (5-5)–(5-7) was suggested for CuBr-catalyzed photodimerization. However, it should be noted that over such a small variation of [BH], a linear relationship between $1/\Phi$ and $1/[\mathrm{BH}]^2$ is not readily distinguishable from a linear relationship between $1/\Phi$ and $1/[\mathrm{BH}]$ for the same data. In fact, we find that the linear-correlation for a least-squares fit of the

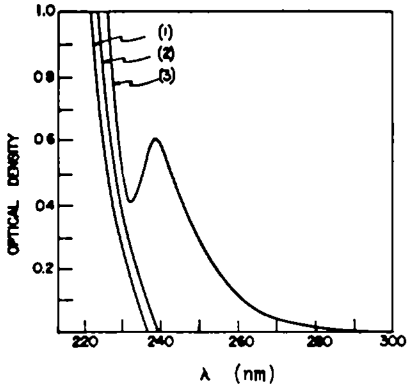


Fig 5-3. Ultraviolet spectra of (1) 7.6×10^{-4}M CuBr in ether, (2) 1.06M bicycloheptene (BH) in ether, and (3) 5.85×10^{-5}M CuBr and 5.3×10^{-2}M bicycloheptene in ether.[89]

reported data[74] is slightly *better* for $1/\Phi$ vs $1/[BH]$ ($R = 0.9905$) than for $1/\Phi$ vs $1/[BH]^2$ ($R = 0.9889$). Furthermore, the assumption that solutions of CuBr in the presence of excess BH contain only a single metal alkene complex was based on UV spectral studies and the assumption that BH–CuBr and $(BH)_2$-CuBr will exhibit substantially different UV spectra.[74] More recent studies employing copper trifluoromethanesulfonate (CuOTf) as catalyst (vide infra) challenge the validity of these assumptions and the mechanism of eqns (5-5)–(5-7).

$$\mathrm{BH{-}CuX} \xrightarrow{h\nu} \mathrm{{}^*BH{-}CuX} \tag{5-5}$$

$$\mathrm{{}^*BH{-}CuX} \longrightarrow \mathrm{BH{-}CuX} \tag{5-6}$$

$$\mathrm{{}^*BH{-}CuX + 2BH} \longrightarrow \mathrm{dimer + BH{-}CuX} \tag{5-7}$$

As noted earlier, CuOTf-alkene complexes containing one, two, three, or even four coordinated C=C bonds are known and these exhibit very similar UV spectra with absorptions at 235 ± 5 nm (ϵ_{max}2950 ± 450) and 274 ± 14 nm (ϵ_{max}2400 ± 900). The UV spectra of CuOTf complexes of BH are typical (Fig. 5-4). Furthermore, ^{1}H-NMR evidence clearly shows that BH forms at least two different complexes with CuOTf in solution.[17] One of these, a 1:1 complex, was also isolated.

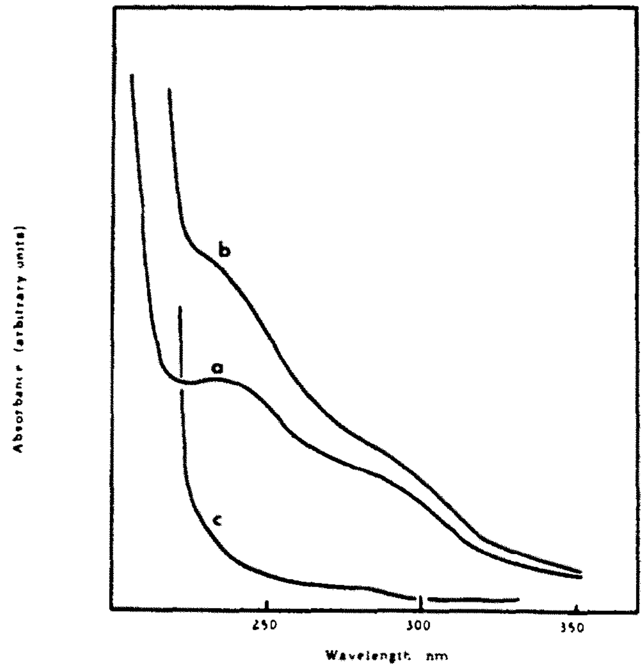


Fig. 5-4 (a) The absorption spectrum of 1:1 CuOTf-bicyclo-[2.2.1]-hept-2-ene (BH) complex in methanol. (b) The spectrum of (a) in the presence of a tenfold excess of BH with BH in the reference cell for balancing. (c) The end adsorption spectrum of BH. The vertical scale is arbitrary in (a)–(c).[91]

With CuOTf as catalyst, irradiation of BH with a medium-pressure mercury vapor lamp affords dimer in 88% isolated yield,[90] more than double the yield obtained with CuBr as catalyst.[74] The dependence of Φ on [BH] was measured over [BH] = 0.10–5.00M.[91] The data clearly show a linear relationship between $1/\Phi$ and $1/[BH]$ but not $1/[BH]^2$ (Fig. 5-5).[91] A general mechanism taking into account the presence of two light absorbing Cu(I)–alkene complexes, a 1:1 and a 1:2 complex, and the possibility of dimer production via photoexcitation of either complex is outlined in eqns (5-8)–(5-13). Since K is not $\ll 1$,[17] and assuming that the 1:1 and 1:2 complexes have nearly identical UV absorption spectra, a linear relationship between $1/\Phi$ and $1/[BH]$ is only predicted (eqn 5-14) for this mechanism if $k_2 \gg k_1$.[91] That is, photoactivation of the 1:1 Cu(I)–alkene does not result in dimer production since deactivation (eqn 5-13) is much faster than the bimolecular association with a ground-state BH (eqn 5-12). The necessary conclusion is that photocycloaddition of BH requires ground state coordination of both reacting C=C

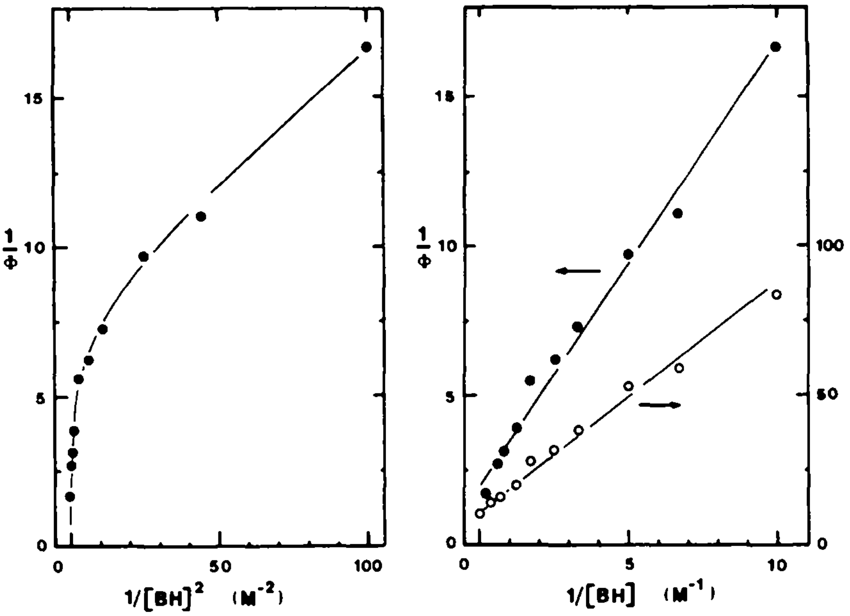


Fig. 5-5. Plot of the quantum yields, Φ, of bicyclo[2.2.1]-hept-2-ene (BH) cyclodimers at varying concentrations of BH keeping [CuOTf] constant at 3.0×10^{-2}M: (●) exo-trans-exo isomer **46**, (○) endo-trans-exo isomer **47**.[91]

bonds with a single Cu(I). This requirement seems to be important for many other copper(I)-catalyzed photocycloadditions (vide infra) although not for intramolecular photocycloaddition of bicyclo[2.2.1]hepta-2,5-diene to give quadricyclane (section 5a).

$$\text{Cu–BH} + \text{BH} \overset{K}{\rightleftharpoons} \text{Cu–(BH)}_2 \tag{5-8}$$

$$\text{Cu–BH} + h\nu \xrightarrow{\phi_1} \text{Cu–BH}^* \tag{5-9}$$

$$\text{Cu–(BH)}_2 + h\nu \xrightarrow{\phi_2} \text{Cu–(BH)}_2^* \tag{5-10}$$

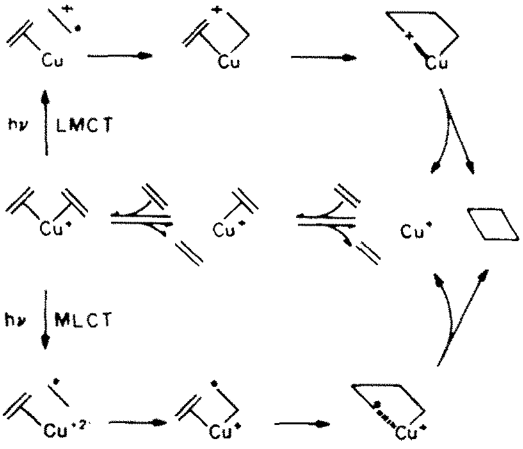
$$\text{Cu–(BH)}_2^* \longrightarrow \text{dimer} \tag{5-11}$$

$$\text{Cu–BH}^* + \text{BH} \xrightarrow{k_1} \text{dimer} \tag{5-12}$$

$$\text{Cu–BH}^* \xrightarrow{k_2} \text{Cu–BH} \tag{5-13}$$

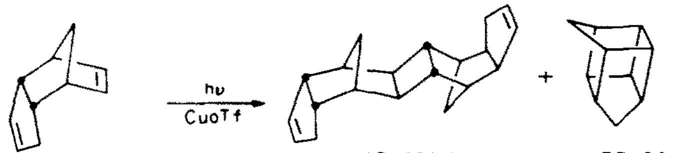
$$\frac{1}{\Phi} = \frac{1}{\phi_2} + \frac{1}{\phi_2 K[\text{BH}]} \tag{5-14}$$

CuOTf-BH exhibits UV absorptions at 236 nm (ε 3400) and 272 nm (ε 2000).[17] The former apparently corresponds to the 239 nm absorption of CuBr-BH.[89] It is tempting to speculate that the shorter wavelength (236 nm) absorption is a metal to alkene ligand charge transfer (MLCT) excitation[92] while the longer wavelength (272 nm) absorption, which is only prominent for the more electrophilic[17] Cu(I) in CuOTf, is probably an alkene ligand to metal charge transfer (LMCT) excitation. It is not clear which of these excitations leads to photocycloaddition. It seems likely that charge transfer in *either* direction could promote intermolecular cycloaddition as suggested above for Cu(I)-catalyzed intramolecular photocycloaddition as bicyclo[2.2.1]hepta-2,5-diene. It is also possible that bond formation in copper(I) catalyzed photocycloadditions is sequential rather than synchronous. Then LMCT and MLCT excitation would lead to cationic or radical cyclization respectively as depicted in scheme 5-4.



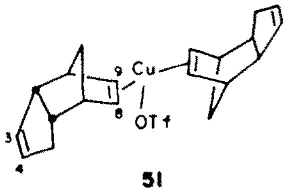
Scheme 5-4.

Photocycloaddition of endo-dicyclopentadiene (**48**) occurs almost exclusively intermolecularly affording **49** selectively[91] in sharp contrast with the intramolecular photocycloaddition of **48** which affords **50** with high energy triplet sensitizers.[93] The strong preference for the formation of **49** in the CuOTf catalyzed reaction confirms the requirement for coordination of both reacting C=C bonds with Cu(I). Thus, endo-dicyclopentadiene forms an isolable 1:2 Cu(I)-alkene complex **51** with CuOTf. The diene coordinates preferentially at the more strained 8,9-C=C bond as an exo-monodentate ligand in **51** and shows little tendency to act as an endo-tetrahapto chelating ligand as in **52**.[17]

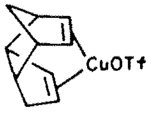


48 **49** (48%) **50** (2%)

Ref 41

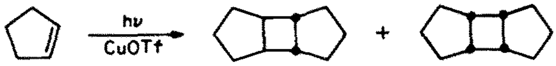


51



52

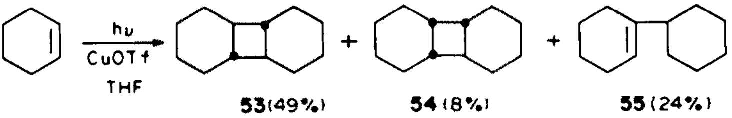
Although neither CuCl nor CuBr catalyzes photodimerization of cyclopentene,[94] CuOTf promotes dimerization analogous to that described above for BH. The greater effectiveness of CuOTf as a catalyst for olefin photoreactions is expected if metal-olefin coordination is important. Thus, trifluoromethanesulfonate is an exceptionally weakly coordinating anion compared to halide ions which compete with alkene for coordination with Cu(I).



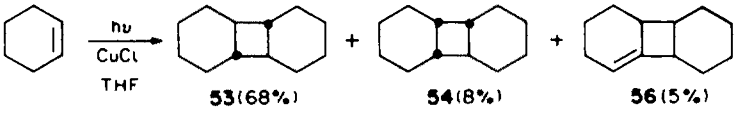
30% 2%

Ref 15

For cyclohexene, copper catalyzed photocycloaddition takes a different course. Doubly trans-fused cyclobutane **53** predominates in spite of a thermodynamic preference for the cis-fused isomers. With CuOTf as catalyst, 1-cyclohexyl cyclohexene (**55**) is also a major product.[15] With CuCl as catalyst, **55** is



not formed.[94] CuCl in neat cyclohexene gives **53** almost exclusively while in ether, tetrahydrofuran or t-butanol solution, **54**, and 3-cyclohexylcyclohexene (**56**) are minor products.[94] Copper(I) bromide and palladium(II) chloride catalyzed similar photoreactions.[94]



Formation of **53** involves conversion of a cis stereochemical relationship of the vinyl hydrogens of *both* cyclohexene monomers into a trans stereochemical arrangement of those hydrogens about the cyclobutane ring. It was noted that this stereochemical outcome could be achieved in two steps, cis→trans isomerization followed by concerted ground-state $2_{\pi a}+2_{\pi s}$ cycloaddition of a trans-cyclohexene intermediate with a molecule of cis-cyclohexene.[15] Since one face of the trans-cycloalkene C=C bond is shielded by a polymethylene bridge, the trans-cycloalkene is restricted to a suprafacial reaction and the cis-cyclohexene must react antarafacially (Fig. 5-6). Such a process conserves orbital symmetry with respect to a C_2 axis of rotation.[95] Although trans-cyclohexene has been suspected as a reactive intermediate in photosensitized ionic addition reactions of cis-cyclohexene,[96] the highly strained trans-cyclohexene intermediate is not stable at room temperature.[97] The latter may be coordinated with copper(I) and thereby derive a degree a stabilization. An analogous complex **2** of trans-cycloheptene is isolable and stable at room temperature (see copper salts section).[16]

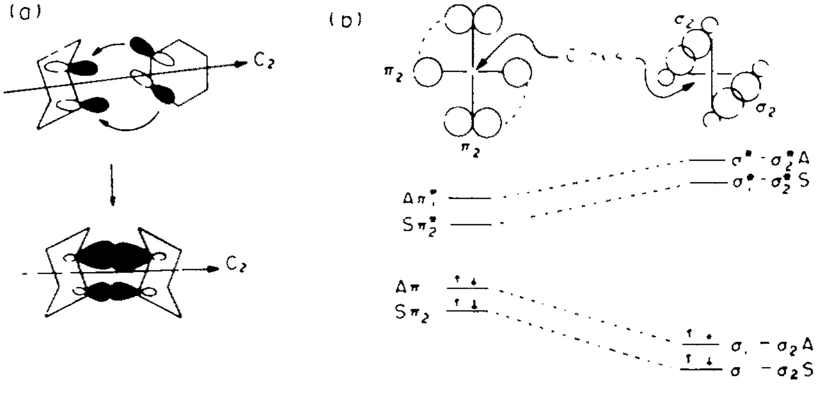
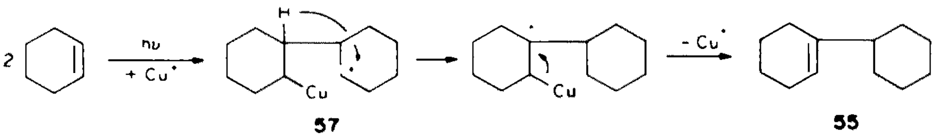
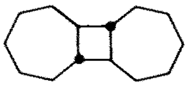


Fig. 5-6. (a) Cycloaddition of trans-cyclohexene (supra-facial) with cis-cyclohexene (antarafacial). (b) Orbital symmetry correlation diagram for the $[2_{\pi a}+2_{\pi s}]$ cycloaddition: $\pi_1 = \pi_s$ = trans-cyclohexene, $\pi_2 = \pi_a$ = cis-cyclohexene.[15]

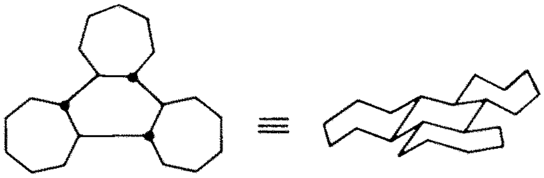
An attractive explanation for the CuOTf catalyzed photogeneration of **55** from cyclohexene involves generation of an intermediate carbenium ion **57** via LMCT excitation and cationic dimerization followed by .3 or two [1.2] hydride shifts and β-elimination of Cu(I)[1d]



Photocycloaddition of cycloheptene is also catalyzed by CuOTf. The major product was originally assumed to be the dimer **58** on the basis of symmetry revealed in its ^{13}C NMR spectrum and analogy with Cu(I)-catalyzed photocycloaddition of cyclohexene.[16] However, more thorough characterization of this major product (m.p. 128–130°) by mass spectroscopy revealed that it is a trimer, probably with



58



59

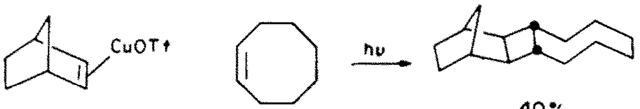
structure **59**.[98] A minor dimeric product (m.p. 66–68°), probably with structure **58**, is also generated.[98] The involvement of an isolable CuOTf complex **2** (see copper salts section 3a)[16] of trans-cycloheptene (t-CH) in the formation of **59** was suggested since heating **2** at 50° in cis-cycloheptene (c-CH) for a short time produces mainly **59**.[98] Although c-CH accelerates the thermal trimerization, crossover experiments revealed that cis-cycloheptene is *not* incorporated in the trimer **59** generated from (t-CH)CuOTf (**2**) heated in c-CH.[98] Furthermore, NMR evidence suggests the existence of a mixed complex **60** (eqn 5-15).[98] Since trans-cyclooctene forms an isolable 1:3 CuOTf-alkene complex,[17] formation of an analogous complex **61** from **60** (e.g. as in eqn 5-16) seems reasonable, and **61** is considered an immediate precursor of **59** (eqn 5-17).[98]

$$\underset{\mathbf{2}}{\text{(t-CH)CuOTf}} + \text{2c-CH} \rightleftharpoons \underset{\mathbf{60}}{\text{(c-CH)}_2\text{(t-CH)CuOTf}} \qquad (5\text{-}15)$$

$$\underset{\mathbf{60}}{\text{3(c-CH)}_2\text{(t-CH)CuOTf}} \rightleftharpoons \underset{\mathbf{61}}{\text{(t-CH)}_3\text{CuOTf}} + \text{2(c-CH)}_2\text{CuOTf} \qquad (5\text{-}16)$$

$$\underset{\mathbf{61}}{\text{(t-CH)}_3\text{CuOTf}} + \text{3c-CH} \xrightarrow{\Delta} \mathbf{59} + \text{(c-CH)}_3\text{CuOTf} \qquad (5\text{-}17)$$

Although CuOTf catalyzes cis→trans isomerization of cis-cyclooctene (c-CO), it does not promote photooligomerization.[91] However, UV irradiation of 1:1 BH-copper complex **62** in the presence of c-CO produces a mixed photocycloadduct.[91]



62

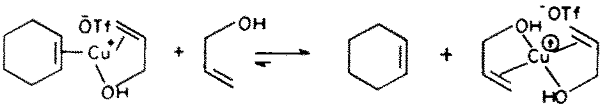
40%

Ref 91

(d) *Acyclic alkenes*

Recently, catalyzed photocycloadditions of functionally substituted alkenes have come under scrutiny since functional groups provide reactive centers for synthetically valuable transformations of the photocycloadducts. Allylic substituents are of special interest since they can facilitate useful transformations of the photoproducts involving cleavage or expansion of the cyclobutane ring (vide infra).

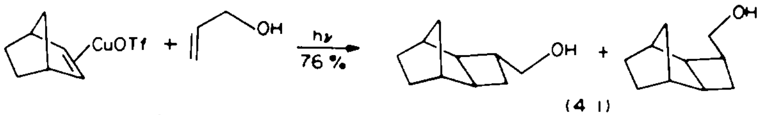
Although cyclohexene photodimerizes in the presence of CuOTf (see section 5a on cyclic monoenes), in allyl alcohol as solvent dimerization is blocked.[99] Apparently cyclohexene, which is a relatively poor ligand, cannot compete with allyl alcohol for coordination sites on copper. The 1:2 complex **64**[100] is strongly favored over the mixed ligand complex **63** required for cross cycloaddition (eqn 5-18). In



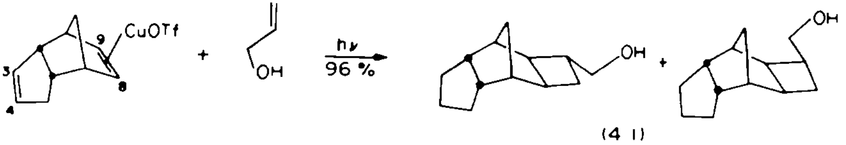
63 64

5-18

contrast, with the more strongly coordinating bicyclo[2.2.1]hept-2-ene or endo-dicyclopentadiene (DCPD) ligands, cross photocycloadditions are observed in the presence of CuOTf.[99] The reaction with

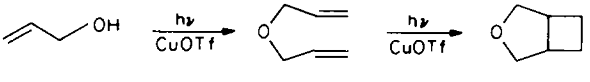


Ref 99



Ref 99

DCPD occurs regiospecifically at the 8,9-C=C bond since DCPD coordinates with Cu(I) preferentially as an exo-monodenate ligand at the 8,9-C=C bond.[17] Thus, allyl alcohol readily participates in Cu(I)-catalyzed photocycloadditions with cyclic alkenes which coordinate strongly with Cu(I). Concurrent photocycloadditions of allyl alcohol with itself were not observed. Photolysis of allyl alcohol in dilute solutions in dioxane in the presence of CuOTf does lead to photocycloaddition. However, the formation of 3-oxa-bicyclo-[3.2.0]heptane (**66**) was shown to involve intramolecular photocycloaddition of diallyl ether (**65**) and not intermolecular photocycloaddition of allyl alcohol.[101] The first step of this sequence is

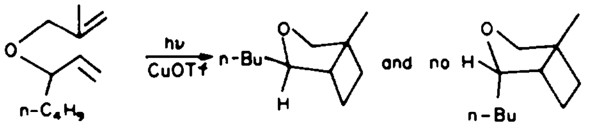


65 **66**

Ref 101

discussed further in section 10a. The **65**→**66** conversion was the first demonstration that CuOTf can catalyze photocycloaddition between *two* acyclic C=C bonds.

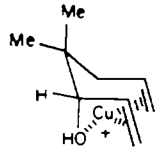
The generality and synthetic utility of this process is evident from the examples presented in Table 5-2.[102] The bicyclic ether products can be oxidized selectively by $NaIO_4$ with RuO_4 as catalyst to provide bicyclic lactones.[102] Table entries 4 and 5 show the high stereoselectivity achievable in such photobicyclizations. For example, photobicyclization of **67** gives **68** with an exo-n-butyl substituent and none of the endo-epimer **69**. Photobicyclization of diallyl ethers is also of value for synthesis of a large variety of multicyclic carbon networks (Table 5-3).[102]



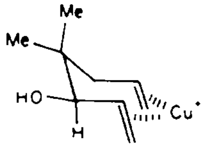
67 **68** **69**

Ref 102

Copper(I) catalyzed intramolecular photocycloaddition provides an effective new route for synthesis of bicyclo[3.2.0]heptan-2-ols **71** by photobicyclization of 1,6-heptadiene-3-ols **70** (Table 5-4).[103] In contrast with the **67**→**68** photobicyclization, the **70**→**71** transformations generally show a great preference for stereoselective generation of the less thermodynamically stable endo-2-hydroxy epimer (see Table 5-4). This selectivity is expected if **70** acts preferentially as a tridentate ligand as in **72** rather than a bidentate ligand as in **73**. Table 5-4 entry d is an exception which confirms the hypothesis. Thus, only for this diene

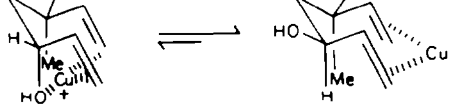


72



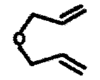
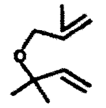
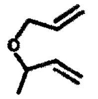
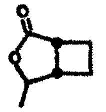
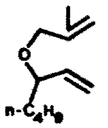
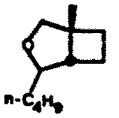
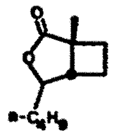
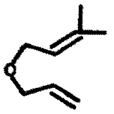
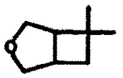
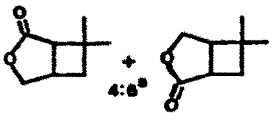
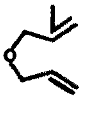
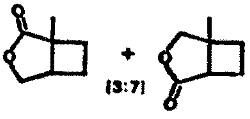
73

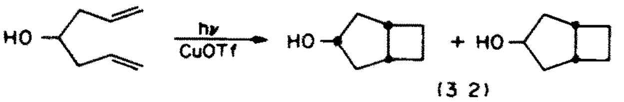
is a bidentate complex **75** favored over a tridentate complex **74** owing to unfavorable steric interference by a methyl substituent in the 5-position. Photobicyclization of 4-hydroxy 1,6-heptadiene with CuOTf as catalyst is also nonstereoselective.[101]



74 **75**

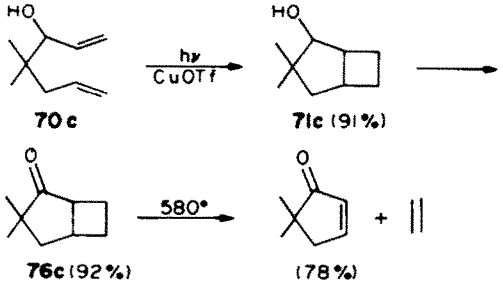
Table 5-2. CuOTf catalyzed photobicyclization of acyclic diallyl ethers and selective oxidation of the resulting 3-oxabicyclo[3.2.0]heptanes[102]

ENTRY	DIALLYL ETHER	PHOTOCYCLIZATION PRODUCT (% yield)		OXIDATION PRODUCT(S)	YIELD (%)	RXN. TIME
1			62		91	30 min
2			56		94	3 hr
3			54		44	6days
4			54		56	30min
5			83		83	5days
6			39			4hr
7			41		65	2hr



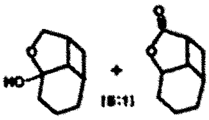
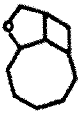
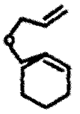
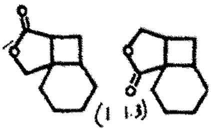
Ref 101

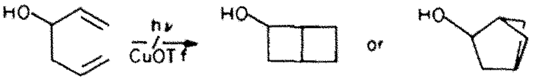
The only previous general method for synthesis of bicyclo[3.2.0]heptan-2-ones (e.g. **76c**) involves $2\pi + 2\pi$ photocycloaddition of cyclopent-2-en-1-ones.[104,105] Copper-catalyzed photobicyclization provides a topologically different route to **76c** by oxidation of **71c**. Furthermore, clean fragmentation of the cyclobutane ring at 580°, facilitated by the neighboring carbonyl functionality, affords cyclopent-2-en-1-ones (scheme 5-5).[106] It should be noted in this context that the success of the **70**→**71** photobicyclizations contrasts with the reported failure of 1,5-hexadiene-3-ol to undergo copper-catalyzed intramolecular photocycloaddition.[101]



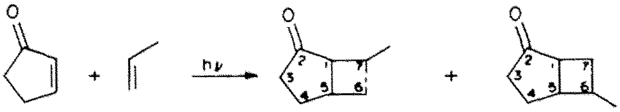
Scheme 5-5.

Table 5-3. CuOTf catalyzed photobycyclization of monocyclic diallyl ethers and selective oxidation of the resulting tricyclic ethers[102]

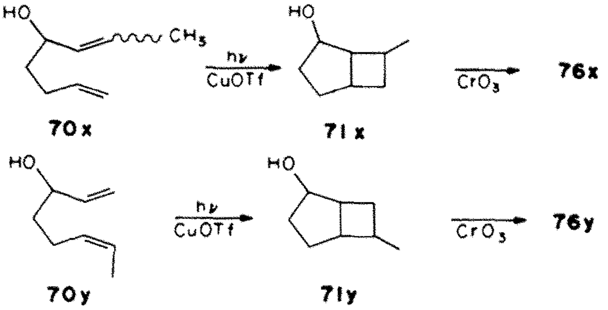
ENTRY	DIALLYL ETHER	PHOTOCYCLIZATION PRODUCT (% yield)		OXIDATION PRODUCT(S)	YIELD (%)	RXN. TIME
1			47		74	4 hr
2			36	 (8:1)	24	3 hr
3			55		56	7 days
4			28		87	30 min
5			35		82	30 min
6			35	 (1 1.3)	78	3 hr
7			94		65	12 hr



The structural specificity of the photobicyclization route to bicyclo[3.2.0]heptan-2-ones, which are versatile intermediates in organic synthesis,[107] will certainly find applications. Thus, whereas intermolecular photocycloaddition affords both **76x** and **76y**, photobicyclization of **70x** or **70y** followed by oxidation necessarily gives only **76x**[108] or **76y**[103] respectively.



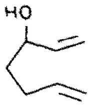
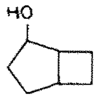
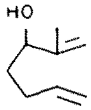
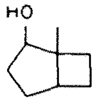
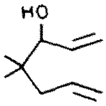
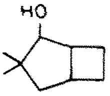
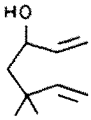
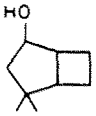
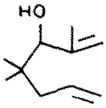
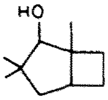
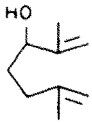
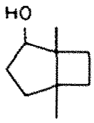
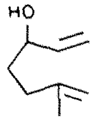
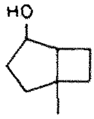
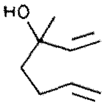
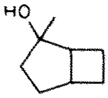
76x (57 43) **76y**



Ref 108

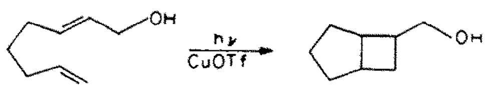
Ref 103

Table 5-4. Photobicyclization of 1,6-heptadiene-3-ols[103]

Entry	Diene **70**	Hyroxybicyclo-alkane **71**	Yield	endo:exo
a			86	9:1
b			81	6:1
c			91	9:1
d			84	3:4
e			83	3:2[a]
f			c	>20:1[b]
g			78	5:1
h			89	>20:1[b]

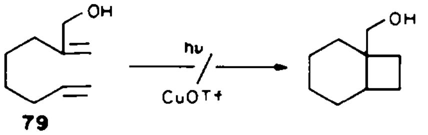
Besides the α-butenylallyl alcohols **70** discussed above, β and γ-pentenylallyl alcohols **77** and **78** also undergo clean photobicyclization in the presence of CuOTf as a catalyst. However no intramolecular photocycloaddition product could be isolated from irradiation of the homologous β-hexenylallyl alcohol

77 96 % Ref 103



78 93 % Ref 103

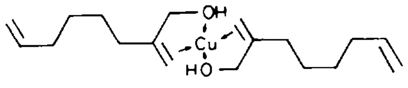
79 in the presence of CuOTf. The contrasting behavior of **77** and **79** probably results from a requirement



79

Ref 103

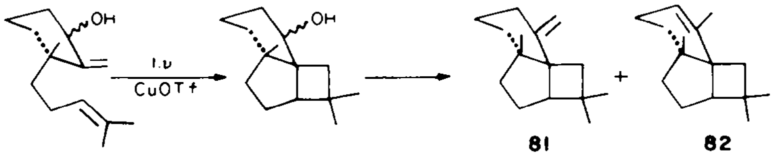
for coordination of both C=C bonds of the photobicyclization substrate with the copper(I) catalyst. This is readily achieved for **77** but less readily for **79** which may prefer to form a 2:1 complex **80**.



80

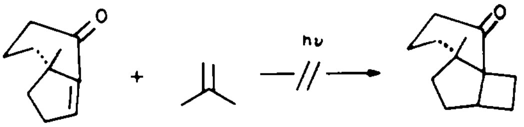
Ref 109

Copper catalyzed photobicyclization is also applicable to the construction of tricyclic ring systems from monocyclic β and γ-(4-pentenyl)-allyl alcohols. This novel synthetic method was applied as a key step in a total synthesis of α-panasinsene (**81**) and β-panasinsene (**82**), sequiterpenes obtained from ginsing.[109] Significantly an alternative synthetic approach to the requisite tricyclic ring system, involving photocycloaddition of isobutylene to an enone,[104] gave none of the required cycloadduct under a variety of conditions.



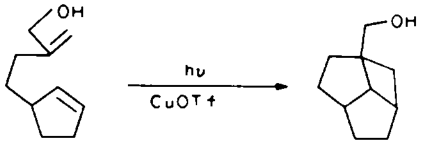
81 **82**

Ref 109



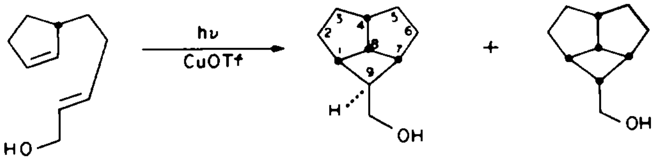
Ref 109

Allylic alcohol **83** is converted cleanly to **84** in excellent yield by UV irradiation in the presence of CuOTf as catalyst.[110] Photobicyclization of trans allylic alcohols **85**–**87** occurs nonstereospecifically



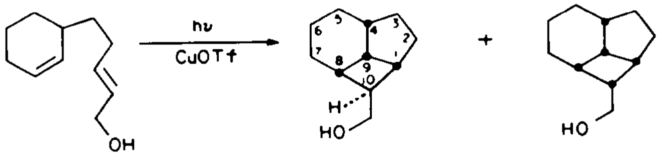
83 **84**

Ref 110



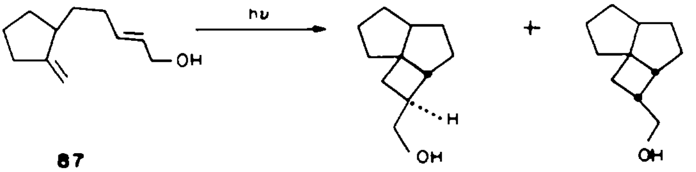
85 (60 %) (33%)

Ref 110



86 78% 16%

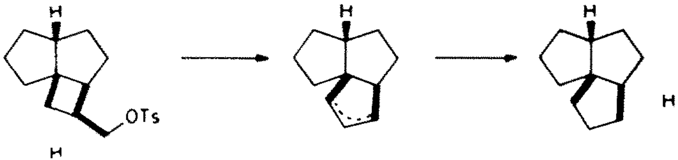
Ref 110



87 68% 23%

Ref 110

probably owing to competing copper(I)-catalyzed geometric isomerization. The utility of copper(I)-catalyzed photobicyclization of allylic alcohols in conjunction with solvolytic ring expansion for construction of a complex multicyclic carbon network was demonstrated with the cyclization product from **87**. Thus, tricyclo[6.3.0.0^{1,5}]undecane (**89**), a triquinane ring system found in the sesqiterpenes isocomene and pentalenic acid,[111] was prepared via tosylate **88**.[110]

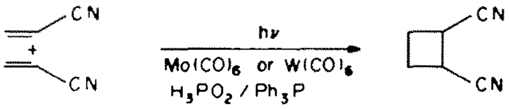


88

89

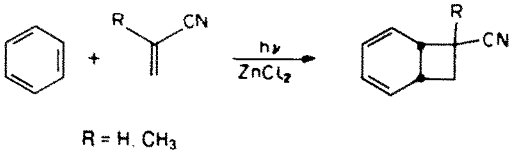
Ref 110

UV irradiation of acrylonitrile in the presence of Mo(CO)$_6$ or W(CO)$_6$ affords 1,2-dicyanocyclobutane.[112] Although acrylonitrile or methacrylonitrile undergo a $2\pi+2\pi$ cycloaddition with benzene



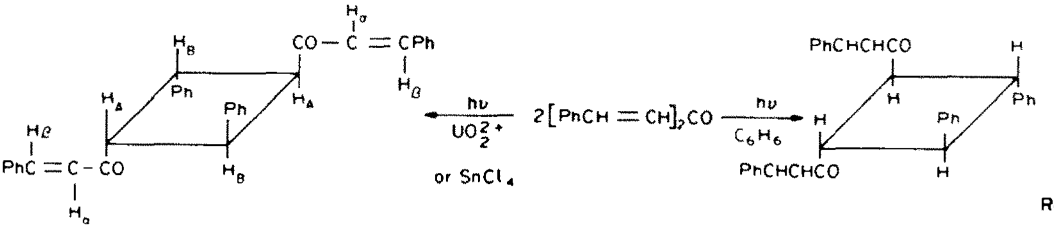
Ref 112

upon UV irradiation, a six fold increase in yield is observed in the presence of ZnCl$_2$ which forms a ground state complex with the reactants.[113] Photocycloaddition of trans,trans-dibenzylideneacetone



Ref 113

(DBA) in the presence of uranyl salts[114] or SnCl$_4$[115] affords head-to-tail dimer **90** in contrast with the photocycloaddition of free ketone which gives head-to-head dimer **91**.[116] A study of the crystal structure



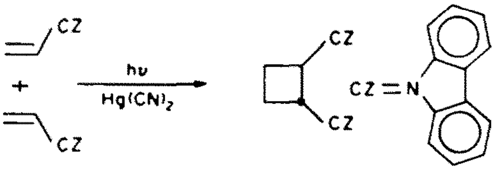
90

91

Ref 116

of bis(DBA)uranyl dichloride did *not* suggest that the uranyl salt influences the orientation of photodimerization by a template effect involving intramolecular reaction of two DBA molecules within the complex. Rather, this study suggested that dimer is produced intermolecularly, between DBA ligands of two molecules of complex, and the orientational effect of complexation results from a steric effect of the uranyl chloride group.[116]

Hg(CN)$_2$ catalyzes photodimerization of N-vinylcarbazole (VCZ) to afford 1,2-trans-dicarbazylcyclobutane whereas VCZ is photopolymerized in the absence of Hg(CN)$_2$.[117] Since Hg(CN)$_2$ has no effect on

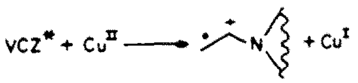


Ref 117

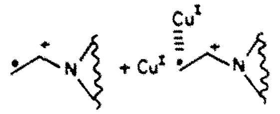
the UV spectrum of VCZ, it was assumed that the mercury salt exerts its catalytic influence after photoexcitation of VCZ, perhaps by facilitating intersystem crossing from a singlet to a triplet excited state. The reaction proceeds especially cleanly in the absence of oxygen.

Copper(II) perchlorate catalyzes *both* photopolymerization and photodimerization of VCZ, and oxygen is required to promote dimerization versus polymerization.[118] A chain mechanism outlined in eqns (5-19)–(5-27) which could account for $\Phi = 15$ was suggested.[118] Since the UV spectrum of VCZ is not altered by $Cu(ClO_4)_2$, the catalytic influence of copper is assumed to follow photoexcitation. Electron transfer from photoexcited VCZ to Cu^{II} generates $VCZ^{+\cdot}$ and Cu^I (eqn 5–20). The importance of VCZ^+ is supported by the observation that the rate of photodimerization is proportional to the donor-number (donating power to a cation) of the solvent. Production of dimer occurs via chain propagation steps 5-24 and 5-25. Polymerization is initiated by a complex of Cu^I and $VCZ^{+\cdot}$ (eqns 5-21 and 5-22). Oxygen, which is consumed during the catalyzed photodimerization, prevents polymerization by removing Cu^I from the system.

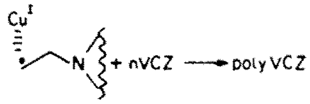
$$VCZ \xrightarrow{h\nu} VCZ^* \qquad (5\text{-}19)$$



(5-20)

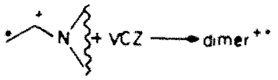


(5-21)

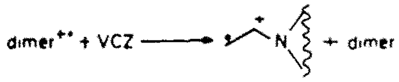


(5-22)

$$Cu^I + O_2 \longrightarrow Cu^{II} + O_2^{\dot{-}} \qquad (5\text{-}23)$$



(5-24)

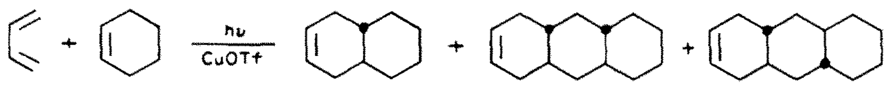


(5-25)

$$O_2^{\dot{-}} \longrightarrow \text{byproducts} \qquad (5\text{-}26)$$

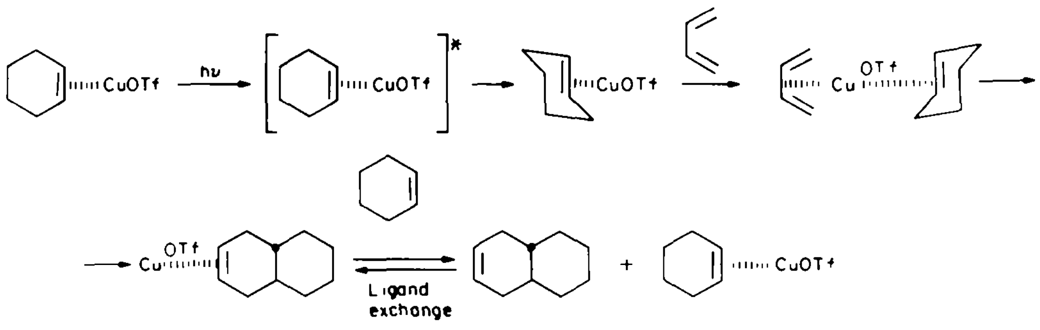
(5-27)

CuOTf catalyzes photoinduced $2\pi + 4\pi$ cycloaddition between cyclohexene and 1,3-dienes. This reaction exhibits several features which contrast with thermal Diels Alder reactions. Foremost is the



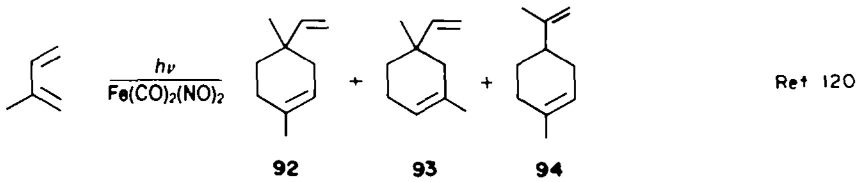
Ref 119

stereoselective generation of trans-Δ^2-octalin rather than a cis-cycloadduct expected for thermal $2\pi_s + 4\pi_s$ cycloaddition. Furthermore, whereas cyclopentene is more reactive than cyclohexene in thermal $2\pi + 4\pi$ cycloaddition, cyclopentene does not react with 1,3-butadiene upon irradiation in the presence of CuOTf as catalyst. A mechanism was proposed for the catalyzed photoreaction (Scheme 5-6) involving a key Cu(I) promoted photochemical cis-trans isomerization and $2\pi_s + 4\pi_s$ cycloaddition of the resulting trans-cyclohexene intermediate.[119]



Scheme 5-6.

Sunlight is reported to markedly accelerate $2\pi + 4\pi$ cyclodimerizations of 1,3-butadiene and isoprene which are catalyzed by $Fe(CO)_2(NO)_2$ or (π-allyl)-$Fe(CO)_2NO$.[120] The major products **92** and **93** are the same for the photoinduced and thermally induced *catalyzed* cyclodimerizations, but differ from the

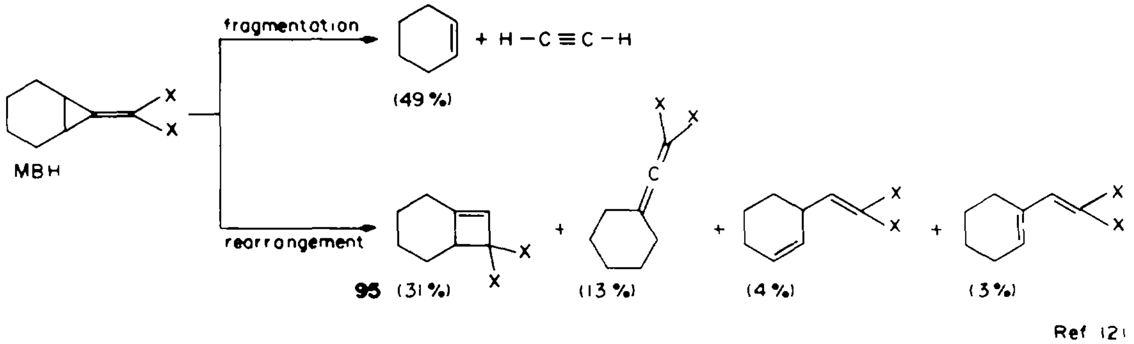


major product **94** of uncatalyzed thermal dimerization. Therefore, thermal or photochemical decomposition of the nominal catalyst was presumed to generate the same "active catalyst" which promotes a thermal cycloaddition.

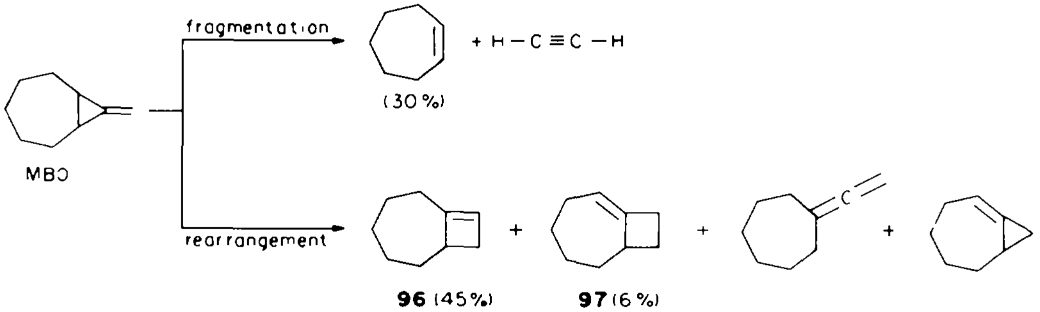
6. SKELETAL REARRANGEMENTS OF ALKENES

(a) *Copper(I) catalysis of alkene rearrangement and fragmentation*

UV irradiation of 7-methylenebicyclo[4.1.0]heptane (MBH) in the presence of CuOTf as catalyst generates an unusual array of products of skeletal rearrangement of fragmentation.[121] The cyclobutene product **95** is highly significant mechanistically (vide infra). The possibility that **95** might be produced

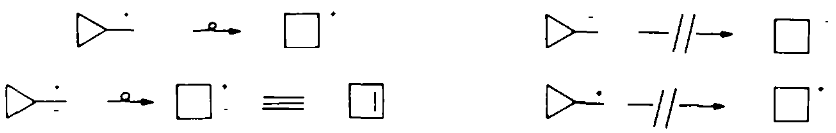


indirectly from 1-vinylcyclohexene via copper(I)-catalyzed photocyclization of this 1,3-diene was excluded by a control experiment. In fact, an earlier claim that CuCl catalyzes a similar rearrangement of 1,3-butadiene[84a,122] was later retracted.[123] The homologous 8-methylene-bicyclo[5.1.0]octane (MBO) upon UV irradiation in the presence of CuOTf also affords a multitude of skeletal rearrangement and fragmentation products.[124] These include cyclobutene **96** and methylenecyclobutane **97**. Photoisomerization of methylenecyclopropanes to give cyclobutenes such as **95** from MBH and **96** from MBO, or methylenecyclobutanes such as **97** from MBO, is unprecedented. Their formation is considered to be presumptive evidence for a reactive intermediate having a vacant orbital on the exocyclic cyclopropyl carbinyl carbon atom. Thus, ring expansion of cyclopropyl derivatives to give cyclobutyl derivatives is

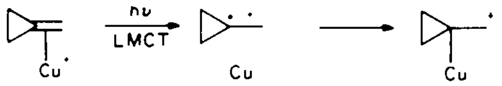


Ref 124

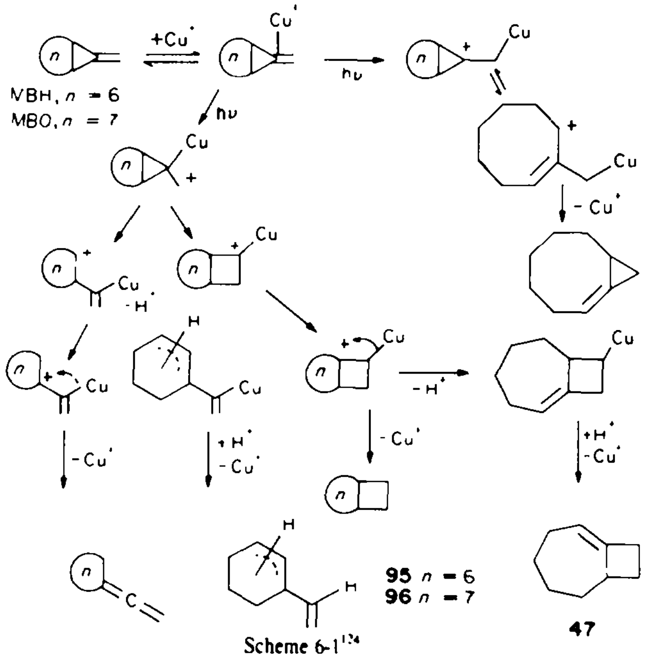
well precedented for cyclopropylcarbinyl carbenes[125] or carbenium ions[126] but not for cyclopropylcarbinyl carbanions or radicals.[127] A cyclopropylcarbinyl carbenium ion intermediate might be produced



from a methylenecyclopropane upon UV irradiation in the presence of copper(I) by LMCT excitation. Thus, electron transfer from the alkene ligand to the copper catalyst might be followed by bonding between the resulting Cu(O) radical and the organic cation radical to afford a η^1-β-copper(I)-carbenium ion intermediate. The overall process, i.e. light-induced transformation of a η^2-copper(I)-alkene complex

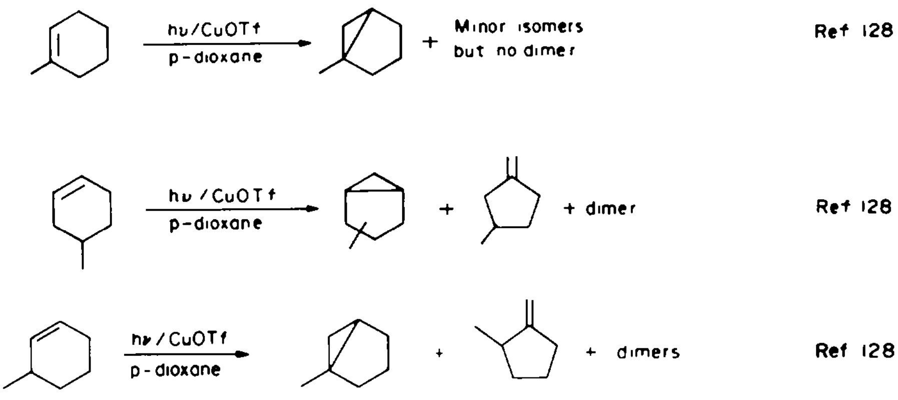


into a η^1-β-copper(I)-carbenium ion, has been termed photocupration.[124] Indeed, photocupration followed by well known carbenium ion reactions *might* account for all of the copper(I)-catalyzed photorearrangements observed for MBH and MBO as indicated in scheme 6-1.[124]

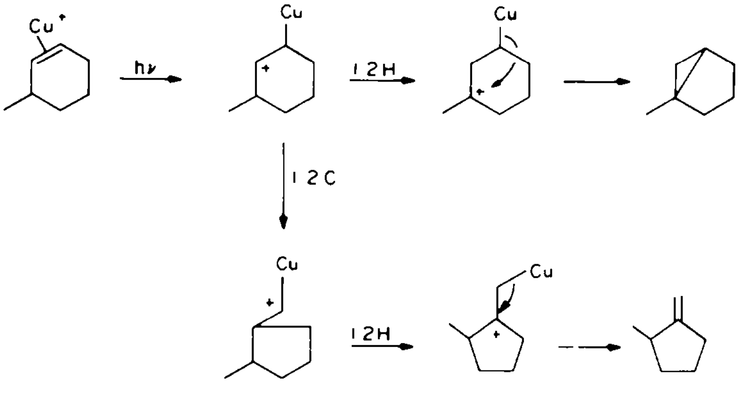


Scheme 6-1[124]

Photodimerization of cyclohexene (section 5c) upon irradiation in the presence of CuOTf is supplanted at very low cyclohexene concentrations by various skeletal rearrangement processes.[128] The primary photoproducts are bicyclo[3.1.0]hexanes and methylenecyclopentanes. The latter products are isomerized in the dark to 1-methylcyclopentenes. The products obtained from various isomeric methylcyclohexenes are typical. A possible mechanism for these rearrangements involving photocupration is

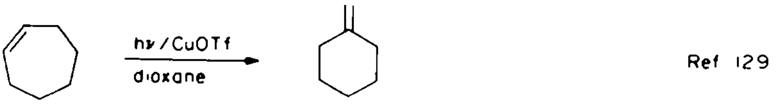


indicated in scheme 6-2 for 3-methylcyclohexene. A similar photorearrangement giving methylene-



Scheme 6-2

cyclohexene occurs upon UV irradiation of cycloheptene in dilute solutions in the presence of CuOTf.[129]

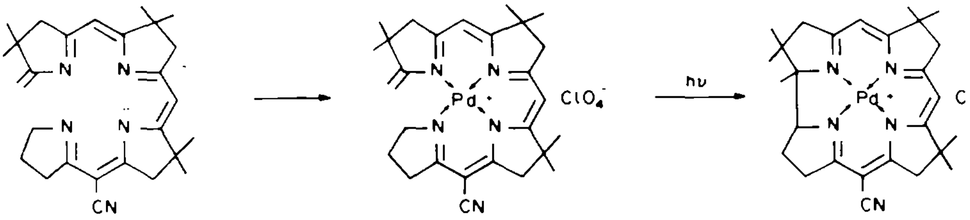


(b) *Photogeneration of alkene metathesis catalysts*

Alkene metathesis catalysts can be photogenerated from $W(CO)_6$ and CCl_4,[130-136] CBr_4,[130c] or MX_n[136] including $TiCl_4$, $ZrCl_4$, $HfCl_4$, and WCl_6, as well as i-$BuAlCl_2$.[137] For the $W(CO)_6$–CCl_4 system, photogeneration of $W(CO)_5$ and $W(CO)_5Cl$ was demonstrated, and assumed to be involved in catalyst activation.[130] Formation of $W(CO)_4Cl_2$ was also suggested[134] but has been questioned.[130c] The identity of the catalytically active entity in this system remains unknown. On the basis of the high stereoselectivity of the reactions catalyzed, the possibility of a halogen-bridged dinuclear structure was suggested.[132] Metathesis can be achieved in the dark with the photogenerated catalyst but continuous irradiation enhances catalytic effectiveness. Kinetic studies revealed that the active catalyst is deactivated by a process requiring the alkene substrate itself.[131] If the active catalyst is generated in the presence of alkene substrate, a small steady state concentration is established, and metathesis ceases soon after termination of irradiation. Similarly, the catalytic effectiveness of $W(CO)_6$-MX_n mixtures was sometimes much greater if the active catalyst was generated in situ, i.e. in the presence of alkene.[136]

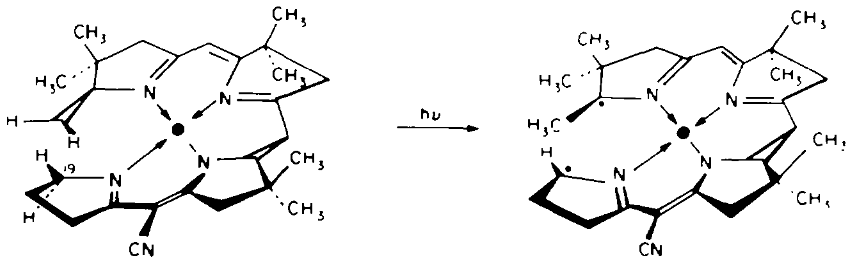
(c) *Metal salt catalysis of cycloisomerizations*

Coordination of the seco-corrinoid ligand **98** with palladium(II) allows photoisomerization to the corrin complex **99**.[138] This cyclization is postulated to involve a light-induced antarafacial sigmatropic 1,16-hydrogen transfer[139] followed by a thermally induced antarafacial electrocyclization.[95] Palladium(II) is a catalyst in the sense that it promotes the process without itself being consumed. No reaction occurs with the corresponding nickel(II) complex. The role of palladium(II) in facilitating cyclization is believed to be that of a template. Tetradentate coordination constraints **98** to adopt a nearly planar conformation in which this ligand coils around the metal ion such that one of the methylene hydrogens in position 19 lies directly underneath (or above) the exocyclic methylidene group as in **100**. The palladium ion also constrains the resulting ligand in **101** to adopt a coiled conformation suitable for antarafacial interaction of the termini of the conjugated 15-center 16-electron-π-system. The catalytic effectiveness of palladium(II) but not nickel(II) may inhere in the stronger tendency of the former than the latter toward planar coordination.[138]



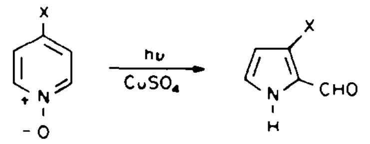
98 **99** (89%)

Ref 138



100 **101**

Though pyridine-N-oxides **102** give low yields of 2-formylpyrroles **103** upon UV irradiation in aqueous solution, a dramatic increase in yields occurs in the presence of certain copper(II) salts (Table 6-1).[140] However, cobalt(II), nickel(II), or Zn(II) do not seem to have any influence upon the photochemistry of **102**. The influence of counteranion on catalytic effectiveness parallels that found in the photoinduced oxidative cleavage of biacetyl to give acetic acid.[141] $CuSO_4$ and $Cu(ClO_4)_2$ were twice as effective as $CuCl_2$. If catalysis of **102** → **103** involves electron transfer, then it must occur from a first and



102 **103**

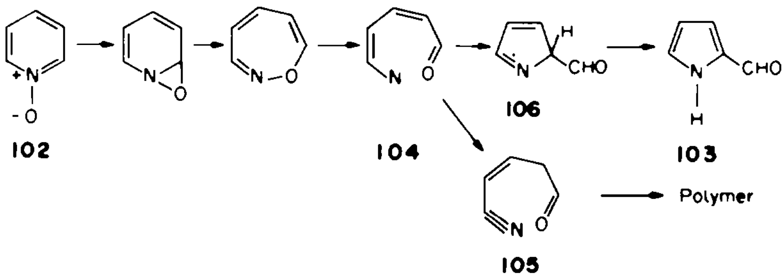
(a) X = H
(b) X = CH_3
(c) X = OCH_3
(d) X = $OCH_2C_6H_5$
(e) X = C_6H_5
(f) X = Cl
(g) X = CN

Ref 140

Table 6-1. Yields of 2-formylpyrroles **103** from pyridine-N-oxides **102** by UV irradiation in the presence and in the absence of copper sulfate[140]

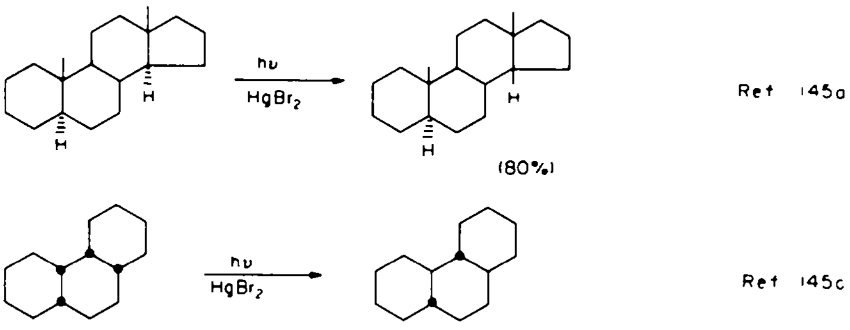
formylpyrrole 103	a	b	c	d	e	f	g
without $CuSO_4$	2.0%	1.5%	12%	4.5%	6.0%	1.6%	4.0%
with $CuSO_4$	42%	32%	40%	32%	33%	35%	40%

then back to a second intermediate since there is no overall change in oxidation level. As a hypothesis, a mechanism was suggested involving electron transfer from the nitrene **104** preventing its isomerization to the corresponding acrylonitrile **105** and favoring ring closure to pyrrolenine **106**.[140] Acrylonitrile derivatives (e.g. **105**) have been trapped during photolysis of pyridine N-oxides.[142] A marked decrease in the yield of 2-formylpyrrole is observed if acetonitrile is employed as cosolvent.[140b] This effect is suggested to result from stabilization of copper(I) and thus interference with back electron transfer.[143]



An alternative hypothesis which should be considered is that a copper(I) species is the actual catalyst which promotes conversion of nitrene **104** into intermediate **106** and that acetonitrile interferes with catalysis by competing with **104** for coordination sites on copper(I). Analogy for such a hypothesis may be found in carbenoid reactions of diazo compounds catalyzed by copper(I) species which can be generated in situ from nominal copper(II) catalysts.[144]

(d) *Mercury(II) bromide catalysis of hydrocarbon epimerization.* Epimerization about unactivated tertiary carbon atoms occur upon 254 nm irradiation in the presence of mercury(II) bromide.[145] This salt has absorption maxima at 198 and 236 nm and slowly decomposes to mercury(I) bromide and subsequently to mercury metal upon irradiation at 254 nm. However, neither mercury(I) bromide nor mercury metal nor cyclohexylmercury(II) bromide catalyze photoepimerization. Bromine radicals, generated by photolysis of mercury(II) bromide, are considered to initiate epimerization by abstraction of tertiary hydrogen since N-bromosuccinimide is also an effective catalyst for the photoepimerizations and since radical scavengers such as oxygen inhibit these isomerizations.[145]

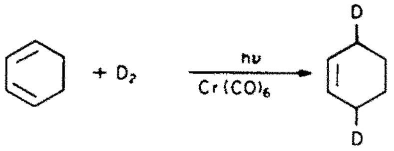


7. HYDROGENATION OF ALKENES

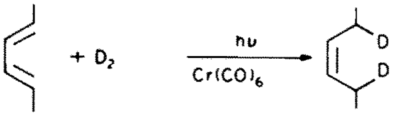
UV irradiation provides a simple and convenient method for generation of thermally active coordinatively unsaturated catalysts for alkene hydrogenation. Generally, however, with a judicious choice of ligands, thermally active catalysts are available which allow hydrogenation under similarly mild conditions without a requirement for photoactivation.

(a) *Chromium, molybdenum and tungsten catalyzed* 1,4-*addition of hydrogen to* 1,3-*dienes*

Although (arene)(Cr(CO)$_3$ complexes catalyze hydrogenation of 1,3-dienes at elevated temperatures,[146] Cr(CO)$_6$ is not similarly effective. In contrast, UV irradiation of 1,3-dienes with a catalytic amount of Cr(CO)$_6$ under an atmosphere of H$_2$ results in selective 1,4-addition of hydrogen at room temperature[147] whereas even prolonged photolysis in the presence of (mesitylene)Cr(CO)$_3$ yields no detectable hydrogenation at 25°.[2] The regiospecificityof photoinduced addition of deuterium with Cr(CO)$_6$ as catalyst allows specific labelling in the allylic positions of the monoene products.[148]



Ref 148



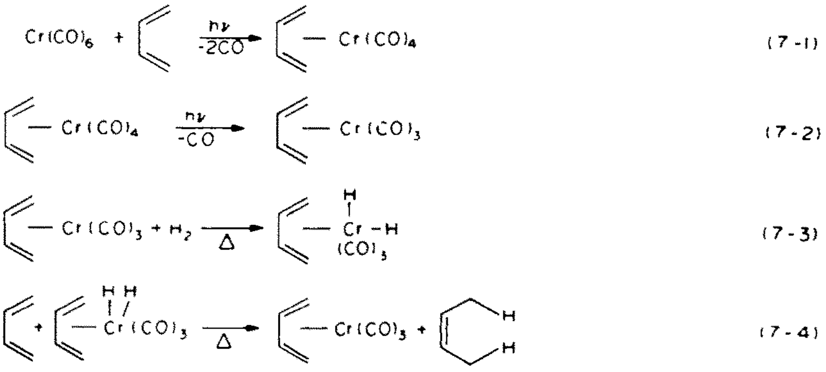
Ref 148

Moreover, reduction of acyclic 1,3-dienes generates cis-monoenes stereoselectively.[148] This stereoselectivity suggests that reduction of acyclic dienes occurs preferentially in an s-cis conformation. That an s-cis conformation is required for reduction is evidenced by the relative rates of reduction of stereoisomeric 2,4-hexadienes: trans,trans > cis,trans ≫ cis,cis.[149,150] Thus cis substituents on the diene sterically disfavor the required s-cis conformation. Cyclohexa-1,3-diene, which is constrained to a planar

107

s-cis conformation, is especially reactive whereas cis,cis-cycloocta-1,3-diene, which prefers a twisted conformation **107** is not reduced.[150a]

The importance of an s-cis conformation arises from its suitability for tetrahapto-coordination with chromium. Thus, (diene)Cr(CO)$_4$ complexes are generated during photoinduced hydrogenation of dienes (eqn 7-1). These complexes were isolated and shown to be intermediates in the photoinduced hydrogenation.[151] Subsequent steps in the mechanism of photogenerated catalysis (scheme 7-1) probably



Scheme 7-1.

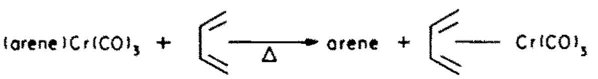
involve photodissociation to give a (diene)-Cr(CO)$_3$ unit (eqn 7-2) which is a thermally active catalyst for diene hydrogenation (eqns 7-3 and 7-4).[151] In fact hydrogenation continues thermally for several hours after cessation of irradiation as shown in the data in Table 7-1.[149] This mechanism accounts for the stereoselective generation of cis-monoalkenes which arise via hydrogen atom addition to the termini of a coordinated cisoid diene. (Arene)Cr(CO)$_3$ could produce a thermally active (diene)Cr(CO)$_3$ by replacement of the arene by a diene ligand (eqn 7-5). Since photoexcitation of (mesitylene)(Cr(CO)$_3$ only yields dissociation of CO (eqn 7-6), such arene complexes are not suitable precursors for photogenerated catalysts. Since the acetonitrile ligands in (CH$_3$CN)$_3$Cr(CO)$_3$ are thermally especially labile, this complex catalyzes 1,4-addition of hydrogen to 1,3-dienes at low temperature (40°) in the dark presumably via

Table 7-1. Chromium carbonyl photocatalyzed hydrogenation of 2-methyl-1,3-butadiene[149]

Time irradiated[a] at 10°, hr	Time thermolyzed at 25°, hr	%hydrogenation
1	0	6.5
1	18	14.3
1	0	6.0
1	15	14.9

[a] $Cr(CO)_6$ initially 2×10^{-3}M, diene initially 10^{-1}M, and hydrogenation product from continuous photolysis and dark thermolysis is 2-methyl-2-butene.

(diene)$Cr(CO)_3$.[152] Similar thermal catalysis of 1,4-addition of hydrogen to 1,3-dienes is also observed with $W(CO)_3(CH_3CN)_3$,[152] and both $Mo(CO)_6$ and $W(CO)_6$ are precursors for photogenerated catalysis for selective H_2 addition to s-cis 1,3-dienes.[149]

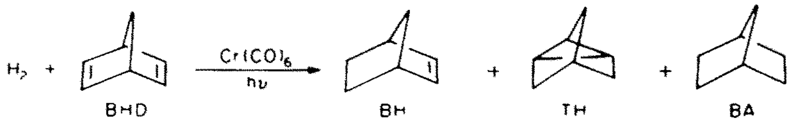


(7-5)

$$(\text{mesitylene})Cr(CO)_3 \xrightarrow{h\nu} (\text{mesitylene})Cr(CO)_2 + CO \qquad (7\text{-}6)$$

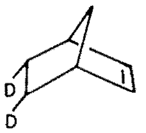
(b) *Chromium, molybdenum and tungsten catalyzed reduction of bicyclo*[2.2.1]*hepta*-2,5-*diene* (*BHD*)

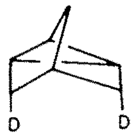
Both $Cr(CO)_6$ and (BHD)$Cr(CO)_4$, which is generated from the former upon irradiation in the presence of BHD, are catalysts for photoinduced hydrogenation of BHD.[147,153] Under 1 atm of H_2 the products are bicyclo[2.2.1]hept-2-ene (BH) and tricyclo[2.2.1.$0^{2,6}$]heptane (TH). At higher H_2 pressures (>40 atm) bicyclo[2.2.1]heptane (BA) becomes a significant product.[154] Deuteriation of BHD affords



Ref 154

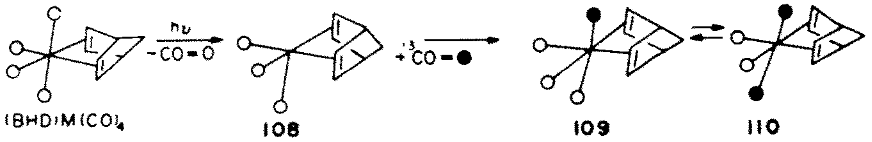
endo,endo-5,6-dideuterio BH and 3,5-dideuterio TH.[148] In spite of extensive investigations of these and



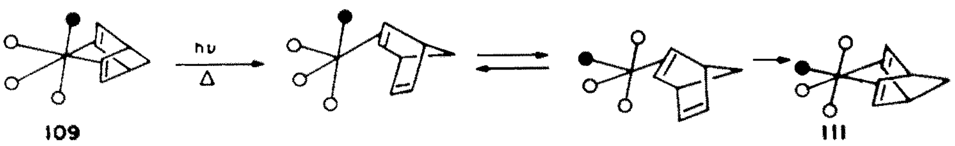


similar reactions with the corresponding molybdenum and tungsten complexes as catalysts, mechanistic understanding remains incomplete.

Important insights come from a study of photoinduced incorporation of ^{13}CO into (BHD)$M(CO)_4$(M = Cr, Mo, W).[155] These complexes readily incorporate ^{13}CO upon photolysis at >280 nm. Furthermore, for the Mo and W derivatives, ^{13}CO incorporation occurs preferentially at an axial position (i.e. cis to the alkene ligand) to give **109** presumably via tricarbonyl intermediate **108**. Upon



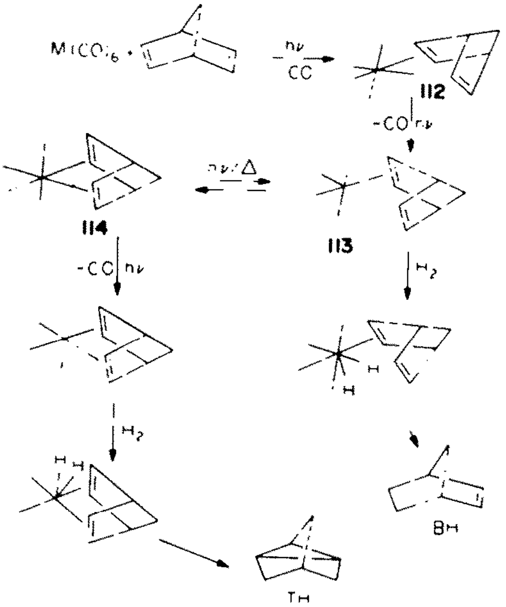
further irradiation a similar process affords **110** in competition with a different process which interconverts **109** with the trans isomer **111**. The **109→111** interconversion, which also occurs thermally, is



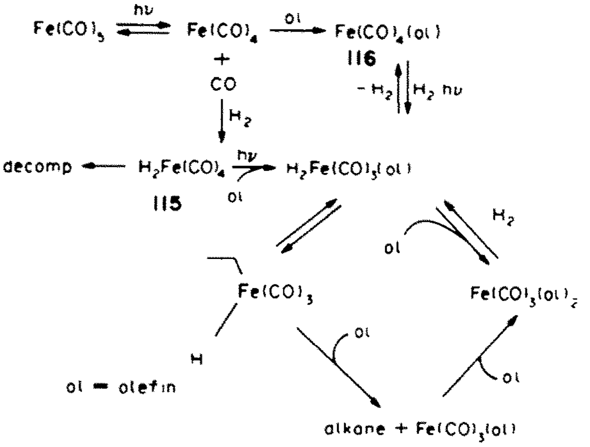
considered to involve thermal or photodissociation of one C=C bond and pseudorotation in a pentacoordinate intermediate. The activation parameters for the thermal **109 → 111** rearrangement closely resemble those observed for thermal substitution processes involving chelate ring-opening. Analogous processes are assumed for (BHD)Cr(CO)$_4$.

Some additional observations are noteworthy. Thus, thermal hydrogenation of (BHD)M(CO)$_4$ occurs under conditions where opening of the metal-alkene chelate is presumed (60°). resulting in exclusive production of BH.[155] Also, photoinduced hydrogenation of BHD with Cr(CO)$_6$ produces TH and BH in a constant ratio of 1.9 but with Mo(CO)$_6$ or W(CO)$_6$ BH predominates strongly ($< 7\%$ TH). However, with (BHD)M(CO)$_4$ as catalyst precursors, product ratios were 0.25–0.50 (M = Mo) and 2.0–4.0 (M = W).

A mechanism which can accomodate all of these observations is outlined in scheme 7-2. Starting with M(CO)$_6$ a pentacarbonyl metal-η^2-BHD complex **112** is formed initially. In fact, the (CO)$_5$W(BHD) species was observed spectroscopically in large quantities upon irradiation of W(CO)$_6$ in the presence of BHD.[155] Photodissociation of CO from **112** gives a tetracarbonyl metal-η^2-BHD complex **113** which can react directly with hydrogen yielding BH or collapse to tetracarbonyl metal-η^4-BHD complex **114**. TH arises only by photodissociation of a CO ligand from **114**. Clearly, production of BH is more likely with M(CO)$_6$ as a catalyst precursor than with (BHD)M(CO)$_4$ (**114**). However, this mechanism does not address the question of bicyclo[2.2.1]heptane (BA) formation. Also, while the rate of BH formation is roughly proportional to H$_2$ pressure as might be expected for scheme 7-2, the rate of TH formation is unexpectedly independent of H$_2$ pressure (Fig. 7-1).[154] Dissociation of CO from **114** must be virtually



Scheme 7-2.



Scheme 7-3.

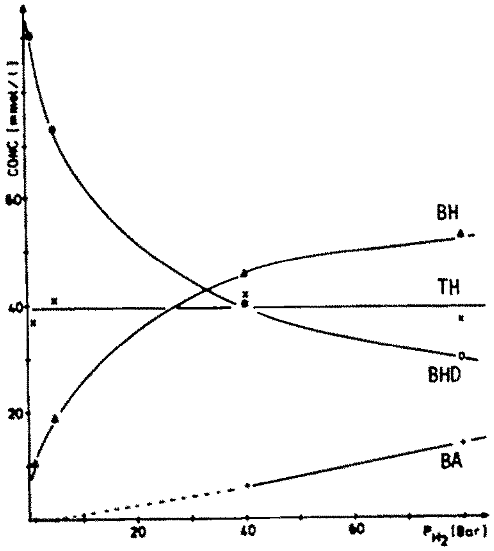


Fig. 7-1. Photochemical hydrogenation of BHD at various hydrogen pressures. -O-O-: concentration of BHD, -Δ-Δ-: concentration of BH, -×-×-: concentration of TH, -+-+-: concentration of BA (mmol l^{-1}) after 1 hr of irradiation.[154]

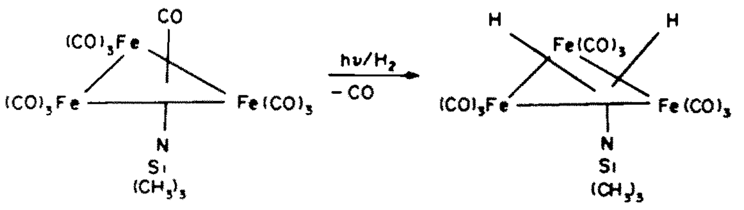
irreversible in competition with reaction of the resulting coordinatively unsaturated intermediate with hydrogen yielding TH.

(c) *Iron, ruthenium and osmium catalyzed hydrogenation*

While hydrogenation of alkenes with $Fe(CO)_5$ as catalyst occurs only at high temperatures (~150°),[156] with UV irradiation such reductions occur even below 0°.[55d] The scope and selectivity of these reductions is indicated by the examples in Table 7-2. Monoalkenes are readily reduced while reduction of 1,3-dienes and alkynes is sluggish. In fact, reduction of monoalkenes is inhibited by conjugated dienes as is photoinduced allylic [1.3] hydrogen shift (Table 7-3), which is also catalyzed by $Fe(CO)_5$ (see section 4c). Isomerization accompanies hydrogenation (Table 7-4) although isomerization is *not* accelerated by hydrogen.[55d] Rearrangement of unsaturated alcohols to carbonyl derivatives occurs with the complete exclusion of hydrogenation.

A multiphoton process was proposed for photoinduced hydrogenation catalyzed by $Fe(CO)_5$ (scheme 7-3). This mechanism includes a purely thermal cycle since quantum yields > 1 were observed.[55d] The photogenerated catalyst is considered to be $(CO)_3FeH_2$(alkene) rather than $(CO)_4FeH_2$ (**115**) since the latter is a very inefficient hydrogenation catalyst at lower temperatures where photoinduced catalysis occurs readily. The inhibitory effect of conjugated dienes is considered evidence for the involvement of $Fe(CO)_3(ol)_2$ in the thermal cycle since removal of this intermediate from the cycle by formation of stable $Fe(CO)_3$(diene) complexes is expected. Photodissociation of a carbonyl ligand facilitates formation of dihydride **115** or monoalkene complex **116**. However, hydrogenation requires generation of further coordinative unsaturation by a second carbonyl photodissociation from **115** or **116**.

Irradiation (≥366 nm) of trinuclear iron complex **117** under an atmosphere of hydrogen generates dihydride complex **118** via photidissociation of a carbonyl ligand. Although **118** is not a catalyst for hydrogenation in the dark, under UV irradiation a catalyst is photogenerated by photodissociation of a



117 **118**

Table 7-2. Photoinduced $Fe(CO)_5$ catalyzed hydrogenation of olefins[a,156]

Starting alkene	Irradiation time, min	Product (% conversion)
Ethylene	**60**	**Ethane (16.7)**
Propylene	**60**	**Propane (46.7)**
***cis*-3-Hexene**	**60**	***n*-Hexane (30.8)**
2-Methyl-2-butene	**60**	**2-Methylbutane (26.9)**
***cis*-3-Methyl-2-pentene**	**110**	**3-Methylpentane (32.0)**
2,3-Dimethyl-2-butene	**60**	**2,3-Dimethylbutane (13.6)**
Cyclopentene	**60**	**Cyclopentane (47.0)**
Cyclohexene	**60**	**Cyclohexane (33.1)**
Cycloheptene	**60**	**Cycloheptane (53.2)**
***cis*-Cyclooctene**	**60**	**Cyclooctane (53.5)**
1-Methylcyclopentene	**60**	**Methylcyclopentane (26.3)**
Methylenecyclopentane	**70**	**Methylcyclopentane (40.0)**
1,2-Dimethylcyclopentene	**60**	**No reaction**
1,2-Dimethylcyclohexene	**60**	**No reaction**
α-Methylstyrene	**60**	**No reaction**
2,3-Pentadiene	**60**	**No reaction**
2-Cyclohexen-1-one	**180**	**Cyclohexanone (4.1)**
***cis*-1,3-Pentadiene**	**300**	**Pentenes (4)**
***trans*-1,3-Pentadiene**	**400**	**Pentenes (8.5)**
***cis,cis*-2,4-Hexadiene**	**315**	**Linear hexenes (30.0)** ***n*-Hexane (4.7)**
***trans,trans*-2,4-Hexadiene**	**305**	**Linear hexenes (35.0)** ***n*-Hexane (4.7)**
Acetylene	**35**	**Ethylene (0.4)**
Diethylacetylene	**60**	**Linear hexenes (~6.0)**
Diphenylacetylene	**160**	***cis*-Stilbene (5.0)** ***trans*-Stilbene (3.5)**

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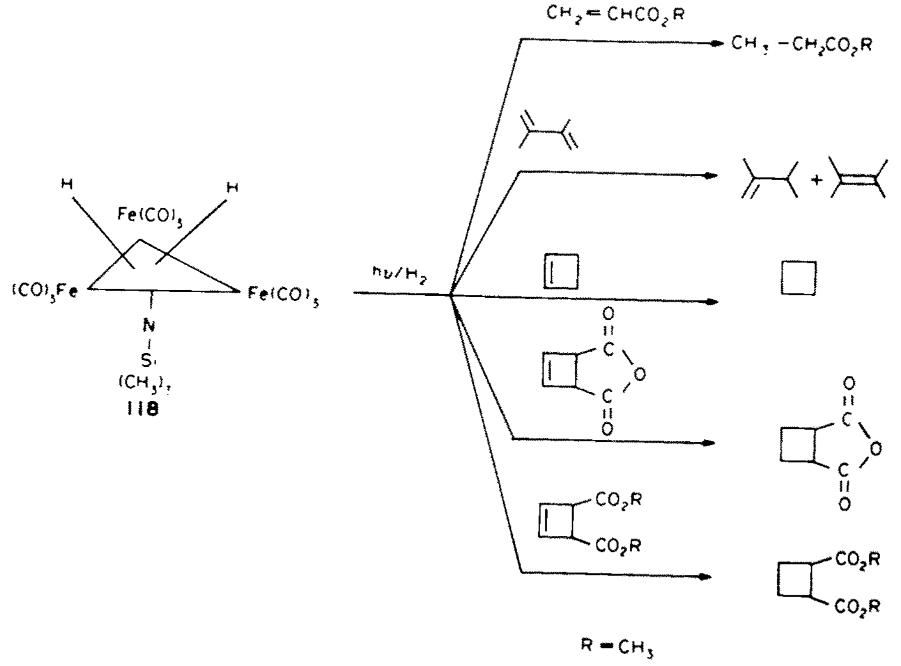
[a] **Irradiation with near-uv (300–380 nm) light ~$10^{-5}-10^{-6}$ einstein/min; $Fe(CO)_5$ is initially 0.011 *M*; temperature is 25°C.**

second carbonyl ligand.[157] In the presence of phosphines, the photodissociated carbonyl is replaced by a phosphine ligand but the phosphine complex is not an effective precursor for photogeneration of a hydrogenation catalyst. The photogenerated catalyst from **118** recombines readily with the dissociated



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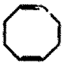
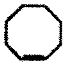
Ref 157

Table 7-3. Quenching of photoinduced $Fe(CO)_5$ catalyzed 1-pentene isomerization by 1,3-dienes[a,55d]

[1-Pentene], *M*	Quencher (*M*)	Irradiation time, min	% conversion to 2-pentene
1.0	None	120	10.2
1.0	 (0.01)	120	6.0
1.0	 (0.1)	120	1.1
1.0	 (1.0)	120	0.2_5
1.0	 (0.01)	120	8.9
1.0	 (0.1)	120	6.2
1.0	 (1.0)	120	1.8

[a] All samples were irradiated in parallel in a 366-nm merry-go-round (~10^{-7} einstein/min) at 20°C. The 3.0-ml degassed ampules contained 0.011 *M* $Fe(CO)_5$ in benzene.

Table 7-4. Photoinduced $Fe(CO)_5$ catalyzed hydrogenation vs isomerization[a,55d]

Olefin (*M*)	Irradiation time, min	Product(s) (% conversion)
 (0.1)	60	 (8.9),  (7.3)
 (0.1)	60	 (30.8), linear hexenes (5.2)
 (0.18)[b]	15	 (5.6),  (17.8)  (71.0)
 (0.1)	60	 (~100)
 (0.1)	60	 (~100)

[a] 25°C, 0.011 *M* $Fe(CO)_5$ in benzene or toluene, 10–14 psi H_2, near-uv irradiation. [b] D_2 used

carbonyl ligand. Thus hydrogenation ceases upon termination of the irradiation unless the carbonyl ligand is swept from the system during photolysis by a stream of hydrogen.[157]

Known catalysts of thermal alkene hydrogenation have been generated in situ by UV irradiation of osmium and ruthenium complexes. Thus irradiation of $Os_3(CO)_{12}$ under hydrogen affords $Os_2H_2(CO)_{10}$ which catalyzes hydrogenation of 1-pentene.[46] $RuHCl(CO)(PPh_3)_3$, is a catalyst precursor for hydrogenation of 1-hexane.[158] $RuHCl(PPh_3)_3$, a known thermally active hydrogenation catalyst,[159] is thus generated in situ from the carbonyl complex by photodissociation of the carbonyl ligand. However, a nonphotochemical method for generation of $RuHCl(PPh_3)_3$ in situ from $RuCl_2(PPh_3)_3$[159a] may actually be preferable since the photochemical route from $RuHCl(CO)(PPh_3)_3$ also generates some $RuHCl(CO)_2(PPh_3)_2$ which is catalytically inactive.[160]

(d) *Cobalt, rhodium and iridium catalyzed hydrogenation*

Light promotes hydrogenation of 1,3-butadiene in the presence of the 2,2′-bipyridine (bpy) complex $CoH_2(bpy)(PBu_3)_2ClO_4$.[161] The role of light in the photoinduced hydrogenation is not known although light was shown to promote reductive elimination of hydrogen from the cobalt complex. Photoinduced extrusion of phosphine may generate a coordinatively unsaturated intermediate which coordinates diene leading to reduction.[1e]

Although $RhH(CO)(PPh_3)_3$ is a thermally active hydrogenation catalyst, its activity is lost owing to a competing thermally irreversible dimer formation (eqn 7-7).[162] Hydrogenation of ethyl acrylate with spent

$$2RhH(CO)(PPh_3)_2 \longrightarrow [Rh(CO)(PPh_3)_2]_2 + H_2 \qquad (7\text{-}7)$$

catalyst can be achieved under continuous UV irradiation.[163] The photoinduced catalytic reduction is similar in rate to the original thermal catalysis. The photoinduced catalysis may arise from photochemical dissociation of the catalytically inactive dimer, or photo-dissociation of carbonyl or phosphine ligands. Similarly, UV irradiation accelerates hydrogenation of cyclooctene in the presence of $RhCl(PPh_3)_3$ in toluene, and the increased rate persists after termination of irradiation.[164] No mechanism has been suggested to explain this photogenerated catalysis. Although $RhCl(PPh_3)_3$ loses thermal catalytic activity owing to dimer formation according to eqn (7-8), UV irradiation of the spent catalyst

$$2RhHCl(PPh_3)_3 \rightarrow [RhCl(PPh_3)_2]_2 + 2\,PPh_3 \qquad (7\text{-}8)$$

induces hydrogenation. While this behavior might be the result of photochemical dissociation of the dimer,[1e] catalytic activity is only generated in the presence of hydrogen. Thus, irradiation does not reverse eqn (7-8).

Hydrogenation of alkenes in the presence of $IrCl(CO)L_2$ ($L = PPh_3$, $P(i\text{-}C_3H_7)_3$, $P(C_6H_{11})_3$, $P(OPh)_3$) is often accelerated upon UV-irradiation.[165] Since the acceleration is greater for some substrates than for others, it is sometimes possible with irradiation to achieve selective hydrogenations not possible thermally. Thus, $IrCl(CO)(PPh_3)_2$ catalyzes selective hydrogenation of 1,3-cyclohexadiene under UV irradiation but not thermally. Furthermore, since hydrogenation of cyclohexene is not accelerated by UV irradiation, reduction of the dienes without further reduction of cyclohexene to cyclohexane is readily achieved photochemically but not thermally.[165b] Similarly, while both 2-butyne-1,4-diol and 2-butene-1,4-diol are hydrogenated slowly in the dark with $IrCl(CO)(PPh_3)_2$ as catalyst, the rate of reduction of the alkyne but not the alkene is strongly accelerated under UV irradiation.[165c] Thus, the alkyne can be selectively hydrogenated to the alkene. For various complexes $IrCl(CO)L_2$, catalytic activity varies with the identity of the phosphorous ligand L, and the effect of L may be different for thermal and photoactivated reductions. For example, with ethyl acrylate as substrate, the most effective catalyst of thermal hydrogenation ($L = P(OPh)_3$) is the least effective catalyst for photoactivated hydrogenation. However the influence of L on catalytic effectiveness also depends on the identity of the substrate so that no generalizations can be made.[165e]

$$HOCH_2C{\equiv}CCH_2OH \xrightarrow[h\nu]{IrCl(CO)(PPh_3)_2} HOCH_2CH{=}CHCH_2OH \qquad \text{Ref. 105c}$$

Under an atmosphere of hydrogen, $IrCl(CO)(PPh_3)_2$ forms a dihydride. Hydrogenation of a substrate S requires coordination with $IrCl(CO)(PPh_3)_2$ as in eqns (7-10)-(7-13).[166] Therefore, irradiation might promote hydrogenation by inducing reductive elimination of hydrogen from the dihydride (eqn 7-9).[167] An additional mode of photoactivation (eqns 7-14 and 7-15) was suggested[165a] which finds analogy with the photochemical behavior of $IrH_3(PPh_3)_3$.[1e] An *irreversible* increase in the concentration of $IrCl(CO)PPh_3$ could result from photoinduced oxidation of a phosphine ligand (eqn 7-16).[166a] Similarly, photodissociation of a CO ligand (en 7-17) that might be swept from the reaction mixture, could *irreversibly* produce $IrCl(PPh_3)_2$ which is known to be a more active hydrogenation catalyst than $IrCl(CO)(PPh_3)_2$.[168]

$$IrH_2Cl(CO)(PPh_3)_2 \overset{h\nu}{\underset{\Delta}{\rightleftharpoons}} IrCl(CO)(PPh_3)_2 + H_2 \qquad (7\text{-}9)$$

$$IrCl(CO)(PPh_3)_2 + S \rightleftharpoons IrCl(CO)(PPh_3)_2S \qquad (7\text{-}10)$$

$$IrCl(CO)(PPh_3)_2S \rightleftharpoons IrCl(CO)(PPh_3)S + PPh_3 \qquad (7\text{-}11)$$

$$IrCl(CO)(PPh_3)S + H_2 \rightleftharpoons IrH_2Cl(CO)(PPh_3)S \qquad (7\text{-}12)$$

$$IrH_2Cl(CO)(PPh_3)S \longrightarrow IrCl(CO)(PPh_3) + SH_2 \qquad (7\text{-}13)$$

$$IrH_2Cl(CO)(PPh_3)_2 \xrightarrow{h\nu} IrH_2Cl(CO)(PPh_3) + PPh_3 \qquad (7\text{-}14)$$

$$IrH_2Cl(CO)(PPh_3) + S \longrightarrow IrH_2Cl(CO)(PPh_3)S \qquad (7\text{-}15)$$

$$\mathrm{IrCl(CO)(PPh_3)_2 + O_2 \xrightarrow{h\nu} IrCl(CO)PPh_3 + Ph_3P{=}O} \qquad (7\text{-}16)$$

$$\mathrm{IrCl(CO)(PPh_3)_2 \xrightarrow{h\nu} IrCl(PPh_3)_2 + CO\uparrow} \qquad (7\text{-}17)$$

Thermally, $IrH_3(PPh_3)_3$ catalyzes hydrogenation of terminal alkenes only.[169] Under UV irradiation $IrH_3(PPh_3)$ catalyzes hydrogenation of 2-hexene[170] presumably owing to generation of the less sterically demanding catalyst, $IrH_3(PPh_3)_2$,[169] by photodissociation of a phosphine ligand (eqn 7-18).[171]

$$\mathrm{IrH_3(PPh_3)_3 \xrightarrow{h\nu} IrH_3(PPh_3)_2 + PPh_3} \qquad (7\text{-}18)$$

(e) *Rhodium catalyzed transfer hydrogenation*

Cyclooctene is produced from 1,5-cyclooctadiene (COD) as a side product during rhodium catalyzed photorearrangement in ether (see rhodium chloride section 4a). The conversion-time profile (Fig. 7-2) reveals that the initial rate of appearance of the 1,4-diene equals the rate of disappearance of 1,5-diene. The rate of cyclooctene formation is initially small but increases rapidly after all of the 1,5-diene has been consumed. Thus, reduction mainly involves 1,4-diene and is inhibited by 1,5-diene. Also, irradiation of 1,4-COD in diethyl ether solution with $[RhCl(1,5\text{-}COD)]_2$ as catalyst gives 40% cyclooctene and 60% rearrangement products after 25% conversion.[36] Deuterium labeling experiments showed that the ether solvent is the source of hydrogen in the reductions. These are the first and only examples of photoinduced transfer hydrogenation. Importantly, rhodium(I) catalyzed thermal hydrogen transfer is insignificant at temperatures well below 120°, even for 1,4-dioxane which is a much more effective hydrogen donor than diethyl ether.[172] The photoinduced hydrogen transfer occurs below 20°. The role of UV light in the hydrogen transfer is most likely the same as in rhodium(I) catalyzed allylic photorear-

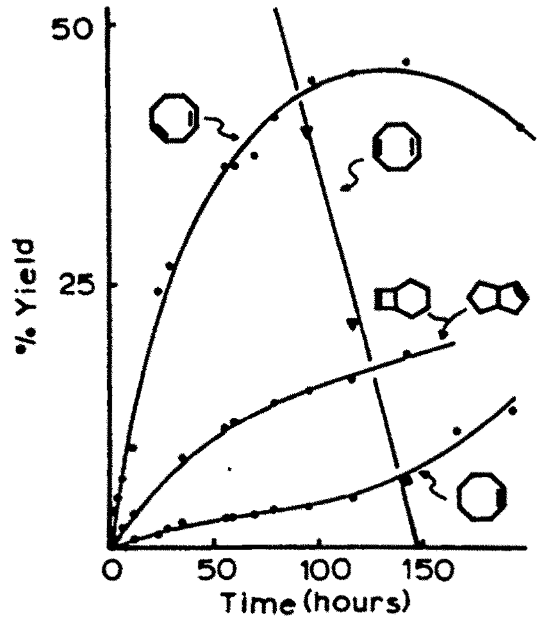
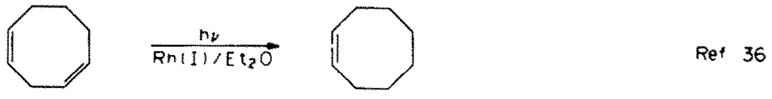


Fig. 7-2. Photolysis of 1,5-cyclooctadiene (COD) in diethyl ether solution in the presence of $[RhCl(1,5\text{-}COD)]_2$ as catalyst.[36]



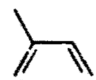
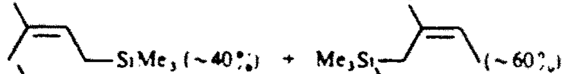
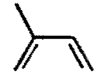
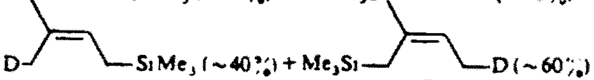
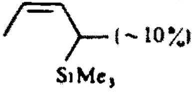
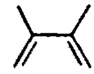
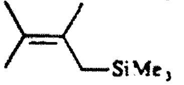
rangements (see scheme 4-2). Photodissociation of an alkene ligand generates a coordinatively unsaturated rhodium(I) species with an enhanced proclivity toward oxidative addition of the α-C–H bond of the ether solvent to rhodium(I), a reaction which is expected[172] to be inhibited by the strongly chelating 1,5-COD ligand. Hydrogenation of the alkene likely occurs by reaction with a rhodium(III) dihydride intermediate which is generated by β-elimination from the initially formed alkylrhodium(III) hydride.

8. ADDITIONS TO ALKENES

(a) *Reactions of alkenes with trialkylsilanes*

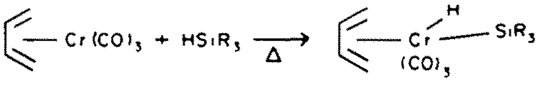
A synthetically valuable 1,4-hydrosilation of 1,3-dienes is achieved in high yields upon UV irradiation of an equimolar mixture of R_3SiH and diene in the presence of $Cr(CO)_6$ as catalyst (Table 8-1).[173]

Table 8-1 Synthesis of allylsilanes from 1,3-dienes by photoinduced $Cr(CO)_6$ catalyzed 1,4-hydrosilation[173]

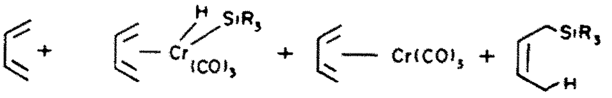
Starting diene	Starting silane	Product(s)[a]
	$HSiMe_3$	
	H_2SiPh_2	
	$HSi(OEt)_3$	
	H_2SiMe_2	
	$HSiMe_3$	
	$DSiME_3$	
	$HSiMe_3$	 
	$HSiMe_3$	

[a] Neat substrates in approximately 1:1 mole ratios. The deoxygenated solutions are saturated in $Cr(CO)_6$ and exposed to two 15W GE Black Light bulbs at 30°.

Although $Mo(CO)_6$ and $W(CO)_6$ are also catalytically active, their ability to promote isomerization (Table 4-5) leading to byproducts makes $Cr(CO)_6$ the catalyst of choice. The hydrosilations generate cis allylsilanes stereoselectively with good regioselectivity for addition of silicon to the least substituted terminus of the diene. These reactions are reminiscent of photoinduced $Cr(CO)_6$ catalyzed 1,4-hydrogenation of 1,3 dienes which requires a cisoid conformation since cis-1,3-pentadiene is unreactive, but the hydrosilation is sterically more demanding since 1,4-disubstituted dienes are unreactive. Irradiation is only required to initiate the reaction and the initial rate under continuous photolysis increases with temperature as expected for a photogenerated thermally active catalyst.[173] The actual catalyst is no doubt (diene)$Cr(CO)_3$ as for the analogous 1,4-hydrogenation (scheme 7-1), and the thermal catalytic cycle involves oxidative addition of silane to Cr(0) (eqns 8-1 and 8-2).[174] Although $(C_6H_6)Cr(CO)_3$



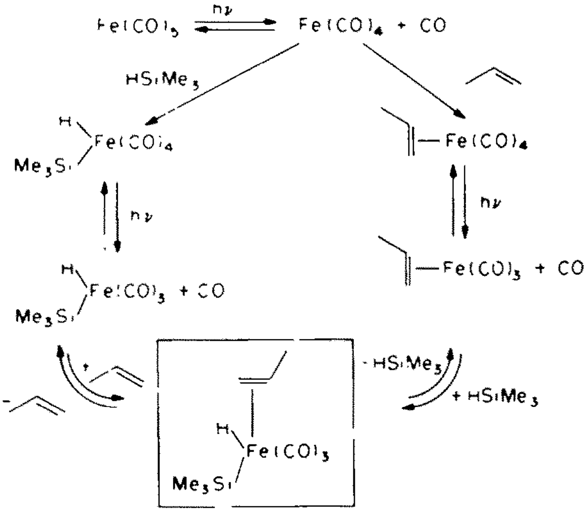
(8-1)



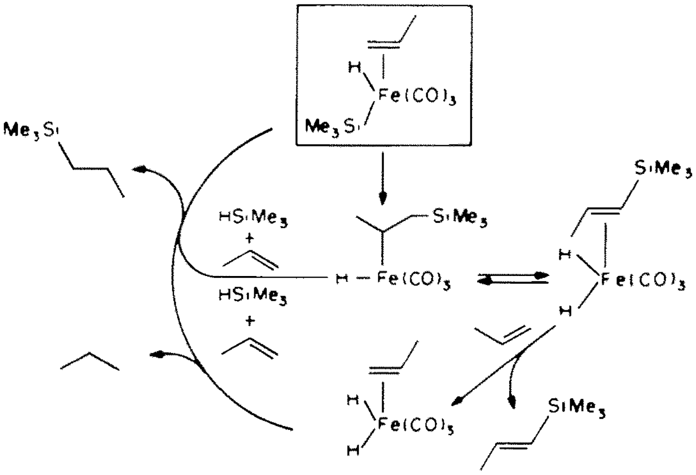
(8-2)

catalyzes nonphotoinduced 1,4-hydrosilation at 175° the synthetic utility of the nonphotochemical reaction is diminished by substantial concomitant dimerization of diene not observed under the thermally milder conditions of the photoinduced reaction.

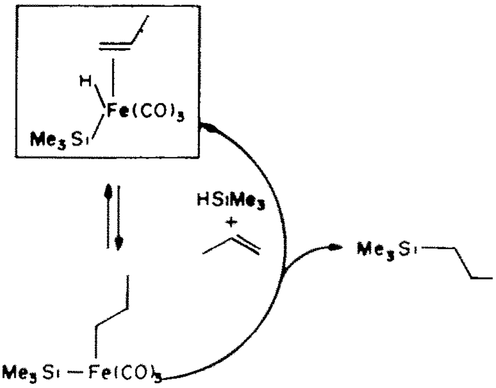
Although $Fe(CO)_5$ catalyzes silation of alkenes without photolysis,[175] near-UV irradiation allows reaction under very mild conditions (Table 8-2).[176] Products include alkylsilanes, alkenylsilanes, and alkanes. The reactions show a strong regioselectivity for C-Si bond formation at the least hindered terminus of the alkene and cyclic alkenes are relatively unreactive. The relative yields of alkyl versus alkenyl silanes varies greatly with the relative concentrations of the reactants as shown in Table 8-3 for the reaction of 1-pentene with Me_3SiH. Formation of alkenyl silane is also favored if the reaction mixture is heated as well as irradiated. Therefore, it is possible to orient the reaction toward the desired product by appropriate choice of experimental conditions. The ratio of alkane to alkenylsilane is generally about 1:1. A quantum yield of 46 for the reaction of 1-pentene with Et_3SiH[55a] reveals a photogenerated catalytic mechanism, and infrared monitoring of the reactions reveals the intermediacy of (alkene)$Fe(CO)_4$ and $(Me_3Si)FeH(CO)_4$, neither of which catalyze the reaction of alkene and silane under the same reaction conditions but in the dark. Therefore, while direct evidence is lacking for such a species, $(R_3Si)FeH(CO)_3$(alkene) was proposed as the actual catalyst which is generated in a multiphoton process according to scheme 8-1. Two competing thermal catalytic cycles (scheme 8-2) then lead to alkylsilane and alkenylsilane plus alkane respectively. A slightly different cycle (scheme 8-3) is also possible for generating alkylsilane. Other mononuclear iron complexes including $Fe(CO)_4(Ph_3P)$, and $Fe(CO)_3(PPh_3)_2$[59] as well as the trinuclear complex $Fe_3(CO)_{12}$ catalyze the reaction of Et_3SiH with 1-pentene affording very nearly the same relative yields of the pentenylsilanes 119–121.[46,59] Thus, the thermally active catalyst generated from $Fe_3(CO)_{12}$ upon irradiation in the presence of silane and alkene is considered to be the same mononuclear species as generated from $Fe(CO)_5$.[46] However, this



Scheme 8-1

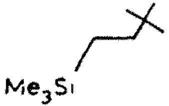
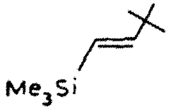
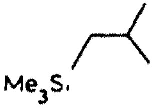
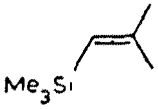


Scheme 8-2.



Scheme 8-3

Table 8-2. Fe(CO)$_5$ photocatalyzed reactions of trialkylsilanes with alkenes[a][176]

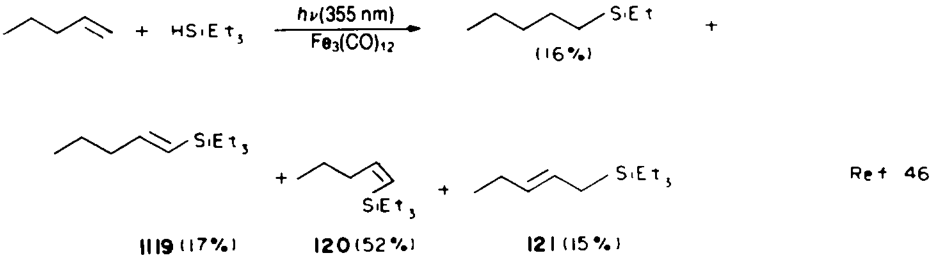
Starting alkene	Starting silane	Irradiation time(h)	Conversion (%) to products	Product distribution (% of products)		
				Alkane	Alkylsilane	Alkenylsilane(s)
Ethylene[b]	HSiEt$_3$	12[b]	>99	None (<1)	SiEt$_4$(>99)	None (<1)
Propylene	HSiMe$_3$	12	>90	Propane (~5)	(n-C$_3$H$_7$)SiMe$_3$ (~90)	(allyl)SiMe$_3$ (*trans*-C$_3$H$_5$)SiMe$_3$ (*cis*-C$_3$H$_5$)SiMe$_3$ } (~5)
1-Butene	HSiMe$_3$	12	>90	n-Butane (~40)	(n-C$_4$H$_9$)SiMe$_3$ (~20)	C$_4$H$_7$SiMe$_3$(~40) (3 isomers)
1-Pentene	HSiMe$_3$	12	>90	n-Pentane (~40)	(n-C$_5$H$_{11}$)SiMe$_3$ (~20)	(*trans*-1-C$_5$H$_9$)SiMe$_3$ (~12 (*cis*-1-C$_5$H$_9$)SiMe$_3$ (trace) isomer I (~22) isomer II (~6)
Cyclopentene	HSiMe$_3$	168	~5	Cyclopentane (~25)	(cyclo-C$_5$H$_9$)SiMe$_3$ (~50)	(cyclo-C$_5$H$_7$)SiMe$_3$ (~23)
t-Butylethylene	HSiMe$_3$	96	~20	2,2-Dimethylbutane (~5)	 (~90)	 (~5%)
Isobutylene	HSiMe$_3$	168	>80	Isobutane (~10)	 (~80)	 (~10)

[a] Reactions were run at 25–35°C using the neat substrates in a 1:1 mole ratio with 0.003 M Fe(CO)$_5$ and a total solution volume of 3.0 mL. [b] Reaction run with 7 mL Et$_3$SiH Fe(CO)$_5$ under 10 psig of ethylene, irradiated with HG arc lamp filtered to isolate the 300–380 nm region.

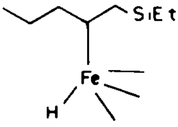
Table 8-3. Photoinduced $Fe(CO)_5$ catalyzed reaction of 1-pentene with Me_3SiH[a,176]

1-Pentene (*M*)	$HSiMe_3$ (*M*)	Concentrations ratio 1-Pentene/$HSiMe_3$	Alkylsilane[b] (%)	Alkenylsilane[b] (%)
0.9	7.5	0.12	66.7	33.3
1.6	6.8	0.24	56.2	43.8
4.8	4.0	1.2	27.3	72.7
7.7	1.3	5.8	3.1	96.9
8.4	0.7	12.0	1.3	98.7
0.9[c]	0.1	9.0	1.8	98.2
0.1[c]	0.9	0.11	44.8	55.2

[a] Degassed, sealed ampoules containing 3.0 ml of the alkene and silane with 0.008M $Fe(CO)_5$ were exposed simultaneously to two 15W GE Black Light bulbs at 30°. After two hours of irradiation the samples were analyzed by VPC. Conversion of the starting materials to silicon-containing products was approximately 50%, based on the least concentrated reagent as the limiting reagent. [b] Percent of total silicon-containing products. [c] Degassed, sealed ampoules containing 7.0 ml of a benzene solution of a alkene and silane with 0.006M $Fe(CO)_5$ exposed to 300–380 nm light for 70 minutes at 25°.

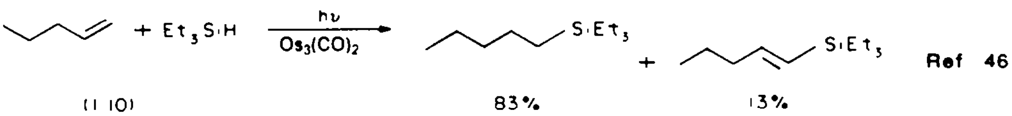


conclusion deserves further scrutiny since the same ratio of **119–121** is also produced upon irradiation of any of these isomers in the presence of $Fe(CO)_5$ which catalyzes their equilibration.[176] $Fe_3(CO)_{12}$ is also an efficient catalyst of photoinduced alkene isomerization (see metal carbonyls section).[46] Thus, it is possible that the observed product ratios are the result of equilibration and do not necessarily reflect the partitioning of various β-silyliron intermediates **122**. Photoinduced reactions of 1-pentene with Et_3SiH



122

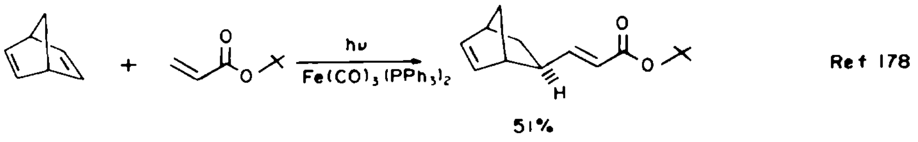
catalyzed by $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are similar to those promoted by $Fe_3(CO)_{12}$ except that different product ratios are obtained under otherwise identical reaction conditions. The osmium catalyst is especially selective for producing alkylsilane versus alkenylsilane.



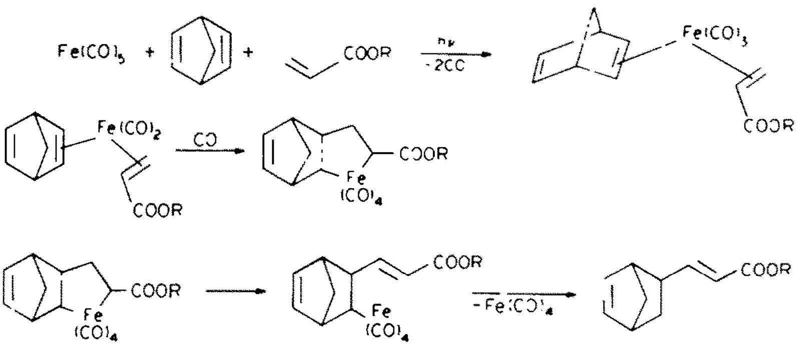
While $Co_2(CO)_8$ and $R_3SiCo(CO)_4$ show thermal catalytic activity toward promoting addition of Et_3SiH to 1-pentene, irradiation significantly enhances yields of n-pentylsilane.[177]

(b) *Additions of C + H to Alkenes*

Photoinduced insertion of one C=C bond of bicyclo[2.2.1]hepta-2,5-diene into the terminal vinyl C–H bond of acrylate esters is catalyzed by $Fe(CO)_5$ or $Fe(CO)_3(PPh_3)_2$.[178] The same reactions can be induced thermally. Irradiation can promote the reaction by facilitating dissociation of carbonyl ligands.



Replacement of two carbonyl groups with alkene ligands (eqn 8-3) followed by cycloaddition is considered to generate a ferracyclopentane intermediate (eqn 8-4) which undergoes β-hydride elimination and reductive elimination of iron (eqn 8-5).[178]

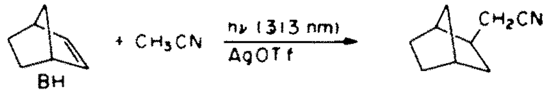


(8-3)

(8-4)

(8-5)

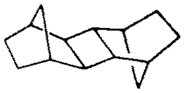
Silver trifluoromethanesulfonate (AgOTf) catalyzes a photoinduced addition of actonitrile to bicyclo[2.2.1]hept-2-ene (BH).[179] Minor amounts of dimers **124**, **46**, and **47**, are also produced, and silver(I)is



Ref 179

123 (93 %)

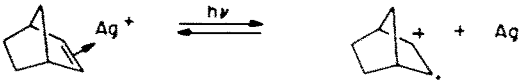
124 (3 %)



46 (1 %)

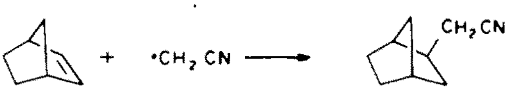
47 (3 %)

reduced and deposited as a silver(0) mirror during the photolysis. The corresponding reaction of CD_3CN affords analogous products but the relative yield of **123**-d_3 is greatly diminished (23%) while the yields of **124**-d_2 (38%), **46**-d_0 (12%), and **47**-d^0 (27%), formed concomitantly, are greater. Despite the similarity of this reaction with a known triplet sensitized process,[180] the AgOTf promoted addition of acetonitrile to BH is considered *not* to involve a triplet mechanism. Rather, a radical chain (eqns 8-8 and 8-9) is proposed which is initiated by photoinduced ligand to metal charge transfer (LMCT) (eqn 8-6) and hydrogen atom abstraction from acetonitrile by an intermediate cation radical (eqn 8-7). The relative rate retardation observed in the Ag(I) promoted photoreaction of CD_3CN with BH arises from a deuterium isotope effect as expected for the C–H bond cleavage involved in the thermal chain reaction (eqn 8-9).

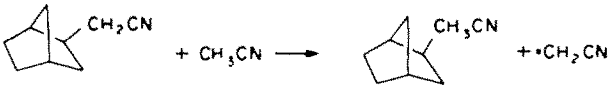


(8-6)

(8-7)



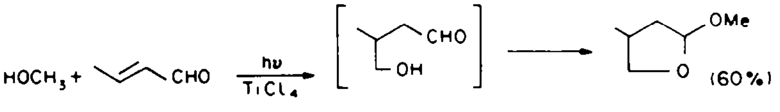
(8-8)



(8-9)

Furthermore, the triplet reaction is quenched by low concentrations of oxygen,[181] whereas the Ag(I) promoted reaction actually requires low concentrations of oxygen (1-5 torr over the solution) and does not occur in thoroughly deoxygenated solutions. The role of oxygen may be to react with Ag(O) to yield $Ag^+O_2^-$·,[182] facilitating chain initiation by preventing back electron transfer (eqn 8-6). Similar additions were observed with propionitrile and several cyclic and acyclic alkenes. However, only alkenes which form light-absorbing (313 nm) ground state complexes with Ag(I) undergo the Ag(I) catalyzed photoreaction. Notably, consistent with a radical chain but not a sensitization mechanism, additions to less reactive alkenes can be promoted by more reactive alkenes. Thus BH substantially enhances the yield of Ag(I) catalyzed photoaddition of CH_3CN to 2-ethyl-1-butene.[179]

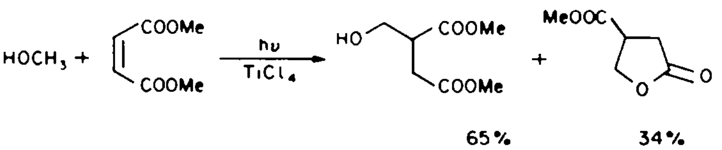
Titanium(IV) chloride catalyzes photoinduced cleavage of a CH bond of methanol and addition of the hydroxymethyl and hydrogen groups to the C=C bond of crotonaldehyde to give **126**, an acetal of the initially formed aldehyde **125**.[183] However, some α,β-unsaturated aldehydes and α,β-unsaturated



125 **126**

Ref 183

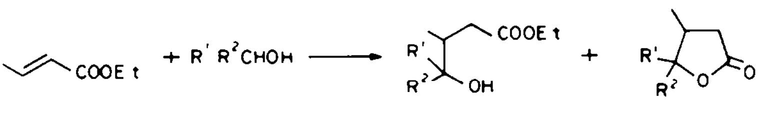
ketones, in general, undergo 1,2-addition rather than 1,4-addition of the hydroxymethyl group (see section 9a on 1, 2 addition to aldehydes and ketones). Tin (IV) chloride catalyzes a similar reaction of crotonaldehyde but is not catalytically active for ketones. Titanium(IV) chloride also catalyzes photoaddition of methanol to the C=C bond of dimethyl maleate.[183] Uranyl chloride is generally effective in



Ref 183

activating the α-C–H bond of alcohols toward addition to the C=C bond of α,β-unsaturated carbonyl compounds including ketones (Table 8-4).[183]

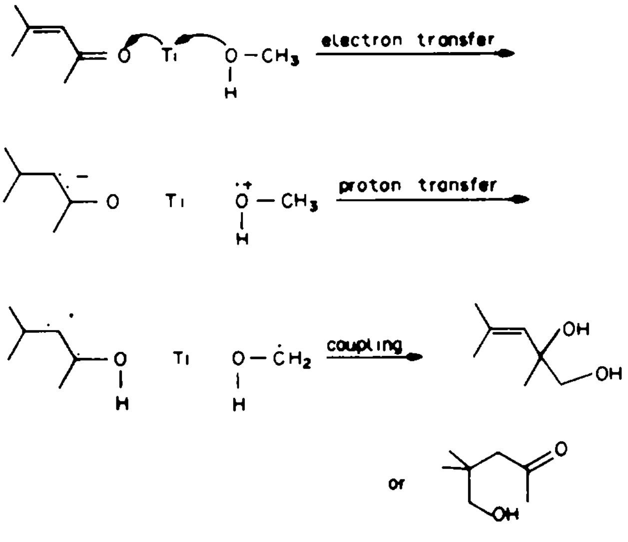
Photochemical 1,4-additions of α-hydroxyalkyl groups by reaction of alcohols with α,β-unsaturated carbonly compounds can also be promoted by aromatic ketones as sensitizers.[184] Although the benzophenone-sensitized additions of alcohols to ethyl crotonate (eqn 8-10) are effected under irradiation for 50–72 hr,[185] very little reaction occurs during 6 hr compared to the corresponding UO_2Cl_2-catalyzed reaction (Table 8-5).[183] Also relative reactivities in the benzophenone-sensitized additions increased in



127 **128**

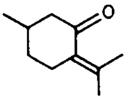
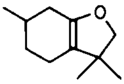
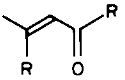
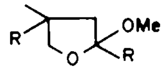
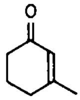
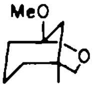
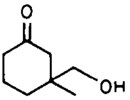
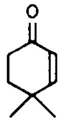
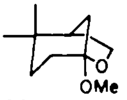
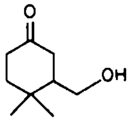
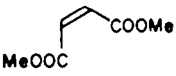
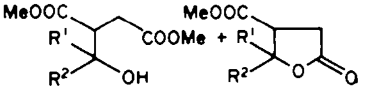
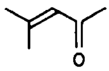
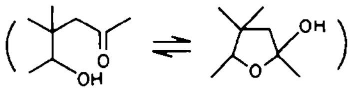
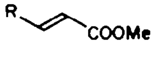
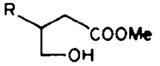
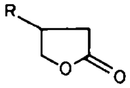
(8-10)

the order methanol < ethanol < 2-propanol, whereas the UO_2Cl_2-catalyzed additions exhibit the opposite order of reactivities (Table 8-5). Thus, while the aromatic ketone-sensitized reactions are considered to involve free α-hydroxyalkyl radicals, a different mechanism not involving free radicals is assumed for the UO_2Cl_2 catalyzed additions of alcohols to carbonyl-conjugated C=C bonds. A similar mechanism is also assumed for $TiCl_4$-catalyzed additions of alcohols to α,β-unsaturated aldehydes, ketones, and esters (scheme 8-4).[183,186] Metal assisted photoinduced electron transfer from the alcohol to the carbonyl compound is followed by proton transfer, imparting a radical character to the α-carbon atom of the alcohol as well as the carbonyl carbon and the β-carbon atom of the enone, and subsequent cross coupling. All these processes are considered to proceed consecutively within the coordination sphere of the metal catalyst, thus providing circumstances favorable for the cross coupling. It is assumed that titanium coordinates strongly with the carbonyl oxygen, thus favoring the 1,2-addition, while uranyl ion coordinates to the π-system more effectively, and induces 1,4-addition. The order of reactivities



Scheme 8-4.[186]

Table 8-4. UO_2Cl_2-Catalyzed reactions of alcohols with α,β-unsaturated carbonyl compounds[183]

Carbonyl Compound	Alcohol	Products (yields %)
	MeOH	 (71)
	MeOH	 R = H (19) R = Me (45)
	MeOH	 (17) +  (2)
	MeOH	 (4) +  (9)
		
	MeOH R', R^2 = H,	(65) (6)
	EtOH R' = H, R^2 = CH_3	(37) (19)
	Me_2CHOH R', R^2 = CH_3	(76) (11)
	EtOH	 (13)
		 + 
R = CH_3	MeOH	(47) (11)
R = H	MeOH	(13) (1)

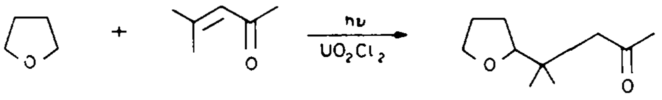
methanol > ethanol > isopropanol is ascribed to the more favorable coordination of the less sterically demanding smaller alcohols to the metal ion.[186]

Uranyl chloride also catalyzes photoactivation of the α-C–H bond of tetrahydrofuran toward

Table 8-5. Photoadditions of alcohols to ethyl crotonate[183]

Alcohol	Product Yields (%)			
	UO_2Cl_2-catalysis		Ph_2CO-sensitization	
	127	128	127	128
Methanol	65	0	0.6	0
Ethanol	39	0	0.6	0
2-Propanol	5	24	1.0	1.3

A solution of ethylcrotonate (1.5 mmol) and UO_2Cl_2 (0.13 mmol) or benzophenone (0.16 mole) in alcohol (12 mL) was irradiated with Pyrex-filtered light from a mercury vapor lamp for 6 hours.



Ref 183

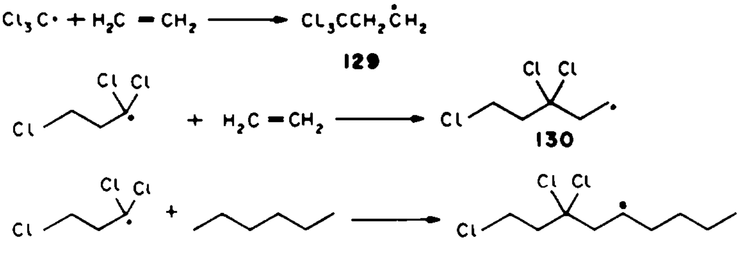
addition to the C=C bond of mesityl oxide. Again, similar photoadditions of ethers to α,β-unsaturated carbonyl compounds are also known with aromatic ketone sensitization.[187]

(c) *Additions of C + halogen to alkenes*

Iron pentacarbonyl thermally catalyzes addition (eqn 8-11, n = 1) and telomerization (eqn 8-11, n > 1) reactions of tetrahalomethanes with alkenes at > 100°.[188] Similar reactions of *gem*-trichloro derivatives occur in the presence of cocatalysts, e.g. nitriles, esters, trialkylphosphites, primary and secondary alcohols, tertiary amines, and amides (eqn 8-12).[189] The rate determining step in these thermally induced reactions is apparently dissociation of a carbonyl ligand to generate the coordinatively unsaturated $Fe(CO)_4$. Since photodissociation can generate this same intermediate at a subambient temperature, UV irradiation has been employed to study the subsequent reactions of $Fe(CO)_4$ in these systems at temperatures as low as −15°C.[190] Under these thermally mild conditions intermediates are sufficiently stable to be studied by the ESR spin trapping technique. In this manner, direct evidence was obtained for generation of $ClFe(CO)_4$ by chlorine atom abstraction from the organic polyhalides and for the intermediacy of organic radicals such as $\cdot CCl_3$ from $XCCl_3$ (X = Cl, Br), $\cdot CHCl_2$ from $CHCl_3$,[190] and $ClCH_2CH_2\dot{C}Cl_2$ from $ClCH_2CH_2CCl_3$.[191b] Adduct radicals **129–131** were also observed.[191]

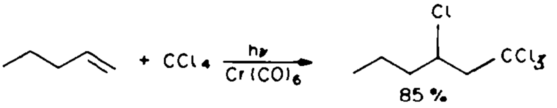
$$Cl_3C-X + CH_2{=}CHY \xrightarrow[Fe(CO)_5]{\Delta} Cl_3C-(CH_2CHY)_n-X \qquad (8\text{-}11)$$

$$R^1R^2CH-CCl_3 + CH_2{=}CHR^3 \xrightarrow[Fe(CO)_5 \;+\; \text{cocatalyst}]{\Delta} R^1R^2CH-CCl_2-(CH_2CHR^3)_n-Cl \qquad (8\text{-}12)$$



Scheme 8-4[186]

UV irradiation of alkenes and CCl_4 in the presence of $W(CO)_6$ produces addition products in competition with photogeneration of metathesis catalysts described in section 6b on photogeneration of alkene metathesis catalysts.[135,136] With $Cr(CO)_6$ as catalyst, exclusively addition and no metathesis is



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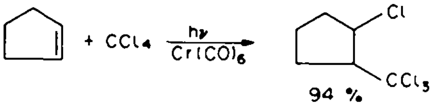
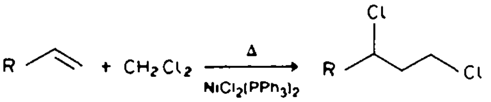


Ref 135

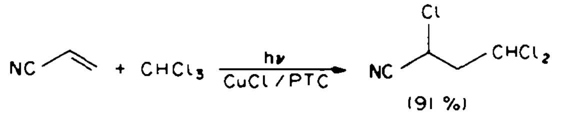
observed.[135] With $Mo(CO)_6$, in general, the addition reaction is much less important than with the tungsten or chromium carbonyls.[135]

Methylene chloride undergoes thermally induced addition reactions at 140–150° with $NiCl_2(PPh_3)_2$ or $NiCl(PPh_3)_3$ as catalyst.[192] $RuCl_2(PPh_3)_2$ and $PdCl_2(PPh_3)_2$ are also effective catalysts albeit less active.



Ref 192

Similar reactions occur under thermally much milder conditions with cuprous chloride as catalyst under UV irradiation at or near room temperature.[193] Thus, CuCl solubilized in $CHCl_3$ or CH_2Cl_2 as solvent and reactant by phase transfer catalysts (PTC), promotes photoinduced additions to acrylonitrile or ethyl acrylate.[193] While CuCl is known to promote analogous reactions of CCl_4 thermally,[194] similar thermally induced reactions of CH_2Cl_2 are unknown.



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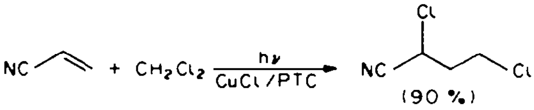

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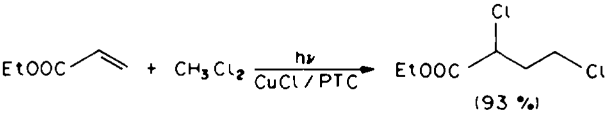
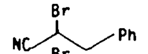
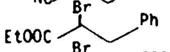
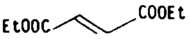
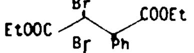
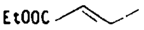
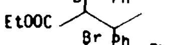
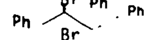
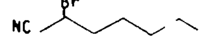
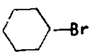
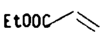
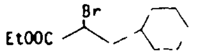


Ref 193

CuCl also catalyzes photoinduced additions of bromobenzene in good yields and alkylmonobromides in low yield to activated alkenes in DMSO solutions (Table 8-6).[193] These reactions have no thermal

Table 8-6. CuCl catalyzed addition of bromobenzene and alkylmonobromides to activated alkenes in DMSO[a,193]

Bromide	Olefin	Adduct	Yield(%)[b]
PhBr			60 (94)[c,d]
PhBr			77
PhBr			75
PhBr			40
PhBr			(95)[c,e]
$n\text{-}C_4H_9Br$			20
			15

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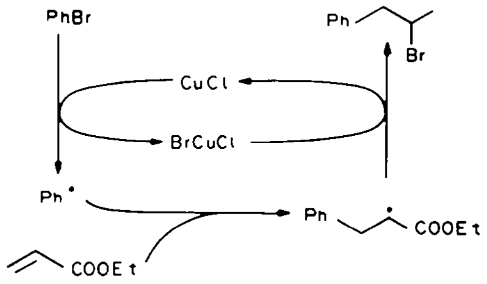
[a] U.V. source; low-pressure Hg lamp, reaction time; 30–40 h, CuCl (0.1 mmol) and alkene (3 mmol), DMSO solvent (20 mL), bromide (9 mmol). [b] Based on charged alkenes and determined by GLC. [c] t-Butylcatechol (0.2 mmol) added and yield based on consumed alkene. [d] Consumption of alkene; 52%. [e] Consumption of alkene; 38%.

analogy and appear to have major significance for applications in organic synthesis. Besides the 1:1 adducts with the bromides, alkenes were consumed in competing telomerization reactions which were suppressed in the presence of t-butylcatechol, a radical inhibitor.[193]

Since similar addition reactions were not produced in radical-induced systems, a free radical chain pathway is not favored for these CuCl catalyzed photoinduced addition reactions. Rather, a photo-redox pathway is preferred.[193] Such a mechanism is illustrated in scheme 8-5.

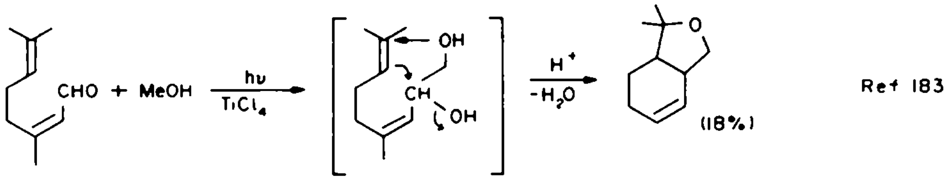


Scheme 8-5.

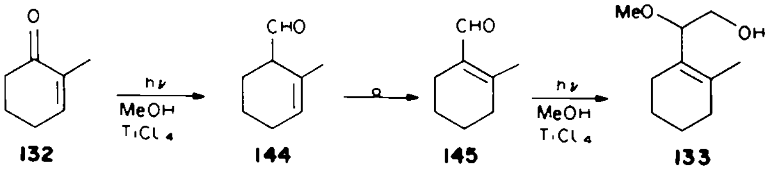
9. ADDITIONS TO C = X AND C ≡ X

(a) 1,2-*Additions to aldehydes and ketones*

As noted above (see section 8b on additions of C + H to alkenes) TiCl$_4$ catalyzes photoaddition of alcohol-derived α-hydroxyalkyl groups to α,β-unsaturated aldehydes in both a 1,4- and 1,2 sense. These reactions were rationalized by a mechanism depicted in scheme 8-4. While the 1,4-additions find analogy in photoreactions sensitized by aromatic ketones, the 1,2-additions are unusual. An example of 1,2-addition to an α,β-unsaturated aldehyde is provided by the reaction of citral with methanol upon UV irradiation in the presence of TiCl$_4$.[183] Titanium(IV) chloride is generally effective in promoting 1,2-addition of alcohol-derived α-hydroxyalkyl groups to α,β-unsaturated ketones (Table 9-1) in contrast with the 1,4-additions promoted by UO$_2$Cl$_2$ (see Table 8-4 above).



A general mechanistic discussion of photoinduced 1,2 and 1,4-addition reaction of alcohols with α,β-unsaturated carbonyl compounds was presented in a previous section (see scheme 8-4). The **132** → **133** conversion is considered to involve initial production of **144** after addition of methaanol to **132**. Subsequent rearrangement to **145** and addition of a second α-hydroxymethyl group ultimately produces **133** after S$_N$2 replacement of an allylic hydroxyl by a methoxy group.[183] S$_N$2′ replacement of the allylic hydroxyl in intermediate **146** occurs during the **134** → **135** conversion. A possible sequence for the formation of **137** is an initial hydroxymethylation followed by aromatization with a methyl group



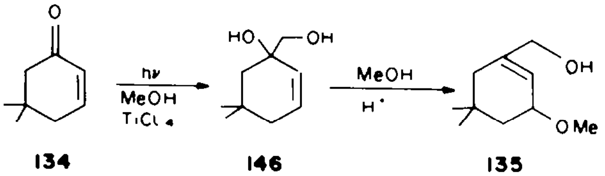
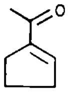
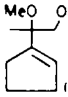
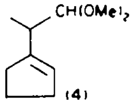
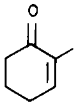
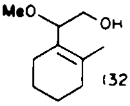
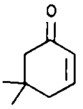
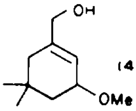
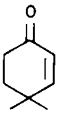
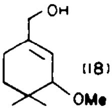
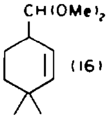
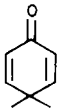
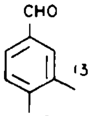
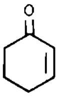
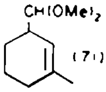
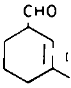
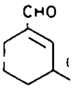
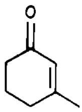
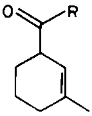
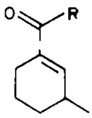
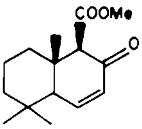
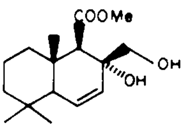
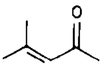
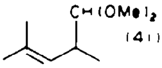
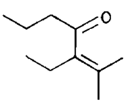
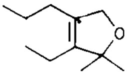
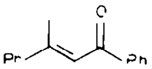
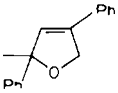
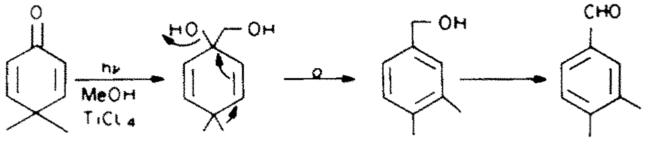


Table 9-1. TiCl$_4$ catalyzed reactions of alcohols with α,β-unsaturated ketones[183,195]

Carbonyl compound	Alcohol	Products (yields, %)		
	MeOH	 (25)	 (4)	
 132	MeOH	 (32) 133		
 134	MeOH	 (45) 135		
	MeOH	 (18)	 (16)	
 136	MeOH	 (32) 137		
 138	MeOH	 (7) 139	 (5) 140	 (3) 141
	R CH$_2$OH			
	R = CH$_3$	(49)	(12)	
	R = CH$_2$CH$_3$	(34)	(9)	
	R = CH$_2$CH$_2$CH$_3$	(30)	(8)	
	R = CH(CH$_3$)$_2$	(39)		
 142	MeOH	 143		
	MeOH	 (41)		
	MeOH	 (62)		
	MeOH			

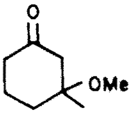
migration in the intermediate **147** to afford **148** which is then oxidized to the aldehyde **137**. The stereoselectivity of the **142**→**143** conversion is noteworthy since it seems to confirm the postulated occurrence of the photoaddition within the coordination sphere of titanium. Thus, addition of the hydroxymethyl group occurs exclusively cis to the methoxycarbonyl group since titanium coordinates to oxygen atoms of both the ester and carbonyl groups in **142**.[183]



136 **147** **148** **137**

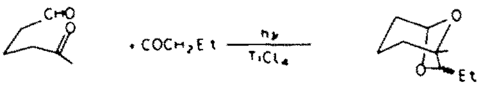
The yields indicated in Table 9-1 are not optimized and higher yields may be achievable since the amount of catalyst employed strongly influences yields as shown in Table 9-2 for the reaction of **138** with methanol. Although the maximum yield of **134**–**141** is obtained when about an equimolar amount of $TiCl_4$ is used, it is evident that $TiCl_4$ functions catalytically rather than stoichiometrically, because the amounts of products exceed the amount of catalyst at low concentrations of $TiCl_4$.[183]

Table 9-2. Effect of $TiCl_4$ catalyst concentration on product yields in the reaction of **138** with methanol[183]

$TiCl_4$ Mol equiv to 138	138 (recovered) (%)	139 (%)	140 (%)	141 (%)	
0.1	12	30	trace	trace	25
0.2	29	49	trace	trace	5
0.5	7	65	trace	trace	6
1.0	0	71	5	3	11
2.0	trace	70	5	2	trace
3.0	4	51	6	3	4
4.0	4	46	8	5	4
5.0	2	30	11	5	trace
10	trace	15	17	2	trace

Solutions of **138** (0.1 g, 0.91 mmol) and varying amounts of $TiCl_4$ in methanol (10 ml) were irradiated with Pyrex-filtered light for 7 h. The yields were determined by NMR analysis, using nitrobenzene as the internal reference.

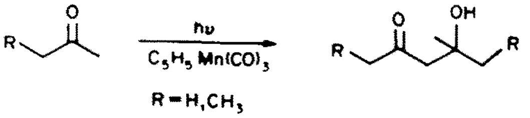
Titanium(IV) chloride also catalyzes 1,2-addition of methanol-derived α-hydroxyalkyl groups to nonconjugated ketone carbonyl groups (Table 9-3).[183,186,196] A similar reaction of n-propanol with ketoaldehyde **149** affords α-hydroxypropylation product **150**.[196b]



149 **150**

Ref 196b

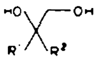
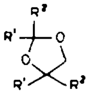
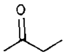
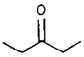
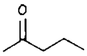
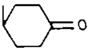
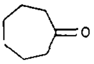
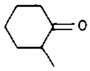
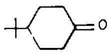
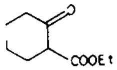
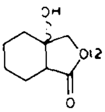
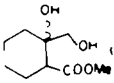
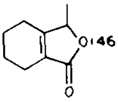
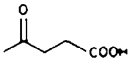
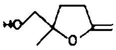
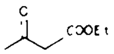
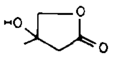
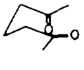
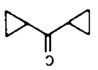
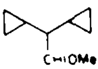
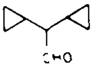
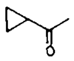
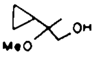
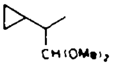
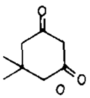
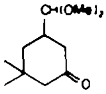
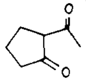
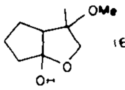
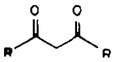
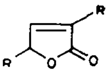
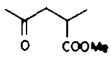
Aldol condensations are catalyzed by (cyclopentadienyl)$Mn(CO)_3$ under UV irradiation.[197] Catalysis



Ref 197

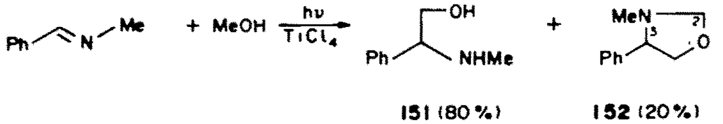
involves formation of an unidentified Mn complex intermediate via photodissociation of a carbonyl ligand.

Table 9-3. $TiCl_4$ catalyzed reactions of saturated ketones with methanol

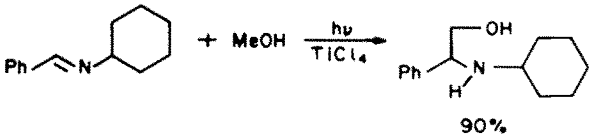
Ketone		Products (yield, %)	
	R^1 R^2		
	CH_3 C_2H_5	54	
	C_2H_5 C_2H_5	55	
	CH_3 n-C_3H_7	68	
	$-(CH_2)_4-$	35	
	$-(CH_2)_5-$	46	20
	$-(CH_2)_6-$	35	
	$-\overset{CH_3}{CH}(CH_2)_4$	42	26
	$-(CH_2)_2\overset{t\text{-}Bu}{CH}(CH_2)_2-$	48	19
	 (23)	 (29)	 (46)
	 (56)		
	 (60)		
	 (85)		
	 (95)	 (trace)	
	 (60)	 (5)	
	 (44 60)		
	 (60)		
	 R = CH_3 (5) R = t-Bu (65)		

(b) *Additions to imines and nitriles*

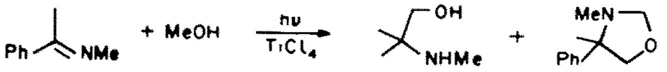
Photoinduced addition reactions of imines with methanol similar to those of the corresponding aldehydes and ketones are catalyzed by $TiCl_4$.[183] The methylene which becomes C-2 in the oxazoladine product **152** most likely arises from formaldehyde which reacts with **151** to produce **152**. Formaldehyde probably is formed from methanol in a $TiCl_4$-catalyzed photooxidation. Such oxidations are considered further in section 11b on oxidation of alcohols.



Ref 183

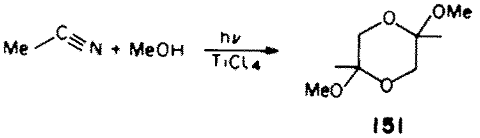


Ref 183

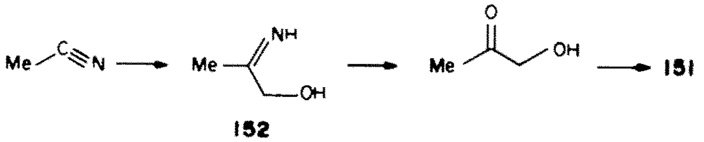


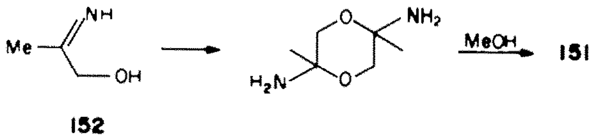
Ref 183

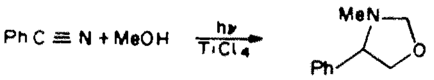
Addition of an α-hydroxymethyl group to acetonitrile is involved in the production of **151** by a $TiCl_4$-catalyzed photoreaction with methanol.[183] Thus, addition of an α-hydroxymethyl group to the C≡N carbon is presumed to afford **152** which upon hydrolysis and dimerization gives **151**. Alternatively, **152** might dimerize first and the resulting **153** could give **151** by methanolysis. The corresponding reaction of benzonitrile[198] is more complex although initial 1,2-addition of an α-hydroxymethyl group to the nitrile is probably involved.[183]



Ref 183



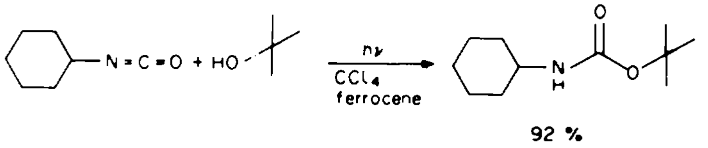




Ref 198

(c) *Additions to isocyanates*

Irradiation with a tungsten lamp accelerates addition of alcohols to isocyanates in CCl_4 solution with ferrocene or butadiene(tricarbonyl)iron as catalyst.[199] The synthetic utility of the catalyzed photoreaction is exemplified by conversion of t-butanol to a urethane which can only be achieved in poor yields thermally. An induction period was detected for the disappearance of isocyanate and the evolution of a

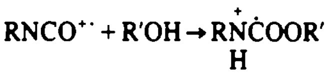


Ref 199

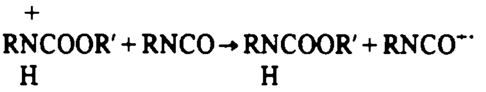
light-absorbing catalytic species was detected.[200] The latter was presumed to be FeCl$_4^-$ since acrylonitrile, which is known to prevent the photogeneration of FeCl$_4^-$ from ferrocene and CCl$_4$,[7a,201] inhibits catalysis of the photoaddition reaction by ferrocene. A photoinitiated short-chain mechanism shown in eqns (9-13)–(9-16) is assumed for the addition.[200]

$$Fe^{3+}Cl^- \xrightarrow{h\nu} Fe^{2+} + Cl\cdot \tag{9-13}$$

$$Cl\cdot + RNCO \rightarrow RNCO^{+\cdot} + Cl^- \tag{9-14}$$



$$RNCO^{+\cdot} + R'OH \rightarrow R\underset{H}{\overset{+}{N}}COOR' \tag{9-15}$$

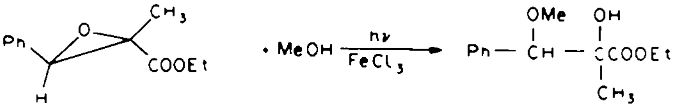


$$\underset{H}{\overset{+}{RN}}COOR' + RNCO \rightarrow \underset{H}{RN}COOR' + RNCO^{+\cdot} \tag{9-16}$$

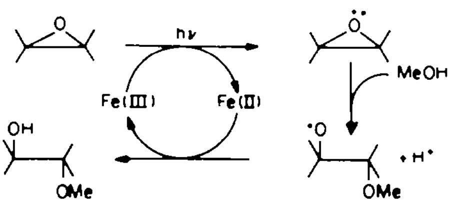
10. SUBSTITUTION REACTIONS

(a) *Aliphatic substitution*

The photochemical ionic addition of alcohols to epoxides is catalyzed by FeCl$_3$ or Fe$_2$O$_3$.[202] Nucleophilic attack by methanol on the epoxide is presumed to be promoted by photoinduced electron transfer from the epoxide oxygen to Fe(III). The electron deficient epoxide oxygen is an activated nucleofuge, and a catalytic cycle depicted in scheme 10-1 might account for the photoaddition.

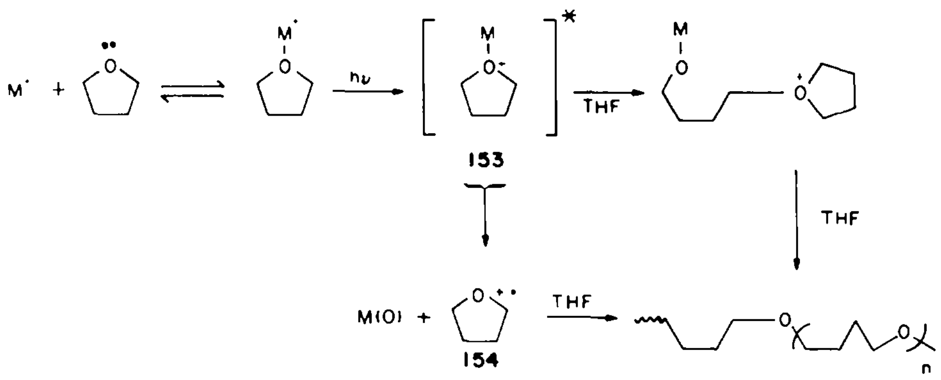


Ref 202



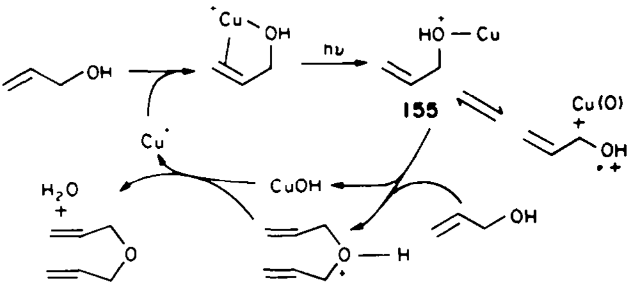
Scheme 10-1.

Similar ligand-to-metal charge transfer (LMCT) excitation is presumed to activate tetrahydroforan (THF) toward nucleophilic attack by a second molecule of THF in metal ion catalyzed photopolymerization of THF.[203] Thus, silver salts—AgBF$_4$, AgPF$_6$, AgSbF$_6$ and AgOTf—or copper salts—(CuOTf)$_2$·C$_6$H$_6$ and Cu(OTf)$_2$—are active initiators of THF photopolymerization. Coordination of THF by the metal seems to be important since alkenes, which compete with THF for coordination sites on the metal, inhibit photopolymerization. Photoactivation of a metal ion—THF complex is considered to generate **153**.[203] The ether oxygen in **153** or the derived cation-radical **154** is an activated nucleofuge susceptible to displacement by a second molecule of THF generating an oxonium ion intermediate. Continued growth of the polymer, which occurs in the dark, probably proceeds via the normal cationic chain mechanism.



Ref 203

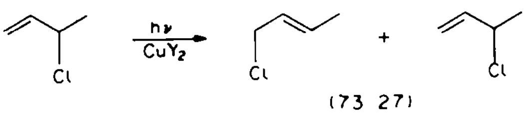
It seems reasonable to assume that a related mechanism (Scheme 10-2) is involved in production of diallyl ether from allyl alcohol upon UV irradiation in the presence of CuOTf.[101] Thus, LMCT excitation



Scheme 10-2.

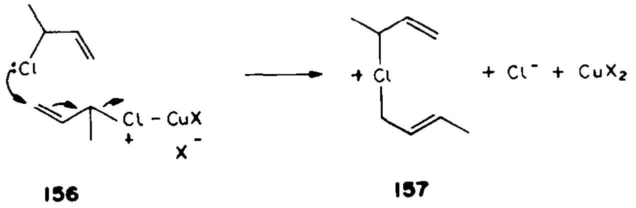
of an alcohol-Cu(I) complex generates **155**. The hydroxyl group in **155** or the derived cation radical is an activated nucleofuge susceptible to displacement by a second molecule of allyl alcohol. The resulting secondary oxonium ion loses a proton to give diallyl ether. The nucleophilic attack on **155** could occur by an S_N2 or an S_N2' process.

It is tempting to speculate that an analogous process might explain Cu(II) catalysis in photoisomerization of 3-chloro-1-butene. Thus, UV irradiation (>250 nm) of 3-chloro-1-butene in the presence of $CuCl_2$, $Cu(OAc)_2$, or $Cu(acetylacetonate)_2$ produces an equilibrium mixture of allylic chlorides.[204] Activation of the allylic chloride might occur by LMCT excitation to produce **156**.



Ref 204

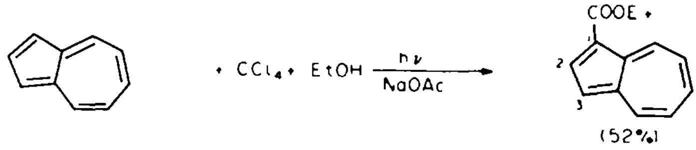
S_N2' attach on **156** by a second molecule of allylic chloride could generate a chloronium intermediate **157** which would react with chloride to generate rearranged allylic halide. However, a plausible alternative



mechanism for catalyzed photoisomerization involves S_H2' reaction of chlorine atoms. Photogeneration of chlorine atoms from $CuCl_2$ is well known,[205] and it may be significant that $CuCl_2$ was the most active catalyst reported.[204]

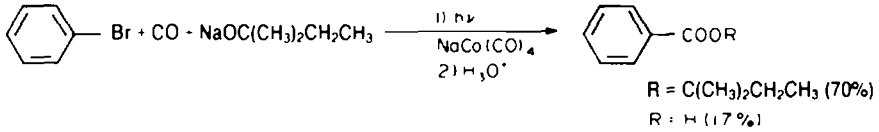
(b) *Aromatis substitution*

Replacement of aryl hydrogen by an alkoxycarbonyl group occurs upon UV irradiation (365 or 313 nm) of azulene in carbon tetrachloride–ethanol (1 : 1) in the presence of sodium acetate and ferrocene as catalyst.[205] In the absence of sodium acetate, 1-chloroazulene is produced instead of ethyl 1-azulenecarboxylate. With $CHCl_3$ in place of CCl_4, 1-formylazulene was obtained (3%) instead of the ester. The ferrocene catalyst is recovered almost quantitatively, and no ethyl ferrocenecarboxylate, the photo-product[207] in the absence of azulene, was detected.



Ref 206

Replacement of aryl halogen by an alkoxycarbonyl group occurs upon UV irradiation (350 nm) of bromobenzene and sodium 1,1-dimethylpropoxide under an atmosphere of CO in the presence of $NaCo(CO)_4$ as catalyst.[208] The coproduction of minor amounts of benzene (3%) appears to be an example of the known cobalt catalyzed reduction of aryl halides which are considered to involve a free radical mechanism.[209] The carbalkoxylation reaction is believed to involve the first example of photo-stimulated $S_{RN}1$ nucleophilic aromatic substitution with $^0Co(CO)_4$ as the nucleophile. The resulting aryl cobalt intermediate reacts with CO and alkoxide to generate the ester product and regenerate the cobalt catalyst as outlined in scheme 10-3.[208] Yields up to about 1800% with respect to cobalt may be obtained.



Ref 208

Initiation step

$C_6H_5Br + NaCo(CO)_4 \rightleftharpoons C_6H_5Br\ NaCo(CO)_4 \xrightarrow{h\nu} [C_6H_5Br]\ Na^{+} + Co(CO)_4$

or $NaCo(CO)_4 \xrightarrow{h\nu} [NaCo(CO)_4]^{*} \xrightarrow{C_6H_5Br}$

Propagation steps

$[C_6H_5Br]^{-}Na^{+} \rightarrow C_6H_5^{\cdot} + NaBr$

$C_6H_5 + NaCo(CO)_4 \rightarrow [C_6H_5Co(CO)_4]\ Na^{+}$

$[C_6H_5Co(CO)_4]\cdot Na + C_6H_5Br \rightarrow C_6H_5Co(CO)_4 + [C_6H_5Br]$

$C_5H_5Co(CO)_4 - CO \rightarrow C_6H_5COCo(CO)_4$

$C_6H_5COCo(CO)_4 + t\text{-}AmONa \rightarrow C_6H_5COOt\text{-}Am + NaCo(CO)_4$

Termination steps

$C_6H_5Co(CO)_4 \rightarrow C_6H_5 + Co(CO)_4$

$C_6H_5 + THF \rightarrow C_6H_6$

$C_6H_5COCo(CO)_4 \rightarrow C_6H_5CO + Co(CO)_4$

$C_6H_5CO + THF \rightarrow C_6H_5CHO$

Hydrolysis

$C_6H_5COCo(CO)_4 + NaOH \rightarrow C_6H_5COOH + NaCo(CO)_4$

$\xrightarrow{NaOH} C_6H_5COONa + H_2O$

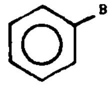
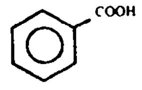
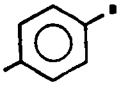
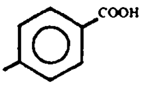
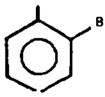
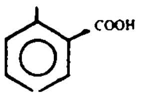
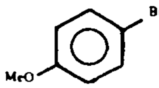
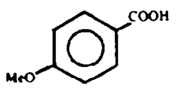
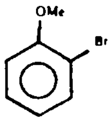
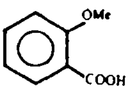
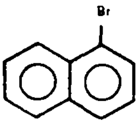
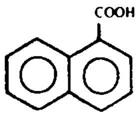
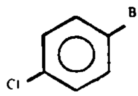
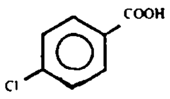
Scheme 10-3.

Under phase transfer conditions, analogous reactions can be achieved with hydroxide instead of alkoxide as nucleophile. Thus, arenecarboxylic acids are prepared in excellent yields (Table 10-1) upon

$$\mathrm{ArX + CO + 2NaOH} \xrightarrow[\mathrm{Co_2(CO)_8/Bu_4NBr} \atop \mathrm{H_2O/benzene}]{h\nu\ (350\,\mathrm{nm})} \mathrm{ArCOONa + NaX + H_2O} \qquad \text{Ref. 210}$$

UV irradiation (350 nm) in the presence of sodium hydroxide, and both $Co_2(CO)_8$ and Bu_4NBr^- as catalysts in a two phase water–benzene mixture under an atmosphere of CO.[210] Under the reaction conditions used, carbonylation of chlorobenzene did not occur and p-bromochlorobenzene could be selectively carbonylated to give p-chlorobenzoic acid. This is unexpected since selective monosubstitutions by $S_{RN}1$ reactions are *not* usually possible.[211]

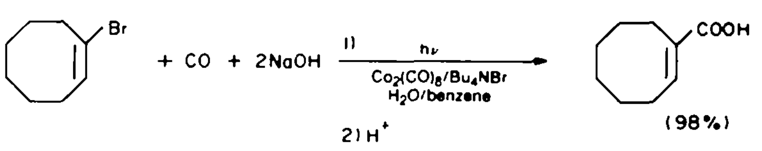
Table 10-1. Cobalt carbonyl catalyzed carbonylation of aryl halides[a,210]

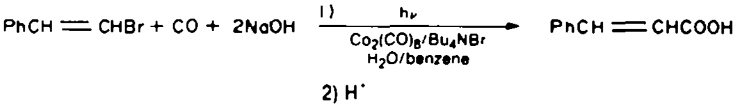
Halide	Reaction time	Acid	Yield(%)[b]
	1.5 h		95
	1.5 h		97
	2.25 h·		96
	2 h		94
	2 h		47[c]
	5 h		96
	1 h		98

(a) Reactions were carried out by simple stirring of the reaction mixture (aryl halide: 20 mmoles, C_6H_6 : 25 ml, 5N NaOH : 50 ml, Bu_4N^+ Br^- : 2 mmoles, Co_2CO_8 : 1 mmole, under a slow stream of carbon monoxide) in a Pyrex flask irradiated by 350 nm ultraviolet lamps in a Rayonet photochemical reactor. Heating was achieved by means of a 100 W tungsten lamp placed under the reaction flask. Reaction temperatures were 65°C. (b) Isolated yields based on aryl halide. (c) Anisole was produced in 45% yield.

(c) *Vinyl substitution*

Under the same reaction conditions which afford arene carboxylic acids from aryl bromides (Table 10-1), vinyl bromides can be converted to vinyl carboxylic acids.[210]


Ref 210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11. OXIDATION

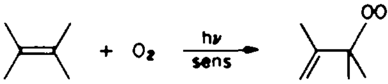
(a) *Oxidation of alkenes*

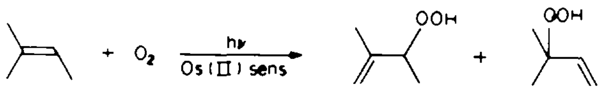
Luminescent ruthenium(II), osmium(II), and irradium(III) complexes are quenched by oxygen with efficient production of singlet oxygen ($^1O_2$) by deactivation of charge-transfer triplet states. The complexes listed in Table 11-1 all catalyze rapid photooxygenation of 2,3-dimethyl-2-butene (eqn 11-1) in methanol solution.[212] As expected for oxygenations involving $^1O_2$, the mole ratio of the two hydroperoxides **158** and **159** from 2-methyl-2-butene formed with the osmium complexes as sensitizers was the same as that obtained using $^1O_2$ generated by Rose Bengal sensitization.[212b] Ru(II) catalyzed photooxygenation of 1,3-cyclohexadiene affords the endoperoxide 2,3-dioxabicyclo[2.2.2]oct-5-ene.

Table 11-1. Ru(II), Os(II) and Ir(III) photosensitizers[a]

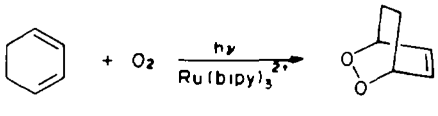
$Os(bipy)_3^{2+}$	$Ru(phen)_2(CN)_2$
$Os(phen)_3^{2+}$	$Ru(phen)_3^{2+}$
$Os(phen)_2(Ph_2phen)^{2+}$	$Ru(bipy)_2(CN)_2$
$Os(phen)_2[(SO_3Ph)_2phen]$	$Ru(bipy)_3^{2+}$
$Ir(bipy)_3^{3+}$	
$Ir(phen)_3^{3+}$	

[a] bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline; Ph_2phen = 4,7-diphenyl-1,10-phenanthroline; $(SO_3Ph)_2phen^{2-}$ = disulfonated 4,7-diphenyl-1,10-phenanthroline.

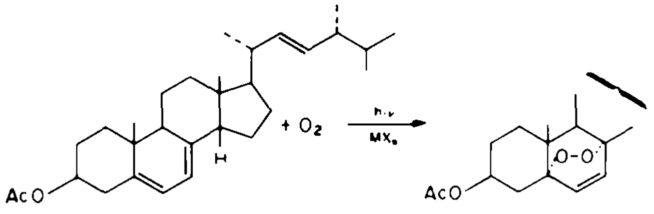

(11-1)


158 **159**

Ref 212 b

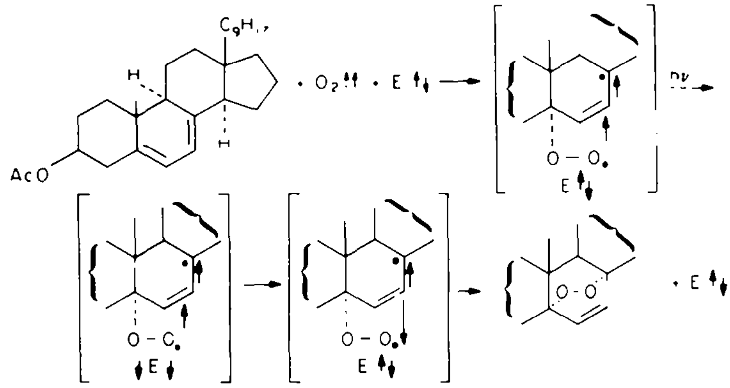

Ref 212 a

Formation of endoperoxides is not limited to reactions involving $^1O_2$. Thus, photooxygenation of ergosteryl acetate (**160**) is catalyzed cleanly and efficiently by nonluminescent Lewis acids including main group ($SnCl_4$, $SnBr_4$, SbF_5) and transition metal halides (WF_6) at −78° upon irradiation with a tungsten lamp.[213] Less efficient photooxygenation is catalyzed by $AlCl_3$, TiF_4, $TiCl_4$ and $PtCl_4$.[213] All MX_n catalysts for photooxygenation of **160** are electrophilic, and are presumed to form complexes with ergosteryl acetate which interact with oxygen and then light leading to endoperoxide as outlined in



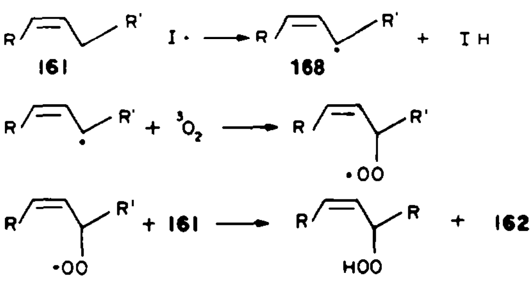
160 (>98 %) Ref 213

scheme 11-1 where E⇅ is an electrophilic, Lewis acid metal halide catalyst.[213] Irradiation converts the singlet (E⇅) complex into a triplet (E⇊) complex and permits, after oxygen insertion, the spin exchange that allows the formation of the peroxide. Whether oxygen is inserted before (as in scheme 11-1) or after singlet to triplet conversion is not defined in the postulated mechanism.[213]



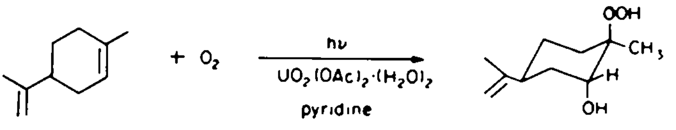
Scheme 11-1.

Formation of allylic hydroperoxides is also not limited to reactions involving $^1O_2$. Thus, autoxidation of alkenes with $^3O_2$ occurs by a free radical chain mechanism as outlined in scheme 11-2. This process is important for the dairy industry since autoxidation of polyunsaturated fatty acid derivatives corresponds to development of rancidity in milkfat. Traces of copper present in dairy products catalyze their photoinduced autoxidation.[214] Autoxidation is enhanced by heat tratment which releases copper from serum proteins allowing it to associate with fat globules where it is effective in catalyzing lipid photooxygenation.[214] Addition of ethylenediaminetetraacetic acid (EDTA) before heat treatment retards oxidation of heat treated cream presumably by complexing copper, making it less available as an oxidation catalyst. Nothing is known about the mechanism of catalysis although it is assumed that irradiation with the copper catalyst promotes initiation, and that subsequent autoxidation proceeds as the usual thermal chain process.

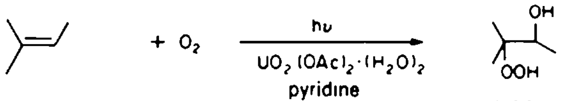


Scheme 11-2.

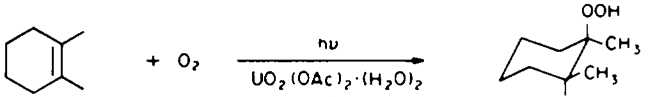
A third type of alkene photooxidation is catalyzed by uranyl acetate. β-Hydroxyhydroperoxides are produced from alkenes and oxygen in the presence of uranyl acetate dihydrate upon irradiation with pyrex filtered UV light. The yields of isolated hydroperoxides are low. However, yields of crude product



(14%)



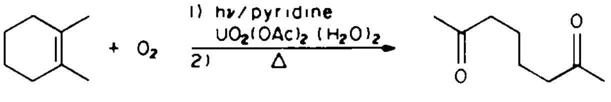
(12%)



163

164 (8%)

are much higher and thermal rearrangement of the crude hydroperoxide **164** affords diketone **165** in 51% yield overall from 1,2-dimethylcyclohexene (**163**).[215] Additions to the cyclohexene derivatives are

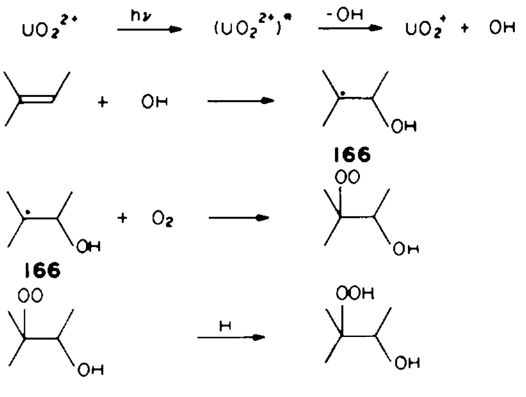


162

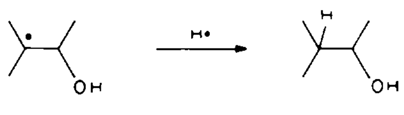
165 (51%)

Ref 215

stereospecifically trans. Additions to the trisubstituted alkenes produce tertiary hydroperoxides regiospecifically. Experiments with $^{18}O_2$ or $H_2{}^{18}O$ reveal that the oxygen atoms in the hydroperoxyl group originate mainly (90%) from molecular oxygen, while the oxygen atom in the hydroxyl group originates, in major part (67%), from the water molecule of hydration in uranyl acetate. A mechanism (scheme 11-3) involving photogeneration of ·OH from $UO_2(OAc)_2(H_2O)_2$ is *not* favored since the oxidation is not affected by radical scavengers (tri-t-butylphenol or p-hydroquinone) and no reaction occurs in the absence of oxygen. It seems that products from the radical **166**, such as an alcohol, should be produced in the absence of oxygen.

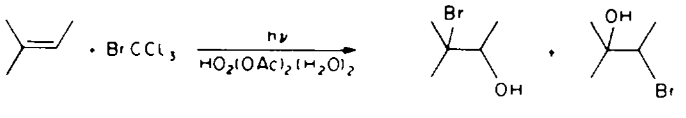


Scheme 11-3.



166

Uranyl acetate catalyzes photochemical formation of bromohydrins from alkenes and various polyhalogenated compounds in the absence of O_2.[215b] The regioselectivity of this reaction contrasts with that found in addition of HOBr to 2-methyl-2-butene which gives **168** selectively.[210] Significantly, the **167** : **168** ratio and the yield of these bromohydrins correlate with the half-wave reduction potentials of the polyhalogenated compounds (Table 11-2).[217] Thus, a novel mechanism was proposed involving "long-range electron-transfer" which is believed to be operative in uranyl acetate promoted photoreactions of alkenes with oxygen (scheme 11-4) or polyhalogenated compounds (scheme 11-5), and also possibility in iron(III) chloride catalyzed photoreactions of alkenes with oxygen and polyhalogenated compounds (vide infra).[217] Electron-transfer from the ^{-}OH ligand to moelcular oxygen through the metal ion and alkene molecule produces an intermediate which is a resonance hybrid of structures **169** and **170**



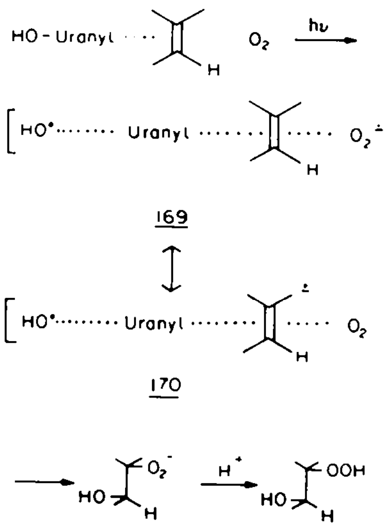
167 (3 : 1) **168**

Ref 216

Table 11-2. Bromohydrin formation and half-wave reduction potential of polyhalogenated compounds[217]

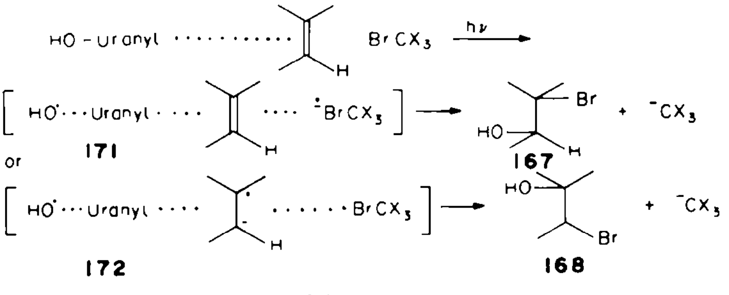
Polyhalogenated compound	Yield[a] (%) 167+168	Ratio[a] 167:168	Recovered olefin (%)	$E_{1/2}$ in DMF (V vs s.c.e.)
$CBrCl_3$	31	3.8	36	-0.18
CBr_4	20	3.0	51	-0.31
CBr_3CN	18	3.0		-0.32[b]
CBr_3COCBr_3	11[c]	2.4[c]		-0.30
$CHBr_3$	5	2.0	73	-0.48
CBr_2F_2	5	2.3	67	-0.66
CH_2Br_2	0		74	-1.48[d]

[a] Irradiation time, 2 h. [b] Determined by a.c. polarography. [c] Irradiation time, 1 h. [d] Value from ref. 218 (in dioxan-H_2O, 8:2).



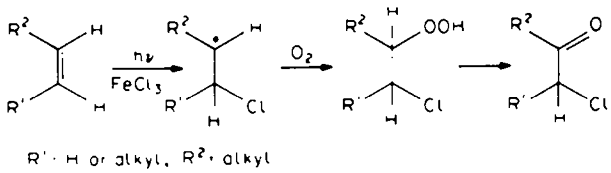
Scheme 11-4.

(scheme 11-4). Once the HO ligand is furnished with radical character through electron-transfer, it adds to the alkene, and successive or probably simultaneous coupling of the resulting carbon radical with oxygen anion radical followed by protonation completes the reaction. Other compounds possessing electron withdrawing character, such as polyhalogenated compounds, instead of oxygen can induce the same type of reactions (scheme 11-5). Resonance hybrid **171** would be favored over **172** as the electron withdrawing ability of $BrCX_3$ becomes stronger. If **171** is involved, a hydroxyl radical attacks the less substituted alkenic carbon producing the more stable carbon radical intermediate, leading to **167** as the final product. On the other hand, if **172** is involved, the hydroxyl radical attacks the more substituted carbon of the alkene anion radical, which has more radical character than the less substituted carbon, and the final product is **168**. As expected for such a mechanism, the yield of bromohydrins **167** + **168** and the product ratio **167**:**168** correlate well with the reduction potentials ($E_{1/2}$) of the polyhalogenated compounds (Table 11-2).[217]

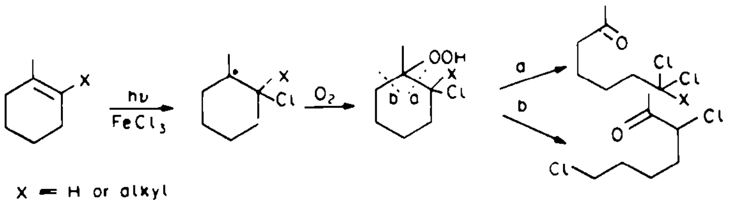


Scheme 11-5

FeCl$_3$ promotes photooxidation of alkenes in pyridine solution (Table 11-3).[219] Mono- and disubstituted alkenes (Table entries 1-7) give α-chloroketones while tri- and tetrasubstituted alkenes (Table entries 8 and 9) afford ring-cleaved dichloroketones upon irradiation with pyrex filtered UV light in pyridine in the presence of an equivalent amount of FeCl$_3$ and excess oxygen. In the absence of oxygen, cyclooctene affords 1,2-dichlorocyclooctene (16%). When an appropriate chlorine source was present, FeCl$_3$ functions catalytically for oxidation of 2-octene (Table 11-4).[219] Chlorides or sulfates of Fe(II), Cu(I), or Cu(II) exhibited weaker activities for promoting photooxidation, 19–42% yields of **173** + **174** from 2-octene compared with 73% with FeCl$_3$ in pyridine-CCl$_4$ 1:1.[219] All of these photooxidations are considered to involve initial vicinal chlorohydroperoxide products which decompose thermally to α-chloroketones if the hydroperoxide is secondary (eqn 11-2) or ring-cleaved dichloroketones if the hydroperoxide is tertiary (eqn 11-3).[219]



(11-2)



(11-3)

Photooxidation of α,β-unsaturated ketones **175** to give dimeric lactones **176** is catalyzed by CuSO$_4$.[220] This catalysis is especially interesting since the enones **175** undergo a different photoreaction in the

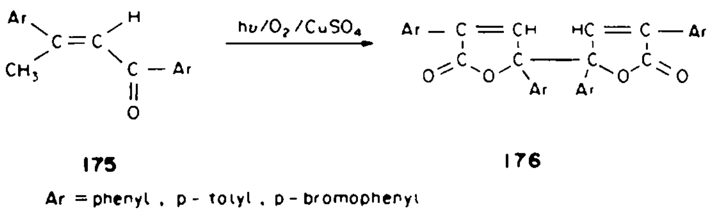
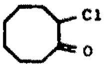
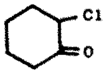
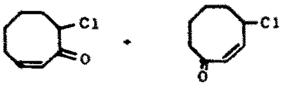
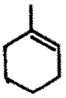
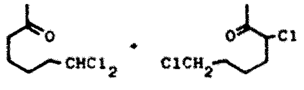
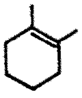
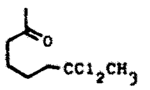


Table 11-3. Photo-oxidation of alkenes in pyridine in the presence of an equivalent amount of $FeCl_3$[219]

Entry	Alkene	Products		Yield[a]
1			b)	37% (40%)
2				33%
3	1-octene	$C_6H_{13}COCH_2Cl$		10%
4	2-octene	 $\underset{Cl}{C_5H_{11}CO\underset{\vert}{C}HCH_3} + \underset{Cl}{C_5H_{11}\underset{\vert}{C}HCOCH_3}$ 173 (1 1 3) 174		43% 50%[c)]
5	$CH_3CH = CHCH_2OH$	 $CH_3CO\underset{Cl}{\underset{\vert}{C}}HCH_2OH$	d)	28%
6	oleyl alcohol	 $C_8H_{17}\underset{O}{\underset{\Vert}{C}}-\underset{H\ \ Cl}{C}(CH_2)_8OH$		33%[c)]
7		 (1 : 2.4)		29%[e)]
8		 (6 : 1)		29%
9				26%

a) Yields were determined by NMR analyses using an internal reference on the crude materials. Values in the parentheses refer to the isolated yields. The amounts of the unreacted starting materials were not determined.

b) Cyclooctene oxide (3%) and *cis*- and *trans*-1,2-dichlorocyclooctane (2%) were identified as by-products.

c) In the presence of tri-t-butylphenol.

d) 2,3-Dichloro-1-butanol (5%) was identified as by-product.

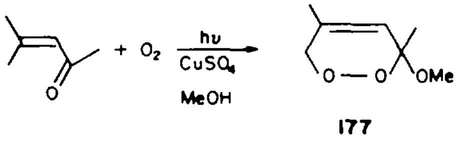
e) Reaction in pyridine-CCl_4 (1 : 1 by volume).

Table 11-4. Iron(III) chloride-catalyzed oxidation of 2-octene by oxygen with CCl_4 or $CHCl_3$[219]

Mole equiv $FeCl_3$ versus 2-octene	Combined yields of 173 and 174[a]	
	in Pyridine-CCl_4	in Pyridine-$CHCl_3$
0	13%	
0.1	46%	
0.5	64%	60%
1.0	73%	

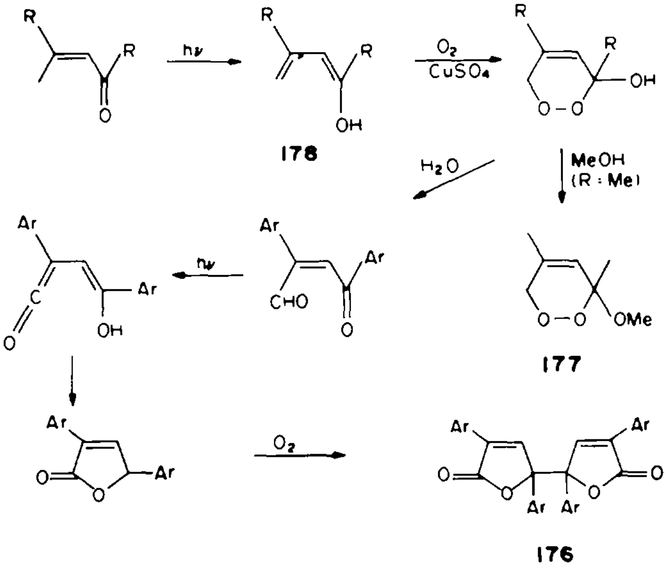
[a] Solutions of 2-octene (0.025 M) and varying amounts of $FeCl_3$ in pyridine-CCl_4 (1:1 by volume) or in pyridine-$CHCl_3$ (1:10 by volume) were irradiated for 1 h under oxygen.

absence of the catalyst, trans→cis isomerization, even in the presence of oxygen. Thus, these catalyzed oxidations apparently are examples of a rare reaction type in which the metal catalyst influences the reaction pattern by interaction with an organic molecule in the excited state or with a transient photogenerated intermediate. Similarly $CuSO_4$ catalyses photooxidation of mesityl oxide to give a cyclic



Ref 220

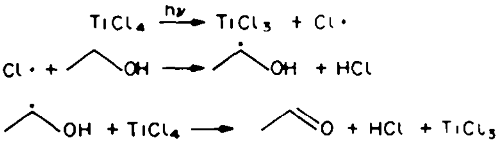
peroxide 177.[220] Generation of both 176 and 177 probably involve addition of oxygen to a photoenol[221] 178 as outlined in scheme 11-6. $CuSO_4$ apparently promotes the addition of oxygen to the photoenol 178.



Scheme 11-6.

(b) *Oxidation of alcohols*

Titanium(IV) catalyzed photooxidation of methanol to formaldehyde was suggested in section 9b to account for the methylene group which becomes C-2 in the oxazolidine product 152 from $TiCl_4$ catalyzed photoreaction of methanol with N-methylbenzaldimine.[183] Also, ethanol affords acetaldehyde with quantum yields approaching unity upon irradiation in the presence of $TiCl_4$.[222] A mechanism outlined in scheme 11-7 was proposed for the latter photooxidation since the production of $TiCl_3$ was detected spectroscopically.[222] Similar stoichiometric photooxidations[223] occur with other primary and secondary alcohols and the relative rates of oxidation correlate with the structures of the alcohols (Table 11-5) in a manner consistent with rate determining generation of the corresponding α-hydroxyalkyl radicals. Since dissolution of $TiCl_4$ in alcohols produces alcoholate complexes, e.g. $Ti(OR)_2Cl_2(ROH)$ by solvolysis,[224]



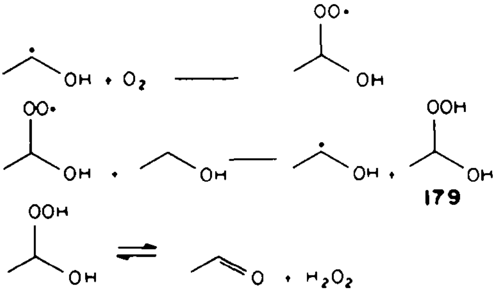
Scheme 11-7.

Table 11-5. Photoreduction of 0.1*M* $TiCl_4$/0.4*M* ROH solutions in 3*M* HCl for 5 hr at 310 nm[223d]

ROH	Conversion of Ti(IV) to Ti(III), %
$C_6H_5CH_2OH$	60
$(CH_3)_2CHOH$	32
CH_3CH_2OH	22
CH_3OH	10

LMCT excitation could occur from Cl^- as suggested in scheme 11-7 or from ^-OR to afford $\cdot OR$, and a mechanism involving alkoxy radicals in place of chlorine atoms might be operative. Participation of $TiCl_4$ in oxidation of α-hydroxyethyl radicals in a secondary dark reaction is supported by the observation that the rate of formation of $TiCl_3$ increases with increased initial concentration of $TiCl_4$ under conditions of total light absorption. Furthermore, photogeneration of α-hydroxymethyl and α-hydroxyethyl radicals from methanol and ethanol respectively and their subsequent oxidation by Ti(IV) in the dark was confirmed by ESR experiments.[225]

With oxygen saturated solutions, photooxidation of ethanol becomes catalytic in $TiCl_4$, and quantum yields in the range of 5–7 are found.[222] Therefore, it is presumed that a thermal radical chain is induced by peroxy radicals (scheme 11-8) produced from reaction of oxygen with α-hydroxyethyl radicals generated according to scheme 11-7. H_2O_2 produced in this thermal chain might regenerate the Ti^{4+} catalyst and initiate further thermal chains by reaction with Ti^{3+} produced in the initial photoreaction.

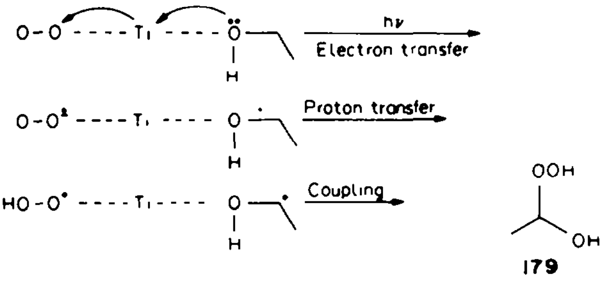


Scheme 11-8.

Alternatively, hydroperoxide **179** might be generated directly by a "long-range electron transfer"

$$Ti^{3+} + H_2O_2 \longrightarrow Ti^{4+} + {}^{-}OH + HO^{\cdot}$$

mechanism (scheme 11-9) which is analogous to scheme 8-4 proposed for $TiCl_4$ catalyzed photoaddition reactions of alcohols.[186]



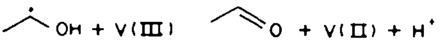
Scheme 11-9.

Sunlight induces oxidation of methanol by oxygen in the presence of a macrocyclic iron(III) complex as catalyst.[226] LMCT excitation is presumed to generate a methoxy radical by homolysis of an iron(III) methoxide intermediate. No details were proposed for the subsequent formation of formaldehyde from the putative methoxy radical.

UV irradiation of vanadium(III) chloride in methanol, ethanol or 2-propanol results in oxidation of the alcohols to formaldehyde, acetaldehyde, and 2-propanone respectively with concomitant formation of V(II).[227] The photogeneration of intermediate α-hydroxyalkyl radicals which react with V(III) to produce additional V(II) in a subsequent dark reaction was confirmed directly by ESR experiments.[224c] The absorption responsible for photooxidation was identified as a ligand to metal charge-transfer (LMCT) excitation. The primary photochemical event was presumed to be generation of an alkoxy radical (eqn 11-4) which rearranges rapidly to an α-hydroxyalkyl radical (eqn 11-5).[224a] The latter reacts with a second equivalent of V(III) in a subsequent dark reaction (11-6). The photooxidation is catalytic in vanadium since, after a short induction period, evolution of hydrogen occurs owing to photoreduction of

(11-4)

(11-5)



(11-6)

protons by V(II) according to scheme 11-10.[224c] With prolonged irradiation of an alcohol solution of

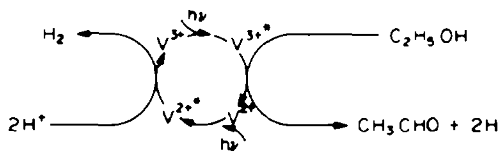
$$V(II) + H^+ \xrightarrow{h\nu} V(III) + H\cdot$$

$$H\cdot + H^+ \longrightarrow H_2^+$$

$$H_2^+ + V(II) \longrightarrow V(III) + H_2$$

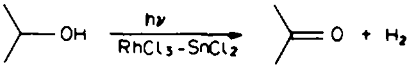
Scheme 11-10.

VCl_3, the number of moles of hydrogen formed exceeds by severalfold the amount of vanadium present. The overall vanadium catalyzed photodehydrogenation of ethanol is summarized in scheme 11-11.



Scheme 11-11[1b]

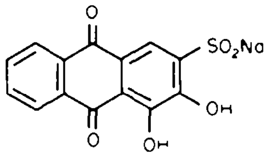
UV irradiation greatly accelerates the rate of dehydrogenation of 2-propanol in the presence of a rhodium(III) chloride-tin(II) chloride catalyst.[228] Since the quantum yield Φ = 1.7 exceeds unity and the



reaction is accelerated by heating, it is presumed that photogeneration of a thermally active catalyst is involved.

(c) *Oxidation of arenes*

Although hydrated Co^{+2} ion catalyzes oxidative decolorization of the red dye Alizarin S (**180**) by H_2O_2, cobalt(III) complexes of the type $[Co(NH_3)_5X]^{2+}$ (X = Br, I, NO_2) are catalytically inactive. Since



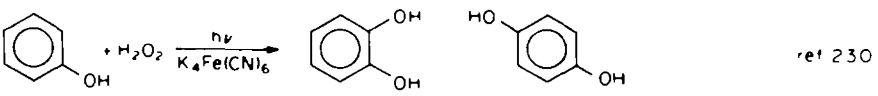
180

these complexes decompose photolytically to hydrated Co^{+2} (eqn 11-7) a Co(II) catalyst for thermally induced oxidation of **180** by H_2O_2 (eqn 11-8) can be photogenerated from the photosensitive Co(III)

$$[Co(NH_3)_5X]^{2+} \xrightarrow{h\nu} Co^{2+} + 5NH_3 + X^- \qquad (11\text{-}7)$$

$$\mathbf{180} + H_2O_2 \xrightarrow{Co^{2+}} \text{colorless products} + H_2O \qquad (11\text{-}8)$$

complexes.[229] Similarly, irradiation of phenol and 35% H_2O_2 in the presence of $K_4Fe(CN)_6$ affords dihydroxybenzenes.[230]



UV irradiation of aqueous solutions of benzene containing Fe(III) salts produces phenol presumably by the photogeneration of hydroxyl radicals (eqn 11-9), generation of phenyl radicals (eqn 11-10), and further oxidation of the latter by a second equivalent of Fe(III).[231] Reactions analogous to eqns (11-9) and (11-10) are considered to be involved in photoinduced oxidative bleaching of aromatic organic dyes (DH) which is catalyzed by Fe(III) salts.[232] However, in the presence of excess oxygen, intermediate dye radicals afford peroxide radicals (eqn 11-11) which regenerate the Fe(III) catalyst by reacting with Fe^{2+} (eqn 11-12). At low Fe^{3+} concentrations, the extent of light absorption and hence the yield of $^\cdot OH$ radicals is proportional to the Fe^{3+} concentration. Therefore, for a given light intensity and time of irradiation, the extent of photooxidative bleaching of the dye is proportional to the Fe^{+3} concentration, and can be exploited as a quantitiative analytical method.[232] Thus, very small quantities of iron can decolorize much larger, more easily measurable quantities of organic dye by catalytic photooxidation.

$$Fe^{3+} + H_2O \rightleftharpoons Fe^{3+}(OH^-) + H^+$$

$$Fe^{3+}(OH^-) \xrightarrow{h\nu} Fe^{2+} + HO^\cdot \tag{11-9}$$

$$HO^\cdot + PhH \longrightarrow H_2O + Ph^\cdot \tag{11-10}$$

$$H_2O + Ph^\cdot + Fe^{3+} \longrightarrow PhOH + H^+ + Fe^{2+}$$

$$DH + {}^\cdot OH \longrightarrow D^\cdot + H_2O$$

$$D^\cdot + O_2 \longrightarrow DOO^\cdot \tag{11-11}$$

$$DOO^\cdot + Fe^{2+} + H^+ \longrightarrow DOOH + Fe^{3+} \tag{11-12}$$

(d) *Oxidative decarboxylation*

UV irradiation of solutions of benzoic acids with iron(III) ions results in oxidative dacarboxylation to produce phenols.[223] A similar photoreaction is presumably involved in iron(III) catalyzed oxidative

$$PhCOOH + Fe^{+3} + H_2O \xrightarrow{h\nu} PhOH + CO_2 + 2Fe^{+2} + 2H^+ \qquad \text{Ref. 233}$$

photodecarboxylationof α-hydroxycarboxylic acids with iodine.[234] The fact that the rate of this reaction is linearly correlated with the inverse of the iron(III) concentrations suggests a complex of iron(III) and the hydroxycarboxylic acid is involved.[234] Presumably LMCT (eqn 11-13) is followed by rapid decarboxylation of the resulting carboxy radical (eqn 11-14). Further oxidation (eqn 11-15 or 11-16) then affords the final aldehyde product. The reactionis catalytic in Fe(III) since any Fe(II) produced is reoxidized to Fe(III) by iodine.

$$RCH(OH)COOH + 2I_2 \xrightarrow[Fe^{+3}]{h\nu} RCHO + 4I^- + CO_2 + 2H^+ \qquad \text{Ref. 234}$$

$$RCH(OH)COOH + Fe^{+3} \longrightarrow RCH(OH)COOFe^{+2} + H^+$$

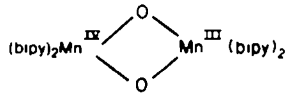
$$RCH(OH)COOFe^{+2} \xrightarrow{h\nu} RCH(OH)COO^\cdot + Fe^{+2} \tag{11-13}$$

$$RCH(OH)COO^\cdot \longrightarrow R\dot{C}H(OH) + CO_2 \tag{11-14}$$

$$R\dot{C}H(OH) + I_2 \longrightarrow RCHO + HI + I^\cdot \tag{11-15}$$

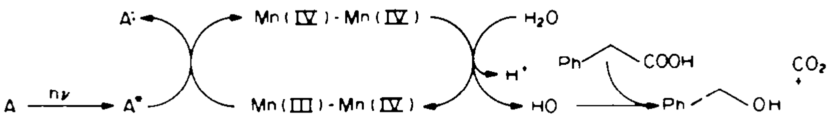
$$R\dot{C}H(OH) + Fe^{+3} \longrightarrow RCHO + Fe^{+2} + H^+ \tag{11-16}$$

The mixed valence binuclear manganese complex **181** catalyzes oxidative photodecarboxylation of phenylacetic acid by dicyanoanthracene (A) to afford benzyl alcohol and the anion radical of A ($A^{\dot{-}}$).[236] The reaction is assumed to involve photoinduced oxidation of **181** by A followed by a dark reaction



181

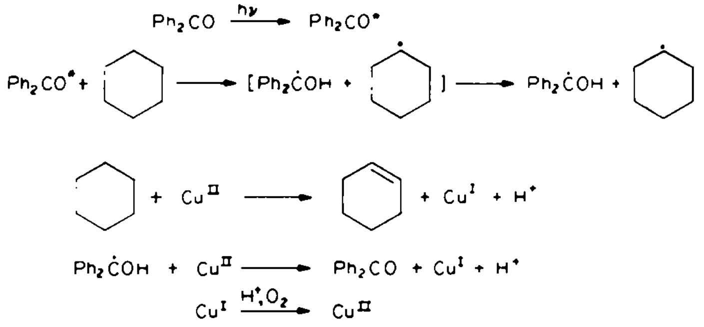
which regenerates **181** with concomitant oxidation of water (scheme 11-12). The resulting hydroxyl radicals produce benzyl alcohol by reaction with phenylacetic acid.[237]



Scheme 11-12.

(e) *Dehydrogenation*

In a sense, any photooxidation by a metal reagent can be made catalytic since there almost certainly exists some pathway for reoxidizing the metal reagent. Potential alternative reaction pathways involving the reoxidant may preclude continuous regeneration of the catalyst. In situ periodic regeneration of the metal oxidant may provide a convenient alternative. Thus, photoinduced dehydrogenation of cyclohexane by copper(II) pivalate is catalyzed by benzophenone, and the Cu(II) oxidant can be regenerated from Cu(I) by periodic treatment of the photolysis mixture with air (scheme 11-13).[237]



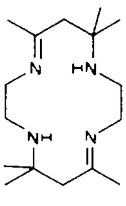
Scheme 11-13.

Photogeneration of hydrogen by dehydrogenation of organic compounds is of considerable interest as a possible means for storage of solar energy. Some examples of metal catalysis of such reactions were presented in the section on oxidation of alcohols. Many reactions of this type are known which involve interception of high energy reagents generated in photoinduced redox reactions by oxidative[238] or reductive [239] quenching of photoexcited metal complexes.

With Ru(bipy)$_3^{2+}$ as a photochemical catalyst and a cobalt(I) complex of the macrocyclic ligand **182** as a thermally active cocatalyst, ascorbic acid (AH$_2$) is photodehydrogenated to dehydroascorbic acid

$$H^+ + HA^- \xrightarrow[\text{Ru(bipy)}_3^{2+}]{h\nu} A + H_2 \qquad (11\text{-}16)$$

$$\text{Co}^{II}\text{L}$$



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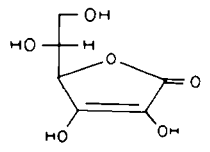
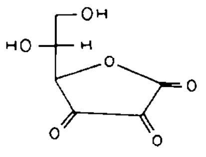


AH$_2$



A

(A) (eqn 11-16). The anticipated mechanism for H_2 evolution is outlined in scheme 11-14 (L = 182).[239] The intermediate $Co^{I}L$ was detected spectroscopically in laser flash photolysis experiments. The photoexcited Ru(II) complex serves as a one electron oxidant toward ascorbate (HA^-) which reductively quenches the photoexcited complex.

$$Ru(bipy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bipy)_3^{2+}$$

$$^*Ru(bipy)_3^{2+} + HA^- \longrightarrow Ru(bipy)_3^{+} + HA^{\cdot}$$

$$Ru(bipy)_3^{+} + Co^{II}L \longrightarrow Ru(bipy)_3^{2+} + Co^{I}L$$

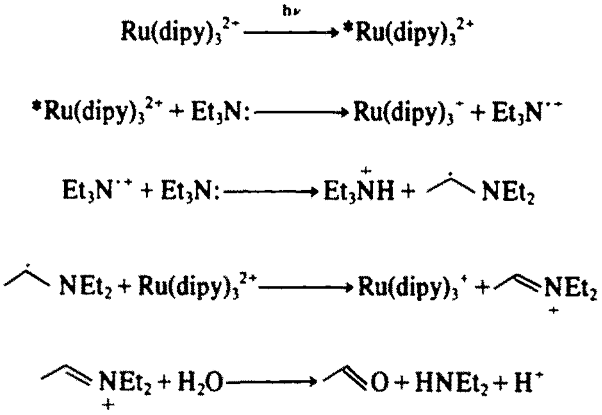
$$Co^{I}L + H^+ \longrightarrow [Co^{III}LH^-] \xrightarrow{H^+} Co^{III}L + H_2$$

$$Co^{III}L + HA^- \longrightarrow Co^{II}L + HA^{\cdot}$$

$$2HA^{\cdot} \longrightarrow HA^- + H^+ + A$$

Scheme 11-14.

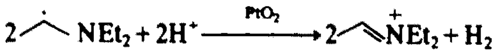
Another example of reductive quenching of a photoexcited complex is found with the analogous Ru(II) complex of 4,4′-dicarboxy-2,2′-bipyridine diisopropylester (dipy) which photooxidizes triethylamine in aqueous acetonitrile to yield acetaldehyde according to scheme 11-15.[240] This photooxidation of



Scheme 11-15.

triethylamine is not catalytic in Ru(II). However, the Ru(II) complex can be regenerated continuously in situ by a dark reaction between the Ru(I) complex and water which is heterogeneously catalyzed by PtO_2 (eqn 11-17), and direct dehydrogenationof α-aminoethyl radicals might also be catalyzed by PtO_2 (eqn 11-18).[240]

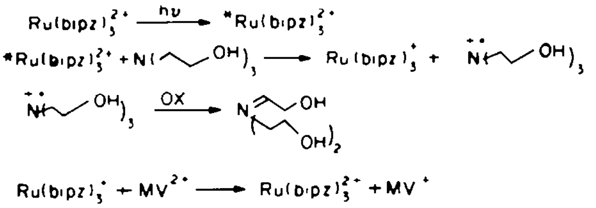
$$2Ru(dipy)_3^{+} + 2H^+ \xrightarrow{PtO_2} 2Ru(dipy)_3^{2+} + H_2 \qquad (11\text{-}17)$$



(11-18)

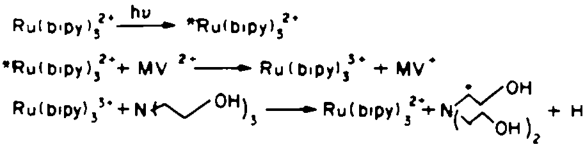
Reductive quenching of the analogous photoexcited Ru(II) complex of 2,2′-bipyridazine (bipz) by triethanolamine (TEA) generates $Ru(bipz)_3^+$ (scheme 11-16).[241] The catalyst is regenerated by reaction with N,N′-dimethyl-4,4′-bipyridinium cation (MV^{2+}). In the absence of MV^{2+} the Ru(I) complex accumulates as evidenced by its characteristic visible spectrum.

In contrast to the reactions of scheme 11-16 with $Ru(bipz)_3^{2+}$, photoexcited $Ru(bipy)_3^{2+}$ is oxidatively



Scheme 11-16.

quenched by MV^{+2} (scheme 11-17).[242] The Ru(II) catalyst is regenerated in a dark reaction involving oxidation of TEA or ethylenediamineteraacetate (EDTA) by Ru(III). Thus, laser flash spectroscopy showed that MV^{2+} quenches the luminescence of *Ru(bipy)$_3^{2+}$ while TEA or EDTA do not.[242a] Hence, minor modifications of the ligands on the Ru(II) catalyst profoundly influence the mechanism by which

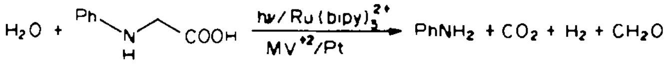


Scheme 11-17.

the amine is dehydrogenated. Since MV$^+$ reacts with water in the presence of a heterogeneous catalyst to produce dihydrogen, metal catalyzed photoredox reactions of either type exemplified by schemes 11-16 and 11-17 are of potential interest for solar energy storage.[243] Cysteine[242b] and other organic

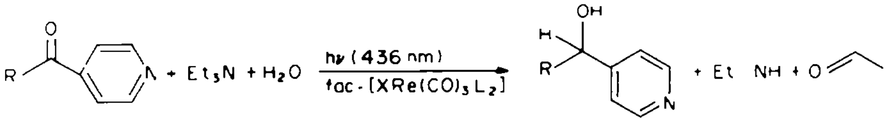
$$2MV^+ + 2H_2O \xrightarrow[\text{catalyst}]{} 2MV^{2+} + H_2 + 2OH^-$$

electron donors[242d] (1,2-diaminocyclohexanetetraacetic acid, N-phenylglycine, iminodiacetic acid, methyliminodiacetic acid, dimethylglycine, bis-hydroxyethylglycine, hydroxyethyltrihydroxypropyl ethylenediamine, allylthiourea, and mercaptoethanol) are oxidized by Ru(III) in photoredox processes analogous to scheme 11-17. In the presence of a heterogeneous platinum catalyst, the case of N-phenylglycine is typical of the overall photoinduced reactions occurring.[242d] Photooxidation of TEA



with H$_2$ evolution also occurs with oxidative quenching of *Ru(bipy)$_3^{2+}$ by Rh(bipy)$_3^{3+}$ instead of MV^{2+}.[243]

Photoinduced dehydrogenation of triethylamine by 4-benzoyl- or 4-acetylpyridine is catalyzed by a Re(I) complex *fac*-[XRe(CO)$_3$L$_2$] (X = Cl and L = 4-benzoylyyridine or X = I and L = 4-acetylpyridine).[244] Since Et$_3$N quenches the luminescence of these complexes, electron transfer from the amine to the excited state of the complex is assumed.



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