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1-ACYL-2-CYCLOPENTENES AND 5-ACYLBICYCLO[2.1.0]PENTANES: PHOTOCHEMICAL AND THERMAL ISOMERIZATIONS

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Abstract—The photochemistry of 1-acyl-2-cyclopentenes varies with the nature of the acyl group. On direct irradiation the aldehyde eliminates carbon monoxide in the singlet excited state, and the aroyl compounds cleave to allyl-aroyl radical pairs both from the singlet and triplet states. In competition to α-cleavage the methyl ketones isomerize in an allylic 1,3-acetyl shift. The lowest-lying reactive triplet of these methyl ketones, characterized as a $^3(\pi, \pi^*)$ state in the case of the 3-phenyl homologue, undergo oxadi-π-methane rearrangement to a mixture of *endo*- and *exo*-5-acetylbicyclo[2.1.0]pentanes.

The ground-state acetylbicyclopentanes react in two ways at elevated temperatures: *endo-exo* stereomutation by selective cleavage of the central cyclopropane bond and reclosure of the 1,3-cyclopentane diradical intermediate, and a rearrangement of the *endo* isomer to 1-acetyl-2-cyclopentenes on a separate potential energy surface involving a formal 1,2-acetyl shift. The unusually large negative entropy of activation for this latter reaction is suggestive of a concerted electrocyclic process in which the electrons of the internal cyclopropane and the C(5)-acetyl bonds participate.

This report concerns investigations which had been initiated six years ago with the aim to study the photochemistry of β,γ-unsaturated "homoconjugated" ketones. The work has mainly centered on 1-acyl-2-cyclopentenes. It has disclosed the specific dependence of 1,3- (in the singlet excited state) and 1,2-acetyl shifts (in the triplet state) on spin multiplicity of the photoexcited methyl ketone representatives, and factors governing the competition between the concerted singlet 1,3-allylic shift (methyl ketones) and the α-cleavage into acyl and allyl radical pairs capable of diffusion (methyl and phenyl ketones). A more recent extension to the exploration of the thermal transformations of 5-acetylbicyclo[2.1.0]pentanes—the triplet photoproducts of the acetylcyclopentenes—has led to the mechanistic differentiation of the *exo*$\rightleftharpoons$*endo* stereomutation and the concurrent *endo*-specific rearrangement to 1-acetyl-2-cyclopentenes.

Our interest in the photochemistry of β,γ-unsaturated carbonyl systems originates from the observation in 1963 that androst-5-en-19-als decarbonylate photolytically, and predominantly so with concurrent intramolecular transfer of the aldehydic hydrogen to the α- and γ-carbons. They afford in quantitative chemical yield a *ca.* 19:1 ratio of the isomeric 5(6)- and 5(10)-olefins (cf. Chart 1: **1** → **2** + **3**).[1] The mechanistic investigation of this reaction included also other similar aldehydes, in particular laurolenal (1-formyl-1,2,3-trimethyl-2-cyclopentene).[2] It was shown that nonplanarity of the C_β=C_γ and the C_α-CHO bonds are prerequisite to the unimolecular decarbonylation, and that the reaction occurs exclusively from the singlet excited state. Fluorescence and singlet-triplet intersystem crossing do not contribute to the dissipation of excitation energy; the quantum yields of reaction are in the order of 0·5. At least two paths are followed by the overall reaction. While a photochemically allowed concerted process—a linear cheletropic elimination of carbon monoxide—remains possible for the major decarbonylation mode (e.g. (*R*)-**4** → (*S*)-**7**, Chart 2; however, a kinetic H/D isotope effect of a mere *ca.* 1·1 renders this less likely), α-cleavage of the aldehydic rotamers to individual allyl-formyl radical pair intermediates (e.g. **5** and **6**) as the primary photochemical process can account for the entire reaction pattern. The secondary reactions of these postulated radical pairs (recombination to starting aldehyde and particularly the disproportionation to products (*R*)- and (*S*)-**7**) would depend on the incipient orientation of the radical components which coincides with that of their rotameric aldehyde precursors. Thus, the radical pair **5** corresponds to the most stable rotamer of the deuteriated aldehyde **4**[4] and its formyl deuterium is suitably oriented for a regiospecific incorporation at C-1. The radical pair **6** results from the predominant among the minor rotamers and offers both the same and an alternative transfer of deuterium (to C-3). A less intimate

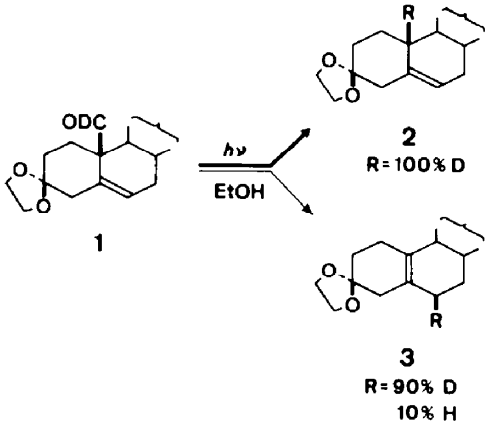


Chart 1.

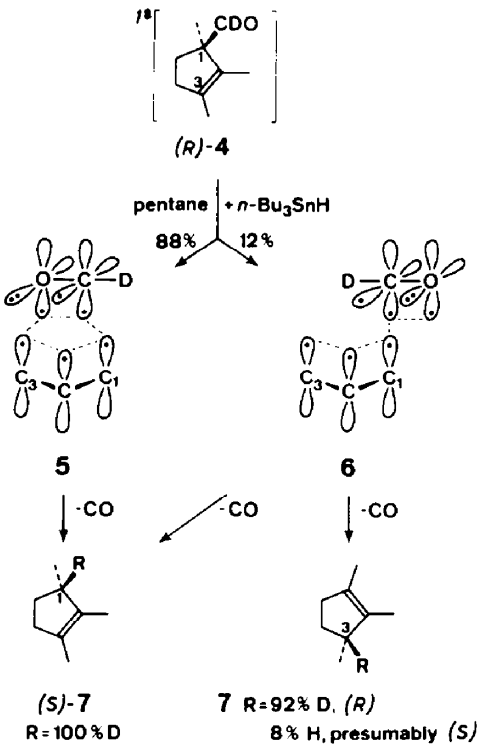


Chart 2.

association in the incipient radical pair of type **6** can accommodate the finding that incorporation at C-3 of a hydrogen from a suitable external donor (ethanol in **1**→**3**, tri-n-butylstannane in (*R*)-**4**→(*R*)-**7**) can compete with the intramolecular transfer of deuterium in the decarbonylation mode involving a double bond shift.

The disproportionation route to decarbonylation via radical pairs emanates also from the photochemistry of α-aryl aldehydes.[5,6] Aliphatic aldehydes of type **8** yield the corresponding cumene (**9**: $\Phi = 0{\cdot}76$), again with full retention of the aldehydic hydrogen when photolyzed in a hydrocarbon solvent. A photo-CIDNP study of **8**[7] discovered a small triplet-born cumyl-formyl radical pair component capable of recombination, disproportionation to **9**, and diffusion to free radicals. The cumyl radicals couple to **10** which constitutes a minor photoproduct. Nonetheless, either a singlet radical pair reacting with a "cage" effect of unity and/or a singlet concerted elimination of carbon monoxide strongly prevail. Finally, both possible disproportionation modes of a singlet-born formyl-benzyl radical pair can become competitive and contribute to the product pattern of appropriate heterocyclic aryl aldehydes. The methylindanyl aldehyde **11**—a benzo homologue of laurolenal (**4**)—still uniformely decarbonylates (→**12**) when photolyzed in deoxygenated pentane, and incorporation of external hydrogen from added stannane occurs to a maximum of 12%. The heteroatom in the dihydrobenzofuranyl system of **13**, however, renders the adjacent methylene hydrogens sufficiently labile to induce parallel decomposition to 5% benzofuran **15** and monodeuterioformaldehyde. In the presence of stannane the responsible radical pair is trapped and a total of 26% hydrogen is incorporated into the dihydrobenzofuran product **14**.

Although the decarbonylation reaction is blocked in ketone homologues of aldehyde **4**, α-cleavage should still be the *a priori* most likely primary photochemical process. Such expectation was fully met in the investigation of phenyl ketones of type **16**.[8] The irradiation of (*R*)-**16** leads to racemization due to a formal 1,3-allylic benzoyl shift, and to the formation of diene **20**, benzaldehyde (**21**), and dimers of the cyclopentenyl radical (**19**). Several analogues of **16** such as the (*R*)-*p*-anisyl ketone and the racemic 2-trideuterio methyl and 1- and 3-desmethyl derivatives were employed additionally in the subsequent more detailed study. The evidence obtained *inter alia* from a chiroptical and mass spectrometric analysis of a crossing experiment and from photolytic CIDNP measurements including the use of carbon tetrachloride as a free radical scavenger, established the reaction paths summarized in Chart 4. The predominant photoreaction is indeed α-cleavage of **16** (and its analogues) to a geminate benzoyl/cyclopentenyl radical pair (**17**). The reaction occurs in approximately 30% yield from the singlet and 70% from the triplet state. The latter is quite short-lived and is quenched only partially in the presence of 2M naphthalene. The radical pair **17** undergoes recombination to *rac*-**16** and disproportionation to **20**+**21** (paths *a*) as well as diffusion to free radicals (**18**) which in turn recombine and disproportionate on random encounter (→**16**, **19**–**21**; paths *c*). The photoracemization of (*R*)-**16** arises *ca.* 40% from pair restitution and 60% from free-radical recombination (the data for the corresponding

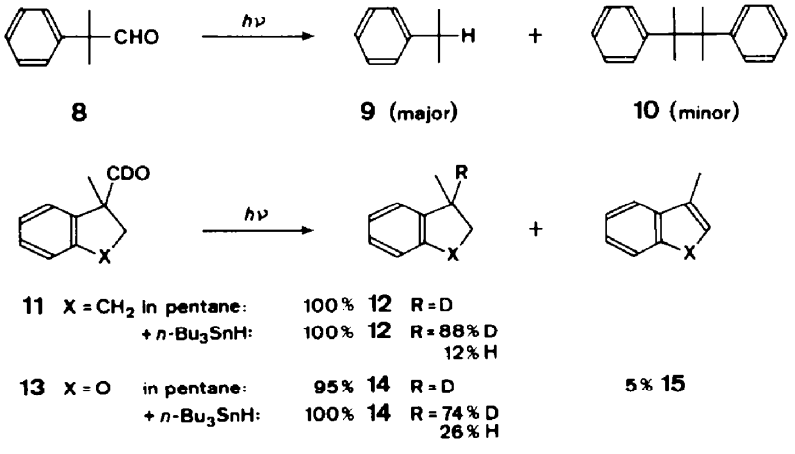
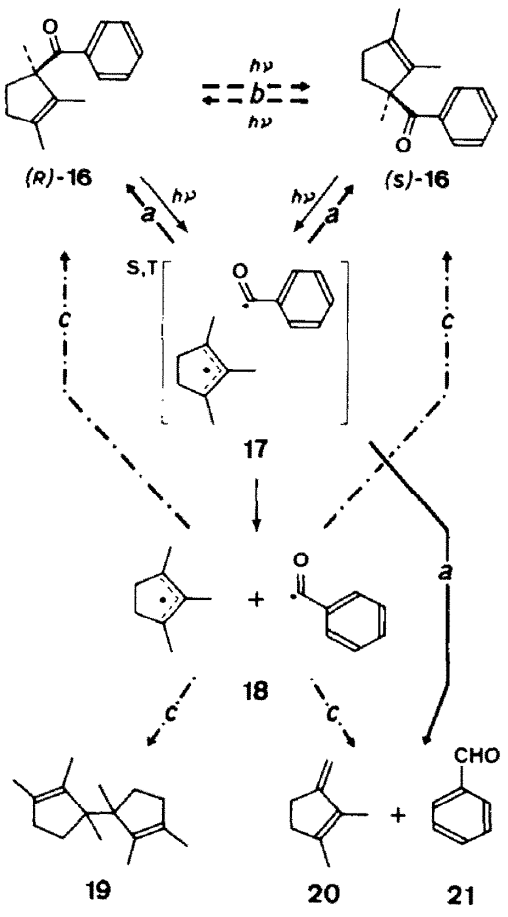


Chart 3.



a = Geminate radical pair reactions,
b = reaction path bypassing polarizable radical intermediates,
c = free radical reactions

Chart 4.

p-anisyl ketone are *ca.* 15% from geminate and 85% from free-radical recombination). Any contribution to ketone isomerization by paths not involving polarizable radical intermediates such as **17** and **18**, e.g. a concerted 1,3-allylic shift (cf. paths *b*) is of minor importance at best.

The fact that the only detectable triplet state reactivity of the phenyl ketone **16** is attributable to α-cleavage (→ **17**) and, possibly, to some allylic 1,3-benzoyl shift, is of a particular interest in the light of an earlier report by Tenney *et al.*[9] that irradiation of 1,2,4,4-tetraphenyl-3-buten-1-one (**22**) affords *trans*-1-benzoyl-2,2,3-triphenylcyclopropane (**23**) in *ca.* 7% yield. The reaction was shown to occur by a 1,2-migration of the benzoyl rather than the 2-phenyl group. The transformation **22** → **23** thus constitutes one of the earliest examples of

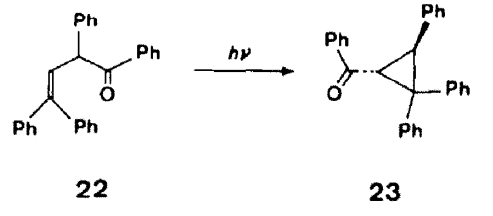


Chart 5.

the rearrangement which is commonly encountered with triplet-excited β,γ-unsaturated ketones (*vide infra*). The occurrence of a similar rearrangement of the phenyl ketone **16** and its *p*-anisyl analogue has been excluded rigorously. A possible rationale for this divergence in reaction paths may reside in the configuration and/or localization of the triplet energy which almost certainly differ in the two molecules. The phosphorescences of the cyclopentenyl phenyl and *p*-anisyl ketones of type **16** are comparable in spectral shape, band positions, lifetime and quantum yield to those of acetophenone and *p*-methoxyacetophenone, respectively (Table 1). The cyclopentene double bond does not influence the—energetically lowest-lying—carbonyl triplet state. One can safely assume that the situation in ketone **22** is different. The triplet energy of the isolated diphenyl ethylene chromophore is >10 kcal/mol lower than that of benzoyl and will therefore most likely prevent a predominant carbonyl configuration of the reactive triplet state.

The product composition resulting from direct irradiation of the β,γ-unsaturated ketone (*R*)-**24** is at first sight reminescent of that of the analogous phenyl ketone (*R*)-**16**.[10,12] A complex mixture of low-yield products is formed, of which only the trimethylcyclopentenyl dimer **19** and 1,2,3-trimethyl-1-cyclopentene have been identified. In addition, racemization of the starting ketone accounts for the major part of the total photochemical reaction of (*R*)-**24**. However, further experimental probing revealed significant differences between the mechanistic characteristics of the two β,γ-unsaturated ketones. The considerable excited singlet-state contribution to the bond cleavage of the aromatic ketone **16** constitutes an unusual finding as quantitative singlet-triplet intersystem crossing normally preceeds any primary photochemical process in phenyl ketones. Thus, 2,4,6-trimethylpivalophenone[13] and α,α-dimethyldeoxybenzoin,[14] which is an aliphatic benzo analogue to **16**, undergo α-cleavage to benzoyl and to *t*-butyl and cumyl radicals, respectively, exclusively in the triplet state. Such is far less generally the case for alkyl ketones (in *t*-butyl alkyl ketones α-cleavage arises from both the singlet and triplet excited states[15]), and spin

Table 1. Phosphorescence data of 1-cyclopent-2-enyl aryl ketones and the corresponding acetophenones[a]

Compound	Phosphorescence 0-0 Band (kcal/mol)	τ_p (msec)	ϕ_p[b]
Acetophenone	73·6	3·5	0·74
1-Benzoyl-1,2,3-trimethyl-2-cyclopentene (**24**)	74	2·3	0·86
1-Benzoyl-1,2-dimethyl-2-cyclopentene	72	2	
4-Methoxyacetophenone	71·8	260	0·68
1-(4-Methoxybenzoyl)-1,2,3-trimethyl-2-cyclopentene	70	107	0·94

[a] Measured in ether-isopentane-ethanol 5:5:2 glass at 77K (ref. 10). - [b] The literature values for acetophenone and 4-methoxyacetophenone (ref. 11) were taken as the references for the determination of phosphorescence quantum yields.

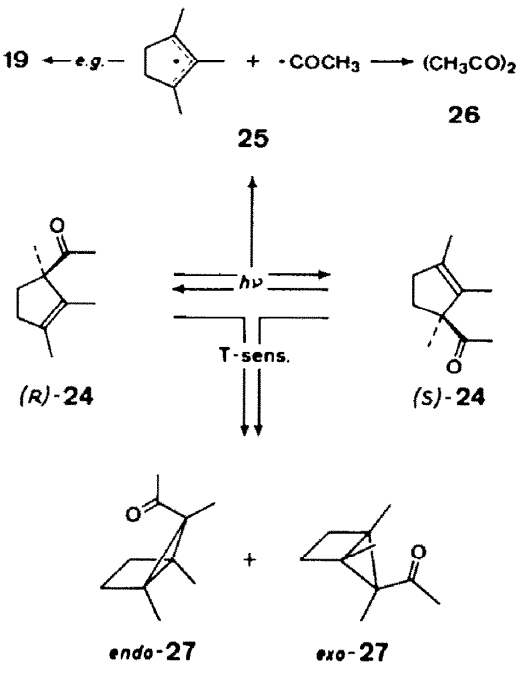


Chart 6.

inversion to the lowest-lying triplet state (T_1) was found virtually not to occur at all in the β,γ-unsaturated methyl ketones of type **24**. Rather, the transformations on direct irradiation proved to be due to the reactivity of a higher excited state and to differ entirely from the T_1 reaction mode of these compounds. In further contrast to the results with the phenyl ketone, the photoracemization of (*R*)-**24** results exclusively from an allylic 1,3-acetyl migration, and radical recombination to racemic ketone is negligible altogether.

The following experiments serve to confirm these statements. Neither the radical cleavage (→**25**) nor the racemization were affected upon the addition of high concentrations of triplet quenchers, 2M 1,3-pentadiene and 1M naphthalene. In the presence of 1M tri-n-butyl stannane reduction of **24** to the secondary alcohol competed with the other photoreactions, and the rate of reduction remained equally unchanged upon addition of 1M naphthalene. The reactive excited state is thus sufficiently long-lived to undergo bimolecular reactions at a rate close to or lower than diffusion control. The nature of the photoracemization is exhaustively documented by three separate observations. A photo-CIDNP study[16] of **24**, while providing *inter alia* otherwise unattained evidence for the formation of biacetyl (**26**), failed to show any polarization effect which could be attributed to racemization through any radical cleavage-recombination sequence. Irradiation of an equimolar mixture of the trideuteriated ketones **28** and (*R*)-**30** (1M each) afforded, after 50% consumption of starting materials exclusively isomeric ketones (**28**, **29**, (*R*)- and (*S*)-**30**). Random intermolecular exchange of acetyl and formation of hexadeuterio ketones had not occurred. Furthermore, the rates of isomerization, (*R*)-**24**→(*S*)-**24** and **28**→**29**, were equal within ±1% in the range up to 13% ketone disappearance.

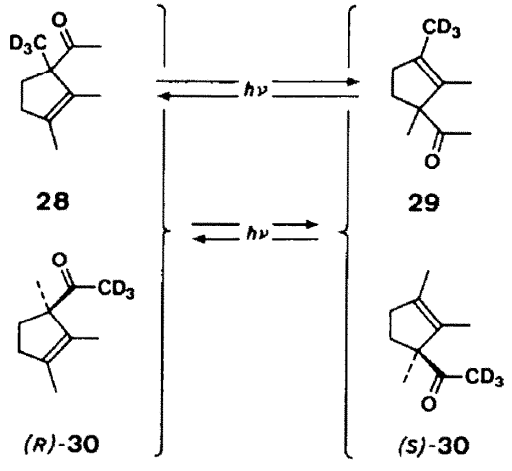


Chart 7.

Table 2. Quantum yields of consumption and product formation of ketones **35**, **36** and **54**[a]

Starting Ketone	Sensitizer	Excitation Wavelength (nm)	Quantum Yield of Consumption	Quantum Yields of Product Formation
35[b]	-	313	0·52 ± 0·02	0·14 ± 0·02 **36**
36[b]	-	313	0·40 ± 0·02	0·06 ± 0·01 **35**
35[c]	acetone (soln.)	254	0·28 ± 0·04	0·14 ± 0·02 *endo*-**37**
				0·04 ± 0·01 *exo*-**37**
35[b,c]	1*M* acetophenone	254	0·05 ± 0·015	0·01 ± 0·002 *endo*-**37**
				0·003 ± 0·001 *exo*-**37**
36[c]	acetone (soln.)	254	0·29 ± 0·03	0·14 ± 0·02 *endo*-**37**
				0·04 ± 0·01 *exo*-**37**
36[b,c]	1*M* acetophenone	254	0·05 ± 0·015	0·01 ± 0·002 *endo*-**37**
				0·003 ± 0·001 *exo*-**37**
54[d]	-	313	0·26 ± 0·03	0·085 ± 0·009 **55**
54	acetophenone (soln.)	313	0·085± 0·009	0·02 ± 0·002 *endo*- + *exo*-**56**
54[d]	0·1*M* benzophenone	366	0·098± 0·01	0·035 ± 0·004 *endo*- + *exo*-**56**
54[d]	0·01*M* thioxanthone	366	0·084± 0·008	0·035 ± 0·004 *endo*- + *exo*-**56**
54[d]	0·01*M* Michler ketone	366	0·083± 0·008	0·047 ± 0·005 *endo*- + *exo*-**56**

[a] All runs at 20°C, in degassed *ca.* 0·1*M* solutions. Quantum yields were determined using the actinometer described by W. Amrein, J. Gloor, and K. Schaffner, *Chimia* **28**, 185 (1974), and by vpc analysis. - [b] Isooctane solution. - [c] *Endo*-**37** is slowly consumed under these conditions. The values given are therefore lower limits for $\Phi_{endo\text{-}37}$ (*cf.* Table 3). - [d] Benzene solution.

The direct population of the energetically lowest-lying triplet state of **24** by sensitization with acetone or acetophenone afforded two new photoisomers, the *endo*- and *exo*-5-acetyl-1,4,5-trimethylbicyclo[2.1.0]pentanes **27**, at the expense of both the photoracemization and the additional product pattern observed on direct excitation of (*R*)-**24**. Sensitizers of lower triplet energies such as diphenyl amine and benzophenone failed to effect any reaction, and acetone proved a considerably more efficient sensitizer than acetophenone while the same product ratio is produced in both experiments (Table 2). These results place the energy of the reactive T_1 state in a narrow range around or below 74 kcal/mol. Analogous rearrangements of the ketones **31**, **33** and **36**—the last is most conveniently prepared by direct irradiation of **35**—to the bicyclopentane isomers **32**, **34** and **37**, respectively, conclusively show that the overall structural change involves a 1,2-migration of the acetyl group and bridging of the 5-membered ring. In each of the sensitized photolyses both stereoisomeric acetylbicyclopentanes are formed as the primary photochemical products. The *endo* component predominates invariably (Tables 2 and 3), whereas the *exo* geometry is favored on thermal equilibration which involves the 1,3-cyclopentane diradical **82** (Chart 21). Furthermore, the *endo*- and *exo*-acetylbicyclopentanes proved photochemically non-interconvertible under the sensitized conditions of their formation as well as on direct irradiation in solution and in the vapor phase at room temperature—a result which contrasts with the experience that cyclopropyl ketones tend to photoepimerize by cleavage and reclosure of an adjacent cyclopropane bond (cf. **38** → **39**[17]). The acetylbicyclopentanes such as *endo*- and *exo*-**37** would have been anticipated by analogy to interconvert via photolytic opening of a lateral cyclopropane bond (e.g. the 1,5-bond to give diradical intermediate **40**), unless rotation around the remaining bond (cf. 4,5 in **40a,b**) is strongly inhibited. Indeed, model considerations indicate that even the least hindered mode of rotation, shown in **40a** and **40b**, encounters substantial, and possibly probibitive, steric

Table 3. *Endo*/*exo* ratios of 5-acetylbicyclo[2.1.0]pentanes obtained by photorearrangement and by thermal stereoequilibration of 1-acetyl-2-cyclopentenes

Compound	*Endo*/*exo* Ratio by Photorearrangement	by Thermal Equilibration
endo/*exo*-**27**	~5 : 1[a]	1 : ~2·5[b]
endo/*exo*-**34**	~3 : 1[a]	1 : 3·8 ± 0·2[c]
endo/*exo*-**37**	~7 : 1[a]	1 : 1·9 ± 0·1[c]
endo/*exo*-**56**	~3 : 1[d]	1 : ≥10[d]

[a] At 5% conversion in acetone-sensitized photolyses (254 nm) of 0·2*M* solutions of **24**, **33**, **35**, and **36**, respectively. – [b] Pseudoequilibrium estimated from plots of product composition (**24** + *endo*- and *exo*-**27**) *vs* time using 0·2*M* solutions of *endo*- and *exo*-**27** in hexachlorobutadiene at 120°C. – [c] Equilibrium calculated from first-order rate constants of stereomutation at 160, 180, 200 and 220° (**34**) and 170° (**37**) using 0·16*M* solutions of *endo*- and *exo*-**34** and -**37** in benzene. – [d] Approximate ratios estimated by NMR analysis of the crude photolysis mixture and after thermal equilibration of the isomers **56** (100°C in benzene-d_6), respectively.

interactions with the *endo* methylene hydrogens. An efficient photochemical deactivation of excited *endo*- and *exo*-**37** (paralleled by comparatively low-yield photochemical decomposition paths to still unidentified products) at the total expense of a conformational equilibration between **40a** and **40b** may thus account for the failure of these ketones to interconvert. Any mechanism of the triplet rearrangement of the acetylcyclopentenes must therefore account for the fact that either the entire process or at least the major path is kinetically controlled.

The results with methyl ketone **24**[12] together with the reports by Hart[18] on the diazabicyclo[2.2.2]octenone **41** and by Ipaktschi[19] on a reinvestigation of the norbornenone **42** (however, *vide infra* for an important revision of these latter results), had for the first time fully revealed

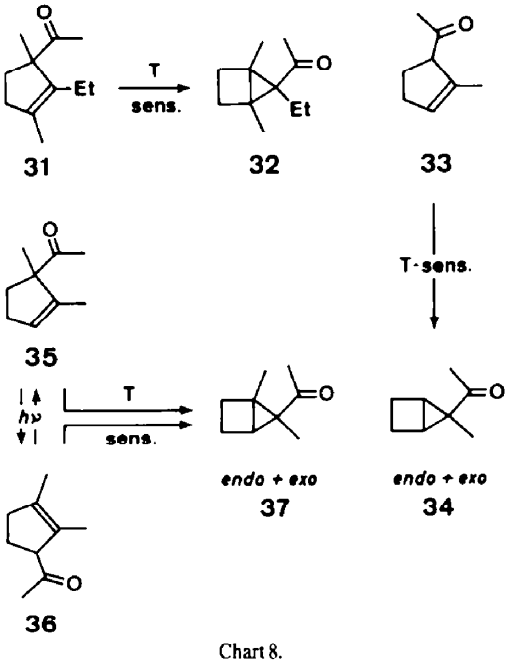


Chart 8.

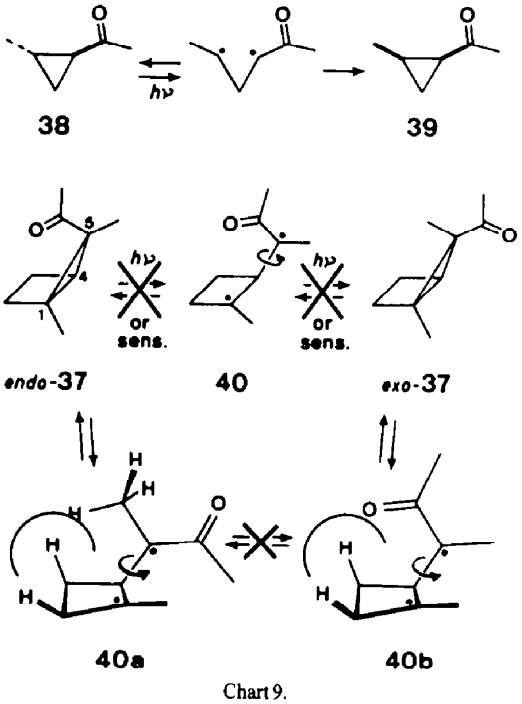


Chart 9.

a photochemical selectivity which in most cases is determined by the mode of excitation and typical of many β,γ-unsaturated ketones: an allylic 1,3-acyl migration upon direct irradiation and, in sensitized runs, a rearrangement involving a formal 1,2-acyl shift and three-ring formation. In view of the formal relationship of the latter process to the di-π-methane rearrangement Dauben[20] appropriately termed the reaction "oxa-di-π-methane rearrangement" (ODPM). The photochemistry of β,γ-unsaturated ketones has since received wide attention and has been reviewed recently by Hixson, Mariano and Zimmerman,[21] and by Houk.[22] The nature of the two reactive states, the rationales for their diverging reactivity and a few mechanistic details of the rearrangements are still a matter of some current debate.

There is a general consensus in the literature that the 1,3-acyl migration of β,γ-unsaturated ketones (other than aryl ketones such as **16**) is in most cases a singlet-excited state process. The conclusion is based on the fact that the reaction is normally observed on direct irradiation only and triplet sensitization gives other reactions including the ODPM rearrangement. This suggests inefficient singlet-triplet intersystem crossing and supports the singlet assignment to such 1,3-shifts. It is not clear whether this inefficiency might be an inherent property of the β,γ-unsaturated ketone, or whether it might result from very fast competing bond cleavage and 1,3-shift reactions. In a few cases only 1,3-acyl migrations have been encountered also in sensitized photolyses. The best documented examples of such triplet 1,3-shifts have been described by Engel. The earlier workers on the norbornenone **42** had missed its triplet isomerization to **43**.[23] In fact, appreciable amounts of the 1,3-acyl shifted compound **43** are formed in addition to the ODPM product **44** on sensitization with acetone, acetophenone, and benzophenone. Both enones then undergo an ODPM rearrangement to **44**. Furthermore, the 1,3-shifts of the ketones **45** and **46** can also be sensitized with acetone.[24] They proved to involve neither free-radical nor cage acyl-allyl recombination, but rather to correspond mechanistically to the similar rearrangements which are initiated selectively by direct irradiation. These can be attributed on compelling grounds to either a concerted symmetry-allowed[3] process (a suprafacial sigmatropic $_{\pi}2+_{\pi}2$ shift; cf. **52**) or a stepwise version via a 1,3-bridged diradical intermediate (cf. **53**) which, however, would seem less likely in bridged β,γ-unsaturated ketones such as **41**, **42** and **47** for steric constraints. The experimental evidence accumulated in the case of methyl ketone **24**[12,16] has been discussed above, and Givens[25] subsequently favored a concerted nature of the 1,3-acyl migration in bicyclo[2.2.2]octenone and benzobicyclo[2.2.2]octadienone (**47**). Direct and sensitized irradiations of **47** furnished the 1,3-shift (**49**) and ODPM products (**48**), respectively. In both runs as well as in the irradiation of **49** naphthalene (**51**) and ketene were formed additionally. This fragmentation is postulated to originate from α-cleavage processes of **47** and **49** via the diradical intermediate **50** which in view of the selective

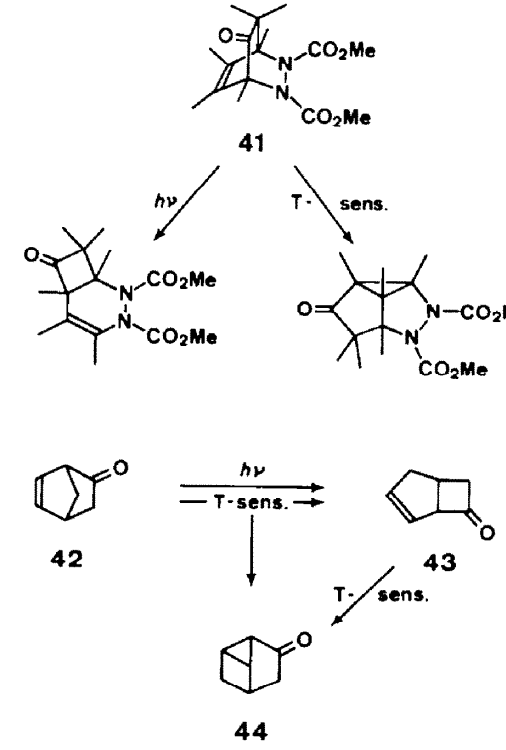
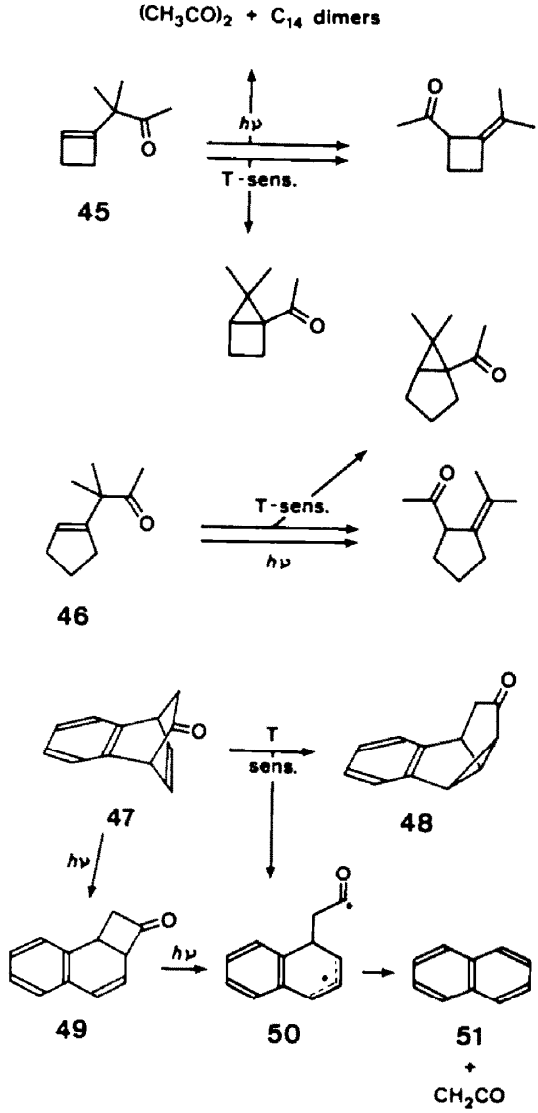


Chart 10.



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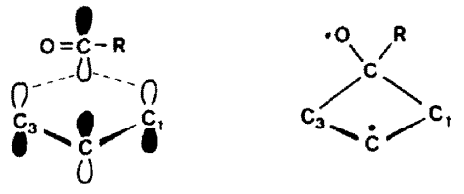


52 53

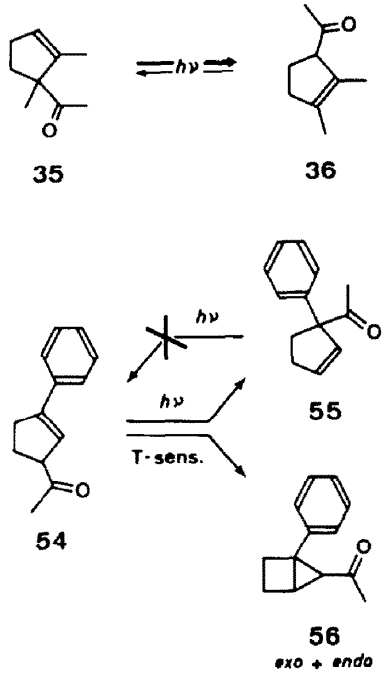
Chart 12.

appearance of **49** on direct photolysis of **47** cannot serve simultaneously as a precursor to the shift product (unless the cyclobutanone **49** is also formed and rapidly consumed on triplet sensitization—a control experiment on this possibility has not been reported). These conclusions are fully corroborated by the results of detailed studies by Nakanishi[26] with steroidal and related β,γ-unsaturated ketones in which a tetrasubstituted (or H/D labeled) α-carbon is transformed into an exocyclic sp^2 carbon and retains its original configuration.

An alternative to the singlet multiplicity of the 1,3-acyl shift is that intersystem crossing is in fact not inefficient but selectively leads to a high-lying triplet state (T_2) which is often above the energy range of the triplet sensitizers used, and which efficiently (Table 2) undergoes a 1,3-shift rather than internal conversion to the lowest-lying T_1 state. CNDO-MO calculations by Houk[27] on *E*-4-hexen-2-one in the appropriate geometry for optimum homoconjugation indicate that the lowest excited singlet configuration is primarily n,π^* (54%) and charge transfer (32%) in nature and that the lowest triplet is predominantly π,π^* (76%). The n,π^* triplet has been estimated to lie within 2 kcal of the acetone triplet (80 kcal/mol).[28] It would be consistent with this estimate that successful energy transfer from acetone resulting in a sensitized 1,3-shift would strongly depend on relatively small structure-related variations in energy of the upper triplet. In the case of **42** (Chart 10), which was shown to have a lowest triplet energy of more than 74 kcal/mol, acetophenone (E_T = 74 kcal/mol) and benzophenone (E_T = 69 kcal/mol) interact with the β,γ-unsaturated ketone in a manner suggesting the formation of an excited complex.[23] The hypothesis of an upper reactive n,π^* triplet would require that this complex leads to 1,3-acyl migration as well although in quantum yields which strongly decrease with sensitizer energy when compared to the quantum yield with acetone. A preference for $S(n,\pi^*) \rightarrow T(n,\pi^*)$ over $S(n,\pi^*) \rightarrow T(\pi,\pi^*)$ intersystem crossing on direct irradiation contrasts with the commonly accepted selection rules by spin-orbit coupling but has been encountered recently in 1-indanones,[29] ketones of admittedly different structural characteristics. Reactions from upper excited states in liquid solution have been observed in several instances, notably with α,β-unsaturated ketones.[30]

A successful correlation of fluorescence and migration efficiencies would constitute a valuable test for the spin multiplicity of the excited state in the 1,3-shift reaction. However, experimental probing with the 1-acetyl-2-cyclopentenes has failed so far in our hands. These compounds, e.g. **35** and **36** with a photostationary equilibrium of approximately 1:2·3,[10] do not exhibit any fluorescence. We may note, furthermore, that the theoretical rationales advanced for the reaction courses of the 1,3-acyl shift and the ODPM rearrangement do not allow for a unified prediction of the excited state nature of the former process. Both singlet and an upper triplet state with n,π^* configuration would be in accord with Houk's arguments based on molecular orbital calculations,[27] while the spin distribution model by Schuster and Underwood[31] cannot be reconciled with a triplet 1,3-shift. Fukui's concept of HOMO-LUMO[32] does not concern any differentiation of multiplicity in this case.

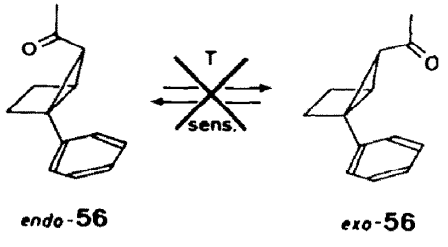
Although the above-mentioned photostationary equilibrium **35** ⇄ **36** in favor of ketone **36** lacking an α-methyl is in accord with a recent report by Engel and Ziffer[33] that the reactivity of β,γ-unsaturated ketones increases towards 1,3-acyl shift processes with increasing α-methyl substitution, an inverse and even more pronounced trend is seen in the phenyl substituted acetylcyclopentene **54**. This compound isomerizes entirely to the α-phenyl ketone **55** when wavelengths are used which are absorbed by both ketones (cf. also Table 2).[34] As with **35** and **36**, triplet sensitization of **54** does not induce 1,3-acetyl migration but furnishes the *endo*- and *exo*-ODPM products **56** instead which again do not interconvert under the conditions of their formation. Ketone **54** had been chosen as an acetylcyclopentene in which the lowest-lying triplet state should closely correspond to the styrene chromophore, and which consequently should have a relatively low-lying $^3(\pi,\pi^*)$ state with little perturbation by the carbonyl. This expectation is met by an intensive phosphorescence of **54**, in EPA at 77 K upon $n \rightarrow \pi^*$ excitation, which exhibits a first band at 483 nm (= 59 kcal/mol) and is superimposable in spectral shape



35 36 54 55 56

exo + *endo*

Chart 13.



endo-56 *exo*-56

Chart 14.

and energy with the very weak triplet emission of 1-phenylcyclopentene. Sensitizations of **54** with acetophenone (E_T 74 kcal/mol), benzophenone (69 kcal/mol), thioxanthone (65 kcal/mol), and Michler ketone (61 kcal/mol) furnished in each case the same *endo-exo* composition of the bicyclopentanes **56**. Both the quantum yields $\Phi_{\rightarrow 54}$ and Φ_{56} are quite similar with the four sensitizers, i.e. they do not fall off with decreasing triplet energy of the donor (Table 2). One may therefore conclude that the lowest-lying (styrene-type) π,π^* triplet of **54** is the excited state responsible for the ODPM rearrangement of **56**. This result is in accord with both the qualitative finding by Dauben[20] that the aliphatic analogue **57** rearranges to **58** upon sensitization with donors of triplet energies as low as 56 kcal/mol (α-acetonaphthone), and with the theoretical prediction by Houk[27] that the ODPM rearrangement should occur from the $^3(\pi,\pi^*)$ state.

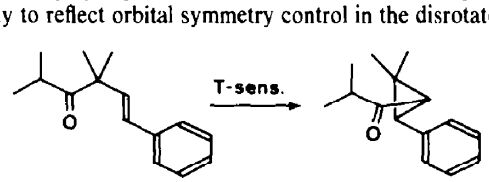
Unfortunately, the exclusively methyl-substituted acetylcyclopentenes do not offer a similarly conclusive test for the configuration of the triplet state leading to ODPM rearrangement. The origin of phosphorescences which have been attributed to several β,γ-unsaturated ketones, appears doubtful and in the case of **42** (p. 646) has recently been shown[23] to be due to impurities. We have observed similar luminescences with all methylated acetylcyclopentenes which disappeared after repeated purifications.

α,β-Unsaturated δ-dioxo systems in which the lowest-lying excited state is the $^3(\pi,\pi^*)$ state of the conjugated ketone moiety, have been shown previously to undergo ODPM-type triplet rearrangements.[36-38] The photochemistry of these systems appears therefore to align in more than a mere formal sense with β,γ-unsaturated monoketones such as **54**.

The more recent mechanistic discussions of the ODPM rearrangement distinguish between concerted pathways and a stepwise variation, i.e. initial bonding between the carbonyl and the β-carbon followed by rearrangement. A concerted mechanism has *a priori* the option of two allowed stereoisomeric paths, $_\sigma 2_a + _\pi 2_a$ and $_\sigma 2_s + _\pi 2_s$ cycloadditions,[3] barring the exclusion of one mode for structural reasons. The former mode constitutes an anti-disrotatory[39] cyclization-migration process, and the latter the syn-disrotatory alternative. The transition-state geometry of the syn-disrotatory reaction is probably less favorable for geometric reasons than the anti-process. Both would be required in order to account for the formation of two stereoisomeric rearrangement products from each of the acetylcyclopentenes **24**, **33**, **35**, **36** and **54** (Table 3), with a preference for the anti-disrotatory path (**59** → *endo*-**66**) in all cases.

Conclusive attempts to rationalize this stereochemical preference appear to be premature. Mariano[39] observed exclusive anti-disrotatory rearrangement of a singlet-excited cyclohexenyl di-π-methane system analogous to our acetylcyclopentenes and considered the stereospecificity to reflect orbital symmetry control in the disrotatory nature and initial orbital overlap in the anti nature of the transformation. The arguments invoked should be valid also for the triplet acetylcyclopentenes.

Yet, a mechanistic interpretation in terms of non-concerted processes via the intermediate cyclopropane carbinyl oxy diradicals **63** and **64**—formal two-step equivalents to the $_\pi 2 + _\pi 2$ cycloaddition paths—is just as satisfactorily reconciled with the stereochemical results. In this mechanism, bonding between the carbonyl carbon and C-2 in **61**/**62** occurs in the initial step. The predominant formation of *endo*-**66** from the ketones **61** would then result from inversion at C-1 by radical displacement of C-6 by C-4 in the diradicals **63** (path *a*), a cleavage of the 3-membered ring by concomitant anti-disrotatory cyclization. Alternatively, the minor *exo*-products **66** would be accessible by retention of configura-



57 **58**

Chart 15.

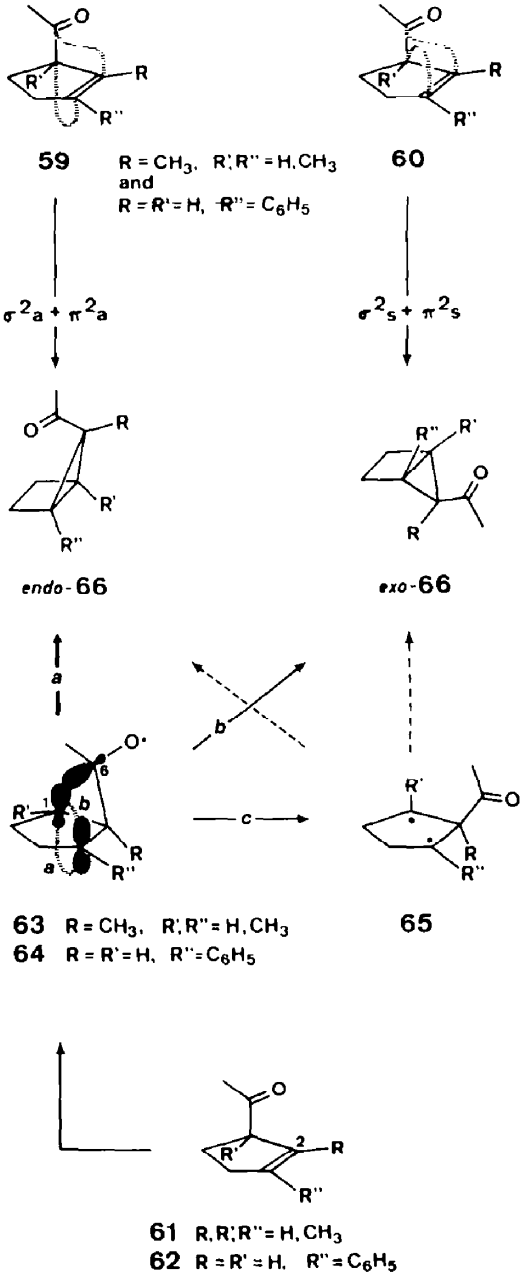


Chart 16.

tion at C-1 in a syn-disrotatory process (path *b*). The preference for path *a* may derive from a better initial overlap between the back orbital lobe at C-1 and the anti lobe at C-4 and/or the requirement of less motion of the two orbitals on the path to the transition state leading to full bonding. Such arguments have been forwarded by Mariano[39] to rationalize the stereospecific di-π-methane triplet rearrangement in the above-mentioned structurally similar cyclohexenyl case. We may note also that path *a* reflects the reactivity expected of a radical in terms of its nucleophilic capacity.

Furthermore, non-assisted opening of the cyclopropane 1,6-bond in **63** and crossing over to localized diradicals of type **65** (path *c*) should also result in a kinetically controlled *endo–exo* product mixture of **66** the composition of which is difficult to anticipate but, barring a coincidence, would differ from the thermodynamically equilibrated ratio (cf. Table 3). Work is presently in progress which is designed to generate diradicals of type **65** via an independent route, and which may eventually differentiate between paths *a*/*b* and *c*.† In particular, a greater preference for path *c* seems a reasonable *a priori* possibility in the case of the phenyl-substituted ketone **54**. Initial bonding (**62**→**64**) could afford here a carbinyl oxy diradical in which ring opening to a 1-phenyl-2-acetylcyclopentane 1,3-diradical (**65**) would profit from both the restitution of a carbonyl group and the benzyl resonance stabilization of one radical site.

A sequence analogous to **62**→**64**→**65**→**66** has been proposed previously for the rearrangements of the steroidal ene-dione **67** to the cyclopropyl diketones **72a,b** and **73a,b** on direct irradiation with wavelength 254 nm which is not absorbed by the products under the reaction conditions.[40] The complete positional scrambling of the CD_3 and CH_3 groups in **72** and **73** is accounted for by the intermediate diradicals **70** and **71** in which the isopropyl radical groupings can rotate around the angular bond prior to ring closure. A synchronous ring opening and cyclization in **68** and **69** analogous to **63**→**66** is possibly prevented here by factors similar to those discussed above for **64** (with the carbinyl substituting for benzyl radical resonance stabilization).

Finally, two claims for fully concerted ODPM rearrangements appear equivocal in one case and incorrect in the other. Photodecomposition of the lactone **74** gave benzobicyclo[2.2.2]octadienone (**47**), its ODPM rearrangement product (**48**), the cyclobutanone **49**, naphthalene (**51**) and ketene.[41] The formation of all these compounds can be formulated to arise from a primary diradical photoproduct **75** as the common intermediate. On the other hand, the triplet ODPM rearrangement of **47** to **48** is not accompanied by the formation of cyclobutanone **49** (Chart 11) and therefore the reaction **47**→**48** cannot proceed via a discrete diradical such as **75** as well. A non-concerted mechanism of the ODPM rearrangement was consequently ruled out with the argument that after initial bridging to **76** the intervention of **75** by ring cleavage would be requisite for the formation of **48**. This assumption is not necessarily valid, however, and the diradical **75**, although probably close-by on the same potential hypersurface,[21] may be avoided on the actual reaction path followed from intermediate **76** onward. A synchronous anti-disrotatory opening of the three-membered ring remains still a just as likely mechanism to lead directly to product **48**. Another result, the triplet transformation **77**→**78**, has been taken erroneously as evidence for a concerted $_\pi 2_a + _\pi 2_a$ cycloaddition.[42] In fact, the structural constraints in product **78** do not allow any other stereochemical result irrespective of the detailed (and possibly stepwise) reaction mechanism.

†*Added in proof*: For the triplet ODPM rearrangement of bicyclo[4.3.0]non-1,6-en-2-one to tricyclo[3.3.1]nonan-2-one unequivocal evidence of a *stepwise* mechanism following paths of type *a*/*b* and/or *c* has now been established: B. Winter and K. Schaffner, *J. Am. Chem. Soc.* **98**, in press (1976).

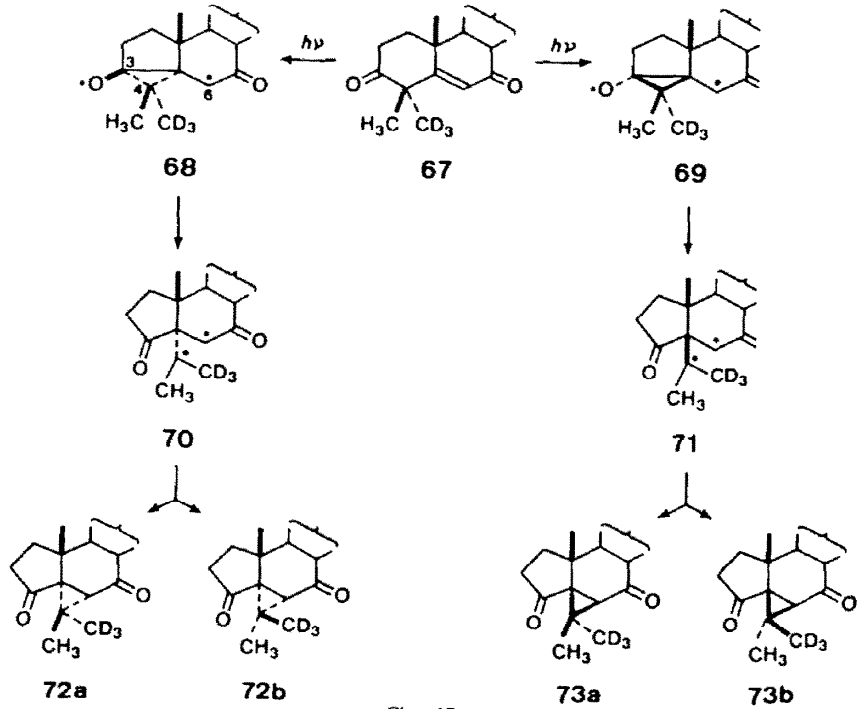


Chart 17.

Unlike some other ODPM rearrangements, the triplet transformation of the 1-acetyl-2-cyclopentenes (Charts 6, 7 and 13) overrides any other triplet photoreactions which compete occasionally in β,γ-unsaturated ketones, and the chemical yield of 5-acetylbicyclopentanes is essentially quantitative in terms of converted starting material and on an analytical scale. This is characteristic of many[19,25,43,44] but not all[24,25] ketones in which the double bond is rigid. The finding in our[12,45] and Jorgenson's[46] laboratory that the bicyclopentanes not only *endo-exo* stereomutate thermally but concurrently rearrange back to the photochemical starting material and to its 1,3-acetyl-shifted isomer on heating was therefore of both analytical and preparative importance adding to mechanistic interest. This thermal cyclopropyl-allylic rearrangement of, e.g. **27**, **32**, **34** and **37** (→**24**, **31**, **33**, and **35** + **36**, respectively) comprises formal cleavage of the central C–C bond and 1,2-migration of the acetyl group.[10] It is a remarkably clean reaction starting from either the *endo* or *exo* isomer and occurs in the vapor phase (gas chromatography) and in inert solvents above *ca.* 130° depending on the degree of methyl substitution, the trimethyl homologue **27** being the most labile. An analogous cyclopropyl-allylic rearrangement had been observed previously by Jorgenson[47] for 5-carbethoxybicyclo[2.1.0]pentanes which, however, require temperatures above 300° for the transformation into the corresponding 1-carbethoxy-2-cyclopentenes.

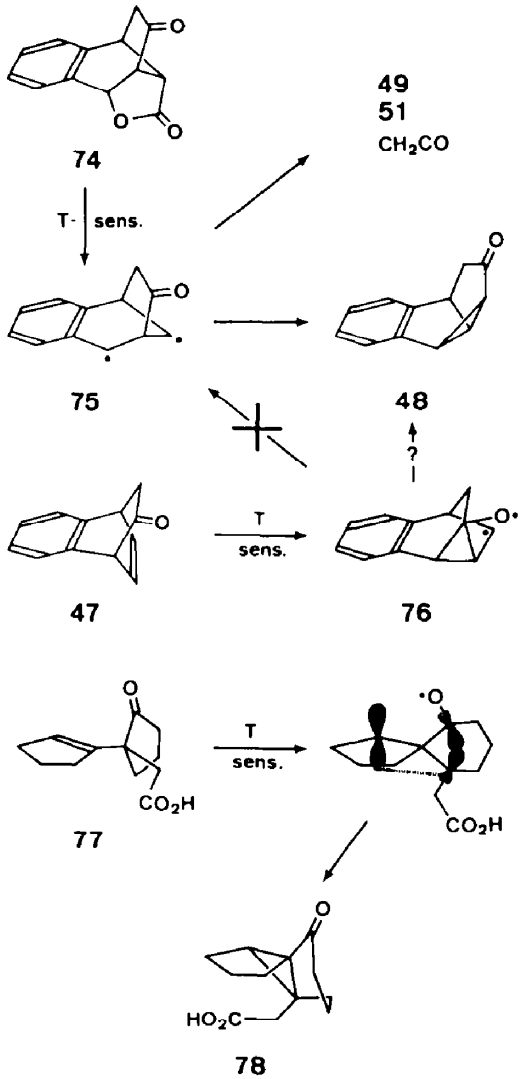


Chart. 18.

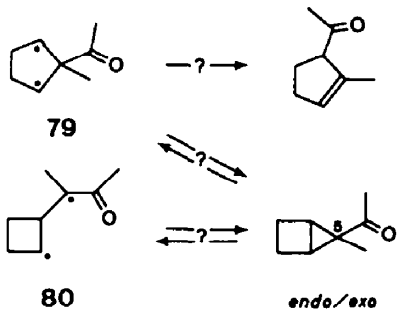


Chart 19.

For the *endo-exo* stereomutation of the 5-acetylbicyclopentanes bond cleavage-recombination processes via the formal diradical intermediates **79** and **80** involving the internal and external cyclopropane bond, respectively, need consideration. The intervention of a planar diradical corresponding to **79** in the ring flip has been presumed for bicyclopentane hydrocarbons[48] and indeed rupture of the central bond was demonstrated experimentally for the isomerization of 5-benzoyloxybicyclo[2.1.0]pentanes.[49] However, while in the latter the π-donating substituent on C-5 lowers the isomerization barrier[50,51] by enhancing the antibonding character in the central bond, the 5-acetyl group can be expected on similar grounds[52] to rather strengthen this bond relative to the lateral bonds through its π-acceptor property. It is pertinent to note, furthermore, that of the two hypothetical diradicals only **79** can serve also as a possible intermediate in the cyclopropyl-allylic rearrangement. As a consequence our investigation[53,54] was focussed on elucidating two major points first: the localization of bond breaking-recombination in the acetylbicyclopentane stereomutation, i.e. the experimen-

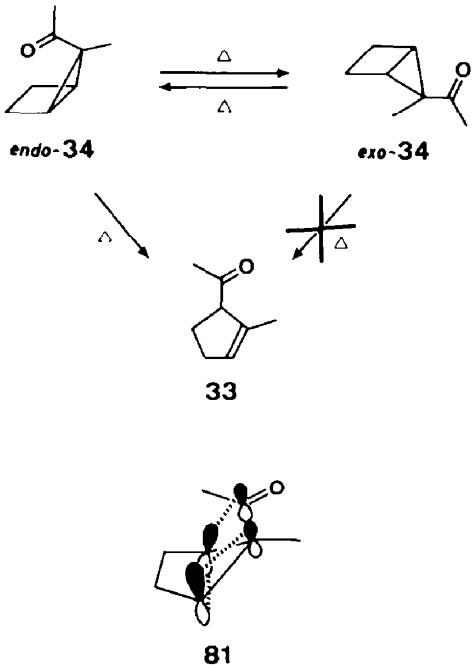


Chart 20.

tal differentiation between **79** and **80**; and a study of the possible connection of the reaction paths followed in the stereomutation and the rearrangement to acetylcyclopentene.

A kinetic analysis of these two thermal isomerizations was first carried out with the *endo*- and *exo*-5-acetyl-5-methylbicyclo[2.1.0]pentanes **34** which are the least labile among this group of ketones and thus best suited for quantitative measurements. The thermolyses of *endo*- and *exo*-**34** were performed in benzene solution in the temperature range 160–220°, compound **33** remaining unchanged under these conditions. Best-fit rate constants were then calculated using programs designed to handle up to four components linked by equilibria,[55] and these data and associated activation parameters are shown in Table 4. The kinetic results provide a clear mechanistic differentiation of *endo–exo* interconversion and cyclopropyl-allylic rearrangement. The order in rate constants, $k_{endo \to exo} > k_{exo \to endo} > k_{endo\ rearr} \gg k_{exo\ rearr}$, shows that the rearrangement occurs with high specificity from the *endo* configuration, and the significant gap in activation entropies between this process and the stereomutation strictly preclude that the two types of reaction involve a common intermediate.

The remarkably large negative entropy of activation for *endo*-**34** → **33** indicates that the rearrangement proceeds through a highly ordered transition state and is suggestive of a concerted electrcyclic process involving the four electrons of the internal cyclopropane and the C(5)-acetyl bonds. Disrotatory opening of the former bond would selectively permit the transfer of the acetyl substituent of *endo*-**34** via a transom of appropriate Möbius topology[56] (cf. **81**). A concerted mechanism has also been tentatively considered by Tufariello[51] and Jefford[56] for the facile and similarly *endo*-selective rearrangements of 5-acetoxybicyclo[2.1.0]pentane and halocyclopropanes, respectively.

After diradical trapping experiments, as one classical chemical approach to the remaining task of differentiating *endo* ⇄ *exo* interconversion paths via intermediates of type **79** and **80** (Chart 19), had failed to give meaningful results, the dimethyl homologues **37** were employed for this purpose. The rate constants, and in particular their ordering in magnitude, for stereomutation and rearrangement to the unsaturated ketones **35** and **36** are quite similar to those found in the monomethyl series (Table 4). Methyl substitution on the bicyclic skeleton therefore does not appear qualitatively to alter the thermal reaction paths. Yet, the bicyclopentanes **37** offer the advantage over **34** that the additional angular methyl group renders these ketones chiral and thus introduces a convenient tool to differentiate between, and to determine the proportion of, the involvement of internal and external cyclopropane bonds in the overall stereoisomerization. A ring flip via an intermediate corresponding to **79** would invert the configuration at the angular carbons and retain that of the apical position C-5. Alternatively, the reaction path involving an **80**-type intermediate would reverse the configurational outcome. It follows that the *exo* enantiomer generated from one enantiomeric form of *endo*-**37** will unequivocally establish the reaction path followed,

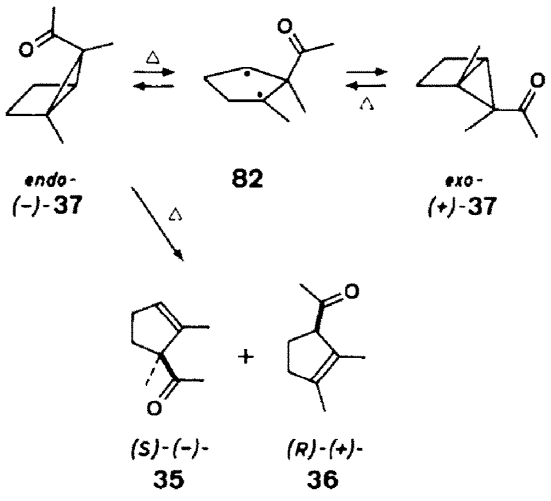


Chart 21.

Table 4. First-order rate constants and activation parameters of the thermal reactions of the *endo*- and *exo*-5-acetylbicyclo[2.1.0]pentanes **34** and **37** in benzene[a]

Reaction	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
endo- → *exo*-**34**	$(9{\cdot}30 \pm 0{\cdot}22){\cdot}10^{-2}$	33·4 ± 0·8	- 1·5 ± 1·7
exo- → *endo*-**34**	$(2{\cdot}42 \pm 0{\cdot}15){\cdot}10^{-2}$	33·9 ± 0·9	- 3·0 ± 2·0
endo-**34** → **33**	$(1{\cdot}96 \pm 0{\cdot}22){\cdot}10^{-3}$	22·2 ± 2·2	-33·0 ± 4·7
exo-**34** → **33**	$2{\cdot}96{\cdot}10^{-7}$ [b]	-	-
endo- → *exo*-**37**	$(6{\cdot}50 \pm 0{\cdot}14){\cdot}10^{-2}$		
exo- → *endo*-**37**	$(3{\cdot}41 \pm 0{\cdot}06){\cdot}10^{-2}$		
endo-**37** → **35**	$(1{\cdot}7 \pm 0{\cdot}2){\cdot}10^{-3}$		
endo-**37** → **36**	$(0{\cdot}8 \pm 0{\cdot}2){\cdot}10^{-3}$		
exo-**37** → **35** + **36**	$2{\cdot}96{\cdot}10^{-7}$ [b]		

[a] Rate constants of *endo*- and *exo*-**34** at 200°, and of *endo*- and *exo*-**37** at 170°. Activation parameters calculated from the rate data at 160, 180, 200, and 220°. Errors are standard deviations, and the correlation factors are 0·998 (*endo*- → *exo*-**34**), 0·997 (*exo*- → *endo*-**34**), and 0·996 (*endo*-**34** → **33**). - [b] This value is the *maximum* rate constant computed to comply with the other rate data.

Table 5. Sensitized photolysis of (*S*)-(−)-1-acetyl-1,2-dimethyl-2-cyclopentene (**35**) and thermal rearrangement of (5*R*)-(−)-5-*endo*- and (5*R*)-(+)-*exo*-acetyl-1,5-dimethylbicyclo[2.1.0]pentanes (**37**)

Starting Compound	Enantiomeric Purity, %[a]	Reaction Conditions	Enantiomeric Purity of Products, %[a]			
			(*S*)-(−)-**35**	(*R*)-(+)-**36**	(5*R*)-(−)-*endo*-**37**	(5*R*)-(+)-*exo*-**37**
(*S*)-(−)-**35**	95	b	-	-	93	94
(5*R*)-(−)-*endo*-**37**	93	c	92	d	94	93
(5*R*)-(+)-*exo*-**37**	94	c	91	d	92	94

[a] Determined by NMR using Pr(HFC)$_3$ shift reagent; estimated error ±5%. - [b] 0·2*M* in acetone + 254 nm, room temperature. - [c] 0·36*M* in benzene, 200°. - [d] Not determined. The optical (+)-rotation of **36** is in agreement with the assigned chirality.

and *vice versa*. Chart 21 and Table 5 summarize the results obtained in such experiments.[54] The optically active *endo*- and *exo*-acetylbicyclopentanes **37** were prepared by acetone-sensitized ODPM rearrangement of (*S*)-(−)-**35**, and each diastereoisomer was thermolyzed at 200°. In both runs the products of stereomutation (including the recovered starting material) had fully retained the original configuration at C-5 and thus demonstrate that the *endo* ⇄ *exo* interconversion occurs—within the limits of experimental error—solely in the ring flip mode involving the formal diradical intermediate **82**.

Acknowledgements—The untimely death of Prof. Margaret J. Jorgenson in 1970 prevented the pursuit as a joint effort of the study of the thermal transformations of 5-acetylbicyclo[2.1.0]pentanes, after explorations into this field had been carried out independently in both her and our laboratories (with Prof. Oskar Jeger). My thanks are due to the able coworkers whose names appear in the literature references to our own contributions. It is appropriate to thank here especially Dr. Hans-Ulrich Gonzenbach, Mr. Jean-Pierre Grosclaude and Miss Inga-Mai Larsson for their most recent enthusiastic efforts to add still unpublished results on the title compounds, and Prof. Stanley J. Cristol for his critical reading of this manuscript. Financial support by the Fonds National Suisse de la Recherche Scientifique and by Firmenich SA, Geneva, is gratefully acknowledged.

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