J. Org. Chem. **1984**, *49*, 1327–1333

Polymer-Bound Iridium Catalysis. Hydrogen Transfer from Formic Acid to Unsaturated Carbon–Carbon Bonds

Jacques Azran and Ouri Buchman

Radiochemistry Department, Nuclear Research Center, Negev, Israel

Milton Orchin

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

Jochanan Blum*

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

Received July 18, 1983

Polystyrene-bound IrCl(CO)(PPh$_3$)$_2$ promotes hydrogen transfer from formic acid to a variety of olefinic substances. The activity of the catalyst increases after the first few uses during which time a substrate–iridium complex is formed. Detailed kinetic studies were carried out with benzylideneacetophenone as the hydrogen acceptor. The catalysis is assumed to proceed by the following steps: (a) cleavage (dissociation) of an Ir–P bond in the supported complex Ⓟ-(PPh$_2$)$_2$IrCl(CO); (b) coordination of the acceptor at the vacated site; (c) oxidative addition of formic acid followed by olefin insertion leading to the formation of an iridium oxopropenyl formate complex; (d) hydrogen transfer from the formate to the iridium accompanied by loss of carbon dioxide; (e) reductive elimination to give the final product. Step d is considered rate detemining on the basis of kinetic isotope effect measurements with HCOOD, DCOOH, and DCOOD. The catalytic activity of the system is decreased by swelling solvents and increased by nonswelling ones. The fully activated, supported catalyst is air stable, essentially leach proof, and capable of being used for an unlimited number of catalytic cycles.

Chlorocarbonylbis(triphenylphosphine)iridium, IrCl(CO)(PPh$_3$)$_2$, has been shown to be an efficient catalyst for selective hydrogen transfer from formic acid to α,β-unsaturated ketones.[1] Recently we found[2] that the activity of the iridium complex is enhanced by anchoring it to a diphenylphosphinated polystyrene to give a catalyst whose structure is represented as Ⓟ-[(PPh$_2$)$_2$Ir(CO)Cl]$_n$.[3]

In this paper we describe the transfer hydrogenation of olefinic double bonds by formic acid (eq 1) in the presence of the above immobilized complex.

$$R^1R^2C{=}CR^3R^4 + HCOOH \rightarrow R^1R^2CHCHR^3R^4 + CO_2 \qquad (1)$$

Results

In our preliminary communication[2] we showed that in the presence of anchored IrCl(CO)(PPh$_3$)$_2$ benzylideneacetophenone, $C_6H_5CH{=}CHCOC_6H_5$, in toluene and boiling formic acid is converted under the conditions given in the Experimental Section into 17% of 1,3-diphenyl-1-propanone, $C_6H_5CH_2CH_2COC_6H_5$, in the first run. Recovery of the catalyst and reuse enhanced its activity. In the third run the catalyst system reached maximum efficiency (69% of reduced product was obtained) that did not change in subsequent cycles.

We now find similar behavior of the iridium catalyst with many other unsaturated compounds, although the number of runs required for full activation of the systems varies with the substrate. Two examples of conversion–turnover profiles for ten successive runs are illustrated in Figure 1.

In contrast to supported IrCl(CO)(PPh$_3$)$_2$, the analogous heterogenized RuCl$_2$(PPh$_3$)$_3$,[4] RhCl(PPh$_3$)$_3$,[5] RhCl(CO)(PPh$_3$)$_2$,[3] and PdCl$_2$(PPh$_3$)$_2$[6] deteriorate in boiling formic acid. Therefore, their performance in reaction 1 is considerably inferior. Conditions that provide transfer reduction of benzylideneacetophenone by supported iridium in 69% yield give yields of only 3%, 4%, 14%, and 42% of 1,3-diphenyl-1-propanone, respectively, with the above catalysts.

Table I. Transfer Hydrogenation of Various Unsaturated Compounds by Formic Acid and a Supported Iridium Catalyst under Comparable Conditions[a]

substrate	yield, %[b]
$C_6H_5CH{=}CHCOC_6H_5$	69
$C_6H_5CH{=}CHCOC_6H_4$-4-CH_3	44
$C_6H_5CH{=}CHCOC_6H_4$-4-F	65
$C_6H_5CH{=}CHCOC_6H_4$-4-Cl	86
4-$CH_3OC_6H_4CH{=}CHCOC_6H_5$	35
4-$CH_3C_6H_4CH{=}CHCOC_6H_5$	44
4-$ClC_6H_4CH{=}CHCOC_6H_5$	70
$C_6H_5CH{=}CHCOCH_3$	30
$C_6H_5CH{=}CHCOC(CH_3)_3$	16
$(C_6H_5)_2C{=}CHCOC_6H_5$	9
$C_6H_5CH{=}C(C_6H_5)COC_6H_5$	99
$C_6H_5CH{=}CHCOOC_2H_5$	17
$C_6H_5CH_2CH{=}CH_2$[c]	32
cyclooctene	50
2,3-dimethylcyclohex-2-enone	0
3,5-diphenylcyclohex-2-enone	0

[a] Reaction conditions: 2.5 mmol of acceptor, 50 mmol of formic acid, 1.9 mL of toluene, 1.8×10^{-2} mequiv of iridium catalyst; 97 °C under argon, 8 h. [b] Yield after full activation of the catalyst. [c] The nonreduced allylbenzene gave the equilibrium mixture of *cis*- and *trans*-1-phenyl-1-propene.[4]

The activation of the supported iridium complex is associated with a change in color from light tan to various shades of yellow characteristic for each substrate. The carbonyl IR absorptions of the freshly prepared polystyrene-bound catalyst (KBr mulls) at 2000, 1958, and 1940 cm^{-1} disappear during the activation and new bands, at high (2140 and 2060 cm^{-1}) and medium wave number regions (1685–1740 cm^{-1}, coordinated substrate) are formed. The 2140 cm^{-1} Ir–H peak is shifted to 1570 cm^{-1} when the catalysis is run in DCOOD instead of in HCOOH. In addition the air sensitivity of the catalyst changes during the activation. While the unreacted beads are highly

---

(1) Blum, J.; Sasson, Y.; Iflah, S. *Tetrahedron Lett.* **1972**, 1015.

(2) Azran, J.; Buchman, O.; Blum, J. *Tetrahedron Lett.* **1981**, *22*, 1925.

(3) Collman, J. P.; Hegedus, L. S.; Cooke, M. P.; Norton, J. R.; Dolcetti, G.; Marquardt, D. N. *J. Am. Chem. Soc.* **1972**, *94*, 1789.

(4) Zoran, A.; Sasson, Y.; Blum, J. *J. Org. Chem.* **1981**, *46*, 255.

(5) Grubbs, R. H.; Kroll, L. C. *J. Am. Chem. Soc.* **1971**, *93*, 3062.

(6) Pittman, Jr., C. U.; Wuu, S. K.; Jacobson, S. E. *J. Catal.* **1976**, *44*, 87.

0022-3263/84/1949-1327$01.50/0

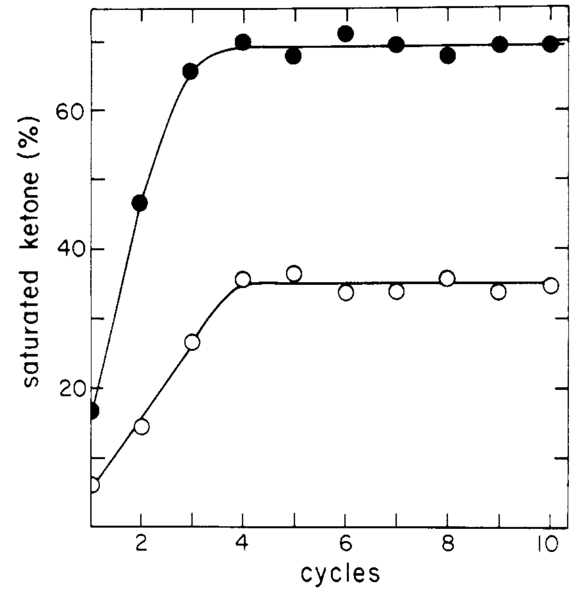


Figure 1. Conversion–turnover profiles for transfer hydrogenation of benzylideneacetophenone (●) and benzylideneacetone (○) under comparable conditions. Each run was performed 8 h under argon with 2.5 mmol of unsaturated ketone, 50 mmol of formic acid, 1.9 mL of toluene, and 1.8 × 10^{-2} mequiv of catalyst containing 3.8% iridium on 2% divinylbenzene cross-linked diphenylphosphinated polystyrene; P:Ir = 3.0; temperature 97 °C.

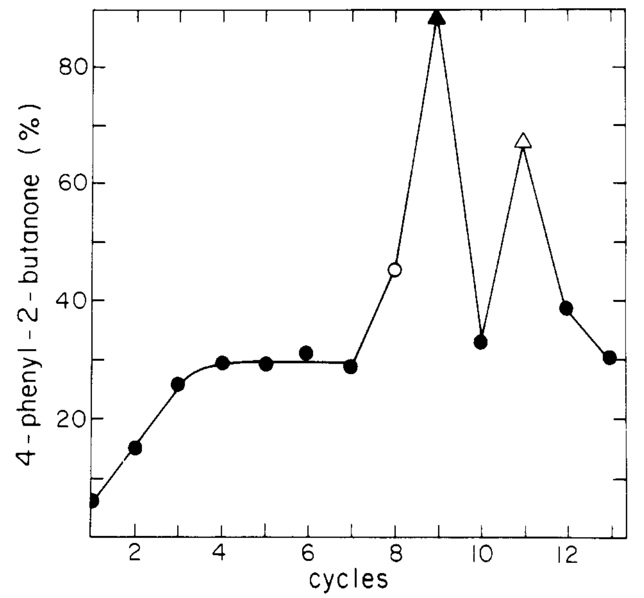


Figure 2. Effect of toluene (●), ethylene glycol (○), decalin (△), and *n*-decane (▲) on the yield of 4-phenyl-2-butanone in transfer hydrogenation of benzylideneacetone (2.5 mmol) by formic acid (50 mmol), 1.8 × 10^{-2} mmol catalyst; and 1.9 mL of added solvent at 97 °C under argon atmosphere. The yields given are those obtained in each run after 8 h.

sensitive to oxygen, they become perfectly air stable after being exposed to the unsaturated hydrogen acceptors for 3–5 runs.

Table I indicates that nonactivated olefins react almost as well as α,β-unsaturated carbonyl compounds. However, the introduction of bulky groups generally exerts a steric effect resulting in diminished conversions. The rapid and quantitative reduction of $C_6H_5CH{=}C(C_6H_5)COC_6H_5$, in which one phenyl group is on each of the unsaturated carbons, is unexpected and not yet quite understood.

The presence of toluene in the reaction mixture serves a mechanical purpose; it prevents the low density beads from floating on top of the reaction mixture and adhering to the upper part of the reaction vessel. In our previous study[4] on catalytic isomerization of allylic compounds by supported $RuCl_2(PPh_3)_3$ toluene and other aromatic hydrocarbons acted as swelling agents. In the absence of such a solvent the reaction rate decreased substantially. In the present catalytic system swelling solvents do not only fail to increase the reaction rate but cause it to slow down. On the other hand typical nonswelling solvents (*n*-decane, decalin) increase the catalytic power of the 2% cross-linked immobilized catalyst. These solvents, however, neither promote nor reduce the activity of the iridium complex on 20% cross-linked polystyrene–divinylbenzene copolymer. An example of this unusual solvent effect (in transfer reduction of benzylideneacetone) is shown in Figure 2.

Similar solvent dependence is observed also with other substrates. For example, when transfer hydrogenation of benzylideneacetophenone (eq 1, $R^1 = R^3 = H$, $R^2 = C_6H_5$, $R^4 = COC_6H_5$) is carried out under the conditions given in the Experimental Section, first for six runs in toluene, followed by successive runs in decalin, toluene, *n*-decane, and decalin, and finally twice in toluene, the respective conversions in the last seven cycles are 69%, 98%, 86%, 99%, 99%, 86%, and 70%. Reactions which are carried out in the absence of any solvent give yields almost as high as in the presence of nonswelling aliphatic hydrocarbons.

It is notable, that this solvent effect is equally pronounced prior to as well as after catalyst activation. For example, the reduction of benzylideneacetophenone is increased already in the first run from 17% to 91% when the toluene is either omitted or substituted by *n*-decane.

As has been demonstrated for several polystyrene-bound metal catalysts, the degree of cross-linking with divinylbenzene can have a substantial influence on the efficiency and selectivity of the catalytic process. (See, e.g., ref 5 and 7–9). In our system the 2% and 20% cross-linked polymeric catalysts behave quite differently. While the conversion of benzylideneacetophenone in the presence of 2% cross-linked beads (conditions as given in the Experimental Section) increases from 17% yield in the first to 69% in the third run, the 20% cross-linked catalyst gives a constant, rather low yield of 25 ± 3% right from the first cycle. (The conversions at the end of each of ten cycles were measured).

In the *absence* of a hydrogen acceptor, boiling formic acid decomposes by the iridium catalyst according to eq 2. Thus it was essential to investigate the possibility that

$$HCOOH \xrightarrow{\text{Ⓟ-}[(PPh_2)_2Ir(CO)Cl]_n} H_2 + CO_2 \qquad (2)$$

molecular hydrogen takes part in the reduction process. We have found that when benzylideneacetophenone is treated with formic acid, toluene, and the supported iridium catalyst in the absence and in the presence of H_2 (1 atmosphere) essentially the same results are obtained in both systems. Experiments under hydrogen but in which the formic acid is replaced by dimethylformamide proved to give a maximum yield of 1,3-diphenyl-1-propanone of 3%. Thus, the reduction appears to be entirely a transfer hydrogenation process for which clean kinetic studies could be anticipated.

Kinetic Studies. A typical conversion–time profile for transfer hydrogenation of benzylideneacetophenone in a

---

[7] Grubbs, R. H.; Kroll, L. C.; Sweet, E. M. *J. Macromol. Sci. Chem.* **1973**, A7, 1047.

[8] Bonds, Jr., W. D.; Brubaker, Jr., C. H.; Chandrasekaran, E. S.; Gibbsons, C.; Grubbs, R. H.; Kroll, L. C. *J. Am. Chem. Soc.* **1975**, *97*, 2128.

[9] Pittman, Jr., C. U.; Smith, L. R.; Hanes, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 1742.

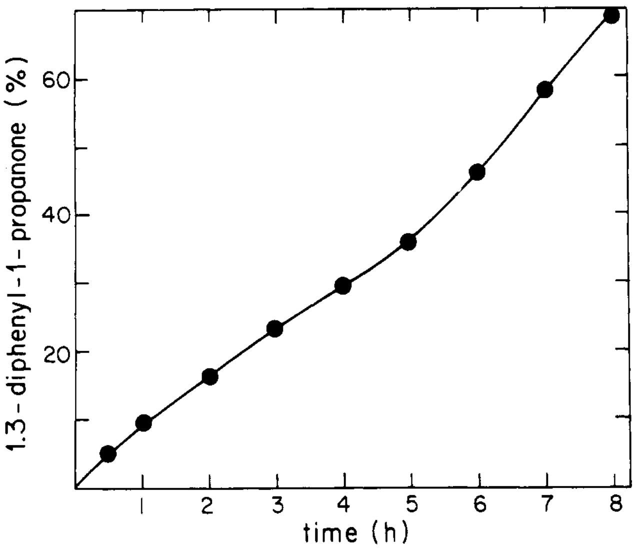


Figure 3. Transfer hydrogenation of benzylideneacetophenone (2.5 mmol) in the presence of 50 mmol of formic acid, 1.9 mL of toluene, and catalyst beads containing 1.8×10^{-2} mequiv of iridium; 97 °C; argon atmosphere, fourth catalytic run.

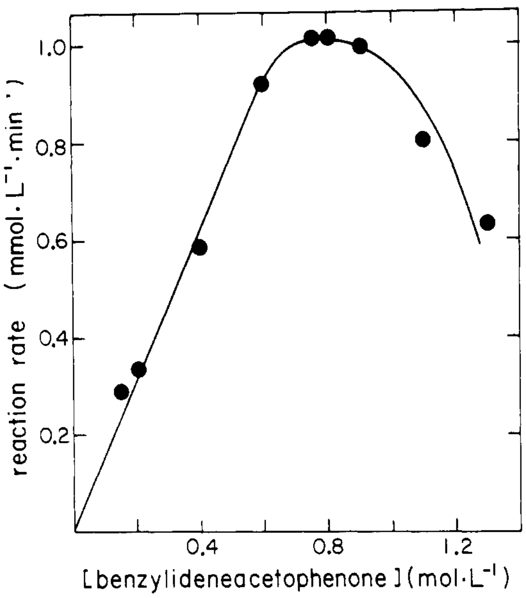


Figure 4. Dependence of initial rate on the concentration of benzylideneacetophenone in formic acid (50 mL) and toluene (1.9 mL) at 97 °C in the presence of 3.95 mmol L^{-1} supported iridium catalyst.

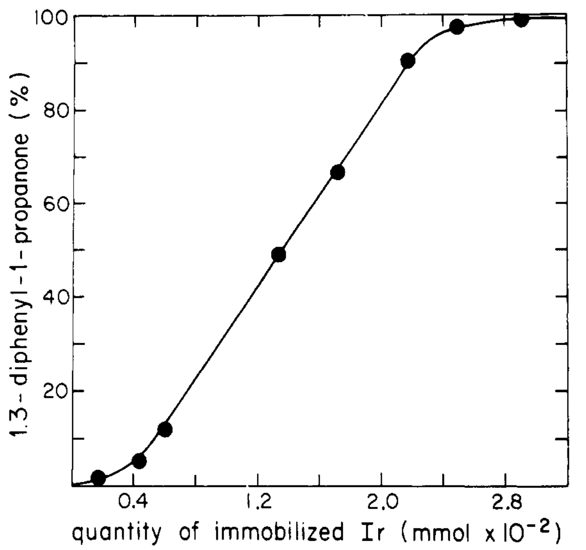


Figure 5. Conversion–catalyst plot for transfer hydrogenation of benzylideneacetophenone under comparable conditions (2.5 mmol of substrate in 50 mmol of formic acid and 1.9 mL of toluene); 97 °C; 8 h. Supported catalyst contained 3.8% iridium on 1.9% diphenylphosphinated 2% cross-linked polystyrene–divinylbenzene, P:Ir = 3.1.

Table II. Initial Rates of Transfer Hydrogenation of Some Substituted Benzylideneacetophenones by Formic Acid and Supported Ir Catalyst[a]

	10^3 (initial rate) mol^{-1} L^{-1}	
X or Y	4-$XC_6H_4CH{=}CHCOC_6H_5$	$C_6H_5CH{=}CHCOC_6H_4Y$-4
Cl	1.20	1.13
F	0.87	
H	0.82	0.82
CH_3	0.60	0.60
OCH_3	0.49	

[a] Reaction conditions: 2.5 mmol of acceptor, 50 mmol of formic acid, 1.8×10^{-2} mequiv of iridium catalyst that has been fully activated for at least 4 runs in the presence of the corresponding substrate; 97 °C; argon atmosphere.

toluene–formic acid mixture is shown in Figure 3.

The plot indicates apparent first-order kinetics during the initial stage of the reaction while the hydrogen donor is still present in large excess. After 5 h, when much of the formic acid has been consumed (as the result of both reactions 1 and 2) the net concentraton of the unsaturated reagent increases and consequently leads to a rate enhancement.

Dependence on Substrate and Catalyst Concentration. A plot of the initial rate of reaction 1 ($R^1 = R^3 = H$, $R^2 = C_6H_5$, $R^4 = COC_6H_5$) against substrate concentration is shown in Figure 4.

The rate is first order in the unsaturated ketone as long as the substrate concentration does not exceed 0.66 M. At higher concentrations the rate dependence deviates from linearity and levels off at ~0.8 M. Above 0.8 M of benzylideneacetophenone, an inverse rate dependence is observed. A similar phenomenon was recently noticed in some other catalytic processes (e.g., in the hydrogenation of cyclohexene by homogeneous and immobilized $RhCl(PPh_3)_3$[10,11]).

In contrast to homogeneous transfer hydrogenation, in which solubility problems and association of the catalyst influence the rate dependence, catalysis 1 (with benzylideneacetophenone as substrate) is first order in the quantity of the supported catalyst up to a level corresponding to 5 mequiv L^{-1}. The dependence of the efficiency of this system on the amount of catalyst used is shown in Figure 5.

Dependence on the Electronic Structure of the Substrate. The influence of the electronic structure of the hydrogen acceptor was studied by employing the substrates shown in Table II in reaction 1 (using fully activated catalysts). Variations in the electronic nature of the substituent cause only small but consistent, changes in the initial rates. When the data are expressed in terms of Hammett correlation the ρ values for reduction of 4-$XC_6H_4CH{=}CHCOC_6H_5$ and of $C_6H_5CH{=}CHCOC_6H_4$-4-Y are very similar (+0.77 and +0.67, respectively).

Kinetic Isotopic Effect. The initial rates of transfer reduction of benzylideneacetophenone by HCOOH, HCOOD, DCOOH, and DCOOD under the conditions

---

(10) de Croon, M. H. J. M.; van Nisselrooij, P. F. M. T.; Kuipers, H. J. A. M.; Coenen, J. W. E. *J. Mol. Catal.* **1978**, *4*, 325.

(11) de Croon, M. H. J. M.; Coenen, J. W. E. *J. Mol. Catal.* **1981**, *11*, 301.

Table III. Effect of Addition of Triphenylphosphine on Reaction 1 ($R^1 = R^3 = H$, $R^2 = C_6H_5$, $R^3 = COC_6H_5$)[a]

catalytic run	P:Ir (mol:mol)	yield of 1,3-diphenyl-1-propanone, %[b]
1	3.1[c]	70
2	3.1[c]	93
3	3.1[c]	93
4	12.3	20.5
5	31.9	2
6	40.0	2
7	58.2	2.8
8	517	65
9	*d*	2
10	*d*	<1

[a] Reaction conditions: 2.5 mmol of benzylideneacetophenone, 1.9 mL of toluene, 50 mmol of formic acid, 2.35 mequiv of catalyst; 97 °C; 8 h; argon atmosphere. [b] Determined by GC. [c] P:Ir in original catalyst; no PPh_3 was added. [d] No PPh_3 was added; P:Ir ratio was not determined.

given in the Experimental Section were determined. The calculated isotope effects for HCOOD, DCOOH, and DCOOD are 1.17, 3.72, and 3.80, respectively. This result suggests that transfer of the formyl but not the hydroxyl hydrogen of the donor occurs in the rate-controlling step of the process.

Effect of Triphenylphosphine and of the P:Ir Ratio. Previously we found that triphenylphosphine inhibits dissociation of phosphines in solutions of $IrCl(CO)(PPh_3)_2$, thereby markedly reducing oxidative addition to this complex.[12] We now find that PPh_3 has a similar effect on the supported catalyst (Table III). It is remarkable, that as long as the molar ratio of added phosphine to iridium is >1 *no* metal leaching is detected by atomic absorption spectrophotometry. Only above this ratio do the iridium–phosphorus bonds, Ⓟ–PPh_2–Ir, start to cleave. Consequently active *homogeneous* complexes are formed and an increase in catalytic activity of the system (during a single run) is observed. At a P:Ir ratio of 517 only $\sim 10^{-5}$ out of the initial 2.35 mmol of Ir are still bound to the polymer.

As metal leaching occurs only when P:Ir > 40, full activity of the system can be obtained by carefully washing the beads from runs 4, 5, or 6 (Table III) and recycling them in the absence of PPh_3. When, however, the beads from the eighth run are recycled hardly any reaction takes place in successive experiments.

The dependence on the P:Ir ratio was also studied by changing the amount of anchored iridium on polystyrene with a constant phosphorus loading. The plots shown in Figure 6 for three catalysts reveal an inverse relationship between the P:Ir ratio and the reaction rate. In transfer reduction of benzylideneacetophenone (conditions as in Table I) by catalysts having P:Ir ratios of 3.76, 5.79, and 8.65 the initial rates were 0.82, 0.41, and 0.11 mmol L^{-1} min^{-1}, respectively.

Many other potential ligands inhibit reaction 1 in the same manner as PPh_3. The effect of sulfuric acid, e.g., is shown in Table IV. Recovery of the activity after acid treatment is very slow compared to the recovery after treatment with PPh_3.

Dependence on Temperature. Reaction 1 ($R^1 = R^3 = H$, $R^2 = C_6H_5$, $R^4 = COC_6H_5$) takes place in the temperature range between 75 and 98 °C with essentially no change in the selectivity. Initial rates were measured at

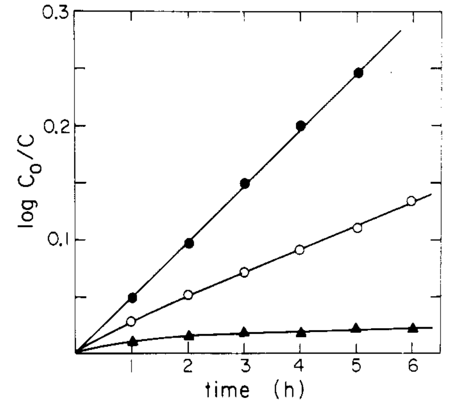


Figure 6. Plots of log C_0/C against time for transfer reduction of benzylideneacetophenone by polystyrene-bound iridium catalysts of P:Ir 8.65 (▲), 5.79 (○), and 3.76 (●). Reaction conditions as in Table I.

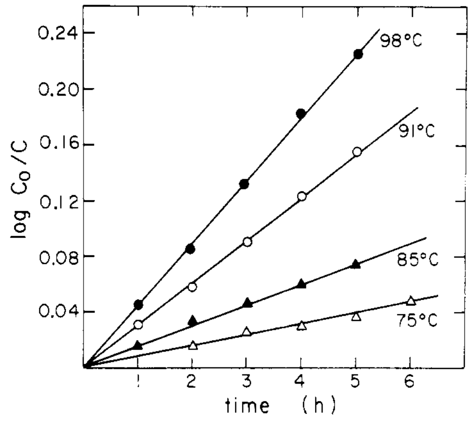


Figure 7. Plot of log C_0/C against time for reaction 1 ($R^1 = R^3 = H$, $R^2 = C_6H_5$, $R^3 = COC_6H_5$) at various temperatures with fully activated supported iridium catalyst. Conditions as in Table I.

Table IV. Effect of Added Sulfuric Acid on Transfer Hydrogenation of Benzylideneacetophenone[a]

catalytic run:	3	4	5	6	7	8	9	10
$[H_2SO_4] \times 10^{-2}$ M		2.4	4.9	24	9			
conversion, %	69	11	7	5	5	6	7	26

[a] Conditions as in Table I.

75, 85, 91, and 98 °C for several substrate concentrations between 0.1 and 0.7 M. From plots of log C_0/C vs. time, such as shown in Figure 7, the reaction constants could be calculated.[13] From the corresponding Arrhenius plot the activation energy E_a(hetero) = 18.3 kcal mol^{-1} is obtained; $H^{\ddagger}$(hetero) (81 °C) = 17.6 kcal mol^{-1}.

Discussion

Following the mechanisms suggested for many other hydrogen-transfer reactions by homogeneous and heterogenized catalysts, we assume the major steps in our process to be (a) activation of the catalyst, (b) activation by complexation of both donor and acceptor, (c) hydrogen transfer within the coordination sphere, and (d) release of products.

Activation of the Catalyst. In analogy with previous suggestions for the activation of homogeneous $IrCl(CO)(PPh_3)_2$[12,14] it can be assumed that the heterogenized

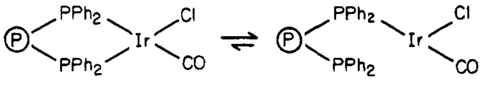
---

[12] Mureinik, R. J.; Weitzberg, M.; Blum, J. *Inorg. Chem.* **1979**, *18*, 915.

[13] We have already shown (ref 4) that it can be assumed that catalytic processes by polystyrene-anchored complexes take place in the spheres of the polymeric catalyst rather than on its surface. Thus, the units of *k*(hetero) become the same as *k*(homo) and direct comparison between the thermodynamic constants in both systems is permissible.

[14] See also: James, B. R.; Menon, N. A. *Can. J. Chem.* **1968**, *46*, 217.

iridium complex releases a polystyryldiphenylphosphine group (*trans* to the Cl ligand) according to eq 3.[15]


(3)

1 2

The release of the phosphine ligand increases the Lewis acidity of the unsaturated metal center and increases its ability to undergo oxidative addition. Recombination of a pendant PPh_2 ligand as well as addition of free PPh_3 [formation of Ⓟ-PPh_2-IrCl(CO)(PPh_3)] results in deactivation. The number of coordinated phosphines depends, of course, on the coordination of available phosphorous atoms in the vicinity of the metal atom. Hence, a high P:Ir ratio favors the formation of **1** while a low ratio causes the coordinatively unsaturated species **2** to prevail.

The mobility of the phosphine-containing polymer chain also plays an important role in establishing the preferred direction of equilibrium 3. If the chains have high mobility, even remote PPh_2 groups can easily be brought into binding distance to the iridium atom. One of the factors that affects chain mobility is the cross-linking in the polystyrene skeleton. Thus, changes in the P:Ir ratio have a great effect on the activation in a 2% divinylbenzene-cross-linked resin, and a much smaller influence in a 20% cross-linked matrix.

An additional factor associated with the chain mobility is the solvent. Good swelling solvents increase the interchain distances and provide high mobility and, therefore, contribute to deactivation of the catalyst [cf. ref 16, 17]. In most cases this "negative" effect of the swelling solvent is masked by its "positive" properties, i.e., its ability to provide fast penetration of the substrate into the pores where metal atoms are located. In our case the deactivation effect of the swelling solvent prevails and nonswelling solvents increase catalytic efficiency. Obviously, the nature of the solvent has only a little effect when the iridium is bound to a nonflexible 20% cross-linked backbone.

The fact that nonswollen beads provide an equal or even greater activity than swollen ones indicates that except for very bulky substrates the unsaturated compounds have little difficulty in moving inside the catalyst channels. Thus, it is understandable that the reaction is not diffusion controlled.

Activation of the Acceptor. The vacant coordination site of structure **2** permits reversible complexation of the unsaturated substrate to the iridium atom (eq 4).

$$\underset{\mathbf{2}}{\text{Ⓟ-PPh}_2\text{-IrCl(CO)}} \underset{}{\overset{\text{olefin}}{\rightleftharpoons}} \underset{\mathbf{3}}{\text{Ⓟ-PPh}_2\text{-IrCl(CO)}(\pi\text{-olefin})}$$
$$\underset{\text{olefin}}{\overset{PPh_3}{\rightleftharpoons}} \underset{\mathbf{4}}{\text{Ⓟ-PPh}_2\text{-IrCl(CO)(PPh}_3)} \quad (4)$$

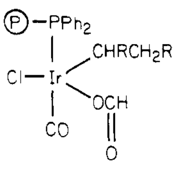
We have recently reported spectroscopic evidence for the formation of the olefin complexes of type **3** during the initial stages of the process.[18] Free PPh_3 is capable of substituting the olefin and hence deactivates the system, but excess olefin causes eventual reformation of **3**.

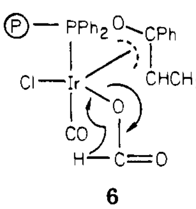
The plot for the rate dependence on the concentration of the substrate (Figure 4) can be represented by the equation $d(\text{rate})/d(S) = aS(1 - S)$ where S is the concentration of the hydrogen acceptor and a is a constant. For low substrate concentration a linear relationship is obtained. When $S \simeq 1$ the rate follows a pseudo-zero-order dependence and when $S \gg 1$ the rate decreases according to $-aS^2$. Such behavior can be expalined in terms of the available free active sites on the metal atoms. At low substrate concentration sufficient unoccupied sites are present and every additional acceptor molecule is immediately activated. After saturation of the free sites the rate remains constant. At still higher concentration of the substrate all active sites are blocked and consequently the rate decreases. A similar rate dependence has already been observed in some other catalyst systems.[10,11,19]

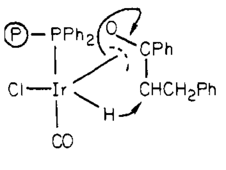
Quantitative IR measurements have indicated that the amount of coordinated substrate increases gradually until the system reaches maximum activity (i.e., at the end of the third or fourth run under our standard conditions). Thus the substrate-Ir complex is a key intermediate in the catalytic cycle. As mentioned already the substrate-containing complex is by far more stable towards oxidation than the unreacted immobilized complex. While the freshly prepared catalyst loses all its catalytic power by brief exposure to air (and substantial metal leaching occurs) the beads become perfectly air stable after being used 3 or 4 times in transfer hydrogenation. No elimination of iridium takes place from fully activated catalyst even when the reactions are conducted under ambient atmosphere.

Activation of the Hydrogen Donor and Interaction with Coordinated Substrate. In some previous studies[20,21] it has been postulated that catalytic reduction of olefins by formic acid involves initial decomposition of the acid into H_2 and CO_2. We have mentioned earlier evidence indicating that in our system this reaction is unimportant. Further evidence that the source of the hydrogen is not the molecular hydrogen obtained from the decomposition of HCOOH comes from the isotope studies. Were H_2 involved, DCOOH and HCOOD would have given the same results and complete hydrogen scrambling would have taken place. We found, however, important kinetic isotope effects[22] and different products resulting from the two labeled formic acids.

We assume that in our case, formic acid activation involves oxidative addition associated with fast alkyl insertion to give **5**. For benzylideneacetophenone this species may exist as an oxypropenyl complex **6**.[23,24]


5


6


7

The value of $k_H/k_D = 1.17$ for HCOOH/HCOOD is consistent with the suggestion that the carboxylic hydrogen transfer (that is involved in the formation of **6**) is not rate controlling.[25] The formyl hydrogen transfer in **6** that

---

[15] Cf., e.g.: Pittman, Jr., C. U.; Ng, Q.; Hirao, A.; Honnick W.; Hanes, R. In "Relations between Homogeneous and Heterogeneous Catalysis"; CNRS: Paris, 1978; pp 49-94.

[16] Regen, S. L. *J. Am. Chem. Soc.* **1974**, *96*, 5275; **1975**, *97*, 3108.

[17] Regen, S. L.; Lee, D. P. *Macromolecules* **1977**, *10*, 1418 and references therein.

[18] Azran, J.; Buchman, O; Höhne, G.; Schwarz, H.; Blum, J. *J. Mol. Catal.* **1983**, *18*, 105.

[19] Ohkubo, K.; Shoji, T.; Yoshinaga, K. *J. Catalysis* **1978**, *54*, 166.

[20] Cf.: Coffey, R. S. *Chem. Commun.* **1967**, 923.

[21] Volpin, M. E.; Kukolev, K. P.; Chernyshev, V. D.; Kolonnikov, I. S. *Tetrahedron Lett.* **1971**, 4435.

[22] Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.

[23] Cf., e.g.: Goetz, R. W.; Orchin, M. *J. Am. Chem. Soc.* **1963**, *85*, 2782.

[24] Sasson, Y.; Blum, J. *J. Org. Chem.* **1975**, *40*, 1887 and references cited therein.

[25] Swain, C. G.; Wiles, R. A.; Bader, R. F. W. *J. Am. Chem. Soc.* **1961**, *83*, 1945.

Table V Isotope Distribution in 1,3-Diphenylpropanone formed by Transfer Hydrogenation of Benzylideneacetophenone and Deuterated Formic Acids[a]

hydrogen donor	deuterium, % (by 70 eV EI mass spectral analysis)				
	d_0	d_1	d_2	d_3	d_4
HCOOD[b]	9.9	34.5	45.9	9.7	
DCOOH[c]	5.6	48.4	34.0	11.1	0.9
DCOOD[c]	0.9	7.1	33.3	57.0	1.7

[a] Reaction conditions: 2.5 mmol of substrate, 50 mmol of labeled formic acid, 1.8×10^{-2} mequiv of supported catalyst, and 1.9 mL of toluene; 97 °C. [b] Determined at 45% conversion. [c] Determined at 92% conversion.

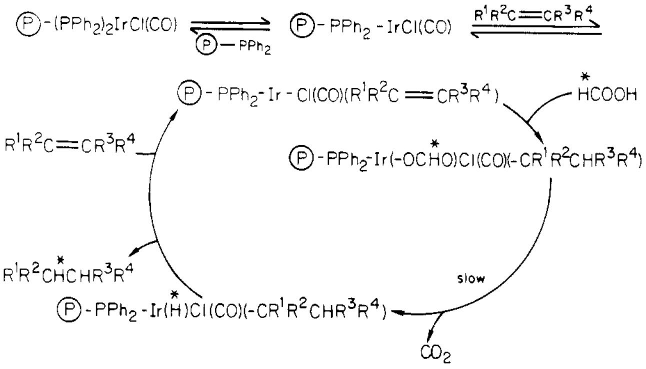
follows is associated with CO_2 elimination and the formation of complex 7. The values of $k_H/k_D = 3.72$ for HCOOH/DCOOH and $k_H/k_D = 3.80$ for HCOOH/DCOOD indicate that not much transfer of hydrogen from H–Ir occurs in the transition state and that such transfer is probably rate controlling.[26,27]

Additional support for the involvement of a metal hydride in the rate-determining step was obtained from an experiment in which benzylideneacetophenone was reduced by formic acid in the presence of polystyrene-anchored $HIr(CO)(PPh_3)_3$. While under the standard conditions given in the Experimental Section supported $IrCl(CO)(PPh_3)_3$ yielded 17% of 1,3-diphenyl-1-propanone in the first catalyst run, the immobilized iridium hydride gave 99%. The activity of the latter catalyst dropped, however, in consecutive runs because the chlorine-free complex is unstable.

The fact that the carboxyl proton of the donor is transferred to the β-carbon atom and the formyl hydrogen to the α-carbon atom of $C_6H_5COC^{\alpha}H{=}C^{\beta}HC_6H_5$ can be deduced also from product analysis in experiments with deuterated formic acids. Table V shows the extent of deuterium incorporation in the products. HCOOD and DCOOH form in addition to the expected monodeuterated products dideuterated and even some trideuterated compounds. The extra deuterium is found predominantly (by 300-MHz ^1H NMR analysis) on the enolizable α-carbon of the product ketone. DCOOD forms a mixture of deuterated 1,3-diphenyl-1-propanones which integrates for one β-hydrogen (2.97 ppm) and only 1/3 α-hydrogen (3.20 ppm). The trideuterated product is $C_6H_5CHDCD_2COC_6H_5$. Similarly, HCOOD yields in addition to $C_6H_5CHDCH_2COC_6H_5$ also $C_6H_5CHDCHDCOC_6H_5$ in a ratio 9:7 as well as small quantities of $C_6H_5CHDCD_2COC_6H_5$. DCOOH forms $C_6H_5CH_2CHDCOC_6H_5$ and $C_6H_5CH_2CD_2COC_6H_5$ as the major mono- and dideuterated products, respectively. None of the deuterated acids gives detectable amounts of the β-dideuterated ketone, $C_6H_5CD_2CH_2COC_6H_5$.

Release of Product. The final product is formed from 7 by reductive elimination followed by complexation with a new substrate molecule to start a new catalytic cycle. We observe a small effect on rate when the nature of the substituent on the substrate varies. However, the electronic influence should be substantial if the reductive elimination were rate controlling.[28] Since mass spectral analysis[18] indicates accumulation of alkyliridium species it can be concluded from both this fact and the small electronic effect that the final step of the process does make some, albeit small, contribution to the overall rate.

Scheme I



The proposed mechanism of the complete catalytic process is presented in Scheme I.

Experimental Section

The deuterated formic acids DCOOH and DCOOD (>98% deuterium) were purchased from Merck, Sharp & Dohme Co; HCOOD was prepared as described by Scribe and Pallaud.[29] Most of the substrates were obtained from commercial sources (of highest grades available) and were freshly distilled in vacuo and degassed or recrystallized before use. Where necessary, α,β-unsaturated ketones were synthesized via aldol condensation of the appropriate ketones and aldehydes in basic media[30] except for 2,3-dimethyl-[31] and 3,5-diphenylcyclohex-2-enone.[32] The reference compounds 1,3-diphenyl-,[33] 1-phenyl-3-(4-chlorophenyl)-,[33] 3-phenyl-1-(4-chlorophenyl)-,[33] 1-phenyl-3-(4-fluorophenyl)-,[33] 1-phenyl-3-(4-methoxyphenyl)-,[33] 3-phenyl-1-(4-methylphenyl)-,[33] and 3-phenyl-1-(4-methylphenyl)-1-propanone[33] as well as 4-phenyl-2-butanone[24] and 2,2-dimethyl-5-phenyl-3-propanone[24] were obtained by our previous method. 1,2,3-Triphenyl-[34] and 1,3,3-triphenyl-1-propanone[35] were prepared according to known procedures.

Anchoring of Catalysts to Diphenylphosphinated Polystyrene Resins. [Cf., e.g., ref 3, 5, 9, and 36]. Typically, a mixture of 1.0 g of 2% cross-linked polymer-bound diphenylphosphine on styrene–divinylbenzene copolymer (0.62 mequiv of P/g, beads 20–60 mesh), 483.6 mg (0.62 meq) of $IrCl(CO)(PPh_3)_2$ and 20 mL of dry, degassed benzene was refluxed under argon for 48 h. The solvent was decanted and the residue was extracted in a Sohxlet apparatus with boiling benzene for 48 h. The beads were dried at 70 °C in vacuo for 48 h. The iridium content of the solid and of the concentrated washing were determined by atomic absorption technique on a Perkin-Elmer Model 403 instrument. The polymeric catalyst contained 3.80% Ir and 1.90% P (molybdenum blue method).

In a similar manner catalyst samples were prepared in which the iridium content was 1.433%, 2.14% and 3.30% and the polymeric backbone was 2% cross-linked polystyrene–divinylbenzene (P content 1.9%). The same technique was also used for the preparation of supported $RuCl_2(PPh_3)_3$, $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $HIr(CO)(PPh_3)_3$, and $PdCl_2(PPh_3)_2$. Several complexes were anchored to 20% cross-linked diphenylphosphinated polystyrene–divinylbenzene copolymers.

Hydrogen Transfer from Formic Acid to Unsaturated Acceptors. A three-necked flask provided with a magnetic bar, a gas inlet, a neoprene rubber seal, and a reflux condenser con-

---

(26) See, e.g.: James, B. R. *Adv. Organometal. Chem.* **1979**, *17*, 319 and references cited therein.

(27) Yurtechenko, E. N.; Anikeenko, N. P. *React. Kin. Catal. Lett.* **1975**, *2*, 65.

(28) Cf., e.g.: Deeming, A. J. *MTP Int. Rev. Sci. Inorg. Chem. Ser. One* **1972**, *9*, 117.

(29) Scribe, P.; Pallaud, R. *C.R. Acad. Sci. Paris* **1963**, 256, 1120.

(30) Nielsen, A. T.; Houlihan, W. J. *Org. React.* **1968**, *16*, 1.

(31) Smith, L. I.; Rouault, G. F. *J. Am. Chem. Soc.* **1943**, *65*, 631.

(32) Meyer, A. Y.; Bergmann, E. D. *Isr. J. Chem.* **1968**, *6*, 735.

(33) Sasson, Y.; Cohen, M.; Blum, J. *Synthesis* **1973**, 359.

(34) Miyano, S.; Sako, Y. *Chem. Pharm. Bull.* **1965**, *13*, 1372.

(35) Shildneck, P. R. "Organic Syntheses"; Wiley: New York, 1956; Collect. Vol. 2, p 236.

(36) Pittman, Jr., C. U.; Jacobson, S. E.; Hiramoto, H. *J. Am. Chem. Soc.* **1975**, *97*, 4774.

nected to a mercury pressure valve was washed with argon and charged with an appropriate amount of catalyst beads containing 1.78×10^{-2} mequiv of transition metal. The flask was placed in a thermostated bath at 97 ± 0.2 °C. The substrate (2.5 mmol) in 1.9 mL of toluene and the formic acid (50 mmol) were injected into the reaction vessel and the mixture was stirred at 97 °C for 8 h. After cooling to room temperature the liquid was withdrawn with a syringe and the solid beads were washed three times with 5-mL portions of toluene. The combined solutions were concentrated and analyzed by gas chromatography on a FID equipped Hewlett-Packard Model 7620 A instrument on either OV-17 or carbowax 20 M columns. The used catalyst beads were washed repeatedly with toluene, dried at 0.05 mm, and stored under argon to await recycling.

The kinetic measurements were carried out in modified reaction flasks in which the catalyst and reactants could be preheated separately in a thermostat oil bath (accuracy ±0.1 °C). After thermal equilibration the solid catalyst and the liquid reactants were mixed. Samples were withdrawn with an air tight syringe at intervals ranging from 10 to 60 min during 5 h. The initial rate was calculated in each case from the average of at least three experiments.

Acknowledgment. We are grateful to the United States-Israel Binational Science Foundation (BSF), Jerusalem, for financial support of this study.

Registry No. $C_6H_5CH{=}CHCOC_6H_5$, 94-41-7; $C_6H_5CH{=}CHCOC_6H_4$-4-CH_3, 4224-96-8; $C_6H_5CH{=}CHCOC_6H_4$-4-F, 399-10-0; $C_6H_5CH{=}CHCOC_6H_4$-4-Cl, 956-02-5; 4-$CH_3OC_6H_4CH{=}CHCOC_6H_5$, 959-33-1; 4-$CH_3C_6H_4CH{=}CHCOC_6H_5$, 4224-87-7; 4-$ClC_6H_4CH{=}CHCOC_6H_5$, 956-04-7; $C_6H_5CH{=}CHCOCH_3$, 122-57-6; $C_6H_5CH{=}CHCOC(CH_3)_3$, 538-44-3; $(C_6H_5)_2C{=}CHCOC_6H_5$, 849-01-4; $C_6H_5CH{=}C(C_6H_5)COC_6H_5$, 4023-77-2; $C_6H_5CH{=}CHCOOC_2H_5$, 103-36-6; $C_6H_5CH_2CH{=}CH_2$, 300-57-2; 4-$FC_6H_4CH{=}CHCOC_6H_5$, 1608-51-1; $IrCl(CO)(PPh_3)_2$, 14871-41-1; formic acid, 64-18-6; cyclooctene, 931-88-4; 2,3-dimethylcyclohex-2-enone, 1122-20-9; 3,5-diphenylcyclohex-2-enone, 10346-08-4.

Singlet Oxygenation and Triazolinedione Addition to Spirofluorene-1,3,5-cycloheptatriene

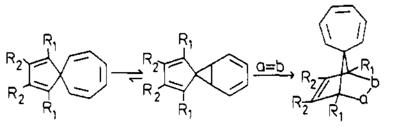
Waldemar Adam,*[1] Heinz Dürr,[2] Karl-Heinz Pauly,[2] Eva-Maria Peters,[3] Karl Peters,[3]
Hector Rebollo,[1,4] and Hans Georg von Schnering[3]

Institut für Organische Chemie, University of Würzburg, Am Hubland, D-8700 Würzburg, West Germany, Departamento de Quimica, Universidad de Puerto Rico, Rio Piedras, Puerto Rico 00931, Fachbereich Chemie, Universität des Saarlandes, D-6600 Saarbrücken 11, West Germany, and Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-7000 Stuttgart 80, West Germany

Received January 27, 1983

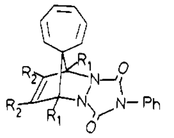
Spirocyclopentadiene-, 1,4-diphenylspirocyclopentadiene-, and 1,2,3,4-tetrachlorospirocyclopentadiene-1,3,5-cycloheptatrienes (**1a–c**) all afford urazoles **3a–c** with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in which cycloaddition takes place at the cyclopentadiene moiety. For spirofluorene-1,3,5-cycloheptatriene (**1d**), however, cycloaddition with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) is forced to take place at the cycloheptatriene site, leading initially to the norcaradiene adduct *N*-methyl-3-spirofluorene-6,7-diazatricyclo[3.2.2.$0^{2,4}$]non-8-ene-6,7-dicarboximide (**6**), which rearranges above 0 °C into the urazole *N*-methyl-9-spirofluorene-7,8-diazabicyclo[4.3.0]nona-2,4-diene-7,8-dicarboximide (**7**). On the other hand, singlet oxygenation produces the tropilidene endoperoxide 2-spirofluorene-6,7-dioxabicyclo[3.2.2]nona-3,8-diene (**8**). Endoperoxide **8** was converted into the diepoxide *syn*-3,4:5,6-diepoxy-7-spirofluorenecycloheptene (**9**) on thermal rearrangement into a mixture of bicyclic peroxides 4-spirofluorene-6,7-dioxabicyclo[3.2.2]non-2-ene (**10**) and 4-spirofluorene-6,7-dioxabicyclo[3.2.2]nonane (**11**) via diimide reduction, into a mixture of epoxy endoperoxides *syn*- and *anti*-2,3-epoxy-4-spirofluorene-6,7-dioxabicyclo[3.2.2]non-8-enes (**12a,b**) via epoxidation with *m*-chloroperbenzoic acid, and into the epoxy enone 6,7-epoxy-3-spirofluorenecyclohepten-4-one (**13**) on triethylamine treatment. X-ray analyses of urazoles **3b** and **7** and endoperoxides **8** and **12b** confirm these structure assignments. The mechanistic implications are discussed.

Spirocyclopentadiene-1,3,5-cycloheptatriene (**1**) exists at room temperature as the norcaradiene valence isomer **N-1**.[5] Although both 1,2-diene moieties are perfectly planar, (4 + 2) cycloaddition takes place preferentially at the cyclopentadiene site (eq 1), despite electronic or steric factors. For example, with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) the respective urazoles **3a–c** are produced.

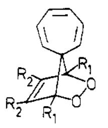


T-1 **N-1** **2** (1)

a, $R_1 = R_2 = H$
b, $R_1 = Ph$; $R_2 = H$
c, $R_1 = R_2 = Cl$
d, $R_1 + R_2 =$ benzo



3



4

Attempted singlet oxygenation also proceeds via preferential attack at the cyclopentadiene moiety, but the resulting endoperoxides **4a–c** are too unstable even for spectral characterization at −60 °C.

Benzo annelation, as in the spirofluorene derivative **1d**, encumbers a (4 + 2) reaction at the cyclopentadiene site,

---

(1) Universität Würzburg and Universidad de Puerto Rico; direct correspondence to Würzburg.

(2) Universität des Saarlandes.

(3) Max-Planck-Institut für Festkörperforschung.

(4) Thanks to the Thyssen Stiftung for a travel grant.

(5) Schönleber, D. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 76.