SHORT COMMUNICATION

Fluorocarbon Derivatives of Iron as Catalysts for the Photochemical Isomerization of 1-Pentene

WILLIAM R. CULLEN and MANGAYARKARASY WILLIAMS

Chemistry Department, University of British Columbia,
Vancouver, B.C., Canada V6T 1W5

The η^3-allyl complex $\underline{1}$ of known structure is prepared by reacting $(C_6H_{11})_2P\overline{C=CC\ell(CF_2)_3}$ with $Fe(CO)_5$ [1]. Derivatives of this type are of interest as potential catalysts because they are stable compounds which could become coordinatively unsaturated by 1) loss of CO from either iron atom, 2) cleavage of the Fe-Fe bond

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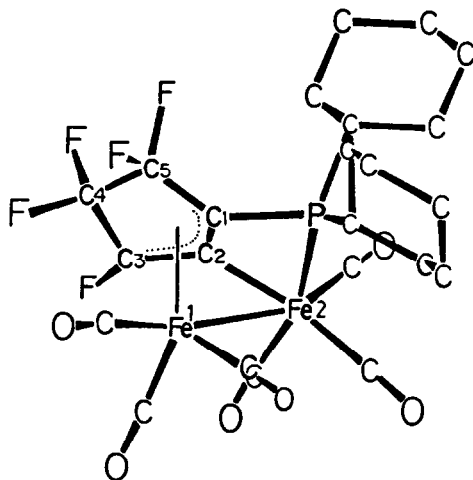
or 3) converting the η^3-allyl system into an η^1-moiety. Schroeder and Wrighton [2] have shown that $Fe(CO)_5$ is a photocatalyst for the isomerization of 1-pentene to cis and trans-2-pentene and postulated that η^3-allyl hydride intermediates such as $(\eta^3-CH_2CHCHC_2H_5)Fe(CO)_3H$

are involved. In this paper we describe the use of $\underset{\sim}{1}$ and related compounds as photocatalysts for the same reaction. It is interesting to note that little is known about the catalytic properties of the numerous fluorocarbon derivatives of the transition metals.

When the diphenylphosphino analogue of $\underset{\sim}{1}$ $(C_6H_5)_2PC\text{=}C\text{=}CF(CF_2)_2Fe_2(CO)_6$ $\underset{\sim}{2}$, and 1-pentene (1:100 mole ratio) are irradiated in benzene solution with near ultraviolet light isomerization takes place to give an equilibrium mixture of the pentenes as shown in Figure 1. (No reaction takes place in the dark.) When the irradiation is carried out starting with the same catalyst and cis-2-pentene or trans-2-pentene the same equilibrium mixture is obtained. The equilibrium values found in this work 1-pentene: trans-2-pentene: cis-2-pentene = 3.8: 73.3:23.0 are very close to those reported by Schroeder and Wrighton (3.0:76.0:21.0).
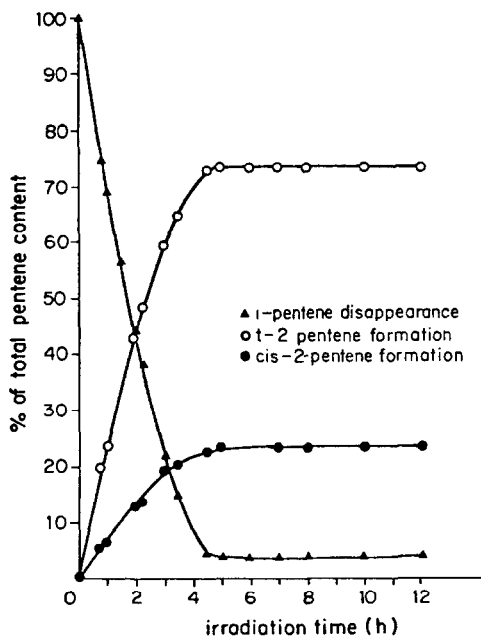

Fig. 1. Photocatalyzed isomerization of 1-pentene using $\underset{\sim}{2}$ as catalyst.

The relative amounts of isomerization of 1-pentene using a number of iron carbonyl derivatives as photocatalysts are compared in Table 1. All three η^3-allyl complexes are catalysts but the

TABLE 1   Isomerization of 1-pentene using iron carbonyl
complexes as photocatalysts[a]

Catalyst		1-pentene (%)	cis-2-pentene (%)	trans-2-pentene (%)
$(C_6H_{11})_2P\overline{C\dot{=}C\dot{=}CF(CF_2)_2Fe_2(CO)}_6$	1	17.9	23.7	58.4
$(C_6H_5)_2P\overline{C\dot{=}C\dot{=}CF(CF_2)_2Fe_2(CO)}_6$	2	3.7	23.0	73.3
$(C_6H_5)_2P\overline{C\dot{=}C\dot{=}CF(CF_2)_3Fe_2(CO)}_6$	3	33.5	22.1	44.4
$(C_6H_{11})_2P\overline{C\dot{=}CP(C_6H_{11})_2(CF_2)_2Fe(CO)}_3$	4	100	-	-
$(C_6H_{11})_2P\overline{C\dot{=}CP(C_6H_{11})_2(CF_2)_3Fe(CO)}_3$	5	100	-	-
$(C_6H_5)_2P\overline{C\dot{=}CC\ell(CF_2)_3Fe(CO)}_4$	6	5.8	28.5	65.8
$(C_6H_5)_2P\overline{C\dot{=}CC\ell(CF_2)_3W(CO)}_5$	7	100	-	-

[a]All experiments used 0.124 mmol of catalyst and 1.2 mmol of 1-pentene
and irradiation was continued for 20.5 h.

best one is the diphenylphosphino derivative 2. In the case of $Fe(CO)_5$
it seems that the actual isomerism is a thermal process which occurs
after photogeneration of the catalyst [2] and because we obtain simi-
lar equilibrium values it is likely that we are also encountering a
process involving carbonyl dissociation.

Although 1 does not easily react with triphenylphosphine one
mole of CO is displaced from 2 at 150°C to give $(C_6H_5)_2P\overline{C\dot{=}C\dot{=}CF(CF_2)_2Fe}$
$(CO)_5P(C_6H_5)_3$, 8. This reaction probably proceeds by a thermal dissoci-
ation of carbon monoxide analogous to the photochemical dissociation
necessary to produce the catalyst.

The structure of 8 can be deduced from the analytical and spec-
troscopic data. The most useful information comes from the ^{19}F and
^{31}P NMR spectra. The former shows a pattern similar to the parent
allyl complex 2 with two AB quartets and a single high field multiplet.
Thus the η^3-allyl moiety is retained. The ^{31}P NMR spectrum shows two
sets of doublets with J(PP)=44.1 Hz. The presence of spin-spin
coupling between the two phosphorus atoms indicates that they are
probably bonded to the same iron atom and the small magnitude of the
coupling suggests [4] that they are in cis positions. Thus it is

likely that 8 has the same structure as 1 with $(C_6H_5)_2P$ replacing the $(C_6H_{11})_2P$ group on Fe^2, and the CO group trans to the Fe-Fe bond replaced by triphenylphosphine. This particular position of sub-stitution is chosen because in related studies [5] it has been found that monosubstitution by phosphines in $(L-L)Fe_2(CO)_6$ deriva-tives ((L-L) is a ditertiary arsine or phosphine ligand of the type shown in 4 and 5) takes place at the position trans to the Fe-Fe bond. However it should be pointed out that since Fe^2 is sigma bonded to C2 of the fluorocarbon group the CO trans to this could be labilized and thus substitution by triphenylphosphine could take place in this position which would also be cis to the $(C_6H_5)_2P$ moiety.

Assuming that photolysis of 1, 2, or 3 results in the disso-ciation of CO groups from Fe^2 it is difficult to envisage that the subsequent thermal isomerization of the pentenes occurs by the same mechanism as proposed by Schroeder and Wrighton [2]. This is because formation of a η^3-allyl hydride intermediate at Fe^2 would involve 7-coordinate iron unless dissociation of all three CO groups takes place. (In this connection it was not possible to replace more than one CO group in 2 by triphenylphosphine in a thermal reaction.) Thus it seems possible that the rest of the cluster is involved in the isomerization.

To continue with the same type of argument, photodissociation of CO from $Fe(CO)_5$ in the presence of H_2 results in the production of $H_2Fe(CO)_4$ which is a good olefin hydrogenation catalyst with considerable selectivity [2]. In contrast compound 2 is not a hydrogenation catalyst under photochemical conditions (1 at H_2, 24 h, benzene solution, olefin : 1 = 100:1) for cyclohexane, cyclo-octadiene, trans-3-hexene, 1-pentene, cis-2-pentene, and trans-2-pentene (olefin isomerization is observed for the pentenes). The two cyclic olefins are not hydrogenated under the same conditions when heated (150°) rather than irradiated.

The failure of 2 to act as a hydrogenation catalyst is probably because the photochemical dissociation of CO results in loss from an iron atom (Fe^2) which is 6-coordinate to start with and thus oxidative addition of H_2 to produce the hydrogenation catalyst would result in a 7-coordinate structure.

The $Fe(CO)_4$ derivative **6** is a good catalyst for pentene iso-
merization (Table 1) probably because at least one CO is easily
dissociated although again the proposed mechanism [2] is difficult
to apply without postulating phosphine and CO dissociation. The
failure of the $Fe(CO)_3$ derivatives **4** and **5** to catalyze the isomeri-
zation may be due to the inherent instability of the complexes [3].
The lack of catalysis by **7** is surprising in view of the known
catalytic ability of $W(CO)_6$ [6] and the belief that reactions
catalyzed by $Fe(CO)_5$ and $W(CO)_6$ proceed along similar pathways [2].

Experimental

The alkenes were obtained from Aldrich Chemical Company Inc. and
Matheson, Coleman and Bell and were used without further purifi-
cation except the cyclic olefins which were distilled over Al_2O_3.
Benzene was refluxed over potassium wire and stored under nitrogen
over molecular sieves. Hydrogen was obtained from Canadian Liquid
Air and was passed through a 'Deoxo' catalytic purifier before use.
The metal carbonyl complexes **1-7** were prepared using well established
procedures [1,3].

An HP 5750 Research Chromatograph unit with thermal conductivity
detector was used for gas chromatographic (GLC) analyses. Separation
of the components of olefin reaction mixtures was accomplished on a
25 ft x 1/8 in. column of 20% propylene carbonate on Chromosorb P.
Mass spectra were run using an AEI MS-9-02 spectrometer and NMR
spectra using a Varian XL 100 instrument.

Isomerization of 1-pentene in the presence of **2**

An evacuated Carius tube containing a benzene solution (1.25 ml)
of 1-pentene (0.135 ml, 1.2 mmol) and **2** (0.0077 g, 0.0124 mmol) was
irradiated with a 200 W Hanovia 654-A36 lamp situated 20 cm from the
reaction tube. The tube was continuously shaken and cooled by an
air stream. At the end of the reaction period the total volatile
components were transferred under vacuum to another tube and the
solution was then analyzed by GLC. The reaction was repeated for
different time intervals using fresh catalyst. The products eluted
from the chromatograph were initially identified by isolation
followed by infrared and nmr spectroscopy. Figure 1 and Table 1
show the results of a number of experiments of this type.

Isomerization of 1-pentene in the presence of the other complexes 2-7

Benzene solutions containing 1-pentene (1.2 mmol) and the iron carbonyl (or tungsten carbonyl) complexes (0.124 mmol) were irradiated for 20.5 h under similar conditions as described above. Table 1 lists the percentage of the isomers of pentene isolated at the end of the reaction.

Attempted hydrogenation reactions of some olefins using 2 as catalyst

A Carius tube containing a benzene solution of the olefin (2.4 mmol) and 2 (.0248 mmol) was cooled and evacuated. One atmosphere of hydrogen was admitted to the Carius tube which was then closed and irradiated for 24 h as described above. At the end of the reaction period the samples were analyzed for saturated products, using GLC.

Reaction of 2 with triphenylphosphine

Triphenylphosphine (0.074 g, 0.28 mmol) and 2 (0.175 g, 0.28 mmol) in benzene (8 ml) were heated in a evacuated Carius tube at 150°C for 46 h. At the end of the reaction period the solution (initially yellow) was red. Removal of solvent gave a red solid which was dissolved in dichloromethane and chromatographed on a Florisil column. A yellow band was eluted with petroleum ether (b.p. 40-60°C). This was identified as unreacted 2 (0.04 g, 22.8% recovery). A 25% diethyl ether - 75% petroleum ether mixture eluted a red band. Evaporation of solvent and recrystallization from hexane afforded red shiny crystals identified as the triphenylphosphine derivative of 2 (0.15 g, 60%) m.p. 206°C (dec.).

The mass spectrum showed a peak at m/e 854 (P^+) followed by peaks corresponding to $[P-n(CO)]^+$ (n = 1-5). The infrared spectrum (PE 457, C_6H_{12} solution) showed $\nu(CO)$ bands at 2055 (vs), 2005 (s), 1980 (m), 1945 (w) cm^{-1}.

The NMR spectra ($CDCl_3$ solution) showed the following bands: ^1H (p.p.m. downfield from TMS) 7.2-7.6 (multiplet); ^{19}F (p.p.m. upfield from $CFCl_3$) 85.28, 87.60, 92.18, 94.53 (AB quartet, area 2) 102.7, 105.0, 106.4, 108.8 (AB quartet, area 2) 170.8 (area 1) all

peaks are multiplets; ^{31}p (p.p.m. upfield from external 80% H_3PO_4) -71.34; -70.21 (doublet) -11.15, -10.04 (doublet). Anal. Calcd. for $C_{40}H_{25}F_5Fe_2O_5P_2$: C, 56.3; H, 2.95. Found: C, 56.6; H, 3.35%.

ACKNOWLEDGMENTS

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