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GROUP VI METAL CARBONYL PHOTOASSISTED ISOMERIZATION OF OLEFINS

MARK WRIGHTON*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)
GEORGE S. HAMMOND
Division of Natural Sciences, University of California at Santa Cruz, Santa Cruz, California 95064 (U.S.A.)
and HARRY B. GRAY
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109 (U.S.A.)

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Summary

UV irradiation of $M(CO)_6$ (M = Cr, Mo, W) in the presence of excess olefin yields light sensitive metal carbonyl—olefin complexes. Photoinduced rearrangement reactions of the olefin, including both *cis—trans* isomerization and 1,3-hydrogen shifts, take place. In addition, photosubstitution of both CO and the olefin occur in $M(CO)_n(\text{olefin})_{6-n}$ complexes with high quantum efficiency. Olefins investigated include the linear pentenes, linear hexenes, 1,4-pentadiene, 1,4-hexadienes, 1,3-pentadienes, 2,4-hexadienes, stilbenes, and *trans*-$C_2H_2D_2$. Photoassistance activity with respect to olefin isomerization depends on the metal in the order W > Mo ≫ Cr. The evidence indicates that both photo and thermal pathways are of importance in olefin rearrangements of $M(CO)_n(\text{olefin})_{6-n}$.

Introduction

A number of transition metal complexes are known to act as homogeneous catalysts for olefin isomerization [1]. General features of the mechanisms for catalyzed olefin isomerization include (1) the formation of coordinatively unsaturated derivatives from the catalytic species; (2) binding of the olefin; and (3) isomerization of the olefin while it is still in the coordination sphere of the metal. Operation of this kind of mechanism requires that the catalyst be substitution-labile in order to allow initial formation of the reactive, coordinatively

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* Author to whom inquiries should be addressed.

unsaturated intermediate, and then to regenerate it by release of the isomerized olefin. Consequently, species which react very slowly in thermal substitution reactions, such as the low-spin d^6 $M(CO)_6$ (M = Cr, Mo, W) complexes [2], are not expected to exhibit catalytic activity at low temperatures. However, these species do become labile and form mixed olefin—carbonyl complexes $M(CO)_n$-$(olefin)_{6-n}$ when mixtures containing the $M(CO)_6$ complexes and the olefin are irradiated at appropriate wavelengths [3]. We have found that the photosubstitution process is accompanied by isomerization of the olefins [4, 5] and Jennings and Hill have reported that olefin dimerization can be induced under similar conditions using $Cr(CO)_6$ [6]. Photoaccelerated olefin isomerization in the presence of the d^8 complex $Fe(CO)_5$ has been known for some time [3]. Elevated temperatures are required for the (arene)$W(CO)_3$, $M(CO)_6$, and $Fe(CO)_5$ thermally catalyzed [3, 7—9] reactions of olefins while the photoassisted reactions are reported to occur at ambient temperatures. In this paper we report results which provide some clues as to the mechanism of the photoassisted isomerizations.

Results

Ultraviolet irradiation of degassed aliphatic hydrocarbon solutions of $M(CO)_6$ (M = W or Mo) and an olefin results in the formation of olefin derivatives of $M(CO)_6$ and *cis—trans* isomerization and double bond migration in the starting olefin. No examples of skeletal rearrangements have been encountered. The photochemical reactions were carried out at room temperature with a greater than ten-fold excess of olefin compared to $M(CO)_6$. Starting olefins, photoassisting agent, and initial isomerization products are set out in Table 1. Full particulars are developed below.

a. Photoassisted isomerization of trans-$C_2H_2D_2$

The slow conversion of *trans*- to *cis*-1, 2-dideuterioethylene by 366nm photolysis of a solution of $W(CO)_6$ and *trans*-$C_2H_2D_2$ provides an example of olefin isomerization which occurs without the presence of an allylic hydrogen. After short photolysis times, $W(CO)_5$(ethylene) is fomred, as evidenced by IR absorptions [10] at 2085, 1972, and 1954 cm^{-1}. Longer irradiation times lead to *trans*-$W(CO)_4$(ethylene)$_2$, which has a single CO IR absorption [10] at 1964 cm^{-1}. Purging the solution with CO accompanied by UV irradiation leads to regeneration of the $W(CO)_6$. Prolonged irradiation of $W(CO)_6$ + *trans*-$C_2H_2D_2$ yields an uncharacterized, brown precipitate and the loss of activity towards photoisomerization of the ethylene. Interestingly, higher intensity irradiation does not necessarily enhance either the rate or the ultimate percentage conversion. Fast precipitate formation and loss of isomerization activity occurred in cases where extremely high intensity irradiation was employed.

b. Photoassisted interconversion of the linear pentenes

Due to the ease of analysis and ready availability of high purity starting materials, detailed studies have been carried out mainly with the linear pentenes. First, it is to be noted that the other two isomers of the linear pentenes are formed as initial products beginning with any one of the three. A typical

TABLE 1

PHOTOASSISTED ISOMERIZATION REACTIONS

Starting Olefin	Photocatalyst	Initial Product(s)
trans-$C_2H_2D_2$	$W(CO)_6$	*cis*-$C_2H_2D_2$
trans-2-Pentene	$W(CO)_6$	*cis*-2-Pentene, 1-pentene
cis-2-Pentene	$W(CO)_6$	*trans*-2-Pentene, 1-pentene
1-Pentene	$W(CO)_6$ $Mo(CO)_6$	*cis*-2-Pentene, *trans*-2-pentene
1-Hexene	$W(CO)_6$	*cis*-2-Hexene (small), *trans*-2-hexene
cis-3-Hexene	$W(CO)_6$	*trans*-2-Hexene, *trans*-3-hexene, *cis*-2-hexene
trans-3-Hexene	$W(CO)_6$	*trans*-2-Hexene, *cis*-2-hexene, *cis*-3-hexene
1,4-Pentadiene	$W(CO)_6$	*trans*-1,3-Pentadiene, *cis*-1,3-pentadiene
cis-1,4-Hexadiene	$W(CO)_6$	*trans,trans*-2,4-Hexadiene, *cis,trans*-2,4-hexadiene, *cis,cis*-2,4-hexadiene
trans-1,4-Hexadiene	$W(CO)_6$	*trans,trans*-2,4-Hexadiene, *cis,trans*-2,4-hexadiene, *cis,cis*-2,4-hexadiene
trans-1,3-Pentadiene	$W(CO)_6$	*cis*-1,3-Pentadiene
cis-1,3-Pentadiene	$W(CO)_6$ $Mo(CO)_6$	*trans*-1,3-Pentadiene
trans,trans-2,4-Hexadiene	$W(CO)_6$	*cis,cis*-2,4-Hexadiene, *trans,cis*-2,4-hexadiene
cis,trans-2,4-Hexadiene	$W(CO)_6$	*trans,trans*-2,4-Hexadiene, *cis,cis*-2,4-hexadiene
cis,cis-2,4-Hexadiene	$W(CO)_6$	*cis,trans*-2,4-Hexadiene, *trans,trans*-2,4-hexadiene
cis-Stilbene	$W(CO)_6$ $Mo(CO)_6$	*trans*-Stilbene
trans-Stilbene	$W(CO)_6$ $Mo(CO)_6$	*cis*-Stilbene

plot of percentage conversion of 1-pentene to *cis*- and *trans*-2-pentene against irradiation time is shown in Fig. 1. The features to be noted are the tendency for the reaction to start slowly, followed by a period of fast conversion, and finally the slow approach to equilibrium. The same general results were obtained in all systems studied except in most cases it was noted that isomerization activity ceased prior to establishment of an equilibrium mixture of olefins. For the linear pentenes, the equilibrium appears to be near 3% 1-pentene, 17% *cis*-

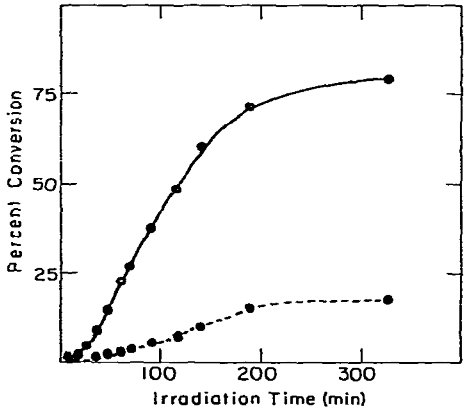


Fig. 1. $W(CO)_6$ photoassisted conversion of 1-pentene to *cis*-2-pentene (————) and *trans*-2-pentene (— — —) at ≈10^{-3} *M* $W(CO)_6$, 5×10^{-2} *M* 1-pentene in degassed isooctane solutions carried out at 366 nm irradiation and 25°.

TABLE 2

$W(CO)_6$ PHOTOASSISTED ISOMERIZATION OF *cis*- and *trans*-2-PENTENE[a]

Starting olefin	Irrdn. time at 313 nm (min)	1-Pentene (%)	*cis*-2 (%)	*trans*-2 (%)
trans-2-Pentene	713	0.28	0.22	99.50
cis-2-Pentene	713	0.07	98.41	1.44
trans-2-Pentene	1436	0.77	0.49	98.74
cis-2-Pentene	1436	0.28	97.28	2.44
trans-2-Pentene	2880	1.51	1.28	97.21
cis-2-Pentene	2880	0.65	93.93	5.42
trans-2-Pentene	7240	1.95	4.58	93.46
cis-2-Pentene	7240	1.23	73.93	24.83

[a] Reaction carried out at 31°; 5.0×10^{-2} *M* in olefin, 2.27×10^{-3} *M* $W(CO)_6$ isooctane solutions irradiated at 313nm in a merry-go-round at $\approx 3 \times 10^{-7}$ ein/min intensity.

-2-pentene, and 80% *trans*-2-pentene, which is approximately the thermodynamic ratio [11]. Table 2 gives percentage conversion starting with *cis*-2-pentene and *trans*-2-pentene under identical conditions. The *cis*-2-pentene appears to be substantially more reactive than the *trans* isomer under these conditions.

Olefin reaction apparently occurs both via photoactivation and thermal activation, as evidenced by the data in Table 3. The absolute number of pentene molecules actually undergoing isomerization in the 3503 min thermolysis is larger than the number of $W(CO)_6$ molecules initially present. *However, no thermal isomerization at 30° is detectable unless the samples are photolyzed. Thus, this system is photocatalytic in the sense that the thermally catalytic species is generated by irradiation.* The data in Table 3 also show that there must be a distinct photochemical process leading to isomerization since the relative rates of production of *cis*- and *trans*-2-pentene are different during the periods of irradiation and the subsequent dark reaction periods.

TABLE 3

PHOTOLYSIS AND THERMOLYSIS OF $W(CO)_6$—1-PENTENE SOLUTIONS[a]

Irrdn. time (min)	Time thermolyzed after photolysis (min)	1-pentene (%)	*trans*-2 (%)	*cis*-2 (%)	(*t*/*c*)
1350	0	96.27	3.22	0.50	6.44
1350	1388	94.67	4.42	0.91	4.90
2744	0	83.74	14.11	2.14	6.64
4226	0	68.85	27.37	3.78	7.31
4233	3503	61.82	31.35	6.83	4.59
7054	0	43.55	48.95	7.60	6.40

[a] Irradiation carried out in a 366nm merry-go-round with $\approx 10^{-3}$ *M* $W(CO)_6$, 5×10^{-2} *M* 1-pentene in isooctane at 30°. Thermolysis was done under identical conditions except samples were protected from the light for the times indicated.

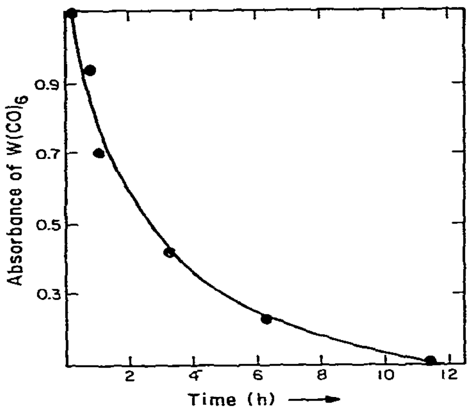


Fig. 2. Disappearance of $W(CO)_6$ upon 366 nm irradiation in the presence of 0.05 *M* 1-pentene at 25°. Absorbance of 1980 cm^{-1} maximum of $W(CO)_6$ is monitored as a function of irradiation time.

The primary photoproduct in every case is undoubtedly $M(CO)_5$(olefin) [4,5]. Evidence that this product competes effectively for the incident irradiation is provided by the observation that the disappearance of $W(CO)_6$ is nonlinear (Fig. 2), even though the remaining concentration is high enough to absorb greater than 99% of the UV light. The $W(CO)_5$(1-pentene) is itself photolabile. Fig. 3 shows the decline of $W(CO)_5$(1-pentene) IR absorption as a function of 313 nm irradiation time. The initial disappearance quantum yield at 313 nm is 0.31 ± 0.05, and is 0.44 ± 0.05 at 366 nm upon irradiation of $W(CO)_5$(1-pentene) in the presence of 2.3 *M* 1-pentene. The disappearance is again nonlinear, evidencing the competition for the incident irradiation by the disubstituted tungsten carbonyl.

The results of an attempt to gain quantitative information regarding light

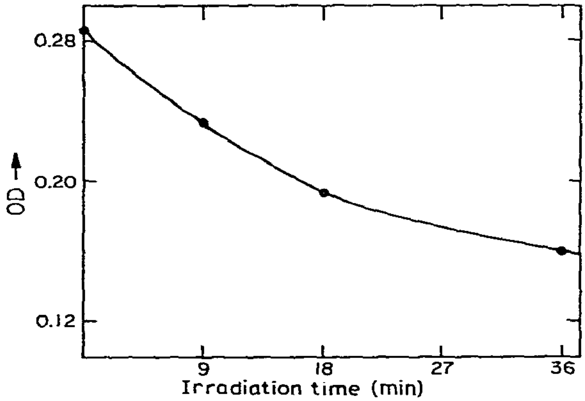


Fig. 3. Disappearance of $W(CO)_5$(1-pentene) as measured by decline in IR absorption upon 313 nm irradiation in the presence of 2.3 *M* 1-pentene at 25°. Quantum yield for diasppearance is 0.31 ± 0.05.

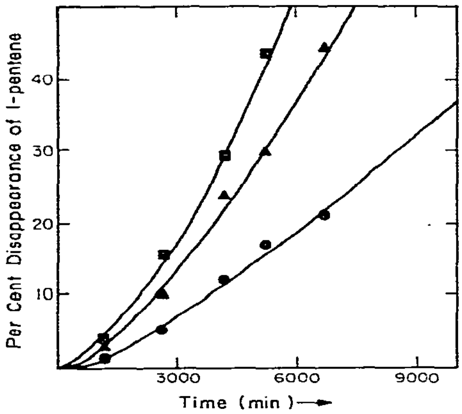
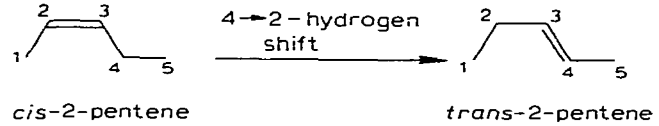


Fig. 4. $W(CO)_6$ photoassisted 1-pentene → 2-pentene conversion at different relative light intensities: 1.0 (●), 2.0 (▲), 3.0 (■). (See Experimental section for details).

intensity effects are shown in Fig. 4. For the range of intensities studied of 1/2/3, conversion of 1-pentene to 2-pentene increases linearly. However, if a sample irradiated at intensity = 1 is exposed three times as long as a sample irradiated at intensity = 3, more isomerization is found, which indicates greater overall quantum efficiency at the lower intensity. This is probably due to the thermal contribution to the rate.

c. Photoassisted interconversion of the linear hexenes

The initial product ratios in the $W(CO)_6$ photoassisted isomerization of some linear hexenes are detailed in Table 4. Several points are to be noted here. First, we find that only products arising from 1,3-hydrogen shifts are found, i.e., there is no direct interconversion of 1-hexenes and the 3-hexenes. Further, the initial product data for the 3-hexenes provide the first conclusive evidence that *cis—trans* isomerization is a competitive reaction without a 1, 3-hydrogen shift. This *cannot* be concluded from the pentene data since a 1, 3-hydrogen shift of one isomer of 2-pentene may yield the other isomer as indicated in eqn.1. Nor is the *trans* → *cis*-dideuterioethylene conversion definitive with respect to the relative importance of *cis—trans* isomerization vs. 1,3-hydrogen shifts.



(1)

Since there appear to be at least two common isomerization products of *cis*- and *trans*-3-hexene and 1-hexene, the initial ratio of these common products could reveal information concerning the active intermediate. The fact that different ratios of *trans*- to *cis*-2-hexene are obtained means that a common intermediate is not involved in the formal 1,3-hydrogen shift that occurs. *In*

TABLE 4

$W(CO)_6$ PHOTOASSISTED ISOMERIZATION OF THE LINEAR HEXENES

Starting olefin	Irrdn. time	Irrdn. λ	% conversion to				
	(min)	(nm)	1-hexene	*t*-2--hexene	*c*-2--hexene	*t*-3--hexene	*c*-3--hexene
1-Hexene	600	366		1.49	[a]	0.00	0.00
	1352	366		3.88	[a]	0.00	0.00
	1900	366		7.31	[a]	0.00	0.00
cis-3-Hexene	3824	313	0.00	1.46	0.96	1.32	
	6152	313	0.00	4.39	2.88	3.29	
	8453	313	0.00	7.92	4.51	4.88	
trans-3-Hexene	3824	313	0.00	11.66	1.74		0.80
	6152	313	0.00	31.13	4.16		1.28
cis-3-Hexene	2433	366	0.000	0.57	1.76	1.06	
	7012	366	0.000	4.93	3.72	3.96	
trans-3-Hexene	2433	366	0.000	7.55	2.03		1.09
	7012	366	0.000	35.47	6.55		2.32

[a] Too small to measure.

a strict sense there appears to be a degree of stereospecificity with *trans*-3-hexene yielding mainly *trans*-2-hexene and *cis*-3-hexene giving a substantial amount of *cis*-2-hexene. Further, it is to be noted here that *trans*-3-hexene is more reactive than *cis*-3-hexene, in contrast to the relative reactivity of *trans*- and *cis*-2-pentene. The ratio of *cis*- to *trans*-2-pentene from 1-pentene is substantially different from that of *cis*- to *trans*-2-hexene obtained from 1-hexene. Finally, the data in Table 4 reveal some modest differences in the ratio of common products of the 3-hexenes, depending on whether 313 nm or 366 nm light is used.

d. $W(CO)_6$ photoassisted hydrogen shifts in 1,4-dienes

The isomerization of 1,4-dienes to yield conjugated 1,3-dienes can be carried out smoothly using $W(CO)_6$ as a photoassistance agent. For 1,4-pentadiene we find that the initial yield of *cis*- to *trans*-1,3-pentadiene is about 1 to 6 using 366 nm excitation. In Table 5 are set out the initial products of the $W(CO)_6$ photoassisted reaction of the isomeric 1,4-hexadienes upon 366 nm excitation.

TABLE 5

$W(CO)_6$ PHOTOASSISTED ISOMERIZATION OF 1,4-HEXADIENES

Starting olefin	Irrdn. time	% conversion to				
	366 nm (min)	*t*, *t*-2, 4-	*c*, *t*-2, 4-	*c*, *c*-2, 4-	*c*-1, 4-	*t*-1, 4-
trans-1,4-Hexadiene	897	4.60	2.29	0.09	0.0	
	1343	5.98	2.93	0.08	0.0	
	2497	9.93	4.81	0.10	0.0	
cis-1,4-Hexadiene	897	0.77	6.38	1.23		0.0
	1343	1.25	8.74	2.18		0.0
	2497	2.43	14.06	3.20		0.0

TABLE 6

$W(CO)_6$ PHOTOASSISTED ISOMERIZATION OF 1,2-DIENES

Starting olefin	Irrdn. time (min)	$\Phi_{313\ nm}$	Product
cis-1,3-Pentadiene	180	0.082	*trans*-1,3-Pentadiene
	460	0.070	
trans,trans-2,4-Hexadiene	175	0.038	*cis,trans*-2,4-Hexadiene
	460	0.026	
	175	0.002	*cis,cis*-2,4-Hexadiene
	460	0.002	
cis,trans-2,4-Hexadiene	175	0.005	*cis,cis*-2,4-Hexadiene
	460	0.010	
	175	0.046	*trans,trans*-2,4-Hexadiene
	460	0.065	
cis,cis-2,4-Hexadiene	175	0.019	*trans,trans*-2,4-Hexadiene
	460	0.019	
	175	0.063	*cis,trans*-2,4-Hexadiene
	460	0.085	

The total lack of interconversion of *trans*- and *cis*-1,4-hexadiene and the fact that 1,3-hexadienes are formed in amounts less than one-tenth that of the 2,4-hexadienes point to considerably diminished reactivity for the internal double bond. Additionally, the lack of a common ratio of 2,4-hexadiene isomeric products shows that there is not a common intermediate leading to conjugation via a 1,3-hydrogen shift. It is attractive from the data available to conclude that the internal double bond is essentially noninteracting. The fact, though, that *trans,trans*-2,4-hexadiene appears to be an initial product from the reaction with *cis*-1,4-hexadiene does not support such a conclusion, unless the *cis*→*trans* isomerization in the four position and the 1,3-hydrogen shift are sequential processes.

e. $M(CO)_6$ *photoassisted cis→trans isomerization of 1,3-dienes*

A preliminary account of the $W(CO)_6$ assisted isomerization of 1,3-dienes has been published [4, 5]. Double bond migration does not accompany the *cis*—*trans* isomerization reactions of the conjugated dienes studied. Table 6 summarizes some quantum yield data for initial isomerization under conditions where initially the $W(CO)_6$ absorbs greater than 99% of the incident 313 nm irradiation. Thus, these figures are minimum values for the actual quantum efficiency of the photoisomerization. The 10^{-2} — 10^{-1} values for the quantum yields are typical for these and the other olefin isomerizations. The significance of the quantum yields is not great because induction periods are observed and no attempt has been made to do a quantitative separation of secondary photochemical isomerization from thermal catalysis by primary or secondary photoproducts.

Some thermal isomerization data are outlined for the 2,4-hexadienes in Table 7. We find that $W(CO)_6$ is far more effective as a thermal isomerization catalyst if the solutions are exposed to UV irradiation prior to the thermolysis.

To test the notion that free 1,3-diene triplet excited states are produced

TABLE 7

EFFECT OF UV IRRADIATION ON THERMAL CATALYTIC ACTIVITY OF $W(CO)_6^a$

Irrdn. ?	Time thermolyzed at 160° (h)	c,c→c,t (%)	c,c→t,t (%)
NO	2	0.00	0.00
NO	41	0.40	1.75
YES	2	3.92	6.00
YES	2	4.12	6.26

[a] Irradiation carried out at 313 nm at room temperature; 2.3×10^{-3} *M* $W(CO)_6$; 0.09 *M* *cis,cis*-2,4-hexadiene in isooctane.

in solution upon irradiation of $W(CO)_n(1,3\text{-diene})_{6-n}$ complexes, we attempted to produce characteristic diene dimers under conditions parallel to those for benzil triplet sensitization [12]. No diene dimers could be detected during photolysis of 0.3 *M* solutions of 2-methyl-1,3-butadiene and 3×10^{-3} *M* $W(CO)_6$, whereas benzil sensitization produced a number of dimers during the same irradiation time. However, irradiation of neat solutions of 2-methyl-1,3-butadiene and $W(CO)_6$ does produce modest yields of as yet uncharacterized dimers; these dimeric species, however, appear to be different from the dimers produced via triplet photosensitization.

f. $M(CO)_6$ photoassisted isomerization of the stilbenes

Several aspects of the $M(CO)_6$ photoassisted isomerization of the stilbenes merit attention [5]. First, we note a substantial difference in the UV—VIS spectral changes which occur upon photolysis of $W(CO)_6$, depending on whether *cis*- or *trans*-stilbene is present (Fig. 5). Secondly, the fact that *cis*-stilbene is formed from *trans*-stilbene unequivocally establishes that electronically excited states can play a key role in these reactions, as the *cis* isomer is present in negligible amounts in a thermodynamic mixture. The stilbenes and the pentenes are

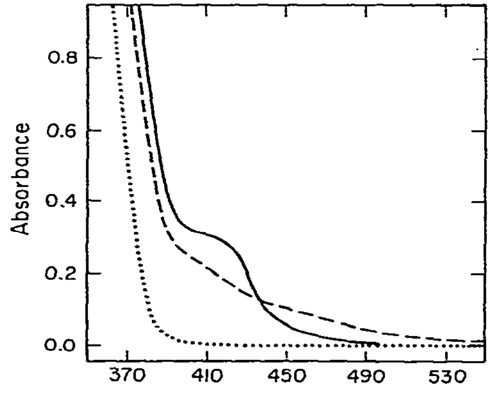


Fig. 5. Initial UV-VIS spectral changes upon 366 nm irradiation of $W(CO)_6$ (. . . .) in the presence of *cis*-stilbene (— — —) and *trans*-stilbene (———).

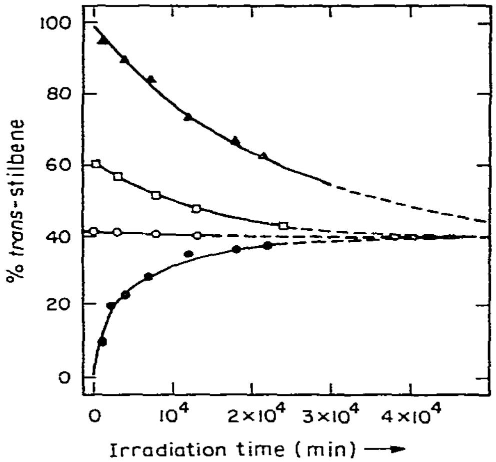


Fig. 6. $W(CO)_6$ photoassisted stilbene interconversion with different initial *trans/cis* stilbene ratios. Total stilbene concentration is ≈0.05 *M*, irradiation is at 366 nm, temperature is 25° and $W(CO)_6$ concentration is $\approx 10^{-3}$ *M*.

the only olefins for which a $M(CO)_6$ photoassisted equilibrium has been achieved. As seen in Fig. 6, *cis*-stilbene is a significant fraction of the mixture at the equilibrium which is attained starting with a solution enriched with either *cis* or *trans*. The stilbenes provide a second example where allylic hydrogens are unnecessary for isomerization to occur.

g. Temperature effect on the $M(CO)_6$ photoassisted isomerization of olefins

We have attempted to obtain quantitative information regarding the temperature dependence. Generally, there is a temperature dependence such that less reaction occurs at lower temperatures. In Fig. 7 we show Arrhenius plots

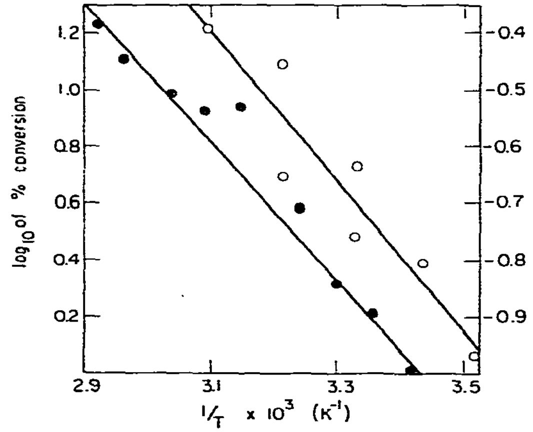


Fig. 7. Arrhenius plots for $W(CO)_6$ photoassisted 1,3-pentadiene (o and right scale) and 1-pentene isomerization (● and left scale).

for the 1-pentene → 2-pentene and the *cis* → *trans*-1,3-pentadiene conversions. The data were obtained on samples that had been irradiated for the same length of time at the same intensity. The activation energy from the plot in Fig. 7 for the $W(CO)_6$ photoassisted 1-pentene isomerization is ≈11.0 kcal/mole. The ratio of *trans*- to *cis*-2-pentene formed changes as a function of temperature, with *cis*-2-pentene becoming substantially more important at the higher temperatures. For example, at 31.6° 0.31% *cis*- and 1.75% *trans*-2-pentene are formed, whereas for the same irradiation time at 66°, 4.92% *cis*- and 8.10% *trans*-2-pentene are produced.

It is to be emphasized that plots such as those in Fig. 7 are likely to be significantly different for different irradiation-thermolysis times since the types of intermediates and the relative importance of thermal vs. photochemical reaction appears to depend on the irradiation time (cf. Table 3). The principal result with the 1,3-dienes and the pentenes is that there is an appreciable temperature effect, consistent with an activation energy of approximately 10 kcal/mole.

h. Thermal olefin exchange in $M(CO)_n(olefin)_{6-n}$ complexes

After isomerization of the coordinated olefin occurs two paths may lead to the appearance of isomerized material in the medium. One of these is a photoexchange process, whereas the second is a thermal path in which coordinated olefin exchanges with excess olefin in the medium. Although no detailed quantitative kinetic studies have been carried out, we find that at room temperature typical $W(CO)_5$(olefin) complexes undergo reaction 2 at a measurable rate. As tungsten complexes are typically the more inert, most especially

$$W(CO)_5(\text{1-pentene}) \xrightarrow[25^\circ]{cis\text{-2-pentene}} W(CO)_5(cis\text{-2-pentene}) + \text{1-pentene} \quad (2)$$

$W(CO)_5$(1-pentene), it follows that any of the olefins listed in Table 1 coordinated to a $M(CO)_5$ group will undergo exchange with excess olefin in the medium.

i. Metal dependence of the photoassisted isomerization

Table 8 shows a comparison of the overall isomerization rates in experiments using $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ as the photoassisting agents. Although essentially all of the incident light is initially absorbed by the $M(CO)_6$ species, the overall rates of isomerization are in the order $W > Mo \gg Cr$ for each case studied. However, in the reaction of 1-pentene, the specific rate of formation of *cis*-2-pentene is higher with molybdenum carbonyl, although the total rate of formation of both isomers is higher in the tungsten system. Chromium carbonyl exhibits no isomerization activity on a comparable time scale.

j. Spectra of complexes

Table 9 records carbonyl stretching frequencies observed in the infrared spectra of the various $W(CO)_5$(olefin) complexes. Definite, if small, changes in the frequencies as a function of the structure of the olefins established in a number of cases that binding to the metal precedes isomerization. Consequently, we *presume* this to be true in all cases.

TABLE 8

EFFECT OF METAL ON PHOTOASSISTED OLEFIN ISOMERIZATION

a. 1-pentene → *cis*-2-pentene + *trans*-2-pentene

Photocatalyst	Irrdn. time (min)[a]	1-pentene (%)	*trans*-2-pentene (%)	*cis*-2-pentene (%)
$Cr(CO)_6$	4042	100.00		
	8600	100.00		
$Mo(CO)_6$	4042	75.81	12.82	11.37
	8600	62.98	19.87	17.15
$W(CO)_6$	4042	66.21	29.53	4.26
	8600	31.36	59.87	8.75

b. cis-stilbene ⇋ *trans*-stilbene

Photocatalyst	Rel. Quantum Yield[b] *trans* → *cis*	*cis* → *trans*
$Cr(CO)_6$	0	—
$Mo(CO)_6$	0.073	0.049
$W(CO)_6$	0.18	1.00

c. cis-1, 3-pentadiene → *trans*-1, 3-pentadiene

Photocatalyst	Irrdn. time (min)[c]	*cis* → *trans* (%)
$Cr(CO)_6$	360	0.00
	820	0.00
$Mo(CO)_6$	360	0.47
	820	0.81
$W(CO)_6$	360	7.52
	820	18.69

[a] Irradiation at 366 nm in a merry-go-round, $\approx 10^{-3}$ *M* $M(CO)_6$, 5×10^{-2} *M* 1-pentene in isooctane.

[b] Irradiation at 366 nm, 5.83×10^{-10} ein/sec.; 1.00 corresponds to observed quantum efficiency of 0.11.

[c] Irradiation at 313 nm in a merry-go-round, $\approx 10^{-3}$ *M* $M(CO)_6$, 4×10^{-2} *M* diene in benzene.

The electronic absorption spectra of the $M(CO)_6$ complexes have already been studied in detail [13, 14]. The lowest energy spin-forbidden and spin-allowed bands have been assigned ${}^1A_{1g} \rightarrow {}^3T_{1g}$ ($t_{2g} \rightarrow e_g$) and ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ($t_{2g} \rightarrow e_g$), respectively. Substitution of CO by a ligand X reduces the symmetry from O_h to at least C_{4v}. For ligands X with a lower ligand field strength than CO, bands arising from ${}^1A_1 \rightarrow {}^3E$ ($e \rightarrow a_1$) and ${}^1A_1 \rightarrow {}^3E$ ($e \rightarrow a_1$) transitions should be at lower energies than the analogous $t_{2g} \rightarrow e_g$ transitions in $M(CO)_6$, as has been found in absorption spectral studies of related $M(CN)_5(X)^{n-}/M(CN)_6^{n-}$ complexes [15, 16]. Since olefins are high in the spectrochemical series, it is not surprising that the UV spectrum of $W(CO)_5$(1-pentene) is little changed from that of $W(CO)_6$ (Fig. 8). Solutions containing the $M(CO)_5$(olefin) complexes are therefore colorless or at most only pale yellow, in sharp contrast to the colors of $M(CO)_5(X)$ (X = oxygen- or nitrogen-donor ligand) solutions, which have maxima in the vicinity of 400 nm [17].

TABLE 9

IR DATA FOR W(CO)$_5$(OLEFIN) COMPLEXES[a]

Olefin	IR bands, cm^{-1} (intensity)		
1-Pentene	2080 (w)	1965 (s)	1952 (s)
cis-2-Pentene	2078 (w)	1958 (s)	1945 (s)
trans-2-Pentene	2078 (w)	1961 (s)	1946.5 (s)
cis-1, 3-Pentadiene	2080 (w)	1967.9 (s)	1950.2 (s)
trans-1, 3-Pentadiene	2080 (w)	1965.5 (s)	1949.0 (s)
70% *trans*-, 30% *cis*-1, 3-pentadiene	2080 (w)	1966.8 (s)	1949.2 (s)
cis-3-Methyl-2-pentene	2076 (w)	1953 (s)	1942 (s)
trans-3-Methyl-2-pentene	2076 (w)	1954 (s)	1941 (s)
cis, cis-2, 4-Hexadiene	2078 (w)	1962 (s)	1947 (s)
cis, trans-2, 4-Hexadiene	2078 (w)	1961 (s)	1946 (s)
trans, trans-2, 4-Hexadiene	2078 (w)	1962 (s)	1946.5 (s)
2-Methyl-butadiene	2080 (w)	1967 (s)	1948 (s)

[a] Pentane or isooctane solutions of the complexes produced by near UV irradiation of W(CO)$_6$ in the presence of the olefin. Maxima are ± 0.5 cm^{-1}.

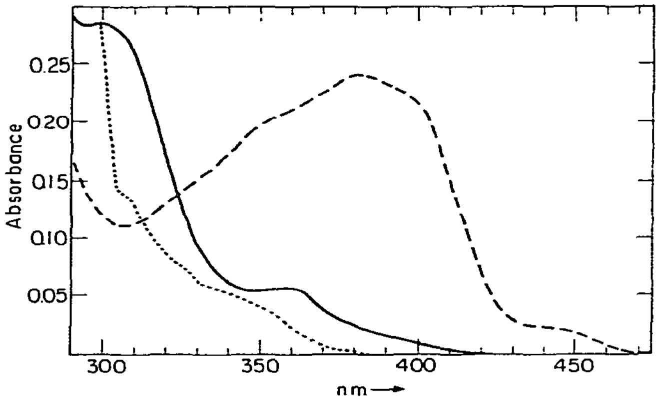


Fig. 8. Electronic absorption spectra of 3.6 × 10^{-5} *M* solutions of W(CO)$_6$ (. . . .), W(CO)$_5$(1-pentene) (———), and W(CO)$_5$(pyridine) (— — —) in isooctane at room temperature in 1.0 cm path length cells.

Discussion

Mechanistic considerations

We have established that the interconversion of olefins can be achieved under mild conditions by irradiation of M(CO)$_6$ solutions containing the olefin. The rate of conversion depends on the central metal, M, the olefin, and the temperature. Evidence points to an interpretation in which both thermal and photo pathways exist for olefin isomerization, after photosubstitution of $M(CO)_6$ to yield $M(CO)_n(\text{olefin})_{6-n}$ complexes.

A general mechanistic scheme must include three features: (i) Formation of the metal carbonyl olefin complexes; (ii) an isomerization path for the coordinated olefin(s), and (iii) appearance of the isomerized olefin as an uncoordinated molecule in the medium. At room temperature step (i) initially only occurs by photolysis (eqns. 3, 4). Step (ii), (eqns. 5, 6) and step (iii),

$$M(CO)_6 \xrightarrow[\text{olefin}]{h\nu} M(CO)_5(\text{olefin}) \tag{3}$$

$$M(CO)_5(\text{olefin}) \xrightarrow[\text{olefin}]{h\nu} M(CO)_4(\text{olefin})_2 \tag{4}$$

$$M(CO)_5(\text{olefin}) \xrightleftharpoons{\Delta \text{ or } h\nu} M(CO)_5(\text{olefin}') \tag{5}$$

$$M(CO)_4(\text{olefin})_2 \xrightleftharpoons{\Delta \text{ or } h\nu} M(CO)_4(\text{olefin}')_2 \tag{6}$$

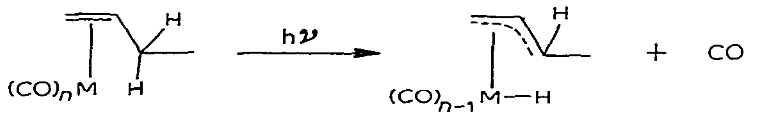
$$M(CO)_5(\text{olefin}') \xrightarrow[\text{olefin}]{\Delta \text{ or } h\nu} M(CO)_5(\text{olefin}) + \text{olefin}' \tag{7}$$

$$M(CO)_4(\text{olefin}')_2 \xrightarrow[\text{olefin}]{\Delta \text{ or } h\nu} M(CO)_4(\text{olefin})_2 + 2\ \text{olefin}' \tag{8}$$

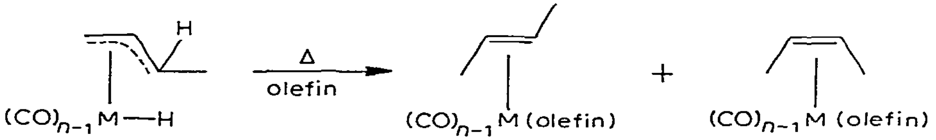
(eqns. 7, 8), could be either thermal or photochemical processes. In the equations, where olefin′ represents an isomerized olefin, we present only the proseses for mono- and disubstituted complexes, although similar reactions probably occur for the more highly substituted carbonyls.

Photosubstitution of the CO and olefins coordinated to the central metals Cr^0, Mo^0, and W^0 is consistent with the changes in bonding that result upon one electron excitation to produce low lying LF excited states [18]. Simultaneous population of $d\sigma^*$ and depopulation of $d\pi$ bonding orbitals should especially enhance the labilities of π-acceptor ligands such as olefins and CO, as we have found. Thermal exchange of olefins does occur and this may account, in part, for the temperature effect found for the 1-pentene and 1, 3-pentadiene photoassisted isomerizations. The activation energies in these cases are not very different from the 7.0 kcal/mole value obtained [19] for acetone dissociation from $W(CO)_5$(acetone).

We now focus on the key step of olefin isomerization. Study [1] of homogeneous catalytic reactions (olefin isomerization, hydrogenation, hydroformylation, ect.) in recent years has led to the assignment of key roles to coordinatively unsaturated intermediates in such processes. Tetracarbonyl monoolefin complexes would be likely candidates in our systems. Equations 9 and 10 represent a possible pathway for photoassisted 1, 3-hydrogen shifts. We observed that thermal dissociation of CO does not occur readily from $W(CO)_5$(olefin), but once the disubstituted olefin complex is formed the generation of the coordinatively unsaturated intermediate can occur readily by thermal or photochemical olefin dissociation. A similar scheme can account for the $Fe(CO)_5$ photoassisted hydrogen shift reactions [3]. Assuming that the π-allyl systems can maintain some stereochemical integrity, such intermediates adequately account

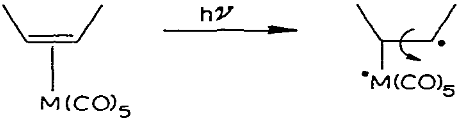


(9)



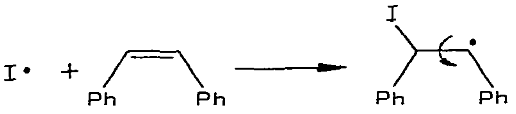
(10)

for dissimilar *trans*/*cis*-2-hexene product ratios from the isomeric 3-hexenes. However, if the isomeric integrity of the π-allyl system does remain intact, a second intermediate must be invoked to account for *cis-trans* isomerization. The fact that both stilbenes and *trans*-$C_2H_2D_2$, which do not possess allylic hydrogens, undergo photoassisted isomerization implicates intermediates having M—olefin σ bonds. One-electron excitation in $M(CO)_5$(olefin) may lead to the rearrangement outlined in eqn. 11. The formation of the σ-bonded olefin may be viewed as a reaction of electronically excited C_{4v} $M(CO)_5$ with an olefin.



(11)

Excited states of $M(CO)_5$ derived from the configuration $e^3b_2^2a_1^1$ should have some reactivity properties in common with ground-state $Co(CN)_5^{3-}$ [$^2A_1$ ($e^4b_2^2a_1^1$)] [20], as both feature a strongly σ antibonding (d_{z^2}) electron. Radical-like reactions of $Co(CN)_5^{3-}$ are well known [21] and include addition to acetylene [22] and other olefins [23]. We may also draw analogy to reversible addition of free radicals to olefins [24], (eqns. 12, 13). It is obvious that an intermediate similar to that in eqn. 11 can account for *cis—trans* isomerization. Further, it could also account for 1, 3-hydrogen shifts if enough activation energy is supplied to yield the most stable organic radical. For example, reaction 14 may occur thermally. It is also to be noted that M—C σ bond formation has been proposed for $Fe(CO)_5$ photoassisted olefin isomerization [3].



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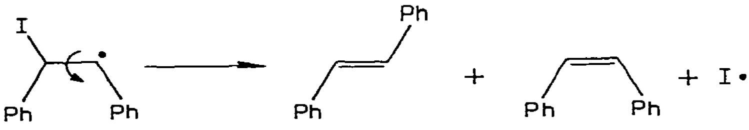
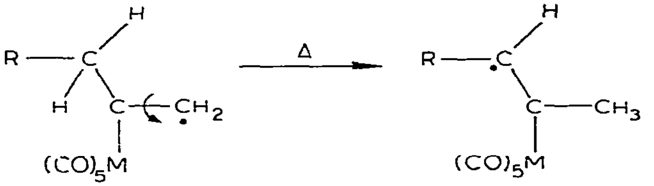


(13)



(14)

There is a third possibility for the stilbene isomerization. Excitation of $M(CO)_5$(stilbene) may yield a ligand-localized (stilbene-like) excited state. Such an intermediate is consisten with the fact that a nonthermodynamic mixture can be obtained in this case. Similar decay paths are thought to be important in the *N*-bonded 2- and 4-styrylpyridines [25]. The likelihood of this "electronic energy migration" mechanism may be enhanced if the interaction of the central metal is with the arene ring. Complexes such as $W(CO)_5$(benzene) are known [26] and a difference in bonding between $W(CO)_5$(*trans*-stilbene) and $W(CO)_5$(alkene) may be inferred from differences in electronic spectra (Figs. 5 and 8). The electronic energy migration mechanism is not likely for the alkenes for two reasons: (1) the lowest intraligand excited state in a simple alkene (>80 kcal/mol) [27] is well above the lowest electronic excited state of the complex, and (2) for the linear pentenes the equilibrium mixture is found to be close to the thermodynamic mixture. The 1, 3-dienes have lowest triplet excited states at about 55 kcal/mol [27] which may be below the lowest LF transitions in the complexes. Unfortunately, we have been unable to achieve equilibration for the 1, 3-dienes.

Structure—reactivity relationships

The most consisten correlation exists between the central metal and isomerization activity. It is found (Table 8) that catalytic activity follows the order W > Mo ≫ Cr. Thus, increasing activity parallels, at least qualitatively, increasing metal carbonyl—olefin complex stability. If we associate stronger binding with larger pertubation of the olefin, it is clear that greater reactivity is expected for the tungsten compounds. The binding strength is likely to be important in another sense, as electronic excited states of $M(CO)_5$(olefin) can decay nonradiatively to give either ligand substitution or the isomerization intermediate. Thus, except in the cases where the ground state substitution rates are slow, electronic excitation may yield absolute rates for substitution which overwhelm decay rates to the isomerization intermediate [18]. Finally, and in this regard, we point out that little or no $W(CO)_6$ photoassisted reaction of *cis*- and *trans*-3-methyl-2-pentene could be detected, although metal complexes are formed. Here the very low reactivity may reflect the relatively small binding interaction of these olefins with tungsten, which is expected since three alkyl substituents are adjacent to the double bond [19].

Apart from the fact that we expect less reactivity with more highly substituted double bonds, little conclusive evidence is available regarding the relationship of reactivity and olefin structure. We have found empirically that the linear pentenes and the stilbenes are the most well behaved of the olefins studied in the sense that both overall yields and conversion rates are good. Isomerization activity is generally good at the outset but ceases prior to complete equilibration, and is accompanied by disappearance of all metal carbonyl species. In such cases a higher olefin concentration may be necessary to prevent formation of substantial amounts of coordinatively unsaturated complexes. Acquiring detailed information regarding structure—reactivity relationships has been inhibited by our lack of knowledge concerning the species actually absorbing light to produce the isomerization intermediate, the nature of such an intermediate, and the relative importance of producing the intermediate via thermal activation. Experiments directed towards clarification of these points are in progress.

Experimental

Chemicals

All alkenes and dienes except *trans*-$C_2H_2D_2$ were obtained from Chemical Samples Co., Columbus, Ohio. The samples were used without further purification. The *trans*-$C_2H_2D_2$ was obtained from Merck Sharp & Dohme of Canada, Ltd., Montreal, Canada. *trans*-Stilbene was purchased from Matheson, Coleman and Bell and the *cis*-isomer was obtained by the benzil-sensitized isomerization of the *trans*-followed by chromatography on alumina (eluting with pentane). Isooctane and n-pentane were spectroquality, obtained from Matheson, Coleman and Bell.

Analyses

Quantitative analyses for *trans*- and *cis*-1, 3-pentadiene, 1-pentene, *cis*- and *trans*-2-pentene, 1, 4-pentadiene, *cis*- and *trans*-1, 4-hexadiene, *cis,cis*-; *trans,cis*-; and *trans,trans*-2, 4-hexadiene, were carried out using a Hewlett—Packard Model 700 gas chromatograph with a flame ionization detector and a recorder equipped with a Disc integrator. A 25′ × 1/8″, 25% β, β'-ODPN column was used, at oven temperatures less than 50°. The isomeric linear hexenes were analyzed using the same GC, except a 20′ × 1/8″ $AgNO_3$ column was employed at room temperature. The stilbenes were analyzed using the GC with a 6′ × 1/8″ 10% UCW-98 column at 180°. Qualitative analysis of *trans*- and *cis*-$C_2H_2D_2$ was by infrared spectroscopy [28]. A Perkin—Elmer 225 Grating spectrometer was used for all IR measurements. Either a Cary 14 or 17 spectrophotometer was used for UV—VIS absorption measurements.

Irradiations

Irradiations were carried out at either 313 or 366 nm in a merry-go-round [29] equipped with a 450 W medium pressure Hanovia Hg lamp and appropriate filters to isolate the desired lines. Both intensity and temperature effects were studied using a modified merry-go-round system. Relative 1/2/3 intensity was achieved by having 3 separate holes for the light for each sample, and either 2, 1 or none of the holes were covered with black tape to achieve the desired intensity. Care was taken to ensure that the light intensity passing through each of the holes was the same. Temperature variation was achieved using a Forma Scientific constant temperature circulating bath.

Typical procedure

Samples (2.5 or 3.0 ml) of either an isooctane or pentane solution of 0.01—0.1 *M* olefin and 10^{-4}—10^{-2} *M* $M(CO)_6$ were placed in 13 × 100 mm test tubes with constrictions. The samples were freeze—pump—thaw degassed three times and hermetically sealed at the constriction. The samples were then irradiated in the merry-go-round for the desired period and analyzed by GC.

High temperature thermolysis procedure

Small (≈ 0.5 ml) samples of the olefin and $M(CO)_6$ in isooctane were degassed in 3 mm ampules and hermetically sealed. The ampules were then placed directly into an oil bath at 160°. One should exercise caution in this procedure: One sample with a small leak exploded.

Photolysis of trans-$C_2H_2D_2$

The photolysis of $M(CO)_6$, *trans*-$C_2H_2D_2$ solutions was carried out using a gas IR cell attached to a test tube containing the isooctane solution of $M(CO)_6$. The *trans*-$C_2H_2D_2$ was condensed with liquid nitrogen into the evacuated cell assembly on a vacuum line. IR analysis of the $C_2H_2D_2$ above the solution of $M(CO)_6$—*trans*-$C_2H_2D_2$ revealed *trans*→*cis* conversion upon irradiation of the $M(CO)_6$ at 366 nm.

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References

1 F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed., Interscience, New York, 1972, pp. 785—799.
2 Organic Synthesis via Metal Carbonyls, Vol. I, I. Wender and P. Pino (Ed.), Wiley, New York, 1968.
3 E. Koerner von Gustorf and F.-W. Grevels, Fortschr. Chem. Forsch., 13 (1969) 366.
4 M. Wrighton, G.S. Hammond and H.B. Gray, J. Amer. Chem. Soc., 92 (1970) 6068.
5 M. Wrighton, G.S. Hammond and H.B. Gray, J. Amer. Chem. Soc., 93 (1971) 3285.
6 W. Jennings and B. Hill, J. Amer. Chem. Soc. 92 (1970) 3199.
7 G.S. Lewandos and R. Pettit, J. Amer. Chem. Soc., 93 (1971) 7087.
8 G.J. Leigh and E.O. Fischer, J. Organometal. Chem., 4 (1965) 461.
9 E.O. Fischer and H.P. Fritz, Angew. Chem., 73 (1961) 353.
10 I.W. Stolz, G.R. Dobson and R.K. Sheline, Inorg. Chem., 2 (1962) 1264.
11 C. Moussebois and J. Dale, J. Chem. Soc. C, (1966) 260.
12 R.S.H. Liu, N.J. Turro and G.S. Hammond, J. Amer. Chem. Soc., 87 (1965) 3406.
13 H.B. Gray and N.A. Beach, J. Amer. Chem. Soc. 85 (1963) 2922.
14 N.A. Beach and H.B. Gray, J. Amer. Chem. Soc. 90 (1968) 5713.
15 D.F. Gutterman and H.B. Gray, J. Amer. Chem. Soc., 93 (1971) 3364.
16 (a) V. Miskowski and H.B. Gray, to be submitted for publication;
(b) G. Geoffroy, M. Wrighton, G.S. Hammond and H.B. Gray, Inorg. Chem., 13 (1974) 430.
17 M. Wrighton, G.S. Hammond and H.B. Gray, J. Amer. Chem. Soc., 93 (1971) 4336.
18 M. Wrighton, H.B. Gray and G.S. Hammond, Mol. Photochem., 5 (1973) 165.
19 M. Wrighton, G.S. Hammond and H.B. Gray, J. Amer. Chem. Soc., 93 (1971) 6048.
20 F.D. Tsay, H.B. Gray and J. Danon, J. Chem. Phys., 54 (1971) 3760.
21 J. Halpern, Accounts Chem. Res., 3 (1970) 386.

22 W.P. Griffith and G. Wilkinson, J. Chem. Soc., (1959) 1629.
23 M.E. Kimball, J.P. Martella and W.C. Kaska, Inorg. Chem., 6 (1967) 414.
24 (a) C. Moussebois and J. Dale, J. Chem. Soc. C, (1966) 264;
(b) M.H. Back and R.J. Coetanovic, Can. J. Chem., 41 (1963) 1396 and 1406;
(c) M.D. Carr, V.V. Kane and M.C. Whiting, Proc. Chem. Soc., (1964) 408.
25 M. Wrighton, G.S. Hammond and H.B. Gray, Mol. Photochem., 5 (1973) 179.
26 I.W. Stolz, H. Haas and R.K. Sheline, J. Amer. Chem. Soc., 87 (1965) 716.
27 (a) S. Sato, Pure Appl. Chem., 16 (1968) 87;
(b) N.J. Turro, Molecular Photochemistry, W.A. Benjamin, New York, 1967.
28 B.L. Crawford, Jr., J.E. Lancaster and R.G. Inskeep, J. Chem. Phys., 21 (1953) 678.
29 F.G. Moses, R.S.H. Liu and B.M. Monroe, Mol Photochem., 1 (1969) 245.