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PHOTOCHEMICALLY INDUCED REACTIONS OF $Ph_2C{=}W(CO)_5$ AND $Ph_2C{=}Mn(CO)_2Cp$

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Summary

The photo-induced degradation of $Ph_2C{=}W(CO)_5$ in n-hexane solution has been investigated, and found to produce tungsten hexacarbonyl and tetraphenylethylene, as well as products of hydrogen abstraction, diphenylmethane and 1,1,2,2-tetraphenylethane. Yields of the organic products are dependent on the concentration of $Ph_2C{=}W(CO)_5$, the olefin being favored in more concentrated solution. Similar products and trends were found when $Ph_2C{=}W(CO)_5$ was thermally degraded in n-heptane. Ligand transfer of the diphenylcarbene ligand was achieved by photolyzing $Ph_2C{=}W(CO)_5$ in diethyl fumarate, which produced diethyl 3,3-diphenyl-1,2-cyclopropanedicarboxylate, and via a thermal reaction of $Ph_2C{=}W(CO)_5$ with $CpMn(CO)_2(THF)$, which produced $Ph_2C{=}Mn(CO)_2Cp$. Photolysis of the latter carbene complex in n-hexane produced the same organic products as those obtained from the photolysis of $Ph_2C{=}W(CO)_5$.

Introduction

Since the synthesis of the first transition metal carbene complex by Fischer and Maasböl in 1964 [1], a myriad of new carbene complexes has been prepared. The nature of the novel metal—carbon bond in these complexes has been the subject of extensive investigations in recent years [2]. Reactions leading to transformations of the carbene ligand do not appear to go through a free carbene intermediate, but rather through the complexed ligand. In the middle transition metal series of carbene complexes, this behavior has been attributed to the electrophilic nature of the carbene carbon. Thermal reactions with nucleophiles capable of substitution take place in which the carbene carbon atom is preferentially attacked, rather than by substitution at the metal. MO calculations predict the LUMO to be mostly centered on the carbene carbon, and have been used to explain the site of attack [3]. There is also experimental evidence in favor of this prediction [4].

In contrast to the extensive chemical reactions of transition metal carbene complexes promoted by thermal means, photochemically induced reactions of this series of organometallic compounds have received surprisingly little attention [5—8]. As part of our current studies on organometallic photochemistry, and in order to further understand the nature and reactivity of the carbene ligand, we chose to investigate the photochemical reactivity of $Ph_2C{=}W(CO)_5$ (I) [9], since no photochemical information is presently available on this system. For comparison, we have also reinvestigated the thermolysis of I [9] and the photolysis of $Ph_2C{=}Mn(CO)_2Cp$ (VI) [7] in hydrocarbon solvents.

Results and discussion

Photolysis of I in n-hexane solution led to the formation of diphenylmethane (II), tetraphenylethylene (III), 1,1,2,2-tetraphenylethane (IV) and tungsten hexacarbonyl (V) as the principal products (eq. 1).

$$\underset{\text{(I)}}{Ph_2C{=}W(CO)_5} \xrightarrow[\text{n-hexane}]{h\nu} \underset{\text{(II)}}{Ph_2CH_2} + \underset{\text{(III)}}{Ph_2C{=}CPh_2} + \underset{\text{(IV)}}{Ph_2CHCHPh_2} + \underset{\text{(V)}}{W(CO)_6} \qquad (1)$$

The yields of the organic products were found to be dependent on the concentration of I (Table 1). As in the concentration of I decreased, the yield of olefin III decreased, whereas the yield of the hydrogen abstraction product II increased. A reinvestigation of the thermolysis of I in n-heptane revealed that in addition to the products previously reported, namely, II, III and V, the hydrogen abstraction product IV was also produced. The ratios of the products were again found to be dependent on the concentration of I, showing somewhat similar trends as the photolyses studies (Table 2). Interestingly, photolysis of I in cyclohexene produced only trace amounts of III (Table 1). When I was thermolyzed in this same solvent, the reported yield of III was also substantially decreased relative to a reaction run in heptane (Table 2).

Hoberg and Korff found that these same organic products were formed from the thermal decomposition of the nickel-ketene complex $(Ph_3P)_2Ni(Ph_2C{=}C{=}O)$ [10]. They postulated the formulation of a diphenylcarbene intermediate, which may have been complexed to the nickel, for the production of II, III and IV.

Tetraphenylethylene (III) is not a characteristic product of free diphenylcarbene generated under the reaction conditions employed [11] *. The olefin III produced in the present study may therefore be the result of a bimolecular reaction involving the decomposition of the carbene complex I, while the hydrogen abstraction produts could result from a unimolecular decomposition. The former process would be favored under more concentrated conditions, with the latter pathway predominating under more dilute solutions, in agreement with the above findings.

In the thermal decomposition of $(CO)_5Cr{=}\overline{CCH_2CH_2CH_2O}$ to produce 2-oxacyclopentylidene dimer, Casey has proposed a mechanism involving the forma-

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* Tetraphenylethylene is, however, produced from diphenyldiazomethane under flash photolysis conditions in benzene solution [12] or by laser-induced reactions [13].

TABLE 1

PHOTOLYSIS OF $Ph_2C{=}W(CO)_5$ IN HYDROCARBON SOLVENTS

Concentration of $Ph_2C{=}W(CO)_5$ (I) ($\times 10^{-3}$ *M*)	Photolysis products (% yield)			
	Ph_2CH_2 (II)	$Ph_2C{=}CPh_2$ (III)	$Ph_2CHCHPh_2$ (IV)	$W(CO)_6$ (V)
28.6 [a]	14	13	25	23
8.62 [a]	21	1.4	24	26
0.271 [a]	37	1	12	24
2.68 [b]	10	Trace	37	22

[a] In n-hexane. [b] In cyclohexene.

tion of a coordinatively unsaturated tetracarbonyl species which reacts with starting material to form a biscarbene intermediate [2e]. A similar bimolecular process may also be occurring in the formation of III from I under photochemical conditions. However, while loss of CO upon irradiation of I may undoubtedly occur, the mechanistic role of any resulting coordinatively unsaturated species in the formation of products II, III and IV cannot be fully elucidated at present, since photolysis of I under a CO atmosphere (up to 2.5 atm) does not substantially inhibit the photodecomposition reaction relative to photolysis of I under N_2.

The formation of II and IV may result from a unimolecular decomposition of I, generating a diphenylmethyl radical via hydrogen abstraction from the solvent. The radical thus produced could either react further with solvent to form II or dimerize to give IV. Such a radical has previously been detected by Wright and Vogler [7] in the photolysis of VI; however, they did not characterize the reaction products. We have now been able to demonstrate that photolysis of VI in n-hexane does indeed produce the hydrogen abstraction products II and IV, as well as the olefin III.

In order to further study the chemistry of I, the carbene complex was irradiated in diethyl fumarate. This reaction led to the formation of diethyl 3,3-diphenyl-1,2-cyclopropanedicarboxylate (VII) as the major product, showing that the diphenylcarbene ligand can be transferred photochemically to an

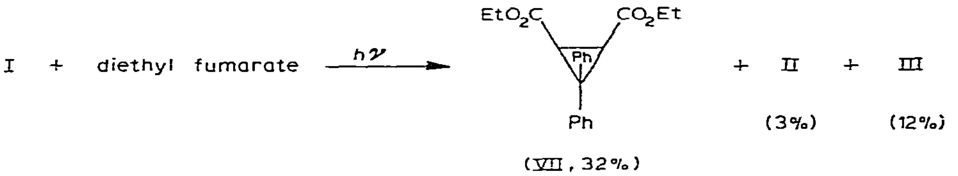
TABLE 2

THERMOLYSIS OF $Ph_2C{=}W(CO)_5$ IN HYDROCARBON SOLVENTS

Concentration of $Ph_2C{=}W(CO)_5$ (I) ($\times 10^{-3}$ *M*)	Thermolysis products (% yield)			
	Ph_2CH_2 (II)	$Ph_2C{=}CPh_2$ (III)	$Ph_2CHCHPh_2$ (IV)	$W(CO)_6$ (V)
28.8 [a]	23	26	7	22
8.66 [a]	19	3	22	23
29.8 [b]	10	35	— [c]	19
— [c,d]	30	13	— [c]	— [c]

[a] In heptane. [b] In heptane; values reported by Casey et al. [9b]. [c] Not reported. [d] In cyclohexene; values reported by Casey et al. [9a].

olefin (eq. 2). Thermal transfer of carbene ligands to olefins has previously been demonstrated [14].



(2)

In addition, thermolysis of I in THF solution in the presence of $CpMn(CO)_2$-(THF) produced VI, which is stable under the reaction conditions employed (eq. 3). This result demonstrates that the diphenylcarbene ligand can likewise

$$I + CpMn(CO)_2(THF) \xrightarrow[35^\circ C]{THF} Ph_2C{=}Mn(CO)_2Cp \quad (3)$$
$$(VI, 49\%)$$

be transferred to another metal. Similar metal-to-metal carbene transfer reactions have previously been reported, but only involving heteroatom-stabilized organometallic carbenes [6,15]. Further studies involving photochemically induced reactions of metal-carbene complexes are in progress in our laboratory.

Experimental

All photolyses were carried out under nitrogen using quartz Schlenk tubes cooled in a water bath and a Hanovia 450 W medium pressure Hg lamp. n-Hexane, n-heptane and cyclohexene were purified by distillation from calcium hydride under nitrogen; diethyl fumarate was vacuum distilled under nitrogen. The reactions were monitored by IR analysis and terminated when the carbonyl absorptions of the starting material were no longer present. Diphenylmethane (II), tetraphenylethylene (III), 1,1,2,2-tetraphenylethane (IV), and diethyl 3,3-diphenyl-1,2-cyclopropanedicarboxylate (VII) were identified by TLC and GLC comparison with authentic samples, and were quantitated using the method of standard addition. A Varian Series 2400 gas chromatograph equipped with a 1.5% OV-101 on Chromosorb W AW/DMS column (5′ × 1/8″) and a FID detector was used for GLC analysis. Separation was achieved by temperature programming at 8°C/min from 160—200°C, and at 4°/min from 200—250°C. IR spectra were recorded on a Beckmann IR-10 spectrophotometer. $Ph_2C{=}W(CO)_5$ (I) [9] and $Ph_2C{=}Mn(CO)_2Cp$ (VI) [8] were prepared by literature methods.

Photolysis of I in hexane

All photolyses were conducted in a similar manner, except for changes in concentration (Table 1). In a typical experiment, 84.5 mg (0.172 mmol) of I were dissolved under nitrogen in 20 ml of hexane (8.62×10^{-3} *M* solution) in a quartz Schlenk tube and photolyzed while stirring for 24 h at 10°C. The initially deep red solution turned a brownish color with the formation of a dark precipitate. The mixture was filtered through a glass frit under nitrogen, and the solvent removed via a water aspirator. The residue was dissolved in 3 ml of methylene chloride and by GLC analysis found to contain 6.2 mg (21%) of II, 0.4 mg (1.4%) of III, and 6.8 mg (24%) of IV. Evaporation of the solvent and sublimation of the residue produced 16 mg (26%) of $W(CO)_6$ (V).

In another set of experiments, two pressure-type Schlenk tubes each containing identical concentrations of I (ca. 9.5×10^{-3} *M*) were photolyzed as above, one under a N_2 atmosphere and the other under a CO atmosphere. The photolyses were carried out at 1 atm pressure and also at 2.5 atm pressure in each case. The disappearance of starting material I was followed by monitoring the CO stretching frequency at 2070 cm^{-1} in the IR spectrum. The changes in absorbance were virtually the same as a function of time for photolyses conducted under either a N_2 or CO atmosphere at a given pressure. The ratios of the organic products formed were also the same for photolyses carried out under either a N_2 or a CO atmosphere, as determined by GLC analyses of the reaction mixtures. The amount of V formed, however, was not the same. Thus, under one atmosphere N_2, 27% of V was produced, whereas under one atmosphere CO, V was formed in 52% yield.

Photolysis of I in cyclohexene

In a quartz Schlenk tube, 131.1 mg (0.163 mmol) of I were dissolved in 100 ml of cyclohexene (2.68×10^{-3} *M*), and the solution was photolyzed at 15°C for 48 h. The reaction mixture was worked up as above to yield 4.5 mg (10%) of II, 16.6 mg (37%) of IV, and 21 mg (22%) of V. Only trace amounts of III could be detected.

Thermolysis of I in heptane

The thermolyses were carried out in a similar manner except for the concentration of I. In a typical experiment, 84.9 mg of I (0.173 mmol) were dissolved under nitrogen in 20 ml of heptane (8.66×10^{-3} *M*) in a 3-neck, round-bottom flask equipped with a reflux condenser, gas inlet and outlet valves, and a Hg overpressure valve. The solution was refluxed for 6 h and worked up as above to yield 5.5 mg (19%) of II, 1.8 mg (3%) of III, 6.4 mg (22%) of IV, and 14 mg (23%) of V.

Photolysis of VI in hexane

In 200 ml of hexane, 179.3 mg (0.553 mmol, 2.76×10^{-3} *M*) of VI were dissolved and the solution photolyzed for 4 h at 15°C. The initially green solution turned red with the formation of a brown precipitate. Workup as in the photolysis of I and GLC analysis indicated that 2.3 mg (3%) of II, 13.4 mg (15%) of III, and 8.6 mg (10%) of IV were produced.

Photolysis of I in diethyl fumarate

In a quartz Schlenk tube, 80.0 mg (0.163 mmol) of I were dissolved in 15 ml of diethyl fumarate and the solution was photolyzed for 48 h at 10°C. The diethyl fumarate was removed by vacuum distillation at 40°C. The residue was dissolved in 15 ml of methylene chloride, the extract was filtered through a frit under nitrogen, and concentrated to ca. 3 ml. By GLC analysis, the solution was found to contain 0.8 mg (3%) of II, 3.2 mg (12%) of IV, and 17.6 mg (32%) of diethyl 3,3-diphenyl-1,2-cyclopropanedicarboxylate (VII):

Thermolysis of I in the presence of $CpMn(CO)_2(THF)$

$CpMn(CO)_2(THF)$ was produced in the usual manner by photolyzing 19.2 mg (0.0941 mmol) of $CpMn(CO)_3$ in 20 ml of THF in a quartz Schlenk tube for 3 h. To this solution were added 46.0 mg (0.0939 mmol) of I dissolved in 10 ml of THF. The resulting mixture was stirred at 35° C for 5 h, during which time the solution turned from red to a light greenish yellow. The solvent was evaporated via a water aspirator, and the residue was extracted with 10 ml of hexane and placed on an alumina column (1.25 × 25 cm, 100—200 mesh, 5% deactivated with H_2O) under nitrogen. Elution with hexane produced a green band which was subsequently eluted with 10/1 hexane/ether. Removal of the solvent yielded 14.3 mg (49%) of VI, which was identified by IR and MS comparisons with an authentic sample.

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