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PHOTOCHEMICAL AND THERMAL REACTIONS OF IRON PENTACARBONYL WITH DIMETHYLDIACETYLENE (DMDA): SPECTRAL CHARACTERIZATION OF REACTION COMPLEXES

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Summary

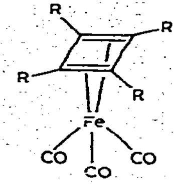
A series of photochemical and thermal reactions has been carried out with iron pentacarbonyl and the conjugated alkadiyne, dimethyldiacetylene (DMDA). One product, (DMDA)$Fe(CO)_6$, was prepared directly from starting materials in tetrahydrofuran under photochemical conditions. Previously, analogs of this complex had been prepared only under thermal conditions from complex intermediates. An X-ray analysis has established the structure of this complex; ^{13}C NMR and other spectral data reported here are in agreement. Under thermal conditions in xylene, three isomeric forms of a tricarbonylferroleiron tricarbonyl, $(DMDA)_2Fe_2(CO)_6$, complex were prepared. Separation and purification of two of these isomers was achieved; selected spectral data are reported. Infrared and mass spectra are also reported for the complex $(DMDA)_2Fe(CO)_4$, resulting from the photochemical reaction of starting materials in cyclohexane.

Introduction

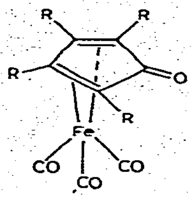
The reactions of iron carbonyls with alkynes and substituted alkynes result in a variety of products [1,2]. It has been noted that in many cases, the complexes formed are of three main types: *(1)* $(alkyne)_2Fe(CO)_3$, a cyclobutadieneiron tricarbonyl derivative (I); *(2)* $(alkyne)_2COFe(CO)_3$, a cyclopentadienoneiron tricarbonyl derivative (II); and *(3)* $(alkyne)_2Fe_2(CO)_6$, a tricarbonylferroleiron tricarbonyl derivative (III) [3]. These products are the result of cyclopolymerization and cyclopolymerization—insertion reactions.

Work has also been done with the reactions of iron carbonyls and alkadiyne compounds, both conjugated and non-conjugated [3—5]. In many cases the complexes formed are analogs of those formed in similar reactions with monoacetylenes.

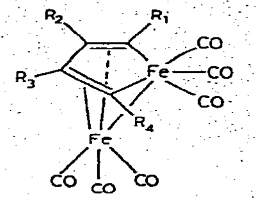
Some photochemical work has been done with iron carbonyls and diphenyl-



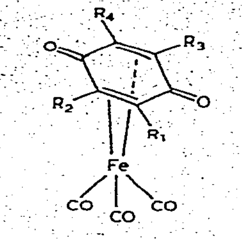
(I)



(II)



(III)



(IV) a, $R_1 = R_2 = R_3 = R_4 = CH_3$
b, $R_1 = R_3 = CH_3$; $R_2 = R_4 = C{\equiv}CCH_3$

acetylene yielding products of the types I—III [6,7]. Dimethyacetylene (DMA) and iron pentacarbonyl are known to react in sunlight to form duroquinoneiron tricarbonyl (IVa) [8]. A preliminary communication [9] reports our photochemical work with dimethyldiacetylene (DMDA) and $Fe(CO)_5$. No other photochemical work has been reported for the alkadiynes.

Results and discussion

Photochemical reactions

(DMDA)Fe(CO)$_6$ (V). (DMDA)$Fe(CO)_6$ was isolated from the reaction of $Fe(CO)_5$ with dimethyldiacetylene (DMDA) in THF under ultraviolet irradiation. The complex was the only one isolated from the reaction. It is air stable in the solid state over several weeks time. In solution it is stable for one to two days at room temperature and for about a week at —10°C.

Recent X-ray work on this complex has determined its structure to be V, see Table 1. [10]. Results of this analysis show six carbon atoms coordinated to the iron atom in approximately an octahedral arrangement. The axial carbonyl carbon atoms make an angle of 166° with the iron atom as vertex and tilt toward the ferrole ring. The ferrole ring is planar and all bond distances are in good agreement with accepted values. Detailed results are reported elsewhere [10].

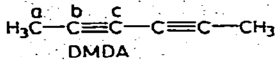
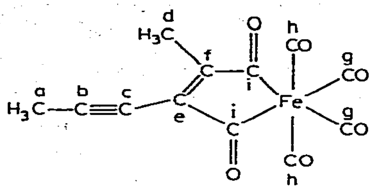
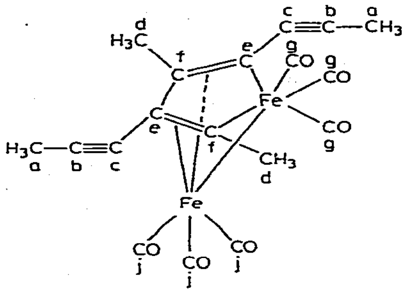
The mass spectrum of the complex is consistent with the known structure. The parent molecular ion is not seen at *m/e* 302, which is not unusual in mass spectrometry [11]. An ion peak at *m/e* 274 is consistent with (DMDA)$Fe(CO)_5^+$. Loss of four carbonyl groups is seen together with loss of iron to give an ion at *m/e* 134 attributed to (DMDA)$(CO)_2^+$.

The carbon-13 spectrum of the complex V displays eleven resonances (Table 1). This number of resonances is consistent with the known structure since the axial carbonyl carbons, h, are magnetically equivalent. Individual assignments were made by comparison to the coupled and decoupled spectra of DMDA and $(DMDA)_2Fe_2(CO)_6$ (Table 1). The assignments are consistent with chemical shifts for other known compounds of similar structure [12—15]. The axial carbonyl carbons, h, were assigned to the resonance at δ 201.3 because this resonance was approximately twice the intensity of the two carbonyl resonances, g. The proton spectrum of V contains two methyl singlets at δ 2.23 and 2.10 (intensity ratio 1 : 1).

The infrared spectrum in the region 2300 to 1600 cm^{-1} in CCl_4 shows one C≡C band (ν 2226w), three C≡O bands (ν 2116m, 2058s(br), 2037s), two bands in the C=O region (ν 1682(sh), 1668s), and one band tentatively assigned as C=C (ν 1614w).

TABLE 1

CARBON-13 CHEMICAL SHIFTS AND COUPLINGS FOR DMDA, V AND VIIIa

Structure	Carbon	δ [a]	J [b]
 $H_3C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3$ DMDA	a	3.7	132(4)
	b	72.0	10(4)
	c	64.4	— (1)
 (V)	a	5.2	
	b	72.8 [c]	
	c	109.8	
	d	13.1	
	e	156.5	
	f	172.1	
	g	198.8	
		199.1	
	h	201.3	
	i	238.7	
		242.4	
 (VIIIa)	a	4.3	132(4)
		5.0	132(4)
	b	92.6	10(4)
		100.6	12(4)
	c	73.8	— (1)
		113.6	— (1)
	d	17.8	130(4)
		30.6	128(4)
	e	131.5	— (1)
		140.0	— (1)
	f	84.9	4(4)
		176.4	7(4)
	g	205.4	— (1)
		206.6	— (1)
		210.1	— (1)
	j	212.4	— (1)

[a] Chemical shifts (δ) in ppm downfield from tetramethylsilane using the relationship: δ(TMS) = δ($CDCl_3$) + 76.9. [b] Coupling constants in Hz; figures in parentheses represent multiplicity of peaks. [c] Chemical shift measured in C_6D_6 because resonance masked in $CDCl_3$.

The complex has four C≡O groups, but two are symmetry related, and one mode (the symmetric one) can be expected to be quite weak. Assignment of the C=O bands was based on the high intensity normally associated with such bands. The assignment of C=C bands is often difficult [11] because they are very weak and can be found from 2000 to 1430 cm^{-1}. Such bands are intensified, however, by conjugation with carbonyls and also by being in ring systems [11]. Tricarbonylferroleiron tricarbonyl complexes (III, R_1 = R_4 = OH) have been oxidized in acidic media with loss of one iron atom as Fe^{2+} and one alkyne moiety to yield alkyneiron hexacarbonyl derivatives [16]. In contrast, the (DMDA)$Fe(CO)_6$ complex (V) is produced directly from starting materials under irradiation. This is the first complex of this type to be synthesized by photochemical conditions.

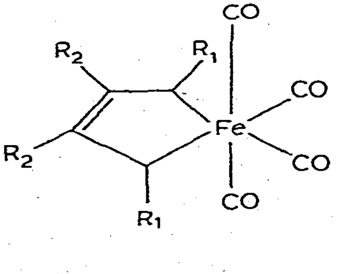
Under identical reaction conditions used to produce (DMDA)$Fe(CO)_6$, dimethylacetylene (DMA) and $Fe(CO)_5$ react to form duroquinoneiron tricarbonyl (IVa) [8]. Removal of the iron—carbon σ-bonds in the (DMDA)$Fe(CO)_6$ complex followed by insertion of a second DMDA group and loss of a carbonyl would lead to the as yet unknown DMDA—duroquinone complex (IVb, and isomers thereof). The complex (DMDA)Fe(CO)$_6$ can be viewed as a possible intermediate in the formation of duroquinones. Irradiation of (DMDA)Fe(CO)$_6$ in the presence of both DMDA and DMA has failed to produce a duroquinone and indeed has only given back starting materials [17]. The stability of this complex may be a result of the conjugation of the double bond, triple bond, and the C=O groups.

(DMDA)$_2$Fe(CO)$_4$ (VI or VII). (DMDA)$_2$Fe(CO)$_4$ was isolated from the reaction of DMDA with Fe(CO)$_5$ in cyclohexane under ultraviolet radiation. A single complex was isolated with proton resonances at δ 2.15 and 1.76 (intensity ratio 1 : 1). A sufficient quantity of this complex was not available for a carbon-13 spectrum. The complex is unstable in vacuum and on alumina chromatography columns. It tends to oil when recovery from organic solvents is attempted. In the solid state, the complex is air stable for several weeks.

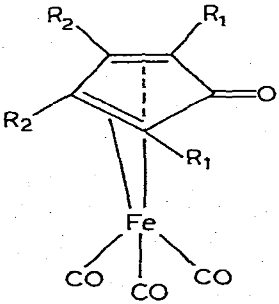
The mass spectrum of the complex gives a peak assumed to be the molecular ion at *m/e* 324. Loss of three carbonyls is followed by loss of iron to give a peak at *m/e* 184 consistent with (DMDA)$_2$CO$^+$.

The infrared spectrum in CCl$_4$ shows one C≡C band (ν 2249w), three C≡O bands (ν 2072s, 2017s, 2007s), and a band and shoulder in the C=O and C=C regions (ν 1663ms(sh), 1656ms). The shoulder at 1663 cm^{-1} is probably an enhanced C=C band. A similar pattern of infrared bands is reported by Hübel and Mérenyi for the diphenyldiacetylene analog (DPDA)$_2$Fe(CO)$_4$ which is suggested to be a cyclopentadienoneiron tricarbonyl type complex (II) [4]. A shoulder at approximately 1663 cm^{-1} is not, however, reported by Hübel and Mérenyi.

Two possible structures, VI and VII, are considered to be compatible with the data. R$_1$ and R$_2$ will be either CH$_3$ or C≡CCH$_3$, respectively. An asymmetric isomer could be expected for each, but such an isomer would have a four peak ^{1}H NMR spectrum. This was never observed. The isolation of a single reaction product could result from more favored kinetics of formation for one of the symmetric structures. Stereospecific products when phenylacetylene is reacted with iron carbonyls have been reported [6,7]. In these cases the phenyl groups are in the R$_1$ positions of the cyclopentadienoneiron tricarbonyl complexes (VII). It has been suggested that the CO attaches to the carbon having the greatest electron density [7]. If this is correct, one would expect the propynyl groups to attach to the ring carbons in the R$_1$ position. The structure VII is favored mainly because of two bands in the C=O, C=C region. Only one would be expected for VI.



(VI)

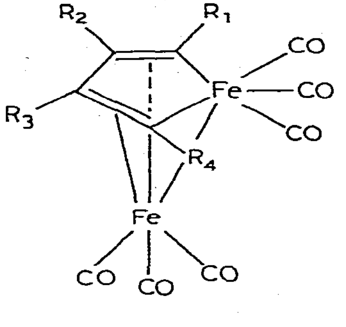


(VII)

Thermal reactions

$(DMDA)_2Fe_2(CO)_6$ (VIII). Three structural isomers of formula $(DMDA)_2Fe_2(CO)_6$ were isolated from the thermal reaction of DMDA with $Fe(CO)_5$. The proton spectrum of VIIIa shows four methyl singlets at δ 2.48, 2.41, 2.13 and 2.08. Isomers VIIIb and VIIIc each have two resonances of equal intensity at δ 2.46 and 2.18, and δ 2.25 and 2.11, respectively.

The three isomers are assumed to be analogs of the DPDA complexes reported [4]. Structural formulation is given as VIIIa, VIIIb and VIIIc. The structural assignments for the DPDA complexes [4] were based on infrared data, with the complex corresponding to VIIIa having two C≡C bands. Isomer VIIIa of the DMDA complex is accordingly assigned [$\nu_{max}(CCl_4)$ 2236w, 2210w (C≡C); 2072m, 2037s, 2004s, 1997(sh), 1951w(br) (C≡O)]. The other two isomers of the DPDA complex were assigned assuming the isomers with the phenylethynyl groups adjacent to the iron atom of the ferrole ring (i.e. $R_1 = R_4 = C{\equiv}CC_6H_5$ and $R_2 = R_3 = C_6H_5$ in VIII) to have the largest shift in the C≡C infrared band. On this basis VIIIc is assigned such that the propynl groups are adjacent to the iron of the ferrole ring. [$\nu_{max}(CCl_4)$. Isomer VIIIb: 2243w (C≡C); 2072m, 2036s, 2009s, 1992(sh), 1950m(br) (C≡O). Isomer VIIIc: 2207w (C≡C); 2073m, 2037s, 2006s, 2000(sh), 1957m (C≡O)].



(VIII)

a, $R_1 = R_3 = CH_3$
$R_2 = R_4 = C{\equiv}C{-}CH_3$

b, $R_1 = R_4 = CH_3$
$R_2 = R_3 = C{\equiv}C{-}CH_3$

c, $R_1 = R_4 = C{\equiv}C{-}CH_3$
$R_2 = R_3 = CH_3$

The carbon-13 chemical shifts and couplings for VIIIa are presented in Table 1. Sixteen resonances are observed, consistent with the structure shown in which the three iron carbonyls, j, are magnetically equivalent. These three carbonyls remained magnetically equivalent even down to −78°C. The three ferrole carbonyls could not be unequivocally assigned. The methyl resonances, a and d, are easily assigned based on the one-bond couplings of ~130 Hz and on their chemical shifts compared to structurally similar methyls in DMDA, and V. The alkyne carbons, c, are singlets and are not easily distinguished from the singlet ring carbons, e. The assignment is based on the expectation that the alkynyl carbons will appear further upfield than the alkenyl carbons [13]. Assuming this assignment to be correct, ring carbons, f, were distinguished from ring carbons, e, by the small two-bond coupling caused by the ring methyls. The downfield resonance within each pair is tentatively assigned to the carbon attached or closer to the ferrole iron. Despite the ambiguities that remain in the individual assignments, it should be emphasized that the chemical shifts, couplings and total number of carbon-13 resonances observed for this complex provides very strong evidence for the proposed structure, VIIIa.

Conclusion

The results indicate that thermal reactions of iron pentacarbonyl with the conjugated diyne, DMDA, yield products which are analogous to those formed with monoalkynes. The photochemical reaction in THF yields the complex V directly, with insertion of two carbonyl groups into the ferrole ring. It is possible that this compound is an intermediate for the formation of a duroquinone complex. Compounds of the complex V type have been previously prepared only from complex intermediates [16]. The photochemical reaction in cyclohexane yields a product which is thought to be similar to that obtained with monoalkynes [4].

Experimental

Physical measurements

Infrared data were recorded with Beckman IR-12 and IR-8 spectrophotometers. X-ray data were collected with a General Electric XRD-7 quarter-circle manual diffractometer by the stationary-crystal, stationary-counter technique. Proton NMR spectra were obtained on Varian T-60 and Varian HA-100 Spectrometers. Carbon-13 spectra were obtained with a JEOL-PS-100/Nicolet 1080 Fourier Transform spectrometer.

Materials

The alumina used for chromatography was Fisher Scientific Co. Adsorption Alumina, 80-200 mesh; it was used as received. Technical grade hexane and cyclohexane were purified by stirring over concentrated sulfuric acid, washing with water, drying over calcium chloride, and distilling from lithium aluminum hydride. Reagent grade acetonitrile was dried over calcium chloride prior to use. Benzalacetone [18], $Fe_2(CO)_9$ [19], and benzalacetoneiron tricarbonyl [20] were prepared according to literature methods. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride prior to use. Dimethylacetylene (DMA) and dimethyldiacetylene (DMDA) were obtained commercially and used as received except that the DMDA used for carbon-13 spectra was sublimed before use. Iron pentacarbonyl was obtained commercially and used as received.

Syntheses

(DMDA)Fe(CO)$_6$(V). DMDA (1.0 g) and $Fe(CO)_5$ (2.0 ml) in 20 ml of THF were irradiated with a Hanovia 679A36 high pressure mercury lamp for 20 min at room temperature. The solvent was evaporated with a stream of nitrogen and the residue vacuum sublimed at room temperature to a Dry Ice/acetone cold finger to obtain the crude product which was then taken up in acetonitrile as a saturated solution at room temperature. The solution was placed at —10°C overnight and filtered, resulting in red-orange crystals of pure $(DMDA)Fe(CO)_6$, 0.5—1.0% yield, m.p. 137°C (dec.). Found: C, 47.91; H, 2.17; Fe, 20.40. $C_{12}H_6FeO_6$ calcd.: C, 47.71; H, 2.01; Fe, 18.49%.

$(DMDA)_2Fe(CO)_4$ (VI or VII). DMDA (1.0 g) and $Fe(CO)_5$ (2.0 ml) in 20 ml of cyclohexane were irradiated under a nitrogen atmosphere with a medium pressure mercury lamp for 25 min at room temperature. The solvent was evaporated with a stream of nitrogen. The residue was taken up in acetonitrile and

filtered rapidly through a 30 ml sintered glass filter two-thirds full of alumina. The filter was washed with additional acetonitrile and the filtrate was evaporated with a stream of nitrogen or simply left in the fume hood to evaporate overnight. The residue was then taken up in a minimum of acetonitrile, and water was added to form a yellow milky solution. Centrifuging for 5 min resulted in an oil layer and a yellow milky aqueous layer which were separated by decantation. The aqueous layer was allowed to evaporate. The resulting pale yellow crystalline solid was filtered and dried by storing in a desiccator, 0.5—1.0% yield, m.p. 95—97°C (dec.). Found: C, 59.51; H, 3.78; Fe, 16.96. $C_{16}H_{12}FeO_4$ calcd.: C, 59.28; H, 3.74; Fe, 17.23%.

$(DMDA)_2Fe_2(CO)_6$(VIII). DMDA (3.0 g) was reacted with $Fe(CO)_5$ (10.0 g) in xylene (7 ml) at 120—130°C for 45 min under a nitrogen atmosphere. At the end of the reaction period, solvent and excess reactants were evaporated under a stream of nitrogen at reaction temperature to leave behind a small residue. The solvents and reactants were collected with a Dry Ice/acetone cold trap. About 75% of the $Fe(CO)_5$ and unknown amounts of DMDA and xylene were recovered. Because of the toxic properties of $Fe(CO)_5$, 10 g was the largest amount handled in a single reaction. After ten reactions were carried out, their residues were combined and chromatographed on a 2 X 7 alumina column with hexane. A yellow band was eluted and the solvent stripped to yield a red-orange oil which solidified to a red-orange solid upon standing.

The product was a mixture of three isomers as determined by proton NMR and designated VIIIa, VIIIb, and VIIIc. Most of the VIIIa was separated by cooling a hot acetonitrile solution of the mixture to room temperature. Recrystallization from saturated acetonitrile at —10°C resulted in red-orange crystals of pure $(DMDA)_2Fe_2(CO)_6$, isomer VIIIa, <0.5% yield, m.p. 113.5—114.5°C. Found: C, 49.88; H, 2.90; Fe, 25.91. $C_{18}H_{12}Fe_2O_6$ calcd.: C, 49.58; H, 2.78; Fe, 25.62%. The filtrate was evaporated with a stream of nitrogen and the residue chromatographed on a 1 X 100 cm alumina column with hexane. As the column eluted, the yellow band spread until it was about 60 cm in length with the leading edge being isomer VIIIa. The trailing edge was VIIIc with VIIIb in the middle. After several successive passes, a pure sample of VIIIc (m.p. 123.0—123.5°C) and an enriched sample of VIIIb (mixed with VIIIc) were obtained. All three isomers had the same yellow color; a pure sample of VIIIb was never obtained. Separation was followed with a Varian T-60 NMR.

During the course of this work, King and Ackermann [21] reported a reaction which gave high yields of tricarbonylferroleiron tricarbonyl type complexes (III). In a similar manner, benzalacetoneiron tricarbonyl (2.6 g) was reacted with DMDA (1.0 g) in benzene (15 ml) under a nitrogen atmosphere for 70 min at 90°C. The reaction mixture was then allowed to cool to room temperature with stirring. The solvent was stripped and the residue chromatographed on a 2 X 10 cm alumina column with hexane. The first yellow band eluted was the desired $(DMDA)_2Fe_2(CO)_6$ (all three isomers). Purification and separation of isomers was the same as previously described. Qualitatively, this method seemed to improve the yield over the original one.

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