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PHOTOCHEMICAL SYNTHESES OF 1,5- AND 1,3-CYCLOOCTADIENE-IRON CARBONYLS.

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1,5-Cyclooctadiene-iron tricarbonyl (I) has been reported as a liquid (n_D^{20} 1.5765) produced photochemically[1)] or thermally[2)] from $Fe(CO)_5$ and 1,5-cyclooctadiene (II), and as an unstable solid melting just below room temperature obtained from refluxing II with $Fe_3(CO)_{12}$ in benzene[3)]. I has also been described in a footnote[4)] as yellow crystals, m.p. 61-63°C, prepared from II and $Fe_2(CO)_9$. Recently the Mössbauer parameters of I have been reported[5)] without any data on its preparation.

The well known isomerization of II to 1,3-cyclooctadiene (III) with catalytic amounts of iron carbonyls[6)] has caused some doubts[7)] as to whether II or III is coordinated in the reported compounds. Therefore in connection with systematic studies of iron carbonyl complexes[8)] we have re-investigated this system.

Illumination of $Fe(CO)_5$ and II yields 1,5-cyclooctadiene-iron tetracarbonyl (IV) as an unstable oil (n_D^{20} 1.575) when only ~ 1/3 of the $Fe(CO)_5$ is reacted. IV can be recrystallized from pentane at -120°C. Structure IV is supported by the degradation with $Ce(NH_4)_2(NO_3)_6$ (V) in C_2H_5OH[9)] to II (Table I), the analytical (all reported compounds gave satisfactory elemental analyses) and IR data (Table I), the mass spectrum[10)] showing peaks at m/e 276, 248, 220, 192, 164 ($[M-(CO)_n]^+$; n = 0 - 4), 110 (butadiene-Fe^+) and 108 (II^+), and the NMR spectrum[11)] with multiplets (m) at 4.53 τ (2 H), 6.8 τ (2 H) and 7.9 τ (8 H) indicating an uncoordinated double bond.

Extended irradiation of $Fe(CO)_5$ and II, however, yields 1,5-cyclooctadiene-iron tricarbonyl (I) as stable orange crystals, m.p. 90-90.5° (from pentane);

[NMR: m 6.6 τ (4 H) and m 8.0 τ (8 H)]. IV obviously is the primary product in this photoreaction.

Decomposition of IV on standing leads to 1,5-cyclooctadiene-bis(iron tetracarbonyl) (VI), yellow crystals, m.p. 85-88°C, which form $Fe_3(CO)_{12}$ on slow heating > 77°C. VI (main product) and I are formed in the reaction of II with $Fe_2(CO)_9$; the melting point of a 1:1 mixture of I and VI is 67.5-68.5°. The conformation of the ring system in VI [NMR: m 6.3 τ (4 H), m 7.3 τ (4 H) and m 8.2 τ (4 H)] and IV is under current investigation.

[1] and [2] are possible pathways from IV to VI. [2] was demonstrated experimentally; however, a simultaneous reaction [1] cannot be ruled out.

$$[1] \quad \text{IV} + Fe_2(CO)_9 \longrightarrow \text{VI} + Fe(CO)_5$$

$$[2] \quad 2\ \text{IV} \longrightarrow \text{VI} + \text{II}$$

According to [1] the predominant formation of VI over IV even in the presence of a large excess of II would require an activation of the uncoordinated double bond in IV compared with II. There is no evidence from the NMR for an interaction of $Fe(CO)_4$ with the free double bond in IV. An analogy to [2] is the formation of butadiene-bis(iron tetracarbonyl) from butadiene-iron tetracarbonyl[12].

1,3-Cyclooctadiene-iron tricarbonyl (VII) [NMR: q 5.24 τ (2 H), m 7.0 τ (2 H), m 8.2 τ (4 H) and m 8.9 τ (4 H)] can be easily obtained in crystalline form (m.p. 36.5-37°C) from the photochemical reaction of $Fe(CO)_5$ and 1,3-cyclooctadiene. VII seems to be thermally less stable than I: this may be due to conformational strain resulting when the conjugated double bonds are forced into one plane by coordination[7].

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TABLE I : Preparation and Spectral Data of I, IV, VI and VII

Iron Carbonyl (Mol)	Cyclo-octadiene (Mol)	Solvent (cc)	Reaction Conditions[a]	CO Evolution (Mol)	Yield[b]	$\nu_{C\equiv O}$[c] (cm^{-1})	UV_{max}[d] ($10^3\ cm^{-1}$)	Degradation
$Fe(CO)_5$ (0.12)	II (0.24)	Pentane (275)	Irradiation[e] at -25°C	0.038	64% IV	2100 2065 1997 1964	~ 36 sh.	95% II 5% III with V
$Fe(CO)_5$ (0.1)	II (0.4)	Benzene (125)	Irradiation at 15-20°C	0.14	47% I	2040 1940- 1945 v.b.	43.4	99% II with V $(\text{Ø}_3P)_2Fe(CO)_3$ with Ø_3P
$Fe(CO)_9$ (0.027)	II (0.11)	Benzene (50)	Stirring in the dark, 20°C	-	30% VI	2098 1995 1965	~ 36 sh.	98% II 2% III $\text{Ø}_3PFe(CO)_4$ with Ø_3P
$Fe(CO)_5$ (0.1)	III (0.15)	Benzene (150)	Irradiation at 15-20°C	0.13	25% VII	2070 1965 v.b.	32.4	99% III with V

[a] All preparations under argon.

[b] On the basis of reacted iron carbonyl. Work up: Removal of excess reagents at 10^{-2} Torr at max. 20°C; low temperature crystallization from pentane.

[c] in CH_2Cl_2, only VII in KBr; v.b. = very broad

[d] in pentane; sh = shoulder

[e] High pressure mercury lamp PHILIPS HP 125 W, SOLIDEX filter.

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