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Preliminary communication

Heptafulvenetricarbonyliron★

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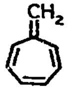
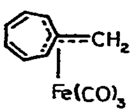
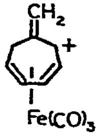
Heptafulvene (I), a highly reactive, conjugated, non-benzenoid hydrocarbon of theoretical interest, has not been isolated to date. Attempts to concentrate a dilute solution of I in propane by evaporation at −60° in vacuum gave only polymer[1]. As expected on theoretical grounds, derivatives containing electron-withdrawing groups on the exocyclic double bond are considerably more stable than the parent molecule[2]. Recently, Kerber and Ehntholt[3] reported the preparation of a stable $Fe(CO)_3$ complex of heptafulvene in which the hydrocarbon is coordinated to the metal as a trimethylene–methane-type ligand (II). Substituted heptafulvenes also form $Fe(CO)_3$ complexes[4].



(I)



(II)



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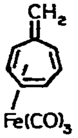

(IV)

In this report we describe the preparation and properties of a heptafulvene–$Fe(CO)_3$ complex which is isomeric with II. Slow addition of triethylamine (3 mmole) to a slurry of III[5] in methylene chloride (20 ml) produced an immediate reaction. The color of the solution became deep yellow and III dissolved completely. Evaporation of the solvent at reduced pressure followed by preparative TLC of the residue on Silica Gel using pentane or carbon disulfide as the eluent afforded a pure sample of (2,3,4,5-*tetrahapto*-methylenecycloheptatriene) tricarbonyliron (IV) as a yellow liquid★★

The NMR spectrum of IV (CS_2) consists of a multiplet at 4.56τ, two singlets at 4.81 and 5.11τ, a doublet at 6.37τ ($J = 7$ Hz) and a triplet at 7.07τ having intensities in the ratio of 4/1/1/1/1. Based on the above spectrum we assign structure IV to the heptafulvene–$Fe(CO)_3$ complex. The absence of a two proton signal at high field (8–9τ) rules out a trimethylene–methane-type structure II [3]. Assignment of the two upfield signals to H_2 and H_5 is consistent with both the chemical shift and splitting expected for

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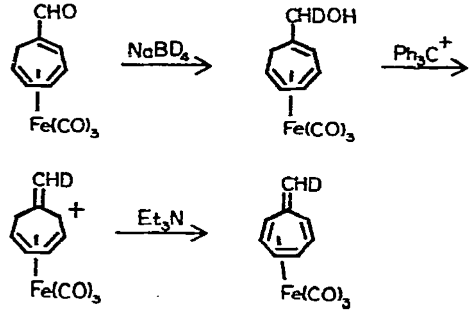
★★Compound II was not detected in the reaction mixture.

protons on the terminal carbons of a cyclic diene–$Fe(CO)_3$ group[5]. In the NMR spectrum of monodeuteroheptafulvene–$Fe(CO)_3$ (V) (Scheme I)[6], the intensity of the singlets at 4.81 and 5.11τ are both reduced by a factor of two, thus confirming the assignment of these signals to the protons on the exocyclic double bond.



Scheme I (V)

The electron impact (EI) and chemical ionization (CI) mass spectra of IV are also consistent with the proposed structure. Although a molecular ion (*m/e* 244) is not observed in the EI mode, abundant fragment ions are evident at *m/e* 216 (M^+–CO), 188 (M^+–2CO). 160 (M^+–3CO), 134 (M^+–3CO–C_2H_2), 104 (M^+–$Fe(CO)_3$), 77 ($C_6H_5^+$) and 56 (Fe^+). In the CI spectrum (CH_4) the quasimolecular ion (QM^+) at *m/e* 245 (M^++1) is the most abundant ion present. Since ionization of the sample by this technique is affected by proton transfer[7] from CH_5^+, a molecular weight of 244 is assigned to the heptafulvene–$Fe(CO)_3$ complex.

Strong bands due to CO ligands on the iron atom appeared at 2040 and 1980 cm^{-1} in the IR spectrum of IV ($CHCl_3$).

A preliminary investigation of the chemistry of heptafulvene–$Fe(CO)_3$ indicates that IV dimerizes slowly at room temperature, forms a 1/1 adduct with dimethylacetylenedicarboxylate (mol. wt. 386, $C_{14}H_{14}O_4Fe(CO_3)$) and is protonated by strong acids such as trifluoroacetic acid. At 78° in benzene the dimerization reaction requires 20 h to go to completion and is unaffected by the presence of either acetic acid or triethylamine. At 100°, neat IV dimerizes in 10 min. A CI mass spectrum of the dimer, $C_{16}H_{16}Fe_2(CO)_6$, shows a QM^+ at *m/e* 489 (M^++1) and fragment ions at *m/e* values corresponding to the successive loss of six CO ligands and two Fe atoms★. Protonation of IV occurs in trifluoroacetic acid but not in acetic acid. Treatment of the protonated species VI with K_2CO_3 in methylene chloride regenerates IV in low yield. Reduction of the salt VI with triethylsilane[8] affords a neutral compound having a molecular weight two mass units higher than IV.

Efforts are presently being made to complete the characterization of the above products and to thoroughly investigate the chemistry of the heptafulvene ring system. Synthetic routes to chromium and molybdenum carbonyl complexes of heptafulvene are also being explored.

★A dimer of IV has also been obtained by Johnson *et al.*[4]

ACKNOWLEDGEMENT

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