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REACTIONS OF ALKALI METAL DERIVATIVES OF METAL CARBONYLS

XII[*]. THE NON-OCCURRENCE OF RING OPENING IN THE REACTION OF SODIUM CYCLOPENTADIENYLDICARBONYLFERRATE WITH 1,2-DIBROMOBENZOCYCLOBUTENE

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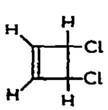
SUMMARY

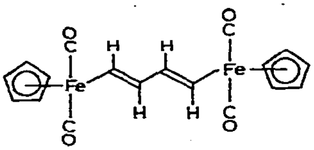
The reaction of 1,2-dibromobenzocyclobutene with $NaFe(CO)_2C_5H_5$in tetrahydrofuran solution gives the deep yellow bimetallic derivative $C_8H_6[Fe(CO)_2C_5H_5]_2$. The proton NMR spectrum and the lack of reactivity towards dienophiles such as tetracyanoethylene show $C_8H_6[Fe(CO)_2C_5H_5]_2$ to be a benzocyclobutene rather than an *o*-xylylene derivative. This indicates that 1,2-dibromobenzocyclobutene, unlike 3,4-dichlorocyclobutene, does not undergo opening of the cyclobutene ring upon reaction with $NaFe(CO)_2C_5H_5$.

INTRODUCTION

The reaction between 3,4-dichlorocyclobutene (I) and $NaFe(CO)_2C_5H_5$ has recently been shown[2–4] to result in ring opening to give the bimetallic butadiene derivative $C_4H_4[Fe(CO)_2C_5H_5]_2$ (II). The related reaction between 1,2-dibromobenzocyclobutene[***] (III)[5] and $NaFe(CO)_2C_5H_5$ has now also been found to give a bimetallic derivative. However, evidence presented in this paper indicates that this bimetallic derivative $C_8H_6[Fe(CO)_2C_5H_5]_2$ is not the *o*-xylylene complex (IV) formed by a ring opening reaction but instead is the benzocyclobutene complex (V).



(I)



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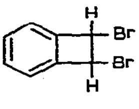

(III)

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[*] For Part XI of this series see ref. 1.

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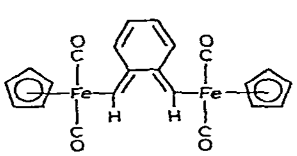
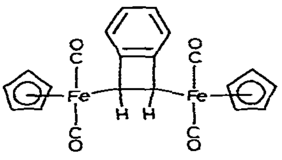
[***] Chem. Abstr. name: 7,8-dibromobicyclo[4.2.0]octa-1,3,5-triene.



(IV)



(V)

EXPERIMENTAL

A nitrogen atmosphere was routinely provided for the following operations: (*a*) carrying out reactions; (*b*) admitting to evacuated vessels; and (*c*) handling filtered solutions of organometallic derivatives. The 1,2-dibromobenzocyclobutene (III) was prepared from α,α,α′,α′-tetrabromo-*o*-xylene and sodium iodide in acetone solution according to the published procedure[5].

Reaction of $NaFe(CO)_2C_5H_5$ with 1,2-dibromobenzocyclobutene (III)

A solution of 10.5 g (30 mmoles) of $[C_5H_5Fe(CO)_2]_2$ in 200 ml of tetrahydrofuran (redistilled over $LiAlH_4$) was stirred with an excess (1.5 g, 65 mmoles) of sodium metal as a 3% amalgam for 2 h at room temperature. After removal of excess sodium amalgam the solution of $NaFe(CO)_2C_5H_5$ was cooled to −78° and treated with a solution of 7.5 g (28.5 mmoles) of 1,2-dibromobenzocyclobutene in 50 ml of the *redistilled* tetrahydrofuran. The resulting reaction mixture was stirred for 3 h at −78° and finally for an additional 13 h at room temperature. Solvent was then removed at 50°/40 mm. The residue was extracted with three 100 ml portions of a 1/3 mixture of dichloromethane and hexane. The filtered extracts were concentrated and then chromatographed on a 2.5 × 70 cm alumina column. The chromatogram was first eluted with a 1/3 mixture of dichloromethane and hexane to remove a very pale yellow band containing some unchanged 1,2-dibromobenzocyclobutene (III). The next band, an intense yellow band, was eluted with the same dichloromethane/hexane mixture. Concentration of this eluate at 25°/40 mm gave 3.5 g (27% yield) of deep yellow crystalline $C_8H_6[Fe(CO)_2C_5H_5]_2$, which was removed by filtration. The analytical sample, m.p. 166–167°, was purified by several recrystallizations from mixtures of dichloromethane and hexane. (Found: C, 57.9, 58.1; H, 3.4, 3.4; Fe, 24.3, 24.5; O, 13.9, 14.2. $C_{22}H_{16}Fe_2O_4$ calcd.: C, 57.9; H, 3.5; Fe, 24.5; O, 14.0%.)

Infrared spectrum (Perkin–Elmer model 621 spectrometer; grating optics)

Cyclohexane solution: ν(CO) frequencies at 2007 (vs), 1960 (vs), and 1947 (vs) cm^{-1}.

Proton NMR spectra (Perkin–Elmer Hitachi R–20 spectrometer; 60 Mc)

(*a*). *1,2-Dibromobenzocyclobutene (III)*. Multiplets in $CDCl_3$ solution at τ 2.95 (at least 12 discernible lines) and τ 4.73 (5 discernible lines) corresponding to the four benzenoid protons and the two saturated aliphatic protons, respectively.

(*b*). $C_8H_6[Fe(CO)_2C_5H_5]_2$ (*V*). Resonances in $CDCl_3$ solution at τ 3.39 (broad, unresolved), τ 5.42 (singlet), and τ 6.21 (singlet) of relative intensities 4/10/2 corresponding to the four benzenoid aromatic protons, the ten protons of the two *pentahapto*-cyclopentadienyl rings, and the two saturated aliphatic protons, respectively.

Mass spectrum (Perkin–Elmer Hitachi RMU 6 mass spectrometer)

The following ions were observed in a mass spectrum of $C_8H_6[Fe(CO)_2C_5H_5]_2$ (V) taken on a sample introduced at 180° into a 220° chamber (relative intensities are given in parentheses): $(C_5H_5)_2Fe_2(CO)C_8H_6^+$ (3), $(C_5H_4)_2Fe_2C_8H_6^+$ (13), $C_{10}H_8FeC_8H_6^+$ (5), $C_5H_5Fe(CO)_2C_8H_6^+$ (43), m/e 262 (5), $C_5H_5Fe(CO)C_8H_6^+$ (30), $(C_5H_5)_2Fe_2^+$ (4), $C_5H_5FeC_8H_6^+$ (100), $C_5H_5Fe_2C_3H_3^+$ (7), $C_5H_5FeC_6H_4^+$ (5), $(C_5H_5)_2Fe^+$ (~72), $C_5H_5Fe(CO)_2^+$ (13), $C_{13}H_{10}^+$ (13), $C_{13}H_9^+$ (23), $C_5H_5FeCO^+$ (20), $C_{11}H_9^+$ (11), $C_{10}H_{10}^+$ (8), $C_5H_5Fe^+$ (74), $C_9H_7^+$ (5), Fe_2^+ (4), $C_8H_6^+$ (87), $C_3H_3Fe^+$ (9), $C_3H_2Fe^+$ (5), C_3HFe^+ (5), $C_6H_4^+$ (27), $C_5H_6^+$ (22), $C_5H_5^+$ (22), $C_5H_3^+$ (12), Fe^+ (32), $C_4H_3^+$ (13), $C_4H_2^+$ (13), $C_3H_4^+$ (10), $C_3H_3^+$ (30). Under these conditions neither the molecular ion nor its doubly charged counterpart was observed.

Reactions of $C_8H_6[Fe(CO)_2C_5H_5]_2$ (V)

(*a*). *Metal carbonyls.* Reaction of $C_8H_6[Fe(CO)_2C_5H_5]_2$ (V) with excess $Fe(CO)_5$ or $C_5H_5Co(CO)_2$ in boiling octane for ≈18 h failed to give any new metal carbonyl derivatives.

(*b*). *Tetracyanoethylene.* Reaction of equimolar quantities of $C_8H_6[Fe(CO)_2C_5H_5]_2$ (V) and tetracyanoethylene in boiling benzene for 4 h gave a mixture of unreacted $C_8H_6[Fe(CO)_2C_5H_5]_2$ (V) and $[C_5H_5Fe(CO)_2]_2$ after chromatography.

(*c*). *Maleic anhydride.* Reaction of equimolar quantities of $C_8H_6[Fe(CO)_2C_5H_5]_2$ (V) and maleic anhydride in boiling benzene for 3 h gave only unreacted $C_8H_6[Fe(CO)_2C_5H_5]_2$ (V) after chromatography.

(*d*). *Diethyl azodicarboxylate.* Equimolar quantities of $C_8H_6[Fe(CO)_2C_5H_5]_2$ (V) and diethyl azodicarboxylate failed to react in tetrahydrofuran at room temperature for 21 h as indicated by the infrared spectrum of the reaction mixture.

(*e*). *Triphenylphosphine.* Reaction of $C_8H_6[Fe(CO)_2C_5H_5]_2$ (V) with three equivalents of triphenylphosphine either in boiling octane or in cyclohexane at room temperature in the presence of ultraviolet irradiation gave only $[C_5H_5Fe(CO)_2]_2$.

DISCUSSION

The following observations indicate that the $C_8H_6[Fe(CO)_2C_5H_5]_2$ formed from 1,2-dibromobenzocyclobutene (III)[5] and $NaFe(CO)_2C_5H_5$ is not the *o*-xylylene complex (IV) but instead has structure (V) with retention of the bicyclic benzocyclobutene system:

(1). The proton NMR spectrum of $C_8H_6[Fe(CO)_2C_5H_5]_2$ has a similar pattern to that in the starting material 1,2-dibromobenzocyclobutene (III) except for the expected upfield shifts arising from the substitution of iron for bromine. The apparent singlet at τ 6.21 assigned to the two protons of (V) in the cyclobutene ring also has a chemical shift outside the normal range for uncomplexed olefinic protons as would be present in the *o*-xylylene derivative (IV).

(2). Reaction of $C_8H_6[Fe(CO)_2C_5H_5]_2$ with the very strong dienophile tetracyanoethylene in boiling benzene does not result in the formation of an adduct but instead in the recovery of some unchanged $C_8H_6[Fe(CO)_2C_5H_5]_2$. An *o*-xylylene complex of structure (IV) has two pairs of conjugated carbon–carbon double bonds and thus should be very reactive towards a dienophile as strong as tetracyanoethylene. The complex $C_8H_6[Fe(CO)_2C_5H_5]_2$ was also unreactive towards the dienophiles maleic anhydride and diethyl azodicarboxylate.

The failure of 1,2-dibromobenzocyclobutene (III) to undergo ring opening upon reaction with $NaFe(CO)_2C_5H_5$ to form an *o*-xylylene complex (IV) may be attributed to the fact that formation of the *o*-xylylene complex (IV) from (III) would result in the destruction of the benzenoid aromatic system in (III).

The structure (V) for the $C_8H_6[Fe(CO)_2C_5H_5]_2$ product actually formed in the reaction between 1,2-dibromobenzocyclobutene and $NaFe(CO)_2C_5H_5$, however, is also unusual in being the first known compound with two transition metals σ-bonded to a pair of saturated vicinal carbon atoms of a hydrocarbon system.

The analogous reactions of the less nucleophilic[7] sodium salts $NaMn(CO)_5$ and $NaM(CO)_3C_5H_5$ ($M = Mo$ and W) with 1,2-dibromobenzocyclobutene in tetrahydrofuran solution were also investigated. However, no compounds analogous to (V) were isolated from any of these reactions. Instead these reactions resulted only in coupling to give $Mn_2(CO)_{10}$ and $[C_5H_5M(CO)_3]_2$ ($M = Mo$ and W), respectively.

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