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Preliminary communication

REACTION OF 5,6-DIMETHYLENE-7-OXABICYCLO[2.2.1]HEPT-2-ENE WITH IRON CARBONYLS

TRISTANO BOSCHI*, PIERRE VOGEL and RAYMOND ROULET
Institutes of Organic Chemistry and of Inorganic and Analytical Chemistry, Place du Château 3, University of Lausanne (Switzerland)

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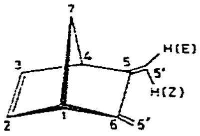
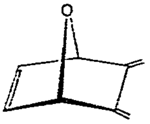
Summary

The photoreaction of 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene with $Fe(CO)_5$ yields initially the *dihapto*-tetracarbonyliron complex, which reacts further to give a *dihapto*-tetracarbonyl-*tetrahapto*-tricarbonyl complex. Deoxygenation of the ligand is observed in the presence of $Fe_2(CO)_9$ in benzene, giving *o*-quinodimethane complexes.

Coordination of a *cis*-dialkylmonoolefin to iron carbonyls seldom yields stable *dihapto*-tetracarbonyliron complexes [1], especially when the ligand offers other coordination sites such as conjugated C—C double bonds**. 5,6-Dimethylenebicyclo[2.2.1]hept-2-ene (I) and 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene (II***) contain a *s-cis*-butadiene group and an endocyclic *cis*-disubstituted C—C double bond. Upon treatment with $Fe_2(CO)_9$, I yields the expected *endo*- and *exo*-5,5′,6,6′-*tetrahapto*-tricarbonyliron complexes together with a mixture of cyclopentanone derivatives [4] arising from the reaction of the π(2,3)-endocyclic double bond. These results suggested the intermediacy of 2,3-η-5,6-dimethylenebicyclo[2.2.1]hept-2-ene·$Fe(CO)_4$ complexes [5], but attempts to isolate them failed



(I)



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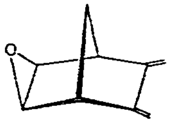

(III)

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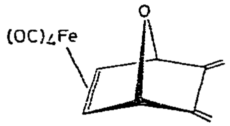
*Present address: Centro Chimica e Technologia Composti Metallorganici Elementi transizione, Facolta di Ingegneria, University of Padua (Italy).

**Dimethylenecyclobutene is known to give 1,2-η-3,4-dimethylenecyclobutenetetracarbonyliron upon treatment with $Fe_2(CO)_9$ [2].

***The triene II was prepared according to ref. 3; we thank Mr. A. Chaouch for technical assistance.

We treated the ether II with iron carbonyls under various conditions, and found that the *dihapto*-tetracarbonyl complex IV is formed and can be isolated in 50% yield by treating II with $Fe_2(CO)_9$ in ether/pentane (36°, 2 days; chromatography on Florisil with n-hexane as eluent). Irradiation of II (pyrex vessel, high pressure Hg lamp, pentane, –80°C) in the presence of $Fe(CO)_5$ in excess gives compounds IV and V in the ratio 4/1 (global yield 30%, after fractional sublimation). IV is first formed; under these conditions, coordination of the *s-cis*-butadiene group occurs only in a subsequent step*.



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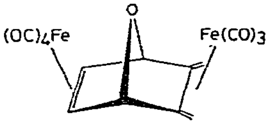

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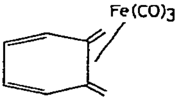

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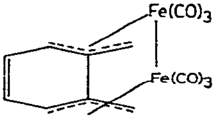

(VII)

The structures of IV and V follow from their physical, analytical and spectroscopic properties and from comparison with tricarbonyliron complexes of the triene I [7] and of the epoxydiene III**.

IV: Yellow crystals, m.p. 47–48°C; Found: C, 49.54; H, 2.74; $C_{12}H_8FeO_5$ calcd.: C, 50.04; H, 2.80%. Mass spectrum (70 eV) m/e^+: 260, 232, 204, 176 (loss of 4 CO); IR (n-hexane): ν(CO) 2097, 2032, 2017, 1984 cm^{-1}; ^1H NMR ($CDCl_3$, δ(TMS) 0 ppm): 5.3 (s; H-5′(*Z*), H-6′(*Z*)), 5.1 (s; H-5′(*E*), H-6′(*E*)), 4.7 (s; H-1, H-4), 3.2 (s; H-2, H-3); ^{13}C NMR (CD_2Cl_2, δ(TMS) 0 ppm, –72°C): 210.3 (s; CO), 145.0 (s; C-5, C-6), 103.1 (t; C-5′, C-6′; ^1J(C-5′, H-5′) 158 Hz), 82.3 (d; C-1, C-4; ^1J(C-1,H-1) 161 Hz), 54.9 (d; C-2, C-3; ^1J(C-2,H-2) 171 Hz).

V: Yellow crystals, m.p. 114–115°C; Found: C, 42.12; H, 1.93. $C_{15}H_8Fe_2O_8$: C, 42.10; H, 1.88%. Mass spectrum (70 eV) m/e^+: 428 (M^+), 400, 372, 344, 316, 288, 260, 232 (loss of 7 CO); IR (n-hexane): ν(CO) 2103, 2061, 2040, 2028, 1991, 1986, 1979 cm^{-1}; ^1H NMR (C_6D_6, TMS): 4.0 (s; H-1, H-4), 2.8 (s; H-2, H-3), 1.7 (d; H-5′(*E*), H-6′(*E*); ^2J(H-5′(*E*), H-5′(*Z*)) 2.2 Hz), 0.2 (d; H-5′(*Z*), H-6′(*Z*)). A crystal structure determination of V is in progress.

Upon more drastic conditions (benzene, 60°C, 36 h), $Fe_2(CO)_9$ brings about an oxygen atom abstraction from the ligand II giving VI (30%) and VII (1%). VI has already been prepared in lower yield by treating α,α'-dibromoorthoxylene with $Fe_2(CO)_9$ [9], and VII is one of the isomers obtained in the photoreaction of VI with $Fe(CO)_5$ [10].

VI: ^{13}C NMR (CD_2Cl_2, TMS, –80°C); δ (ppm) 217.1, 207.9 (CO, exchange blocked, intensity ratio 1/2), 132.1 (d; C-2, C-3; ^1J(C-2,H-2) 167 Hz), 128.7 (d; C-1, C-4; ^1J(C-1,H-1) 161 Hz), 99.5 (s; C-5, C-6), 35.3 (t; C-5′, C-6′; ^1J(C-5′,H-5′) 160 Hz)

Deoxygenation of unsaturated ethers by iron carbonyl anions is known to occur easily when the ether can equilibrate with an epoxide isomer as in the case

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[*] An analogous *dihapto*-tetracarbonyl-*tetrahapto*-tricarbonyldiiron complex of 9-oxabicyclo[4.2.1]nona-2,4,7-triene has been reported; it was formed by complexation of the corresponding 2,3,4,5-η-$Fe(CO)_3$ complex [6].

[**] A crystal structure determination of the *exo-tetrahapto*-tricarbonyliron complex of III has been carried out [8].

of the oxepine/benzene oxide system [11]. It can not be excluded that the oxygen bridge in the iron complexes of II migrates and forms an epoxide intermediate which readily undergoes deoxygenation.

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