

(CYCLOOCTATETRAENE OXIDE)DIIRON HEXACARBONYL: PREPARATION AND THERMOLYSIS

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SUMMARY

The preparation of (cyclooctatetraene oxide)diiron hexacarbonyl is described and its thermolysis compared with that of the uncomplexed epoxide.

INTRODUCTION

Cyclooctatetraene oxide (I) is the photo-precursor to the labile and theoretically interesting oxacyclononatetraene (oxonin)¹. However, (I) is *thermally* quite unreactive, and only at 260° does it finally rearrange to cycloheptatriene-3-carboxaldehyde². The reason for this thermal inertness is not clear. Recently, several groups have shown that transition metals can greatly increase rates of otherwise sluggish pericyclic reactions, possibly via formation of intermediate π -complexes³. Consequently, we wished to prepare a transition-metal π -complex of (I) to see whether coordination would affect the rates or change the products of its thermal, pericyclic, reactions. This report describes the preparation and thermolysis of (cyclooctatetraene oxide)-diiron hexacarbonyl (II).

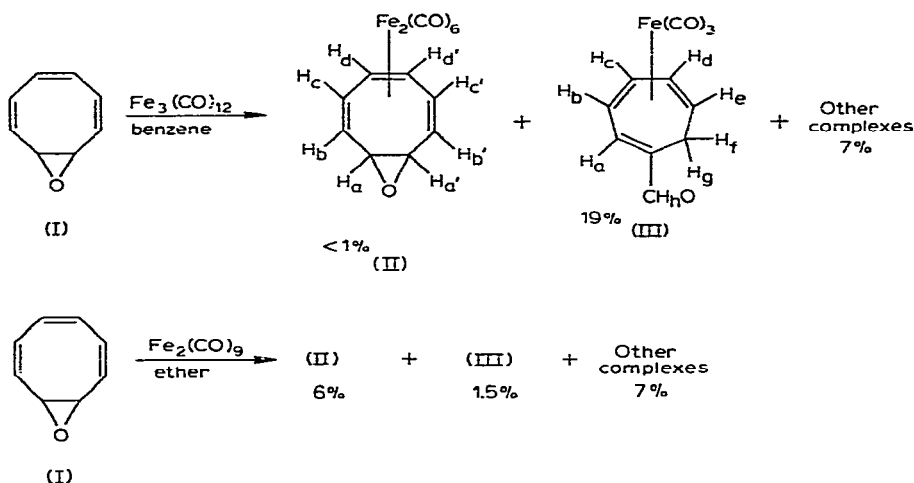
RESULTS AND DISCUSSION

Reaction of (I) with $\text{Fe}_3(\text{CO})_{12}$ in refluxing benzene failed to give an epoxide complex, but instead produced the aldehyde (III) (19%) and small amounts (7%) of complexes of cyclooctatetraene and cyclooctatrienone (*vide infra*). Structure (III) was assigned on basis of the mass spectrum (M^+ 260), IR spectrum (cyclohexane) [$\nu(\text{C}\equiv\text{O})$ 2050, 1995, 1990 cm^{-1} ; $\nu(\text{C}=\text{O})$ 1682 cm^{-1} ; $\nu(\text{C}=\text{C})$ 1640 cm^{-1}] and NMR spectrum (C_6D_6) (τ 7.05–8.38, 4 H multiplet, $\text{H}_{b,c,f,g}$; τ 5.53, 2 H multiplet, $\text{H}_{c,d}$; τ 3.93, 1 H doublet, J 8 Hz, H_a ; τ 0.97 1 H singlet, H_h). Of the eight possible (cycloheptatrienecarboxaldehyde)iron tricarbonyl complexes, only (III) would show a single uncoordinated olefinic proton, split into a doublet.

Milder conditions [$\text{Fe}_2(\text{CO})_9$ in diethyl ether] did produce (II) in a maximum yield of 6%, together with a large amount of polymer, (cyclooctatetraene)iron tri-

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carbonyl (1.6%), (cyclooctatetraene)diiron pentacarbonyl (3%), (cyclooctatrienone)-iron tricarbonyl (1%), (cyclooctatrienone)diiron hexacarbonyl (0.6%) and (III) (1.5%).



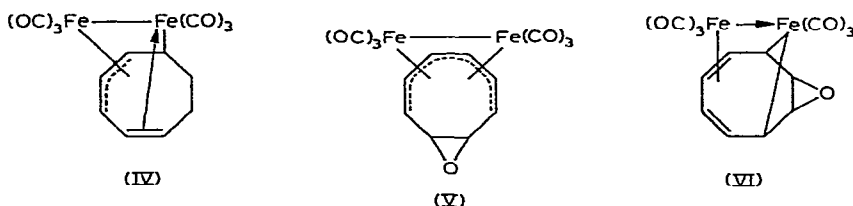
No iron tricarbonyl complex of (I) could be isolated but the large amount of polymer may be evidence for polymerization of such a species. The cyclooctatetraeneiron carbonyls, which are formed (*ca.* 5%) under all conditions (petroleum ether, diethyl ether, methylene chloride, hexane, benzene, octane; 25°–125°) are probably produced via prior deoxygenation by $\text{Fe}_2(\text{CO})_9$, followed by complex formation.

The small amounts of aldehyde and ketone complexes formed in non-aromatic solvents (3%) might result from reaction of (I) or (II) with traces of acid in the $\text{Fe}_2(\text{CO})_9$. However, under conditions where no (II) was isolated (refluxing benzene or toluene), the yield of (III) greatly increased, and (III) became the principal product (*vide infra*).

To our knowledge, (II) is the first reported epoxide-transition-metal complex*. Its structure follows from the mass spectrum (M^+ 400), IR spectrum (cyclohexane) [$\nu(\text{C}\equiv\text{O})$ 2078, 2048, 2005, 1997, 1988, 1949 cm^{-1}] and NMR spectrum (CS_2) (τ 6.87, 2 H singlet, $\text{H}_{a,a'}$; τ 6.70, 2 H multiplet, $\text{H}_{c,c'}$; τ 5.95, 2 H doublet, $\text{H}_{b,b'}$; τ 4.49, 2 H multiplet, $\text{H}_{d,d'}$; J_{ab} 0 Hz, J_{bc} 6.5 Hz, J_{cd} 9.0 Hz, $J_{dd'}$ 11 Hz). The NMR absorptions were assigned as follows. The 2 H singlet at τ 6.87 should be due to H_a and $\text{H}_{a'}$ since the corresponding epoxide protons in (I) also appear as a discrete singlet. Apparently, the dihedral angle between the epoxide protons and the adjacent protons is *ca.* 90° in both (I) and (II). Irradiation at τ 6.70 collapses the other multiplets into singlets, thus securing this resonance as due to H_c and $\text{H}_{c'}$. Irradiation at τ 5.95 changes the multiplet at τ 6.70 into the mirror image of that at τ 4.49. These multiplets analyze as an AA'XX' system, indicating that the resonance at τ 5.95 must be due to H_b and $\text{H}_{b'}$. This is confirmed by decoupling the multiplet at τ 4.49, upon which the resonance at τ 6.70 collapses to a doublet. The NMR spectrum of (II), surprisingly, is temperature-independent (to *ca.* -80°), in contrast to that of the related (cyclooctatriene)diiron and

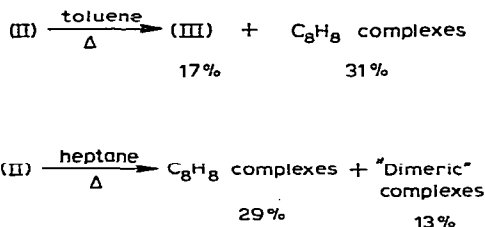
* X-ray structure determination is in progress (R. Eiss, Oregon Graduate Center).

(cyclooctatetraene)diruthenium hexacarbonyls⁴. The latter molecules have dissymmetric structures (IV), but are fluxional in solution and undergo an oscillatory rearrangement which interconverts the two mirror images^{4,5}. Upon lowering the temperature, the rearrangement is slowed so that with (IV), broadening of the NMR spectrum begins to occur at -15° , with final resolution⁴ at -87° . The symmetrical and static spectrum of (II) suggests that it may *not* be fluxional and may possess either of the symmetrical structures (V) or (VI) which have also been proposed for diiron hexacarbonyl complexes⁶.



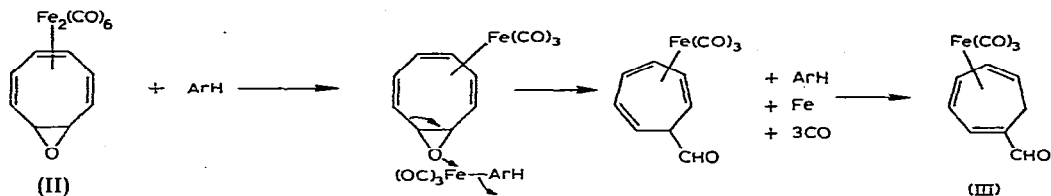
Thermolysis of (II) revealed that coordination opens pathways unavailable for (I), itself. Under conditions in which (I) is inert (refluxing toluene, 3 h) (II) was converted to a mixture of (III) (17%) and cyclooctatetraene complexes [$C_8H_8Fe(CO)_3$, 25%; *trans*- $C_8H_8Fe_2(CO)_6$, 4%; $C_8H_8Fe_2(CO)_5$, 2%]. The same products in similar yields were obtained in benzene.

Thermolysis in refluxing heptane (15 h) also gave deoxygenation [$C_8H_8Fe(CO)_3$, 23.5%; *trans*- $C_8H_8Fe_2(CO)_6$, 3%; $C_8H_8Fe_2(CO)_5$, 2.5%], together with two substances (13%) (not further investigated) for which mass spectral analysis gave the formulas $(C_8H_8O)_2Fe_2(CO)_4$ and $(C_8H_8O)_2Fe(CO)_2$. No traces of (III) could be detected. Thermolysis in dioxane gave similar results.



The deoxygenations must be effected by iron(0), although the pathways are not clear. Formation of $C_8H_8Fe(CO)_3$, however, indicates that an *intramolecular* mechanism may be of importance. The appearance of the cycloheptatriene-1-carboxaldehyde complex (III) at temperatures as low as 80° reveals that coordination markedly lowers the barrier to rearrangement, since (I) affords the corresponding 1-carboxaldehyde (via the 3-carboxaldehyde) only on pyrolysis² at 330° . Moreover, aromatic solvents seem to be necessary for rearrangement to (III). In fact, reaction of (I) with $Fe_3(CO)_{12}$ in benzene leads directly to (III), probably via (II).

A tentative mechanism involves solvent-assisted dissociation of (II), with formation of a transient areneiron tricarbonyl complex. This species might act as a Lewis acid and catalyze the ring contraction. Subsequent hydrogen transfer leads to (III), which is probably the thermodynamically-favored aldehyde complex.



Because this work is the only reported study of the thermolysis of an $\text{Fe}_2(\text{CO})_6$ complex, the generality of the novel arene-assisted iron-iron bond cleavage is unknown. Further experiments on thermolyses of $\text{Fe}_2(\text{CO})_6$ complexes are in progress.

EXPERIMENTAL

All reactions and separations were carried out under nitrogen. Proton NMR spectra were recorded on Varian HA-60 and T-60 spectrometers. IR spectra were measured on a Beckman IR-10 spectrophotometer. Mass spectra were recorded on an Atlas CH-9 spectrometer. Melting points were determined in air and are uncorrected. Elemental analyses were by Dornis and Kolbe, Mülheim, Germany.

Known compounds were identified by comparison of IR and NMR spectra with authentic samples.

Preparation of (cyclooctatetraene oxide)diiron hexacarbonyl (II)

To a solution of cyclooctatetraene oxide⁷ (10 g, 83 mmoles) in 250 ml of anhydrous ether was added diiron nonacarbonyl (50 g, 137 mmoles). The mixture was flushed with nitrogen and heated to reflux for 60 h. The resulting brown mixture was filtered, the solvent evaporated and the residue extracted with petroleum ether, giving a red-orange solution. The extract was concentrated and chromatographed on a neutral alumina column (activity 3). Elution with petroleum ether gave an orange-red band containing $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ (0.35 g, 1.6%) and *trans*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$ (0.16 g, 0.5%). Next was eluted a yellow band consisting of (II). Recrystallization from petroleum ether gave pale yellow rhomboids, m.p. 128–130° decomp. (Found: C, 42.10; H, 2.13. $\text{C}_{14}\text{H}_8\text{Fe}_2\text{O}_7$ calcd.: C, 42.05; H, 2.00%).

Elution with petroleum ether/benzene (1/1) gave a red-brown band containing $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_5$ (0.71 g, 2.3%) followed by a yellow band containing (III). The latter substance was identical with that obtained from thermolysis of (II) (*vide infra*).

Elution with a 1/2 mixture of petroleum ether/benzene gave a yellow band containing (cyclooctatrienone)iron tricarbonyl (0.20 g, 0.9%), followed by a yellow-orange band containing (cyclooctatrienone)diiron hexacarbonyl (0.20 g, 0.6%).

Thermolysis of (II) in toluene

A solution of (cyclooctatetraene oxide)diiron hexacarbonyl (0.24 g, 0.6 mmoles) in 10 ml of toluene was heated to reflux for 3 h. The toluene was taken off at reduced pressure and the residue extracted with petroleum ether. The extract was concentrated and chromatographed on a neutral alumina column (reactivity 3). Elution with petroleum ether gave an orange-red band containing $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ (0.036 g, 25%) and *trans*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$ (0.008 g, 3.6%). Elution with petroleum ether/benzene (1/1) gave a red-brown band containing $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_5$ (0.005 g, 2.1%) and a yellow

band containing (III). Evaporation of the solvent from the yellow fraction gave an oily solid which was recrystallized from petroleum ether to give a yellow powder. Sublimation (70°/0.02 mm) gave yellow crystals of (III), m.p. 88–90°. (Found: C, 50.76; H, 3.12; Fe, 21.56. $C_{11}H_8FeO_4$ calcd.: C, 50.76; H, 3.15; Fe, 21.54%.)

Thermolysis of (II) in n-heptane

A solution of (cyclooctatetraene oxide)diiron hexacarbonyl (0.44 g, 1.1 mmoles) in 30 ml of n-heptane was heated to reflux for 15 h. The n-heptane was taken off at reduced pressure and the residue extracted with petroleum ether. The extract was concentrated and chromatographed on a neutral alumina column (reactivity 3). Elution with petroleum ether gave an orange-red band containing $C_8H_8Fe(CO)_3$ (0.064 g, 23.5%) and *trans*- $C_8H_8Fe_2(CO)_6$ (0.013 g, 3.1%). Elution with petroleum ether/benzene (1/1) gave a red-brown band containing $C_8H_8Fe_2(CO)_5$ (0.010 g, 2.5%). Next was eluted a yellow band which afforded a yellow solid on evaporation of solvent. TLC showed the presence of two components for which mass spectral analysis gave the formulas $(C_8H_8O)_2Fe_2(CO)_4$ and $(C_8H_8O)_2Fe(CO)_2$.

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