Ring Expansion in Some Organometallic Compounds of Iron

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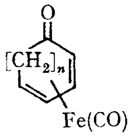
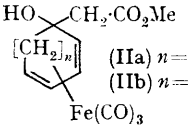
CHANGES in the size of organic ring systems have previously been noted in only two reactions of organometallic complexes. Pauson[1] observed the contraction of a seven- to a six-membered ring in the reaction of the tricarbonyl-(π-tropylium)-chromium cation with sodium cyclopentadienide, whilst Fischer and Breitschaft[2] observed the expansion of a six- to a seven-membered ring in the reaction of the complexes (π-C_5H_5)M(π-C_6H_6) (M = Cr or Mn) with acetyl chloride and aluminium bromide. We report a series of reactions involving the expansion of a six- to a seven- and a seven- to an eight-membered ring with iron tricarbonyl adducts: this reaction may have general applicability.

In our study of co-ordinated ligands we have examined the reactions of the iron tricarbonyl complexes of cyclohexa-2,4-dienone[3] (Ia) and cyclohepta-2,4-dienone[4] (Ib). Under the conditions of the Reformatskii reaction, both ketones react with methyl α-bromoacetate and zinc to give the expected hydroxy-esters (II). Both hydroxy-esters react with trityl fluoroborate in dichloromethane to give dienyl salts, and in each case the organic product is triphenylmethanol. The n.m.r. spectrum of the salt derived from the six-membered ring homologue reveals that a ring-expansion has occurred to give the dienyl salt (IIIa). On attempted recrystallisation of (IIIa) from water we obtained the 1-methoxycarbonylcycloheptatriene complex (IV), the i.r. spectrum of which shows a strong band at 1610 cm.$^{-1}$ due to the unco-ordinated double bond. In concentrated sulphuric acid protonation of (IV) occurs to produce (IIIa). The n.m.r. spectrum of the salt derived from the seven-membered ring alcohol (IIb) indicates that the salt is the straightforward product (IIIb), but on attempted recrystallisation from water the neutral compound (V) is obtained. The triene complex (V) is soluble in concentrated sulphuric acid and its n.m.r. spectrum in this solvent corresponds to the tricarbonyl-(1-methoxycarbonylcyclo-octadienyl)-iron cation. On dilution with water, (V) is recovered unchanged.

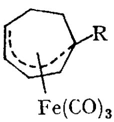
A study of the enol reactions of the two ketones provides an illustration of a fundamental difference between the six- and seven-membered ring compounds. Thus, although iron tricarbonyl complexes of cycloheptatriene are well known,[5] the corresponding benzene compounds have not been isolated.[6] In the Mannich reaction of ketones with dimethylamine and formaldehyde an enol intermediate is generally assumed; thus for the six-membered ring an arene intermediate would be required. Under the conditions of the Mannich reaction the cycloheptadienone complex (Ib) gave the α-dimethylaminomethyl derivative (VI) in 88% conversion, but under the same conditions the six-membered homologue decomposed extensively and we recovered only 20% of starting material with no detectable α-aminomethylation.



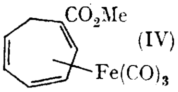
(Ia) $n=1$
(Ib) $n=2$



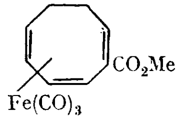
(IIa) $n=1$
(IIb) $n=2$



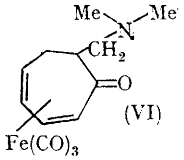
(IIIa) $R=CO_2Me$
(IIIb) $R=CH_2 \cdot CO_2Me$



(IV)



(V)



(VI)

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