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SYNTHESIS OF CYCLIC KETONES VIA IRON TRICARBONYL COMPLEXES

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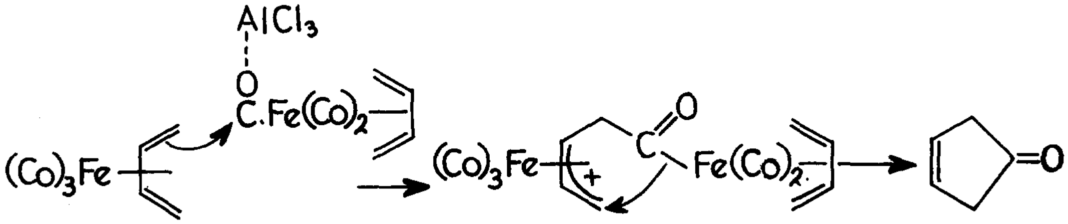
In our earlier studies[1] on the reaction of tricarbonyl-cyclooctatetraene-iron(1) with aluminium chloride we observed the formation of the cyclic ketonic complex (2). This product was formally derived by the addition of carbon monoxide to the starting material. We envisaged that this type of reaction could be extended to the synthesis of cyclopentenones from tricarbonyl-1,3-dieneiron complexes *via* the mechanism[†] shown below :



We initially examined the reaction of the quinodimethane complex (3;R=H) since this should give the stable product 2-indanone (4;R=H). This complex had previously been prepared[2] in 5% yield by the reaction of α, α[1] dibromo-*o*-xylene with $Fe_2(CO)_9$, but it can be prepared in much higher yield (35%) by reaction of the dibromide with $Na_2Fe(CO)_4$. When this complex (3;R=H)(1 mole) was reacted with anhydrous $AlCl_3$ (1.1 mole) in benzene at room temperature an orange gum rapidly separated out of solution. After stirring for 2 hours the mixture was

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[†] The mechanism by which these reactions occur is currently under investigation but it is known to be independent of CO concentration.

worked up in the usual way to give 2-indanone (4;R=H) in 48% yield.

The quinodimethane complex (3;R=H) behaves as a normal aromatic compound and not as a **diene**. It reacts very readily with acetyl chloride at 0° to give a high yield of the complex (3;R=CO.Me) as yellow crystals m.p. 78-80° (from pentane)(Found:C, 54.9; H, 3.7; M, 286.$C_{13}H_{10}FeO_4$ requires C, 54.6; H, 3.5%; M, 286) $\nu_{max.}$(hexane) 2056, 1990 and 1690 cm^{-1}. δ ($CDCl_3$) 8.2(1H,s), 7.88 (1H, d, J 8Hz), 7.50 (1H, d, J 8Hz), 2.60 (3H,s), 2.50 (2H,m) and 0.36 (2H,m).

The substituted complex (3;R=CO.Me) reacted readily with $AlCl_3$ to give 5-acetyl-2-indanone (4;R=CO.Me) as colourless plates (45%) m.p. 96-98°. (Found C, 75.5; H, 5.7.$C_{11}H_{10}O_2$ requires C,75.8; H,5.8%) $\nu_{max.}$ 1756 and 1682 cm^{-1}. $\lambda_{max.}$(EtOH) 253 nm. δ($CDCl_3$) 7.90 (1H,s), 7.85 (1H, d, J 9Hz.), 7.40 (1H, d, J 9Hz.), 3.60 (4H,s) and 2.60 (3H,s).

The synthesis of (4;R=CO.Me) from (3;R=H) can be carried out by adding 1 mole of $CH_3COCl/AlCl_3$ in CH_2Cl_2 dropwise to a solution of the complex (1 mole) in CH_2Cl_2 at 0°, stirring for 2 minutes and then adding more $AlCl_3$ (1.5 moles) and stirring at room temp. for 2 hours. Work up in the usual way gave (4;R=CO.Me) (42%).

Reaction of the isoindene complex (5)[2] with $AlCl_3$ did not give the expected bicyclic ketone (6) but instead gave the iron tricarbonyl complex (7) which was isolated by chromatography as yellow crystals (46%) m.p. 100-102° (Found: C, 57.5; H, 3.6; M, 312.$C_{15}H_{12}FeO_4$ requires C, 57.7; H, 3.8%; M, 312) $\nu_{max.}$(hexane) 2066, 2012, 1992 and 1645 cm^{-1}. The difference in the course of the reaction is probably due to steric factors since the bicyclic ketone (6) is a very strained system.

When the tetralone complex (7) was reacted with carbon monoxide (80 ats, 30°) a new complex (8) was obtained as a colourless oil, $\nu_{max.}$(hexane) 2104, 2056, 2036, 2026, 1702 and 1653 cm^{-1}. The absorptions at 2104, 2056, 2036 and 2026 are typical of an $Fe(CO)_4$ complex[1] and the absorption at 1702 was assigned to the bridging acyl group[1]. The complex (8) was unstable and readily lost CO to reform (7). The interpretation of the ^{1}H n.m.r. spectra of the complex (7) and (8) was aided by the use of a Europium shift reagent (see Table).

Reaction of tricarbonyl-butadieneiron with $AlCl_3$ gave a low yield (ca.5%)

of a mixture of 2- and 3-cyclopentenone, the major product being unreacted starting material (80%). Reaction of substituted tricarbonyl-butadieneiron complexes also gave low yields of cyclopentenones and further studies are in progress to extend this work to a general synthesis of cyclopentenones in good yield.

TABLE

^{1}H n.m.r. Absorptions

(0.2M solutions in $CDCl_3$; δ values, *J* in Hz.)

Shift on addition of 0.05m moles of $Eu(FOD)_3$ is shown in brackets

	Compound (7)	Compound (8)
8-H	8.6,m (1.2)	8.18,m (0.7)
6,7-H	7.6,m (0.24)	7.48,m (0.1)
5-H	7.3,m (0.2)	7.22,m (0.2)
4-H	4.25,s (0.3)	3.70,d,*J* 1.5, (0.32)
2-H	2.75,bs (0.9)	3.60, d, *J* 1.5, (1.06)
3-Me	1.4,s (0.37)	1.28,s (0.24)
3-Me	0.6,s (0.32)	0.98,s (0.32)

ACKNOWLEDGEMENTS

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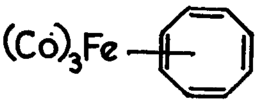
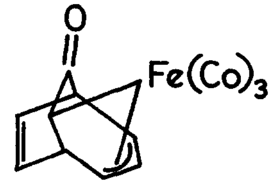
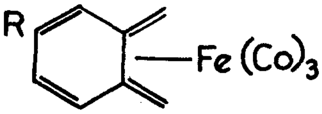

(Co)3Fe

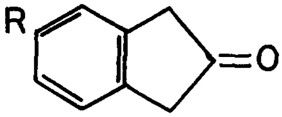
(1)


O
Fe(Co)3

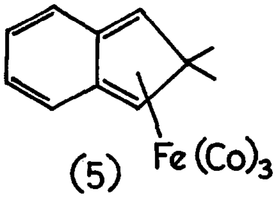
(2)


R
Fe (Co)3

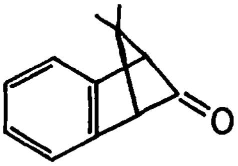
(3)


R
O

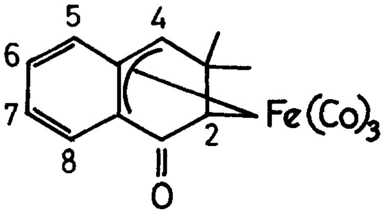
(4)


Fe (Co)3

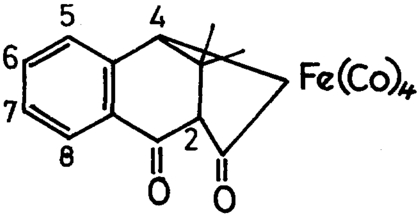
(5)


O

(6)


5
4
6
7
8
2
Fe(Co)3
O

(7)


5
4
6
7
8
2
Fe(Co)4
O
O

(8)