Electrophilic Substitution Reactions of Co-ordinated Cyclo-octatetraene

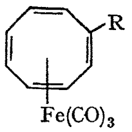
By B. F. G. JOHNSON, J. LEWIS,* A. W. PARKINS, and G. L. P. RANDALL
(*Department of Chemistry, University College, London, W.C.*1)

CYCLO-OCTATETRAENE does not readily undergo electrophilic substitution reactions employing the *usual* organic methods, and substituted derivatives are in general prepared by indirect means (see, *e.g.*, ref. 1). It is now well established that the reactivity of olefins is modified on co-ordination to metal-containing units (see, *e.g.*, ref. 2). This led us to examine the reactivity of cyclo-octatetraene co-ordinated to iron tricarbonyl.

Cyclo-octatetraeneiron tricarbonyl (I) reacted with phosphorus oxychloride in dimethylformamide, and a red solid was isolated (60%), $C_{12}H_8O_4Fe$ (II). The i.r. spectrum (CCl_4) showed absorptions due to CO stretching vibrations of both co-ordinated carbonyl (2060s, 2000s, and 1988s cm.$^{-1}$) and aldehyde group (1680 cm.$^{-1}$). Elemental analysis was satisfactory, and the molecular weight of the complex was determined from the mass spectrum. The n.m.r. spectrum (100 Mc./sec. in CS_2 with Me_4Si as internal standard at 30°) showed a singlet at τ 0·72, a doublet at τ 3·91, a complex multiplet centred at τ 4·66 and a triplet at τ 5·62. The signals at τ 3·91 and τ 5·62 showed some fine structure. This spectrum is temperature dependent, and dependence studies are best interpreted in terms of a fluxional system.

Oxidation with Ce^{4+} in water–ethanol (1 : 10) displaced the iron tricarbonyl unit to give the free aldehyde C_9H_8O (IX) in good yields. This provides a useful synthetic method for the production of cyclo-octatetraene derivatives directly from the parent hydrocarbon. In the mass spectrum of this aldehyde an intense molecular ion *m/e* 132 and an ion *m/e* 104 corresponding to the loss of a CO group were observed, together with the appropriate metastable peak at *m/e* 82. Other peaks corresponding to the fragmentation of a cyclo-octatetraene unit were also present.

Reduction of (II) with sodium borohydride in ethanol gave the alcohol $C_{12}H_{10}O_4Fe$ (III) in 80% yield. The mass spectrum showed a molecular ion *m/e* 274 and the i.r. spectrum confirmed the presence of an alcoholic OH group. When (II) was reacted with methyl Grignard reagent, a secondary alcohol $C_{13}H_{12}O_4Fe$ (IV) was produced. Both alcohols (III) and (IV) readily undergo hydroxide-ion abstraction with hexafluorophosphoric acid to produce the salts $C_{12}H_9O_3FePF_6$ (VI) and $C_{13}H_{11}O_3FePF_6$ (V), respectively. These undergo nucleophilic addition reactions to produce a variety of substituted cyclo-octatetraene complexes $C_{12}H_9O_3YFe$ (III) where Y = OH, (VII; Y = MeO, CN, or C_4H_8NO) and $C_{14}H_{14}O_4Fe$ (VIII).

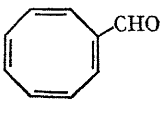


(I) R=H
(II) R=CHO
(III) R=CH_2OH
(IV) R=MeCHOH

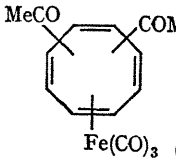
(VII) R=CH_2Y
(VIII) R=MeCHOMe
(X) R=MeCO

$[C_{10}H_{11}Fe(CO)_3]^+$ PF_6^-
(V)

$[C_9H_9Fe(CO)_3]^+$ PF_6^-
(VI)



(IX)



(XI)

In addition, the co-ordinated cyclo-octatetraene undergoes acetylation reactions under *typical* Friedel–Crafts conditions to yield amongst other products mono- and di-acetyl derivatives $C_{13}H_{10}O_4Fe$ (X) and $C_{15}H_{12}O_5Fe$ (XI). Reduction of (X) with sodium borohydride in ethanol gives the secondary alcohol (IV). In contrast the Friedel–Crafts' reactions of cyclo-octatetraene with acetyl bromide or propionyl chloride and aluminium trichloride gives a 2—3% yield of *o*-methyl- or *o*-ethyl-cinnamaldehyde, respectively. The main portion of the cyclo-octatetraene is polymerised under these conditions.[3]

The electrophilic substitution reactions of cyclo-octatetraeneiron tricarbonyl are obviously related to those of cyclobutadieneiron tricarbonyl.[2]

(*Received, March* 28*th*, 1969; *Com.* 442.)

---

[1] G. Schroder, "Cyclooctatetraen", Verlag Chemie, Weinheim, 1965.
[2] M. L. H. Green, "Organometallic Compounds," vol. II, Methuen, London, 1968.
[3] A. C. Cope, T. A. Liss, and D. S. Smith, *J. Amer. Chem. Soc.*, 1957, **79**, 240.