Mercuration of Cyclobutadienyliron Tricarbonyl

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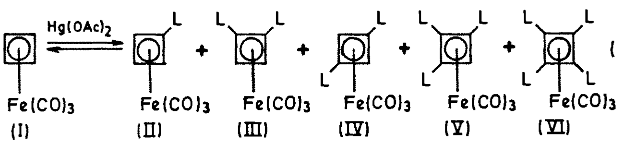
Summary The mercuration of cyclobutadienyliron tricarbonyl proceeds with unusual ease and leads to all possible mercurated derivatives of the parent system

IN the case of a few particular aromatic systems, notably thiophen and pyrrole, the mercuration reaction proceeds very readily and can result in permercurated derivatives [1,2] Although the details are not clear, the reaction is generally considered to involve electrophilic substitution [3] We report now that mercuration of cyclobutadienyliron tricarbonyl (I), which has previously been found to undergo electrophilic substitution reactions,[4] also proceeds extremely readily and, like the heterocyclic systems mentioned above, leads to polymercurated derivatives

The ease with which cyclobutadienyliron tricarbonyl is mercurated is demonstrated in the following reaction Treatment of equimolar quantities of (I) and mercuric acetate in acetic acid for 30 min at room temperature leads to an equilibrium mixture of all possible acetoxymercury derivatives (II—VI, L = HgOAc) (reaction 1)



The analysis of the mixture is determined by treatment of the product solution with KI_3 whereby the mercury derivatives are converted into the corresponding iodo-derivatives (II—VI, L = I) The iodo-compounds can be separated by chromatography over alumina, their physical properties and the extent to which they are found in the total crude reaction mixture which, in turn, reflects the ratio of the corresponding mercury derivatives are given in the Table The ratio of these products showed no significant change when the mercuration was carried out for longer periods

The reversibility of the mercuration of (I) is shown by allowing pure monoacetoxymercury cyclobutadienyliron tricarbonyl to stand in acetic acid, after 30 min all possible mercury derivatives, together with the parent complex, are observed in solution The tetra-acetoxymercury complex (VI, L=HgOAc) also disproportionates in acetic acid to yield all the possible mercury derivatives

Competition experiments between the complex (I) and ferrocene indicated that they are of comparable reactivity towards mercuration However, the disposition of the mercury atoms in the ferrocene system has not been studied in detail, in particular no evidence has been obtained for the existence of higher than dimercurated derivatives [6]

Properties and distribution of iodocyclobutadienyliron carbonyl derivatives obtained from the equilibrium reaction (1)

Compound[a]	M p	N m r (τ)	Mole ratio[b]
Parent (I)		6 04	12 0
Monoiodo (II)	5°	5 83(2), 5 50(1)	5 5
1 2-Di-iodo (III)	72°	5 37(J_{HH}0)[c]	2 0
1,3-Di iodo (IV)	[d]	5 52	0 5
1,2,3,-Tri-iodo (V)	39—40°	5 05	1 0
1,2 3,4-Tetraiodo (VI)	116—117°		1 0

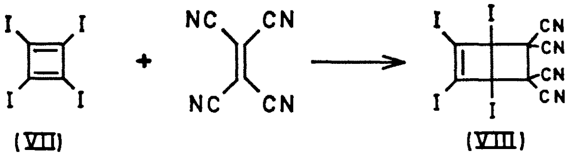
[a] Satisfactory elemental analysis was obtained for each iodocyclobutadienyliron tricarbonyl complex

[b] The ratio of products was determined by n m r integration The amount of tetraiodo product present was found by isolation and also estimated by addition of a known amount of toluene to the weighed n m r sample then by difference in the total integration of the ligand protons The two methods gave reasonable agreement

[c] The orientation of the two iodine atoms in complexes (III) and (IV) was determined from the magnitude of the hydrogen coupling constants revealed in the ^{13}C satellite proton spectrum (ref 5)

[d] The product was liquid at room temperature but small amounts of compound (III) remained as an impurity

The mercuration reaction followed by treatment with KI_3 offers a simple method of synthesis of the various iodinated cyclobutadiene complexes which have hitherto been unavailable through direct halogenation of (I) Thus, heating (I) at 60—70° in acetic acid with an excess of $Hg(OAc)_2$, followed by treatment with KI_3, affords the tetraiodo-derivative (VI) in 33% yield. Tetraiodocyclobutadiene (VII), liberated from the complex (VI) through oxidative decomposition with ceric ion, reacts with tetracyanoethylene to yield the substituted bicyclohexene derivative (VIII) †



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