The Structure and Some Reactions of the Iron Tricarbonyl Complex of Thebaine

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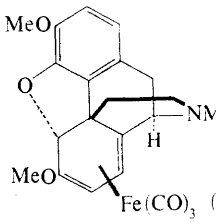
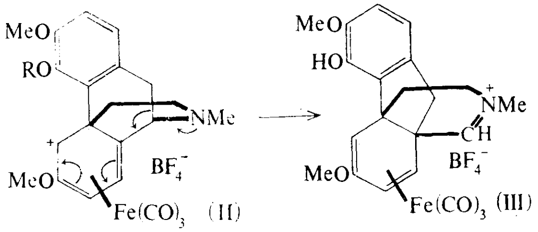
THE opium alkaloid thebaine reacts with triirondodecacarbonyl or ironpentacarbonyl to give the adduct (I). The detailed chemistry of (I) will be reported elsewhere, but it should be noted that complexing profoundly changes the properties of the methoxycyclohexadiene ring and adjacent structures. For example, cleavage of the oxide ring occurs readily with aqueous fluoroboric acid to the salt (II; R = H) and in the presence of acetic anhydride to the salt (II; R = Ac).



(I)

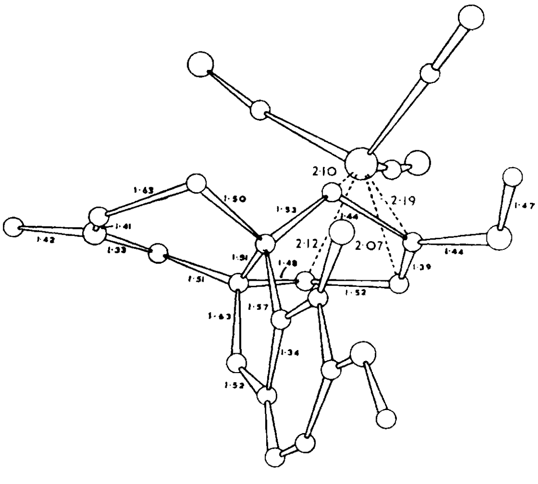


Refluxing the salt (II; R = H) in a solvent such as ethanol causes rearrangement which is new in the morphine series despite the large number of carbonium ion rearrangements already observed. The structure has been shown by *X*-ray analysis to be (III), in which ring-contraction had occurred.

Important intramolecular bond-lengths are shown in the Figure; the Fe(CO)$_3$ group is bound to the "butadiene" structure, the bond-lengths in which are similar to those reported[1] for a variety of such complexes. Estimated standard deviations of the metal–carbon bond-lengths average 0·01 Å; those of the C–C, C–N, and C–O values average 0·03 Å (R = 0·11 for 1200 independent reflexions). The n.m.r. spectrum can be completely assigned on the basis of the solid-state structure.

Other rearrangements of similar carbonium ions result in final production of an aromatic ring;[2] the present rearrangement reflects the stability of the iron–"butadiene" bond[3] compared with the iron–arene bond which would result from the usual types of rearrangement.

Accepting the demonstrated absolute configuration of thebaine[4] and that the bridge and Fe(CO)$_3$ groups remain on the same sides of the molecules in (III) as they are in (I), then formulae (I) and (III) and the Figure represent absolute configurations.



FIGURE

We are indebted to the Science Research Council for support of these studies.

(*Received, March* 21*st*, 1968; *Com.* 357.)

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[1] M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, 1967, **5**, 93.
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[4] J. Kalvoda, P. Buchschacher, and O. Jeger, *Helv. Chim. Acta*, 1955, **38**, 1847.