Reaction of Methylenecyclopropanes with Enneacarbonyldi-iron: a New Route Tricarbonyltrimethylenemethaneiron Complexes

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STABILIZATION of unstable organic molecules, including cyclobutadiene,[1] carbene,[2] *o*-quinodimethane,[3] and benzyne[4] as transition-metal ligands has been studied. Trimethylenemethane (I) has also received attention because of the maximum bond order possible for the central carbon atom,[5] and the triplet ground electronic state.[6] The stabilisation of the reactive species as the tricarbonyliron complex (IIa) was first achieved by reduction of 3-chloro-(2-chloromethyl)-propene with enneacarbonyldi-iron.[7] We report a convenient synthesis of tricarbonyliron complexes of substituted trimethylenemethanes, from readily accessible methylenecyclopropane derivatives (III).[8]

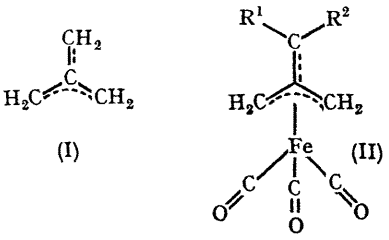
An equimolar mixture of 1-methylene-2-phenylcyclopropane (IIIb) and enneacarbonyldi-iron in benzene was stirred at room temperature for 5 hr. under nitrogen to give tricarbonyl(phenyltrimethylenemethane)iron (IIb) (40%). The structure was confirmed by comparison of the i.r. and n.m.r. spectra with those of an authentic specimen. Similarly 2-methyl-2-phenyl- and 2,2-diphenyl-methylenecyclopropane [(IIIc) and (IIId)] gave (IIc) (60%) and (IId) (50%). Methylenecyclopropane (IIIa) itself, however, gave butadienetricarbonyliron (*ca.* 2%) rather than (IIa). As might be expected, the mass spectra of the trimethylenemethane complexes (IIb—d) exhibited characteristic cracking patterns arising from successive loss of carbon monoxide, and other fragmentations showed close resemblance to those of the original methylenecyclopropanes.

Introduction of phenyl groups into the trimethylenemethane portion of the complex does not greatly affect the principal carbonyl frequencies (Table).[9] This might imply that, in agreement with the result of the *X*-ray diffraction study,[10] the phenyl ring is not coplanar with the plane of the adjacent sp^2 carbon atom even in solution.

Tricarbonyl(trimethylenemethane)iron complexes

	M.p.	νCO (cm.$^{-1}$ (in CCl_4)* Narrow band	Broad band
(IIa)	32·5—33·0°	2061m	1995s, 1966w
(IIb)	63—64	2058m	1996s, 1966w
(IIc)	Oil	2087w, 2054m, 2010m	1993s, 1960w
(IId)	157—158	2057m	1995s, 1965w

* The values are believed to be accurate to ±1 cm.$^{-1}$.



a; $R^1=R^2=H$
b; $R^1=H$, $R^2=Ph$
c; $R^1=Me$, $R^2=Ph$
d; $R^1=R^2=Ph$

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