The *ortho*-Metallation Reaction of Thiobenzophenones with Di-iron Enneacarbonyl

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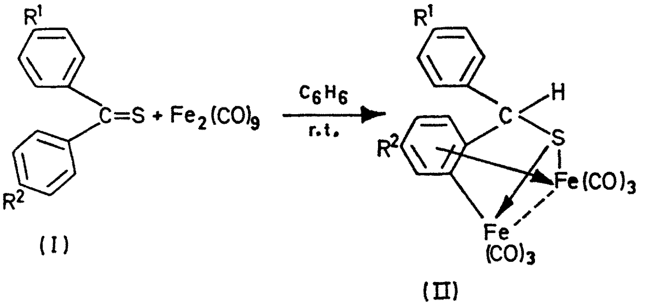
Summary Thiobenzophenones react with di-iron enneacarbonyl [$Fe_2(CO)_9$] in benzene at room temperature to form *ortho*-metallated products.

THE reaction of carbon disulphide with metal carbonyls such as $Fe_2(CO)_9$[1] and dicobalt octacarbonyl[2] results in the formation of complexes having a sulphur and/or carbon atom co-ordinated to the metal. To our knowledge, there have been no publications concerning the reaction of thioketones and simple metal carbonyls.[3] We now report the isolation of *ortho*-metallated products[4] by treatment of thiobenzophenones with $Fe_2(CO)_9$.

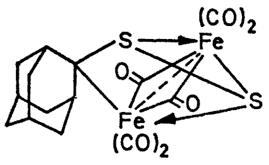


(I)

(II)

Reaction of the appropriate thiobenzophenone (I; $R^1 = R^2 = H$, OMe, NMe_2),[5] with $Fe_2(CO)_9$ in anhydrous benzene at room temperature for 36 h (work-up by column chromatography of the reaction mixture on Florisil using pentane or pentane–benzene as eluant) gave crystalline red or purple-red air-stable complexes (II; $R^1 = R^2 = H$, OMe, NMe_2), in good to excellent yields. The structure (II) for these complexes was elucidated on the basis of elemental analyses,† molecular weight as determined by vapour-pressure osmometry and mass spectrometry, and spectral results. For example, (II; $R^1 = R^2 =$ OMe) gave the following pertinent data: m.p. 96—98° (s.t.); a vapour pressure osmometrically determined molecular weight of 542 [538 calc.]; mass spectrum shows the parent molecular ion peak at m/e 538 as well as peaks at m/e 510 $[M - CO]^+$, 482 $[M - 2CO]^+$, 454 $[M - 3CO]^+$, 426 $[M - 4CO]^+$ 398 $[M - 5CO]^+$, 370 $[M - 6CO]^+$, 112 $[Fe_2]^+$, and 56 $[Fe]^+$; i.r. spectrum (CCl_4) exhibits intense terminal metal carbonyl stretching bands at 2069, 2033, and 1995 cm^{-1} and a shoulder at 1976 cm^{-1} (no absorption bands due to bridging carbonyls); n.m.r. spectrum ($CDCl_3$) displayed singlets at 3·70 (OCH_3, complexed ring), 3·83 (OCH_3, uncomplexed ring), and 5·43 p.p.m. (CH–S), quartets centred at 6·28 and 6·67 p.p.m. (J 8 Hz, two protons on adjacent carbons of complexed benzene ring), a quartet centred at 7·20 p.p.m. (J 9 Hz, protons of uncomplexed benzene ring), and a broad absorption centred at 7·63 p.p.m. (isolated proton of complexed benzene ring)—relative integration of 3·0 : 3·0 : 1·0 : 2·0 : 4·0 : 1·0. The unsymmetrical thioketone, 4-methoxythiobenzophenone, reacted with $Fe_2(CO)_9$ to form (II; R^1 = OMe, R^2 = H, m.p. 131·0—131·5°) and (II; R^1 = H, R^2 = OMe, m.p. 125·0—126·0°). The latter complex was eluted after the former on acidic alumina using petroleum or petroleum–ether as eluant. Pauson and his co-workers[6] have obtained complexes analogous in some respects to (II) by treatment of Schiff bases with $Fe_2(CO)_9$.

We are currently investigating the cleavage of (II) with various reagents as well as the reactions of non-aromatic thioketones with $Fe_2(CO)_9$. For instance, (III) is the major complex formed in the reaction of adamantanethione[7] with $Fe_2(CO)_9$. This tentative structure was assigned on the basis of its i.r., n.m.r., and mass spectra and its elemental analysis. Carbon–iron σ-bond formation occurs in (III), like in (II) and in addition, the adamantane complex has bridging carbonyls and an extra sulphur atom. Dispiro[1,3-dithietan-2,2′ : 4,2″-adamantane], the dimer[7] of adamantanethione, failed to react with $Fe_2(CO)_9$, indicating that (III) did not result *via* initial dimerization of the thioketone. The additional sulphur atom in the quite unstable complex (III) may arise *via* an intermolecular process.



(III)

Acknowledgments are made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Foundation of the State of New York, for support of this research.

(*Received, July* 16*th*, 1971; *Com.* 1225.

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† Satisfactory (±0·4%) C, H, S, and Fe analyses were obtained for all new compounds.

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[5] The thiobenzophenones (I; $R^1 = R^2$ = OMe, NMe_2) were commercial products while (I; $R^1 = R^2$ = H, and R^1 = H, R^2 = OMe) were prepared according to A. Schönberg and E. Frese, *Chem. Ber.*, 1968, **101**, 701.

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