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Preliminary communication

REACTION OF DIPHENYLCYCLOPROPENETHIONE WITH $\text{Mn}(\text{CO})_5^-$: RING CLEAVAGE, ALKYLATION, AND REDUCTION

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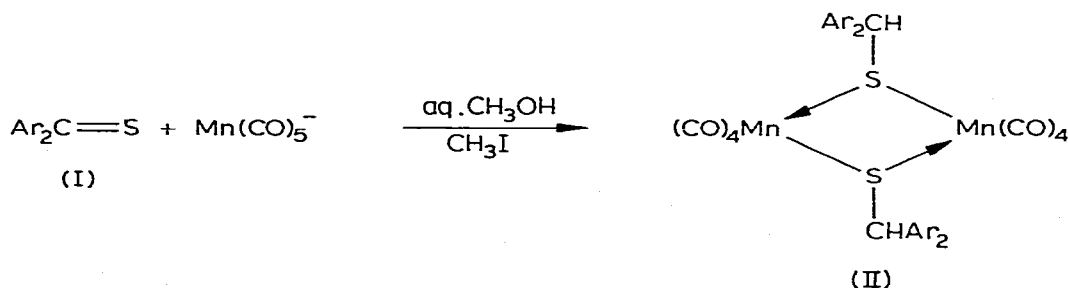
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Summary

Alkylation, reduction, and ring opening of diphenylcyclopropenethione to a π -allyl complex occurs on treatment with $\text{Mn}(\text{CO})_5^-$ and methyl iodide in aqueous methanol.

Thiobenzophenones (I) react with manganese pentacarbonyl anion and methyl iodide in aqueous methanol to give dimanganese octacarbonyl complexes (II) [1]. This reaction is believed to proceed via charge-transfer and radical intermediates



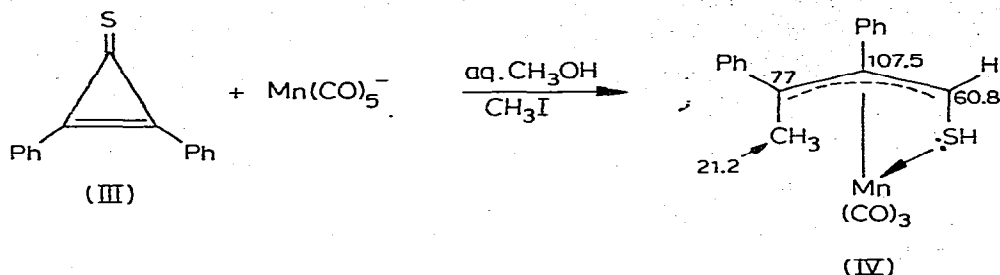
[2]. This communication describes the novel reaction of diphenylcyclopropenethione(III) with the metal carbonyl anion. It was of considerable interest to learn the effect of an α,β -double bond, and of ring strain*, on the reaction course.

Treatment of III with $\text{Mn}(\text{CO})_5^-$ (generated from $\text{Mn}_2(\text{CO})_{10}$ and NaOH) [4] for four hours at room temperature, followed by addition of an equimolar amount of methyl iodide gave the yellow, crystalline, air-stable π -allyl complex, IV, m.p. 179–180°C**. The ^1H NMR spectrum (CDCl_3 , TMS as internal standard) exhibited a singlet at δ 2.23 ppm (3H, CH_3), doublets at δ 1.73 ppm

* See ref. 3 for examples of metal carbonyl induced cleavage reactions of the strained azirine heterocycles.

** Satisfactory elemental analysis (C, H, S, Mn) and osmometric molecular weight were obtained for IV.

(1H, SH, $J = 2$ Hz) and δ 5.13 ppm (1H, CH), and a multiplet at δ 7.13–7.48 ppm (10H, Ph). The ^{13}C NMR chemical shifts (CDCl_3) for the methyl and π -allyl carbons of IV are noted with the structure (in addition, eight aromatic carbon resonances were observed at δ 124.8, 127.5, 128.0, 128.2, 128.6, 129.8, 136.8,



and 139.6 ppm. The chemical shifts for the methyl carbon, and for the π -allyl carbons bearing a phenyl group, are in good agreement with literature data for other π -allyl complexes [5, 6]. Terminal metal carbonyl stretching bands were observed in the infrared at 2005 cm^{-1} , 1931 cm^{-1} , and 1907 cm^{-1} . Absorption bands at similar positions have been reported for other $\text{Mn}(\text{CO})_3$ complexes [7, 8]. The mass spectrum of IV displayed a molecular ion peak at m/e 378, followed by successive loss of three carbonyl groups.

Complex IV is the first example, to our knowledge, of a sulfur-donor ligand π -allyl manganese complex. Furthermore, an unusual hydrogenation of the thione group occurs in the conversion of III to IV. In addition, alkylation takes place at a phenyl substituted carbon, rather than at the carbon or sulfur atom of the thiocarbonyl group [9]. In contrast, for thiobenzophenones, hydrogen abstraction from solvent to give II from I is a much more facile process than alkylation.

The mechanism of this interesting ring-cleavage reaction, and a determination of the reaction sequence (i.e. ring opening, alkylation, reduction), is currently being investigated.

Acknowledgments

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