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A NEW AND FACILE ROUTE FROM A THIAPHANE TO A CYCLOPHANE VIA IRON PENTACARBONYL

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Summary

2,11-Dithia[3,3]paracyclophane is converted into [2.2]-paracyclophane in 62% yield by treatment with $Fe(CO)_5$ in refluxing toluene.

Introduction

Cyclophanes have become of considerable interest to organometallic chemists during the last few years. This is reflected in numerous papers, mostly dealing with (a) the complexation of the aromatic rings of cyclophanes with metal atoms [1] or some common organometallic species such as $M(CO)_3$ ($M = Cr$, Mo, W) and $(\eta^5\text{-}C_5H_5)Fe^+$ [2] and (b) the behaviour of the sulphur atoms in the thiaphanes towards metal carbonyls [3] or some metal salts [4]. In one of these papers [3a] Koray and Ziegler studied the reaction of 2,6,15,19-tetrathia[7.7]paracyclophane with $Fe(CO)_5$ and found to their surprise, that this metal carbonyl brought about efficient elimination of the 1,3-dithiapropane unit from the thiaphane. It was assumed, that this elimination occurred by a radical mechanism. Unfortunately what happened to the fate of the residual *p*-xylyl radicals was not established; these could have been polymerized to polyparaxylene.

It seemed of interest to try this reaction with a more familiar to a thiaphane, namely 2,11-dithia[3.3]paracyclophane, and to see whether it was possible to achieve sulphur extrusion and obtain [2.2]paracyclophane in one step. Thiaphanes are usually converted into cyclophanes by pyrolysis of their sulfones or by photolysis with trialkylphosphites.

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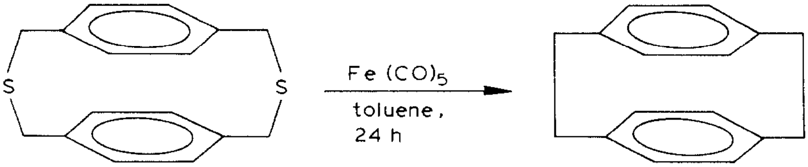

Fig. 1. Conversion of 2,11-dithia[3.3]paracyclophane into [2.2]paracyclophane.

Results and discussion

2,11-Dithia[3.3]paracyclophane was converted into [2.2] paracyclophane in 62% yield by treatment with $Fe(CO)_5$ in refluxing toluene. The identity of the [2.2]paracyclophane was confirmed by comparison of its melting point and mass- and ^{1}H-NMR spectra with those of an authentic sample. The yield depends greatly upon the degree of the dilution. The optimum condition proved to involve refluxing of a 0.0025 *M* solution of thiaphane in toluene with 58 mmol (8 ml) of $Fe(CO)_5$ for 24 h. This is consistent with the fact that at high dilution cyclization of radicals favoured over polymerization. The [2.2]paracyclophane is isolated readily by sublimation from the reaction residue, which also contains reactive iron powder, iron sulphide and polymeric material. If the reaction is carried out with $Fe_2(CO)_9$ in a lower boiling solvent such as ether or hexane sulphur extrusion does not occur and it seems that higher temperatures are essential. Another significant requirement seems to be the presence of the benzylic carbon–sulphur bonds in the starting compound. This is reflected in the fact that the reaction of $Fe(CO)_5$ with dibenzyl sulphide yields 1,2-diphenylethane (60%), whereas the same reaction with benzyl,2-phenylpropylsulphide gives no 1,3-diphenylpropane, 1,2-diphenylethane again being the main organic product.

These observations and the need for higher temperatures (boiling point of toluene) indicate, that the reaction probably proceeds through an intermediate iron complex. In fact a red iron compound was isolated when the reaction was stopped after 2–3 h [5]. Spectral data (IR, FD-mass, ^{1}H- and ^{13}C-NMR) and the elemental analysis show, that in this thiaphane-iron complex a $Fe(CO)_3$ group has been inserted into one of the four benzylic carbon–sulphur bonds and a $Fe(CO)_4$ moiety is coordinated to one of the sulphur atoms. Unfortunately a complete structure determination of this compound by a X-ray analysis has not yet been possible because of the very bad quality of the crystals. Elucidation of the structure of this complex should throw much light on this new desulphurization reaction.

Experimental

500 mg (1.84 mmol) of 2,11-dithia[3.3]paracyclophane [6] and 8 ml (58.24 mmol) of $Fe(CO)_5$ are refluxed in 750 ml toluene under nitrogen for 24 h. Metallic iron, iron sulphide and polymeric material are filtered off. The residue on the filter is washed thoroughly with hot dichloromethane and the combined extracts, which also contain unreacted $Fe(CO)_5$, are evaporated under reduced pressure. The remaining solid is sublimed at 120°C/0.05 Torr. The sublimate is crystallized from chloroform/cyclohexane, yield: 237 mg (62%); m.p. 284–286°C, mass spectrum: M^+ 208; ^{1}H NMR ($CDCl_3$, TMS) δ (ppm) 3.1 (s, 8H), 5.0 (s, 8H).

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5 The compound can be prepared in a much better yield by photolysis of the thiaphane with $Fe(CO)_5$ in benzene. It is the main product of this reaction and no [2.2]paracyclophane is obtained.

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