Syntheses of Cyclophanes by Photochemical Extrusion of Sulphur

By Virgil Boekelheide,* I. David Reingold, and Mark Tuttle

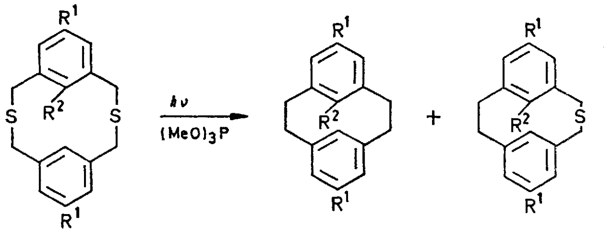
(*Department of Chemistry, University of Oregon, Eugene, Oregon* 97403)

Summary Irradiation of dithiacyclophanes in the presence of trimethyl phosphite gives the corresponding cyclophanes in good yield, and this procedure has allowed the synthesis of [2,2](2,6)pyridinoparacyclophane (**8**).

Until recently, the only good general method for synthesizing cyclophanes has been the Wurtz reaction.[1] The formation of dithiacyclophanes generally occurs in excellent yield, and they have been used as precursors for syntheses of cyclophanes in two ways: (i) the extrusion of sulphur has been accomplished by a two-step reaction sequence of a Stevens rearrangement followed by a Hofmann elimination;[2] (ii) the extrusion of sulphur has been accomplished by conversion into the corresponding bis-sulphone followed by elimination of sulphur dioxide on pyrolysis.[3] It had been reported that irradiation of sulphides alone in the presence of trivalent phosphorus derivatives leads to extrusion of sulphur.[4] We now report that irradiation of dithiacyclophanes in the presence of trimethyl phosphite provides a convenient, high-yield, single-step synthesis of cyclophanes.

For example, the condensation of 3,5-bis(bromomethyl)toluene and 3,5-bis(mercaptomethyl)toluene gave *anti*-6,15-dimethyl-2,11-dithia[3,3]metacyclophane (**1**), m.p. 98–99°, in 45% yield.† Irradiation of (**1**) (300 mg) in trimethyl phosphite (8 ml) at 24° using Vycor tubing and a Hanovia 450 w high-pressure mercury lamp for 18 h gave (**3**), identical in all respects with a known sample,[5] in 85% yield. When the irradiation was carried out for shorter periods, the yield of (**3**) was lower and the intermediate product (**5**), m.p. 116—117°, corresponding to a single extrusion of sulphur was isolated.

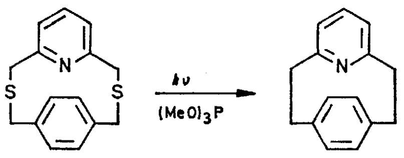
Similarly, the condensation of 2,6-bis(bromomethyl)toluene with 1,3-bis(mercaptomethyl)benzene gave (**2**), m.p. 104—105°, in 38% yield. Irradiation of (**2**) in trimethyl phosphite at room temperature for 48 h gave (**4**),[6] in 49% yield. At shorter irradiation times, n.m.r. monitoring showed the presence of the intermediate monosulphide, (**6**).



(1) R^1 = Me, R^2 = H
(2) R^1 = H, R^2 = Me

(3) R^1 = Me, R^2 = H
(4) R^1 = H, R^2 = Me

(5) R^1 = Me, R^2 = H
(6) R^1 = H, R^2 = Me



(7) (8)

Sutherland and his co-workers have studied the comparative steric requirements of the pyridine nitrogen lone pair *versus* a benzene carbon–hydrogen bond with respect to conformational flipping in the [2,2]metacyclophane series.[7] In contrast to [2,2]metacyclophane, which shows no change in its n.m.r. spectrum up to 200°, the corresponding [2,2]metaparacyclophane exhibits n.m.r. coalescence at 157° using a 100 MHz spectrometer.[8] It was of interest to see whether the present procedure might provide (**8**), the pyridine analogue of [2,2]metaparacyclophane,

† Satisfactory elemental analyses and spectral data have been obtained for all new compounds.

and if so, to examine the n.m.r. spectrum of (**8**) and its temperature dependence.

Condensation of 2,6-bis(mercaptomethyl)pyridine and *p*-xylylene dibromide gave (**7**), m.p. 177—178°, in 48% yield. Irradiation of (**7**) in trimethyl phosphite gave (**8**), m.p. 83—84°. At room temperature the four *para*-bridged aromatic protons of (**8**) appear as a singlet. Separation into the two separate signals corresponding to the respective conformational isomers is observed only at quite low temperatures, with coalescence occurring at −50°, using a 100 MHz spectrometer. Although the transition state for conformational flipping in the case of the [2,2]metaparacyclophane skeleton is probably different to that for the [2,2]metacyclophanes, the conclusion is that the pyridine nitrogen lone pair has appreciably smaller steric requirements than an aromatic carbon–hydrogen bond.

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