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PHOTOEXTRUSION REACTIONS: SO_2 EXTRUSION AS A ROUTE TO CYCLOPHANES

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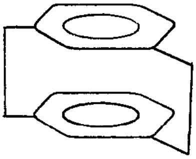
The synthesis of cyclophanes has captured considerable attention over the past two decades leading to the development of several new methods for entry into this class of strained molecules.[1] Some of the more recently applied methods are the Wittig rearrangement[1b] of bis-sulfides and pyrolysis of bis-sulfones.[1d] The sulfur analogs have been most extensively studied because the thiacyclophanes are formed in relatively high yields by nucleophilic substitution reactions.[1] We wish to report an efficient route to cyclophanes 1, 2, and 3 by photoextrusion of SO_2 from bis-sulfones.[2]



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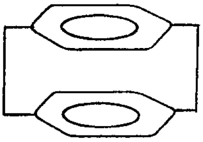

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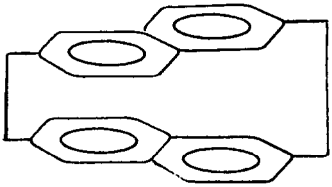
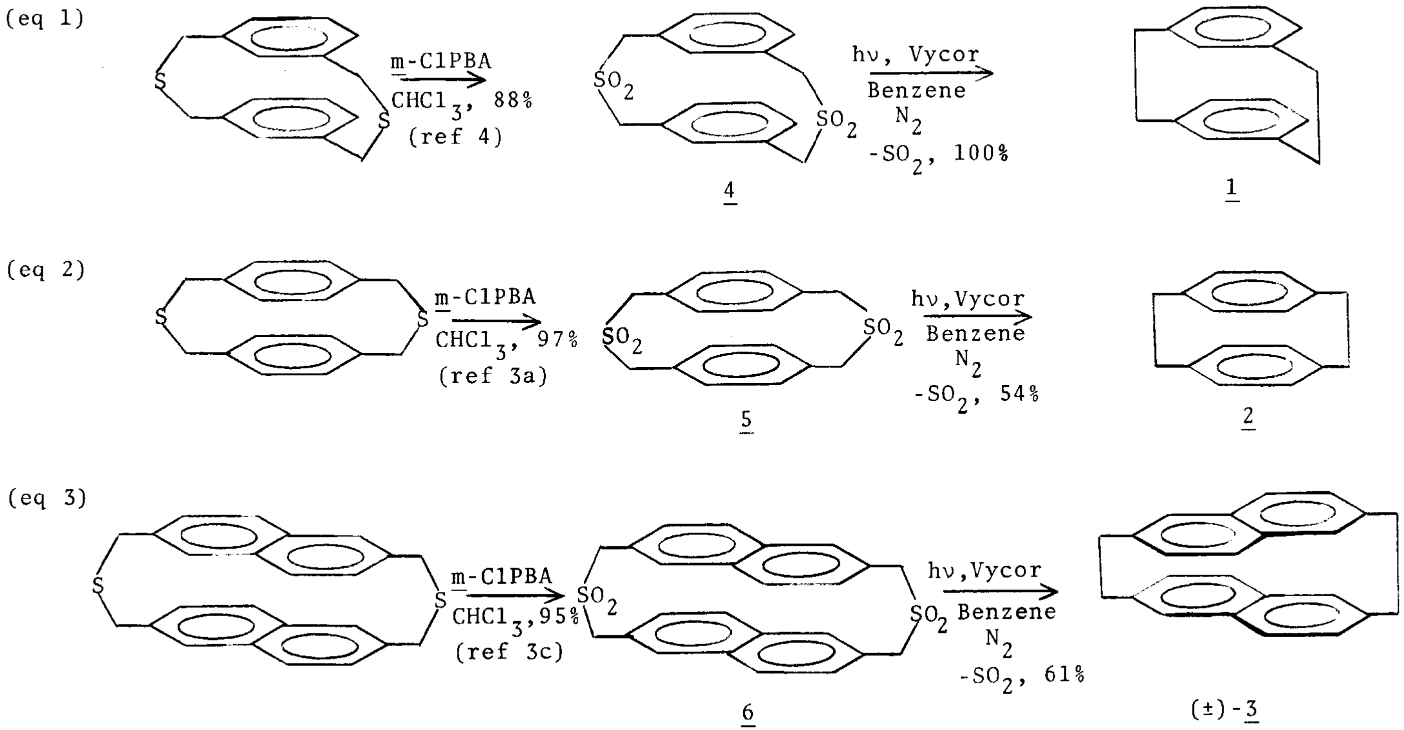


(±)-3

As shown in the Scheme, the sulfones were readily prepared by m-chloroperbenzoic acid oxidation of the known bis-sulfides.[3] The sulfones were irradiated as fine suspensions in benzene to the cyclophane products which were isolated by a short column chromatography.

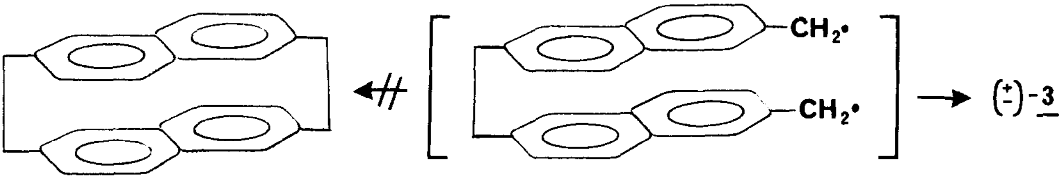
Scheme

Synthesis and Photochemistry of Sulfones 4, 5, and 6



In a typical run, 250 mg of 2,11-dithia-2,2,11,11-tetraoxo(3.3)metacyclophane (4)[1d,4] was irradiated through Vycor as a finely divided suspension in 800 ml of benzene. The solution was continually purged with a stream of oxygen-free nitrogen in order to remove SO_2 as it formed. After 21 hours, the benzene was removed and the residue treated with chloroform. The chloroform-insoluble material (143 mg) proved to be mainly unreacted 4. The remaining chloroform-soluble fraction was chromatographed on silica gel to yield 69.4 mg (100%,based on recovered sulfone) of 2,2-metacyclophane (1).[5] Similarly, 2,11-dithia-2,2,11,11-tetraoxo[3.3]para-cyclophane(5)[6] gave 2,2-paracyclophane (2) in 54% yield.

Entry into the naphthalenophanes through photoextrusion of SO_2 was achieved with 2,15-dithia-2,2,15,15-tetraoxo[3.3](2,6)naphthalenophane (6)[3d] in 61% yield. Conversion of 6 was carried to 100% completion in this study. None of the meso isomer was observed under these direct irradiation conditions paralleling the results from the thermolysis of 6 at 300° which also gave only the d,l isomer of 3 as reported by Haenel and Staab[3e]. Presumably the same diradical intermediate 7 is formed in both reactions which closes exclusively to (±)-3.[7]



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Although no attempt was made to optimize the yields of these photoextrusion reactions, the yields compare favorably with the currently available methods including pyrolysis of sulfones[1d,3d,8,9], *e.g.* 5 ($\xrightarrow{\Delta}$2, 16%)[1d] and 6 ($\xrightarrow{\Delta}$(±)-3, 48%)[3d,e],and photolysis of the sulfides in the presence of triphenylphosphite developed by Boekelheide[1c] and Brink[10]. Overall yields of pure cyclophanes 1, 2, and 3 by the photoextrusion of sulfur dioxide from the readily available arylmethyl bromides (5 steps) are 67%, 38%, and 36%, respectively. Furthermore, the method represents a very convenient synthetic sequence, for separation of the cyclophane from the sulfone is easily accomplished by trituration of the crude photolysate with chloroform.

Additional work which will extend this study to other applications of sulfone photoextrusions is in progress.

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2. a) A single report of SO_2 photoextrusion in a cyclophane synthesis has appeared (W. Rebafke and H. A. Staab; *Angew. Chem.*, **85**, 831 (1973)). We thank Professor V. Boekelheide for bringing this to our attention.
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