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A NEW AND CONVENIENT SYNTHESIS OF AZULENES FROM 6-N,N-DIMETHYLAMINOFULVENE AND THIOPHENE 1,1-DIOXIDES.

By David Copland, Derek Leaver,* and William B. Menzies
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ.

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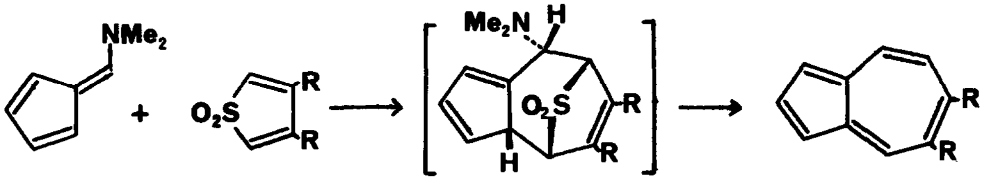
The cycloaddition reactions of fulvenes with dienes,[1] heterodienes[2] and 1,3-dipoles[3] have been studied recently by several groups of workers and it has been recognised that the fulvenes may function either as 2π- or as 6π-addends. 6-N,N-Dimethylaminofulvene (1) shows a particularly marked propensity for [6+4]cycloaddition and this periselectivity has been rationalised by Houk and his coworkers[4] using the Frontier M. O. method. When the 4π-addend is a 5-alkoxycarbonyl-2-pyrone, such cycloadditions to the fulvene (1) are followed by spontaneous loss of dimethylamine and carbon dioxide, thus providing a convenient synthesis of azulenes, albeit in low yield.[5] We now report an improved route to azulenes based on similar principles but utilising thiophene 1,1-dioxides (2) as the 4π-components.* The reactions are believed to take the course outlined in the Scheme though there is no direct evidence for the intermediate cycloadducts (3).



1 2 3 4

a: R=H a: R=H
b: R=Cl b: R=Cl

Formation of azulene (4a), as shown by the appearance of a blue colour and by t. l. c., commenced at room temperature when the fulvene (1) was added, under nitrogen, to a solution of thiophene 1,1-dioxide[6] (2a) (approx. 1 equiv.) in tetrahydrofuran. The reaction was completed by raising the temperature slowly to reflux and, after 3 hr., azulene (33%) was isolated by chromatography on alumina in pentane. A similar reaction with 3,4-dichlorothiophene 1,1-dioxide[7] (2b) proceeded more rapidly and gave 5,6-dichloroazulene (4b) (46%), blue plates, m.p. 58-59°, δ ($CDCl_3$) 7.30-7.35 (H-1 and H-3), 7.41 (d, H-7), 7.88 (t, H-2, $J_{1,2}$ 3.7Hz), 8.03 (d, H-8, $J_{7,8}$ 11Hz), 8.52 (s, H-4).

Despite the moderate yields, we believe that this reaction provides a highly convenient route to azulene; the fulvene (1) is obtainable[8] in one stage from cyclopentadiene, and a solution of thiophene dioxide (2a) is easily prepared from the commercially available 2,5-dihydro-compound by addition of bromine and dehydrobromination[6b] with powdered sodium hydroxide in tetrahydrofuran. Work-up of the reaction mixture is straight-forward since no chromatographically mobile products other than azulene are formed. The hitherto unknown 5,6-dichloro--azulene (4b) is a useful source of other azulenes with uncommon substitution patterns since the chlorine at C-6 is susceptible to nucleophilic displacement (e. g. by secondary amines and by thiolate anions).

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* Professor K. N. Houk has kindly informed us that similar observations, which are shortly to be published, have been made independently in his laboratory.