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NOVEL CYCLOADDITION-ELIMINATION REACTIONS OF 2,5-DIPHENYL-1,4-DITHIIN-1,1-DIOXIDE WITH ELECTRON-DEFICIENT ACETYLENIC COMPOUNDS

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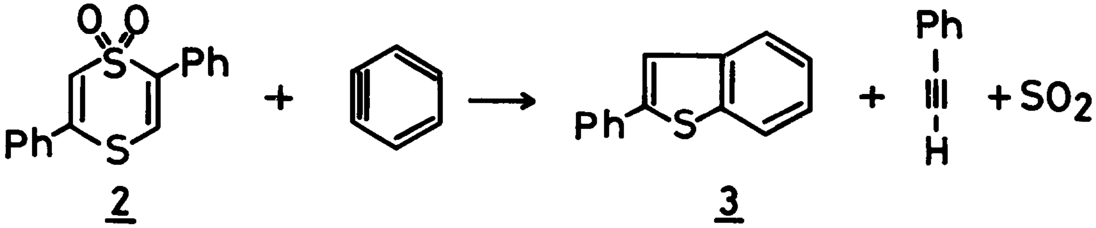
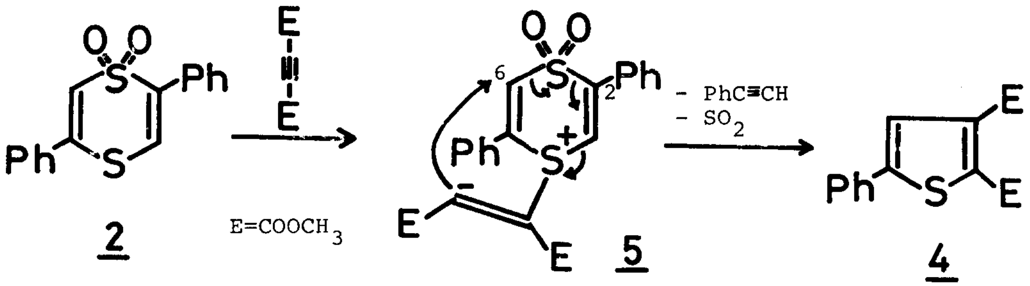
Thermal elimination reactions of sulfur, sulfur monoxide, and sulfur dioxide have been well known[1)]. Our observation[2)] of an unusual reaction in which the Diels-Alder adducts of 2,5-diphenyl-1,4-dithiin (1) extrude sulfur and give rise to naphtho[2,1-b] or [1,2-b]thiophenes prompted us to investigate the cycloaddition reaction of its 1,1-dioxide, 2. In sharp contrast to 1, 2 is thermally stable and undergoes no extrusion of sulfur dioxide upon heating[3)]. We now report the novel cycloaddition-elimination reactions of 2 with benzyne as well as with dimethyl acetylenedicarboxylate, which appear to provide the first example of thioethylene moiety involved in 1,3-cycloaddition.

Anthranilic acid and iso-amyl nitrite were refluxed with 2 in a mixture of methylene dichloride and acetone for 20 hr, during which the evolution of sulfur dioxide was observed. Separation of the reaction mixture by column chromatography on alumina yielded 27 % of 2-phenylbenzo[b]thiophene (3) along with 60 % of unreacted 2. Phenylacetylene was also detected in the reaction mixture by vpc. The structural assignment of 2 was based on analytical and spectral data[4)].



A similar elimination of phenylacetylene and sulfur dioxide occurred when 2 was refluxed with dimethyl acetylenedicarboxylate in o-dichlorobenzene for 15 hr. Chromatography of the reaction mixture on silica gel afforded dimethyl 5-phenylthiophene-2,3-dicarboxylate (4) in 19 % yield and most of the unchanged 2 was recovered. The structure of 4 was deduced from analytical and spectral data, and from comparison with other possible isomers[5)].

These reactions can be best rationalized by the initial attack of the



electron-deficient tripple bond to a sulfur atom[7] in 2 to form a dipolar species, 5, which may undergo cyclization resulting in the elimination of sulfur dioxide and phenylacetylene. It is interesting to note that an inorganic fragment is extruded in the retro-cycloaddition reaction accompanying the loss of an organic fragment[8]. The regioselective cyclization at C-6 rather than C-2 of 5 is another characteristic feature of these reactions. Further studies on the mechanism are now in progress.

References and Notes

1) B. P. Stark and A. J. Duke, "Extrusion Reactions" Pergamon, Oxford, 1967.

2) K. Kobayashi and K. Mutai, Chemistry Lett., 1149 (1977).

3) W. E. Parham in "Organic Sulfur Compounds", Vol. 1, N. Kharasch Ed., Pergamon, New York, 1961, Chapter 22.

4) S. H. Groen, R. M. Kellogg, J. Buter and H. Wynberg, J. Org. Chem., 33, 2218 (1968).

5) The spectral data revealed that the product is one of the three possible isomers of dimethyl phenylthiophenedicarboxylate, but was identical neither with dimethyl 2-phenylthiophene-3,4-dicarboxylate[6], m.p. 70-71 °C, nor with dimethyl 4-phenylthiophene-2,3-dicarboxylate, m.p. 93-95 °C, IR(nujol) 1725, 1710 cm^{-1}, NMR(CDCl$_3$) δ3.90(3H,s), 3.95(3H,s), 7.43(5H,s), 7.49(1H,s). The latter compound was prepared from acetophenone and dimethyl succinate followed by treatment with sulfur. For 4; m.p. 91-93 °C, IR(nujol) 1730, 1700 cm^{-1}, NMR(CDCl$_3$) δ3.97(3H,s), 4.00(3H,s), 7.35-7.70(6H,m). Addition of a shift reagent caused reasonable induced-shifts in the nmr spectra of each isomer.

6) K. T. Potts and U. P. Singh, J. Chem. Soc., Chem. Comm., 569 (1969).

7) Thioacetylenes are reported to react with benzyne affording a similar type of 1,3-cycloadduct. See H. H. Wasserman and J. M. Fernandez, J. Amer. Chem. Soc., 90, 5322 (1968). As to the 1,3-dipole, $^{+}C=\underset{|}{C}-S^{-}$, as an intermediate, see F. M. Benitez and J. R. Grunwell, Tetrahedron Lett., 3413 (1977).

8) The cycloadduct of sulfene undergoes thermolysis to give the product due to the extrusion of sulfur dioxide and methylene, but the fate of methylene fragment has not been identified. See J. F. King and E. G. Lewars, Can. J. Chem., 51, 3044 (1973).