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A NOVEL PHOTOREARRANGEMENT OF 2,5-DIARYL-1,4-DITHIIN-1,1-DIOXIDE ACCOMPANIED BY EXTRUSION OF SULFUR DIOXIDE

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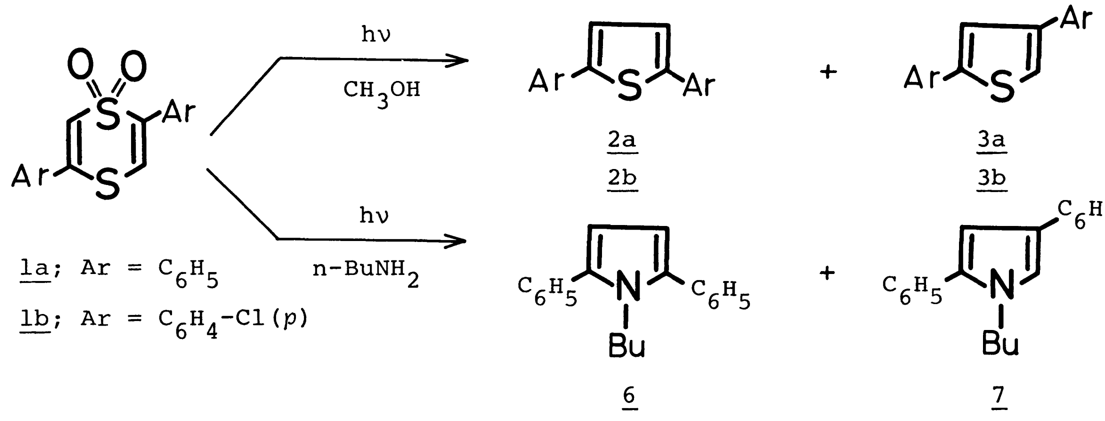
Photolysis of the title compound afforded 2,5-diarylthiophene. The mechanism involving the valence isomerization to thioketone was supported by the photolysis in n-butylamine, which gave pyrrole derivatives.

Photochemical ring transformation of five membered heterocyclic systems has been the subject of extensive studies.[1] In particular, the fascinating photorearrangement of arylthiophenes has attracted considerable interest since the work of Wynberg and co-workers.[2] We report herein an unusual formation of rearranged thiophene in photochemical ring contraction of a six membered heterocyclic compound, 2,5-diaryl-1,4-dithiin-1,1-dioxide (1a and 1b).

A solution of 1a in methanol (*ca.* 1.5×10^{-3} M) was irradiated with a high pressure mercury lamp through a Pyrex filter under nitrogen for 30 min. After removal of the solvent the photolysates were chromatographed on alumina to give 2,5-diphenylthiophene (2a) (4%) and 2,4-diphenylthiophene (3a) (1%). Although intractable mixture other than unreacted 1a (25%) was also eluted on chromatographic separation, the thiophene products were easily collected by monitoring their strong fluorescence. The isomeric thiophenes were identified by comparison with authentic samples.[2] Irradiation of *p*-chlorophenyl derivative 1b similarly gave rearranged thiophene 2b (3%) as well as thiophene 3b (1%) solely due to the loss of sulfur dioxide. The structure of 2b, mp 161-162 °C, NMR ($CDCl_3$): δ 7.20 (2H, s), 7.42(8H, broad q, J=8 Hz), was deduced from the spectral properties.

Although photochemical elimination of sulfur dioxide is frequently reported in the literature,[3] the extrusion concomitant with the rearrangement seems pretty rare. Based on the photorearrangement of arylthiophene explored by Wynberg[2] one might suspect that 2a is a secondary photoproduct derived from initially formed 3a. However, this possibility is ruled out by the finding that no detectable amount of 2a was obtained when 3a was irradiated. Thus 2a should be formed directly from 1a *via* a photochemical process.

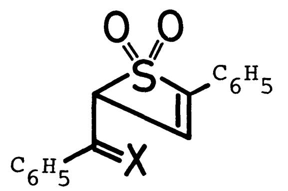
Among a number of possible mechanisms envisaged the most plausible one seems to involve the valence isomerization to thioketone 4 bearing a thiete dioxide moiety. Subsequent intramolecular cyclization of 4 followed by the extrusion of sulfur dioxide would give rise to 2a. Alternatively, 4 might eliminate sulfur dioxide prior to the cyclization, leading to cyclopropenyl thioketone 5 as an



1a; Ar = C_6H_5

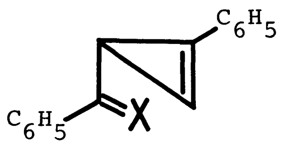
1b; Ar = C_6H_4-Cl(p)

2a 2b 3a 3b 6 7



4; X = S

8; X = N-Bu



5; X = S

9; X = N-Bu

intermediate. This rationale by analogy of the van Tamelen-Whitesides mechanism[4)] of thiophene photorearrangement was supported by the photolysis carried out in n-butylamine as solvent. Thus, when 1a was irradiated in n-butylamine under nitrogen at 0 °C for 8 h, 1-butyl-2,5-diphenylpyrrole (6) (2%), 1-butyl-2,4-diphenylpyrrole (7) (5%), and 2,4-diphenylthiophene (3) (1%) were obtained by chromatography. The structure of the isomeric pyrroles was identified by direct comparison with authentic samples.[5,6)] The formation of the pyrroles is most reasonably interpreted in terms of the conversion of the thioketone intermediate into 8 or 9 by a ground state aminolysis.[7)]

It is interesting to note that the photochemical behaviour of 1a is remarkably different from that of the corresponding sulfoxide.[8)] The scope of the photochemistry in thiophenes appears now to extend to involve the thiophene equivalent of six membered heterocyclic systems.

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