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REACTIONS OF 2,5-DIPHENYL-1,4-DITHIIN SULFONES WITH SODIUM AZIDE

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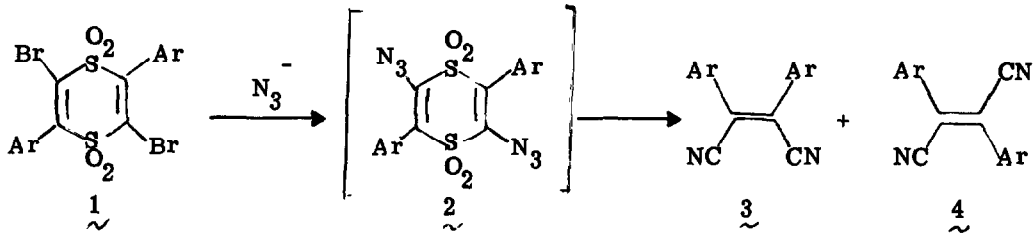
Summary A number of unanticipated transformations were observed when various 2,5-diphenyl-1,4-dithiin sulfones were treated with sodium azide. These include a fragmentation to give 1,2-dicyano-1,2-diphenylethene, the formation of 2,5-diphenyl-1,4-thiazine-1,1-dioxide, and the rearrangement of 3-bromo-2,5-diphenyl-1,4-dithiin-1,1-dioxide to its 2-bromo- isomer. Possible mechanism for these unusual reactions are discussed.

In conjunction with continuing studies of vinyl azides capable of undergoing thermolysis to zwitterionic species (zwittazido cleavage)[1], we report here an investigation of the reactions of variously substituted derivatives of 1,4-dithiin sulfones with sodium azide. Because of the structural similarity of azide derivatives in this series to azidoquinones, analogous thermolysis pathways were expected, but not realized. Initial studies involved the reaction of 2,5-dibromo-3,6-diphenyl-1,4-dithiin-1,1,4,4,-tetraoxide (1a)[2] with sodium azide in HMPA. It was anticipated that this would result in the corresponding 2,5-diazido derivative 2a and that this would undergo fragmentation at elevated temperatures to give two equivalents of cyanophenylsulfene. Such a prediction was based upon the observation that 2,5-diazido-3,6-diphenyl-1,4-benzoquinone cleaves to two equivalents of cyanophenylketene in refluxing benzene.[3] However, this analogy did not hold since it was observed that treatment of 1a with excess (4 eq) sodium azide at ambient temperature or below (-10^0) results in rapid evolution of gas and no azido derivatives or sulfene products could be isolated. Instead, a 54% yield of a 3:1 mixture of, respectively, the Z- and E-isomers of 1,2-dicyano-1,2-diphenylethene[4], 3a and 4a was obtained. It is of interest to note that the major product is the thermodynamically less stable Z-isomer, 3a, and that this appears to be the kinetically favored product. Thus, when the Z- or E-isomers alone were subjected to the reaction conditions, they slowly converted to an equilibrium mixture having a Z:E ratio of 1·4. Approximately a 10% conversion of 3a to 4a was realized after 4 hr, the length of time required for the conversion of 1a to 3a and 4a.

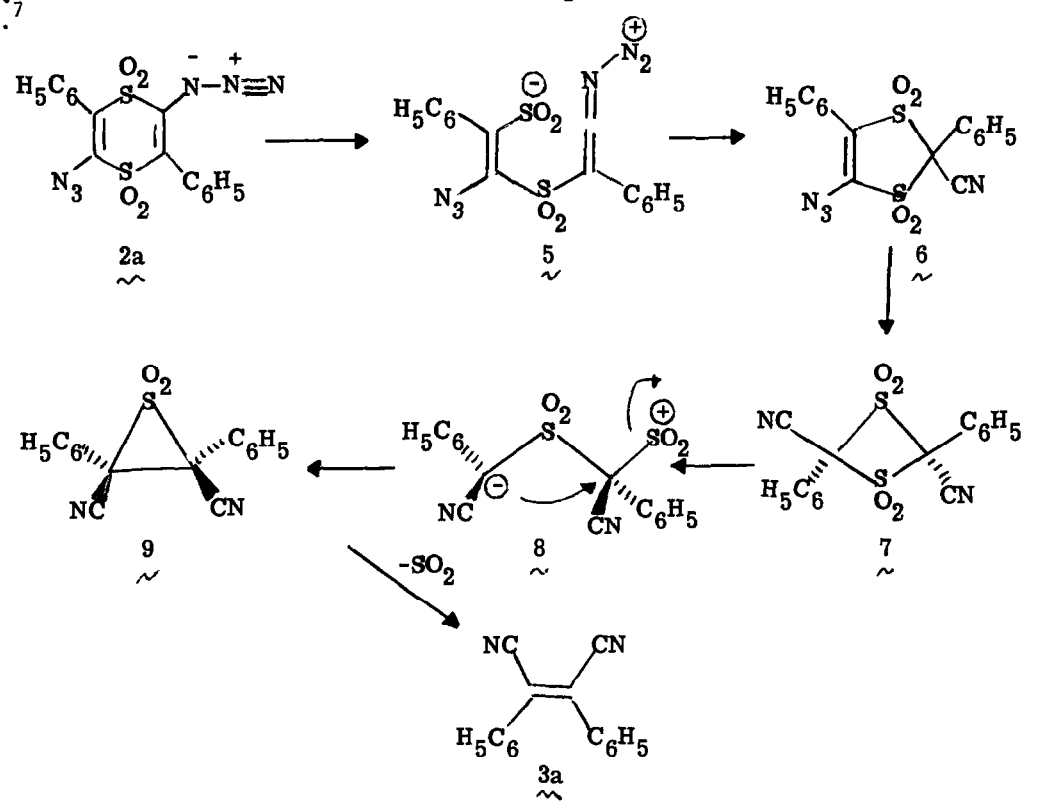
Although a number of possible mechanisms can be envisaged for this unusual transformation, that which is operative must involve a series of intramolecular ring contractions rather than a fragmentation to, for example, cyanophenylsulfene which dimerizes and loses SO_2 to give the alkenes. This conclusion is based upon the observation that no crossover products were observed when an equal mixture of 1a and its p-bromophenyl analog, 1b[5], was subjected to the

reaction conditions; only the alkenes 3a,b and 4a,b were detected Thus, a possible mechanism



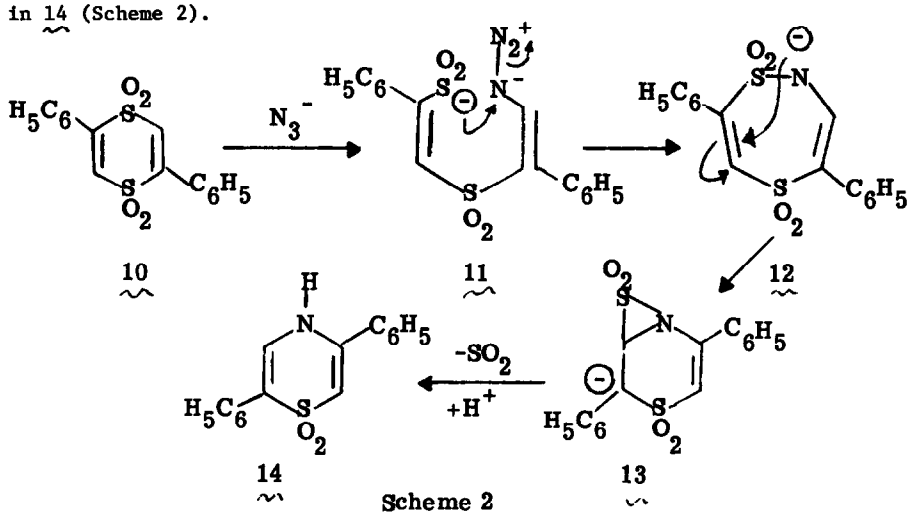
Ar = a) $-C_6H_5$, b) $-C_6H_4$-pBr

which accounts for the intramolecular nature of the reaction as well as the Z-isomer enhancement is outlined in Scheme 1. The first step is assumed to be the formation of the diazide 2a. This then undergoes azide-assisted ionization to the iminodiazonium ion 5, a transformation which is rare but not without precedent. [6] Ring closure of 5 would give 6 which can repeat the above steps to give 7. Here, the E-isomer would be expected to predominate on the basis of steric considerations. Heterolysis of 7 would result in the zwitterion 8 and this would give 9 upon ring closure. Stereospecific loss of SO_2 from the episulfone, 9, would then result in 3a.[7]



Scheme 1

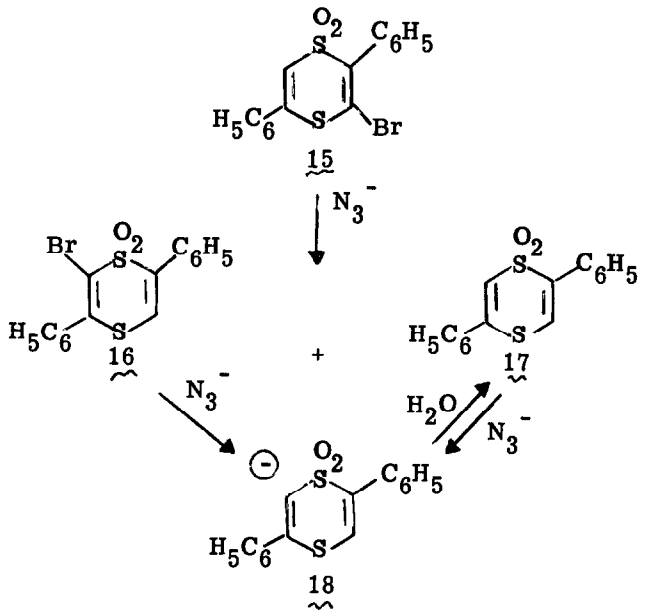
A comparative study was made utilizing 2,5-diphenyl-1,4-dithiin-1,1,4,4-tetraoxide (10)[8]. Here the dithiin contains no halogen leaving groups, but is still capable of addition-elimination with sulfinate displacement. This apparently controls the course of the reaction since the observed product was the thiazine 14(43%)[9]. Such is viewed as arising from the vinyl azide 11 which gives 12 upon ring closure. Subsequent intramolecular Michael addition to 13 and loss of SO_2 results in 14 (Scheme 2).



10 11 12 13 14

Scheme 2

Attention was next turned to the reaction of 3-bromo-2,5-diphenyl-1,4-dithiin-1,1-dioxide[10] (15) with sodium azide. This compound, unlike the disulfone, 10, would not be amenable to sulfinate displacement. On the other hand, displacement of the 3-bromo substituent is feasible and, in view of the results reported here, this was anticipated. However, to our surprise, we observed that treatment of 15 with excess (4 eq) of sodium azide in HMPA for 24 hr at ambient temperature resulted in its conversion to the 2-bromo isomer 16.[11] In addition, the debrominated compound, 2,5-diphenyl-1,4-dithiin-1,1-dioxide[8] (17) was formed as a minor product. Under the conditions described, the reaction proceeds to 50% completion, and the respective products were isolated in 32% and 18% yields. The possibility exists that the 2-bromo isomer 16 functions as the precursor to 17 since when 16 was subjected to the reaction conditions, it debrominated to give 17 in 15% conversion. Evidence for the intermediacy of the anion 18 in this transformation was obtained when 16 was treated with sodium azide in HMPA:D_2O (30·1) at 40° for 40 hr. This resulted in deuterium incorporation to give 2-deuterio-3,6-diphenyl-1,4-dithiin-1,1-dioxide in > 85% yield. The same compound was also obtained in > 90% when 17 itself was subjected to these conditions. Thus, the carbanion 18 is easily accessible and can be generated by either proton or bromonium ion abstraction from the 2- position of the corresponding 1,4-dithiin-1,1-dioxides.[12] The mechanistic details for the more intriguing conversion of 15 to 16 remain unresolved and will require appropriate labeling studies before concrete conclusions can be drawn.



Acknowledgement· The authors wish to thank the National Science Foundation for financial support of this work (77-02102).

References and Notes

1. H. W. Moore, Acc. Chem Res , 1979, 12, 125.
2 Prepared in 80% yield by the oxidation (H_2O_2/CH_3CO_2H) of 2,5-dibromo-3,6-diphenyl-1,4-dithiin, mp, 332-334°, ir (nujol, cm^{-1}) 1614, 1325, 1150, ^{1}HNMR (DMSO-d_6,δ) 7 8 bs; mass spec (m/e,%) 490 (24.6); 202 (48.0) 182 (100) For a reference to the starting dibromodithiin see· W. E. Parham, I. Nicholson, and V. J. Traynelis, J Am. Chem. Soc., 1956, 78, 850.
3. W. Weyler, Jr., W. G Duncan, and H. W. Moore, J. Am. Chem Soc , 1975, 97, 6187.
4. D. G. Coe, M. M Gale, R. P. Lindstead, and C. J. Timmons, J. Chem. Soc., 1957, 123, W. V Sargeant and C J. Timmons, ibid., 1964, 2222, M. Weizman, and S. Patai, J. Am. Chem. Soc., 1949, 71, 2587
5 Prepared in 62% yield by a procedure analogous to that used for 1a; mp 312-314°, ir (nujol, cm^{-1}) 1610, 1300, 1130, ^{1}HNMR (DMSO-d_6,δ) 7.70, anal. C, 29 59, H, 1.19, Br, 49.20.
6. G. Smolinsky and C. A. Pryde, J. Org. Chem , 1968, 33, 2411.
7 Stereospecific loss of SO_2 from episulfones (Ramberg-Backland) is well documented. See, for example, F. G. Bordwell, J M. Williams, E. B Hoyt, and B J. Jarvis, J Am. Chem Soc., 1968, 90, 429.
8. H H. Szmant and J. Dixon, J Am. Chem Soc., 1953, 75, 4354.
9 Characteristic structural data for 14 follows. mp, 217-218°; ir (nujol, cm^{-1}) 3310, 1640, ^{1}HNMR (DMSO-d_6,δ) 6.12 s 1H, 7.12 s 1H, 7.60 m 10H, 10 6 bs 1H, mass spec M^+, 283, anal. C, 67 75; H, 4 57
10. Prepared as described by W E Parham, I. Nicholson, and V J. Traynelis, J. Am. Chem. Soc , 1956, 78, 850. The structure was unambiguously established by x-ray crystallography. See, H. A. Levi and R. J. Doedens, Acta Cryst., 1980, B36, 1959.
11. Prepared in 97% yield by bromination of 2,5-diphenyl-1,4-dithiin-1,1-dioxide, mp, 146-148°, ir (nujol, cm^{-1}) 1620; ^{1}HNMR ($CDCl_3$,δ) 7.50 m 10H, 7.10 s 1H; mass spec., M^+, 378; anal. C, 50.70, H, 2.80 For a reference to the starting sulfone see, H. H Szmant and L. M. Alfonso, J. Am Chem Soc., 1956, 78, 1064.
12. Alkene protons adjacent to a sulfone group have previously been shown to be reasonably acidic See, C. P Broaddus, J Am Chem Soc , 1966, 88, 3863.

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