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CHARACTERISTIC BEHAVIOR OF N-(PHENYLSULFONYL)BENZOHYDRAZONOYL AZIDE. BASE-INDUCED DECOMPOSITION TO BENZONITRILE AND CYCLIZATION TO A TETRAZOLE

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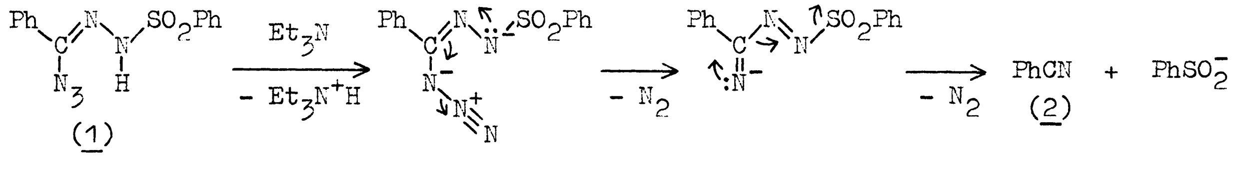
N-(Phenylsulfonyl)benzohydrazonoyl azide decomposed to give benzonitrile on treatment with triethylamine at room temperature, and cyclized to 5-phenyl-1-(phenylsulfonyl)aminotetrazole on heating in benzene, along with the formation of benzonitrile and other products.

Although hydrazonoyl azides may be an interesting type of species in view of their potential reactivity, only a little attention has been paid to them.1,2) Hydrazonoyl azides, such as N-arylbenzohydrazonoyl azides, have been reported to undergo no cyclization to tetrazoles, in spite of their structural analogy to imidoyl azides.2a) In the present communication, we would like to describe a novel base-induced decomposition of N-(phenylsulfonyl)benzohydrazonoyl azide3) (1) to benzonitrile (2) and the first cyclization of hydrazonoyl azide to tetrazole, the formation of 5-phenyl-1-(phenylsulfonyl)aminotetrazole (3) from 1.

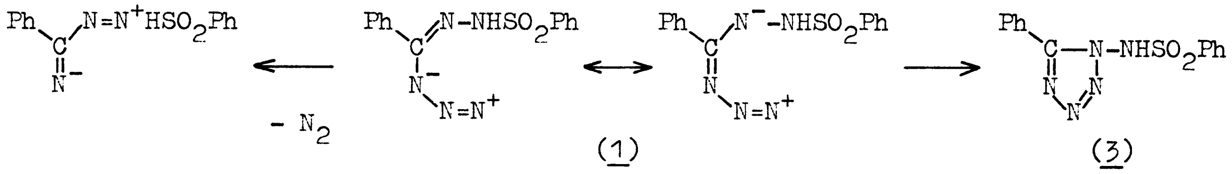
Base-induced Decomposition of 1: To a solution of 1 (5 mmol) in 15 ml of acetonitrile, a solution of triethylamine (10 mmol) in acetonitrile (5 ml) was added at room temperature; hereupon the mixture turned deep yellow immediately with the evolution of nitrogen. The reaction was slightly exothermic. From the reaction mixture, 2 (yield: 91%) was detected by GLC. Triethylammonium benzenesulfonate (0.2 mmol) was obtained as the benzene-insoluble fraction after removal of solvent from the mixture. From the benzene-soluble fraction, 2 (3.2 mmol)4) and small amounts of diphenyl disulfide (4, 0.1 mmol), S-phenyl benzenethiosulfonate (5, 1.1 mmol), and 4-phenyl-1-(phenylsulfonyl)semicarbazide (6, trace) were separated by means of column chromatography (silica gel, hexane — benzene — diethyl ether — ethanol). On the other hand, the similar treatment of N-phenyl-3) (7) and N-(p-nitrophenyl)benzohydrazonoyl azide2a) (8) resulted in no formation of 2. On heating under reflux in acetonitrile, however, 7 and 8 afforded 2 in a 55 and 62% yield (GLC), together with benzene or nitrobenzene (46%), respectively.5)

Benzenesulfinic acid gives 4, 5, and benzenesulfonic acid by disproportionation;6) thus, the base-induced formation of 2 from 1 can be formulated as follows:



The unique reactivity of 1 should be ascribed to the strong electron-withdrawing property of phenylsulfonyl group and its being a good leaving group.
The formation of 2 via the thermal process of hydrazonoyl azides can be interpreted analogously by the intermediacy of a zwitter ion, N^-=C(Ph)-N=N^+HAr.

Cyclization of 1 to Tetrazole 3: When 1 (5 mmol) was heated for 10 h in dry benzene (30 ml) under reflux, tetrazole 3[7] (0.7 mmol) was formed together with 2 (1.4 mmol), 6 (1.8 mmol), 4 (0.1 mmol), and 5 (0.8 mmol).[8] In acetonitrile, 3 was obtained in a diminished yield. The strong electron-withdrawing nature of phenylsulfonyl group probably contributes to the tetrazole formation; that is to say, the 1,5-dipole structure of 1 may be stabilized owing to the reduced electron density at the amino nitrogen, and the formation of intermediate zwitter ion leading to 2 may be also depressed to some extent:



(1) (3)

This type of contribution can not be expected for the N-aryl group in compounds 7 and 8. On the other hand, since the thermal decomposition of 1 to 2 gives benzenesulfinic acid as mentioned above, the secondarily formed benzenesulfonic acid may catalyze the Curtius-type rearrangement[2a] of 1 leading to the formation of 6.

References
1) M. E. C. Biffin, J. Miller, and D. B. Paul; W. Lwowsky, in "The Chemistry of the Azide Group," ed. by S. Patai, Interscience, London (1971), p. 90, 93, and 517.
2) a) A. F. Hegarty, J. B. Aylward, and F. L. Scott, Tetrahedron Lett., 1259 (1967); J. Chem. Soc. (C), 2587 (1967).
b) L. Caranti and G. Zecchi, Tetrahedron Lett., 21, 559 (1980).
3) Hydrazonoyl azides were prepared by the reaction of the corresponding chloride with sodium azide. Compound 1 could be obtained in a 85−90% yield by application of the method for 8[2a] and was purified by reprecipitation with hexane from the acetone solution. Mp. 118−120 °C (dec.); IR (KBr, cm^{-1}): 3164 (N-H), 2130 (N_3), 1613 (C=N), 1307, 1160 (SO_2). For compound 7, the reaction was carried out by using DMF as the solvent under ice-cooling. Yield: 82−88%; mp. 79−81 °C (dec.) (benzene−hexane); IR (KBr, cm^{-1}): 3345 (N-H), 2140 (N_3), 1597 (C=N). These compounds gave satisfactory analytical data (C, H, N).
4) Appreciable losses of 2 attended the removal of solvent.
5) 1-Aryl-4-phenylsemicarbazide was also obtained as a by-product.
6) a) E. Vinkler, F. Klivengi, and J. Szabo, Acta Chim. Acad. Sci. Hung., 15, 384 (1958); (b) J. L. Kice and K. W. Bowers, J. Am. Chem. Soc., 84, 605 (1962).
7) Mp. 183−184 °C (benzene); IR (KBr, cm^{-1}): 3062 (N-H), 1362, 1175d (SO_2), 1265, 1087, 983 (1,5-disubstituted tetrazole ring). Found: C, 51.72; H, 3.69; N, 23.39%. Calcd for $C_{13}H_{11}N_5O_2S$: C, 51.82; H, 3.68; N, 23.24%.
8) Isolated yields by column chromatography (silica gel) except that of 2 (by GLC).

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