Decomposition of 2-Azidosulphonylbenzophenones. Unusual Rearrangement Products

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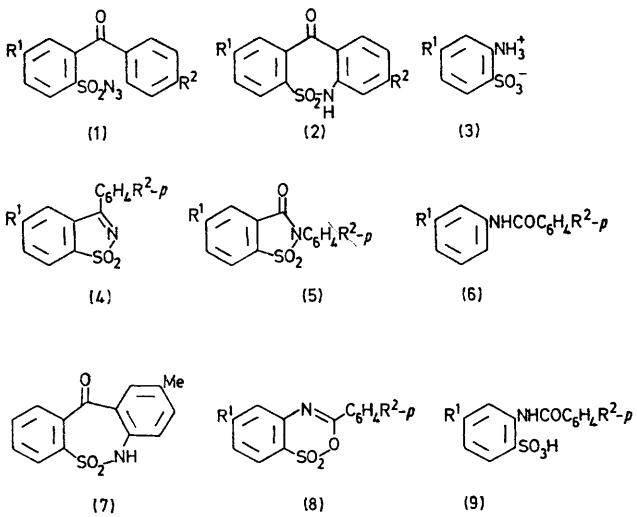
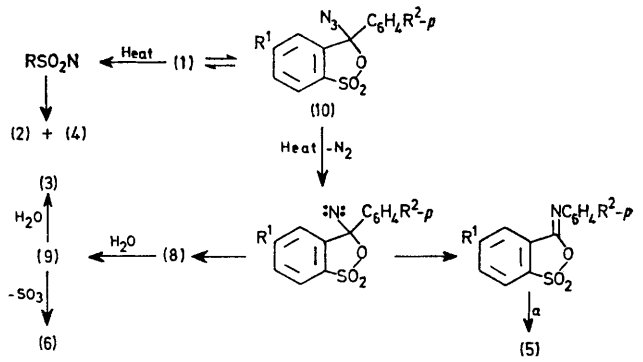
Summary Thermal decomposition of 2-azidosulphonylbenzophenones gives the 7-membered cyclisation products in addition to products in which nitrogen is bound to the *ortho*-position originally bearing the carbonyl group; ring chain tautomerism of the sulphonyl azides with 3-aryl-3-azidobenzo[*d*][2,1]oxathioles followed by decomposition of the latter and 1,2-aryl shifts is proposed to explain formation of the rearranged products.

INTRAMOLECULAR cyclisation of sulphonylnitrenes has led to a variety of new heterocyclic ring systems.[1] We now report the decomposition of 2-azidosulphonylbenzophenones which, in addition to the desired cyclisation products, leads to an unusual rearrangement in which the nitrene nitrogen gets bound to the aryl *ortho*-carbon atom originally bearing the carbonyl group.



(1) (2) (3) (4) (5) (6) (7) (8) (9)

a; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = Me$
c; $R^1 = Me$, $R^2 = H$



SCHEME. [a] D. Y. Curtin and L. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 637, discuss the related rearrangement of isophthalimide to phthalimide.

Thermolysis of the azide (**1a**),† in Freon 113 at 100 °C gave the dioxide (**2a**) (3·5%),‡ orthanilic acid (**3a**) (15%), the dioxides (**4a**) (1%)[2] and (**5a**) (1%),[3] and benzanilide (**6a**) (1%). Only one other example of the cyclisation of a sulphonylnitrene to give a seven-membered ring had been reported previously,[1] namely the formation of dibenzo-[*b*,*f*][1,4,5]oxathiazepine 5,5-dioxide. The azide (**1a**) (38%) was recovered. When the *para*-methyl compound (**1b**) was similarly decomposed, (**2b**) (5%), m.p. 235—236 °C, (**3b**) (35%), (**4b**) (2%), (**5b**) (3%), *p*-toluic acid (26%), and (**6b**) (2%) were isolated. The isomeric cyclisation product

† All new compounds gave correct analyses and spectral data (i.r., n.m.r., and mass) consistent with the proposed structures.

‡ A yield of 7% was obtained when the thermolysis was carried out in chlorobenzene at 150 °C. The *N*-methyl derivative, m.p. 158—159 °C, was identical with a sample prepared from *o*-$HO_2CC_6H_4SO_2N(Me)Ph$ by treatment with PCl_5 in CS_2, followed by $AlCl_3$ in nitrobenzene at 50 °C.

(**7**) was not detected.§ When the thermolysis was carried out at 140 °C for 10 h, (**8b**) (33%), m.p. 144—146 °C, was isolated [ν 1633 (C=N), 1360, and 1190 (SO_2) cm^{-1}] which gave (**3a**) and ethyl *p*-methylbenzoate on treatment with ethanol. Decomposition of (**1c**) in Freon 113 at 140 °C gave (**2c**) (6%), m.p. 203—204 °C, (**6c**) (1%), and a compound [presumably (**8c**), m.p. 138–145 °C] which, on recrystallisation, gave (**9c**), m.p. 183 °C, identical with an authentic sample prepared by benzoylation of sodium 2-amino-4-toluenesulphonate. Treatment of (**9c**) with ethanol gave (**3c**).

Compounds (**4**) probably arise by the known[4] dehydration of the hydrogen-abstraction product. To account for the array of non-sulphonylnitrene derived products it is suggested that ring–chain tautomerization[5] of some undecomposed (**1**) to 3-aryl-3-azidobenzo[*d*][2,1]oxathioles (**10**) occurs; decomposition of the latter to the alkylnitrene and 1,2-aryl shifts would give the observed products (Scheme) (a concerted nitrogen elimination aryl shift is also possible). Other mechanisms, *e.g.* intramolecular 1,3-dipolar addition of the azide to the carbonyl group followed by loss of nitrogen and rearrangement, appear less likely since (**5**) would then be expected to be the main product.

The oxathiazine (**8b**) is thermally stable in chlorobenzene at 140 °C. The benzanilides are, therefore, probably formed by desulphonation of (**9**).[6]

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§ An authentic sample of the *N*-ethyl derivative of (**8**), m.p. 154—155 °C, was prepared from *o*-$HO_2CC_6H_4SO_2NEt(C_6H_4Me$-*p*) by treatment with PCl_5 in CS_2 followed by heating with $AlCl_3$, and was found to be different from the *N*-ethyl derivative of (**2b**), m.p. 118—119 °C.

[1] R. A. Abramovitch, C. I. Azogu, and I. T. McMaster, *J. Amer. Chem. Soc.*, 1969, **91**, 1219; R. A. Abramovitch and R. G. Sutherland, *Fortsch. Chem. Forsch.*, 1970, **16**, 30; R. A. Abramovitch and W. D. Holcomb, *Chem. Comm.*, 1969, 1298; *J. Amer. Chem. Soc.*, 1975, **97**, 678.

[2] R. A. Abramovitch, B. Purtshert, E. M. Smith, P. C. Srinivasan, M. Humber, and G. M. Singer, *J.C.S. Perkin I*, 1974, 2589.

[3] H. Watanabe, R. L. Gay, and C. R. Hauser, *J. Org. Chem.*, 1968, **33**, 900.

[4] I. Remsen and A. P. Saunders, *Amer. Chem. J.*, 1895, **17**, 347.

[5] Some other known examples of ring–chain tautomerism are: *o*-benzoylbenzamide ⇌ benzo[*c*]oxoline (M. Ahmed and J. M. Vernon, *J.C.S. Perkin I*, 1975, 2048); *o*-formylbenzoyl chloride ⇌ 3-chlorophthalide (M. Renson, *Bull. Soc. Chim. belges*, 1961, **70**, 77); *o*-formylbenzenesulphonyl chloride ⇌ 3-chlorobenzoxathiazoline (J. F. King, B. L. Huston, A. Hawson, and J. Komeny, *Canad. J. Chem.*, 1971, **49**, 943); *o*-formylbenzenesulphonic acid ⇌ 3-hydroxybenzoxathiole (K. A. Freeman and C. D. Ritchie, *J. Assoc. Offic. Agric. Chemists*, 1957, **40**, 1108 (*Chem. Abs.*, 1958, **52**, 6067a); benzophenone-2-sulphonamides ⇌ 3-hydroxy-3-phenyl-2,3-dihydrobenzisothiazole 1,1-dioxide (H. Watanabe, C.-L. Mao, I. T. Barnish, and C. R. Hauser, *J. Org. Chem.*, 1969, **34**, 919).

[6] H. Suschitsky, J. Martin, and O. Meth-Cohn, *J.C.S. Perkin I*, 1974, 2451.