The Reaction of Sulphonyl Azides with Tetracyclone. *O*- and *N*-Sulphonyl-2-pyridones

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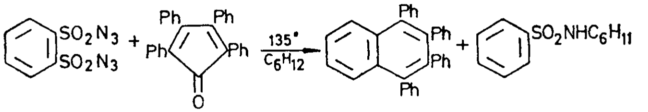
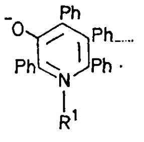
Summary Tetracyclone forms tetraphenyl-2-pyridone and tetraphenyl-2-pyridyl sulphonates with sulphonyl nitrenes, and traps intermediate azepines as the $(4 + 2)\pi$ and $(6 + 4)\pi$ adducts and benzyne from benzene-*o*-disulphonyl azide; no benzyne is formed in the hydrogen-abstraction by sulphonyl nitrenes from benzene.

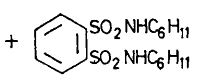
It was anticipated that benzyne might be formed on heating benzene-*o*-disulphonyl azide (**1**)† by loss of N_2 (2 mol. equiv.) and of SO_2 (2 mol. equiv.). Since benzyne is known to react with sulphonyl azides to give triazoles[1] tetracyclone (**2**) was used to try and intercept it. Thermolysis of (**1**) in cyclohexane containing (**2**) (1·1 equiv.) at 135° gave tetraphenylnaphthalene (**3**) (6%), the expected benzyne adduct, together with products of nitrene insertion into the solvent (**4**) (8%) and (**5**) (12%). In addition, however, there was isolated tetraphenyl-2-pyridone (**6**) (18%). Thus, (**1**) does give rise to benzyne, but in relatively low yield.



(1) (2) (3) (4)



(11)



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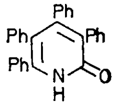
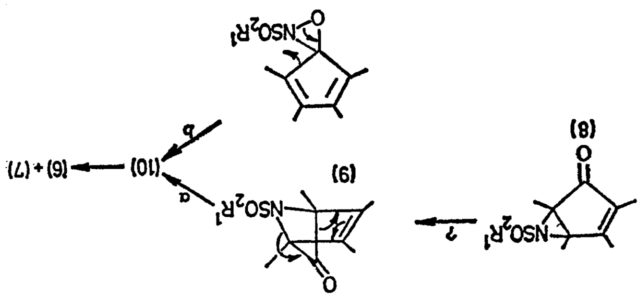
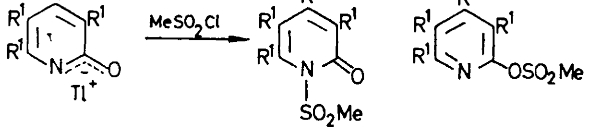


(6)

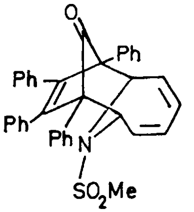
The unusual formation of (**6**) seems to be a general reaction of sulphonyl azides with tetracyclone. Thus, the decomposition of methanesulphonyl azide at 135° in methylene bromide containing tetracyclone gave methanesulphonamide (26%), (**6**), (12%), and tetraphenyl-2-pyridyl mesylate (**7**) (12%). No reaction occurred between the azide and tetracyclone at 80°, thus pyridone formation does not involve a 1,3-dipolar addition of azide to (**2**)[2] but suggests rather that a nitrene is the reactive intermediate.



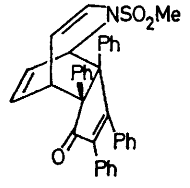
Three possible methods of addition of a nitrene to (**2**) can account for the formation of (**6**) and (**7**): (i) 1,2-addition to give (**8**) followed by rearrangement to the 1,4-adduct (**9**) and then rearrangement to the *N*-sulphonyl-2-pyridone (**10**); (ii) direct 1,4-addition to give (**9**); (iii) 1,2-addition to C=O and then rearrangement to (**10**). There is some precedent for this last possibility in that methylene is known to give an oxiran with acetone.[3] This was tested by heating methanesulphonyl azide with fluorenone in methylene bromide; an addition to the carbonyl would lead to a phenanthridone, while both 1,2- and 1,4-addition to the cyclopentadienone portion are unlikely. In fact, no phenanthridone was formed, a small amount of a monobromo-9-fluorenone was isolated and 9-fluorenone was recovered together with methanesulphonamide (67%) (abstraction from CH_2Br_2). Singlet ethoxycarbonyl nitrene has been shown[4] to undergo exclusive 1,2-addition to conjugated olefins, but the vinylaziridine so formed undergoes thermal rearrangement to the apparent 1,4-adduct. On the other hand, its reaction with pyrrole and with 2,5-dimethylthiophen has been formulated as going *via* the 1,4-adduct.[5] In the present study, no 3-hydroxypyridine derivative (**11**) [expected from ring-opening of (**8**)] was observed. Thus, path (a) is followed, perhaps, but not necessarily, preceded by formation of (**8**).



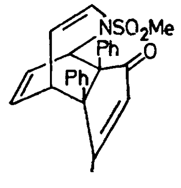
(12) (R^1 = H) (13) (R^1 = H)
(10) (R^1 = Ph) (7) (R^1 = Ph)



(14)



(15a)



(15b)

To understand the conversion (**10**) → (**6**) + (**7**) model studies were carried out on 2-pyridone and its tetraphenyl derivative. Mesylation of thallium(I)-2-pyridone at room temperature in ether gave *N*-mesyl-2-pyridone (**12**) (48%) and 2-pyridyl methanesulphonate (**13**) (52%). When (**12**) was heated alone at 175° or in methylene bromide at 135° it rearranged quantitatively to (**13**).[6]

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† All new compounds have been fully characterized by i.r., n.m.r., m.s. and microanalysis.

Methanesulphonation of thallium(I)-3,4,5,6-tetraphenyl-2-pyridone in ether suspension at room temperature gave (**6**) (27%) and (**7**) (72%).‡ No (**10**) was detected. It appears that (**10**) is formed but is unstable (probably due to steric hindrance by the 6-Ph group) and either rearranges to (**7**) or eliminates methylene sulphene (or its equivalent) to give (**6**). With the bulkier *ortho*-disubstituted benzene elimination probably takes place before any *N* → *O* migration can occur.

It has been suggested that in the decomposition of sulphonyl azides in aromatic solvents the unsubstituted sulphonamide is formed by the simultaneous abstraction of two hydrogen atoms from the aromatic nucleus which leads to a benzyne[7]. Thermolysis of $MeSO_2N_3$ in benzene containing tetracyclone (1·1 equiv.) at 135° gave methanesulphonanilide (23·5%), (**6**) (1·4%), (**7**) (1%), the $(6 + 4)\pi$ adduct (**14**) (1·7%) and a $(4 + 2)\pi$ adduct (**15a** or **15b**) (9·7%), but no 1,2,3,4-tetraphenylnaphthalene. This suggests that a benzyne is not formed in this reaction and an alternative mechanism must be sought to account for the formation of hydrogen abstraction products.

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‡ (**7**) is stable to the reaction conditions and to the chromatographic procedure used in the separation of (**6**) and (**7**) so that (**6**) is not formed by the hydrolysis of (**7**) during workup.

[1] W. Ried and M. Shoen, *Chem. Ber.*, 1965, **98**, 3142.

[2] Such reactions with strained and unstrained double bonds occur at much lower temperature than 135°; R. A. Wohl, *J. Org. Chem.*, 1973, **38**, 3862; R. A. Abramovitch, G. N. Knaus, M. Pavlin, and W. D. Holcomb, *J. Org. Chem.*, submitted; R. A. Abramovitch, and R. G. Sutherland, *Fortschr. Chem. Forsch.*, 1970, **16**, 1.

[3] J. N. Bradley and A. Ledwith, *J. Chem. Soc.*, 1963, 3480.

[4] A. Mishra, S. N. Rice, and W. Lwowski, *J. Org. Chem.*, 1968, **33**, 481.

[5] K. Hafner and W. Kaiser, *Tetrahedron Letters*, 1964, 2185.

[6] This is to be contrasted with, say, the relative thermodynamic stabilities of *N*- and *O*-benzoylphenanthridone in which the *N*-benzoyl derivative is the product of thermodynamic and the *O*-benzoyl derivative the product of kinetic control (D. Y. Curtin and J. H. Engelmann, *Tetrahedron Letters*, 1968, 3911).

[7] R. A. Abramovitch, J. Roy, and V. Uma, *Canad. J. Chem.*, 1965, **43**, 3407; R. A. Abramovitch and V. Uma, *Chem. Comm.*, 1968, 797.