The Decomposition of *ortho*-secondary Amino-substituted Arylsulphonyl Azides and Carbonyl Azides

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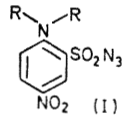
Summary In general arylsulphonyl azides with secondary amino-groups as *ortho*-substituent give thiadiazole dioxides in good yield on pyrolysis in chlorobenzene, while the corresponding carbonyl azides give the expected isocyanates.

IN pursuing our studies of *o*-substituted-t-anilines[1] we pyrolysed a series of benzenesulphonyl azides (Ia—i). With a carefully purified azide the main product was a thiadiazole dioxide in 60—80% yield. The thiadiazole dioxides obtained were of three types: (i) the new mesoionic system (II) from the azides (Ia and Id—f); (ii) the dealkylated product (IIIa) from the azide (Ib); (iii) the alkenyl-substituted products (IIIb—d) from the 7-, 8-, and 9-membered azides (Ig—i). This new type of cyclisation is analogous to the formation of pyridine *N*-imides (IV)[2] or dimethylaniline *N*-imides (V)[2] from the decomposition of benzenesulphonyl azide in pyridine or dimethylaniline respectively. The analogous cyclisation (VI → VII) has also been observed.[3]

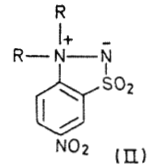
The formation of the ring-opened (IIIb—d from Ig—i) and the dealkylated product (IIIa from Ib) probably arises from the expected thiadiazole dioxides (II) by a Cope-type elimination. By comparison, the perhydroazepine *N*-oxide (VIII) which could be regarded as an oxygen analogue to the *N*-imide (IIg) also ring-opens to form (IX) even at low temperature.[4] An analogous interaction, which requires coplanarity of the participating centres,[5] is feasible with the thiadiazole dioxides (IIb and IIg—i) as borne out by molecular models (Stuart–Brigleb).

The course of the reaction was changed when the azides were incompletely purified. Under these conditions the dimethyl compound (Ia) gave a complex mixture consisting of inter- and intra-molecular sulphonylnitrene-insertion as



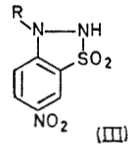
(I)

a ; R=Me
b ; R=Et
c ; R—R=$(CH_2)_4$
d ; R—R=$(CH_2)_5$



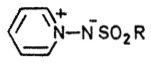
(II)

e ; R—R=$(CH_2)_2O(CH_2)_2$
f ; R—R=$(CH_2)_2NMe(CH_2)_2$
g ; R—R=$(CH_2)_6$
h ; R—R=$(CH_2)_7$
i ; R—R=$(CH_2)_8$

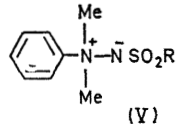


(III)

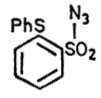
a ; R=Et
b ; R=$(CH_2)_4CH=CH_2$
c ; R=$(CH_2)_5CH=CH_2$
d ; R=$(CH_2)_6CH=CH_2$
e ; R=$(CH_2)_5Cl$



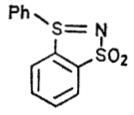
(IV)



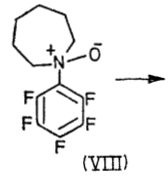
(V)



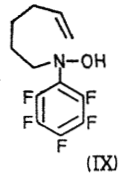
(VI)



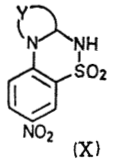
(VII)



(VIII)

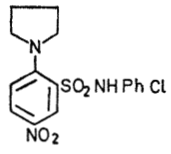


(IX)

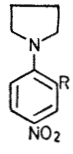


(X)

a ; Y=$(CH_2)_4$
b ; Y=$CH_2CH_2OCH_2$
c ; Y=$(CH_2)_5$
d ; Y=$(CH_2)_3$

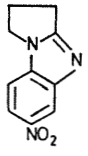


(XI)

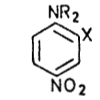


(XII)

a ; R=H
b ; R=SO_2NH_2
c ; R=NH_2



(XIII)



(XIV)

(R as in I)
a ; X=CON_3
b ; X=NCO

well as proton-abstraction products while the piperidine, the morpholine and the perhydroazepine derivatives (Id, e, and g) gave mainly the thiadiazines (X a—c) respectively, in good yield. It is significant that the cyclic sulphonamide (Xa) was also obtained when the thiadiazole (IId) was heated in piperidine. Decomposition of the pure azides (Id, e, and g) proceeded normally in the presence of traces of base or acid but gave the thiadiazines (X a—c) when traces of base hydrochloride were added.

Addition of acid to the thiadiazole (IId) resulted in ring-opening to give the chloride (IIIe) in good yield. The action of various electrophiles and nucleophiles on this system is under investigation.

The pyrrolidinobenzenesulphonyl azide (Ic) was pyrolysed to give various products some of which sugggest a nitrene intermediate. Thus sulphonylnitrene insertion into the solvent produced (XI; *o*-, *m*-, and *p*-isomers; 1% of each) while intramolecular insertion led to (Xd), and hydrogen abstraction to (XIIb). A Curtius-type rearrangement is responsible for the formation of the amine (XIIc) and the imidazole (XIII). The loss of the sulphonyl azide group (XIIa) is also a reaction characteristic of sulphonylnitrenes.[6] It would appear that the greater strain involved in forming the cyclic *N*-imide fused to a 5-membered ring renders cyclisation to give thiadiazoles unfavourable in this case.

The carbonyl azides (XIVa) bearing an *ortho*-amino-substituent behaved normally in that only the isocyanates (XIVb) were isolated on decomposition. However, anchimeric assistance of the *ortho*-substituent is probably involved since the decomposition is spontaneous even at 0°.

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[3] R. A. Abramovitch, C. I. Azogu, and I. T. McMaster, *J. Amer. Chem. Soc.*, 1969, **91**, 1219.
[4] M. Bellas, D. Price, and H. Suschitzky, *J. Chem. Soc.* (*C*), 1967, 1249.
[5] A. C. Cope and E. R. Trambuk, *Org. Reactions*, 1960, **11**, 317.
[6] Ref. 2, p. 259.

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