Thermal Reaction of Arylsulphinylamines with Aryl Azides

By L. BENATI, G. DE LUCA, G. MACCAGNANI, and A. TUNDO*

(*Istituto di Chimica Organica e Industriale, Università Viale Risorgimento*, 4-40136XXX, *Bologna, Italy*)

Summary The thermal or photochemical reaction between aryl azides and *N*-sulphinylanilines has been investigated; two possible mechanisms—direct cycloaddition of the azide to the N=S double bond or nitrenic insertion on the same bond—are discussed.

THE addition of carbenes to carbon–carbon multiple bonds is a well known process. Recently,[1] the first example of carbene addition to a non-carbon multiple bond has been reported. However, addition of nitrenes to carbon multiple bonds is relatively unknown,[2] due to the intervention of the nitrene precursor, usually the azide, in the addition process.

We report what we believe to be the first example of the reaction between aryl azides (or nitrenes) and compounds with a non-carbon multiple bond, namely arylsulphinylamines.

When equimolar quantities of the aryl azide (I) and the aryl-*N*-sulphinylamine (II) were allowed to react in boiling chlorobenzene for 72 h, the products shown in reaction (1) were isolated or detected for all the examples (a—f). (V) is the main product.

The same products were obtained by irradiation (Hanau 100 W high-pressure immersion lamp) of equimolar amounts of (I) and (II) in benzene at room temperature.

The reaction products were identified by g.c. Separation was also achieved by column chromatography and the products identified by i.r. and n.m.r. spectra and, when solid, by mixed m.p. with authentic samples.

$$\underset{\text{(I)}}{Ar^1N_3} + \underset{\text{(II)}}{Ar^2NSO} \rightarrow \underset{\text{(III)}}{Ar^1N{:}NAr^1} + \underset{\text{(IV)}}{Ar^2N{:}NAr^2} + \underset{\text{(V)}}{Ar^2N{:}NAr^1}$$

$$+ Ar^1NH_2 + Ar^2NH_2 + Ar^1NSO + Ar^2NSO + S + SO_2 \qquad (1)$$

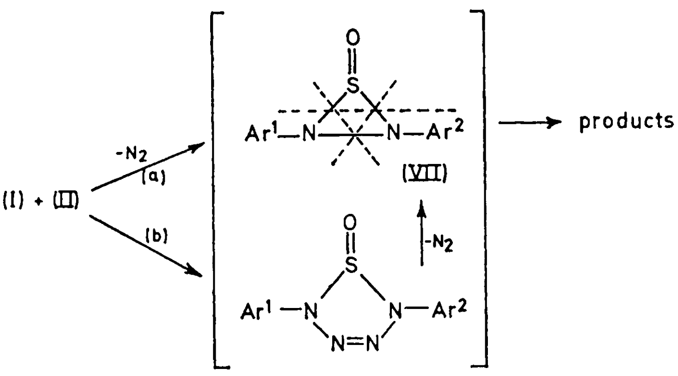
a; $Ar^1 = Ph$, $Ar^2 = p\text{-}MeC_6H_4$
b; $Ar^1 = p\text{-}MeC_6H_4$, $Ar^2 = Ph$
c; $Ar^1 = Ph$, $Ar^2 = p\text{-}ClC_6H_4$
d; $Ar^1 = p\text{-}ClC_6H_4$, $Ar^2 = Ph$
e; $Ar^1 = Ph$, $Ar^2 = p\text{-}OMeC_6H_4$
f; $Ar^1 = p\text{-}OMeC_6H_4$, $Ar^2 = Ph$

The total yield of azo-compounds (IV) and (V), calculated by g.c. was *ca.* 60%, based on the *N*-sulphinylaniline used.

The formation of sulphur and sulphur dioxide suggests that SO was probably given off during the reaction.

When the reaction was carried out between phenyl azide and the sulphinyl derivative $Ph\text{-}C_6H_4\cdot NSO\text{-}o$ (IV), carbazole was obtained as well as the expected products.

In our opinion, the experimental results indicate the probable intermediacy of the three-membered-ring compound (VII) (see Scheme).



SCHEME

The results so far obtained do not allow a distinction to be made between path (a) and (b), i.e. between nitrene addition to the N=SO bond and the concerted cycloaddition of the azide on the same bond. The reaction does not take place at temperatures < 110 °C, a fact which supports path (a).

The formation of the products can be rationalized as arising from different decompositions of the cyclic intermediate (VII), namely extrusion of SO, Ar^1N:, or Ar^2N: and recombination of the latter two to yield the azo-derivatives (III)—(V). In the case of the sulphinyl derivative (VI), the biphenyl-nitrene gives[3] the carbazole by intramolecular attack on the neighbouring phenyl ring.

The thermal decomposition of *N*-sulphinylamines to nitrenes is not possible under our experimental conditions. This reaction has been carried out successfully only at 800 °C and in a very low yield.[4]

We thank C.N.R. for financial support.

(*Received, 27th March* 1972; *Com.* 506.)

---

[1] J. O. Stoffer and H. R. Musser, *Chem. Comm.*, 1970, 481.

[2] R. A. Abramovitch in 'Essays on Free-radical Chemistry,' *Chem. Soc. Special Publ.*, 1970, no. 24, 361.

[3] P. A. S. Smith and B. B. Brow, *J. Amer. Chem. Soc.*, 1951, **73**, 2435; P. A. S. Smith and J. H. Hall, *ibid.*, 1962, **84**, 480.

[4] P. A. S. Smith in 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, p. 154.