The Photolysis of *N*-Sulphinylaniline in the Presence of Diphenyldiazomethane

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Summary The photolysis of *N*-sulphinylaniline in the presence of diphenylcarbene leads to *N*-diphenylmethyleneaniline the reaction proceeds by addition of a carbene to the nitrogen–sulphur double bond

THE reactions of carbenes with carbon–carbon multiple bonds and carbon–hetero-atom multiple bonds have been known for many years We report what we believe to be the first example of the addition of a carbene to a non-carbon multiple bond Although the chemistry of *N*-sulphinylaniline (I) has been well documented in the literature[1,2] little attention has been given to the photolytic reactions of this compound In view of the fact that the carbon analogue, phenyl isocyanate reacts with diphenylcarbene (II) to yield 2,2-diphenylindolin-3-one[3] we studied the reaction of (I) with (II)

Irradiation (Hanovia **450** w high-pressure immersion lamp) of equimolar amounts of *N*-sulphinylaniline (I) and diphenyldiazomethane in hexane gave *N*-diphenylmethyleneaniline (III) benzophenone (IV) tetraphenylethylene (V), benzophenone azine (VI), and several other minor products The photolysis was carried out under a constant stream of nitrogen† in order to inhibit the formation of benzophenone from diphenylcarbene and air[4] (Scheme 1)

$$\underset{(I)}{PhNSO} - N_2CPh_2 \xrightarrow[\text{Hexane}]{h\nu} \underset{(III)}{PhN{=}CPh_2} + \underset{(IV)}{Ph_2C{=}O}$$

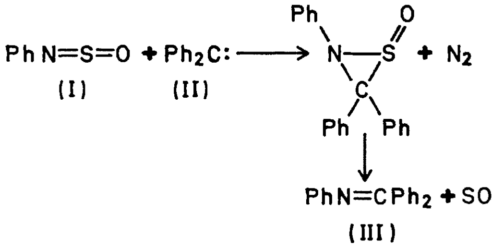
$$+ \underset{(V)}{Ph_2C{=}CPh_2} + \underset{(VI)}{Ph_2C{=}N{-}N{=}CPh_2}$$

SCHEME 1

The reaction products were identified by gas chromatography using an SE-30 liquid-phase column The reaction mixture was also subjected to preparative gas chromatography and the corresponding products identified by their i r spectra and, in the case of *N*-diphenylmethyleneaniline (III), mixed m p of authentic samples The yield of *N*-diphenylmethyleneaniline calculated by gas chromatography using CCl_4 as an internal standard, was 67% based on *N*-sulphinylaniline used

The preparative gas chromatography of a portion of the reaction product yielded a small amount of a blue oil which, upon standing, decomposed to a brown-white solid While structural proof of this oil is not yet available it may be thiobenzophenone ‡

On passing nitrogen through a neutral permanganate solution manganese dioxide was produced This indicates that SO gas is probably given off and supports the suggested mechanism (Scheme 2)



SCHEME 2

SO gas is isoelectronic with oxygen and its presence could account for the formation of benzophenone and thiobenzophenone This mechanism is analogous to the reaction between triphenylphosphine and *N*-sulphinyl-*p*-toluenesulphonamide[6] Compounds (V) and (VI) are by-products of the photolysis of diphenyldiazomethane[7]

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† Commercial grade nitrogen was passed through traps of a basic pyrogallol solution concentrated H_2SO_4 and then solid KOH prior to use

‡ Thiobenzophenone is a blue oil which upon standing decomposes to benzophenone SO_2, and various sulphides (ref 5)

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[3] J C Sheehan and I Lengyel *J Org Chem* 1963 **28** 3256

[4] H Staudinger E Anthes and F Pfenninger *Ber* 1916 **49**, 1298

[5] G Gattermann and H Schulze *Ber* 1896 **29** 2944

[6] A Senning *Angew Chem* 1965 **77** 379

[7] J March 'Advanced Organic Chemistry Reactions Mechanisms and Structure," McGraw Hill, New York 1968 p 165