

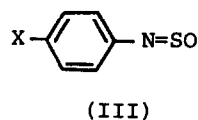
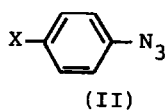
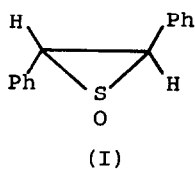
NOVEL SYNTHESIS OF N-SULPHINYLAMINES FROM SULPHUR MONOXIDE AND AZIDES

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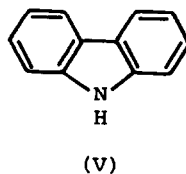
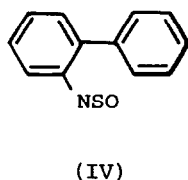
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We have previously reported<sup>1</sup> a reaction in which sulphur monoxide, generated in situ from thiiran 1-oxide derivatives such as (I), substitutes the nitrogen molecule of diazoalkanes to give thione S-oxides (sulphines). This finding prompted us to apply the same reaction to azides (II). In this case the electrophilic attack of sulphur monoxide on the nucleophilic  $\alpha$ -nitrogen of (II) would have given a closely-related substitution leading to the N-sulphinyl derivatives (III). Reaction of equimolar quantities of (I) and (II) in boiling dichloromethane until decomposition of (I) was complete (ca. 3 h), gave (III) with the reported yields plus trans-stilbene and unreacted (II). The reaction products were identified by comparison with authentic samples and the yields estimated by g.c..



a: X = OCH<sub>3</sub>  
b: CH<sub>3</sub>  
c: H  
d: Cl

a: yield = 45%  
b: 24%  
c: 22%  
d: 15%



We think that the present reaction proceeds by electrophilic attack of the SO molecule on the nucleophilic  $\alpha$ -nitrogen of the azide. Therefore we exclude the possibility that the reaction involves a nitrene intermediate derived from the thermolysis of the azide. This conclusion is supported by the following considerations:

- i) the reaction temperature is too low to allow any thermolysis<sup>2</sup> of the azide to nitrene;
- ii) in no case was any azo compound or aniline found;<sup>3</sup>
- iii) the direction of the substituent effect, which can be estimated from the given reaction yields, is in line with an electrophilic attack at the  $\alpha$ -nitrogen of the azide;<sup>3</sup>
- iv) finally when we produced sulphur monoxide in the presence of 2-azidobiphenyl in the above-reported conditions, besides the unreacted azidobiphenyl, only the corresponding N-sulphinyl compound (IV) was formed (in 18% yield). No carbazole (V) could be detected, and it is known<sup>4</sup> that as soon as 2-biphenylnitrene is formed it gives the carbazole (V) by intramolecular attack on the neighbouring phenyl ring.

#### REFERENCES

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