Photochemical Synthesis of Phenazine *N*-Oxide

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Summary Irradiation of a solution of *N*-acetyl- or *N*-benzoyl-2′-methylthio-2-nitrodiphenylamine in benzene gave 1-methylthiophenazine 5-oxide in 50 and 85% yield, respectively.

THE formation of azaheterocycles by photocyclization of an aromatic nitro-group with an ethylenic, acetylenic, or azomethine bond has been investigated,[1] but there have been no reports of a similar photocyclization with an aromatic C=C bond.

We have found that aromatic nitro-groups react photochemically with an aromatic C=C bond provided an ortho-acylamido-group is present. The present results provide a new preparative method for phenazine *N*-oxides and also have interesting mechanistic implications with respect to the photochemistry of the nitro group.

The diphenylamine (Ia), prepared from 2-nitrophenyl phenyl sulphide *via* Smiles rearrangement and subsequent methylation,[2] was readily converted into several *N*-alkyl and acyl derivatives (Ib—e).† In an attempted preparation of the phenazine 5-oxide (II), a possible intermediate for the synthesis of naturally occurring 1-substituted phenazines, the acetyl and benzoyl derivatives (Ib and c) were irradiated.

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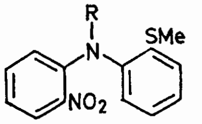
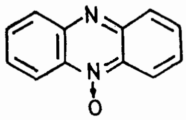
† All new compounds described herein gave satisfactory microanalytical results and spectral data consistent with their structures.



(I)

a; R=H c; R=Bz
b; R=Ac d; R=Me
e; R=Bu^n



(II)

A solution of (Ib) in benzene (5 mg/ml) was irradiated under nitrogen with a high-pressure mercury arc lamp surrounded by a water-cooled Pyrex filter for 24 h. After evaporation, chromatography of the residue gave the phenazine (II), m.p. 213° (50%). T.l.c. showed the presence of other products‡ which could not be isolated. The structure of (II) was confirmed by spectral data and deoxygenation to 1-methylthiophenazine.[3] Similar irradiation of the *N*-benzoate (Ic) also afforded (II) in higher yield (85%).

In contrast, (Ia) and the *N*-alkyl derivatives (Id and e) were inert to irradiation for 30 h and were recovered almost quantitatively.

Thus the photochemical formation of (II) appears to occur only when an acyl group is attached to the NH group of (Ia), but is as yet obscure.

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‡ Photolysis of phenazine *N*-oxides has been studied (*cf*. C. Kaneko, S. Yamada and M. Ishikawa, *Tetrahedron Letters*, **1970**, 2329). Some of the by-products may result from further photolysis of the initially formed (II). Similar irradiation of *N*-acetyl-2-nitrodiphenylamine gave phenazine 5-oxide in only 5% yield, and other undetermined products.

[1] H. A. Morison, 'The Chemistry of the Nitro and Nitroso Group,' ed. H. Feuer, Wiley–Interscience, New York, part **1**, **1969**, p. 165.
[2] W. J. Evans and S. Smiles, *J. Chem. Soc.*, **1935**, 181.
[3] Y. Kidani and K. Ukai, *Chem. Pharm. Bull.* (*Japan*), **1966**, **14**, 293.