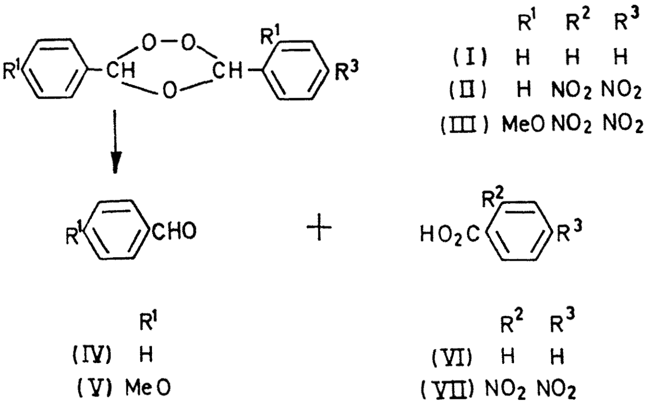
Reactions of Some Stilbene Ozonides with Dimethyl Sulphoxide and Dimethylformamide

By R M ELLAM* and J M PADBURY
(*Department of Chemical Sciences, The Hatfield Polytechnic, Hatfield, Herts*)

Summary Some stilbene ozonides react with dimethyl sulphoxide, dimethylformamide, and primary, secondary and tertiary amines to give a single aldehyde and a single acid in quantitative yield

THE recent report[1] that ozonides are readily solvolysed by alcohols prompts us to report our observations on the reactions of some stilbene ozonides with dimethyl sulphoxide, dimethylformamide, and amines The ozonides

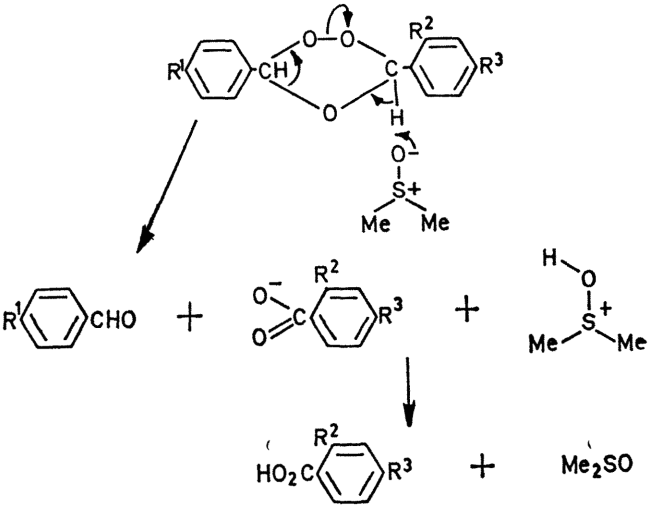
(I—III) dissolve in the anhydrous solvent (dimethyl sulphoxide, dimethylformamide, or amine) in a mildly exothermic reaction to give a single aldehyde and a single acid, in quantitative yield (Scheme 1).



SCHEME 1

Both *cis*- and *trans*-stilbene ozonides (I) give benzaldehyde (IV) and benzoic acid (VI) in quantitative yield, and with no appreciable difference in the rates of reaction of the two isomers With the unsymmetrical *trans*-ozonides (II and III),† 2,4-dinitrobenzoic acid (VII) is the sole acid produced, and benzaldehyde (IV) and anisaldehyde (V) are, respectively, the sole aldehydes produced. The possibility of solvolysis occurring during the aqueous work-up of the products may be discounted since the ^{1}H n.m.r. spectra of the ozonides in dimethyl sulphoxide show the complete absence of the signals due to the ozonide ring methine protons (observed in CCl_4 and $CDCl_3$ as solvents) and the presence of the characteristic aldehyde-proton signals.

The mechanism we suggest involves attack by the solvent (acting as a base) on one of the slightly acidic methine protons in the ozonide ring. In the unsymmetrical ozonides (II, III) the base preferentially attacks the more acidic proton adjacent to the strongly electron-withdrawing 2,4-dinitrophenyl ring. The reaction with dimethyl sulphoxide is shown in Scheme 2; the reaction with dimethylformamide probably involves attack by, and subsequent protonation of, the oxygen atom of the dimethylformamide.[2]



SCHEME 2

The acid–base nature of the reaction seems to be confirmed by the reaction with amines: thus n-butylamine, diethylamine, piperidine, and triethylamine all give products identical with those obtained in dimethyl sulphoxide and dimethylformamide. Alternatively, the mechanism could be stepwise rather than concerted with cleavage of the oxygen–oxygen bond as the initial step. The possibility of direct nucleophilic attack on the oxygen–oxygen bond seems less likely for these particular ozonides in view of their lack of reaction with other nucleophiles (*e.g.* methanol, ethanol).

This method of cleaving stilbene ozonides gives different products from those obtained by the normal oxidative and reductive work-up procedures,[3] and the direction of cleavage appears to be controlled by electronic effects. We are currently extending this investigation to other ozonides and bases.

(*Received, June* 21*st*, 1971; *Com.* 1006.)

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† Correct elemental analyses have been obtained for these new compounds.

[1] R. Criegee and H. Korber, *Chem. and Eng. News*, **1971**, **49**, no. 15, 31.

[2] R. J. Gillespie and T. Birchall, *Canad. J. Chem.*, **1963**, **41**, 148.

[3] P. S. Bailey, *Chem. Rev.*, **1958**, **58**, 988.