

Base Catalysed Dehydration of α -Alkoxybenzyl Hydroperoxides: Applications to Zwitterion Trapping Reactions in Ozonolysis

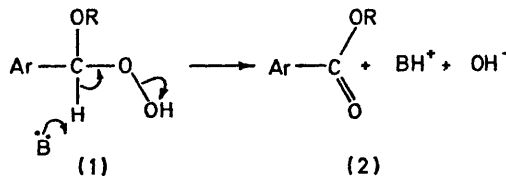
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Summary α -Alkoxybenzyl hydroperoxides are converted rapidly and quantitatively at room temperature into the corresponding alkyl benzoates by primary, secondary, and tertiary amines and by dimethyl sulphoxide.

PREVIOUSLY, analyses of mixtures of the two α -alkoxy hydroperoxides and the two carbonyl fragments obtained from the ozonolysis of unsymmetrical olefins in the presence of alcohols have involved either the isolation of each individual component¹ or only partial analyses.² The ozonolysis of *trans*-stilbene in the presence of primary and secondary alcohols (methanol,² ethanol, n-propanol, isopropyl alcohol) produces one mole equivalent of benzaldehyde, and one mole equivalent of the α -alkoxybenzyl hydroperoxide (**1**) as determined by iodometric titration. Treatment of (**1**) with primary, secondary, or tertiary amines, or dimethyl sulphoxide converts it quantitatively into the corresponding alkyl benzoate (**2**) in a mildly exothermic reaction at room temperature. Similarly with unsymmetrically-substituted stilbenes, the mixtures of α -alkoxybenzyl hydroperoxides obtained are also converted

quantitatively into the corresponding alkyl esters. The mechanism we suggest is shown in the Scheme and is analogous to those put forward for the base catalysed decompositions of stilbene ozonides³ and primary and secondary alkyl peroxides.⁴



SCHEME

By using the above reaction however, all four components from an unsymmetrical olefin may be readily and quantitatively analysed using g.l.c. Thus some ten unsymmetrically-substituted *trans*-stilbenes were ozonised in the presence of various alcohols, treated with diethylamine, and quantitatively analysed by g.l.c. using a suitable internal

standard. In all cases material balances of not less than 97% were obtained, based on the weights of all four products and the amount of stilbene consumed.

The dehydration of samples of the mixtures of α -alkoxybenzyl hydroperoxides may also be effected quantitatively, and the products simultaneously analysed, by direct injection onto g.l.c. columns having a basic support material (*e.g.* Chromosorb G; pH 8.5) at temperatures in the range 100–150 °C. That this is a base catalysed rather than a thermal dehydration was indicated by addition of the hydroperoxide mixture to a stirred suspension of the

column support material in methylene chloride at room temperature and observing the formation of the esters spectroscopically (i.r.). The main advantage of the treatment with base prior to g.l.c. analysis is that any side reactions of the hydroperoxides may be prevented immediately on completion of the ozonolysis: α -alkoxy-4-methoxybenzyl hydroperoxides for example, decompose relatively quickly after completion of the ozonolysis.

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³ R. M. Ellam and J. M. Padbury, *Chem. Comm.*, 1971, 1094.

⁴ N. Kornblum and H. E. De la Mere, *J. Amer. Chem. Soc.*, 1951, **73**, 880.