Oxiran Formation in the Base-catalysed Reaction of Long-chain Alkyldimethylsulphonium Salts and Carbonyl Compounds in Benzene–Water

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Summary Oxirans can be synthesized in high yields, by stirring a heterogeneous mixture of lauryldimethylsulphonium salt and a carbonyl compound in benzene–aqueous sodium hydroxide at room temperature.

Previously, we have found that the base-catalysed H–D exchange reactions of long chain alkyldimethylsulphonium salts in water are much faster than the corresponding reaction of shorter chain alkylsulphonium compounds.[1] The enhanced rate is accounted for by the ease of carbanion formation (ylide) from a long chain alkylsulphonium salt on a micellar surface. We now report results of the application of this system to the synthesis of oxirans.

Table 1. *Yields* (%) *of product in reaction of* PhCHO *in* C_6H_6–NaOH *in the presence of* $C_nH_{2n+1}S^+Me_2I^-$ *after* 6 h *stirring*

	$\overline{PhCH\cdot CH_2\cdot O}$		$C_nH_{2n+1}SMe$	PhCHO	$PhCH_2OH$	
NaOH	$n=12$	$n=1$	$n=12$	$n=12$	$n=12$	$n=1$
5N	23	0	24	51	0	0
10N	62	2—3	64	16	0	Trace
15N	81	9	83	3	0	Trace

It is well known that oxirans can be prepared in high yield by the reaction of trimethylsulphonium ylide with carbonyl compounds, usually in DMSO or THF[2] under anhydrous conditions, and Hatch has reported that oxirans can be prepared even in aqueous media.[3] However, the reaction is limited to those of very active carbonyl compounds such as benzaldehyde, whereas, the following system is applicable to a wider range of carbonyl compounds.

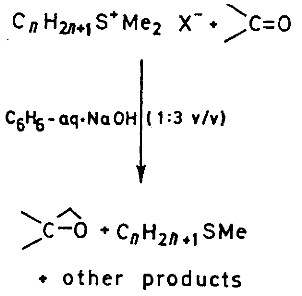
TABLE 2. *Effect of counterion* (X) *on yield of oxiran, after* 10 h *stirring in* C_6H_6–15N-NaOH

>C=O	X	Oxiran (%)
PhCHO	Cl	86
Cyclohexanone	Cl	88
	I	27
PhCOMe	Cl	85
1,1,1-Trimethylbicyclo[2,2,1]heptan-2-one	Cl	40[a]

[a] Starting ketone recovered (60%).

Typically, benzaldehyde (2·37 mmol) and lauryldimethylsulphonium halide (2·37 mmol) were added to a stirred heterogeneous mixture of benzene (2·5 ml)† and aqueous NaOH (7·5 ml), and the mixture was stirred a further 6—10 h at room temperature. After work-up, the yields of the products were determined by g.l.c. (Tables 1 and 2).

Table 1 indicates that lauryldimethylsulphonium salt ($n = 12$) is a better reagent than trimethylsulphonium salt ($n = 1$) for the formation of oxirans. It is interesting that the side reactions (Cannizarro, aldol, *etc.*) do not occur, presumably owing to protection of the carbonyl compound and the product (in benzene) from contact with the base (in water). In fact, when the reaction was carried out in the absence of benzene, significant side reactions were observed. Table 2 shows that lauryldimethylsulphonium chloride is a better reagent than the corresponding iodide. This accords with our previous observation that the rates of H–D exchange of lauryldimethylsulphonium halides increase in the order Cl > Br > I.[1]



The above procedure is simple and may have advantages over known procedures.[2] A disadvantage is the formation of the non-volatile lauryl methyl sulphide compared to the volatile dimethyl sulphide, which does not interfere with the isolation of oxirans. The lauryl methyl sulphide can be recovered by distillation and reconverted into lauryldimethylsulphonium halide.

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† Methylene dichloride and toluene give similar results to benzene.

[1] k_{rel} values for H–D exchange of the methyl groups of normal $C_nH_{2n+1}S^+Me_2X^-$ in D_2O–NaOD (40° C) are: 81 (X = Cl), 53 (Br), 42 (I) when $n = 12$ (under micellar conditions), and 1·0 (invariant to change of X) when $n = 1$; T. Okonogi, Y. Yano, and W. Tagaki, presented at the 27th Meeting of Japan Chemical Society, October, 1972, and submitted to *J. Org. Chem.*

[2] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 3782; 1965, **87**, 1353; H. O. House, in 'Modern Synthetic Reactions', Benjamin, California, 1972, p. 709.

[3] M. J. Hatch, *J. Org. Chem.*, 1969, **34**, 2133.