

Simple, Inexpensive Synthesis of Oxiranes from Carbonyl Compounds. Generation of Sulfonium Ylides from the Ternary System Methanol–Sulfuric Acid–Dimethyl Sulfide

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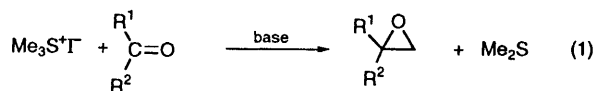
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Reaction conditions are described for the transformation of benzaldehyde and a series of ketones into epoxides, *in situ*, in the ternary system: methanol–sulfuric acid–dimethyl sulfide.

The original Corey synthesis¹ of oxiranes from the reaction of non-stabilised ylides and carbonyl compounds [eqn. (1)] has been gradually modified and improved. For example, the use of trimethylsulfonium chloride^{2,3} obviates the necessity for bases such as sodium hydride in non-aqueous media, allowing ylide formation in aqueous sodium hydroxide. Epoxidation through sulfonium iodides⁴ and methyl sulfates⁵ and polymer-supported fluorosulfonates⁶ has also been effected in heterogeneous alkaline media under catalytic phase-transfer conditions; a related procedure involves the use of lauryldimethyl sulfonium salts.⁷

The original and modified oxirane syntheses^{2–7} require isolation and purification of sulfonium salts prior to ylide generation and ensuing epoxidation. An ideal method would entail generation of the sulfonium salt, thence the ylide, *in situ* from inexpensive precursors, with subsequent epoxidation of the carbonyl compound in the same vessel. We describe such a process below.



It is known that dialkyl sulfides can be alkylated by alcohols in acidic media.^{8,9} During the course of a wider study of alkylations of dimethyl sulfides we showed that trimethylsulfonium hydrogen sulfate ($\text{Me}_3\text{S}^+\text{HSO}_4^-$) could be generated by adding methanol (0.156 mol) slowly to a stirred mixture of sulfuric acid (98%; 0.237 mol) and dimethyl sulfide (0.316 mol) while the temperature was kept < 25 °C; the presence of $\text{Me}_3\text{S}^+\text{HSO}_4^-$ was confirmed by comparing the ¹H NMR spectrum of the product with that of analytically pure hygroscopic material† prepared from trimethylsulfonium iodide, concentrated sulfuric acid and 30% hydrogen peroxide. This study led to the notion that the ternary system, methanol–concentrated sulfuric acid–dimethyl sulfide could be used to generate $\text{Me}_3\text{S}^+\text{HSO}_4^-$, that subsequent addition of base would generate the ylide ($\text{Me}_2\text{S}^+\text{CH}_2^-$) and that these reactions and subsequent epoxidation could be effected in one pot; successful realisation of the new method is exemplified for epoxide formation from benzaldehyde.

Experimental

Concentrated sulfuric acid (0.316 mol) was added over 1 h to dimethyl sulfide (0.316 mol) the temperature of the reaction mixture being kept < 30 °C. Methanol (0.156 mol) was then

Table 1 Epoxidation of carbonyl compounds *via* sulfonium salts

Carbonyl compound	Yield of epoxide (%)
Benzaldehyde ^a	55
Benzophenone ^b	78
4-Phenylbutan-2-one ^b	72
3-Methylbutan-2-one ^b	47
Cyclohexanone ^b	55
<i>tert</i> -Butylcyclohexanone ^b	71 ^c
1-(2,4-Dichlorophenyl)pentan-1-one ^b	86

^a The method used was identical with that described in the text. ^b Ketone was added before the first aliquot of potassium hydroxide. ^c The product consisted of a *ca.* 1:1 mixture of diastereoisomers.

added to the mixture over 30 min with the temperature < 35 °C. After the mixture had been stirred for 5 h, Bu^tOH (0.048 mol) was added to it followed by solid potassium hydroxide (0.58 mol) in 10 equal aliquots over 2.5 h. Benzaldehyde (0.15 mol) was added after the seventh KOH aliquot and an alkaline pH had been achieved. The mixture was stirred at room temperature for 12 h and subjected to conventional pentane/aqueous work-up. Styrene oxide (55%), identical (¹H NMR, IR) with an authentic sample was isolated. Examples of starting materials that can be used in the new method, and yields of epoxide produced are shown in Table 1. The yields quoted are not optimised.

In summary, a simple one-pot procedure for epoxide synthesis is described, with considerable advantages over existing procedures.^{1–7} The overall process is inexpensive with the volatile by-product dimethyl sulfide (b.p. 38 °C) being easily recovered and reused. Optimisation and the extension of this methodology to other systems is being investigated.

References

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† M.p. 20–21 °C (recrystallised from ethanol at –78 °C); δ [²H₆]-DMSO) 2.91 (s, 9 H, CH₃S⁺) and 7.4–7.6 (s, 1 H, HSO₄[–]). Accurate data from elemental analysis were obtained.