

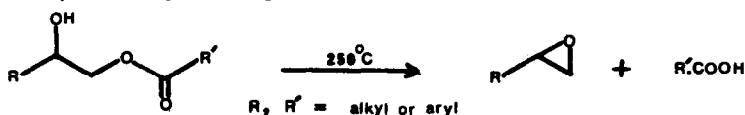
NEIGHBOURING GROUP PARTICIPATION - A NOVEL REARRANGEMENT
OF VICINAL HYDROXY-ESTERS TO EPOXIDES

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We were interested in preparing a number of terminal epoxides of commercial importance from performic acid and the appropriate olefins. The *in situ* performic acid is a reagent of choice, but suffers from the disadvantage of yielding substantial quantities of glycols at the expense of epoxides^{1,2}. Therefore, chances of achieving a commercially acceptable process very much depended on our ability to regenerate epoxides from unwanted glycols. We now report such a preparation from glycols via their mono-esters in acceptable yields.

The process involves mono-esterification of the glycol, followed by thermal isomerisation in liquid phase at 200-250°C to form the epoxide. Alternatively, since the epoxide formation from hydroxy-esters is accompanied by the elimination of the organic acid, the reaction on glycols can also be carried out directly with a catalytic amount of a high-boiling acid such as *m*-toluic acid and a trace quantity of sodium acetate. The reaction is particularly useful for the preparation of stable, terminal epoxides; however, secondary rearrangements are observed with more reactive oxiranes.



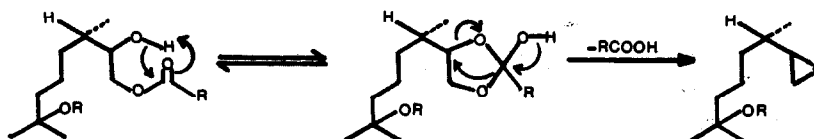
DIOL (POSITIONS INDICATED)	METHOD *	% YIELD OF ** DISTILLATE	% COMPOSITION OF DISTILLATE BY G. L. C.		
			EPOXIDE	CARBONYL DERIV.	ALLYLIC ALC. & OTHERS
Octane (1,2)	A	60	100	-	-
Tetradecane (1,2)	A	68	40.6	-	59.4
2-Alkoxy-2,6-dimethyl- octane (7,8)	A & B	95 (A) 82 (B)	97.0	3.0	-
2,6-Dimethyloct-7-ene (2,3)	A	71	36.2	-	63.8
α -Phenylethane (α,β)	A	50	10.0	77.3	12.7
Cyclododecane (cis;1,2)	B	60	37.0	54.5	8.5

* METHOD A. Neat hydroxy-acetate was isomerised without an additive.

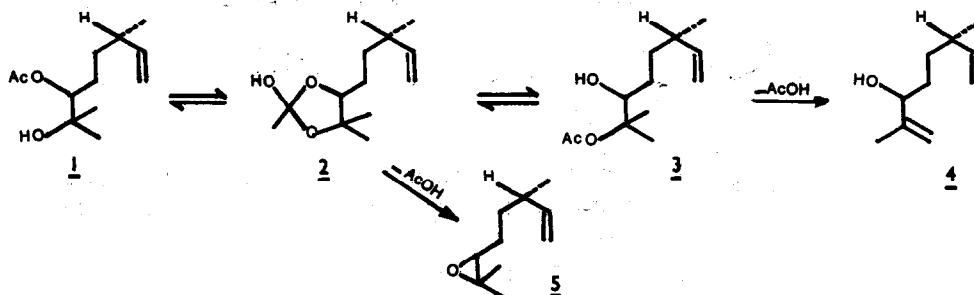
METHOD B. Glycols were treated directly with *m*-toluic acid (5% by weight) at 200-250°C.

** In each case the entire reaction mixture was distilled through a Fenske column followed by G.L.C. analysis of the weighed distillate. Unlike Ref. 3, all reactions were conducted in neutral or acidic media.

We believe that the mechanism of epoxide formation from a terminal mono-ester in our case can best be explained by invoking the intermediacy of a tautomeric, cyclic ortho-monoester formed by neighbouring group participation.^{4,5} This intermediate collapses under the conditions of its generation to give an epoxide and the acid. It is not known which of the two oxygen atoms is eliminated; this aspect is under investigation.



Further support for the ortho-monoacetate as the crucial intermediate in epoxide formation came from the observation that conditions under which hydroxy-acetates were smoothly converted into epoxides left the corresponding diacetates unchanged. It seems reasonable to assume that the absence of the hydroxyl proton in diacetates prevented intramolecular cyclisation. Also, when a non-terminal 1,2-hydroxyacetate such as (1) was subjected to thermal rearrangement, the allylic alcohol (4) was the major reaction product, while only a small amount of the epoxide (5) was formed. This can be rationalized by postulating an equilibrium between the initial hydroxy-acetate and the isomeric ester (3), through the intermediate ortho-monoacetate (2). The hydroxy-acetate (3) with its less stable tertiary ester function is readily pyrolysed to the allylic alcohol (4).



All substrates as well as products had satisfactory analyses and structure proof. The (+) and (-)-erythro and threo-epoxides from 2-alkoxy 2,6-dimethyloct-1-ene were also reduced with LAH to the corresponding and known alkoxyelgenols with pleasant sandalwood odour⁶.

REFERENCES.

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