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THE ACTION OF MERCAPTOACETIC ACID ON A TRIALKYL EPOXIDE

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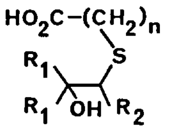
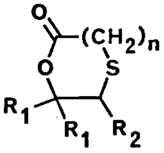
Abstract: The reaction between 2,3-epoxy-2-methylpentane and mercaptoacetic acid yields a 3:4 mixture of the thialactone (2a) and the hydroxyacetate (3b). Using milder reaction conditions, only the mercaptoester (3a) is formed, which has been shown to be an intermediate in the formation of the acetate (3b). The reactivity of mercaptoacetic acid towards the epoxide is not due solely to the action of the mercapto or carboxylic acid group and therefore may result from the formation of cyclic intermediates.

Although nucleophilic addition to the oxirane ring has been much studied, little work has been carried out on either polyalkyl epoxides or the addition of mercaptoacids. More recent studies[2] have shown that various mercaptoacids add to epoxides to give the hydroxyacid (1), and the lactone (2), which is in accordance with the expected nucleophilicity of the functional groups of the mercaptoacids.

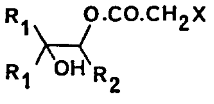


(1)



(2)

(a) R_1=Me, R_2=Et, n=1



(3)

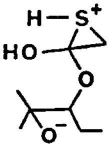
(a) R_1=Me, R_2=Et, X=SH

(b) R_1=Me, R_2=Et, X=H

We have carried out a similar study on the addition of mercaptoacetic acid to 2,3-epoxy-2-methylpentane; our interest in this epoxide lies in its being a model for epoxidized natural rubber. A mixture of mercaptoacetic acid (1.89g) and 2,3-epoxy-2-methylpentane (2.0g) in chloroform (5ml) was refluxed and the reaction monitored by h.p.l.c. analysis. Initially a product was observed which, as reaction continued, was consumed, together with the starting materials and two major products were observed (66h). These were separated by preparative h.p.l.c. and found to be the expected thialactone (2a, 0.33g)[3] and, surprisingly, the hydroxyacetate (3b, 0.44g).[4,5]

The initial product, which could be an intermediate in the formation of either 2a or 3b or both, was formed as a major product when the reaction was carried out at room temperature for 24 h. It was separated by preparative h.p.l.c., giving the hydroxymercaptoester (3a, 0.38g).[6] In order to investigate its intermediacy, the mercaptoester (3a, 0.15g) in chloroform (2ml) was refluxed in the presence and absence of mercaptoacetic acid (0.07g) for 90 h. In both cases, the intermediate was efficiently converted to only the hydroxyacetate 3b (h.p.l.c. analysis).

In view of these findings, the actions of a monofunctional thiol and/or carboxylic acid towards 2,3-epoxy-2-methylpentane were also investigated. The reaction conditions were the same as those used in the formation of the mercaptoester 3a, using, as required, acetic acid and/or n-hexanethiol. In no case could reaction be observed after 24 h. It seems likely that the addition of a carboxylic acid moiety may be anchimerically assisted *via* a cyclic sulphonium ion, 4; such intermediates are known to form in other reactions.[7] We have found that, in the reaction between the epoxide and acetic acid, much more vigorous conditions are required (150°C; 3 h) to produce detectable quantities of the acetate (3b). However, we are not at present able to assess the extent of any steric and inductive effects, which may be significant in these reactions.



(4)

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References and Notes

1. Present address: Fasson(Nederland)bv, Research and Technology, P.O.Box 28, 2300 AA Leiden, The Netherlands.
2. K.Jankowski, R.Coulombe, and C.Berse, *Bull.Acad.Pol.Sci.Ser.Chim.*, 19 (11-12), 661 (1971).
3. NMR(CCl_4) δ 4.02(1H,t,*J* 6,CH-O),3.7-3.55 and 3.17-3.0(2H,ABq,CH_2-S), 1.6(2H,m,$C\underline{H}_2$-Me), 1.35(3H,s,CH_3CS),1.30(3H,s,CH_3CS),1.07(3H,t,*J* 7, $C\underline{H}_3$-CH_2). IR(neat) 1740(CO)cm^{-1}.
4. NMR(CCl_4) δ 4.65(1H,dd,*J* 4,10,CHO),2.04(3H,s,CH_3CO),1.95(1H,br,OH),1.6(2H,m,$C\underline{H}_2$Me), 1.13(6H,s,$\underline{Me}_2$COH),0.88(3H,t,*J* 7,$C\underline{H}_3CH_2$). IR(neat)1730(CO)cm^{-1}. Found: S, <0.5%.
5. The formation of the acetate is not due to contamination of the mercaptoacetic acid by acetic acid, which was found to be present in a concentration of only 360 μg/g (ion-exchange chromatography).
6. NMR($CDCl_3$) δ 4.68(1H,dd,*J* 9,3,CH-O),3.48(1H,br,OH),3.21(2H,d,*J* 9,CH_2S),1.97(1H,t,*J* 9,SH), 1.57(2H,m,$C\underline{H}_2$Me),1.15(6H,s,Me_2COH),0.90(3H,t,*J* 7,$CH_2\underline{Me}$). IR(neat) 3460(OH),2560(SH), 1725(CO)cm^{-1}.
7. E.S.Gould, 'Mechanism and Structure in Organic Chemistry', Holt, Rinehart and Winston, New York, 1959, p.561.

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