

α, β -EPOXY SULFIDES

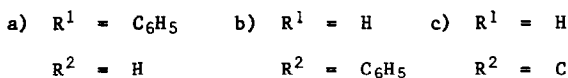
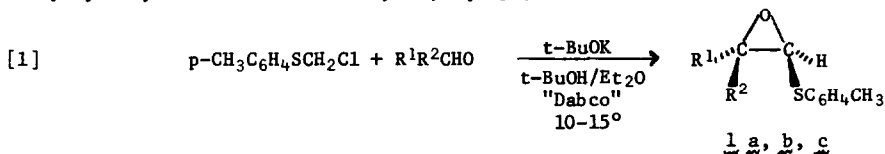
A NEW SULFUR-SUBSTITUTED OXIRANE

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We have demonstrated the applicability of the Darzens condensation to the synthesis of the new functional groups α, β -epoxy sulfone (1) and α, β -epoxy sulfoxide (2), in which an oxirane ring is substituted with tetracoordinate hexavalent sulfur and tricoordinate tetravalent sulfur, respectively. It was of interest to determine whether the final member of the series, in which the substituent is dicoordinate divalent sulfur, could be prepared. This has been realized and we report here the preparation of α, β -epoxy sulfides by the reaction of chloromethyl p-tolyl sulfide with aldehydes, eq. [1].



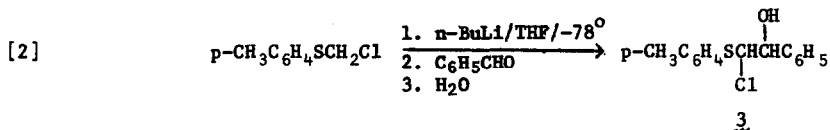
The Darzens condensation with chloromethyl p-tolyl sulfide and benzaldehyde by the procedure reported earlier (1) gave only poor conversion to epoxides 1a and 1b, and much starting material was recovered unchanged. Corey and Seebach reported (3) that the metalation of methyl phenyl sulfide with n-butyllithium, which otherwise gave poor yields or required a long reaction period to give good conversion to phenylthiomethyl lithium, could be effectively catalyzed by using 1,4-diazabicyclo[2.2.2]octane ("Dabco"). We find that by using Dabco, good yields of α, β -epoxy sulfide can be obtained. This suggests that in our t-BuOK/t-BuOH system, in the absence of Dabco, the concentration of p-tolythiochloromethyl carbanion is very low. This conclusion is supported by the fact that, whereas in the absence of Dabco some chloromethyl p-tolyl sulfide can be recovered unchanged, in all our experiments using

Dabco cis- and trans-1,2-bis [p-tolylmercapto]-ethylene (2) was obtained as a by-product, presumably by a displacement-elimination reaction involving p-tolylthiochloromethyl carbanion.¹



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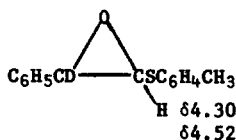
Several attempts to effect condensation with the less reactive carbonyl group of a ketone have failed; formation of 2 becomes the kinetically more favorable process. Whereas the first step in the Darzens condensation is reversible, the low temperature metalation-condensation scheme used by Durst (4) for phenylsulfinylchloromethyl carbanion with ketones is kinetically controlled. In an experiment with benzaldehyde, using the Durst procedure, only a trace of chlorohydrin 3 (eq. [2]) could be detected,² the major product being 2. It is interesting to note that Schöllkopf, in his study of the reaction of α -halosulfides with olefins to form



cyclopropanes, observed that the yield of side-product was greater with lithium alkyl base than with potassium t-butoxide (5).

Epoxy sulfides 1a and 1b were obtained in a ratio of 1:4.5 and could be separated by recrystallization from ether.^{3,4} The epoxymethine protons of 1a (trans) were centered at δ 4.32 and δ 3.83 with a coupling constant of 2.0 Hz; for 1b (cis), at δ 4.60 and δ 4.18 with a coupling constant of 4.5 Hz; and for 1c at δ 4.22 and δ 2.80 with a coupling constant of 4.5 Hz. The chemical shift assignments were made on the basis of those observed for 4, prepared from

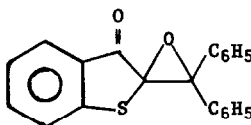
1. This observation has been noted by Schöllkopf in the metalation of chloromethyl phenyl sulfide with n-butyllithium or potassium t-butoxide (5).
2. Infrared and n.m.r. spectra of the reaction mixture, except for the ($s = 0$) in the i.r., were like those obtained for the chlorohydrin from chloromethyl p-tolyl sulfoxide.
3. All new compounds gave satisfactory elemental and mass spectrometric analyses, and all structures were confirmed by i.r. and n.m.r. spectroscopy.
4. 1b, a solid, m.p. 59-60.5°C, crystallizes from the solution. The isomer 1g is a viscous oil which can be freed of 1b by successively concentrating and cooling the ether solution until no more crystalline 1b is obtained. The oil remaining after evaporation of the ether was pure 1a by i.r. and n.m.r. analysis.



4

benzaldehyde-d; the α -proton is at lower field. Only the cis-epoxide has been obtained in the case of 1c, and the cis isomer was the major component in the mixture of 1a and 1b. We reported the predominant formation of a less soluble cis isomer from benzaldehyde in our synthesis of α,β -epoxy sulfoxides (2).

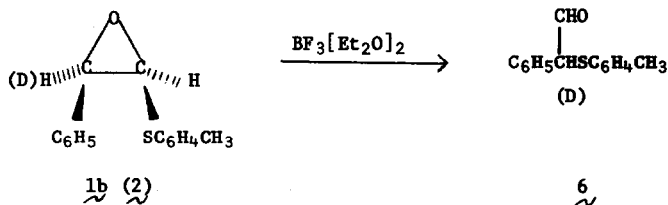
With the possible exception of compound 5, α,β -epoxy sulfides have to our knowledge not been reported.⁵ Within the limitations cited, our procedure allows a simple preparation of this



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new functional group, and its properties are being investigated. In this regard we find that 1b rearranges with boron trifluoride etherate in a manner analogous to that reported (2, 7) for α,β -epoxy sulfoxides and sulfones; in particular, treatment of 1b or 2 with BF_3 etherate (eq.[3]) gave phenyl (*p*-tolylthio) acetaldehyde (6) with exclusive migration of the *p*-tolylthio group.⁶

[3]



5. While 5 may be an epoxy sulfide in a formal sense, it is at the same time an epoxy ketone and indeed its method of preparation is that well known for α,β -epoxy ketones (6).
6. The n.m.r. spectrum of 6 shows an aldehydic proton and a benzylic proton, centered at $\delta 9.48$ and $\delta 4.56$, respectively, with coupling constants of 4.5 Hz.

Investigation of the rearrangement of epoxides 1a, and 1c is underway, and a completely general method for effecting a Darzens condensation of chloromethyl sulfides with aldehydes and ketones is being sought.

Acknowledgement

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