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α,β-EPOXY SULFOXIDES AND SULFONES.

THERMAL AND ACID CATALYZED REARRANGEMENTS.

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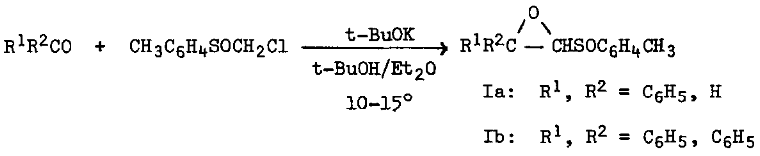
The synthesis of α,β-epoxy sulfoxides (1) and sulfones (2,3) has been described recently. This communication reports the thermal and acid catalyzed rearrangements of α,β-epoxy sulfoxides Ia and Ib and of the corresponding α,β-epoxy sulfones, IIa and IIb, as examples of what appears to be a general method and the one of choice for the synthesis of β-carbonyl sulfoxides and sulfones.[1]

We have found that the Darzens condensation reported earlier (2) as a general synthesis for α,β-epoxy sulfones works equally well for the sulfoxide analogs, eq. [1]. Whereas in the case of the α,β-epoxy sulfone IIa only the trans-epoxide was formed (2), the α,β-epoxy sulfoxide Ia appears to be predominantly cis, on the basis of n.m.r. coupling constants. The epoxymethine protons of Ia were centered at τ5.47 and 5.92 with a coupling constant of 3.5 Hz, well outside the range normally found for trans-epoxides but within the range found for the cis-isomers (4). The n.m.r. spectrum of the residue remaining from recrystallization showed, in addition to the set of doublets with J = 3.5 Hz, a second set of doublets of about the same chemical shifts but with J = 1.5 Hz, indicating that some trans-isomer was present. The difficulty of predicting

[1]



$$R^1R^2CO + CH_3C_6H_4SOCH_2Cl \xrightarrow[\text{t-BuOH/Et}_2\text{O}\ \ 10\text{-}15^\circ]{\text{t-BuOK}} R^1R^2C\overset{O}{-}CHSOC_6H_4CH_3$$

Ia: $R^1, R^2 = C_6H_5, H$

Ib: $R^1, R^2 = C_6H_5, C_6H_5$

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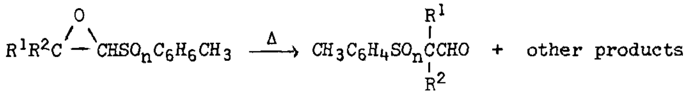
[1] Similar rearrangements have been observed for several examples of α,β-epoxy sulfoxides and sulfones. The four examples reported here are those for which the details are most complete; a comprehensive report will be published later. Professor T. Durst and his group at the University of Ottawa have obtained results which are similar to ours and it was decided to submit our work for simultaneous publication.

the stereochemistry of the final products from a Darzens-type condensation is well known (5); our observation could be explained by precipitation of a less soluble cis isomer. In general, however, the Darzens-type condensation appears to be an excellent method for the preparation of sulfur-substituted oxiranes, without some of the complications encountered in syntheses starting from the halohydrins (1,3).[2]

THERMAL REARRANGEMENT

We have observed that most α,β-epoxy sulfoxides and sulfones decompose slowly when left at room temperature, and more rapidly when heated. Once decomposition had begun, it appeared to be autocatalytic, consuming all of the material. The major product from all of the thermal decompositions was the β-carbonyl sulfoxide or sulfone resulting from an intramolecular migration of the p-tolylsulfinyl or p-tolylsulfonyl group, respectively, eq. [2].[3]

[2]



$$R^1R^2\overset{O}{C-C}HSO_nC_6H_6CH_3 \xrightarrow{\Delta} CH_3C_6H_4SO_n\overset{R^1}{\underset{R^2}{C}}CHO \quad + \quad \text{other products}$$

$R^1 = C_6H_5$

$R^2 = C_6H_5$ or H

$n = 1$ or 2

Rather unexpectedly, cis-2-phenyl-1-(p-tolylsulfinyl)-1,2-epoxyethane (Ia) was unchanged after heating for 6 h at 50°; unfortunately, no trans-isomer was available for comparison. Three compounds were obtained from the thermal decomposition of 1,1-diphenyl-2-(p-tolylsulfinyl)-1,2-epoxyethane (Ib). In addition to the major product, diphenyl(p-tolylsulfinyl)acetaldehyde (IIIb, eq. [2], $R^1 = R^2 = C_6H_5$, $n = 1$), a second carbonyl compound, 2-phenyl-2-(p-tolylsulfinyl)-acetophenone (IVb) was obtained, as well as some material having infrared absorptions for sulfoxide but none for carbonyl. The former (IVb) must arise by migration of a phenyl group from C_β to C_α; the latter has not been identified.[4] Although the rearrangement to form IVb might

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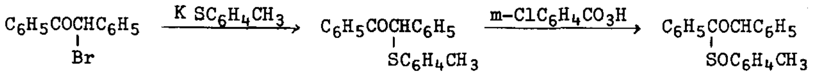
[2] D.F. Tavares, R.E. Estep, and J.R. Obst, to be published.

[3] All new compounds gave satisfactory elemental analyses, and all structures were confirmed by i.r. and n.m.r. spectroscopy.

[4] It has been established that this compound is not diphenyl p-tolyl sulfoxide, which might have been expected from a deformylation of IIIb, by analogy with the thermal rearrangement of IIb.

require the formation of an apparently objectionable α-sulfinyl carbonium ion, analogous migrations have been reported for the acid induced rearrangements of α,β-epoxy ketones (6,7). The structure IVb was confirmed by independent synthesis, eq. [3].[5]

[3]



$$\underset{Br}{C_6H_5COCHC_6H_5} \xrightarrow{K\,SC_6H_4CH_3} \underset{SC_6H_4CH_3}{C_6H_5COCHC_6H_5} \xrightarrow{m\text{-}ClC_6H_4CO_3H} \underset{SOC_6H_4CH_3}{C_6H_5COCHC_6H_5}$$

Thermal rearrangement of *trans*-2-phenyl-1-(*p*-tolylsulfonyl)-1,2-epoxyethane (IIa) gave phenyl-(*p*-tolylsulfonyl)acetaldehyde (Va, eq. [2], $R^1 = C_6H_5$, $R^2 = H$, $n = 2$), together with other sulfur containing compounds known to be formed in the thermal decomposition of *p*-toluenesulfinic acid (8.9). The thermally more labile 1,1-diphenyl-2-(*p*-tolylsulfonyl)-1,2-epoxyethane (IIb) gave the expected diphenyl(*p*-tolylsulfonyl)acetaldehyde (Vb, eq. [2], $R^1 = R^2 = C_6H_5$, $n = 2$) and some diphenylmethyl *p*-tolyl sulfone, presumably by deformylation of Vb.[6]

REARRANGEMENT WITH BORON TRIFLUORIDE

The acid-catalyzed rearrangement of α,β-epoxy ketones has been studied extensively by House (10). The products were aldehydes and ketones, and in some cases each diastereoisomer produced a different isomerization product (6a); usually, however, fission of the oxirane ring with intramolecular migration of the acyl group was observed. We have found that boron trifluoride etherate gives an essentially quantitative conversion of α,β-epoxy sulfoxides and sulfones to β-carbonyl sulfoxides and sulfones, respectively, eq. [2]. Treatment of Ia with BF_3 etherate gave a rapid conversion to phenyl(*p*-tolylsulfinyl)acetaldehyde (IIIa), while Ib gave a mixture of IIIb and IVb as before (thermal), within 15 min. Longer contact of Ib with BF_3 etherate gave a more complex mixture and the amount of IVb relative to IIIb was diminished. Both the α,β-epoxy sulfones IIa and IIb rearranged with exclusive migration of the *p*-tolylsulfonyl group (eq. [2]) to give Va and Vb, respectively; no other rearrangement products could be detected (8).

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[5] This sequence of reactions fails to give the possible α,β-epoxy sulfide (G.W. Griffin, private communication).

[6] We have found that pure Vb will not deformylate with heat alone, suggesting that some of the other decomposition products from IIb are involved. T. Durst (private communication) obtained diphenylmethyl *p*-tolyl sulfone from 1,1-diphenyl-2-chloro-2-phenylsulfinylethane with base in an attempt to form the epoxide.

All of the β-carbonyl sulfoxides and sulfones which we have observed in the foregoing rearrangement studies have been stable, white, crystalline compounds and all formed 2,4-dinitrophenylhydrazones. Unfortunately, only one of each possible cis-trans pair of epoxides was available, so the stereochemical dependence of these rearrangements is unknown.

Acknowledgement

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