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THERMAL AND ACID-CATALYZED REARRANGEMENT OF α-EPOXY SULFOXIDES AND SULFONES

T. Durst and K.-C. Tin

Department of Chemistry, University of Ottawa, Ottawa 2, Canada

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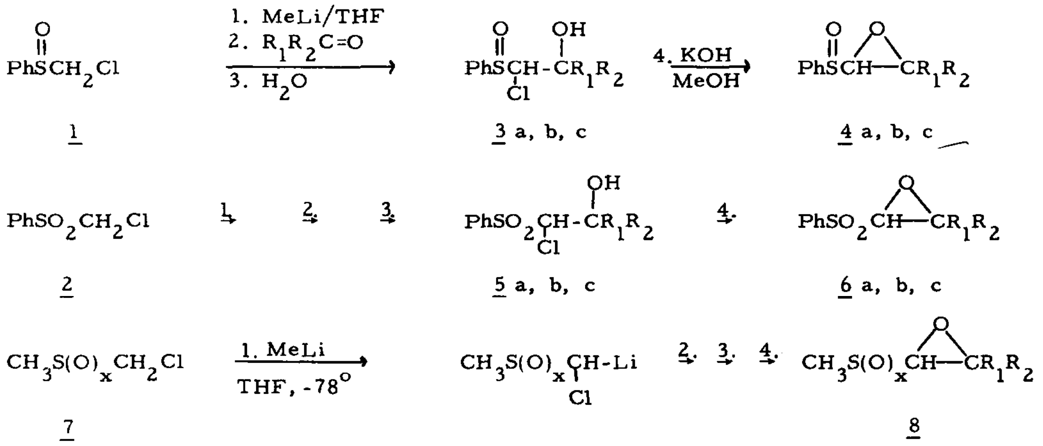
Recently we reported the metallation of chloromethyl phenyl sulfoxide 1 and chloromethyl phenyl sulfone 2 (1) and shown that this allows a simple preparation of a new functional group i.e. α-epoxy sulfoxides 4 and an easy access to a variety of α-epoxy sulfones 5, a group of substances not readily available by previously published procedures (2) Scheme I. Since our initial report, Tavares and co-workers have shown that the reaction of chloromethyl aryl sulfones and sulfoxides with ketones and aldehydes leads directly to α-epoxy sulfones (3) and α-epoxy sulfoxides (4) respectively. The extension of the Tavares procedure may be limited to sulfones and sulfoxides which cannot undergo a Ramberg-Backlund type rearrangement (5). The low temperature metallation reaction holds no such restrictions and we have prepared the lithio derivatives from both chloromethyl methyl sulfoxide (7, x=1) and chloromethyl methyl sulfone (7, x=2). Condensation of these derivatives with ketones and aldehydes leads to adducts which are easily converted to epoxides (1).

Scheme I

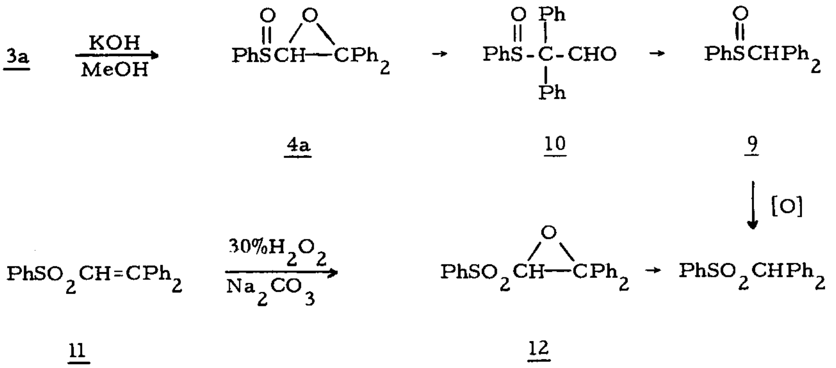


a) $R_1=R_2$ = Ph; b) $R_1=R_2$ = CH_3; c) R_1 R_2 = $(CH_2)_5$

In the course of investigating the epoxide formation from the adducts 3 and 5, we have discovered a thermal and acid catalyzed rearrangement which parallels those reported for a number of other negatively substituted epoxides, for example, α-halo (6), α-keto (7), α-carbomethoxy (8) and α-phosphonate ester epoxide (9).[1]

Reaction of 3a, the adduct from benzophenone and chloromethyl phenyl sulfoxide, with 5% KOH in methanol for 10 min. at room temperature failed to give the expected epoxide 4a, (10) in contrast to the behavior of 3b and 3c which gave the epoxides 4b and 4c respectively in greater than 90% yield. Instead we obtained a virtually quantitative yield of benzhydryl phenyl sulfoxide 9. The formation of 9 can be rationalized as involving initial formation of 4a followed by rearrangement to the aldehyde sulfoxide 10 and finally deformylation. Scheme II. The product 9 was identified by oxidation to benzhydryl phenyl sulfone. The latter compound was also obtained by reaction of 2 with benzophenone in refluxing MeOH/MeONa (20% yield), and by hydrogen peroxide/Na_2CO_3 treatment of the unsaturated sulfone 11. Both of these procedures presumably involve rearrangement of the intermediate epoxy sulfone 12.

Scheme II



The rearrangement of the epoxy sulfone 6b to the formyl sulfone 13 was carried out at 130° (37% yield) or in ether solution catalyzed by BF_3 (72% yield). Deformylation of 13 (5% KOH/MeOH) afforded quantitatively isopropyl phenyl sulfone. The thermal and acid catalyzed rearrangements of a number of other epoxy sulfones and sulfoxides are recorded in the Table.

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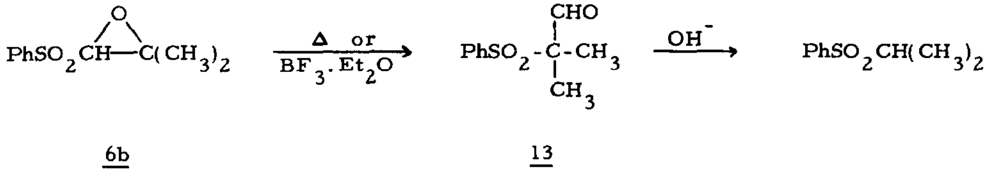
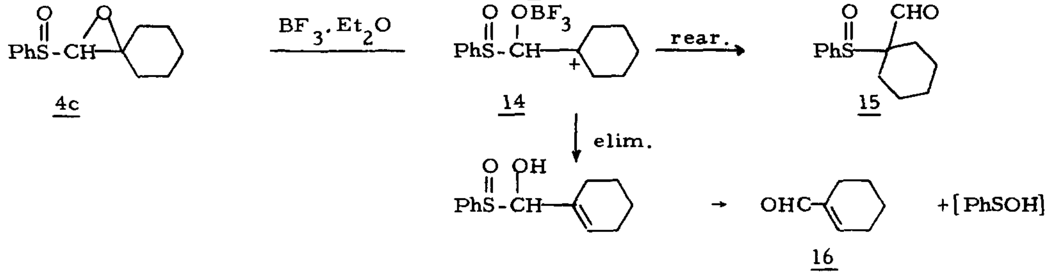
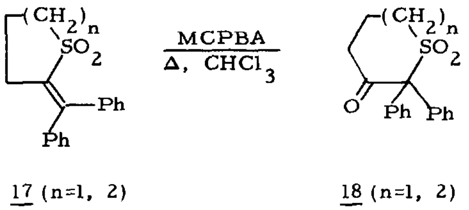
[1] We have also learned that Professor Tavares and his group have made similar observations and have agreed to communicate our results at this time.



The acid catalyzed rearrangement probably proceeds via the intermediate 14. Such a species, which can undergo either rearrangement or proton elimination, would account for the formation of the rearranged sulfone 15 and Δ-1-cyclohexene carboxaldehyde 16 in the rearrangement of 4c. A similar ratio of rearrangement to elimination was observed for the epoxy sulfone 6c.



The rearrangement of epoxy sulfoxides and sulfones represents an interesting possibility for ring enlargement and thus a potential route to medium size sulfur containing rings which are generally difficult to prepare from acyclic precursors. Several examples indicating the feasibility of such a scheme have already been carried out. Epoxidation of 17 (n=1, 2) with *m*-chloroperbenzoic acid in refluxing chloroform leads directly to the ring enlarged products 18 in greater than 90% yield. A study of the generality of ring enlargement reaction together with rearrangement of epoxides bearing other sulfur functions will be reported shortly.



TABLE

Epoxide	Rearr. Method	Product	Yield (%)[1]
4a[2]	thermal	$Ph_2CHSOPh$[3]	95
4c	$BF_3.Et_2O$	15	36
4c	thermal	16[3]	68
6b	thermal	13	37
6b	$BF_3.Et_2O$	13	72
6c	$BF_3.Et_2O$	15	34
12[2]	thermal	Ph_2CHSO_2Ph[3]	70
17 (n=1)[2]	thermal/acid	18 (n=1)	90
17 (n=2)[2]	thermal/acid	18 (n=2)[2]	91

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1) Yields refer to purified product; 2) epoxide not isolated; 3) product derived from subsequent reaction of initial rearrangement product.

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REFERENCES

1. T. Durst, J. Am. Chem. Soc., 91, 1034 (1969).
2. M. Ballester, Chem. Rev., 55, 283 (1955).
3. P. F. Vogt and D. F. Tavares, Can. J. Chem., 47, 2875 (1969).
4. D. F. Tavares, private communication.
5. L. A. Paquette, Acc. of Chem. Research, 1, 209 (1968).
6. R. N. McDonald and R. N. Steppel, J. Am. Chem. Soc., 91, 784 (1969); R. N. McDonald and T. E. Tabor, J. Org. Chem., 33, 2934 (1968); R. N. McDonald and T. E. Tabor, J. Am. Chem. Soc., 89, 6573 (1967).
7. H. O. House and G. D. Ryerson, J. Am. Chem. Soc., 38, 979 (1961).
8. S. P. Singh and J. Kagan, J. Am. Chem. Soc., 91, 6198 (1969).
9. M. Sprecher and D. Kost, Tetrahedron Letters, 703 (1969); C. E. Griffin and S. K. Kundu, J. Org. Chem., 34, 1532 (1969).
10. All new compounds reported herein gave acceptable analyses and had spectroscopic properties in agreement with the assigned structures.