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REGIOCHEMISTRY AND STEREOCHEMISTRY OF OXIRANE RING-OPENING WITH SILYL HALIDES

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Abstract: The ring-opening of various styrene and stilbene oxides with silyl halides was examined. The regiochemistry of ring-opening was independent of the silyl halide used, but the stereochemistry of ring-opening was sensitive to both the choice of halide and the steric bulk of groups attached to silicon.

The electrophilic opening of oxiranes with various silicon reagents is of interest for converting oxiranes to allylic alcohols.[1] Regiochemical and stereochemical details of such reactions are fairly well defined for mono- and 1,2-disubstituted oxiranes but not for those capable of opening to give more stable carbenium ions. Variation of regiochemistry and stereochemistry with respect to the silicon reagent has not been addressed.

We examined the ring-opening of oxiranes with silyl bromides and iodides in acetonitrile. The regiochemistry of ring-opening was independent of the nature of the attacking species, but the stereochemistry of ring-opening was sensitive to both the nature of the halogen and the nature of the hydrocarbon groups attached to silicon.

Trimethylsilyl iodide (TMSI), trimethylsilyl bromide (TMSBr), tert-butyldimethylsilyl iodide (BDMSI), tert-butyldimethylsilyl bromide (BDMSBr), and tert-butyldiphenylsilyl iodide (BDPSI) were prepared by adding bromine or iodine to a dry acetonitrile solution of the appropriate (phenylseleno)silane.[1e] The resulting silyl halide solutions (~1 M) were added dropwise to a stirred solution of the oxirane in acetonitrile (~1 M). For TMSI and BDMSI, the oxirane solutions were cooled to -78°C before addition of the halide, and the reactions were quenched by adding saturated sodium bicarbonate solution immediately after addition was complete. Reactions with TMSBr were stirred for 1 h at 0°C before quenching. Reactions with BDMSBr and BDPSI were warmed for 1-3 h at reflux to give complete reaction.

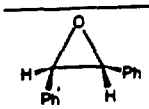
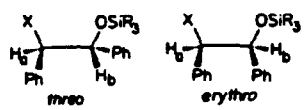
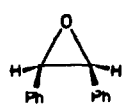
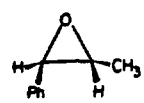
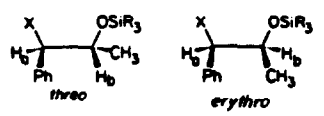
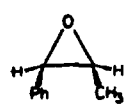
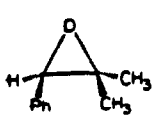
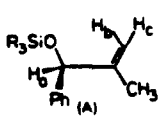
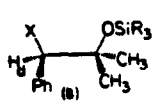
The products of reaction were isolated by chromatography on silica gel (9/1 hexane/ether), and product ratios were determined by VPC and 90 MHz ^{1}H NMR techniques. BDMSBr and BDPSI gave only silylated halohydrins or allylsilyl ethers. TMSI and BDMSI, in addition to silylated iodohydrins, gave 1-5% of olefinic products of mixed stereochemistry from deoxygenation of the oxiranes.[2] In addition, TMSI and BDMSI gave 1-3% of diphenylacetaldehyde from reaction with both cis- and trans-stilbene oxides. Diphenylacetaldehyde was isolated in 5% yield from the reaction of TMSBr with cis-stilbene oxide.

The regiochemistry of ring-opening was independent of the silyl halide used

(see Table I). The regiochemistry of the silyl ethers was assigned on the basis of ^{1}H NMR chemical shifts,[3] which were compared with those of the corresponding halohydrin.[4,5] Ring-opening occurs in the direction of greatest carbenium ion stability, as would be expected for initial electrophilic attack of silicon on oxygen to give an onium species followed by partial or complete cleavage of the carbon-oxygen bond, and subsequent nucleophilic attack by halide. The distribution of products from the opening of β,β-dimethylstyrene oxide is consistent with the observation that, in solution, the tert-butyl carbenium ion is ~1 kcal/mole more stable than the methylbenzyl carbenium ion.[6]

The data in Table I suggest considerable positive charge development on the carbon of the bond being cleaved before the nucleophile becomes involved and that the stereochemical outcome of cleavage of this bond is sensitive to both the halogen and the hydrocarbon groups attached to silicon.

Table I. Stereochemistry of Oxirane Ring-Opening with Silyl Halides.

OXIRANE	PRODUCTS	(threo/erythro) TMSI	TMSBr	BDMSI	BDMSBr	BDPSI
	 threo erythro	>99:1	20:80	>99:1	30:70	30:70
	J_{ab}(Hz) 7.8-8.2 / J_{ab}(Hz) 6.7-7.4	>99:1	86:14	>99:1	83:17	80:20
	 threo erythro	45:55	11.89	51:49	27:73	9:91
	δCH_3 1.00-1.08 / δCH_3 1.20-1.38	—	—	55:45	84:16	—
	 (A)	A/B 90:10	—	90:10	88:12	—
		δH_a 4.81		4.77	4.77	
		δH_b 5.07		5.07	5.07	
		δH_c 5.07		5.07	5.07	
	 (B)	δH_d 4.40		4.43	4.60	

The stereochemistry of the halohydrin ethers was established in two ways. The vicinal methine coupling constants for threo and erythro pairs were determined for the products from the stilbene oxides and compared with literature values for the corresponding chlorohydrins.[4] The stereochemistries for products derived from cis- and trans-β-methylstyrene oxides were determined from the chemical shifts of the methyl doublets. The methyl doublets are consistently at

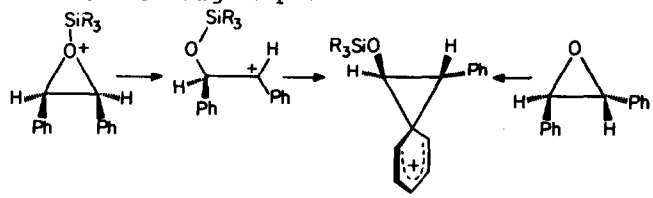
lower field in the erythro than in the threo isomers in a series of 1,2-disubstituted 1-arylpropanes.[5] The halohydrin ethers were converted to oxiranes of well-defined stereochemistry by treatment with an excess of tetrabutylammonium fluoride in tetrahydrofuran.[7] Silyl fluoride should be lost through a trans elimination, thus relating oxirane and halohydrin ether stereochemistries.

The most striking differences in stereochemistries were observed for trans-stilbene oxide. TMSI and BDMSI gave complete retention of stereochemistry (threo product) at the carbon undergoing cleavage, but the bulkier BDPSI gave mostly inversion (erythro product). TMSBr and BDMSBr gave mostly inversion.[8]

With cis-stilbene oxide, TMSI and BDMSI were completely stereospecific, giving the threo-iodohydrin silyl ether from cleavage with inversion. The other silicon reagents were stereoselective toward inversion, but 14-20% of products of retention (erythro) were observed (Table I).

Similar results were obtained from the β-methylstyrene oxides. TMSI and BDMSI gave mixtures of nearly equal amounts of products of inversion and retention, but TMSBr, BDMSBr, and BDPSI gave mostly inversion peroducts (Table I).

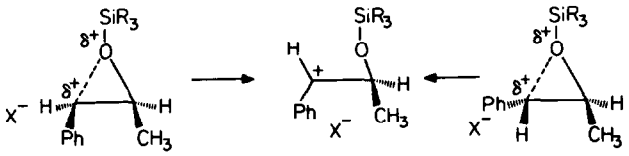
The stereospecificity observed for both cis- and trans-stilbene oxide to give only the threo product upon ring-opening with TMSI or BDMSI suggests a common intermediate from each of the oxiranes, presumably a phenonium ion. The isolation of small amounts of diphenylacetaldehyde from these product mixtures is further support for the involvement of a phenonium ion. As shown below, one oxirane, presumably cis-stilbene oxide, would undergo C-O bond cleavage, rotation, followed by phenyl participation to give an intermediate directly accessible from the other oxirane simply by phenyl participation. Furthermore, the intervention of a phenonium suggests a late involvement of the nucleophile, iodide, in the transition leading to products.



The use of TMSBr and BDMSBr allows the intermediate onium species to be intercepted earlier in the transition state by bromide, which should be a better nucleophile than iodide in acetonitrile.[9] With TMSBr no diphenylacetaldehyde is observed from trans-stilbene oxide, which would require cleavage and rotation for a phenonium ion, but cis-stilbene oxide gives measurable amounts. The observations that inversion does not occur stereospecifically for either cis- or trans-stilbene oxide with TMSBr and BDMSBr argues against extensive involvement of phenonium ions. Alternatively, bromide attacks the cyclic onium species before rupture and, although backside attack to give inversion is preferred, a significant amount of frontside attack by the nucleophile occurs to give products of retention.

The bulky BDPSI could sterically promote inversion in two ways. The initial silyl onium species might sterically prevent phenonium ion formation, or the bulky silyl group might hinder attack from the same face in either the phenonium ion or the initial onium species.

Similar arguments can be used for the results with cis- and trans-β-methylstyrene oxide. Although a phenonium ion is not observed here, a freely rotating benzyl carbenium ion is a possibility which would explain the nearly 1:1 mixtures of inversion and retention observed for TMSI and BDMSI.[10] The silyl bromide gives mostly inversion by attack of the nucleophile before cleavage.



An alternative explanation that best explains the results with BDPSI is that products of retention become more likely the further the C-O bond is stretched, which will be a function of the strength of the nucleophile. With BDPSI, frontside attack by iodide to give retention is sterically hindered, but with TMSI and BDMSI it is not.

In conclusion, the regiochemistry of oxirane ring-opening is fairly independent of the silyl halide used. However, the stereochemistry of ring-opening might be varied by judicious choice of halogen and the steric bulk at silicon.

References and Notes

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2. TMSI has been used for preparative deoxygenation of oxiranes: Denis, J. N.; Magnane, R.; Van Eenoo, M.; Krief, A. Nouveau J. Chem. 1979, 3, 705-707.
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4. Lasne, M. C.; Masson, S.; Thuillier, A. Bull. Soc. Chim. Fr. 1973, 1751.
5. Schmid, G. H. Can. J. Chem. 1968, 46, 3415; Garratt, D. G. ibid. 1979, 57, 2180.
6. Arnett, E. M.; Larsen, J. W. in "Carbonium Ions," G. A. Olah and P.v.P. Schleyer, Eds., Vol. 1, Wiley: New York, 1968.
7. Threo isomers gave cis-oxiranes and erythro isomers gave trans-oxiranes. The product ratios for oxirane mixtures were identical with the product ratios of halohydrin ether mixtures. Oxirane formation was more rapid than equilibration of the silyl ethers by Bu_4NX in THF.
8. The composition of product mixtures from TMSBr reactions was quite sensitive to the temperature of reaction. At room temperature, deoxygenation pathways became significant as well as diphenylacetaldehyde formation.
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10. No amide products from a Ritter reaction were observed. Under the conditions of reaction with dry (distilled from P_2O_5) acetonitrile and short reaction times, this is not surprising. For the Ritter reaction with benzyl alcohols, see: Parris, C. L.; Christenson, R. M. J. Org. Chem. 1960, 25, 331.

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