

Thermal reactions of oxiranes

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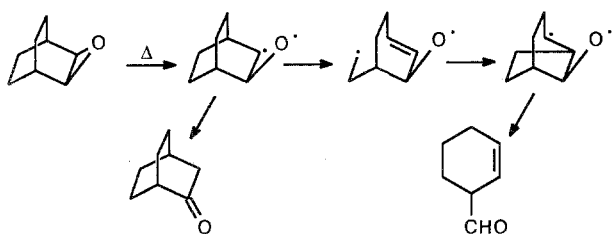
The pyrolytic reactions of tetramethylethylene oxide, cyclopentene oxide, cyclohexene oxide, cyclooctene oxide, 1,2-epoxyethylbenzene, 1,2-epoxy-2-phenylpropane, 1,2-epoxy-1-phenylpropane, and 1,2-epoxy-1,2-diphenylethane were investigated at 600 °C using a conventional pyrolysis flow system. The products are mainly due to thermal cleavage of the oxirane ring followed by rearrangement to give carbonyl compounds.

Key words: oxiranes, pyrolysis, rearrangement, cleavage; biradical, decomposition.

Thermal rearrangements of oxiranes sealed *in vacuo* in pyrex tubes are well known (see, for example, Ref. 1). Thermolysis of simple oxiranes under these conditions gives complex mixtures of products that predominantly consist of aldehydes and ketones.¹ Hudrlik *et al.*² gave a useful short list of references to kinetic and preparative studies of the thermal decomposition of simple oxiranes in which the rearrangement to give a carbonyl compound is often the main reaction.

The results of most gas-phase studies suggest the intermediacy of biradicals. The thermal rearrangement of bridged cyclobutene oxiranes to cycloalkenylaldehydes³ and the pyrolytic rearrangement of norbornene oxide at 550 °C⁴ (Scheme 1) are typical examples. These results are similar to those reported by Crandall,⁵ who studied the acid catalyzed rearrangement of norbornene oxide.

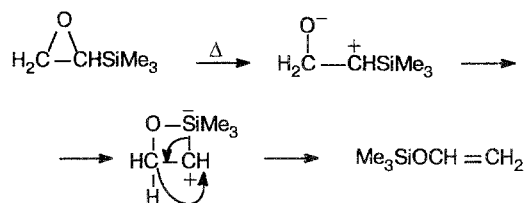
Scheme 1



The rearrangement of α,β -epoxysilanes (Scheme 2) that occurs at 600 °C at a pressure of 0.2–0.7 Torr and gives a number of silyl vinyl ethers in high to moderate yields is preparatively useful.²

Dehydration of 2,3-dimethylbutane-1,2-diol (pinacol) to give 3,3-dimethylbutan-2-one (pinacolone) and 2,3-dimethylbutadiene in the presence of alumina⁶ or copper⁷ at high temperatures was reported to involve an oxirane intermediate. Therefore, it was of interest to

Scheme 2



investigate the pyrolytic reactions of oxiranes at high temperatures and to consider the difference between thermolysis in a flow system and thermolysis under static conditions in which some oxiranes were reported to give complex mixtures of products. This paper presents the results of a comprehensive pyrolytic study of various oxiranes.

Results and Discussion

We studied pyrolysis of tetramethylethylene oxide, cyclopentene oxide, cyclohexene oxide, cyclooctene oxide, 1,2-epoxyethylbenzene, 1,2-epoxy-2-phenylpropane, 1,2-epoxy-1-phenylpropane, and 1,2-epoxy-1,2-diphenylethane, yielding mixtures of products of various compositions.

Tetramethylethylene oxide. The liquid pyrolysate contained mainly the starting oxirane (59–61 %) and pinacolone (3,3-dimethylbutan-2-one, 10–13 %). In addition, small amounts of two unidentified compounds having the same molecular mass (m/z 100) as the starting material were obtained.

Cyclopentene oxide. The starting material was recovered unchanged.

Cyclohexene oxide. The liquid pyrolysate contained mostly the starting oxirane (>95 %) and only traces of cyclohexadiene, cyclohexene, and cyclopentanecarboxaldehyde.

Cyclooctene oxide. The liquid pyrolysate consisted of cyclooctanone (68–71 %) and cycloheptanecarboxaldehyde (12–14 %). In addition, traces of unidentified compounds were found.

1,2-Epoxyethylbenzene (styrene oxide). The liquid pyrolysate contained 2-phenylethanal (phenylacetaldehyde, 57–60 %), toluene (18–20 %), and 1,2-diphenylethane (8–10 %).

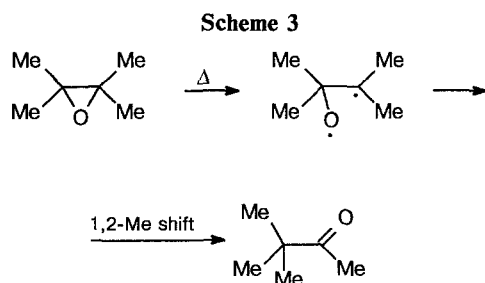
1,2-Epoxy-2-phenylpropane. The pyrolysate consisted of 2-phenylpropanal (50–54 %), phenylethylene (31–34 %), and acetophenone (8–9 %).

1,2-Epoxy-1-phenylpropane. The pyrolysate contained 1-phenylpropan-2-one (44–46 %), ethylbenzene (10–13 %), 2-phenylpropanal (6–8 %), diphenylethane (4–6 %), and the starting epoxide (9–12 %). Trace amounts of toluene and phenylethylene were also detected.

1,2-Epoxy-1,2-diphenylethane (stilbene oxide). The pyrolysate contained the starting oxirane (40–43 %), α -phenylacetophenone (13–15 %), 1,1-diphenylethylene oxide (9–11 %), and 2,2-diphenylethanal (6–9 %). In addition, small amounts of diphenylmethane and 1,2-diphenylethylene were obtained.

The inherent strain in the oxirane ring ($E = 27.2 \text{ kcal mol}^{-1}$) is nearly equal to that in cyclopropane ($E = 27.5 \text{ kcal mol}^{-1}$). Therefore, it is not surprising that the activation energy of the monomolecular thermal decomposition of oxirane to ethanal is comparable to that of the corresponding rearrangement of cyclopropane to propene.¹⁰ According to the literature data, substituents in oxiranes have an effect on ring opening and on rearrangement. For example, the trimethylsilyl group in α,β -epoxysilanes facilitates rearrangement,² while the phenyl substituent in 1,2-epoxyethylbenzene has an effect on the direction of ring opening.¹¹

In the study of the pyrolysis of tetramethylethylene oxide (600 °C) we found that most of the starting oxirane was recovered unchanged, and the only identified product was 3,3-dimethylbutan-2-one. This result is consistent with the reported data¹² on the inertness of epoxides derived from tetrasubstituted alkenes. The reaction product is formed through opening of the oxirane ring to form the intermediate biradical followed by migration of the methyl group (Scheme 3).



Of oxygen-bridged bicyclic molecules, *viz.*, cyclopentene oxide, cyclohexene oxide, and cyclooctene oxide,

only the latter undergoes pyrolysis to any significant degree. The low reactivity of cyclopentene oxide and cyclohexene oxide is not surprising, as the cyclopentane and cyclohexane rings have far less strain energies ($E = 7.3$ and $1.4 \text{ kcal mol}^{-1}$, respectively) than the cyclooctane ring ($E = 11.5 \text{ kcal mol}^{-1}$).¹³ The cyclooctane ring as such is more susceptible to rearrangement, which also relieves the additional strain created by the oxirane ring. The stability of cyclohexene oxide at 600 °C has been reported by Hudrlik *et al.*² Therefore, under the conditions of pyrolysis, cyclooctene oxide readily rearranges into cyclooctanone and cycloheptanecarboxaldehyde (*cf.* the strain energy of the cycloheptane ring, $E = 7.8 \text{ kcal mol}^{-1}$).¹³

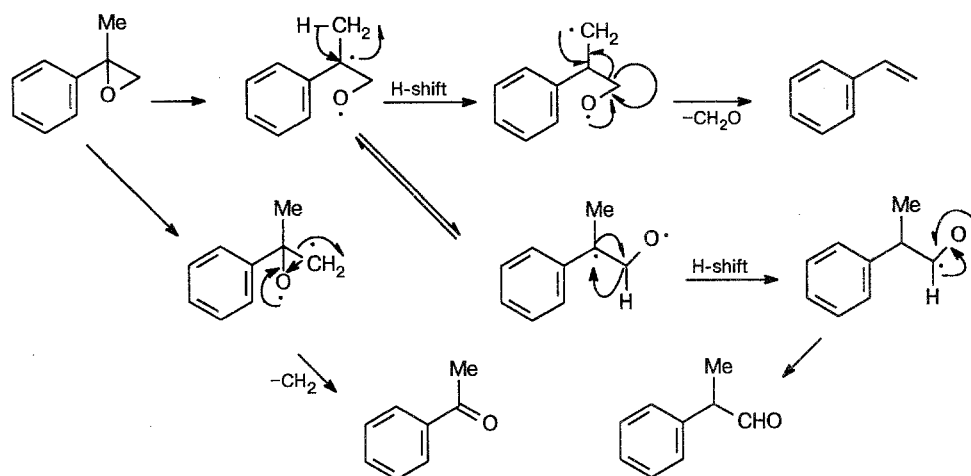
It has been reported that thermolysis of 1,2-epoxyethylbenzene at 500 °C affords mostly toluene, while its thermal rearrangement at 200–300 °C leads to phenylethanal.¹¹ However, at 600 °C only partial rearrangement was observed.² Under our pyrolytic conditions, the rearrangement of 1,2-epoxyethylbenzene gave mostly phenylacetaldehyde and small amounts of toluene and 1,2-diphenylethane resulting from fragmentation. The absence of acetophenone in the mixture of products indicates that the oxirane ring cleaves preferentially at the α -position due to the inductive effect of the phenyl group.

Pyrolysis of two isomeric oxiranes, 1,2-epoxy-2-phenylpropane and 1,2-epoxy-1-phenylpropane, gave mostly products of rearrangement, namely 2-phenylpropanal and 1-phenylpropan-2-one, respectively. This result once again confirms that cleavage of the C—O bond bearing the phenyl group in the oxirane ring is preferred (Scheme 4). In the case of 1,2-epoxy-1-phenylpropane, in which the C(2) atom is bound to the methyl group, a small amount of 2-phenylpropanal resulting from cleavage of the other C—O bond was also obtained. All the other products formed in the pyrolysis of both substrates result from thermal fragmentation.

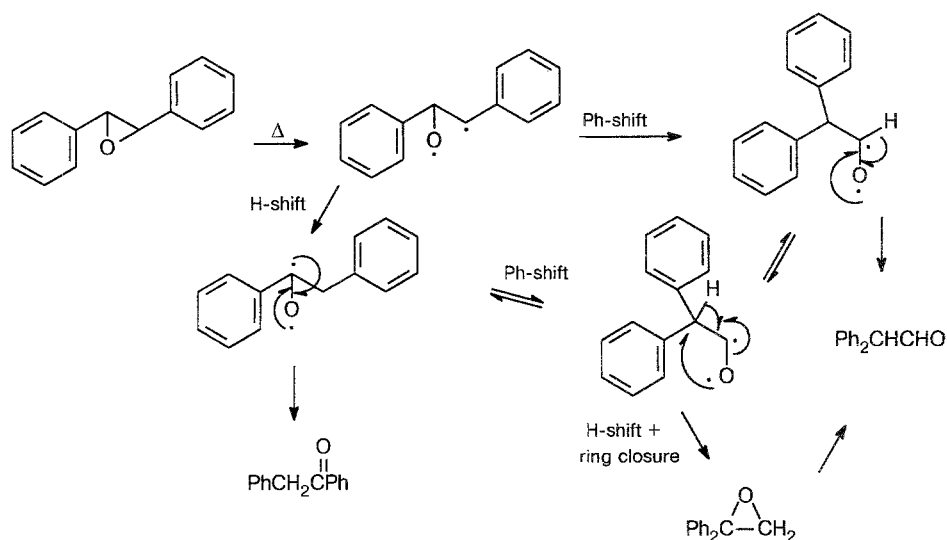
The last of the oxiranes investigated was 1,2-epoxy-1,2-diphenylethane. The mixture of products formed from this compound contained almost 50 % of the starting oxirane. The rearrangement products obtained were α -phenylacetophenone and 1,1-diphenylethylene oxide. These products are formed by cleavage of the oxirane ring to give a biradical followed by migration of hydrogen or phenyl, respectively. 2,2-Diphenylethanal, which was also isolated, may have been formed either by rearrangement of the starting oxirane or by rearrangement of the initially formed 1,1-diphenylethylene oxide (Scheme 5). The recovered starting oxirane may be due to the reverse closure of the oxirane ring in the intermediate biradical formed by the initial cleavage of the ring.

Pyrolysis of all of these substrates at temperatures below 600 °C gave only unchanged starting materials, while increase in the temperature to 700 °C led to thermal degradation yielding mixtures of products that were difficult to separate. High-pressure pyrolysis at

Scheme 4



Scheme 5



600 °C at greater duration of contact also led to extensive fragmentation.

Experimental

Preparation of the oxiranes. The cyclopentene oxide, cyclooctene oxide, and 1,2-epoxyethylbenzene used were commercial samples from Aldrich Chemicals. The other oxiranes were prepared by oxidation of the corresponding C=C double bonds by peracetic acid according to the standard literature procedure.⁸

Flash vacuum pyrolysis of the oxiranes. The apparatus used was based on the design of W. D. Crow (Australian National University). A similar setup has been described in the monograph by Brown.⁹ The oxiranes were volatilized from a horizontal inlet tube, through a 30×2.5 cm silica tube loosely packed

with glass wool and heated under vacuum (10^{-1} – 10^{-3} Torr) to 600 °C by a Carbolite Eurotherm MTF-12/38A tube furnace. Under these conditions the contact time of the substrates was in the range 1–10 ms.

The pyrolyses were generally carried out using 200–500 mg samples. The products were collected using a trap cooled with liquid nitrogen and then dissolved out of the trap in CDCl_3 (volatile products) or in CH_2Cl_2 (solids; the solvent was then evaporated). Each pyrolysis was carried out in triplicate.

The products were analyzed by NMR spectroscopy (80 MHz for ^1H and 75 MHz for ^{13}C) and GC-MS (using a Hewlett-Packard 5890A gas chromatograph coupled to a Finnigan Incos mass spectrometer with computerized data processing and library search).

The yields were estimated by adding known amounts of internal standards and comparing the NMR signals and/or relative areas of chromatographic peaks.

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References

1. A. Rosowky, in *Heterocyclic Compounds with 3- and 4-Membered Rings*, Ed. A. Weissberger, New York, 1964, Pt. 1, 231.
2. P. F. Hudrlik, C. N. Wan, and G. P. Withers, *Tetrahedron Lett.*, 1976, 1449 (see Ref 10 in this paper).
3. D. L. Garin, *J. Org. Chem.*, 1969, **34**, 2355.
4. D. L. Garin, *Can. J. Chem.*, 1969, **47**, 4071.
5. J. K. Crandall, *J. Org. Chem.*, 1964, **29**, 2830.
6. L. Schmerling, B. S. Friedman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, 1940, **62**, 2448.
7. L. P. Kyriakides, *J. Am. Chem. Soc.*, 1914, **36**, 985.
8. C. C. Price and D. D. Carmelite, *J. Am. Chem. Soc.*, 1966, **88**, 4041.
9. R. F. C. Brown, in *Pyrolytic Methods in Organic Chemistry*, Academic Press, New York, 1980.
10. K. Pihlaja and E. Taskinen, in *Physical Methods in Heterocyclic Chemistry*, Ed. A. R. Katritzky, Academic Press, New York, 1974, **6**, 199.
11. J. M. Watson and B. L. Young, *J. Org. Chem.*, 1974, **39**, 116.
12. D. H. Aue and R. N. Reynolds, *J. Am. Chem. Soc.*, 1973, **95**, 2027.
13. E. M. Engler, J. D. Andose, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1973, **95**, 8005; A. Greenberg and J. F. Liebman, in *Strained Organic Molecules (Organic Chemistry Series of Monographs)*, Academic Press, New York, 1978, **38**, 66.

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