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MASS SPECTRA OF AROMATIC EPOXIDES : CASES OF ALKYL AND ARYL MIGRATION.

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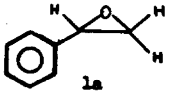
Several cases of methyl migration upon electron impact in mass spectrometry have recently been reported (1). Migration of larger groups however, e.g. phenyl, seems to be very rare (2)(3).

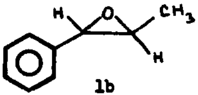
We have found that aromatic epoxides, such as styrene oxide 1a, trans 1-phenyl-1,2-epoxypropane 1b, cis 1-phenyl-1,2-epoxypropane 1c, 1-phenyl-2-methyl-1,2-epoxypropane 1d, cis and trans stilbene oxide 2 and 3, and tetraphenylethylene oxide 4, undergo a rather unexpected fragmentation, involving rearrangement of phenyl or alkyl groups. Moreover, comparison of the mass spectra of these compounds affords a rough estimate of the "migratory aptitude" of the various substituents.

Heating these epoxides in a stainless steel vessel at 150º for 20 minutes does not induce any detectable modification, as shown by I.R. spectroscopy. A small CO stretching band appears after one hour. Tetraphenylethylene oxide, when heated at 240º for 10 minutes, is recovered unchanged.

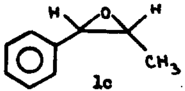
As the temperature of the ion source and of the inlet system was maintained at 150º, the rearrangements must be due essentially to electron impact.



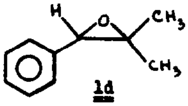
1a



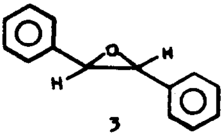
1b



1c



1d



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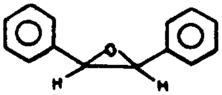

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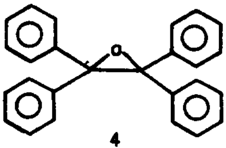

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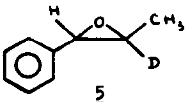
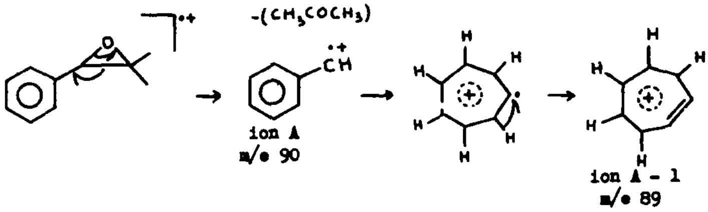


5

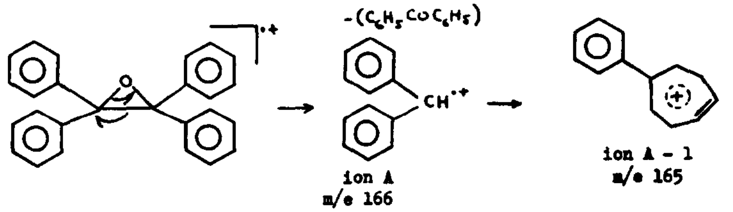
Two competing mechanisms have to be considered.

a) Elimination of one neutral fragment of aldehyde or ketone.

The base peak in the spectra of 1a, 1b, 1c and 1d, 2 and 3 occurs at m/e 90 (ion A). Ion A gives rise to ion A - 1 (m/e 89) (metastable peak at m^* 88). Their formation may be rationalized as follows (compound 1d) :



The same mechanism applies in the case of tetraphenylethylene oxide :

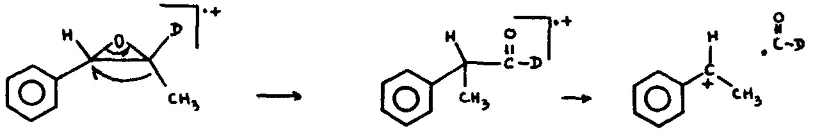


b) Opening of the oxirane ring and migration of hydrogen, alkyl or phenyl groups.

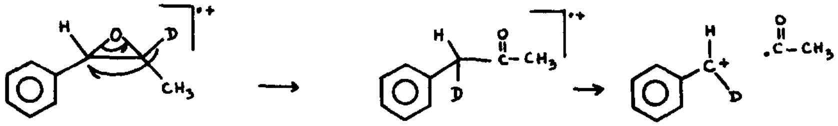
The mass spectra of the cis and trans isomers 1b and 1c are identical. It is therefore possible to discuss the mechanism of fragmentation of these epoxides with the aid of the deuterated compound 5, regardless of its stereochemistry.

In the mass spectrum of 1b, peaks are found at m/e 91 and m/e 105. The peak m/e 91 is shifted to m/e 92 in the mass spectrum of 5. On the contrary, the peak m/e 105 is partly shifted to m/e 106. The remaining m/e 105 peak is in fact a doublet(as shown by high resolution mass spectrometry), which can be attributed to a C_7H_5O ion (95%) and to a C_8H_9 ion (5%).

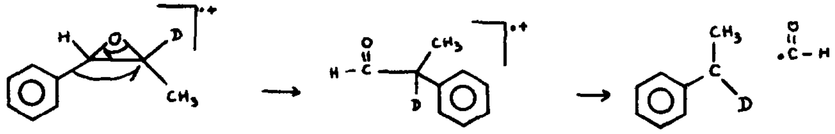
The following mechanism explains the fragmentation pattern. Upon electron impact, all the possible rearranged species are formed :



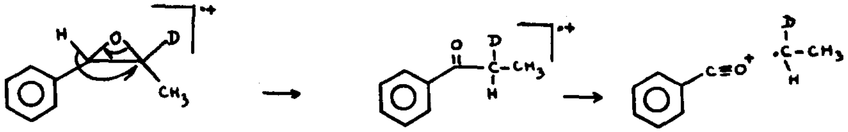
ion B m/e 105



ion C m/e 92

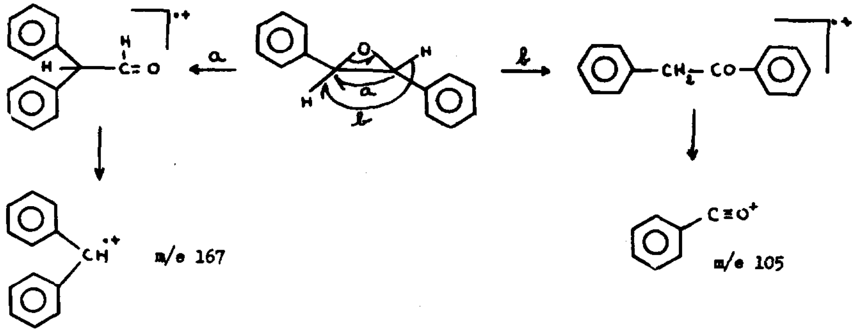


m/e 106 ion D

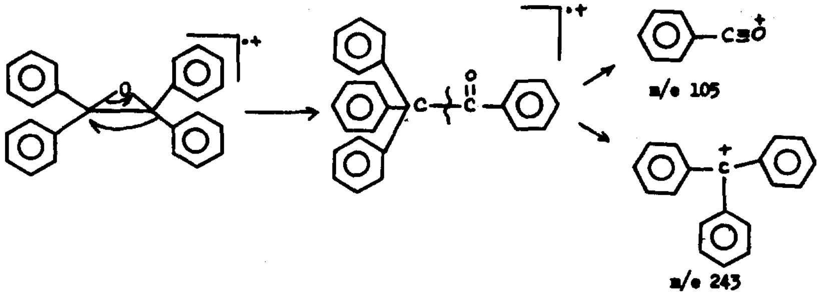


ion E m/e 105

Peaks at m/e 105 and 167 are found in the spectra of cis and trans stilbene oxide and can be explained in the same way :



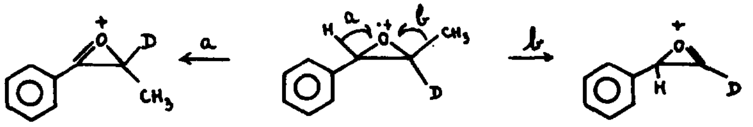
Finally, the mass spectrum of tetraphenylethylene oxide shows one peak at m/e 105 and one at m/e 243 :



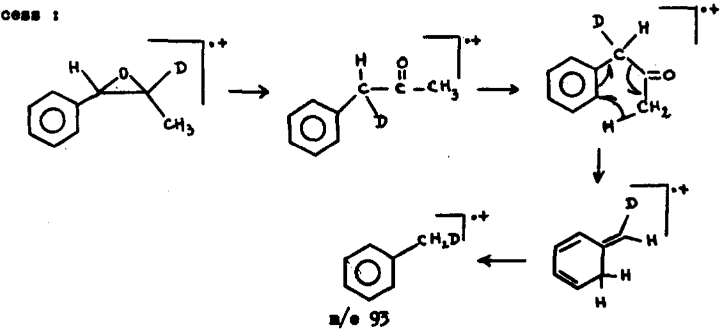
Although there is only one rearranged intermediate ketone in the case of this highly symmetrical compound, the non oxygenated ion is so stable that it appears as one of the major peak.

From the intensities of the various peaks in the spectrum, and since the stability of the various fragments (ion B and $^{+}CD = O$ vs ion C and .CHO) is obviously about the same, it seems that migration of a phenyl group is much easier than migration of a methyl group.

Two other points deserve to be briefly discussed. a) In the spectra of 1a, 1b, 1c, or 1d, there is a big M - 1 peak, which is due to the expected elimination of the benzylic hydrogen (fragmentation a). A rather weak M -15 peak appears in the spectra of 1b, 1c and 1d according to the following mechanism (fragmentation b) :



b) When low energy electrons (12 eV) are used, the spectrum of 5 is modified: although the ratio of m/e 106 to m/e 105 is about the same as with 70 eV electrons, the m/e 90 peak is absent. There is still a m/e 92 peak, but a new peak is observed at m/e 93, which may be due to the following fragmentation process :



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(3) K. G. Das, P. Funke and A.K. Bose, J. Am. Chem. Soc., 86, 3729 (1964)