Mass Spectra of Glycidic Esters and Amides: Examples of Migrations of Alkoxy- and Amino-Groups

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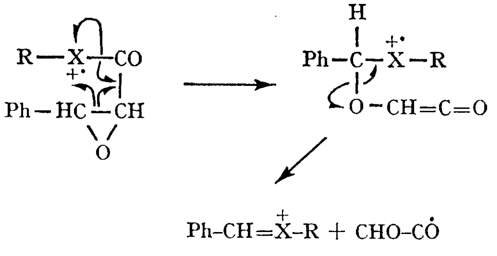
THE importance of migrations induced by electron impact, leading to rearranged ions, has been emphasised in a number of recent papers,[1] and some aromatic epoxides have been shown to undergo migrations of alkyl or aryl groups before fragmentation.[2]

We have examined the mass spectra of a number of β-phenylglycidic esters and amides, and have shown that in all cases concerted loss of C_2HO_2 is an important process, often leading to the base peak of the spectrum. The process, which must involve a rearrangement of the molecular ion, is best formulated as follows:—

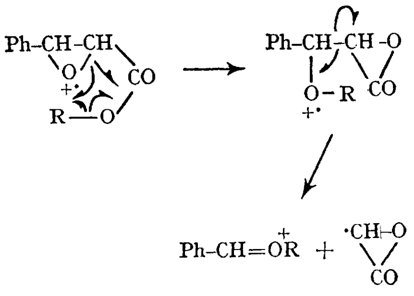


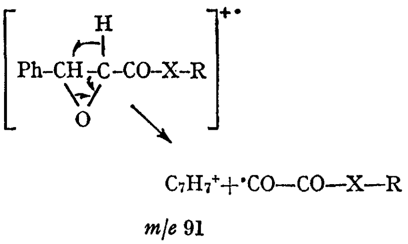
[R–X=Alkyl-O, or Alkyl-NH, or NH$_2$]

Production of the stable oxonium or iminium cation is no doubt a driving force in this rearrangement and elimination. These species undergo the expected further decompositions, thus the oxonium cation from ethyl $\alpha\beta$-epoxy-β-phenylpropionate eliminates ethylene, a typical reaction of such an ion.[3]

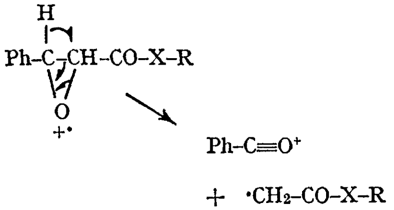
$$\underset{m/e\ 135}{\mathrm{PhCH{=}\overset{+}{O}CH_2{\cdot}CH_3}} \rightarrow \underset{m/e\ 107}{\mathrm{PhCH{=}\overset{+}{O}H}} + \mathrm{CH_2{=}CH_2}$$

An alternative mechanism for the initial rearrangement involving alkyl rather than alkoxyl migration seems unlikely, since although it would explain the observed loss from glycidic esters:





and



its operation would predict the loss of C_2H_2ON (56 mass units) from the corresponding amides, rather than the observed C_2HO_2 (57 mass units).

Alternative fission pathways of the molecular ion involve hydrogen migrations, and lead to tropylium ion or benzoyl cation.

These migrations and fissions are formally analogous to those described by Audier and co-workers.[2]

A complete analysis of the spectra of all the compounds examined will be reported elsewhere. Spectra were determined with an AEI MS9, with a heated inlet system (220°). The compositions of ions discussed were in all cases verified by high-resolution mass spectrometry, with tris(perfluoro)butylamine as a standard.

(*Received, July* 12*th,* 1966; *Com.* 491.)

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[1] P. Brown and C. Djerassi, *J. Amer. Chem. Soc.*, 1966, **88**, 2469; C. Djerassi, A. M. Duffield, F. Komitsky, Jr. and L. Tökes, *ibid.*, p. 860; B. R. Webster, *Chem. Comm.*, 1966, 124; R. R. Arndt and C. Djerassi, *ibid.*, 1965, 578; J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson, and G. Schroll, *ibid.*, p. 403.

[2] H. E. Audier, J. F. Dupin, M. Fétizon, and Y. Hoppilliard, *Tetrahedron Letters*, 1966, 2077.

[3] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds", Holden-Day, San Francisco, 1964, p. 51.