## OXYGEN REARRANGEMENT PROCESSES IN MASS SPECTROMETRY

## J. K. MACLEOD

Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T., Australia

(Received 29 April 1969; accepted 29 April 1969)

Abstract—The recent publication<sup>1</sup> concerning oxygen rearrangement processes in the mass spectra of aromatic and unsaturated esters parallels an investigation by the author on similar compounds. Some further definitive aspects of this study are reported here.

THE MASS spectrum (Fig. 1) of methyl- $\beta$ -phenyl isovalerate (1), showed a peak at  $m/e \, 135 \, (10\% \, \text{Rel. int.})$  whose composition was determined by accurate mass measurement to be  $C_9H_{11}O$ . Deuterium exchange of the  $\alpha$ -hydrogens afforded the 2,2-dideutero-derivative (II), the mass spectrum of which revealed no shift of the  $m/e \, 135$  ion. The electron-impact spectra of the homologous compounds (III) and (IV),



FIG. 1. Mass spectrum of methyl- $\beta$ -phenyl-isovalerate.

exhibited oxygen rearrangement peaks at m/e 121 (C<sub>8</sub>H<sub>9</sub>O:12% Rel. int.) and m/e 107 (C<sub>7</sub>H<sub>7</sub>O:4% Rel. int.) respectively. No diffuse metastable peaks were evident, however, in the three spectra for the formation of the rearrangement ion from any of the higher mass peaks.



In their publication,<sup>1</sup> Kadentsev *et al.* proposed a route for the formation of the rearrangement species involving initial loss of the alkyl function on the ester group followed by cyclization and retro-diene-like scission (Scheme 1).



SCHEME 1

One observed metastable peak only was quoted, purportedly for the rearrangement process  $m/e \ 163 \rightarrow m/e \ 107$  in the mass spectrum of 2-cyanopropanol-2- $\alpha$ -methyl- $\beta$ -phenyl-propionate (V). This assignment must be viewed with caution, however, since the observed value of the metastable peak ( $m/e \ 69.7$ ) was considerably removed from the calculated value of 70.2 and would correspond more closely with a metastable peak for the transition  $m/e \ 119 \rightarrow m/e \ 91$  (calculated value 69.6). Both the  $m/e \ 119$  and 91 peaks appear quite prominently in the mass spectrum of V. Also the mass spectra of I and II showed a strong metastable peak at 69.7 for  $m/e \ 119 \rightarrow m/e \ 91$ .



We considered that an alternate fragmentation scheme (Scheme 2) was feasible, involving direct production of the rearrangement ion a from the molecular ions of I, II, III and V particularly since the evidence in support of Scheme 1 appeared rather tenuous.



In order to define the breakdown pathway, the origins of the rearrangement peaks at m/e 135, 121 and 107 in compounds I (and II) III and IV respectively have been investigated using Jennings'<sup>2</sup> method for the observation of pure metastable spectra. In all cases an intense metastable parent ion was observed at an m/e value corresponding to the  $[M - 15]^+$  ions (Table 1). This result would imply that fragmentation Scheme 1 proposed by Kadentsev *et al.* is the more valid of the two representations of the rearrangement process.

Compound	Daughter ion [D] <sup>+</sup> (m/e)	Helipot ratio R	Parent ion $[P]^+$ $[P]^+ = [R \times D]^+ (m/e)$	Molecular ion $[M]^+$ $(m/e)$
(I)	135	1.315	177	192
(II)	135	1.329	179	194
(III)	. 121	1.352	163	178
(IV)	107	1.395	149	164

TABLE 1. ANALYSES OF PURE METASTABLE SPECTRA

A further feature of this oxygen migration process is that, unlike many other observed electron-impact-induced rearrangements,<sup>3</sup> the peak intensity of the fragment ion a in the mass spectra of compounds I, III and IV decreased very rapidly at low ionizing voltages compared with the intensity of the ion formed by simple benzylic cleavage. This indicated that the rearrangement ion a was formed via a secondary decomposition process since direct production of such species from the molecular ion is usually associated with a low frequency factor with concomitant enhancement of peak intensity for the rearrangement species relative to ions arising from simple bond cleavages at lower electron energies.<sup>3</sup>

## EXPERIMENTAL

All spectra were recorded on a GEC/AEI MS-902 double-focusing mass spectrometer using a trap current of 100  $\mu$ A, source temperature 150° and 70 volt-electrons, except where stated. Samples were introduced into the ionizing chamber via an all-glass heated inlet system (AGHIS) operating at 200° with the inlet line and re-entrant probe at 150°. Accurate mass measurements were performed at a resolution of 20,000 (10% valley definition) using heptacosafluorotributylamine as reference compound.

Compounds I and III were prepared by methylation, using diazomethane, of the corresponding acids prepared by established procedures.<sup>4,5</sup>

Methyl hydrocinnamate (IV), was prepared by methylation of hydrocinnamic acid, obtained by catalytic reduction of cinnamic acid (B.D.H. reagent grade).

The  $\alpha$ -d<sub>2</sub> derivative (II) of methyl- $\beta$ -phenylisovalerate (I) was prepared by NaOMe/MeOD exchange.

All compounds were purified by v.p.c. on a 10% Apiezon L column operating at 175°C.

For the observation of pure metastable spectra, a circuit similar to that described by Jennings<sup>2(b)</sup> was used.

## REFERENCES

- 1. V. I. Kadentsev, B. M. Zolotarev, O. S. Chizov, Ch. Shachidayatov, L. A. Yanovskaya and V. F. Kucherov, Org. Mass Spectrom. 1, 899 (1968).
- (a) M. Barber and R. M. Elliot, ASTM Committee E-14, 12th Annual Conference on Mass Spectrometry and allied topics, Montreal, June 1964; (b) K. R. Jennings, Proceedings of the Fourth Annual MS-9 Mass Spectrometer Users Conference, Manchester, April 1966.
- 3. D. H. Williams and R. G. Cooks, Chem. Commun. 663 (1968).
- 4. J. F. J. Dippy and J. T. Young, J. Chem. Soc. 3919 (1955).
- 5. G. Baddeley and W. Pickles, J. Chem. Soc. 2855 (1957).