(4) (a) J. Cornelisse and E. Havinga, *Chem. Rev.*, **75**, 353 (1975); (b) R. Beugelmans, M. T. Le Goff, J. Pusset, and G. Roussi, *J. Chem. Soc., Chem. Commun.*, 377 (1976).
(5) (a) J. A. J. Vink, C. M. Lok, J. Cornelisse, and E. Havinga, *J. Chem. Soc., Chem. Commun.*, 710 (1972); (b) S. Nilsson, *Acta Chem. Scand.*, **27**, 329 (1973); (c) K. Mizuno, C. Pac, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 553 (1975).
(6) M. M. Baizer, Ed., "Organic Electrochemistry", Marcel Dekker, New York, N.Y., 1973, Chapter XII.
(7) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, p 289.
(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", 3rd ed, Chapman and Hall, London, 1975, p 41.
(9) D. H. R. Barton and R. C. Cookson, *Q. Rev. Chem. Soc.*, **10**, 44 (1956).
(10) Using the viscosity (η_{20} = 0.35891 cP) reported by S. Minc and L. Werblan, *Rocz. Chem.*, **40**, 1537 (1966).
(11) (a) A. Weller in "The Exciplex", M. S. Gordon and W. R. Ware, Ed., Academic Press, New York, N.Y., 1975, Chapter 2; (b) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970); (c) A. Weller, *Fast React. Primary Processes Chem. Kinet., Proc. Nobel Symp., 5th*, 413 (1967); (d) H. Beens and A. Weller, *Acta Phys. Pol.*, **34**, 593 (1968).
(12) (a) C. Lewis and W. R. Ware, *Mol. Photochem.*, **5**, 261 (1973); (b) W. R. Ware, D. Watt, and J. D. Holmes, *J. Am. Chem. Soc.*, **96**, 7853 (1974).
(13) (a) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Am. Chem. Soc.*, **94**, 3679 (1972); (b) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).
(14) R. S. Nicholson, *Anal. Chem.*, **38**, 1406 (1966).
(15) (a) P. J. Kropp, *J. Am. Chem. Soc.*, **91**, 5783 (1969); (b) *ibid.*, **95**, 4611, (1973); (c) S. Fujita, Y. Hayashi, T. Nômi, and H. Nozaki, *Tetrahedron*, **27**, 1607 (1971); (d) S. Fujita, T. Nômi, and H. Nozaki, *Tetrahedron Lett.*, 3557 (1969); (e) M. P. Servé and A. W. Bryant, *ibid.*, 2663 (1972); (f) H. M. Rosenberg and M. P. Servé, *J. Org. Chem.*, **37**, 141 (1972).
(16) R. Bonneau, J. Joussot-Dubien, L. Salem, and A. J. Yarwood, *J. Am. Chem. Soc.*, **98**, 4329 (1976).
(17) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).
(18) D. R. Arnold and A. J. Maroulis, unpublished results.
(19) (a) M. D. Bentley and J. A. Lacadie, *Tetrahedron Lett.*, 741 (1971); (b) W. S. Trahanovsky and M. P. Doyle, *ibid.*, 2155 (1968).
(20) F. L. Scott, *Chem. Ind.* (*London*), 224 (1959).
(21) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **81**, 1050 (1959).
(22) (a) J. F. Garst in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 9; (b) J. F. Garst, *Acc. Chem. Res.*, **4**, 400 (1971).
(23) A. D. Grebenyuk and I. P. Tsukervanik, *J. Gen. Chem. USSR* (*Engl. Transl.*), **25**, 269 (1955).
(24) G. W. Gokel and D. J. Cram, *J. Org. Chem.*, **39**, 2445 (1974).
(25) B. M. Trost, *J. Am. Chem. Soc.*, **89**, 1847 (1967).

The Loss of C_2H_2O and of C_3H_4O from the Molecular Ions of 3-Phenylpropanal as Studied by Field Ionization Kinetics. Isomerization of the Molecular Ions of 3-Phenyl-2-propen-1-ol

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Abstract: As a result of carrying out field ionization kinetic studies upon the decompositions of labeled analogues of the molecular ions of 3-phenylpropanal we are able to show that the expulsion from these ions both of C_2H_2O and of C_3H_4O proceeds almost exclusively through a mechanism analogous to the McLafferty rearrangement. As the reaction time increases from $10^{-10.2}$ to $10^{-9.6}$ s it is found that some interchange begins to occur between the hydrogen atoms in the aldehydic, benzylic, and ortho positions of the benzene ring. The detailed field ionization kinetic data suggest that this interchange results from the occurrence of two distinct hydrogen exchange mechanisms: (1) interchange between the aldehydic and benzylic hydrogens, and (2) interchange between the aldehydic and ring ortho hydrogens. Similarities between the field ionization mass spectra of 3-phenylpropanal and spectra from its isomer 3-phenyl-2-propen-1-ol suggest that at least some of the molecular ions of the latter isomerize very rapidly to the structure of the molecular ions of the former. Further evidence to support this hypothesis is derived from electron impact ionization studies in which the kinetic energy released in the expulsion of C_2H_2O from the molecular ions of the two compounds has been measured.

Introduction

Until recently it has only been possible to investigate the mechanistic details of gas-phase ionic fragmentation reactions by studying the information contained in the conventional electron impact (EI) mass spectra of specifically labeled precursor neutral molecules. However, such spectral information provides only a time-integrated view of all the decompositions occurring in the first 10^{-6} s after ionization. Unfortunately it is frequently observed that extensive interchanges take place between the hydrogen and/or carbon atoms prior to decomposition. These interchanges can be specific, nonspecific, or incomplete at the time of observation so that it is often difficult to interpret the data obtained from the EI spectra of the labeled compounds. It is frequently difficult to separate the mechanism(s) of decomposition(s) from the interchange process(es), since the rates of interchange are generally comparable with the rates of decomposition.

Field ionization (FI) mass spectrometry and field ionization kinetics (FIK) provide methods whereby even processes which occur extremely rapidly may be studied. In the FIK method decompositions of molecular ions occurring in the first 10^{-11} to 10^{-9} s after ionization can be studied. The technique involves measuring the abundance of fragment ions as a function of field emitter potential while maintaining the electric sector voltage and magnetic field constant. The detection system of the instrument thus remains focused upon ions of some specific m/e value formed at a point in space close to the emitter where they acquire some specific energy (8.45 keV in our experiments). Increasing the emitter potential thus allows one to see decompositions of molecular ions occurring at ever-increasing distances from the emitter, which of course correspond to longer lived molecular ions.[1] The power of FIK has already been demonstrated in numerous cases (see ref 2), and this has prompted us to reexamine the decompositions of the molecular

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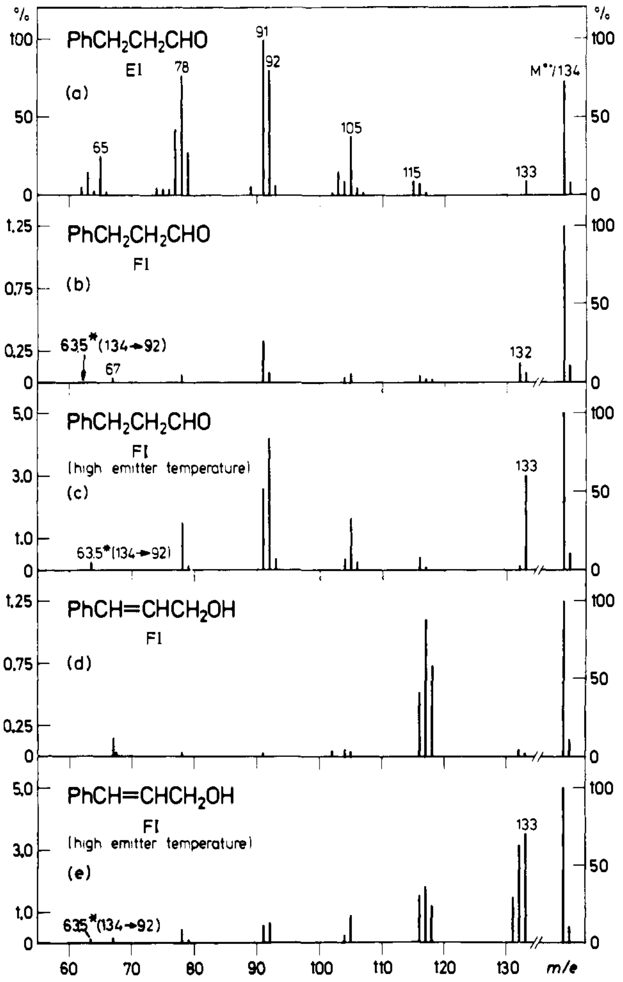


Figure 1. (a) The EI spectrum of 3-phenylpropanal (from ref 3a); (b) and (c) the FI spectra of 3-phenylpropanal at emitter currents of ~0 (b) and 40 mA (c); (d) and (e) the FI spectra of 3-phenyl-2-propen-1-ol at emitter currents of 0 (d) and 40 mA (e).

ions of 3-phenylpropanal which have previously been observed to show extensive hydrogen interchange[3a] when studied under EI conditions.

Upon EI, 3-phenylpropanal ($C_6H_5C^3H_2C^2H_2C^1HO$) decomposes predominantly by the loss either of C_2H_2O (*m/e* 92, rel intensity 80) or of C_3H_4O (*m/e* 78, rel intensity 76) (see Figure 1a). By ^{13}C labeling it has been shown[3b] that in these fragmentations only the carbon atoms of positions 1 and 2 and 1, 2, and 3, respectively, are involved. On the basis of the results from deuterium labeling in the side chain and in the ring it was further concluded that the hydrogen atoms of position 2 are transferred to the aromatic ring in the formation of the ions *m/e* 92 and 78 as well as in the initiation of the hydrogen interchange process. Recently it has been found[4] that the molecular ions of the isomeric 3-phenyl-2-propen-1-ol also eliminate C_2H_2O and C_3H_4O upon EI, but by entirely different mechanisms as indicated by a partial hydrogen scrambling in the elimination process of C_2H_2O.

In this study, emphasis has been placed upon the elucidation of the mechanisms of these fragmentations and of the hydrogen interchange processes. It has also been noticed that upon EI the aldehyde and the isomeric unsaturated alcohol behave rather similarly and the final section of this paper concerns the probable isomerization of the molecular ion of the alcohol to that of the aldehyde.

Experimental Section

A Varian MAT 711 double focusing mass spectrometer was used for both the FI and FIK measurements. The emitter, a 10-μm activated tungsten wire, was heated during the experiments by passing a current of a few mA along it. The electric sector was set to transmit ions with a kinetic energy corresponding to 8450 ± 30 V.[5a] The sample pressure in the ion source was approximately 5×10^{-6} Torr.

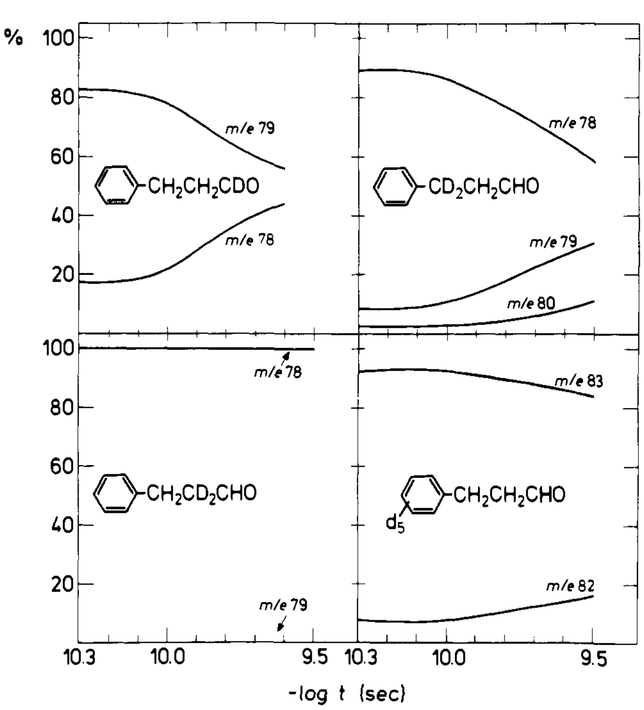


Figure 2. Percentage ion currents of $(M - C_3H_xD_{4-x}O)^{+\cdot}$ ions formed following FI of 3-phenylpropanal-*1*-d_1, 3-phenylpropanal-*2*-d_2, 3-phenylpropanal-*3*-d_2, and 3-pentadeuteriophenylpropanal as a function of molecular ion lifetimes.

Samples were introduced into the ion source (110 °C) via a cooled direct insertion probe (−10 °C for the aldehydes and 25 °C for 3-phenyl-2-propen-1-ol). Prior to the introduction of 3-phenylpropanal-*2*-d_2 the ion source and the inlet system were pretreated with D_2O and under these conditions no significant back exchange was observed.

Spectral data were recorded on line, stored, and then processed by the Varian Spectro System 100 (sampling frequency 6 KHz).[5b] The computer was programmed to produce output data in the form of log time plots of the normalized rate[6] and/or abundance of the fragment ion current (in percentage of the molecular ion current). The time scale was calculated from the electrostatic potential distribution between the emitter and the slotted cathode according to the method of Falick.[7] The FIK curves shown in Figures 2 and 3 represent the average of nine scans; standard deviations are close to 2%. The FI spectra of 3-phenylpropanal and 3-phenyl-2-propen-1-ol given in Figure 1 were measured under similar conditions on the same day and as shown represent the average of three scans each.

The kinetic energy release measurements were performed on an AEI MS902S double focusing mass spectrometer under conditions of good energy resolution with the samples being introduced through a variable leak valve. The metastable ion peak shapes were measured by increasing the acceleration voltage while keeping the electric sector voltage fixed. The kinetic energy releases were calculated on the basis of the peak widths[8] of the metastable peaks at 25, 50, and 75% of peak heights.

3-Phenylpropanal-*1*-d_1 and 3-phenylpropanal-*3*-d_2 were prepared as described previously.[3a] 3-Phenylpropanal-*2*-d_2 was prepared by H/D exchange on two GC columns in tandem at 180 °C.[9] The first section was operated under acidic conditions (H_3PO_4) and the second section of the column consisted of Chromosorb WAW (45–60 mesh) coated with 25% Carbowax 20M, both pretreated with D_2O. 3-Pentadeuteriophenylpropanal was prepared by oxidation of the corresponding alcohol,[10] which was made by reduction[11] of 3-pentadeuteriophenyl-2-propenecarboxylic acid. This latter was synthesized from benzaldehyde-d_5 and malonic acid.[12] The aldehydes were all purified by GC prior to use. 3-Phenyl-2-propen-1-ol was purified by successive recrystallizations from an ether–pentane solvent mixture.

The deuterium contents of the labeled aldehydes were estimated from their FI spectra to be as follows: $C_6H_5CH_2CH_2CDO$, 97% d_1; $C_6H_5CH_2CD_2CHO$, 92.3% d_2 and 7.4% d_1; $C_6H_5CD_2CH_2CHO$, 96.5% d_2 and 3.3% d_1; $C_6D_5CH_2CH_2CHO$, 95.9% d_5, 3.9% d_4, and 0.2% d_3.

Results

1. Loss of C_3H_4O from the Molecular Ion of 3-Phenylpropanal. Upon FI, 3-phenylpropanal exhibits a fragmentation pattern showing the same nominal masses as are seen upon EI (cf. Figures 1a and 1b). Thus the FI spectrum shows peaks at *m/e* 133 $(M - H)^+$, 132 $(M - H_2)^{+\cdot}$, 116 $(M - H_2O)^{+\cdot}$, 115 $(M - (H + H_2O))^+$, 105 $(M - CHO)^+$, 92 $(M - C_2H_2O)^{+\cdot}$, 91 $(M - C_2H_3O)^+$, and 78 $(M - C_3H_4O)^{+\cdot}$.

In the region corresponding to *m/e* 78 of the unlabeled compound the FI spectrum of $C_6H_5CH_2CH_2CDO$ shows two ions of measurable intensity: *m/e* 79 $(M - C_3H_4O)^{+\cdot}$ and 78 $(M - C_3H_3DO)^{+\cdot}$. Similarly $C_6H_5CD_2CH_2CHO$ shows three fragment ions: *m/e* 80 $(M - C_3H_4O)^{+\cdot}$, 79 $(M - C_3H_3DO)^{+\cdot}$, and 78 $(M - C_3H_2D_2O)^{+\cdot}$. The FI spectrum of $C_6D_5CH_2CH_2CHO$ shows *m/e* 83 $(M - C_3H_4O)^{+\cdot}$ and 82 $(M - C_3H_3DO)^{+\cdot}$, but with $C_6H_5CH_2CD_2CHO$ it is predominantly *m/e* 78 $(M - C_3H_2D_2O)^{+\cdot}$ that is observed. Although the fragment ion peaks seen in the FI spectra result from a combination of genuine unimolecular gas-phase fragmentations and emitter surface induced fragmentations (which are not time resolved), the FI spectra of the deuterated 3-phenylpropanals clearly imply that the aldehydic hydrogen atom (position 1) is the principal (85%) itinerant hydrogen involved in the loss of C_3H_4O:

$$(C_6H_5CH_2CH_2CDO)^{+\cdot} \xrightarrow{85\%} (C_6H_5D)^{+\cdot} + C_3H_4O$$

This also holds true under FIK conditions (unimolecular gas-phase reactions only). In Figure 2 the various fragment ion currents (abundances) are presented as functions of molecular ion lifetime (FIK curves). At $10^{-10.2}$ s the deuterium atom in the molecular ion of $C_6H_5CH_2CH_2CDO$ is transferred to the ring to the extent of 83% in the fragmentation process. The exclusive fragmentation to *m/e* 78 $(M - C_3H_2D_2O)^{+\cdot}$ in the case of $C_6H_5CH_2CD_2CHO$ shows that the α hydrogen (deuterium) atoms (position 2 of the side chain) are not involved in the fragmentation on the time scale examined here. The curves for $C_6H_5CD_2CH_2CHO$ show that at $10^{-10.2}$ s the hydrogen (deuterium) atoms of position 3 may transfer to the ring, but only to the extent of about 10%. The ring hydrogen atoms do not interchange with the side chain to any significant extent as may be seen from the FIK curves for $C_6D_5CH_2CH_2CHO$.

2. Loss of C_2H_2O from the Molecular Ion of 3-Phenylpropanal. Figure 3 shows as a function of the molecular ion lifetime of $C_6H_5CH_2CH_2CDO$ the ion currents (abundances) of the $(M - C_2H_2O)^{+\cdot}$ and $(M - C_2HDO)^{+\cdot}$ ions. At $10^{-10.2}$ s it is seen that the aldehydic deuterium atom is transferred almost exclusively (>93%) in the fragmentation process (similarly the normal FI spectrum indicates that the D transfer is of the order of 90%).

Discussion

The above data clearly demonstrate that at very short times ($\leq 10^{-10.2}$ s) the loss of C_2H_2O and of C_3H_4O from the molecular ions of 3-phenylpropanal occur by the transfer of the aldehydic hydrogen atom. This differs from an earlier conclusion based only on EI studies.[3a] Presumably the transfer takes place to the ortho position of the ring via a six-membered transition state (cf. ref 13) and thus resembles the McLafferty rearrangement.[14] In addition it is found from EI metastable decompositions in the first field-free region that the *m/e* 78 ions resulting from the elimination of C_3H_4O appear to originate both from the molecular ions *and* from the $(M - 28)^{+\cdot}$ ions. Therefore, it appears that the process involves the consecutive[17] expulsion of carbon monoxide and ethylene.[18]

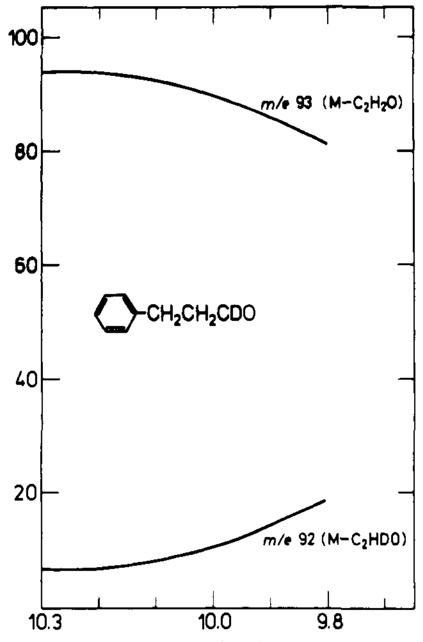
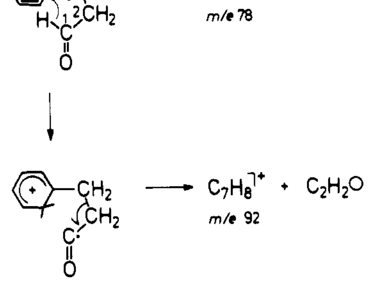


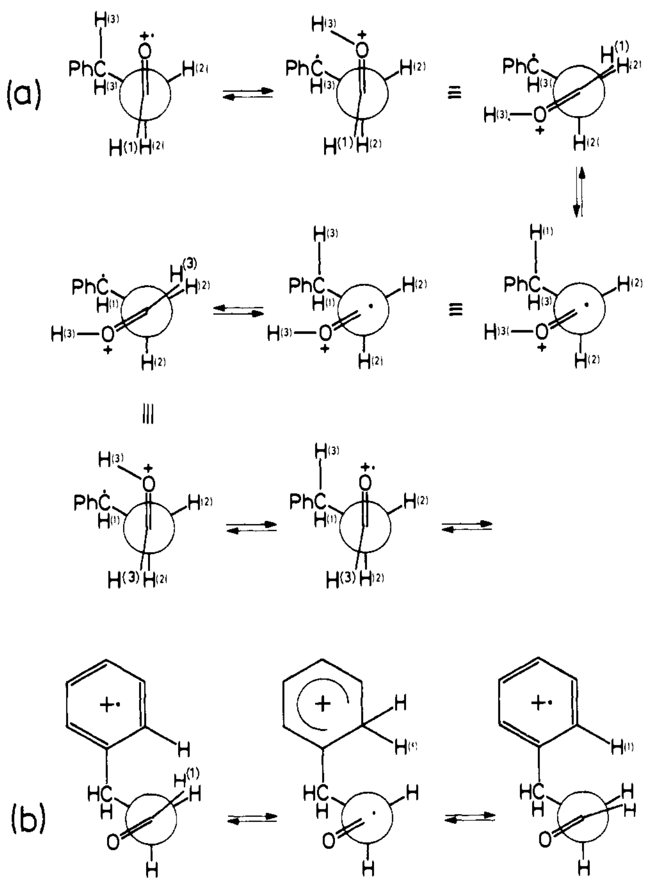
Figure 3. Percentage ion currents of $(M - C_2H_xD_{2-x}O)^{+\cdot}$ ions formed following FI of 3-phenylpropanal-*1*-d_1 as function of molecular ion lifetime.

Scheme I. Proposed Mechanisms for the Losses of C_2H_2O and C_3H_4O from 3-Phenylpropanal



Hydrogen Interchange Processes. The FIK curves (Figures 2 and 3) show that except in the case of $C_6H_5CH_2CD_2CHO$ the relative abundances of the $(M - C_3H_xD_{4-x}O)^{+\cdot}$ and $(M - C_2H_xD_{2-x}O)^{+\cdot}$ ions formed from the various labeled molecular ions are time dependent. The fragment ions which are formed from the molecular ions of $C_6H_5CH_2CH_2CDO$ and $C_6H_5CD_2CH_2CHO$ exhibit qualitatively similar time dependences, while for $C_6D_5CH_2CH_2CHO$ the time dependence is not so marked. The simplest explanation of these observations is that two separate hydrogen interchange processes occur: (a) between the aldehydic and benzylic hydrogen atoms (Scheme IIa) and (b) between the aldehydic and ring hydrogen atoms (Scheme IIb). If one assumes charge localization on oxygen, then process (a) may be visualized as a series of hydrogen atom transfers initiated by hydrogen abstraction from position 3 of the side chain by the radical site on the oxygen atom. Alternatively, if the charge resides initially in the phenyl ring, then the initial step will be proton abstraction from position 3 by one of the lone pairs of electrons on the oxygen atom. In either case there may then follow an exchange of the aldehydic and the remaining benzylic hydrogen atoms. Finally a migration of the oxygen-bonded hydrogen atom back to the benzylic position produces a new specifically hydrogen ex-

Scheme II. (a) Proposed Mechanisms for the Interchange Process between the Aldehydic and Benzylic Hydrogen Atoms; (b) between the Aldehydic and Ortho Hydrogen Atoms



changed molecular ion species (e.g., $(C_6H_5CH_2CH_2CDO)^{+\cdot} \rightarrow (C_6H_5CHDCH_2CHO)^{+\cdot}$). (Interchange processes in benzylic systems have been reviewed recently.[13])

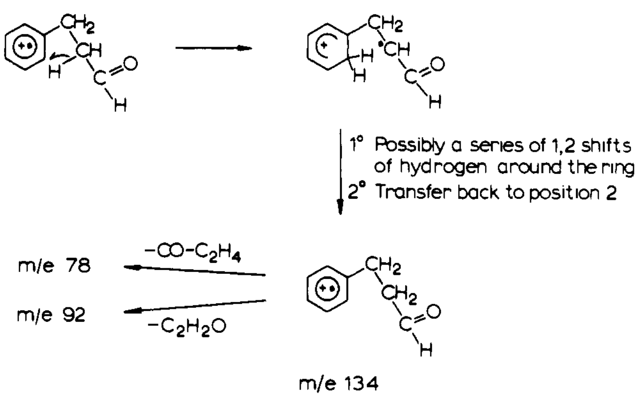
Process (b) is rationalized in Scheme IIb in terms of exchange between the aldehydic and the ortho hydrogen atoms. This mechanism is compatible with that proposed for the loss of C_2H_2O and of C_3H_4O. The less sizable decrease at longer times in the abundance of the $(M - C_3H_4O)^{+\cdot}$ ions formed from $C_6D_5CH_2CH_2CHO^{+\cdot}$ is in accordance with these two proposed interchange processes. This implies that the loss of C_3H_4O and of C_2H_2O occurs almost exclusively through the transfer of the aldehydic hydrogen atom to the ring. Process (b) requires one further transfer of the originally exchanged ortho hydrogen atom via process (a). So, in the event of a simultaneous interchange occurring between the ring hydrogen atoms and both the aldehydic and benzylic hydrogen atoms one would have expected to have observed a more pronounced time dependence of the abundance of the $(M - C_3H_4O)^{+\cdot}$ ions formed from $C_6D_5CH_2CH_2CHO^{+\cdot}$ than was actually observed.

On the FIK time scale the hydrogen atoms of position 2 of the side chain do not participate in any interchange processes.[20a] However, the previously published EI results[3a] show that on a microsecond time scale both these and the ring hydrogen atoms interchange extensively.[20b] One might therefore infer that these hydrogens mutually interchange, possibly as suggested in Scheme III.

Table I. Kinetic Energy Releases T (meV) for the Reaction $134^{+\cdot} \rightarrow 92^{+\cdot} + 42$

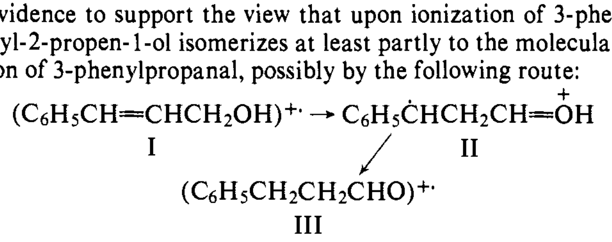
Compd	$T_{25\%}$	$T_{50\%}$	$T_{75\%}$
$C_6H_5CH_2CH_2CHO$	42 (±3)	20 (±1)	7 (±1)
$C_6H_5CH{=}CHCH_2OH$	44 (±2)	20 (±1)	8 (±1)

Scheme III. Rationalization of the Exchange between the Hydrogen Atoms from Position 2 with the Phenyl Ring Hydrogens in the Molecular Ion of 3-Phenylpropanal at Times $>10^{-9.6}$ s



Isomerization of the Molecular Ion of 3-Phenyl-2-propen-1-ol. The EI spectra of 3-phenylpropanal[3a] and the isomeric 3-phenyl-2-propen-1-ol[4a] are almost identical and differ only slightly in relative peak intensities. A metastable peak (second field-free region) corresponding to the loss of C_2H_2O is present in both spectra as it is in the normal FI spectra. It has also been reported[4a] that for the alcohol a metastable peak is observed for the loss of C_3H_4O, but we have been unable to confirm this latter result working on two different mass spectrometers. It seems that extensive rearrangements will be required if the alcohol molecular ions are to undergo the eliminations of either C_2H_2O or C_3H_4O. Recent labeling experiments[4b] do in fact indicate that *all* the hydrogen atoms participate in the elimination of C_2H_2O, possibly as a result of an isomerization of the alcohol molecular ions to the structure of those of the aldehyde. To find support for this hypothesis, the FI spectra of the isomeric compounds were examined at both ambient and high emitter temperatures. Unlike the EI spectra, the FI spectra of the aldehyde and alcohol are significantly different at ambient temperature (compare Figures 1b and 1d). The FI spectrum of the alcohol exhibits intense fragment ion peaks corresponding to the loss from the molecular ions of OH· (*m/e* 117), H_2O (*m/e* 116), and H_2O + H· (*m/e* 115), while only a weak peak is seen for the loss of C_3H_4O and virtually no peak for loss of C_2H_2O. Upon heating the emitter the spectrum of the alcohol changes so as to somewhat resemble that of the aldehyde (compare Figures 1c and 1e). The peaks at *m/e* 78, 92, and 105 in the alcohol spectrum become stronger at the expense of those in the $(M - H_2O)^{+\cdot}$ region of the spectrum. (Unfortunately these peaks are too weak to be studied by FIK with our existing instrument.) This may be interpreted as meaning that sufficient thermal energy becomes available[22] to enable a certain proportion of the alcohol molecular ions to undergo isomerization to aldehyde molecular ions in less than $10^{-10.2}$ s. This hypothesis is supported by kinetic energy release measurements on the elimination of C_2H_2O from the two compounds (first field-free region EI metastables); see Table I.

The kinetic energy release obtained from the widths of the metastable peaks at 25, 50, and 75% of their heights are sufficiently similar to indicate that the $(M - C_2H_2O)^{+\cdot}$ ions are formed along the same potential energy surface and hence from molecular ions of very similar structures. The metastable peak shapes for the losses of C_3H_4O are too weak to be accurately measured, but qualitatively they are similar in shape. The observation of two metastable peaks for the formation of the *m/e* 105 ions (unlabeled systems) show that these are formed both from the molecular ions by loss of ·CHO and from the $(M - H)^+$ ions by the loss of CO. The shapes of the metastable peaks for these two fragmentations of the aldehyde and the alcohol are very similar. There are thus several good pieces of evidence to support the view that upon ionization of 3-phenyl-2-propen-1-ol isomerizes at least partly to the molecular ion of 3-phenylpropanal, possibly by the following route:



$$\underset{\text{I}}{(C_6H_5CH{=}CHCH_2OH)^{+\cdot}} \rightarrow \underset{\text{II}}{C_6H_5\dot{C}HCH_2CH{=}\overset{+}{O}H}$$
$$\swarrow$$
$$\underset{\text{III}}{(C_6H_5CH_2CH_2CHO)^{+\cdot}}$$

(Note that ion II is identical with one of the intermediates in Scheme II.) Considering decompositions in the same time window, it seems that ions III are slightly more excited than those generated directly from 3-phenylpropanal, since the ratio of the intensities of the metastable peaks in the first field-free region for the loss of C_2H_2O and of C_3H_4O are ≈ 150 for 3 phenyl-2-propen-1-ol and ≈ 200 for 3-phenylpropanal (AP *m/e* 78 − AP *m/e* 92 $\approx$ 1.4 eV in both cases).[23]

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References and Notes

(1) (a) H. D. Beckey, "Field Ionization Mass Spectrometry", Pergamon Press, Oxford, 1971; (b) P. J. Derrick, "International Review of Science", Vol. 5, "Mass Spectrometry", A. Maccoll, Ed., Butterworths, London, 1975, Series 2, p 1.
(2) B. N. McMaster, *Spec. Period. Rep.; Mass Spectrom.*, **3**, 33 (1975).
(3) (a) A. Venema, N. M. M. Nibbering, and T. J. de Boer, *Org. Mass Spectrom.*, **3**, 583 (1970); (b) A. Venema and N. M. M. Nibbering, *ibid.*, **9**, 628 (1974).
(4) (a) H. Schwarz, C. Köppel, and F. Bohlmann, *Org. Mass Spectrom.*, **7**, 881 (1973); (b) C. Köppel and H. Schwarz, *ibid.*, **11**, 101 (1976).
(5) (a) J. van der Greef, C. B. Theissling, and N. M. M. Nibbering, *Adv. Mass Spectrom.*, in press; (b) J. van der Greef, F. A. Pinkse, C. W. F. Kort, and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Phys.*, **25**, 315 (1977).
(6) H. D. Beckey, K. Levsen, and P. J. Derrick, *Org. Mass Spectrom.*, **11**, 835 (1976).
(7) A. M. Falick, *Int. J. Mass Spectrom. Ion Phys.*, **14**, 313 (1974).
(8) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973.
(9) W. J. Richter, M. Seen, and A. L. Burlingame, *Tetrahedron Lett.*, 1235 (1965).
(10) R. Partch, *Tetrahedron Lett.*, 3071 (1964).
(11) E. I. Snyder, **32**, 3531 (1967).
(12) A. I. Vogel, "Practical Organic Chemistry", Longmans, London, 1959, p 719.
(13) J. L. Holmes in ref 1b, p 207.
(14) Related hydrogen transfers to an aromatic ring via a six-membered intermediate have been reported for alkylbenzenes,[15] 3-phenylpropanol,[16a] 3-phenylpropyl bromide,[16b] 1-phenyl-2-propanol,[16a] and 2-phenylethanol.[16c] For an extensive review on the McLafferty rearrangement see D. G. I. Kingston, J. T. Bursey, and M. M. Bursey, *Chem. Rev.*, **74**, 215 (1974).
(15) (a) J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, **81**, 4116 (1959); (b) F. W. McLafferty, "Mass Spectrometry of Organic Ions", F. W. McLafferty, Ed., Academic Press, New York, N.Y., 1963, p 337; (c) D. A. Lightner, G. B. Quistad, and E. Irwin, *Appl. Spectrosc.*, **25**, 253 (1971).
(16) (a) N. M. M. Nibbering and T. J. de Boer, *Tetrahedron*, **24**, 1415 (1968); (b) *ibid.*, **24**, 1427 (1968); (c) *Org. Mass Spectrom.*, **1**, 365 (1968).
(17) Consecutive one-step expulsions of two (or more) neutral fragments have been reported frequently in the literature, and were first observed by K. R. Jennings [*Chem. Commun.*, 238 (1966)]; see also T. W. Bentley, *Spec. Period. Rep.: Mass Spectrom.*, **3**, 59 (1975).
(18) The heats of formation of carbon monoxide and ethylene are −26.4 and 12.5 kcal mol^{-1}, respectively.[19]
(19) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Ions", NSRDS-NBS 26, National Bureau of Standards, Washington, D.C., 1969.
(20) (a) The FIK experiments do show an increase in the ratio of the ion currents of the $(M - C_2HDO)^{+\cdot}$ and $(M - C_2H_2O)^{+\cdot}$ ions at the emitter potential (high voltage) which corresponds to decompositions occurring in the focusing region ($\approx 10^{-8}$ to 10^{-7} s).[21] This indicates that the interchange process starts at longer times. Similar observations are made concerning the loss of C_3H_4O. It may be added that metastables corresponding to the loss of C_2H_2O, C_2HDO, and C_2D_2O are seen in the normal FI spectrum of 3-phenylpropanal-*2-d*$_2$. (b) Results analogous to those described in ref 20a are found for 3-pentadeuteriophenylpropanal.
(21) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Am. Chem. Soc.*, **94**, 6794 (1972).
(22) K. Levsen and H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 51 (1972).
(23) Appearance potential measurements were performed using the semilog plot method of F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

Electroorganic Chemistry. 31. Reductive Cyclization of Nonconjugated Olefinic Ketones to Cyclic Tertiary Alcohols[1]

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Abstract: The electroreduction of a series of nonconjugated olefinic ketones in a mixed solvent of methanol and dioxane or in *N,N*-dimethylformamide gave intramolecular cycloaddition products, namely, cis-1,2-dialkyl alicyclic tertiary alcohols, in excellent yields. This reductive cyclization showed remarkable regio- and stereoselectivities, in which the reaction always took place between the inner carbon atom of the double bond and the carbonyl carbon atom, and the product was exclusively the cis isomer. Some bicyclic tertiary alcohols or nitrogen heterocycles were synthesized satisfactorily by this new cyclization.

The electrochemical reduction of organic compounds has been recognized as a promising method for the formation of a carbon-carbon bond.[2] For instance, the electroreductive coupling of a carbonyl group with ketones,[3] alkyl halides,[4] carbon dioxide,[4] activated olefins,[5,6] pyridine,[7] or cyanamide[8] has been reported to be a versatile tool to form a new carbon-carbon bond.

Although the reaction of organometallic reagents is also an effective method for bringing about carbon-carbon bond formation,[9] the attempts to synthesize cyclic tertiary alcohols by the intramolecular reactions of organometallic reagents formed from halo ketones are generally unsuccessful owing to the extreme difficulty of the generation of such organometallics.[10]

In the present study, we wish to describe a novel electrochemical method for syntheses of five- and six-membered cy-

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