

per sample, but most of that time is actually involved in pumping out the lines and involves no loss of operator time.

#### ACKNOWLEDGMENT

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# Mass Spectrometric Analysis

## Molecular Rearrangements

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► Structure determination by mass spectrometry has been hampered by the relatively unpredictable possibilities of molecular rearrangement. Classification of such anomalies as more random or more specific rearrangements is proposed. The former appear to involve a higher energy reshuffling process in which various atoms or groups are equilibrated in the molecule. The latter can yield either specific ions of high abundance through formation of a sterically favorable transition state or more stable products. Further classification according to whether the ions and neutral species involved contain an odd or even number of electrons has been useful in correlating these rearrangements. Mechanisms are proposed for several rearrangement classifications.

PROBABLY the greatest drawback to unequivocal molecular structure assignment from a mass spectrum is the possibility of molecular rearrangement during ion formation—i.e., ion fragments are found in the mass spectrum that cannot be formed by simple cleavages of a bond or bonds of the molecule—such as  $C_2H_5^+$  in the spectrum of  $CH_3CH(CH_3)_2$ . Examination of a large number of spectra shows that rearrangements are very common. There are few molecules (other than diatomic) that do not exhibit this phenomenon in their mass spectra to some extent.

Further information on the nature of these rearrangements would also help to elucidate the effects of bom-

bardment of molecules with high energy particles. Some striking similarities have been shown between radiolysis and mass spectrometry (6, 33), including recent evidence for similarity in rearranged products (43).

The relative abundance of a rearranged ion depends on the relative activation energy and stability of products of the rearrangement reaction, as compared to other possible reaction paths.

Many mechanisms have been postulated to explain the variety of rearrangements observed in various individual spectra (14, 18, 19, 24-26, 30, 34, 35, 40, 41, 47-49, 52, 55). The chief similarity of these proposals is that all involve intramolecular rearrangement of the molecule-ion. To bring these diverse observations together for comparison on a common basis, it is proposed that these rearrangements can be classified according to the amount of randomization in the molecule, with further characterization as to whether there is an odd or even number of bonding electrons in the original ion and products. Some rearrangements appear to involve a relatively high degree of activation of the molecule, with considerable exchange of atoms. In other molecules the rearrangements are of lower energy and much more specific, and are usually caused by the strong influence of a functional group. Field and Franklin (15) have pointed out recently that the activation energy for molecular ion decomposition or rearrangement is small compared to the neutral molecule, and that the rate

of rearrangement depends on the energy and entropy of the activated state required for the process. Thus the more randomized rearrangements are ones where several reaction paths are nearly equal in energy and entropy requirements so that a number of rearranged ions are possible, usually of reduced abundance. The more specific rearrangements usually have one path more favorable than the rest, so that the rearranged ion(s) may be dominant in the spectrum. Most of this paper is devoted to the latter specific rearrangements, because the former have been considered previously.

#### EXPERIMENTAL

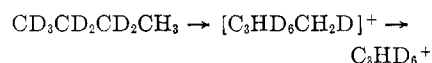
Except where otherwise noted, the mass spectra were obtained on a 90° sector-type instrument (8) equipped with a heated inlet system (7) usually run at 200° C. These were part of the file of 4500 mass spectra at the Spectroscopy Laboratory, The Dow Chemical Co., Midland, Mich., examined for this study. Percentage figures in parentheses refer to the relative abundance of the particular peak in relation to the total ion abundance. The samples giving spectra containing anomalous rearrangement peaks were checked for impurities in many cases by vapor phase chromatography.

#### RANDOM REARRANGEMENTS

Random rearrangements are characterized by a more general reshuffling and isomerization of the excited molecule-ion. This often leads to a family

of rearranged ions of minor intensity, in contrast to the specific rearrangements discussed later. There is usually little energy difference between the various atomic arrangements taking part or produced, so that rearrangement is somewhat an equilibration of parts of the molecule. Various parts of the ion rearranged are structurally similar, having no (or weak) functional groups.

Hydrocarbons typically undergo more random rearrangements, as illustrated by the spectrum of  $C_3D_7CH_3$  (34). The presence of such ions as  $C_3HD_6$  (3.1%),  $C_3H_2D_5$  (3.8%), and  $C_2HD_4$  (1.1%) vs.  $C_3D_7$  (20%) and  $C_2D_5$  (3.2%), shows that 1-2, 1-3, 1-4, and 2-3 exchange of hydrogen and deuterium must be taking place.



It is pointed out that this lack of complete equilibration shows that the  $H \rightarrow D$  exchange is slower than the rate of the  $C-C$  bond break.

The relative amounts of the  $CH_3^+$  and  $C_2H_3^+$  ions found in the spectra of 10  $C_5H_8$  isomers are similar, irrespective of whether rearrangement is necessary for their formation (14). Several authors (5, 10, 16, 29, 54) have shown that the ion and radical obtained when  $R_1 - R_2 + e \rightarrow R_1^+ + R_2 + 2e$  do not necessarily have the structures given by simple bond cleavage.

In the spectrum of  $CH_3CD_3$ , (49) such rearrangement could account for the presence of the ions  $C_2HD_3$  and  $C_2H_2D$  in addition to the energetically expected  $C_2H_2D_2$ . Similarly, the loss of  $H$  from  $HC \equiv CCD_3$  is statistically equivalent to the loss of  $D$  (13). The spectrum of *o*-deuterophenol,  $C_6H_5OD$ , shows in such ions as  $C_3D$  that the deuterium atom can migrate randomly to the ring to a considerable extent (42).

Perhalogen compounds can give rearrangements similar to those found with hydrocarbons. For example, the mass spectrum of  $CBrF_2CF=CFBrF_2$  shows a significant  $C_3Br_2F_3$  ion. The amount of this ion differs appreciably for the *cis*- and *trans*-isomers (purified by gas chromatography), probably illustrating an entropy effect in the transition state.

These more randomized rearrangements can also involve a shuffling of the atoms making up the molecular skeleton. Thus, relative amounts of the  $C^{13}H_3$ ,  $C^{13}H_2$ ,  $C_2^{13}H_5$ , and  $C^{13}C^{13}H_5$  ions found in the spectrum of  $C^{13}H_3CH-(CH_3)_2$  are the same as those in the spectrum of  $CH_3C^{13}H(CH_3)_2$  (55). Skeletal rearrangement is shown even in the resonance-stabilized *s*-triazine molecule by the presence in the spectrum of the ions  $C_2^+$  and  $C_2H^+$ , occurring in low relative abundance (27). It is possible that some of the rearrange-

ments of hydrogen in the previous spectra cited are caused by skeletal changes also (14, 34).

There are several cases of hydrocarbon spectra that seem to involve lower energy rearrangement paths through intermediates or products of unusual stability. For some isotope-labeled tertiary hydrocarbons, Rylander and Meyerson (47) have proposed a cationated cyclopropane intermediate that accounts quantitatively for the rearrangement ions formed by the loss of at least three carbon atoms. The cyclopropane ring equilibrates the tertiary carbon with two of its substituent carbon atoms, effectively exchanging them to form the rearranged product. The more general mechanism of Field and Franklin (15) is essentially similar to this, although it does not predict the isotope distribution in the products. The first authors have also proposed formation of a tropylium ion intermediate to account for exchange of both carbon and hydrogen atoms between the alpha and ring positions in the spectra of many alkyl benzenes (48).

#### SPECIFIC REARRANGEMENTS

Rearrangements of greater specificity are characterized by strong driving forces leading to degradation routes of lower energy requirements, such as by functional groups or polarity in the molecule, and by stability of the rearranged products. A sterically favorable intermediate leading to a rearranged product can contribute to its probability for formation. Sometimes a probable degradation route gives an unstable product which can be stabilized by rearrangement—e.g., the lactone example below. Many of these specific rearrangements can be viewed as a cleavage where the lost fragment on the original ion is replaced by part of that fragment (37). Many such ions from hydrogen atom replacement rearrangement are of the same molecular weight or one mass unit greater than that of a lower member of the homologous series that includes the original molecule.

Because molecular bonding is accomplished by electron pairs, molecules have an even number of bonding electrons. The less stable free radicals have an odd number of bonding electrons because of their unpaired electron. Similarly, as pointed out by Friedman and Long (18) and others, ion stabilities are, in general, greater for those ions with an even number of electrons—e.g., in hydrocarbon spectra the most abundant fragment ions are those at odd mass numbers, as  $C_3H_5^+$ ,  $C_3H_7^+$ ,  $C_4H_9^+$ , etc. Biradicals are an exception, of course.

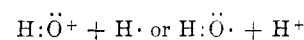
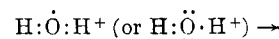
The stability of the products appears

to be a prominent factor in most of the specific rearrangements. It is useful here to classify such rearrangements according to whether the decomposing ion and its products contain odd (O.E.) or even (E.E.) numbers of electrons as follows:

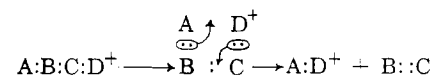
- A. O.E. ion  $\rightarrow$  O.E. ion + E.E. molecule (single rearrangement)
- B. O.E. ion  $\rightarrow$  E.E. ion + O.E. radical (double rearrangement)
- C. Cyclic O.E. ion  $\rightarrow$  E.E. ion + O.E. radical (single rearrangement)
- D. E.E. ion  $\rightarrow$  E.E. ion + E.E. molecule (single rearrangement)
- E. Ion  $\rightarrow$  E.E. ion + E.E. molecule + others (multiple rearrangements and bond cleavages)

In each individual reaction above, except *E*, it is assumed that the only products are another positive ion and a neutral fragment (no negative ions). The rearranging unit(s) is either an atom (mainly hydrogen) or a group (as  $CH_3$ ). The classifications listed do not include all of the possible ones, but only those found to be of common occurrence. Indeed, ions can be found which fulfill these requirements without rearrangement taking place—e.g., for *D*, most even-electron ions do not need to rearrange to give even electron products.

**A. Single Rearrangement. O.E. Ion  $\rightarrow$  O.E. Ion + E.E. Molecule.** With the molecular ion [formed initially under electron bombardment (46)], or most of the other odd-electron ions, a simple homolytic cleavage, or rupture of a one-electron bond, yields the even electron ion and radical.

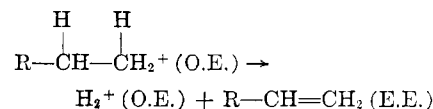


Transfer of a group from one cleavage fragment to the other, however, makes possible the formation of an odd-electron ion and a molecule,



and thus can be favored when these products are more stable than those from simple cleavage (with equivalent activation energies).

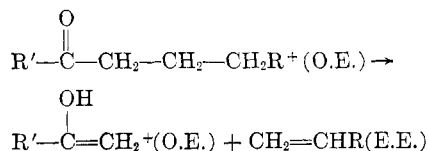
A common rearrangement ion in hydrocarbon spectra is  $H_2^+$ . Unless hydrogens on the same carbon are involved, the other product is an even-electron olefin or cyclic molecule.



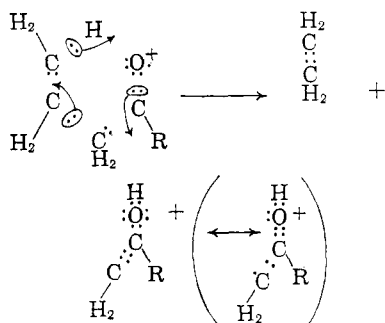
There is evidence for the similar formation of  $CH_4^+$  in some hydrocarbon spectra (30), but neither of these ions is usually abundant. The relative abundances of the rearranged ion  $Cl_2^+$  in *cis*- and *trans*-1,2-dichloroethylene are

0.24% and 0.05%, respectively (1), showing the steric influence on the activation energy.

The migration of hydrogen on cleavage of a bond beta to an electron withdrawing group is a prime example of a specific rearrangement, both in the high relative abundance and specificity of the rearranged ions that it yields, and in the large number of compound classes in which it is found (21, 22, 24, 25, 35, 38, 52).

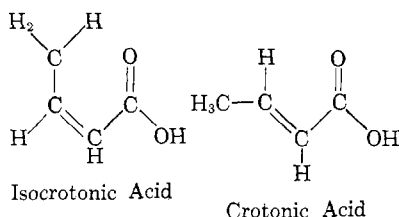


The polar unsaturated groups such as carbonyl (in aldehydes, ketones, amides, esters, etc.), nitrile, phosphate, sulfite, etc., thus often give such specific rearranged ions as the largest peak in their spectra (nitro and nitrite are apparently exceptions). A possible general mechanism is:

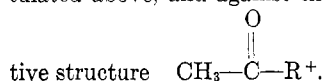


Thus, the replacement rearrangement of hydrogen allows the formation of the stable ethylene molecule and odd-electron ion (here probably of fairly high stability) from the odd-electron molecular ion, with the cyclic intermediate favoring a lowered activation energy.

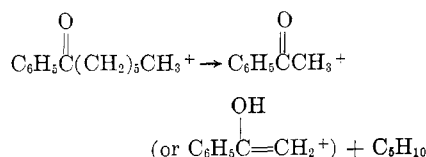
Further evidence for a cyclic intermediate is seen in the fact that the  $m/e$  60 rearrangement peak (involving here the migration of two hydrogen atoms) for isocrotonic acid (25) is significant (2%), while the crotonic acid it is not appreciable (35).



Recent work (51) gives evidence from appearance potential measurements in support of the rearranged structure containing the hydroxyl group, as postulated above, and against the alternative structure



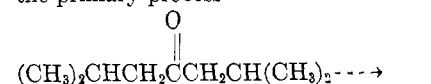
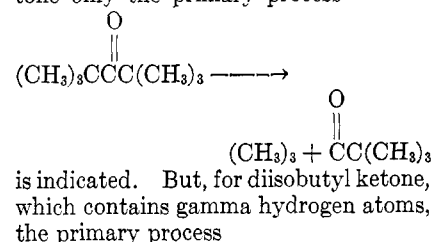
Meyerson and Rylander (40) point out that the existence of a metastable ion of  $m/e$  75.8 in the spectrum of phenyl *n*-hexyl ketone can be accounted for by  $m/e$  190<sup>+</sup>  $\rightarrow$  120<sup>+</sup> + 70—i.e., the similar rearrangement



This evidence for the neutral olefin or cycloalkane formation postulated above is encouraging, because it cannot occur in the spectrum. The rearranged ion shown is abundant (68% of base peak) in the spectrum.

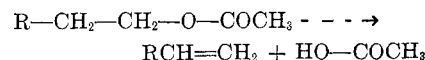
Energetically, rearrangement is favored over simple bond cleavage as the migration of the hydrogen atom allows the formation of the double bond, thus making a new bond for each one broken. This double bond formation favors migration of the hydrogen atom beta, not alpha, to the bond cleaved, which is in agreement with the observation (35) that this rearrangement does not occur where there are only  $\alpha$ -hydrogens available. Thus the spectrum of butyric acid gives this rearranged ion as the largest peak, while in propionic acid it is insignificant (25). This  $\alpha$ -hydrogen migration would yield an unstable diradical. The other class of rearrangements involving formation of the even-electron molecule, discussed in D, below, exhibits this same specificity.

With ketones, the main mass spectral cleavages (35, 52) are strikingly similar to their behavior on vapor phase photolysis. Thus, (28) for di-*tert*-butyl ketone only the primary process



is also observed, corresponding to the specific mass spectral rearrangement discussed above. Photolysis of esters,

$\text{R}-\text{C}(\text{OR}')_2$  (2) shows the same specificity of hydrogen migration in cleavage of either R or R'. In the photolysis of carbonyl compounds such a rearrangement is known as a Norrish type II mechanism (56). The pyrolysis of acetates to give acetic acid and the corresponding olefin is well known.

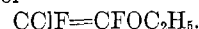


A check of further similarities between such mass spectral rearrangements and photolysis or high energy irradiation, to see if mass spectra can be used to predict results of such chemical processes, is planned.

Rearrangement of substituents farther removed than the beta position is indicated for some compounds. This could give a cyclic even-electron molecule in place of the olefin as the other product. The spectrum of

$\text{C}_6\text{H}_5\text{OCH}_2\text{CCH}_3$  shows 3%  $m/e$  94 ( $\text{C}_6\text{H}_5\text{OH}$ ), even though such a cyclic molecule would apparently involve a three-membered ring.

Other functional groups characteristically show this rearrangement also. Thus trimethylsilyl ethers,  $\text{ROSi}(\text{CH}_3)_3$ , give a prominent rearrangement to the corresponding  $\text{HOSi}(\text{CH}_3)_3$  when R is ethyl or greater (50). Diethyl peroxide ( $\text{C}_2\text{H}_5\text{O}$ )<sub>2</sub> has  $\text{C}_2\text{H}_5\text{OOH}$  (8%) and  $\text{HOOH}$  (0.03%) in its spectrum (1). The peak corresponding to the rearranged ion  $\text{CClF}=\text{CFOH}$  is large in the spectrum of

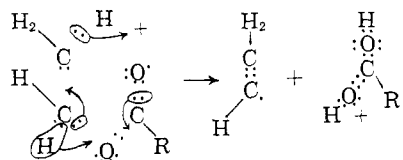


The presence of chain atoms as oxygen or nitrogen in the alpha position helps such rearrangement, probably because of their ability to donate their nonbonding electrons. Thus the lower effectiveness of the phenyl group gives 0.3% (after correction for heavy isotope contribution) of the rearranged  $m/e$  92 peak in propylbenzene, while the added oxygen in phenyl ethyl ether makes the corresponding rearrangement peak at  $m/e$  94 the largest in the spectrum. Even vinyl phenyl ether gives a large (10%)  $m/e$  94. Also, if the hydrogen is substituted on an oxygen atom, the rearrangement seems markedly increased. Thus the analogous 2-phenylethanol shows a strong (19%)  $m/e$  92 peak in contrast to the *n*-propylbenzene. Both these and the phenyl ethyl ether case may involve rearrangement of the hydrogen to a resonance-stabilized seven-membered ring instead of to the substituted benzene ion, etc. The tropylium ion has been used to explain other mass spectral phenomena (48) (see above).

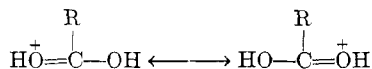
In connection with the 2-phenylethanol rearrangement, it is conclusively shown by the spectra of  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OD}$  (20),  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)-\text{CH}_2\text{OD}$  (20), and  $\text{C}_6\text{H}_5\text{CH}_2\text{CHDOH}$  (12) that the hydrogen rearranging on cleavage of the bond to the  $-\text{CH}_2\text{OH}$  function comes mainly from the hydroxyl group and not the hydrogens alpha to the cleaved bond.

**B. Double Rearrangement. O.E. Ion  $\rightarrow$  E.E. Ion + O.E. Radical.**

With a strong electron-withdrawing substituent plus the  $\alpha$ -oxygen or nitrogen atom, as in esters, amides, carbonates, carbamates, phosphates, etc., an ion with two hydrogen atoms rearranged is formed as well as the monorearrangement product (23, 35, 53).



The additional rearrangement can also involve the  $\gamma$ -hydrogen in place of the  $\beta$ -hydrogen shown here. The rearrangement of the second H is much different from the first, because a radical is formed in place of the molecule. Because a second migration involving either the  $\beta$ - or  $\gamma$ -hydrogen gives radicals of similar stability (in this example, identical radicals), steric factors are probably the main determinants. Also quite different from the case of the first H migration is the resonance stabilization possible for the even-electron ion thus formed which can contribute to the driving force for this phenomenon.



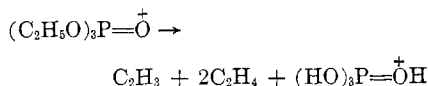
The possible alternative ion structure,  $\text{R}-\text{C}(\text{OH})=\text{O}^+$ , would not exhibit this resonance stabilization. The mass spectra of 2- and 3-D-*sec*-butyl acetate have recently been run (45).

<i>m/e</i>	2-D Spectrum	3-D Spectrum	2-D Spectrum
43	100	100	100
60	0.88	0.85	0.17
61	2.20	2.94	4.24
62	1.62	1.28	15.6
87	17.0	14.7	0.69
88		1.75	

The 2-D spectrum shows that both of the hydrogen atoms rearranged in the formation of the *m/e* 61 peak come from the  $\gamma$ - or  $\delta$ -carbon atoms 60% of the time, even though here the beta-hydrogen is in the labile tertiary position. Thus the gamma and delta positions supply 80% of the two rearranged hydrogens. The 3-D spectrum shows that 15% of these, or roughly one fifth involve one of the two secondary gamma-H atoms. Thus the choice of these *vs.* the other three  $\gamma$ -hydrogens available is roughly statistical, or, more probably, the  $\delta$ -hydrogens are also involved.

Carboxylic acids have the extra  $\alpha$ -oxygen atom, although not next to the cleaved bond. Simple acids—e.g., *n*- and isovaleric (25)—show an appreciable double rearrangement (*m/e* 61) peak as well as the highest peak at *m/e* 60 from rearrangement of one hydrogen atom. Cyclohexylacetic acid with its four  $\gamma$ -hydrogen atoms gives a strong (58%) *m/e* 61. In cyclohexane carboxylic acid the formation of this peak, found in 0.7% abundance, actually involves a triple rearrangement. This *m/e* 61 ion would be stabilized by resonance in the same way as the ester product above.

Triethyl phosphate rearranges a total of four hydrogen atoms on cleavage of the three O—C linkages (35).



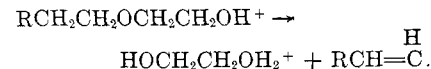
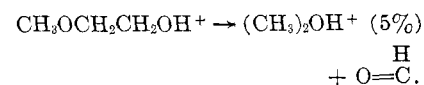
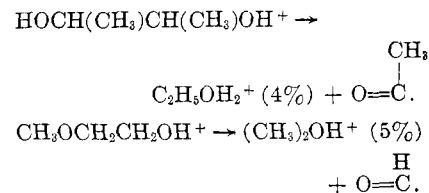
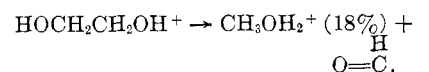
The product ion has many resonance forms.

Double rearrangements are also formed with compounds containing electron-donating groups. The even-electron hydronium (11) and ammonium (9) ions, *m/e* 19 and 18, are common anomalies in the spectra of alcohols and amines, respectively.

The mass spectrum of isobutyl alcohol shows a large (13%) rearranged peak of *m/e* 33, probably the oxonium-type ion  $\text{CH}_3-\text{OH}_2^+$  (9). Spectra of the deuterated analogs  $(\text{CH}_3)_2\text{CDCH}_2\text{OH}$  and  $(\text{CH}_3)_2\text{CHCHDOH}$  (12) show that this ion contains the 1-hydrogen and not the 2-hydrogen atom. This is

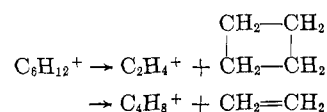
in isoamyl alcohol (9). The similarity of such rearrangements in these compounds and the corresponding amines was pointed out by Beynon (4).

Similar significant ions in some glycol (39) and alkoxy alcohol (44) spectra may arise through:

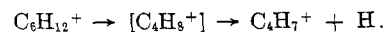


### C. Single Rearrangement. O.E. Cyclic Ion $\rightarrow$ E.E. Ion + O.E. Radical.

Two bond ruptures are necessary to produce fragment ions from the cyclic molecular ion. If these are simple homolytic cleavages, they will give an odd-electron ion and a diradical, in contrast to an acyclic compound. To obtain more stable products, several alternative paths are possible, as illustrated for the degradation of cyclohexane. The diradical may be stabilized by formation of an unsaturated or cyclic isomer requiring no rearrangement.



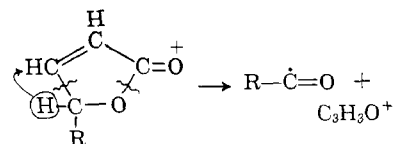
Loss of a substituent from the odd-electron ion would give an ion with an even number of electrons



Finally, as pointed out by Friedman and Long (18), cleavage could be accompanied by rearrangement to yield the even-electron ion with an additional substituent.

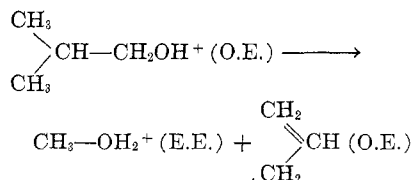


In the spectra of  $\gamma$ -crotonolactone and  $\beta$ -angelica-lactone, the formation of *m/e* 55, the largest peak, involves cleavage of the weak 3- and 5-bonds (18). Stabilization of the carbonyl ion then requires migration of one of the hydrogens available in the neutral radical.



However, hydrogen migration through a cyclic six-membered ring intermediate to the oxygen atom, as is favored for acyclic carbonyl compounds, would give the unlikely diradical ion

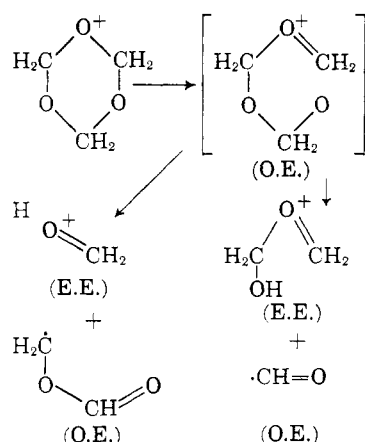
consistent with the following mechanism:



Construction of a model of the molecule shows this is sterically favorable. The resonance stabilization possible for the propenyl radical may contribute to such analogous rearrangements as  $\text{H}_3\text{O}^+$  in isopropyl alcohol and  $\text{C}_2\text{H}_5\text{OH}_2^+$

$\text{HC}=\text{CH}-\text{C}=\text{OH}^+$ . Rearrangement to the adjacent carbon atom would give the more stable ion,  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{O}^+$ . This vicinal hydrogen shift is similar to the second hydrogen migration of the double rearrangement of esters, etc., described in *B* above. Both involve formation of the even-electron ion and a radical, and illustrate again that the migration of an atom substituted in a particular position is usually found only where a neutral molecule is to be formed by the rearrangement.

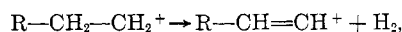
Langer (30) notes the  $m/e$  31 and 61 rearrangement peaks in the spectrum of trioxane, but prefers a mechanism to explain these involving migration of a hydrogen atom to another methylene group, which accounts also for the  $\text{CH}_3^+$  observed. A modification of an alternative suggestion (30) might be preferred because of the stability of the products produced.



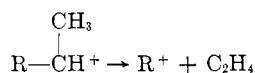
**D. Single Rearrangement. E.E. Ion  $\rightarrow$  E.E. Ion + E.E. Molecule.** Further degradation of an even-electron ion to another even-electron ion and a molecule can usually occur without rearrangement, as



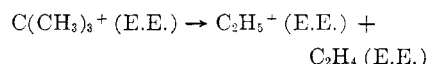
Sometimes rearrangement in the product molecule is necessary to produce an even-electron ion by a minimum energy process, as



or

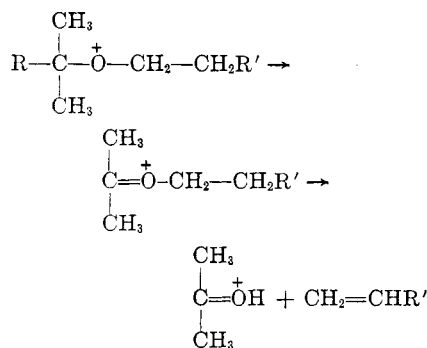


In certain cases, migration of an extra group to the ion itself may be necessary. Some of these, such as



have been discussed (see above) under Random Rearrangements because of the over-all similarity to other hydrocarbon rearrangements. Other examples of this type of rearrangement that give very prominent peaks occur

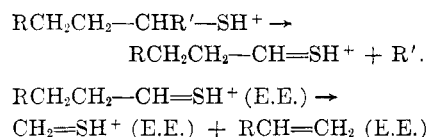
in alpha-branched secondary and tertiary amines, ethers (36, 44), and sulfides (32), etc.



Except for O—C bond rupture to give the  $\text{CH}_2\text{CH}_2\text{R}^+$  ion, which requires transfer of the localized positive charge of the oxygen atom (11, 19) to the alkyl group, this rearrangement is necessary to give even-electron products from further degradation of the abundant

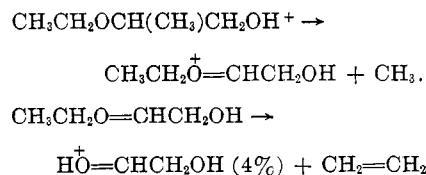
$(\text{CH}_3)_2\text{C}=\text{O}^+\text{CH}_2\text{CH}_2\text{R}'$ . The availability of a hydrogen substituted at the beta position or beyond is necessary for the rearrangement, in the same way as found previously for rearrangements producing a neutral molecule. However, a cyclic intermediate for this mechanism would only involve the four-membered ring, in contrast to the more stable six-membered ring intermediate proposed in *A*, above, for the analogous odd-electron ion rearrangement.

In secondary and tertiary mercaptans (32) where the branches are  $\text{C}_2$  or greater, a significant rearrangement ion results from the following probable mechanism:



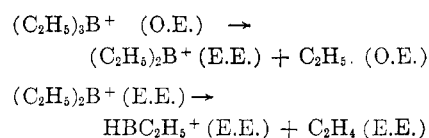
There is a striking similarity to the ether case above, although here the group that contributes the rearranged hydrogen is lost from the  $\alpha$ -carbon atom instead of the hetero atom. Tertiary mercaptans can also give a  $m/e$  47 peak by loss of three alkyl groups and rearrangement of two hydrogen atoms (32).

2-Alkoxyethanols substituted in the 1- or 2- positions show a combination of these effects (44).



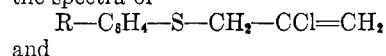
The largest peak in the mass spectrum of triethyl borine  $(\text{C}_2\text{H}_5)_3\text{B}$  is

$m/e$  41  $(\text{HBC}_2\text{H}_5)$  analogous to the sizable  $m/e$  43  $(\text{HBOCH}_3)$  in the spectrum of methyl borate,  $(\text{CH}_3\text{O})_3\text{B}$  (31). The mechanism

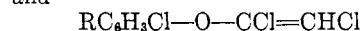


is suggested. It can be seen that further degradation of the  $(\text{C}_2\text{H}_5)_2\text{B}^+$  ion to even-electron products requires a rearrangement. The analogous  $\text{HC}(\text{C}_2\text{H}_5)_2$  rearrangement peak,  $m/e$  71, in the spectrum of the nonane  $(\text{C}_2\text{H}_5)_4\text{C}$  is of much lower relative intensity (0.7%) but here the cationated cyclopropane mechanism (47) gives large  $m/e$  43 and 57 ions. It is interesting that in the cases of the ether, borane, and hydrocarbon cited above, the oxygen, boron, and carbon, respectively, to which the hydrogen apparently migrates are of such diverse electronegativities.

**E. Multiple Bond Cleavage, Multiple Rearrangement.** Although it is possible by classification in the above categories to explain many anomalous ions, there still remain spectra for which the present experience is inadequate. Higher ethers (36) show a characteristic ion corresponding to loss of HOH from the parent molecule, and dimethyl acetal gives a  $\text{C}_3\text{H}_5^+$  ion (8). Both of these cases involve loss of the oxygen atom from within the molecule (breaking two bonds), with reunion of the two fragments. These may require higher energies similar to the random rearrangements, but do give more specific products. Prominent ions in the spectra of



and



are formed by the losses of the elements of  $\text{HClS}$ , and  $\text{COCl}$ , respectively, a similar ejection of a group in the interior of a molecule.

The largest peak in the spectrum of the cyclic dimethylphosphinoborane trimer,  $[\text{—P}(\text{CH}_3)_2\text{—BH}_2\text{—}]_3$ , is  $\text{B}(\text{CH}_3)_2^+$  (17). Here all four original bonds to the boron atom are cleaved, with rearrangement of two methyl groups.

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The author wishes to thank R. S. Gohlke, H. H. Freedman, and D. O. Schissler for very helpful discussions and R. S. Gohlke for checking various samples for impurities and purifying others. He also thanks M. C. Hamming, Koppers Co., Inc., who ran the mass spectra of 2- and 3-D-sec-butyl acetate and supplied the data. These compounds were obtained from H. C. Brown and Benjamin Repka, Purdue University, Lafayette, Ind.

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## Mass Spectra of Esters

### Formation of Rearrangement Ions

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► Important fragmentation peaks in the mass spectra of 31 aliphatic esters have been correlated with molecular structures. Each type of ester produced a characteristic major rearrangement peak. A possible process for the formation of these rearrangement ions is discussed. Examples are given of the use of both rearrangement and fragmentation peaks for the identification of esters.

MASS spectral correlation studies have been carried out on several classes of hydrocarbons (2, 16). The mass spectra of various oxygen-containing compounds have been investi-

gated, including aliphatic acids by Happ and Stewart (14), ethers by McLafferty (20), and aldehydes by Gilpin and McLafferty (11). Correlation studies at this laboratory on alcohols, ketones, acetals, trimethylsilyl derivatives, and esters have been described (7, 8, 23, 25, 26).

Previous investigations of the mass spectra of esters have been limited primarily to methyl (1, 18) and aromatic esters (12). Newton and Strom have compared the spectra of isopropyl and isopropenyl acetate (22). Several investigations of the formation of rearrangement ions in mass spectra have been reported (1, 6, 9, 10, 15, 17, 21, 27).

Rearrangement and normal fragmentation ions have been studied in the mass spectra of 31 esters, ranging from methyl formate (mass 60) to decyl acetate (mass 200).

#### EXPERIMENTAL

Spectra were obtained on a Consolidated Model 21-103 mass spectrometer equipped with a mercury orifice system for introducing samples. The ionizing voltage was 70 volts and the temperature of the ion source was controlled at 250° C.

Compounds were used as obtained without further purification. The source for each compound is given in Table I.