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Intramolecular Hydrogen Transfer in Mass Spectra. I. Rearrangements in Aliphatic Hydrocarbons and Aromatic Compounds[‡]

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Contents

I. Introduction

If any chemical reaction could truly be called ubiquitous, the rearrangement of hydrogen in molecules subjected to mass spectrometric analysis would certainly qualify. A molecule in the vapor phase may be bombarded with electrons over a wide energy range (electron-impact ionization), or subjected to high electric fields (field ionization) or to photon impact (photoionization) or collision with an ionized atom, group, or molecule (charge-transfer ionization), in order to produce an ionized nondecomposed species, the molecular ion. This species will in general be produced with a range of energies in excess of the ionization potential (IP), which is the energy just sufficient to produce the molecular ion. For those ions with sufficient internal energy, unimolecular decomposition (fragmentation) will be rapid on the mass spectrometer time scale (*i.e.*, decomposition within about 10^{-6} sec after ionization), and one or more fragment ions will be detected. The energy required to produce any given fragment is the appearance potential (AP) of that fragment. Molecular ions formed with energies just in excess of the ionization potential may not have sufficient energy to decompose by the lowest energy pathway and will thus be collected and detected as such. Since the molecular ion may formally be viewed as a cation radical (eq 1), hydrogen rearrangement is logically to be expected in its fragmentation,[1] since both cations and radicals are well known to undergo hydrogen rearrangements in solution chemistry. In this part of the review hydrogen rearrangements of aliphatic hydrocarbons and various aromatic compounds will be discussed, while the McLafferty rearrangement and related reactions will be covered in the second part. A projected third part will cover rearrangements involved in loss of HX or ketene, together with rearrangements in various nitrogen and sulfur compounds. Emphasis has been placed on electron-impact-induced rearrangements, since these are the most commonly encountered, but rearrangements induced by other methods of ionization will be discussed where appropriate. The literature through mid-1972 has been covered for this review.

$$M + e \longrightarrow M^{\cdot +} + 2e \qquad (1)$$

Before we discuss hydrogen rearrangements in particular, it will be helpful to review briefly some of the evidence on which the mass spectrometrist bases his proposed mechanisms of ionic decomposition, so that the ion structures and mechanisms proposed in the main part of this review can be understood in the perspective of current thinking on the subject.

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(1) F. W. McLafferty, *Chem. Commun.*, 78 (1966).

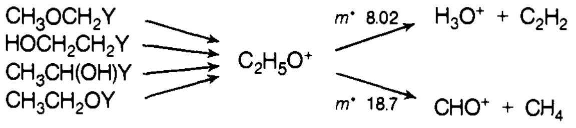
A. Ion Structures

A knowledge of the structure of ions in the mass spectrometer is crucial to a realistic discussion of mass spectrometric mechanisms. Unfortunately, the methods available for the determination of ion structures are at best limited in their application, and the conclusion of two recent reviews of the subject[2] was that our knowledge of ion structures is at present very poor. Nevertheless, useful information can be obtained in certain cases from studies of the thermodynamic properties of ions, derived from ionization and appearance potential data and other measurements of heats of formation. The technique is not widely used because of the experimental difficulties involved in the accurate determination of ionic properties. Nevertheless, when these quantities are available, useful information can be obtained on the structure of ions. For example, measurements of the heats of formation of the $C_3H_7^+$ cation from *n*-alkanes and from a variety of *n*-propyl and isopropyl compounds have shown that ions generated from propane and other *n*-alkanes have a heat of formation of about 195 kcal mol^{-1}, while ions generated from precursors such as 1-chloropropane and propane-1-thiol have heats of formation around 215 kcal mol^{-1}.[3-5] The conclusion may be drawn that ions from *n*-alkanes have the isopropyl structure, requiring a hydrogen rearrangement for its formation from *n*-alkanes larger than propane. Work in this area has been reviewed,[6] in addition to discussions in the reviews previously cited.[2]

A second approach to the determination of ion structures is by the correlation of metastable transitions. If an ion decomposes in the source of the mass spectrometer within about 10^{-6} sec after its formation, the daughter ion so formed will be accelerated and analyzed as such. If the ion decomposition is delayed to the range of 10^{-5} to 10^{-6} sec, however, formation of the fragment ion may occur after acceleration of the undecomposed parent ion but before mass analysis in a magnetic deflection instrument. The result is that a broad and diffuse peak is observed in the mass spectrum, at a position m^* given by eq 2, where m_2 is the daughter ion mass and m_1 that of

$$m^* = m_2^2/m_1 \qquad (2)$$

the parent ion. By use of this equation, a given product ion may of course be related to its parent. The usefulness of metastable ions in the determination of ion structures arises because the intensity of a metastable ion, when compared with the intensity of a suitable reference ion, is a measure of the number of parent ions which decompose to a specific daughter ion within a specific time period. Since the rate of decomposition of a parent ion will depend on its structure and energy, the intensity of a metastable ion will reflect the structure and energy of its parent ion. In particular, when a parent ion decomposes *via* two or more competing pathways, the ratio of metastable ion intensities for the two pathways should be the same for all ions of the same structure and energy. An elegant application of this criterion was made in the assignment of structures to the decomposing ion of formula $C_2H_5O^+$ from a variety of precursors.[7] The first group of precursors of the $C_2H_5O^+$ ion gave a ratio of metastable intensities [*m*/*e* 8.02]/[*m*/*e* 18.7] of less than 0.01, while the remaining three groups of precursors all had this ratio around 2.0. This evidence strongly suggests that compounds in the last three groups fragment *via* an ion $C_2H_5O^+$ of common structure, and thus implies hydrogen rearrangement in the fragmentation of at least one molecular type. Caution is necessary in interpreting results which are less clear-cut than this one, however, since ions of the same structure derived from different origins may show some variation in metastable abundance ratios because of varying energy distributions in precursor ions and differing rates of formation of the fragments.[8] It should also be borne in mind that a study of metastable peak intensities can only yield information on the structure of decomposing ions. This technique is silent on the subject of the structure of ions which do not decompose before they reach the collector, and it is quite possible that in some cases these will have different structures from ions of the same composition which do decompose.



While a metastable peak is generally assumed to be indicative of a one-step process, this is not always the case, as was recognized in early studies on the origins of metastable peaks.[9] Recent examples of two or multistep processes which give rise to a single metastable peak include the loss of two molecules of acetylene from the $C_7H_7^+$ ion in the spectrum of toluene,[10] the loss of CO and HO from a fragment ion formed from pyridoxol,[11] the loss of H_2O and CH· from ergosterol,[12] and the loss of H_2O and HO· from dinitrophenylhydrazones.[13]

The "metastable defocusing" technique, to which reference is made here occasionally, produces metastable peaks by operating a double-focusing mass spectrometer so as to defocus the ion beams responsible for normal peaks and more efficiently focus those giving rise to metastable peaks.[14-16] Ions decomposing in the region between the source and the electrostatic analyzer, which would normally fail to pass through the analyzer, are given sufficient energy to pass through and be collected. Using this method, one may determine all of the ions which produce a given ion (on the metastable time scale, *ca.* 10^{-5} sec) or, in some instruments, all of the fragment ions formed from a given ion (on the metastable time scale). In addition to the advantages of increased sensitivities for metastable detection and ease of interpretation of results, this technique also allows the direct study of consecutive transitions in the mass spectrometer.[10,17] The related technique of "ion kinetic energy

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(2) (a) T. W. Bentley and R. A. W. Johnstone, *Advan. Phys. Org. Chem.*, **8**, 152 (1970); (b) M. M. Bursey and M. K. Hoffman in "Mass Spectrometry: Techniques and Applications," G. W. A. Milne, Ed., Wiley, New York, N. Y., 1971.

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(4) J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

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(6) (a) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, N. Y., 1957; (b) A. G. Harrison, "Topics in Organic Mass Spectrometry," A. L. Burlingame, Ed., Wiley-Interscience, New York, N. Y., 1970.

(7) T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5021 (1966).

(8) J. L. Occolowitz, *J. Amer. Chem. Soc.*, **91**, 5202 (1969).

(9) J. A. Hipple, *J. Phys. Colloid Chem.*, **52**, 456 (1948).

(10) K. R. Jennings, *Chem. Commun.*, 283 (1966).

(11) D. C. DeJongh, S. C. Perricone, and W. Korytnyk, *J. Amer. Chem. Soc.*, **88**, 1233 (1966).

(12) J. Seibl, *Helv. Chim. Acta*, **50**, 263 (1967).

(13) S. D. Sample and C. Djerassi, *Nature (London)*, **208**, 1314 (1965).

(14) M. Barber and R. M. Elliott, 12th Annual Conference on Mass Spectrometry, Montreal, Canada, ASTM E-14, 1964.

(15) K. R. Jennings, *J. Chem. Phys.*, **43**, 4176 (1965).

(16) J. H. Futrell, K. R. Ryan, and L. W. Sieck, *J. Chem. Phys.*, **43**, 1832 (1965).

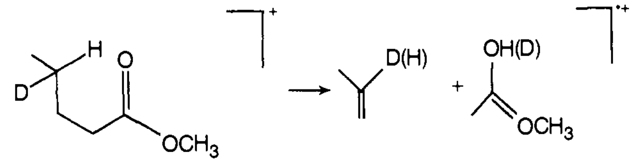
(17) E. Tajima and J. Seibl, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 245 (1969).

spectroscopy," in which ion beams differing in kinetic energy are collected with no mass analysis, also provides information on decomposition pathways.[18]

Finally, the technique of ion cyclotron resonance[19,20] may be used to assign structures to ions by observing their ion-molecule reactions. This approach was used, for example, in the assignment of structures to the product ions of the double McLafferty rearrangement,[21] and this example will be discussed in more detail in Part II.

B. Labeling Studies

Probably the single most useful technique used to trace the course of hydrogen rearrangements has been the use of molecules specifically labeled with deuterium. This technique is valuable because most of the chemical properties of deuterium are identical with those of the hydrogen it replaces, but it is easy to distinguish deuterium from hydrogen mass spectrometrically. There are many pitfalls for the unwary in the use of deuterium labeling, but the two most important ones are the fact of the isotope effect and the possibility of label scrambling prior to or during fragmentation. In the first case, because the zero-point energy of the carbon-deuterium bond is lower than that of the carbon-hydrogen bond, correspondingly more energy is required to break the carbon-deuterium bond. Thus, when a fragmentation process involves transfer of hydrogen, replacement of the hydrogen by deuterium results in the operation of an isotope effect—the discrimination against transfer of deuterium when equivalent hydrogen is available.[22] Thus, unless all equivalent hydrogen atoms have been replaced by deuterium, the fragmentation process is likely to be disproportionately weighted toward the transfer of hydrogen. In the case of the McLafferty rearrangement of partially deuterated methyl pentanoate, for example, an isotope effect of 0.92 was observed.[23] Isotope effects of up to 0.50 have been observed in the spectra of hydrocarbons; thus an effect of 0.80 discriminating against deuterium is operative in the γ-hydrogen rearrangement of butylbenzene.[24]



The problem of hydrogen scrambling is in many respects a more serious one than that of the isotope effect, which has not historically been a major source of confusion, and has served on occasion to direct attention to mechanistic details that were not otherwise apparent. Synthetic routes to the introduction of deuterium are generally quite specific, and if it is assumed that the position(s) of the labeled atom(s) in a molecular ion corresponds to that in the neutral molecule from which the ion is formed, then a knowledge of the fate of the label in subsequent fragmentations often allows the proposal of reasonable ion structures and fragmentation mechanisms. It is apparent, however, that in many cases rearrangement is not specific, and it is helpful to distinguish three possible types of hydrogen rearrangement: (a) *specific*, in which a specific hydrogen atom (or atoms) rearranges to a different site in the ion during fragmentation; (b) *nonspecific*, in which hydrogen atoms from more than one site in the precursor ion rearrange to a given site during fragmentation by the intermediacy of transition states of different ring sizes; (c) *hydrogen scrambling*, in which positional identity of the labels is wholly or partially lost before fragmentation. In practice it is difficult to distinguish experimentally between nonspecific rearrangement and hydrogen scrambling, although in a recent paper[25] this distinction was made for the rearrangement of phenyl *n*-butyl ether. The occurrence of hydrogen scrambling, while of interest in its own right, complicates the interpretation of the spectra of deuterium-labeled compounds and on occasions makes it impossible to draw mechanistic conclusions from labeling studies.

In spite of these potential pitfalls, deuterium labeling is the most powerful weapon in the chemist's armamentarium for the study of hydrogen rearrangements. Since hydrogen is present in most organic compounds, the mass spectrometric hydrogen rearrangement, whether specific or random, is observed in the case of virtually every compound studied in the mass spectrometer.

C. Metastable Peaks

In addition to their use in characterizing ion structures and confirming reaction pathways, the intensity of a metastable peak can frequently provide a clue as to whether or not a specific fragmentation proceeds *via* a rearrangement. Rearrangement reactions generally have lower activation energies than simple bond cleavages because the energy required for cleavage of a bond is at least somewhat compensated for by the formation of a new bond. However, the rate of a rearrangement reaction is reduced by the necessity for the molecule to assume a certain steric configuration before rearrangement can occur. According to the quasi-equilibrium theory,[26,27] fragmentations with low activation energies and low "frequency factors" are likely to show substantial metastable peaks, and it has been stated[28] that rearrangement can be excluded if a process which produces an abundant product ion does not also have an abundant corresponding metastable ion. However, because of various instrumental factors governing the actual observed intensities of metastable peaks, this criterion for rearrangement processes must be used with caution.

D. Conclusion

From the foregoing discussion it should be clear that our knowledge of the mechanisms by which ions decompose in the mass spectrometer is based on evidence which is at best fragmentary and incomplete. The biggest handicap to any discussion of mass spectral mechanisms is our lack of knowledge of the structures of decomposing and product ions in all but a few cases. Because of this, it might appear foolish to attempt to represent ionic structures in this review. However, the rearrangements to

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(18) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 313 (1969).

(19) J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, **40**, 123 (1969).

(20) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

(21) G. Eadon, J. Diekman, and C. Djerassi, *J. Amer. Chem. Soc.*, **92**, 6205 (1970).

(22) J. Delfosse and J. A. Hipple, Jr., *Phys. Rev.*, **54**, 1060 (1938).

(23) J. K. MacLeod and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 5182 (1967).

(24) J. K. MacLeod and C. Djerassi, *Tetrahedron Lett.*, 2183 (1966).

(25) A. N. H. Yeo and C. Djerassi, *J. Amer. Chem. Soc.*, **94**, 482 (1972).

(26) H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 1.

(27) R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass Spectrom.*, **2**, 137 (1969).

(28) F. W. McLafferty and R. B. Fairweather, *J. Amer. Chem. Soc.*, **90**, 5915 (1968).

be discussed are more easily understood with the aid of structural formulas, and for this reason alone such formulas have been used liberally. It should be clearly understood that the use of a structural formula does not imply that the ion in question has been investigated and shown to have that particular structure. Cases where ionic structures have been established beyond reasonable doubt will be discussed specifically in the text.

Finally, the possibility that molecules might rearrange prior to ionization should be carried in mind. Such rearrangements could occur, for example, by thermal isomerization of molecules in the heated inlet system of the mass spectrometer, or by thermal dehydration or rearrangement in the source prior to ionization. Studies of several systems have been reviewed, and it is shown that these preionization reactions do occur in some cases.[29]

II. Rearrangements in Aliphatic Hydrocarbons and Group IV Alkyls

A. Introduction

The investigation of hydrocarbons, particularly aliphatic ones, goes back to the earliest days of mass spectrometry. The discovery that organic compounds fragment on impact with electrons of sufficiently high energy itself included the first observation of intramolecular hydrogen transfer in gaseous hydrocarbon ions.[30] Processes occurring in the lower alkanes studied in this work were later shown to include the rearrangements

$$C_3H_7^+ \longrightarrow C_3H_5^+ + H_2 \tag{3}$$

$$C_3H_5^+ \longrightarrow C_3H_3^+ + H_2 \tag{4}$$

Six years later, in 1937, the study of decompositions of gaseous organic ions as a subject of interest in its own right began, and again aliphatic hydrocarbons were used as the test substrates.[31,32] Two factors explain this early interest in hydrocarbons. In the first place, their volatility made it possible to obtain good spectra with even the simplest inlet system, and, secondly, it seemed logical to begin systematic studies of the fragmentation of organic molecules with representatives of their simplest class, which would presumably show the most easily interpretable reactions. This assumption proved not to be the case, and the widespread occurrence of both hydrogen and carbon-skeletal rearrangements in aliphatic hydrocarbons led most chemists to conclude that little information of structural importance could be obtained from mass spectra. It was not until the late 1950's, when a sufficient number of organic compounds containing heteroatoms had been investigated, that it was generally realized that useful structural information can be obtained from mass spectra.

In spite of, or perhaps because of, the complexity of the fragmentations undergone by hydrocarbons on electron impact, a large amount of elegant experimental and theoretical work has been carried out on them. This interest is largely explained by the use of mass spectrometry in the petroleum industry for petroleum and gasoline analyses, both qualitative and quantitative, and it is no accident that some of the best work in this area has come from workers in the petroleum industry. Noteworthy also is the development of the quasi-equilibrium theory (QET) using propane as a model compound,[33] and later formulations of the theory continued to use hydrocarbons as model compounds.[26,34-38]

Because of the wealth of papers dealing with the fragmentations and rearrangements of hydrocarbons, it is impossible to do justice in anything short of a monograph to all the work that has been done. We have chosen instead to discuss illustrative examples at some length, and to present the remainder of the data in tabular form for those readers interested in specific examples.

B. Rearrangements in Alkanes

In spite of the deceptively simple appearance of the mass spectra of alkanes, these compounds undergo extensive rearrangement on electron impact. The major documented rearrangements of a number of alkanes are listed in Table I. Hydrogen rearrangements fall into the following basic types.

(a) Elimination of molecular hydrogen from the molecular ion.

$$CH_4^{\cdot+} \longrightarrow CH_2^{\cdot+} + H_2 \tag{5}$$

Since this reaction involves rearranging bonds to hydrogen atoms, it can be classified as a hydrogen rearrangement.

(b) Elimination of a neutral alkane from the molecular ion.

$$CH_3CH_2CH_2CH_3^{\cdot+} \longrightarrow CH_3CH{=}CH_2^{\cdot+} + CH_4 \tag{6}$$

$$CH_3(CH_2)_4CH_3^{\cdot+} \longrightarrow C_4H_8^{\cdot+} + C_2H_6 \tag{7}$$

(c) Elimination of molecular hydrogen from odd- or even-electron fragment ions.

$$CH_3CH_2CH_3^{\cdot+} \longrightarrow C_2H_4^{\cdot+} \longrightarrow C_2H_2^{\cdot+} + H_2 \tag{8}$$

$$CH_3CH_2CH_3^{\cdot+} \longrightarrow C_3H_7^{\cdot+} \longrightarrow C_3H_5^+ + H_2 \tag{9}$$

(d) Hydrogen rearrangement accompanying skeletal rearrangement.

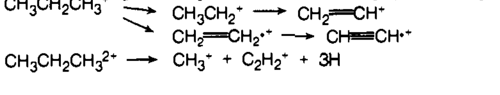
$$(CH_3)_2CHCH_3^{\cdot+} \longrightarrow C_2H_5^+ + C_2H_5^{\cdot} \tag{10}$$

(e) Hydrogen scrambling preceding or accompanying fragmentation.

Rearrangements of all these types except (d) are shown by propane, and we shall discuss the fragmentations of this compound in some detail as examples of hydrogen rearrangements in alkanes.

The mass spectrum of propane[39] can be explained in terms of the fragmentations shown in Scheme I. Major

SCHEME I



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(29) H. Budzikiewicz, *Z. Anal. Chem.*, **244**, 1 (1969).

(30) H. R. Stewart and A. R. Olson, *J. Amer. Chem. Soc.*, **53**, 1236. (1931).

(31) L. G. Smith, *Phys. Rev.*, **51**, 263 (1937).

(32) P. Kusch, A. Hustrulid, and J. R. Tate, *Phys. Rev.*, **52**, 843 (1937).

(33) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952).

(34) A. Kropf, E. M. Eyring, A. L. Wahrhaftig, and H. Eyring, *J. Chem. Phys.*, **32**, 149 (1960).

(35) E. M. Eyring and A. L. Wahrhaftig, *J. Chem. Phys.*, **34**, 23 (1961).

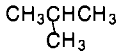
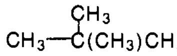
(36) M. I. Vestal, *J. Chem. Phys.*, **43**, 1356 (1965).

(37) J. C. Tou, L. P. Hills, and A. L. Wahrhaftig, *J. Chem. Phys.*, **45**, 2129 (1966).

(38) M. I. Vestal in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley-Interscience, New York, N. Y., 1968, p 59.

(39) Catalog of Mass Spectral Data. American Petroleum Institute, Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., Spectrum No. 3.

TABLE I. Hydrogen Rearrangements in the Mass Spectra of Alkanes[a]

Alkane	Fragment ion formed by rearrangement		Comment[b]	Ref
CH_4	$CH_2{\cdot}^+$	$(M - H_2){\cdot}^+$	N, E, D	*c–f*
	$H_2{\cdot}^+$		I	31
	H_3^+		I	31
C_2H_6	$C_2H_4{\cdot}^+$	$(M - H_2){\cdot}^+$	N	*g–i*
	CH_3^+	$(M - CH_3)^+$	HS, D	*i, j*, 48
$CH_3CH_2CH_3$	$C_3H_6{\cdot}^+$	$(M - H_2){\cdot}^+$	N, HS, E, D	*k*, 45
	$C_3H_4{\cdot}^+$		E, D	
	$C_2H_4{\cdot}^+$	$(M - CH_4)^+$	N, E, D	16, 45
	$CH_3^+ + C_2H_3^+$		SR, E, D, C	39
$CH_3CH_2CH_2CH_3$	$C_4H_8{\cdot}^+$	$(M - H_2){\cdot}^+$	HS, D	*g, l*
	$C_3H_6{\cdot}^+$	$(M - CH_4){\cdot}^+$	I, D, E	*g, m–q*
	$C_3H_7^+$	$(M - CH_3)$	HS, D	*r*
 $CH_3\underset{\displaystyle CH_3}{C}HCH_3$	$C_2H_5^+$		SR, E	s–*u*
	$C_3H_6{\cdot}^+$	$(M - CH_4)$	I, D	46
	$C_4H_8{\cdot}^+$	$(M - H_2)$	I	*g*
 $CH_3{-}\overset{\displaystyle CH_3}{C}(CH_3)CH_3$	$C_2H_5^+$		SR, E, C	*v–x*
	$C_2H_3{\cdot}^+$		SR, E, C	*v–x*
C_6H_{14}	$(M - CH_3)^+, (M_1 - C_2H_5)^+$		SR	*y*
$CH_3(CH_2)_4CH_3$	$C_5H_{11}^+$	$(M - CH_3)$	HS, D	*z*
	$C_5H_{10}{\cdot}^+$	$(M - CH_4)$	HS, D	*z*
	$C_4H_8{\cdot}^+$	$(M - C_2H_6)$		*z*
	$C_3H_8{\cdot}^+$	$(M - C_3H_6)$	I, D	*aa*
	$C_3H_7^+$		M	*bb*
C_7H_{16}	$C_4H_9^+$		M	*cc*
n-C_8H_{18}	C_1–C_4 ions		D, HS	*dd–ii*
n-C_9H_{20}	C_1–C_4 ions		C, HS	*dd–gg*
n-$C_{10}H_{22}$	$C_9H_{19}^+$	$(M - CH_3)^+$	D, M, C, SR	*y, jj–ll*
	C_1–C_4 ions		HS, D	
$C_{12}H_{24}$	C_1–C_5 ions		HS, D	*ii*
$C_{12}H_{26}$	C_1–C_5 ions		HS, D, C	*ii, mm*
$C_{16}H_{34}$	$(M - \text{alkane}){\cdot}^+$		I, M, F	*nn*
$C_{26}H_{54}$	$(M - R)^+$		D, SR	*oo*
$RC(CH_3)CHR'$	$(M - CH_4){\cdot}^+$		I, M	*pp–tt*

[a] Only the major rearrangement pathways have been indicated for each compound in the table. For further information, consult the references listed. [b] The various types of evidence used by the author(s) of the cited papers to support the occurrence of hydrogen rearrangement were as follows: C, ^{13}C labeling; D, deuterium labeling; E, studies of the energetics of ion formation; F, data are for field ionization spectra; HS, hydrogen scramble (partially or completely) before formation of this ion; HR, hydrogen rearrangement occurs in the formation of this ion; I, rearrangement implicit in the structure(s) of the fragment ion(s); IS, ion structure(s) studied; M, ion decomposition pathway confirmed by metastable peaks; N, neutral fragment lost in one step; R, rearrangement suggested by similarity of spectrum with that of an isomeric compound; SR, skeletal rearrangement observed. [c] A. Langer, J. A. Hipple, Jr., and D. P. Stevenson, *J. Chem. Phys.*, **22**, 1836 (1954). [d] E. Lindholm, *Z. Naturforsch. A*, **9**, 535 (1954). [e] V. H. Dibeler and F. L. Mohler, *J. Res. Nat. Bur. Stand.*, **45**, 441 (1950). [f] Ch. Ottinger, *Z. Naturforsch. A*, **20**, 1232 (1965). [g] J. A. Hipple, Jr., R. E. Fox, and E. U. Condon, *Phys. Rev.*, **69**, 347 (1946). [h] J. A. Hipple, Jr., *ibid.*, **53**, 530 (1938). [i] L. D'Or, J. E. Collin, and J. Longrée, *Bull. Classe Sci. Acad. Roy. Belg.*, **52**, 518 (1966). [j] Y. Amenomiya and R. F. Pottie, *Can. J. Chem.*, **46**, 1741 (1968). [k] J. Delfosse and W. Bleakney, *Phys. Rev.*, **56**, 256 (1939). [l] W. H. McFadden and A. L. Wahrhaftig, *J. Amer. Chem. Soc.*, **78**, 1572 (1956). [m] R. E. Fox and A. Langer, *J. Chem. Phys.*, **18**, 460 (1950). [n] P. Ausloos and S. G. Lias, *ibid.*, **45**, 524 (1966). [o] O. Osberghaus and Ch. Ottinger, *Phys. Lett.*, **16**, 121 (1965). [p] Ch. Ottinger, *Z. Naturforsch. A*, **22**, 20 (1967). [q] I. Hertel and Ch. Ottinger, *ibid.*, **22**, 40 (1967). [r] R. Liardon and T. Gäumann, *Helv. Chim. Acta*, **54**, 1968 (1971). [s] R. E. Honig, *Phys. Rev.*, **75**, 1319A (1949). [t] D. P. Stevenson and J. A. Hipple, Jr., *J. Amer. Chem. Soc.*, **64**, 1588 (1942). [u] I. Omura, *Bull. Chem. Soc. Jap.*, **34**, 1227 (1961). [v] F. W. Lampe and F. H. Field, *J. Amer. Chem. Soc.*, **81**, 3238 (1959). [w] A. Langer and C. P. Johnson, *J. Phys. Chem.*, **61**, 891 (1957). [x] A. Langer and C. P. Johnson, *ibid.*, **61**, 1010 (1957). [y] C. Corolleur, S. Corolleur, and F. G. Gault, *Bull. Soc. Chim. Fr.*, 158 (1970). [z] R. Liardon and T. Gäumann, *Helv. Chim. Acta*, **52**, 528 (1969). [aa] R. Liardon and T. Gäumann, *ibid.*, **52**, 1043 (1969). [bb] W. F. Haddon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 4745 (1968). [cc] G. Khodadi, R. Botter, and H. M. Rosenstock, *Int. J. Mass. Spectrom. Ion Phys.*, **3**, 397 (1969). [dd] I. V. Goldenfield and I. Z. Korostyshevsky, *ibid.*, **3**, 404 (1969). [ee] M. V. Gur'ev and M. V. Tikhomirov, *Zh. Fiz. Khim.*, **32**, 2731 (1958). [ff] M. V. Gur'ev, M. V. Tikhomirov, and N. N. Tunitskii, *ibid.*, **32**, 2847 (1958). [gg] M. V. Gur'ev, M. V. Tikhomirov, and N. N. Tunitskii, *Tr. Khim. Khim. Teckhnol.*, **1**, 453 (1958). [hh] D. S. Weinberg and M. W. Scoggins, *Org. Mass Spectrom.*, **2**, 553 (1969). [ii] S. Meyerson, *J. Chem. Phys.*, **42**, 2181 (1965). [jj] J. R. Morandi and B. Jensen, *J. Org. Chem.*, **34**, 1889 (1969). [kk] R. E. Rhodes, M. Barber, and R. L. Anderson, *Anal. Chem.*, **38**, 48 (1966). [ll] T. W. Shannon, T. E. Mead, C. G. Warner, and F. W. McLafferty, *ibid.*, **39**, 1748 (1967). [mm] J. H. Beynon, R. A. Saunders, A. Topham, and A. E. Williams, *J. Phys. Chem.*, **65**, 114 (1961). [nn] H. D. Beckey and P. Schulze, *Z. Naturforsch. A*, **20**, 1329 (1965). [oo] N. Dinh-Nguyen, R. Ryhage, S. Ställberg-Stenhagen, and E. Stenhagen, *Ark. Kemi*, **18**, 393 (1961). [pp] A. Herlan, *Brennst.-Chem.*, **50**, 204 (1969). [qq] A. Herlan, *ibid.*, **46**, 264 (1965). [rr] G. Remberg, M. Spiteller-Friedman, and G. Spiteller, *Org. Mass Spectrom.*, 1, 87 (1968). [ss] E. D. McCarthy, J. Han, and M. Calvin, *Anal. Chem.*, **40**, 1475 (1968). [tt] A. Herlan, *Org. Mass Spectrom.*, **4**, 425 (1970).

fragmentation pathways include the loss of hydrogen atoms or molecules to form a series of ions at *m/e* 43–36, the loss of a methyl group to yield an intense ion $C_2H_5^+$ at *m/e* 29, and the loss of CH_4 to yield a weaker ion at *m/e* 28.

Studies with ^{13}C-labeled propane showed that no detectable skeletal rearrangement occurred prior to formation of the base peak due to the ethyl cation; thus $CH_3{}^{13}CH_2CH_3$ yielded $CH_3{}^{13}CH_2^+$ only.[40] That this process was a simple one was deduced earlier from appearance potential data.[41] However, studies with deuterium-labeled propanes indicated that a small amount of hydrogen scrambling precedes or accompanies formation of the ethyl cation.[42,43] Thus $CD_3CH_2CD_3$ yields ions at *m/e* 33 and 34 attributable to CD_3CDH^+ or $CD_2HCD_2^+$ and $CD_3CD_2^+$.

Hydrogen scrambling occurs in some of the ions decomposing by loss of hydrogen. There is good evidence from heats of formation that the $C_3H_7^+$ ion has the iso-

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(40) D. P. Stevenson, *J. Chem. Phys.*, **19**, 17 (1951).

(41) D. P. Stevenson, *J. Chem. Phys.*, **10**, 291 (1942).

(42) F. E. Condon, *J. Amer. Chem. Soc.*, **73**, 4675 (1951).

(43) C. Lifshitz and M. Shapiro, *J. Chem. Phys.*, **46**, 4912 (1967).

propyl structure,[3,44] and the finding that $CH_3CD_2CH_3$ loses a deuterium atom but not a hydrogen atom in metastable transitions[45] and in normal mass spectra[41,46] indicates that hydrogen scrambling does not precede formation of the isopropyl ion. Some scrambling does occur, however, in secondary C_3 ions losing molecular hydrogens, as indicated by analysis of their metastable transitions.[45] Such studies of metastable transitions only give information about the weakly excited ions undergoing these transitions, and the results may not be directly applicable to normal mass spectra. However, earlier studies of the normal spectra of specifically labeled deuteriopropanes indicated that label scrambling does occur before loss of H_2 from the molecular ion,[41] although the results can be explained equally well by the postulate of multiple pathways for H_2 elimination.[42] The first-order decay constant k_1 has been measured for the metastable transition $C_3H_7^+ \rightarrow C_3H_5^+ + H_2$ for the $C_3H_7^+$ ion generated from a variety of sources.[47] No significant variation in k_1 was observed, and thus the initial preparation does not have much effect on this decomposition, nor probably on structure. It was shown that the metastable transition is not a collision-induced dissociation. The observation that scrambling does not precede loss of H· from ionized propane while it does precede loss of CH_3· and H_2 may be explained by the larger energy requirements of the latter reactions.

The formation of the ion $C_2H_4\cdot^+$ in the mass spectrum of propane arises at least in part by the one-step loss of methane from the molecular ion, as indicated by a metastable transition corresponding to this reaction,[16,45] although inexplicably its intensity differs by a factor of 300 in the references cited. The elimination reaction to form this ion could in principle occur by a 1,2 pathway (eq 11) or a 1,3 pathway (eq 12). It was early proposed that the

$$CH_3CH_2CH_3\cdot^+ \longrightarrow CH_3CH\cdot^+ + CH_4 \qquad (11)$$

$$CH_3CH_2CH_3\cdot^+ \longrightarrow CH_2{=\!=}CH_2\cdot^+ + CH_4 \qquad (12)$$

1,3 elimination represented the lowest energy pathway,[46,48] and this was confirmed by a study of the elimination in $CH_3CD_2CH_3$ using charge-exchange ionization;[49] the 1,3 elimination has an appearance potential of 11.7 eV as compared with about 12.2 eV for the 1,2 process. As would be expected from these results, elimination of CD_4 from $CD_3CH_2CD_3$ is observed in its normal mass spectrum, but surprisingly no metastable transition for this loss could be detected in spite of the presence of a strong metastable peak for CH_4 loss from $CH_3CD_2CH_3$.[42] These and other results were originally explained on the basis of the QET assuming two distinct rate constants for 1,2 and 1,3 elimination,[50] but later reinterpretation showed this explanation to be incorrect.[43] The QET does offer a satisfactory explanation for these results when the different energy level spacings of the deuterated products are taken into account.[43]

The ion CH_3^+ in the mass spectrum of propane appears to be formed largely from doubly charged molecular ions by the processes shown in eq 13a–c. This is indicated by ionization efficiency curves[51] and by measurement of the energy released in the formation of this ion.[52] Not surprisingly, hydrogen and skeletal rearrangement are observed in these high-energy processes, and $CH_3{}^{13}CH_2CH_3$ yields $^{13}CH_3^+$ as well as CH_3^+,[40] while CH_3CHDCH_3 yields CH_2D^+.[53]

$$C_3H_8^{2+} \longrightarrow CH_3^+ + C_2H_2^+ + 3H \qquad (13a)$$

$$\longrightarrow CH_3^+ + C_2H_3^+ + 2H \qquad (13b)$$

$$\longrightarrow CH_3^+ + C_2H_4^+ + H \qquad (13c)$$

The structure of the $C_3H_7^+$ ion from various sources other than propane has been the subject of some recent work.[54] In these studies the structure of the $C_3H_7^+$ ion was examined by ion cyclotron resonance (icr),[54a,b] by *ab initio* molecular orbital calculations,[54d] and by radiolysis and electron-impact studies.[54c] Earlier results have been concisely reviewed.[54b] The conclusion was reached from the latest icr work that *sec*-propyl ions undergo little isomerization on the time scale required for icr reactions (*ca.* 10^{-3} sec), while almost no *n*-$C_3H_7^+$ ions retain their structure, most isomerizing to *sec*-$C_3H_7^+$. Protonation of cyclopropane produced propyl ions of reactivity identical with that of *sec*-$C_3H_7^+$, suggesting either that isomerization to *sec*-$C_3H_7^+$ occurs or that the heat of formation of c-$C_3H_7^+$ is significantly higher than that of *sec*-$C_3H_7^+$.[54b] This result is in agreement with the most recent theoretical calculations,[54d] which indicated that *sec*-$C_3H_7^+$ is the lowest energy structure, with forms of *n*-$C_3H_7^+$ and c-$C_3H_7^+$ of unusual geometry being the next most stable states, approximately 17 kcal above that of *sec*-$C_3H_7^+$.

The higher alkanes show hydrogen rearrangements which are basically similar to those observed in propane, although the detailed mechanisms may differ from case to case. In summary, then, the alkanes undergo hydrogen rearrangement in the loss of alkane fragments from the molecular ion and in the loss of molecular hydrogen from the molecular ion or from fragment ions. Little or no hydrogen rearrangement (scrambling) is observed prior to fragmentations involving simple bond cleavage, such as formation of the M − CH_3 ions. Some higher alkanes, particularly those with branched chains, also show skeletal rearrangement accompanying hydrogen rearrangement, and examples of this process are given in Table I.

C. Rearrangements in Unsaturated Hydrocarbons

The mass spectrometry of alkenes has recently been reviewed,[55] so some aspects of this discussion are abbreviated. Hydrogen rearrangements occur ubiquitously and extensively in the molecular ions of alkenes and alkynes, in contrast to the situation in alkanes where little rearrangement takes place prior to most fragmentations. A practical consequence of this is that the mass spectra of, for example, monoolefins with the double bond in different positions are generally very similar,[55a] and the implications of this for the structural determination of these

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(44) B. Steiner, G. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961).

(45) C. Ottinger, *J. Chem. Phys.*, **47**, 1452 (1967).

(46) F. E. Condon, H. L. McMurray, and L. V. Thornton, *J. Chem. Phys.*, **19**, 1010 (1951).

(47) G. A. Muccini, W. H. Hamill, and R. Barker, *J. Phys. Chem.*, **68**, 261 (1064).

(48) D. O. Schissler, S. O. Thompson, and J. Turkevich, *Discuss. Faraday Soc.*, **10**, 46 (1951).

(49) J. H. Futrell and T. O. Tiernan, *J. Chem. Phys.*, **39**, 2539 (1963).

(50) C. Lifshitz and M. Shapiro, *J. Chem. Phys.*, **45**, 4242 (1966).

(51) D. P. Stevenson and J. A. Hipple, *J. Amer. Chem. Soc.*, **64**, 2769 (1942).

(52) T. Tsuchiya, *J. Chem. Phys.*, **36**, 568 (1962).

(53) D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **18**, 11 (1950).

(54) (a) M. L. Gross, *J. Amer. Chem. Soc.*, **93**, 253 (1971); (b) D. J. McAdoo, F. W. McLafferty, and P. F. Bente, III, *ibid.*, **94**, 2027 (1972); (c) S. G. Lias, R. E. Rebbert, and P. Ausloos, *ibid.*, **92**, 6430 (1970); (d) L. Radom, J. A. Pope, V. Buss, and P. v. R. Schleyer, *ibid.*, **93**, 1813 (1971).

(55) E. J. Kuchar in "The Chemistry of Alkenes," J. Zabicky and S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1970, p 312.

(55a) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier, Amsterdam, 1960, pp 262-263.

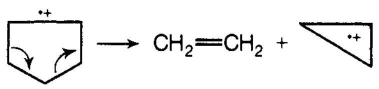
compounds have been discussed.[56] Even the simplest alkene, ethylene, appears to scramble its hydrogens prior to fragmentation, as indicated by the fact that *cis*- and *trans*-1,2-dideuterioethylenes give identical spectra.[57]

The major documented hydrogen rearrangements undergone by unsaturated aliphatic hydrocarbons are summarized in Table II. The simpler olefins, propene through pentene, have been studied the most thoroughly, and we shall confine ourselves to a detailed discussion of their spectra.

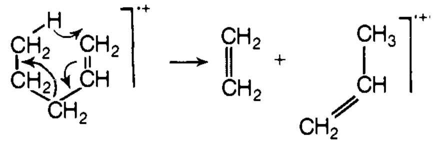
Propene loses a hydrogen atom to give the ion $C_3H_5^+$, and a methyl group to yield $C_2H_3^+$. The formation of these ions has been studied using deuterium-labeled compounds,[58,59] but the results and more particularly the interpretation of these results differ. From a study of the spectra of $CD_3CH{=}CH_2$, $CH_3CD{=}CH_2$, and $CH_3CH{=}CD_2$, McFadden concluded that the $C_3H_5^+$ ion was formed by loss of hydrogen from the two terminal positions, with little loss from the central carbon atom. The occurrence of relatively rapid 1,3 shifts and slower 1,2 shifts was thus proposed. Smith and his coworkers, however, concluded from their study of $CH_2DCH{=}CH_2$, $CH_3CD{=}CH_2$, and $CH_3CH{=}CHD$ that complete hydrogen randomization preceded formation of the $C_3H_5^+$ ion. A similar discrepancy appears in the analysis of hydrogen rearrangement preceding loss of methyl; according to McFadden, about 20% of the molecular ions of $CH_3CD{=}CH_2$ show D transfer to the CH_3 fragment lost,[58] while Smith claims 55% equilibration.[59] These differences may be explained by isotope effects of unknown size, and the use of different experimental conditions,[56] but an alternative explanation has been advanced.[60] Using McFadden's original data, these authors interpret the composition of the ions formed by loss of a methyl group from $CD_3CH{=}CH_2$ in terms of a mechanism involving rapid 1,2 shifts, rather than rapid 1,3 shifts. The discrepancy between this mechanism and McFadden's results on the formation of the allyl ion may again be explained by the unknown size of the primary isotope effect on the formation of this ion. Labeling with ^{13}C also appears to indicate that cleavage and isomerization are competitive and of similar rates for the loss of methyl.[61]

Hydrogen rearrangements occur extensively in the isomeric butenes. Thus four isomers of butene show the same metastable transitions, suggesting isomerization to a common structure(s) prior to fragmentation. Hydrogen migration is required to explain the loss of C_2H_4 from isobutylene.[62,63]

Thermochemical studies of the formation of $C_3H_5^+$ and $C_2H_4\cdot^+$ from the isomeric butenes, methylcyclopropane and cyclobutane, suggest that the isomers essentially lose their identities before fragmentation, confirming the conclusion drawn from metastable transitions. Any differences in 70-eV spectra can be explained as being the result of shifts in internal energy distribution caused by the inequality of heats of formation of molecular ions in their ground states.[64] Rearrangements in the formation of the $C_3H_5^+$ ion from 1- and 2-butenes have been studied by both deuterium[60,65a] and ^{13}C labeling.[65a] The formation of ions due to the loss of $CHD_2\cdot$ from $DCH_2CH{=}CHCH_2D$ showed that 1,3 shifts cannot be the sole mechanism of rearrangement in this compound, since such shifts could never place both deuterium atoms on the same carbon.[60] This result supports earlier studies on $CD_3CH_2CH{=}CH_2$, which gave essentially random retention of deuterium in the $C_3(H,D)_5^+$ ion, again excluding a pure 1,3-shift mechanism.[65a] Studies with $^{13}CH_3CH_2CH{=}CH_2$ showed that the labeled carbon is retained in 75% of the $C_3H_5^+$ ions, indicating complete randomization of carbon atoms prior to or during formation of this ion.[65b] This result, together with earlier work by Rylander and Meyerson,[66] suggests that the butenes fragment *via* the methylcyclopropane cation as the intermediate responsible for skeletal and much of the hydrogen randomization. This explanation avoids the need to postulate an unattractive series of 1,2 hydrogen atom or hydride shifts. However, other workers dispute the significance of ring formation in mass spectral fragmentations, basing their evidence on label scrambling in cyclopentane.[60] They argued that if formation of the cyclopropane ion were a favorable process, then the loss of ethylene from cyclopentane should occur as shown below without label scrambling (a separate experiment indicated that label scrambling in trideuterio-*n*-pentane is insignificant). In fact, label scrambling in 1,1-dideuteriocyclopentane was observed, leading these authors to conclude that the loss of ethylene occurs at least in part from open-chain radical ions. While this evidence does not disprove the existence of some fragmentation *via* the cyclopropane ion, the question of the exact nature of the intermediate in this and similar fragmentations is still open.



Hydrogen rearrangement in pentene has also been studied by deuterium labeling.[60] The ion formed by loss of ethylene from 1-pentene was originally predicted to arise by a McLafferty rearrangement (eq 14).[67] However, analysis of the spectra of variously labeled 1-pentenes showed that neither a simple six- nor a four-membered transition state could account for the observed data; instead, ethylene is lost primarily from the terminal double bond plus a fourth hydrogen from position 3, 4, or 5, in that order.[60] A scheme involving a series of 1,2 shifts of hydrogen was invoked to explain this result, but rearrangement *via* the ethylcyclopropane cation could also explain it. Similarly, the loss of methyl from 1-pentene is preceded or accompanied by hydrogen rearrangement; thus, for example, 22% of the deuterium atoms in $CH{=}CHCHDCH_2CH_3$ are lost as methyl in the formation of the ion $C_4H_7^+$. The loss of ethyl from the saturated



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[56] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 1.

[57] E. I. Quinn and F. L. Mohler, *J. Res. Nat. Bur. Stand., Sect. A*, **65**, 93 (1961).

[58] W. H. McFadden, *J. Phys. Chem.*, **67**, 1074 (1963).

[59] S. R. Smith, R. Schor, and W. P. Norris, *J. Phys. Chem.*, **69**, 1615 (1965).

[60] B. J. Millard and D. F. Shaw, *J. Chem. Soc. B*, 664 (1966).

[61] H. H. Voge, C. D. Wagner, and D. P. Stevenson, *J. Catal.*, **2**, 58 (1963).

[62] L. D'Or, J. Lorquet, and J. Momigny, *Ann. Soc. Sci. Bruxelles*, **71**, 53 (1957).

[63] J. C. Lorquet, *Bull. Soc. Roy. Sci. Liege*, **27**, 161 (1958).

[64] G. G. Meisels, J. Y. Park, and B. G. Giessner, *J. Amer. Chem. Soc.*, **92**, 254 (1970).

[65] (a) W. A. Bryce and P. Kebarle, *Can. J. Chem.*, **34**, 1249 (1956); (b) G. G. Meisels, J. Y. Park, and B. G. Giessner, *J. Amer. Chem. Soc.*, **91**, 1555 (1969).

[66] P. N. Rylander and S. Meyerson, *J. Amer. Chem. Soc.*, **78**, 5799 (1956).

[67] F. W. McLafferty, *Anal. Chem.*, **31**, 2072 (1959).

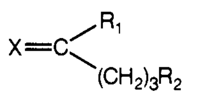
TABLE II. Hydrogen Rearrangements in the Mass Spectra of Unsaturated Aliphatic Hydrocarbons[a]

Hydrocarbon	Fragment ion(s) formed by rearrangement	Comment	Ref
$CH_2{=}CH_2$	CH_3^+, $H_2^{\cdot+}$	D, R	32, 57
$CH_3CH{=}CH_2$	$C_3H_5^+$ (M − H)	D, HS	58, 59
	$C_2H_3^+$ (M − CH_3)	D, HS	58, 59, 61
$CH_3CH_2CH{=}CH_2$	$C_3H_5^+$ (M − CH_3)	HR, SR	65, 66
$CH_3C(CH_3){=}CH_2$	$C_2H_4^{\cdot+}$	I	63
C_4H_8 isomers	$C_3H_5^+$, $C_2H_4^{\cdot+}$	M, R, E	62, 64
$CH_3CH_2CH_2CH{=}CH_2$	$C_3H_6^{\cdot+}$ (M − C_2H_4)	I, D, HR	60
		I, F	69
	$C_4H_7^+$, $C_3H_5^+$	HS	60
$(CH_3)_3CCH{=}CHC(CH_3)_3$	$C_6H_{10}^{\cdot+}$, etc.	R	*b*
$CH_3C{\equiv}CH$	$C_3H_3^+$ (M − H)	HS, IS	70–73
$RC{\equiv}CH$	Secondary alkyl ions	HR	75
	$C_3H_3^+$	F, HR	74
$CH_2{=}CHCH{=}CH_2$	$C_3H_3^+$, $C_2H_4^{\cdot+}$, CH_3^+	HS	78–82
$RCH{=}C{=}CHCH_3$	$C_5H_8^{\cdot+}$	I	*c*
$RCH{=}C{=}CHC_2H_5$	$C_5H_7^+$	I	*c*
$RC{\equiv}CCH{=}CH_2$	$C_3H_3^+$	I	*d*
Polyacetylenes		HR	76, 77
Linear and branched-chain trienes and tetraenes	Various		*e*

[a] See footnotes *a* and *b*, Table I. [b] P. Natalis and J. L. Franklin, *Bull. Soc. Chim. Belg.*, **75**, 328 (1966). [c] A. A. Polyakova, K. I. Zimina, A. A. Petrov, and R. A. Khmel'nitskii, *Zh. Obshch. Khim.*, **30**, 2977 (1960). [d] A. A. Polyakova, K. I. Zimina, A. A. Petrov, and R. A. Khmel'nitskii, *ibid.*, **30**, 912 (1960). [e] V. I. Khvostenko, V. P. Yur'ev, I. Kh. Aminev, G. A. Tolstikov, and S. R. Rafikov, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **202**, 861 (1972).

end of 1-pentene also involved hydrogen rearrangement. Since this cleavage yields the stabilized allyl cation, it would be expected to occur more readily, and this can explain the observation that cleavage is competitive with hydrogen exchange.[60]

The McLafferty rearrangement and other hydrogen rearrangements have been studied in some 1,1-dialkyl-substituted alkenes of general structure **1a–d.**[68] The results of these studies differ somewhat. Kraft and Spiteller state that the McLafferty rearrangement is site-specific, with no isomerization preceding rearrangement.[68b] Mayer and Djerassi, on the other hand, state that isomerization *does* take place before the McLafferty rearrangement, even under mild ionization conditions.[68a] Hydrogen rearrangement does certainly precede other fragmentations of these olefins; thus, for example, **1b** (R_1 = CH_3, R_2 = C_2H_5) loses $\cdot CH_2D$ and $\cdot CHD_2$ as well as the expected $\cdot CH_3$ from the molecular ion.[68a]



1a, X = CH_2
b, X = CD_2
c, X = CHR
d, X = CR_2

Hydrogen rearrangements also occur in the field ion spectra of alkenes. Thus ethylene is lost from the molecular ions of 1-pentene and other terminal olefins,[69] a process which must involve hydrogen rearrangement.

Hydrogen rearrangements occur extensively in the electron-impact induced spectra of alkynes. Thus the hydrogens of propyne are essentially completely scrambled prior to formation of $C_3H_3^+$.[70,71] The structure of the ion from propyne and other sources[70–72] is the same and has been suggested to be propargyl[70–72] or cyclopropenyl.[73] A $C_3H_3^+$ ion is also formed in the field ion spectra of pentyne and other alkynes, and it has been proposed that this ion may be the cyclopropenyl ion and thus require a rearrangement in its formation.[74] In larger 1-alkynes, deuterium rearrangement on electron impact does not occur prior to the formation of alkyl ions generated by *β* cleavage[75] (eq 15). The formation of ions of general formula C_nH_{2n-3} (starting with the M − 1 species) does involve considerable hydrogen scrambling, however, and studies at different ionizing energies indicate that several competing paths may lead to a given ion. The spectra of polyacetylenes may be explained by hydrogen migration along the chain.[76]

$$RCH_2C{\equiv}CH^{\cdot+} \longrightarrow R^+ + \cdot C_3H_5 \qquad (15)$$

Two recent papers discuss the mass spectra of various simple alkynes in some detail.[77] Interested readers are referred to these papers for a full discussion of the fragmentations of the class of compounds, but it should be noted that some hydrogen rearrangement occurs prior to the formation of some fragments, while hydrogen scrambling is extensive in the ions which arise by multiple fragmentation pathways. Hydrogen rearrangement occurs of course also in such fragmentations as the McLafferty

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(68) (a) K. K. Mayer and C. Djerassi, *Org. Mass Spectrom.*, **5**, 817 (1971); (b) M. Kraft and G. Spiteller, *ibid.*, **2**, 865 (1969).

(69) H. D. Beckey and P. Schulze, *Z. Naturforsch. A*, **20**, 1335 (1965).

(70) F. H. Coats and R. C. Anderson, *J. Amer. Chem. Soc.*, **79**, 1340 (1957).

(71) J. Collin and F. P. Lossing, *J. Amer. Chem. Soc.*, **80**, 1568 (1958).

(72) J. Collin and F. P. Lossing, *J. Amer. Chem. Soc.*, **79**, 5848 (1957).

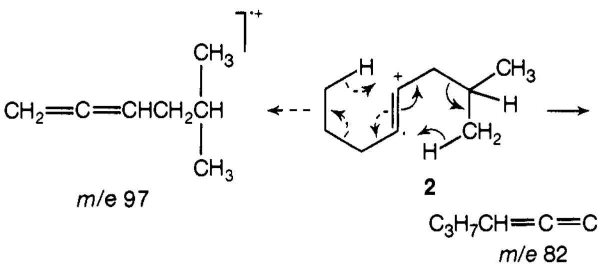
(73) F. W. McLafferty in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, p 93.

(74) B. C. Patterson and M. Seakins, *Trans. Faraday Soc.*, **63**, 1863 (1967).

(75) Z. Dolejšek, V. Hanuš, and K. Vokacc, *Advan. Mass Spectrom.*, **3**, 503 (1966).

(76) (a) E. J. McWhorter and M. Anchel, *J. Org. Chem.*, **30**, 2359 (1965); (b) R. T. Aplin and S. Safe, *Chem. Commun.*, 140 (1967); (c) F. Bohlmann and H. Bethke, *Chem. Ber.*, **104**, 11 (1971), and preceding papers.

(77) (a) H. Luftmann and G. Spiteller, *Org. Mass. Spectrom.*, **5**, 1073 (1971); (b) P. D. Woodgate, K. K. Mayer, and C. Djerassi, *J. Amer. Chem. Soc.*, **94**, 3115 (1972).



rearrangement, which becomes important in branched-chain alkynes such as **2**. Hydrogen scrambling appears not to precede this rearrangement, as shown by the fragmentations indicated for **2**.[77b]

As would be expected from the preceding discussion, aliphatic dienes also undergo extensive hydrogen rearrangement. Thus 1,3-butadiene loses a methyl group (a process which in itself requires hydrogen rearrangement) with complete scrambling of hydrogens either preceding or accompanying this fragmentation.[78,79] This result has been explained by proposing that isomerization to 1,2-butadiene takes place prior to fragmentation.[79] Other ions formed in the spectrum of 1,3-butadiene which require hydrogen transfer are $C_2H_4\cdot^+$ [80] and CH_3^+,[81] whose appearance potentials have been examined; the latter is formed with excess kinetic energy.

In summary, it is clear that hydrogen rearrangements do indeed occur widely in the mass spectra of unsaturated acyclic hydrocarbons. Hydrogen scrambling in the molecular ion appears to be complete or very nearly so prior to the higher energy decompositions involving bond cleavage. On the other hand, scrambling does not occur extensively prior to the formation of ions by a rearrangement pathway, which would have a lower energy of activation, although multiple pathways of rearrangement are common in this situation.

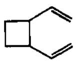
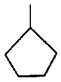
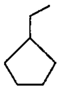
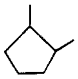
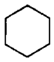
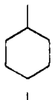
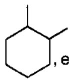
D. Rearrangements in Saturated Alicyclic Hydrocarbons

With the background of the preceding sections on rearrangements in alkanes and alkenes, it should come as no surprise to find that alicyclic hydrocarbons also undergo extensive hydrogen rearrangement. Table III lists the major documented rearrangements undergone by these hydrocarbons.

The structure of the $C_3H_6\cdot^+$ ion generated from cyclopropane has been studied by ion cyclotron resonance spectroscopy.[82] In principle this ion would have the structure of ionized propane, formed with hydrogen rearrangement, or a cyclic structure with three equivalent carbon atoms. Other structures such as the trimethylene radical cation are also possible. The icr results indicated not only that the $C_3H_6\cdot^+$ ion generated from cyclopropane has a different reactivity toward ammonia than the ion from propene,[82a] but also that the three carbon atoms of the former ion are equivalent,[82b] supporting its formulation as a cyclic ion. Thus hydrogen rearrangement does *not* occur in this particular reaction.

The major fragmentation reactions of the simple saturated monocyclic hydrocarbons include the loss of any alkyl substituent present and the loss of ethylene. In addition, unsubstituted cyclic hydrocarbons such as cyclohexane show loss of alkyl groups, a process which must involve hydrogen rearrangement.

TABLE III. Hydrogen Rearrangements in Cycloalkanes[a]

Cycloalkane	Fragment ion formed by rearrangement		Comment	Ref
	CH_3^+	$(M - C_2H_3)^+$	I	*b, c*
	$C_3H_5^+$	$(M - H)^+$	E	86
	$C_2H_5^+$	$(M - C_2H_3)^+$	I	*d*
	$C_4H_7^+$	$(M - H)^+$	E	*e*, 86
	CH_3^+		D, HS	*e*
	$C_7H_9^+$	$(M - CH_3)^+$	I	*f–h*
	$C_4H_7^+$	$(M - CH_3)^+$	D, HS	*i*, 60
	$C_3H_6\cdot^+$	$(M - C_2H_4)\cdot^+$	D, HS	60
	$C_5H_9^+$	$(M - CH_3)^+$	D, C, E	83–87
	$C_4H_8\cdot^+$	$(M - C_2H_4)\cdot^+$	D, C, E	83–87
	$C_5H_9^+$	$(M - C_2H_5)^+$	D	84
			I	*j, k*
	$C_5H_9^+$	$(M - CH_3)^+$	I	84
	$C_4H_8\cdot^+$	$(M - C_2H_4)^+$	D	84
	$C_5H_{10}\cdot^+$	$(M - C_2H_4)\cdot^+$	D	84
	C_6H_{10}	$(M - CH_4)\cdot^+$		84
, etc.	CH_4^+, $C_2H_5^+$, $C_3H_7^+$		I, E	*l–o*

[a] See footnotes *a* and *b*, Table I. [b] F. H. Field, *J. Chem. Phys.*, **20**, 1734 (1952). [c] P. Natalis, *Bull. Soc. Roy. Sci. Liege*, **29**, 94 (1960). [d] P. Natalis and J. Laune, *Bull. Soc. Chim. Belg.*, **73**, 944 (1964). [e] J. Laune, *Ind. Chim. Belge*, **27**, 245 (1962). [f] E. F. H. Brittain, C. H. J. Wells, and H. M. Paisley, *J. Chem. Soc. B*, 503 (1969). [g] E. F. H. Brittain, C. H. J. Wells, and H. M. Paisley, *ibid.*, 304 (1968). [h] H. M. Paisley, E. F. H. Brittain, and C. H. J. Wells, *ibid.*, 185 (1969). [i] P. Natalis, *Bull. Soc. Roy. Sci. Liege*, **27**, 201 (1958). [j] P. Natalis, *Bull. Soc. Chim. Belg.*, **66**, 5 (1957). [k] J. Momigny and P. Natalis, *ibid.*, **66**, 26 (1957). [l] P. Natalis, *ibid.*, **72**, 416 (1963). [m] P. Natalis, *ibid.*, **75**, 668 (1966). [n] P. Natalis, *ibid.*, **69**, 519 (1960). [o] P. Natalis, *ibid.*, **73**, 961 (1964).

On the face of it, loss of the alkyl group from an alkylcycloalkane ought to be a simple process involving fracture at the ring to produce an alkyl radical and a cycloalkyl ion. However, as so often in mass spectrometry, the simple obvious explanation turns out to be only partially correct. Thus studies with methylcyclopentane-*CH*$_3$-^{13}C indicated that the label is retained in about half the $C_5H_9^+$ ions formed, suggesting that molecular ions which dissociate to $C_5H_9^+$ undergo ring opening and hydrogen rearrangement to hexene ions, which could then lose a methyl group from either end of the chain.[83] More detailed studies of the ions produced from both deuterium and ^{13}C-labeled methylcyclopentane indicated that the label retention in the $C_5H_9^+$ ions is actually nearer to 40%, suggesting that two pathways—one simple, one with rearrangement—operate in the loss of methyl from methylcyclopentane (eq 16).[84,85] The simple pathway A would lead to 100% loss of ^{13}C label, while the rearrangement pathway B would give 50% loss of the ^{13}C label (ignoring isotope effects). The combination of both

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(78) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, p 138.

(79) A. B. King, *J. Phys. Chem.*, **68**, 1409 (1964).

(80) J. L. Franklin and A. Mogenis, *J. Phys. Chem.*, **71**, 2820 (1967).

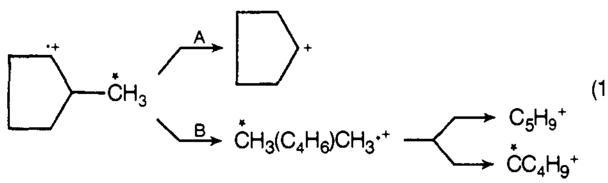
(81) (a) T. Tsuchiya, *Bull. Chem. Soc. Jap.*, **35**, 1221 (1962); (b) T. Tsuchiya, *Shitsuryo Bunseki*, 11, 100 (1963).

(82) (a) M. L. Gross and F. W. McLafferty, *J. Amer. Chem. Soc.*, **93**, 1267 (1971); (b) M. L. Gross, *ibid.*, **94**, 3744 (1972).

(83) D. P. Stevenson, *J. Amer. Chem. Soc.*, **80**, 1571 (1958).

(84) S. Meyerson, T. D. Nevitt, and P. N. Rylander, *Advan. Mass Spectrom.*, **2**, 313 (1963).

(85) S. Meyerson, *Appl. Spectrosc.*, **22**, 30 (1968).



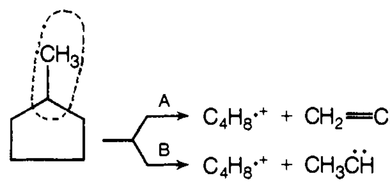
(16)

pathways could then lead to the observed 40% loss of label. The finding that label retention in the $C_5H_9^+$ ion is a function of ionizing voltage confirmed the operation of two pathways.[84,85] Further measurements involving changes in the ion repeller potential suggested that the difference between Stevenson's original work[83] and the later results[84] could be explained in large part by differences in the instrumental parameters used for the experiments.[85]

In contrast to methylcyclopentane, methylcyclohexane forms the $(M - CH_3)^+$ ion almost exclusively by a path analogous to A, that is, by loss of the original side chain.[84] This may be explained by the fact that ring strain is close to zero in methylcyclohexane. Evidence from heats of formation also supports the finding that ring opening occurs in methylcyclopentane but not in methylcyclohexane.[86,87] These results point out the sensitivity of mass spectra to subtle enthalpic and entropic effects corresponding to energies that are minute beside the energy of the impinging electrons.

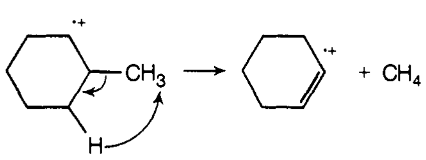
Loss of $CH_3\cdot$ from cyclohexane and other unsubstituted cycloalkanes, which is a moderately important process in these compounds, must involve hydrogen rearrangement. It presumably occurs by ring opening and hydrogen rearrangement to an alkene ion radical, followed by bond cleavage. In the case of cyclopentane, an analysis of the spectrum of 1,1-dideuteriocyclopentane suggested that some scrambling of hydrogens occurs (to the extent of about 25%) in ions decomposing to $C_4H_7^+$.[60] This scrambling occurs, of course, in addition to the hydrogen rearrangement necessitated by the reaction.

The loss of ethylene from cyclopentane has already been alluded to in the preceding section; labeling evidence suggests that ring opening with subsequent hydrogen rearrangement occurs prior to formation of the $M - C_2H_4$ ion.[60] Similar studies on cyclohexane have not been carried out, but it is likely that scrambling occurs in this case also. In the methylcycloalkanes the situation is more complex, with loss of C_2H_4 occurring largely from the ring in both methylcyclopentane[83,84] and methylcyclohexane.[84] In both cases some loss of C_2H_4 does involve the methyl group, however, and such loss must involve either hydrogen rearrangement (path A) or, improbably, the formation of an unstable carbene product (path B) (eq 17). Ethylcyclopentane loses C_2H_4 essentially completely from the ring, although loss of C_3H_6 from the side chain does occur, in analogy to C_2H_4 loss from the side chain of methylcyclopentane.



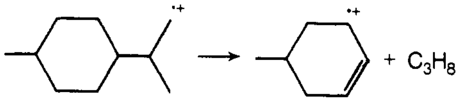
(17)

The alkyl cycloalkanes also show moderate peaks corresponding to loss of the side chain plus a hydrogen. The origin of the peripatetic hydrogen has not been established with certainty, and although the mechanism indicated in eq 18 was tentatively proposed[84] for this reaction, the verdict must be "not proven" in the absence of more detailed evidence.



(18)

Hydrogen rearrangements also occur freely in the decomposition of the more complex cycloalkanes represented by various terpenes, substituted decalins, and the steranes. Loss of C_3H_8 from menthane (eq 19) involving at least transfer of a hydrogen atom to the isopropyl group has been observed both in field ionization[88] and electron impact spectra.[89] Extensive hydrogen rearrangements must take place in the decomposition of the monoterpenes, since the spectra of isomeric compounds are similar,[90-93] but very little detailed study of these rearrangements has been done. Thus the spectra of the isomeric thujanes are similar,[94] and almost all terpenes have common metastables.[95] A labeling study with camphane-*8*-^{13}C indicates that specific processes are responsible for the C_8 and C_9 ions but that extensive rearrangements must take place for species with fewer carbon atoms; attempts were made to justify the distribution of ^{13}C found by suggesting structures for intermediates.[96] A common loss from bicyclic monoterpenes is C_3H_7, even when the closest structural unit is the isopropylidene bridge.[89-93,97] In the bicycloalkane series, loss of alkyl groups from the decalins,[98] methyldecalins,[99] and hexahydroindans[100] requires hydrogen migration before fragmentation, as does loss of certain alkyl fragments or alkane molecules from alkylspiropentanes.[101] These rearrangements correspond to the simpler loss of alkyl groups from cycloalkanes and alkyl + H fragments from alkylcycloalkanes discussed earlier.



(19)

Among the polycyclic hydrocarbons, rearrangements in steranes are general.[91] The definitive papers on the fragmentation of cholestane,[102,103] summarizing the results of a heroic investigation involving the synthesis of molecules labeled with deuterium in virtually all the carbon atoms, indicated that hydrogen rearrangements occur frequently and unpredictably in the spectra of these com-

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(86) R. F. Pottie, A. G. Harrison, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 3204 (1961).

(87) M.-T. Praet, *Org. Mass Spectrom.*, **4**, 65 (1970).

(88) H. D. Beckey and H. Hey, *Org. Mass Spectrom.*, **1**, 47 (1968).

(89) G. von Bünau, G. Schade, and K. Gollnick, *Z. Anal. Chem.*, **244**, 7 (1969).

(90) T. Gilchrist and R. I. Reed, *Experientia*, **16**, 134 (1960).

(91) R. I. Reed, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 637.

(92) R. Ryhage and E. von Sydow, *Acta Chem Scand.*, **17**, 2025 (1963).

(93) Yu. Ya. Efremov, *Dokl. Akad. Nauk SSSR*, **170**, 597 (1966).

(94) G. Ohloff, G. Uhde, A. F. Thomas, and E. Kovats, *Tetrahedron*, **22**, 309 (1966).

(95) H. C. Hill, R. I, Reed, and M. T. Robert-Lopes, *J. Chem. Soc. C*, 93 (1968).

(96) L. Friedman and A. P. Wolf, *J. Amer. Chem. Soc.*, **80**, 2424 (1958).

(97) A. F. Thomas and B. Willhalm, *Helv. Chim. Acta*, **47**, 475 (1964).

(98) P. Natalis, *Bull. Soc. Chim. Belg.*, **72**, 264 (1963).

(99) S. Meyerson and A. W. Weitkamp, *Org. Mass. Spectrom.*, **2**, 603 (1969).

(100) P. Natalis, *Bull. Soc. Chim. Belg.*, **72**, 374 (1963).

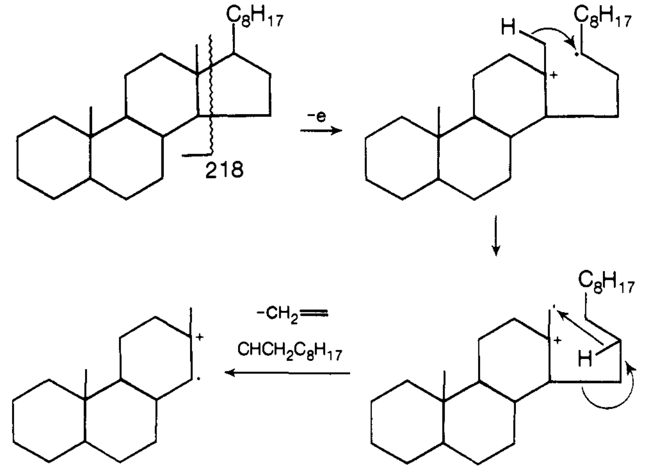
(101) P. Battioni, L. Vo-Quang, and Y. Vo-Quang, *Bull. Soc. Chim. Fr.*, 3942 (1970).

(102) L. Tökes, G. Jones, and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 5465 (1968).

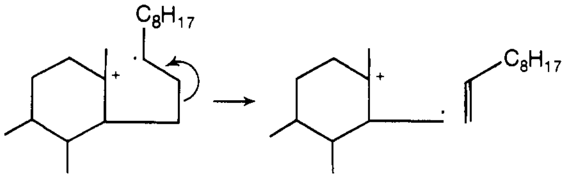
(103) C. Djerassi, *Advan. Mass Spectrom.*, **4**, 199 (1968).

pounds. The characteristic ring D fragmentation of steroids, for example, which yields ions at *m/e* 218 and *m/e* 217, involves hydrogen rearrangement. Fragmentation to yield the *m/e* 218 ion, far from being the simple cleavage it might appear to be, actually involves a double hydrogen rearrangement, as indicated in Scheme II.

SCHEME II



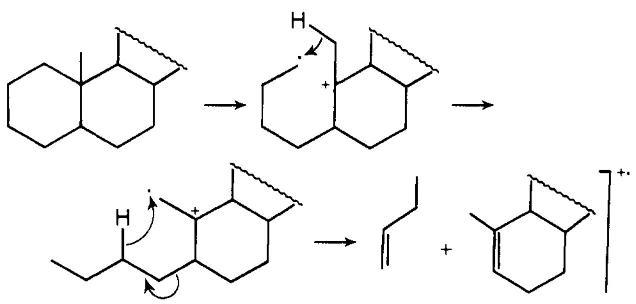
On the other hand, formation of the ion of mass 232 in the spectrum of cholestane proceeds by simple cleavage of ring D (eq 20), while loss of a methyl radical occurs exclusively by expulsion of one of the angular methyl functions rather than loss of a ring methylene group with associated hydrogen migration.



(20)

Sometimes apparently small changes can make a large difference in the reaction pathways observed. Thus androstane does not give intense characteristic ions at *m/e* 217 and 218 on fragmentation, but does give an intense ion at *m/e* 203, which was shown to arise *via* the double hydrogen rearrangement indicated (Scheme III).[104a]

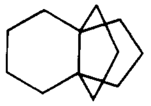
SCHEME III



This paper reports in detail the results of a complete investigation of the fragmentation of androstane labeled with deuterium in various positions. A recent paper[104b] discusses the spectra of *D*-homoandrostane and *D*-homopregnane and shows that the characteristic ring D and ring A cleavages in these compounds are completely analogous to those observed in androstane and pregnane. In contrast, the mass spectral behavior of the D-nor compounds is significantly different from that of the parent compounds. The very abundant *m/e* 218 ion, for example, is produced without the reciprocal hydrogen transfer observed in the normal and homo series (Scheme II).

A study of metastable peaks in the spectrum of cholestane indicated that those ions which had more than one mode of formation, as indicated by the metastable peaks, were exactly those with the most complex labeling patterns.[105] Thus the complex labeling patterns observed could result in part from multiple pathways, as well as from hydrogen transfers within the steroid skeleton. In spite of this evidence, however, there are enough cases on record where hydrogen rearrangement in the steranes is unambiguous to leave no doubt that such rearrangements do occur commonly in these compounds.

Hydrogen rearrangements have been shown to occur also in various pentacyclic triterpenes;[106] in addition to the earlier references cited in this paper, other citations of hydrogen rearrangements, without labeling, in di-[107] and triterpenes[108,109] are available. Hydrogen migrations have also been postulated to explain fragment peaks in propellanes (**3**a),[110] while the loss of a methyl radical on photoionization of tricyclo[3.2.1.0^{2,4}]octane (**3b**) demands hydrogen rearrangement.[111]



3a

3b

In summary, hydrogen rearrangements in cycloalkanes are common and are associated primarily with fragmentations involving the cleavage of the ring. Most rearrangements are relatively nonspecific, but a few specific rearrangements do occur in more complex compounds such as the steranes.

E. Rearrangements in Unsaturated Alicyclic Hydrocarbons

The observation of hydrogen rearrangements in the fragmentation of both alkenes and cycloalkanes implies that they will occur *a fortiori* in the fragmentation of cycloalkenes and other unsaturated alicyclic hydrocarbons. Such proves to be the case, and these rearrangements are summarized in Table IV. Of particular significance to structural elucidation is the observation that frequently the spectra of isomeric hydrocarbons, and particularly isomeric unsaturated alicyclic hydrocarbons, are identical or nearly so. Thus the formation of $C_3H_3^+$ from cyclopropene, allene, and methylacetylene with essentially identical heats of formation requires identical structures for the ion from all three (propargyl or cyclopropenyl), unless there are several structures whose heat of formation is accidentally the same.[112] Similarly, the spectra of several isomeric C_5H_8[113] and C_7H_{10}[114] hydrocarbons are very similar, suggesting isomerization to common structures

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(104a) L. Tökes and C. Djerassi, *J. Amer. Chem. Soc.*, **91**, 5017 (1969); (b) G. Eadon, S. Popov, and C. Djerassi, *ibid.*, **94**, 1282 (1972).

(105) C. C. Fenselau and F. P. Abramson, *Org. Mass Spectrom.*, **2**, 915 (1969).

(106) J. Karliner and C. Djerassi, *J. Org. Chem.*, **31**, 1945 (1966).

(107) H. E. Audier, S. Bory, G. Defaye, M. Fétizon, and G. Moreau, *Bull. Soc. Chim. Fr.*, 3181 (1966).

(108) K. Persaud, *Advan. Mass Spectrom.*, **4**, 171 (1968).

(109) J. P. Kutney, G. Eigendorf, and I. H. Rogers, *Tetrahedron*, **25**, 3753 (1969).

(110) J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron Suppl.*, **8**, 279 (1966).

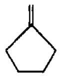
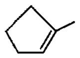
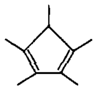
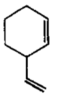
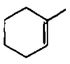
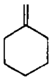
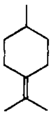
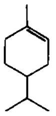
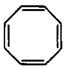
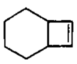
(111) C. E. Brion, J. S. Haywood Farmer, R. E. Pincock, and W. E. Stewart, *Org. Mass Spectrom.*, **4**, 587 (1970).

(112) K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *J. Amer. Chem. Soc.*, **84**, 3980 (1962).

(113) F. L. Mohler, E. G. Bloom, L. Williamson, C. E. Wise, and E. J. Wells, *J. Res. Nat. Bur. Stand.*, **43**, 533 (1949).

(114) Reference 56, p 65.

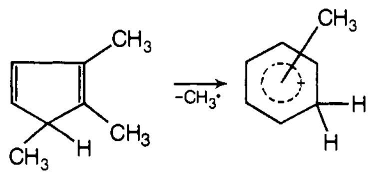
TABLE IV. Hydrogen Rearrangements in Cycloalkenes and Related Compounds[a]

Cycloalkene	Fragment ion formed by rearrangement		Comment	Ref
	$C_3H_3^+$	$(M - H)^+$	E	112
			E, I	87
			M, R, E, I	87, 119
	$C_nH_{2n-5}^+$		R	118
			M, R	119
	$C_7H_9^+$	$(M - CH_3)$	I	*b–d*
	$C_5H_7^+$	$(M - C_2H_5)^+$	I, D	122
	C_6H_9	$(M - CH_3)^+$	I, D	122
	$C_6H_7^+$	$(M - H)$	D, H	*e–g*
	$C_7H_{11}^+$	$(M - C_3H_7)^+$	D	97, 123–124
	$C_7H_{10}\cdot^+ + C_3H_8$		I	89
			E	*h, i*
	C_7H_9	$(M - CH_3)$	I	*j*
Methyl esters of communic acid isomers			I	*k*
Spiro olefins				*l*
Bicyclic alkenes				*m*

[a] See footnotes *a* and *b*, Table I. [b] E. F. H. Brittain, C. H. J. Wells, and H. M. Paisley, *J. Chem. Soc. B*, 503 (1969). [c] E. F. H. Brittain, C. H. J. Wells, and H. M. Paisley, *ibid.*, 304 (1968). [d] H. M. Paisley, E. F. H. Brittain, and C. H. J. Wells, *ibid.*, 185 (1969). [e] M. I. Gorfinkel' and V. A. Koptyug, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 109 (1967). [f] M. I. Gorfinkel', T. P. Sosedkina, and V. A. Koptyug, *Zh. Obshch. Khim.*, **37**, 1448 (1967). [g] J. L. Franklin and S. R. Carroll, *J. Amer. Chem. Soc.*, **91**, 6564 (1969). [h] S. Meyerson, *ibid.*, **85**, 3340 (1963). [i] J. L. Franklin and S. R. Carroll, *ibid.*, **91**, 5940 (1969). [j] S. F. Chappell and R. F. Clark, *Chem. Ind. (London)*, 1198 (1962). [k] P. W. Atkinson and W. D. Crow, *Tetrahedron*, **26**, 1935 (1970). [l] G. D. Christiansen and D. A. Lightner, *J. Org. Chem.*, **36**, 948 (1971). [m] C. M. Cimarusti and J. Wolinsky, *ibid.*, **36**, 1871 (1971).

prior to or during fragmentation. Such isomerizations, of course, must be accompanied by one or more hydrogen rearrangements. A study of the mass spectra of isomers has been initiated,[115-117] and these papers dealing with fragmentation of various cyclic alkenes and alkanes indicate a large measure of isomerization prior to decomposition. Unfortunately deuterium labeling was not carried out on these isomers, and thus the mechanisms proposed for their fragmentation must be regarded as only tentative.

Methyl-substituted cyclopentadienes fragment with only a small indication of positional isomerism in their spectra; the formation of $C_nH_{2n-5}^+$ proceeds with rearrangement to form a more stable ion, and the spectra of these compounds are similar to those of the isomeric cyclohexadienes.[118] It was concluded that the major fragment ions from the methylcyclopentadienes do not retain the cyclopentadienyl structure but undergo rearrangement, probably to form a cyclic benzenium-type ion (eq 21).



(21)

Compounds may fragment through common intermediates even when their mass spectra differ substantially.

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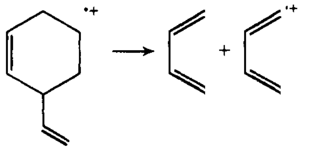
(115) E. F. H. Brittain, C. H. J. Wells, and H. M. Paisley, *J. Chem. Soc. B*, 304 (1968).

(116) E. F. H. Brittain, C. H. J. Wells, and H. M. Paisley, *J. Chem. Soc. B*, 185 (1969).

(117) E. F. H. Brittain, C. H. J. Wells, and H. M. Paisley, *J. Chem. Soc. B*, 503 (1969).

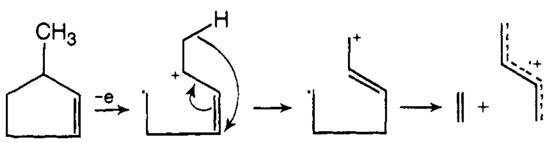
(118) A. G. Harrison, P. Haynes, S. McLean, and F. Meyer, *J. Amer. Chem. Soc.*, **87**, 5099 (1965).

Thus several C_6H_{10} isomers, including cyclohexene and two methylcyclopentenes, gave spectra with significant intensity differences in their major peaks. In spite of this, metastable transitions and appearance potential data indicated that fragmentation pathways are the same for all the molecules, thus implicating skeletal and/or hydrogen rearrangements in at least some of the decompositions.[119] In the particular case studied, rearrangement probably did not occur in the fragmentation of ionized cyclohexene to ionized butadiene (the retro-Diels–Alder reaction[120]) since label scrambling was not observed in the retro-Diels–Alder reaction of 4-vinylcyclohexene (eq 22).[121] Presumably the methylcyclopentenes and other compounds investigated isomerized to an intermediate which could decompose to give ionized butadiene and ethylene as fragmentation products. Scheme IV indicates one possibility for this in the case of 3-methylcyclopentene, although in the absence of deuterium labeling such a scheme is merely a rationalization of the observed products.



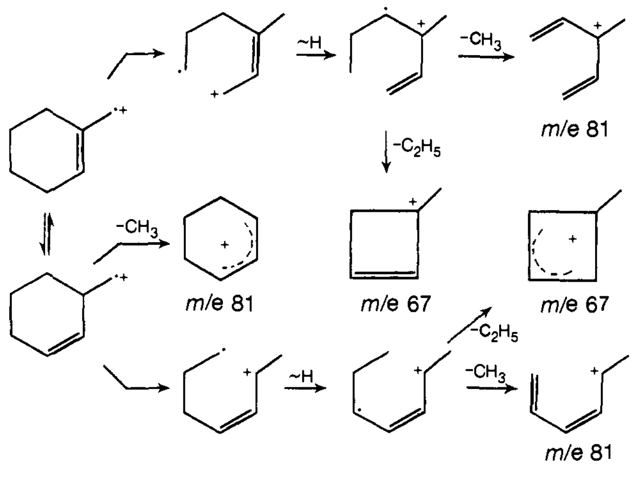
(22)

SCHEME IV



Deuterium labeling is available in the case of 1-methylcyclohexene.[122] The two most abundant ions in the spectrum (after the molecular ion) are the ions at *m*/*e* 81 (M − CH_3) and *m*/*e* 67 (M − C_2H_5), and the formation of both involves hydrogen rearrangement. Approximately 60% of the M − CH_3 ion is formed by direct loss of the substituent, but 40% is formed by a pathway involving hydrogen rearrangement. Similarly, loss of the ethyl group must involve hydrogen rearrangement, and two possible pathways were suggested on the basis of labeling results. These pathways are summarized in Scheme V, although other pathways undoubtedly contribute to the formation of the observed ions. The fragmentation of methylenecyclohexane was also studied in this work, and analysis of the spectrum of the 2,2,6,6-d_4 labeled compound indicated that hydrogen transfer to the exocyclic methylene group must occur before formation of the M − CH_3 ion.

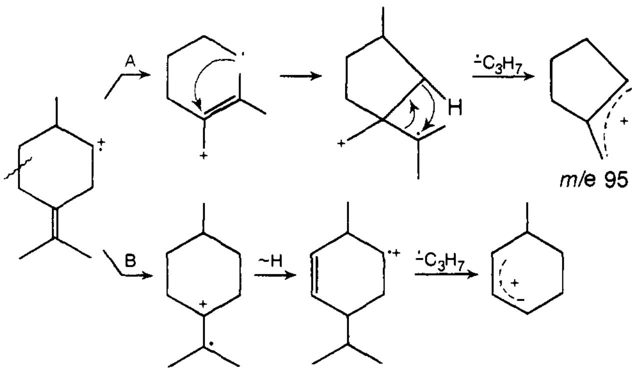
SCHEME V



Hydrogen rearrangements are common in the mass spectra of various terpene and steroid hydrocarbons, but relatively little deuterium labeling work has been done on these compounds and the occurrence of most rearrangements must be inferred from the nature of the product ions and by analogy to the spectra of simpler molecules.

The loss of C_3H_8 has been noted in menthenes and menthadienes and, of course, must involve a hydrogen rearrangement.[89] The loss of $C_3H_7\cdot$ from $\Delta^{4(8)}$-menthene has been ascribed to ring contraction[97] and hydrogen transfer[123] as preceding steps (paths A and B, Scheme VI). The hydrogen transfer mechanism was demonstrated as being more in concert with observations in deuterium-labeling studies.[123,124] This hydrocarbon apparently does not undergo extensive hydrogen scrambling before some of its fragmentations; specific transfer of some hydrogen atoms was observed as occurring through six-membered transition states.[124]

SCHEME VI



The spectra of some steroids with unsaturated side chains have been investigated by deuterium labeling, and the mechanism of an intriguing fragmentation involving loss of the entire C-17 substituent with rearrangement of two hydrogens was elucidated.[125] The mechanism proposed is shown in Scheme VII and involves a skeletal rearrangement as well as the double hydrogen rearrangement. The first of the two hydrogen atoms migrating to the side chain was shown to originate from the C-17 position as indicated, but the second hydrogen migrated from the C-12, C-14, or C-16 positions in the approximate ratios 7:2:5. Such rearrangement peaks remain at low voltage, and spectra from 13 to 15 eV ionizing voltage are therefore not interpretable in terms of simple cleavages, though the spectra are considerably less complicated and more useful as fingerprints for compounds.[126] Labeling studies have been carried out on one class of diterpenes—podocarpa-3,11,18-triene derivatives[127a]—and a study of the influence of double bond location in the spectra of diterpenes includes several postulations of hydrogen rearrangement as well.[127b] Labeling studies have also been carried out on some pentacyclic triterpenes.[106]

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(119) R. E. Winters and J. H. Collins, *Org. Mass Spectrom.*, **2**, 299 (1969).

(120) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1956).

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(122) T. H. Kinstle and R. E. Stark, *J. Org. Chem.*, **32**, 1318 (1967).

(123) D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

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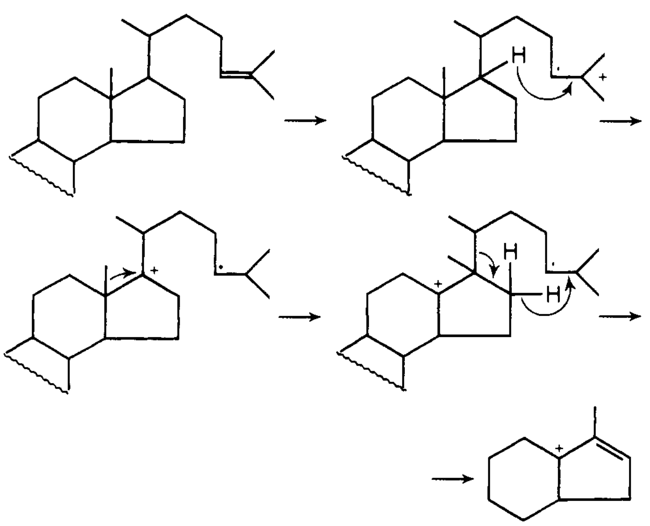
(126) K. Hirota and P. Nakane, *Tetrahedron Lett.*, 5909 (1968).

(127) (a) C. R. Enzell and R. Ryhage, *Ark. Kemi*, **26**, 425 (1967); (b) H. E. Audier, S. Bory, M. Fetizon, and M.-T. Anh, *Bull. Soc. Chim. Fr.*, 4002 (1966).

SCHEME VII



F. Rearrangements in Group IV Alkyls

The molecular ions of the group IV alkyls decompose initially by radical elimination, thereby producing even-electron ions (eq 23). In subsequent fragmentation pro-

$$R_4M + e \longrightarrow R_4M^{\cdot +} \longrightarrow R_3M^+ + R\cdot \qquad (23)$$

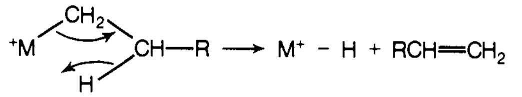
cesses the dominant feature is the tendency to form further even-electron ions, and thus loss of an alkene fragment with concomitant hydrogen rearrangement (eq 24)

$$R_3M^+ \longrightarrow R_2M^+H + \text{alkene} \qquad (24)$$

is a common reaction of these ions where possible. General features of the mass spectra of the group IV organometallics have been reviewed,[128,129] and this section will concentrate on hydrogen rearrangements accompanying the fragmentations of the group IV alkyls.

Mass spectra of group IV alkyls were obtained very early by Aston in his determination of isotopic compositions,[130] but detailed investigations of these compounds have only been carried out in recent years. Silane itself gives $SiH_2{\cdot}^{+}$[131] by loss of H_2 from the molecular ion as shown by thermochemical measurements.[132] Likewise the molecular ion of disilane loses H_2. The molecular ion of CH_3SiH_3 loses CH_4 by similar arguments,[133] and the negative ion forms Si^- by a loss of either $CH_4 + 2H$ or $H_2 + CH_3\cdot + H\cdot$.[133] These types of losses are found in the other methylsilanes as well,[134] and in addition to losses of methane from various fragments there are also losses of C_2H_4 from $Si(CH_3)_3{}^+$, $SiHCH_3{}^+$, $CH_3SiCH_2{}^+$, and $Si(CH_3)_2{\cdot}^{+}$.[131,134] Appearance potentials relating to some of these losses have been measured.[135] There is also a $C_2H_3{}^+$ ion in the spectrum of $HSi(CH_3)_3$, the formation of which must involve both skeletal and hydrogen rearrangement. The spectra of all the tetramethyl group IV compounds have been compared; a small peak in the spectrum of $(CH_3)_4Pb$ seems to correspond to loss of CH_2, which is quite uncommon otherwise.[136]

As already noted, alkene elimination is an important fragmentation process for all group IV metal alkyls, frequently giving strong metastable ions. It is a general reaction for even-electron ions containing the grouping RCH_2CH_2M and is probably a β-elimination process (eq 25). In the case of olefin elimination from R_3Si^+ cations,



$${}^{+}M{-}CH_2{-}CH(H){-}R \longrightarrow M^+ - H + RCH{=}CH_2 \qquad (25)$$

at least, deuterium labeling supports this formulation of the reaction as a site-specific 1,2 elimination.[137] Alkene elimination from odd-electron parent ions is rarely observed; on the mechanism suggested it would require a pentacoordinate transition state which is probably unfavorable compared with radical elimination.[128] Elimination of ethylene from ethylsilanes,[138] -germanes,[138b-141] -stannanes,[138b,141-144] and -plumbanes[138,142,145-147] has been observed including decomposition from the molecular ion.[142] It is seen also in reactions of doubly charged ions from $Ge_2(C_2H_5)_6$.[139] In addition to the four-center mechanism proposed, reaction *via* a five-center transition state has been invoked in special cases such as the loss of C_2H_4 from $(C_2H_5)_3SnSnH_2{}^+$.[142] Frequently losses of H_2 are also observed here from fragments.[138] Loss of higher alkenes from larger alkyl groups attached to group IV metals has also been observed (ref 139, 141, 143, 144, 146, 148–151). Sometimes the olefin lost contains fewer carbons than the alkyl group.[138,150] Lead alkyls, in particular, show abundant ions formed by rearrangement of alkyl groups, and in tetra-*n*-propyllead the $MePb^+$ ion is the most abundant in the spectrum. Occasionally the neutral lost from an R_nM^+ fragment is not an olefin but MH_2. This latter claim is substantiated by metastable peaks for Ge,[151] but for C the claim is not supported.[141]

Molecule elimination by cleavage of two M–X bonds with charge retention on the metal is a common reaction and is most favorable for the heavier metals. In some cases, as in eq 26,[138] this can involve a hydrogen rear-

$$C_2H_5Ge^+H_2 \longrightarrow C_2H_5Ge^+ + H_2 \qquad (26)$$

rangement. A similar type of fragmentation is sometimes observed from odd-electron ions (eq 27).

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(128) D. B. Chambers, F. Glockling, and J. R. C. Light, *Quart. Rev., Chem Soc.*, **22**, 317 (1968).

(129) M. I. Bruce in "Mass Spectrometry," Vol. I, The Chemical Society, London, 1971, p 189.

(130) F. W. Aston, "Mass Spectra and Isotopes," 2nd ed, Edward Arnold and Co., London, 1924.

(131) G. P. Van der Kelen, O. Volders, H. van Onckelen, and Z. Eeckhaut, *Z. Anorg. Allg. Chem.*, **338**, 106 (1965).

(132) P. Potzinger and F. W. Lampe, *J. Phys. Chem.*, **73**, 3912 (1969).

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(134) T. Tamás and K. Ujszászy, *Acta Chim. Acad. Sci. Hung.*, **56**, 125 (1968).

(135) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **66**, 155 (1962).

(136) V. H. Dibeler, *J. Res. Nat. Bur. Stand.*, **49**, 235 (1952).

(137) T. H. Kinstle, P. J. Ihrig, and E. J. Goeltert, *J. Amer. Chem. Soc.*, **92**, 1780 (1970).

(138) (a) N. Y. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, and V. M. Vdovin, *Zh. Obshch. Khim.*, **36**, 89 (1966); (b) J. J. de Ridder and G. Dijkstra, *Rec. Trav. Chim. Pays-Bas*, **86**, 737 (1967).

(139) F. Glockling and J. R. C. Light, *J. Chem. Soc. A*, 717 (1968).

(140) R. A. Khmel'nitskii, A. A. Polyakova, A. A. Petrov, F. A. Medvedev, and M. D. Stadnichuk, *Zh. Obshch. Khim.*, **35**, 773 (1965).

(141) D. B. Chambers, F. Glockling, J. R. C. Light, and M. Weston, *Chem. Commun.*, 281 (1966).

(142) D. B. Chambers, F. Glockling, and M. Weston, *J. Chem. Soc. A*, 1759 (1967).

(143) M. Gielen and G. Mayence, *J. Organometal. Chem.*, **12**, 363 (1968).

(144) S. Boue, M. Gielen, and J. Nasielski, *Bull. Soc. Chim. Belg.*, **77**, 43 (1968).

(145) V. H. Dibeler and F. L. Mohler, *J. Res. Nat. Bur. Stand.*, **47**, 337 (1951).

(146) E. I. Quinn, V. H. Dibeler, and F. L. Mohler, *J. Res. Nat. Bur. Stand.*, **57**, 41 (1956).

(147) M. R. Chate and K. N. Bhide, *Indian J. Chem.*, **2**, 243 (1964).

(148) I. L. Agafonov, V. I. Farman, Y. N. Tsinovoi, N. V. Larin, and V. A. Umilin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1289 (1968).

(149) J. L. Occolowitz, *Tetrahedron Lett.*, 5291 (1966).

(150) A. Carrick and F. Glockling, *J. Chem. Soc. A*, 623 (1966).

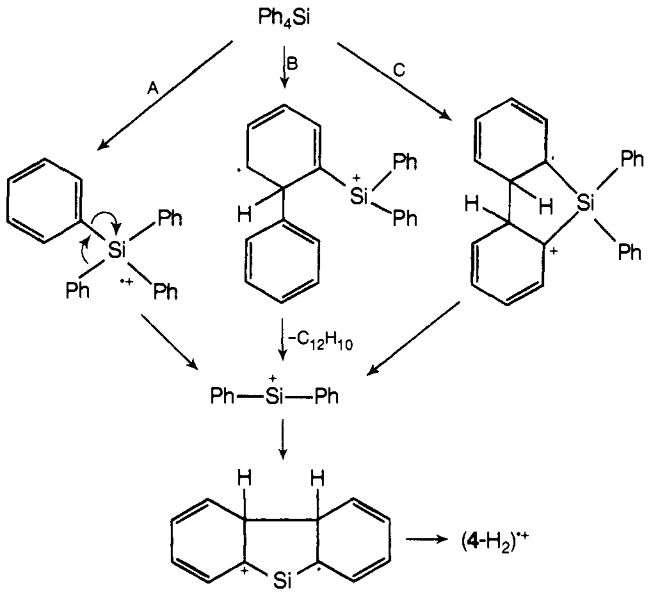
(151) J. J. de Ridder, G. van Koten, and G. Dijkstra, *Recl. Trav. Chim. Pays-Bas*, **86**, 1325 (1967).

$$Et_3GeH^{\cdot +} \longrightarrow Et_2Ge^{\cdot +} + C_2H_6 \qquad (27)$$

Phenyl-substituted group IV atoms lose benzene in an analogous reaction (eq 28).[139,141,142] Benzene is also lost from tetrabenzylgermane.[139] Typical aromatic rearrangements involving hydrogen are observed in tetraphenylsilane,[152] and the loss of $C_{12}H_{10}$ from tetraphenyl derivatives of group IV elements has been studied.[153] It was concluded that this loss involves elimination of a biphenyl molecule, and three possible pathways were suggested for the reaction (Scheme VIII).

$$Ph_2M^{+}H \longrightarrow PhM^{+} + C_6H_6 \qquad (28)$$

SCHEME VIII



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Pathway A does not involve hydrogen rearrangement, and some support for this pathway came from the observation that inter-ring hydrogen scrambling was not observed. An alternative explanation would be that pathways B and/or C operate irreversibly, so that any hydrogen scrambling in the biphenyl part of the intermediate would not show up in the product ion. This product ion, PhSiPh·+, loses H· and H_2, possibly *via* the cyclized intermediate **4**, since loss of H_2, HD, and D_2 was observed from partially deuterated tetraphenylsilanes.

The $(C_6H_5CH_2)_2Ge^+$ ion loses stilbene,[139] in a reaction involving both hydrogen and skeletal rearrangement. In aryltrimethylstannanes, SnH^+ is observed,[154] as it is in other stannanes as well. It has recently been shown[155] that SnH^+ arises by loss of ethyl from $^+SnMe_2$ in the spectrum of $SnMe_4$, rather than loss of CH_2 from ^+SnMe as previously thought.[138b] Various reactions of group IV allyls were also investigated; thus tetraallyltin loses propylene from its molecular ion (**5**) and allene from the ion **6**, with hydrogen rearrangement in each case.[155]

$$\underset{\mathbf{5}}{Sn(C_3H_5)_4^{\cdot +}} \longrightarrow Sn(C_3H_5)_2C_3H_4^{\cdot +} + C_3H_6$$

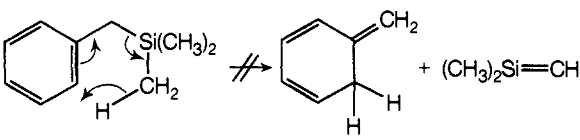
$$\underset{\mathbf{6}}{Sn(C_3H_5)^{\cdot +}} \longrightarrow SnH^{\cdot +} + C_3H_4$$

Various α-phenyl-ω-trimethylsilylalkanes show interesting skeletal rearrangements.[137,156,157] Many of these do not involve hydrogen rearrangement, but hydrogen scrambling is observed prior to the loss of ethylene from **7**, possibly *via* a ring-expansion mechanism (see section III.B).[137]

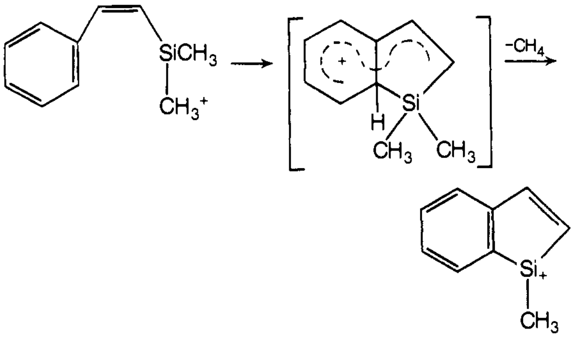
$$C_6H_5CD_2CH_2\overset{H}{\underset{+}{Si}}C_6H_5$$

7

One important hydrogen rearrangement that does *not* occur in these compounds is that of eq 29,[157] in spite of the fact that rearrangements of this type are important in the spectra of propylbenzenes and related compounds (section III.D). Hydrogen rearrangement must occur in the loss of CH_4 from 1-phenyl-2-trimethylsilylethylene, which may occur by the pathway shown (eq 30).[156b] This loss is preceded by hydrogen scrambling, which also occurs in the negative-ion spectra of phenylsilanes.[153,158]

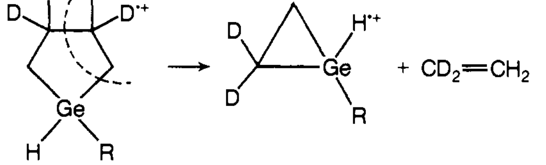


(29)



(30)

Heterocycles containing group IV elements show the presence of rearrangements too: several five-membered heterocycles have losses of methyl and ethyl;[159] the loss of benzene from 1-phenyl heterocycles involves a hydrogen atom from the 1 or 2 position;[160] in germacyclopentane only C-2 and C-3 are incorporated into the ethylene produced (eq 31).[160] The effect of ring size in sila ring compounds has been studied; the spectra of 1,1-dimethylsilacyclobutane (**8**) and 1-methylsilacyclopentane (**9**) are nearly the same,[161] suggesting rearrangement during fragmentation.



(31)

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(152) P. N. Preston and N. A. Wier, *Inorg. Nucl. Chem. Lett.*, **4**, 279 (1968).

(153) J. H. Bowie and B. Nussey, *Org. Mass Spectrom.*, **3**, 933 (1970).

(154) M Gielen and J. Nasielski, *Bull. Soc. Chim. Belg.*, **77**, 5 (1968).

(155) M. Fishwick and M. G. H. Wallbridge, *J. Chem. Soc. A*, 57 (1971).

(156) (a) W. P. Weber, R. A. Felix, and A K. Willard, *Tetrahedron Lett.*, 907 (1970); (b) W. P. Weber, A. K. Willard, and H. G. Boettger, *J. Org. Chem.*, **36**, 1620 (1971).

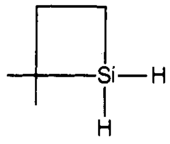
(157) M. E. Freeburger, B. M. Hughes, G. R. Buell, T. O. Tiernan, and L. Spialter, *J. Org. Chem.*, **36**, 933 (1971).

(158) J. H. Bowie and B. Nussey, *Chem. Commun.*, 17 (1970).

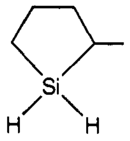
(159) A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 2920 (1965).

(160) A. M. Duffield, C. Djerassi, P. Mazerolles, J. Dubac, and G. Manuel, *J. Organometal. Chem.*, **12**, 123 (1968).

(161) N. Y. Chernyak, R. A. Kheml'nitskii, T. V. D'yakova, V. M. Vdovin, and T. N. Arkhipova, *Zh. Obshch. Khim.*, **36**, 96 (1966).



8



9

Compounds containing more than one group IV atom show similar losses of olefin to those of the previous compounds.[142,162,163] In compounds with intervening methyl groups between Si atoms, losses of alkylsilanes are observed.[164] In tetrasiladamantanes with Cl or H on the apical silicon atoms, methyl is lost from the molecular ion; D-labeling suggests that some H comes from the apical positions.[165]

In conclusion, the almost complete lack of deuterium-labeling data in this field should be noted. While many of the rearrangements have "obvious" mechanisms, these have in the past turned out to be incorrect in other areas, and the same might be true here. The existence of many different isotopic species in the heavier elements makes the interpretation of the results more difficult, but computer programs are available to deal with such situations,[166] and there seems every reason to confirm some of the postulated mechanisms with hard experimental data.

G. Rearrangements in the Production and Decomposition of Aliphatic Hydrocarbon Ions from Sources Other than Hydrocarbons

Alkyl ions are produced in the fragmentation of most organic compounds, and any attempt to document all the known examples would result only in an indigestible mass of information. However, the formation of hydrocarbon ions from some smaller functionally substituted molecules has been studied, and some of these results will be presented in this section.

Hydrogen scrambling has been observed to precede the formation of the methyl ion from CH_3CD_2OH,[167] and the thermodynamics of its formation from ethylene oxide has been measured.[168] Small ions such as methyl have also been observed in the spectra of some aromatic compounds, including furans,[169] benzene (section III.A), thiophenol,[170] and several bisaryl compounds.[171] The origin of the carbon atom lost in the case of diphenyl sulfide has been studied, and it was found that all the carbon atoms of the original molecule have an essentially equal chance of being lost as $CH_3\cdot$.[172] Such reactions clearly involve extensive hydrogen rearrangement, but the exact mechanism cannot be deduced with our present knowledge. Formation of $CH_3\cdot$ has also been observed from deuterated aldehydes[173] and unsaturated lactones.[174]

Among other small alkyl ions there is a tendency toward rearrangement, as a number of important scrambling studies indicate. The ethyl ion from dihydrothiophene dioxide has been studied.[175] The $C_2H_3\cdot^+$ and $C_2H_5^+$ ions from various ethyl chlorides have been studied with respect to metastable peak shapes.[176] The propyl ion from 1-bromobutane-*1,1*-d_2 is 86% d_0 and 14% d_2, but 0% d_1, indicating little hydrogen scrambling prior to its formation.[177] Two recent papers[54,178] summarize the available evidence for the structure of the $C_3H_7^+$ ion and conclude on the basis of ion-molecule reactivities (as studied by ion cyclotron resonance spectroscopy) that initially formed *n*-propyl ions isomerize to *sec*-propyl ions within 10^{-3} sec. Propyl ions formed by protonation of cyclopropane have identical reactivity with that of *sec*-propyl ions, suggesting that the former ions also isomerize to the latter.

The butyl ions from *n*-butyl halides undergo complete scrambling of carbon and hydrogen atoms before the metastable loss of CH_4, and in general any butyl ion studied isomerizes to a common structure or structures before the metastable loss of CH_4 or C_2H_4.[179] Similarly, generation of $C_4H_7^+$, $C_5H_9^+$, $C_6H_{11}^+$, $C_5H_7^+$, and $C_6H_9^+$ individually from various halide precursors showed that the metastable decompositions of each ion were essentially independent of the particular precursor used. It is thus highly probable that the isomeric ions rearrange to common intermediates (or mixtures of intermediates) before decomposition *via* competing metastable transitions.[180]

The *tert*-butyl cation, generated from *tert*-butyl bromide or iodide, decomposes by loss of CH_4 with randomization of its hydrogens,[181] while the formation of the $C_4H_9^+$ ion incorporating the isopropyl group of 3,4-epoxymenthane requires migration of at least one hydrogen atom.[182] Hydrogen scrambling before alkyl ion formation from penta- and hexamethylene oxide has been studied.[183]

Ion structural studies have also been carried out on the $C_6H_{13}^+$ and $C_8H_{17}^+$ ions from alkyl bromides and iodides[184] and the $(C_nH_{2n-3})^+$ and $(C_nH_{2n-4})^+$ (n = 7, 8) ions generated from bicyclic and unsaturated halides and steroids.[184] In each case isomerization to a common structure or mixture of structures was observed prior to decomposition in most of the examples studied. Other examples of hydrogen rearrangements in the ions produced from bicyclic compounds include the (retro-Diels-Alder + 1) ion from norbornane and 2-substituted norbornanes,[185] the $C_7H_{11}^+$ ion from 2-norbornyl chloride prior to decomposing by loss of C_2H_4,[186] the $(M - CHO)^+$ ion

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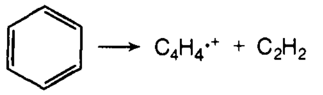
from nortricyclanone,[187] and various ions from 7-ketoandrostanes.[188]

Hydrogen rearrangements are also observed in the formation of various odd-electron ions from nonhydrocarbon sources. Thus the formation of $C_2H_4^+$ from ethanol, ethylamine, ethanethiol,[189,190] and ethyl halides[191] must involve hydrogen rearrangements; the formation and subsequent decompositions of the ion radicals $C_4H_8\cdot^+$ and $C_6H_{12}^+$ indicate decomposition from common states in each case.[192] These and related reactions will be discussed further in Part III of this review. A Cope-type rearrangement in substituted vinyl ethers involves a hydrogen rearrangement,[193] as does the loss of CH=C(OH)OR from 4-alkoxy-1-decalones.[194] Other odd-electron hydrocarbon ions are produced in the spectra of various natural products, including steroids,[195,196] steroidal sapogenins,[197] and coumarins.[198]

III. Rearrangements in Aromatic Compounds

Aromatic compounds undergo a large number of fragmentation processes on electron impact, many of which involve hydrogen rearrangement. In this section we will first discuss the intriguing group of reactions in which aromatic hydrogens are scrambled with respect to each other and to the carbon skeleton prior to or during various fragmentation processes. An example of this type of reaction is that preceding loss of acetylene from benzene (eq 32). The next section will cover reactions of aromatic compounds involving ring expansion to a tropylium ion or its heterocyclic analog (eq 33). The third section deals with rearrangements in phenyl-substituted alkenes and alkynes, while the fourth section includes rearrangements of aromatic compounds in which side-chain hydrogens are transferred to an aromatic ring (eq 34). After sections on miscellaneous rearrangements in alkylbenzenes and in other aromatic compounds, the chapter ends with a discussion of proximity effects in the fragmentation of aromatic compounds.



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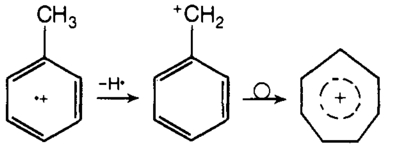

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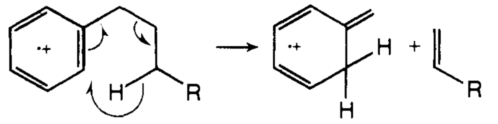

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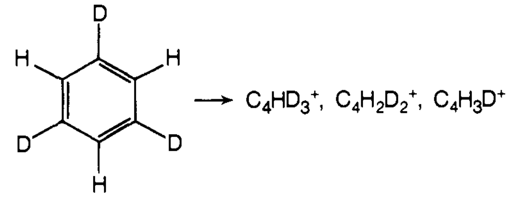
A. Scrambling of Aromatic Hydrogens without Ring Expansion

Scrambling of hydrogen atoms in aromatic compounds, including heterocyclic compounds, has been known for several years, but this intriguing reaction has been studied most extensively in the last 4 years. In this section we shall first discuss the experimental evidence for hydrogen scrambling and the carbon scrambling associated with it, and then turn to a discussion of possible mechanisms for the process.

Hydrogen scrambling as observed in benzene has served as a prototype of scrambling in more complex compounds. There is complete scrambling of protium and deuterium before loss of acetylene in benzene-*1,2,3-d*$_3$ and benzene-*1,3,5-d*$_3$;[199] similarly, in benzene-*1,3,5-d*$_3$ and benzene-*1,4-d*$_2$ there is complete scrambling before metastable processes.[200] Thus, for example, benzene-*1,3,5-d*$_3$ (**10**) could only lose C_2HD in the absence of scrambling, whereas in actual fact losses of C_2H_2, C_2HD, and C_2D_2 were observed in the statistical ratio of 1:2:1 expected for complete randomization of hydrogens.[199,200] Possible mechanisms for this scrambling will be discussed later, but it may be noted that they include isomerization *via* valence isomers of benzene, in analogy with known photochemical transformations.[201] These mechanisms have been tested by the application of ^{13}C labeling to benzene.[202-204]



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In addition to the scrambling of hydrogen on a presumably intact carbon skeleton (but see below, p 210), benzene undergoes fragmentations that must involve ring opening. Thus the spectra of benzene and hexa-1,3-dien-5-yne are nearly identical, so that it has been suggested that the $C_6H_6\cdot^+$, $C_6H_5^+$, and $C_6H_4\cdot^+$ ions are all acyclic.[205] However, the spectra of 1,3- and 2,4-hexadiyne are appreciably different from that of benzene,[206] and hence the degree of isomerization of benzene is limited. Hydrogen rearrangement must also occur in the decomposition of $C_6H_6^{2+}$ (eq 35). This decomposition occurs

$$C_6H_6^{2+} \longrightarrow C_5H_3^+ + CH_3^+ \qquad (35)$$

with the release of kinetic energy in a metastable pro-

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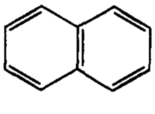
cess,[207-210] the total energy release being 2.67 ± 0.1 eV, though one must bear in mind that values may be affected by collector slit discrimination. If this energy is made equal to coulombic repulsion energy and the charges are assumed to reside as far apart as possible in the doubly charged ion, then the charge separation is found to be 5.14 Å, a distance matched by a linear all-cis configuration of the carbon atoms.[209] The application of ion kinetic energy spectra to the problem[211,212] resulted in a value of 2.33 eV, or 6.2 Å for the intercharge distance, so that trans junctions in the linear structure are required.

Returning to the question of hydrogen scrambling in aromatic systems, scrambling of aromatic hydrogens is also observed in naphthalene (**11**),[199] phenanthrene (**12**),[199] and biphenyl (**13**).[213]



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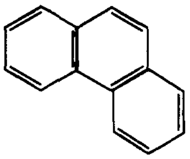

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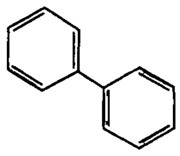

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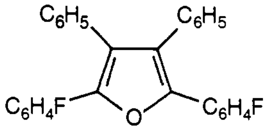
Other fragmentations which must involve hydrogen rearrangement are observed for naphthalene and azulene,[214] doubly charged naphthalene,[208,211] phenanthrene,[215] triptycene,[216,217] triply charged biphenyl,[211,218] triply charged 9,10-diphenylanthracene,[219,220] singly charged 9,10-diphenylanthracene,[220] and the polyphenyls.[221] A theoretical treatment of rearrangements in biphenyl has appeared.[222]

Randomization of the aromatic hydrogens also occurs in various heterocyclic analogs of benzene. Scrambling has been observed prior to elimination of HCN from pyridine,[223] and the methylpyridines and quinoline,[224] but extensive randomization of hydrogen does not precede loss of CHO from furan[225] or loss of HCN from thiazole.[213] In agreement with this finding, very little skeletal rearrangement occurs in the phenylated furan **14**, formation of $FC_6H_4CO^+$ exceeding that of the rearranged ion $C_6H_5CO^+$ by approximately an order of magnitude.[226] Somewhat surprisingly, the corresponding eliminations from the benzo derivatives do involve hydrogen randomization; thus loss of both HCN and DCN is observed from **15**,[213] with more extensive scrambling occurring in ions of longer lifetime decomposing in the field-free regions than in ions decomposing in the source.



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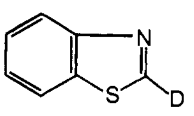

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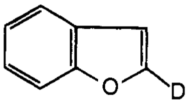
Similarly, the mass spectra of benzofuran-*2-d* (**16**) and *-5-d*[227] indicate partial scrambling of H/D prior to loss of CHO from the molecular ion. In the case of the thiophenes, however, both carbon and hydrogen scrambling are observed. Thus studies of deuterium-labeled thiophenes such as thiophene-*2,5-d*$_2$ (**17**) indicated that considerable but not complete hydrogen randomization precedes the formation of such ions as CHS^+ and $C_2H_2S^+$,[225,228,229] while studies of ^{13}C-labeled thiophenes[229,230] indicate that substantial carbon scrambling occurs prior to formation of the major fragment ions, although the exact interpretation of the extent of scrambling differs somewhat in the papers cited.



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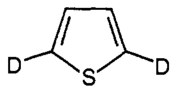

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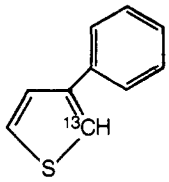
Substituent scrambling occurs in phenylated thiophene,[226] and a recent study[231] has shown that this occurs essentially independently of any ring-carbon scrambling in 3-phenylthiophene-2-^{13}C (**18**) and two bromo derivatives. Ring-carbon scrambling does occur, however, in benzothiophene-2-^{13}C (**19**),[232] and hydrogen randomization precedes acetylene loss in benzothiophene-*2,3-d*$_2$.[213]



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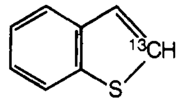

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Hydrogen scrambling has also been observed in 2,3-diphenyl- and 2,3,5-triphenylpyrrole-*N-d* (**20**),[233] cinnoline-*3,4-d*$_2$ (**21**) and related compounds,[234] carbazole,[199,235] and dibenzothiophene,[236] but randomization

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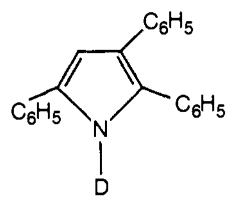

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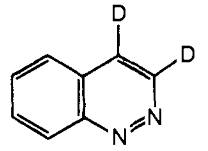
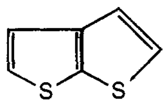


21

does not occur to any significant extent prior to the formation of the major ions from oxazoles,[237] isoxazoles,[238] or pyrazoles.[239] Carbon-skeletal randomization is observed in the fragmentation of 2-phenylthiophene[240] and in the thienothiophenes **22** and **23**.[241]



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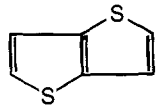

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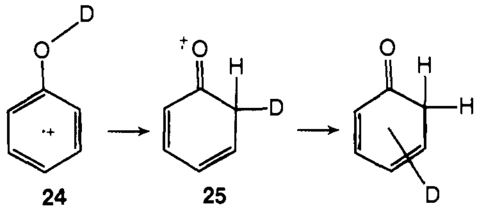
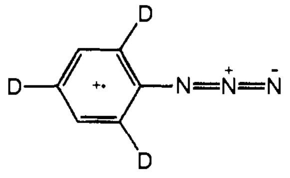
Hydrogen scrambling also occurs widely in the fragmentation of many substituted phenyl and heterocyclic compounds. In the case of alkyl-substituted benzenes, this scrambling can be accommodated by ring expansion to the tropylium ion, discussed in the next section, but in most other cases different mechanisms are required. In many cases the molecular ions of monosubstituted benzenes decompose *via* loss of a fragment not containing hydrogen, and in these cases it is impossible at present to determine the degree of scrambling in the molecular ion. Even in these cases, however, it is frequently possible to detect scrambling in fragment ions, and in the following discussion both types of scrambling will be mentioned.

Hydrogen rearrangement involving at least some hydrogen scrambling has been shown to occur prior to the formation of ions such as $C_3H_4^+$ from phenol, thiophenol, and aniline.[242] Thus phenol-*O*-d_1 (**24**) yields fragments corresponding to $(M - CO)^+$ and $(M - CHO)^+$ in the parent compound, and in the latter case only about 33% of the hydroxylic hydrogen is lost, implying partial randomization of this hydrogen and the aromatic hydrogens.[242] The mechanism of CO loss has been proposed to proceed *via* the keto form (**25**),[243] and equilibration may well occur during the lifetime of this ion (**25** ⇌ **26**).



24 **25** **26**

Benzonitrile loses HCN after randomization of hydrogen; it was thought initially that the randomization was removed at low voltage,[244] but this proved not to be the case.[245] There is likewise randomization of hydrogen before the loss of HCN from the 1- and 2-cyanonaphthalenes[213] and phenyl isocyanide,[246] although 1-naphthyl isocyanide apparently loses HCN by removal of the peri hydrogen.[247] The $M^+ - N_2$ ion from phenyl-*1,3,5*-d_3 azide (**27**) eliminates HCN and C_2H_2 subsequent to hydrogen scrambling.[248]



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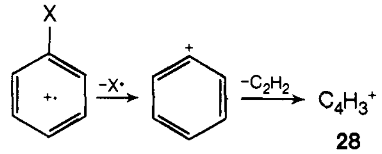
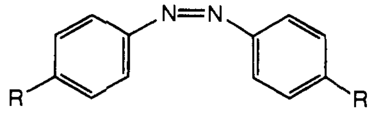
Although as previously noted the extent of hydrogen scrambling in the molecular ions of compounds which do not lose a small fragment containing hydrogen cannot be ascertained, it is possible to measure the amount of scrambling in the $C_6H_5^+$ ion derived from the molecular ion of these compounds. Thus hydrogen scrambling before fragmentation of the $C_6H_5^+$ ion derived from C_6H_5Cl,[199,249] C_6H_5Br,[199,249] C_6H_5I,[249] C_6H_5NO,[250] $C_6H_5NO_2$,[251] and $C_6H_5OC_6H_5$[249] has been observed (eq 36).

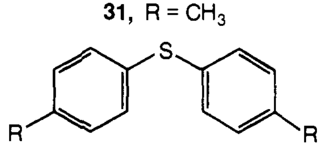


28 (36)

Hydrogen randomization is also observed in the loss of the bridging group from a number of bis(aryl) compounds. Thus scrambling precedes or accompanies the loss of N_2H and N_2H_2 from azobenzene (**29**) and the loss of CHS from diphenyl sulfide (**30**).[171] The 4,4′-dimethyl homologs of **29** and **30** (**31** and **32**, respectively) also undergo extensive hydrogen scrambling prior to loss of the bridging group but in addition appear to fragment by some pathways involving the loss of an unscrambled methyl group.[171]



29, R = H
31, R = CH_3



30, R = H
32, R = CH_3

Other compounds in which randomization of aromatic hydrogens before or during specific fragmentation pro-

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(237) J. H. Bowie, P. F. Donaghue, H. J. Rodda, R. G. Cooks, and D. H. Williams, *Org. Mass Spectrom.*, **1**, 13 (1968).

(238) J. H. Bowie, R. K. M. R. Kallury, and R. G. Cooks, *Aust. J. Chem.*, **22**, 563 (1969).

(239) B. K. Simons, R. K. M. R. Kallury, and J. H. Bowie, *Org. Mass Spectrom.*, **2**, 739 (1969).

(240) W. D. Weringa, H. J. M. Sinnige, and M. J. Janssen, *Org. Mass Spectrom.*, **5**, 1399 (1971).

(241) A. Bugge, *Acta Chem. Scand.*, **25**, 1504 (1971).

(242) J. Momigny, *Bull. Soc. Roy. Sci. Liege*, **22**, 541 (1953).

(243) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

(244) R. G. Cooks, R. S. Ward, and D. H. Williams, *Chem. Commun.*, 850 (1967).

(245) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *J. Chem. Soc. B.*, 149 (1969).

(246) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Org. Mass Spectrom.*, **1**, 910 (1968).

(247) B. Zeeh, *Org. Mass Spectrom.*, **1**, 315 (1968).

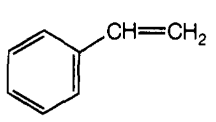
(248) D. G. I. Kingston and J. D. Henion, *Org. Mass Spectrom.*, **3**, 413 (1970).

(249) D. H. Williams, S. W. Tam, and R. G. Cooks, *J. Amer. Chem. Soc.*, **90**, 2150 (1968).

(250) I. R. King and G. W. Kirby, *J. Chem. Soc. C*, 1334 (1966).

(251) F. Benoit and J. L. Holmes, *Chem. Commun.*, 1031 (1970).

cesses has been observed include the following (the ion observed to detect scrambling is indicated after the compound): triphenylmethane, $(M - H)^+$,[217,252] $(M - CH_3)^+$,[217] $(M - CH_4)^+$;[217] diphenylmethane, $(M - H)^+$, $(M - CH_3)^+$;[217,253,254] styrene (**33**), $(M - C_2H_2)^+$;[255-257] stillbene (**34**), $(M - H)^+$, $(M - CH_3)^+$;[233,258-262] phenylacetylene, $(M - C_2H_2)^+$;[263] 1-phenylpropyne-*3,3,3-d*$_3$ (**35**), $(M - H)^+$;[264] diphenylacetylene $(M - C_2H_2)\cdot^+$;[265] anisole, $(C_6H_7^+)$;[266] diphenylmethanol, $(M - C_6H_6)\cdot^+$;[267] triphenylphosphine, triphenylphosphine oxide, and related substances,[268] various alkylidenetriphenylphosphoranes (**36**),[269] 1-arylanthra-9,10-quinones (**37**), $(M - H)^+$;[270] hydrocinnamaldehyde (**38**), $(M - C_2H_2O)^+$, $(M - C_3H_4O)^+$;[271] and various halo-substituted biphenyls, $(M - HX)^+$.[272]



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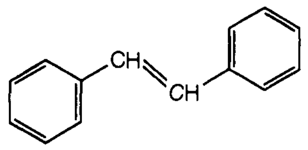

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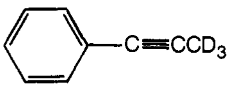

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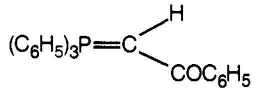

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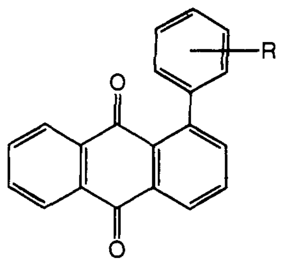

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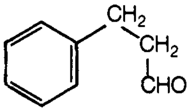

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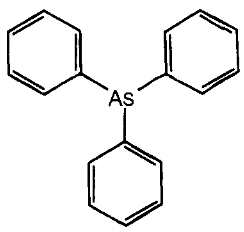
Lest the large number of examples of hydrogen randomization cited give the impression that this reaction is ubiquitous, it should be pointed out that specific losses of aromatic hydrogen atoms do occur; the fragmentation of some of the heterocyclic compounds previously mentioned (furan, oxazoles, isoxazoles, and pyrazoles) provides one example, while certain fragmentations of most of the compounds cited undoubtedly proceed without hydrogen randomization.

Scrambling of aromatic hydrogens has also been observed in negative-ion mass spectrometry, specifically in the cases of triphenylarsine (**39**) and tetraphenylsilane (**40**).[158]



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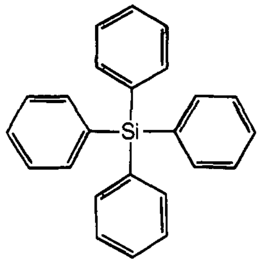

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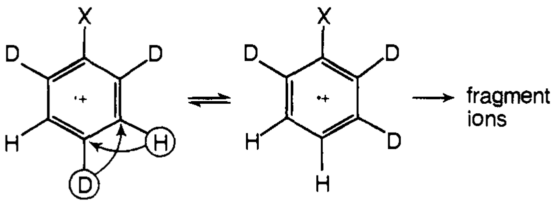
The widespread occurrence of hydrogen randomization processes in aromatic compounds has naturally produced much interest and speculation concerning the mechanism by which scrambling occurs. It should be noted that at least three different types of scrambling may be involved in any fragmentation loosely described as "hydrogen scrambling." In the first place, aromatic hydrogens may simply rearrange on an intact carbon skeleton ("pure" hydrogen scrambling). Secondly, the carbon atoms of the carbon skeleton may themselves be scrambled with respect to each other (carbon scrambling). Finally, any substituents on the aromatic system may scramble with respect to the carbon atom(s) to which they are bonded. In both of these latter two situations hydrogen scrambling inevitably occurs, but it is almost incidental to the other type of scrambling taking place. In the discussion of examples of hydrogen scrambling up to this point, we have not been concerned with differentiation between these various types of scrambling, but it is convenient at this point to use them as a basis for the various possible mechanisms of hydrogen scrambling.

1. Simple H/D reciprocal shifts on the intact carbon skeleton of the molecular ion, possibly involving reversible formation of σ or π complexes between the aromatic ring and its hydrogen atoms ("pure" hydrogen scrambling, Scheme IX).[199]

SCHEME IX



2. Randomization of the ring carbon atoms *via* ionized valence-bond isomers of the aromatic system (carbon scrambling, Scheme X). This mechanism was first suggested by Jennings,[200] and later by Williams[225,249] in analogy to the photochemical isomerization of benzene.[201]

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(252) V. K. Potapov, D. N. Shigorin, A. D. Filyugina, and V. V. Sorokin, *Zh. Fiz. Khim.*, **40**, 2332 (1966).

(253) K. D. Berlin and R. D. Shupe, *Org. Mass Spectrom.* **2**, 447 (1969).

(254) T. K. Bradshaw, J. H. Bowie, and P. Y. White, *Chem. Commun.*, 537 (1970).

(255) J. L. Franklin and S. R. Carroll, *J. Amer. Chem. Soc.*, **91**, 5940 (1969).

(256) E. I. Quinn and F. J. Mohler, *J. Res. Nat. Bur. Stand.*, **62**, 39 (1959).

(257) A. Venema, N. M. M. Nibbering, and T. J. de Boer, *Org. Mass Spectrom.*, **3**, 1589 (1970).

(258) P. F. Donaghue, P. Y. White, J. H. Bowie, B. D. Roney, and H. J. Rodda, *Org. Mass Spectrom.*, **2**, 1061 (1969).

(259) R. A. W. Johnstone and B. J. Millard, "Some Newer Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davis, Ed., United Trade Press, Ltd., London, 1967, p 28.

(260) J. H. Bowie and P. Y. White, *Aust. J. Chem.*, **24**, 205 (1971).

(261) H. Güsten, L. Klasinc, J. Marsel, and D. Milirojevic, *Org. Mass Spectrom.*, **5**, 357 (1961).

(262) J. H. Bowie and P. Y. White, *Org. Mass Spectrom.*, **6**, 135 (1972).

(263) S. Safe, *Chem. Commun.*, 534 (1969); S. Safe, *J. Chem. Soc. B*, 962 (1971).

(264) S. Safe, W. D. Jamieson, W. R. Pilgrim, and S. Wolfe, *Can. J. Chem.*, **48**, 1171 (1970).

(265) S. Safe, *Org. Mass Spectrom.*, **3**, 239 (1970).

(266) F. Meyer and A. G. Harrison, *Can. J. Chem.*, **42**, 1762 (1964).

(267) D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Chem. Soc. B*, 522 (1968).

(268) D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, **90**, 966 (1968).

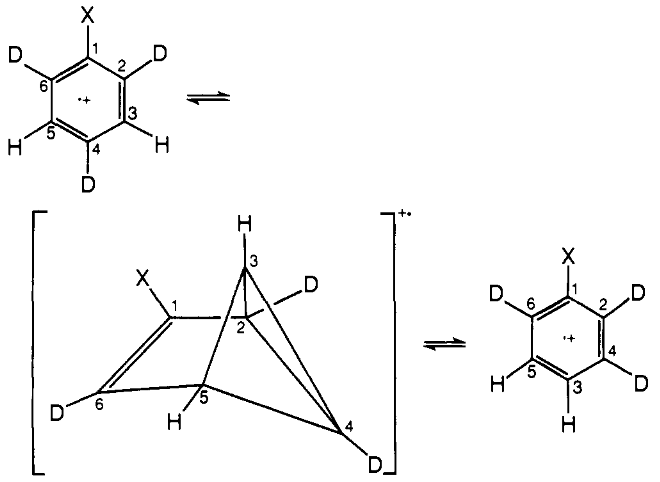
(269) R. G. Cooks, R. S. Ward, D. H. Williams, M. A. Shaw, and J. C. Tebby, *Tetrahedron*, **24**, 3289 (1968).

(270) D. R. Buckle and E. S. Waight, *Org. Mass Spectrom.*, **1**, 273 (1968).

(271) A. Venema, N. M. M. Nibbering, and T. J. de Boer, *Org. Mass Spectrom.*, **3**, 583 (1970).

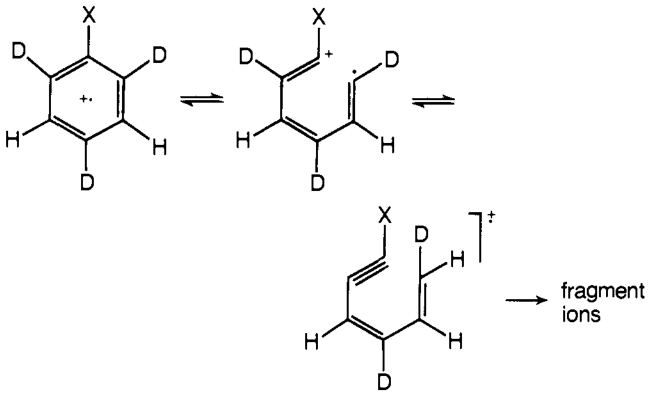
(272) S. Safe, *Org. Mass Spectrom.*, **5**, 1221 (1971); S. Safe and O. Hutzinger, *J. Chem. Soc., Perkin Trans. 1*, 686 (1972).

SCHEME X



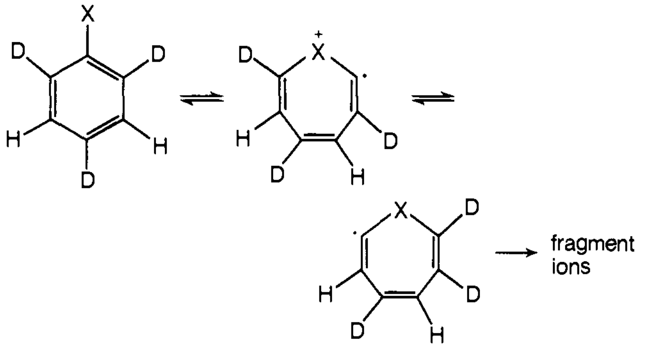
3. Opening of the aromatic ring (Scheme XI) and hydrogen randomization *via* the intermediacy of such species as ionized hexadienynes.[199] The extensive hydrogen scrambling observed in unsaturated aliphatic compounds has been documented in section II.C of this review, and an open-chain ion if formed would certainly be expected to randomize its hydrogens.

SCHEME XI



4. Randomization of hydrogen in certain cases could also occur *via* the intermediacy of ring-expanded molecules. Such a pathway is known to operate in toluene and various other alkylbenzenes and will be considered in detail in the next section. It could also be a significant pathway for scrambling in other cases[273] (substituent scrambling, Scheme XII). Other mechanisms of substituent scrambling analogous to those for hydrogen scrambling, Scheme IX, may also operate.

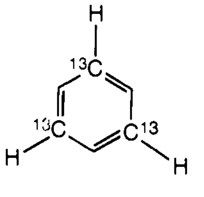
SCHEME XII



A distinction between these possible mechanisms of hydrogen scrambling may be made in various ways. Mechanism 2, for example, requires that a given hydrogen atom (and also any substituent X) remain bonded to its original carbon atom throughout the course of the rearrangement, while mechanisms 1, 3, and 4 require scrambling of hydrogen independent of any other scrambling. Mechanisms 1, 2, and 3 all require that any substituent X remain bonded to its original carbon atom, unless substituent scrambling occurs by an independent pathway. Substituent scrambling can be accommodated under mechanism 4, however, if random insertion of X into C–C bonds is postulated, as has been shown to occur in the case of toluene.[274,275]

Experimental information on the nature of the rearrangement process has come primarily from ^{13}C-labeling studies. The situation is clearest in the case of benzene and certain heterocyclic compounds, where mechanism 4 cannot operate, and we shall discuss these first.

A ^{13}C-labeling study with benzene-*1,3,5*-$^{13}C_3$ (**41**) indicated that the carbon atoms are completely randomized before metastable decomposition in the first field-free region of a double-focusing instrument,[202] with losses of C_2H_2, $^{13}CCH_2$, and $^{13}C_2H_2$ being observed in the statistical ratios of 1:2:1. This observation provided necessary but not sufficient proof for the operation of mechanism 2. A double-labeling experiment with benzene-*1,2*-$^{13}C_2$-*3,4,5,6*-d_4 (**42**) showed that about 30% of the ions $C_3H_3^+$ and C_4H_4 arise by paths in which the carbon atoms are scrambled *without* breaking C–H bonds, demanding rearrangement *via* mechanism 2 for at least this 30% of decomposing ions.[203] In the remaining 70% of the ions the hydrogens are scrambled over and beyond whatever carbon scrambling occurs. However, studies of the decomposition of benzene-*1*-^{13}C-*1-d* (**43**) in the first field-free region of a double-focusing mass spectrometer showed that complete scrambling of *both* carbon and hydrogen atoms occurred before metastable decomposition.[204] The discrepancy between this result and the previous one presumably arises because ions decomposing in the first field-free region have average lifetimes about ten times longer than those ions decomposing in the source region, thus allowing sufficient time for complete scrambling to occur. Whatever the detailed results concerning the relative importance of carbon and independent hydrogen scrambling in benzene, it is clear that mechanism 2 provides a significant pathway for hydrogen randomization, but that rearrangement by other mechanisms such as 1 and/or 3 must be proceeding concurrently with valence isomerization.



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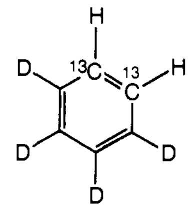

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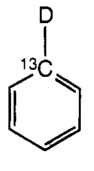

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The situation is somewhat different in the case of rearrangement of various heterocycles. Pyridine, for example, scrambles its hydrogens prior to loss of HCN,[223] and it might reasonably be expected that mechanism 2 should apply here also. However, pentaphenylpyridine does not scramble its phenyl groups (as shown by the *p*-fluoro la-

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(273) J. D. Henion and D. G. I. Kingston, *Chem. Commun.*, 258 (1970).

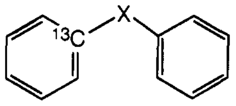
(274) K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *J. Amer. Chem. Soc.*, **90**, 2983 (1968).

(275) A. S. Siegel, *J. Amer. Chem. Soc.*, **92**, 5277 (1970).

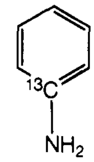
beling technique)[276] and hence cannot be isomerizing *via* valence isomers. Perhaps the difference between phenyl and hydrogen substituents is enough to make mechanism 2 energetically unfavorable, but this example does at least indicate that valence isomerization is not ubiquitous. Furthermore, it is difficult to rationalize the results of scrambling studies in bicyclic aromatic compounds on the basis of valence isomerization. Thus the observation of hydrogen scrambling in benzofuran but not in furan itself is the opposite of what would be predicted on the basis of mechanism 2, and it may very well prove that the structure of the decomposing ion in these cases is quite different from that of the neutral molecule. Even in the case of benzene the intuitive feeling that the cyclic form is favored because of delocalization is given the lie by molecular orbital calculations which show that the benzene radical cation is an order of magnitude less aromatic than benzene itself (RE = 0.04).[277]

Recent results for the 3-phenylthiophene system (**18**)[231] have been interpreted to suggest that substituent isomerization occurs by way of group migration only after ring opening, while ring-atom scrambling (which does not compete effectively with substituent migration in these examples) is limited to cyclic molecular ions. If this result turns out to be a general one, it would imply that hydrogen scrambling in aromatic compounds occurs primarily by mechanism 3, with some additional scrambling by mechanism 2 occurring in certain cases.

Hydrogen scrambling in substituted aromatic compounds, and especially in substituted benzenes, is further complicated by the possibility that the substituent could participate in the randomization process (mechanism 4). That such participation does occur in some cases is indicated by ^{13}C labeling studies on diphenyl sulfide (**44**)[273] and diphenyl ether (**45**).[278] In both cases extensive scrambling of the bridging atom occurred with respect to its associated carbon atoms prior to elimination of CS or CO, respectively. This result should be contrasted with the observation that label scrambling does *not* occur prior to elimination of CO from phenol,[204,279] but scrambling of the label with respect to sulfur does occur prior to elimination of CS from thiophenol.[279] Various other substituted benzenes have been studied by ^{13}C labeling, with results that are dependent on the nature of the side chain. Thus the spectrum of aniline-*1*-^{13}C (**46**) reveals that 92%[280] (93%[281]) of the HCN eliminated from the molecular ion is lost as $H^{13}CN$, implying that a ring-expanded ion such as **47** is formed only to a small extent, if at all, by decomposing ions. Loss of HCN probably occurs from the tautomeric ion **48**. The spectra of methylpyridines and ^{13}C-labeled methylquinolines have been examined, and it is probable that these do ring expand to an ion analogous to **47**; these results will be discussed in the next section. Loss of NO and CO from *p*-nitroaniline-*1*-^{13}C (**49**) proceeds with essentially no loss of label,[282] implying no carbon-skeletal rearrangement prior to CO loss, in agreement with arguments based on studies of metastable transitions.[283] Similarly, loss of CO from thionylaniline-*1*-^{13}C (**50**) proceeds without loss of the labeled carbon,[284] as does also loss of CO from phenyl-*1*-^{13}C butyl ether (**51**)[285] and nitrobenzene.[282] These findings have mechanistic and structural implications for the specific steps involved in these fragmentation processes, but for our purposes they may merely be noted as examples of fragmentations which proceed without extensive carbon scrambling.



44, X = S
45, X = O



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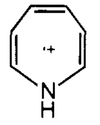

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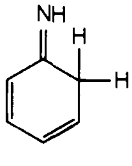

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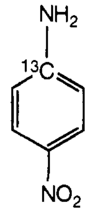

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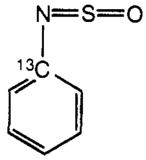

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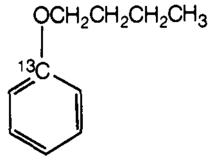

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In contrast, the odd-electron ion $C_6H_5N\cdot^+$ from phenyl azide is rearranged to a considerable extent preceding HCN loss, as shown by a study of phenyl-*1*-^{13}C azide.[286] Likewise, stilbene loses $CH_3\cdot$ from its molecular ion with extensive scrambling of a ^{13}C label, and, although there has been disagreement about the precise nature of the pathways involved, it is clear that at least the major pathway involves either complete or nearly complete carbon skeletal randomization.[233,258-262] Studies on styrene labeled in the side chain with ^{13}C show that it is not necessary to assume ring expansion to explain the observed hydrogen scrambling,[255-256] since label retentions corresponding to fragmentation of an eight-membered ring were only observed with low-energy ions.[257] Loss of C_2H_2 from the $C_6H_5^+$ ion formed by decomposition of iodobenzene-*1*-^{13}C occurred with statistical loss of C_2H_2 and $^{13}CCH_2$, again implying complete randomization of the carbon skeleton prior to this fragmentation.[204]

An alternate approach to the question of skeletal rearrangement in aromatic compounds employs a study of substituent effects as a function of beam energy and has

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(276) M. M. Bursey and T. A. Elwood, *J. Org. Chem.*, **35**, 793 (1970).

(277) R. C. Dougherty, *J. Amer. Chem. Soc.*, **90**, 5780 (1968).

(278) D. G. I. Kingston and J. D. Henion, unpublished observations; J. D. Henion, Ph.D. Thesis, 1972.

(279) A. Siegel and K. L. Rinehart, Jr., Abstracts, 158th National Meeting of the American Chemical Society, New York, Sept 1969, No. ORGN 66.

(280) A. V. Robertson and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 6992 (1968).

(281) K. L. Rinehart, A. C. Buchholz, and G. E. Van Lear, *J. Amer. Chem. Soc.*, **90**, 1073 (1968).

(282) F. Benoit and J. L. Holmes, *Chem. Commun.*, 1031 (1970).

(283) B. Davis and D. H. Williams, *Chem. Commun.*, 412 (1970).

(284) A. S. Siegel, *Org. Mass Spectrom.*, **3**, 875 (1970).

(285) P. D. Woodgate and C. Djerassi, *Org. Mass Spectrom.*, **3**, 1093 (1970).

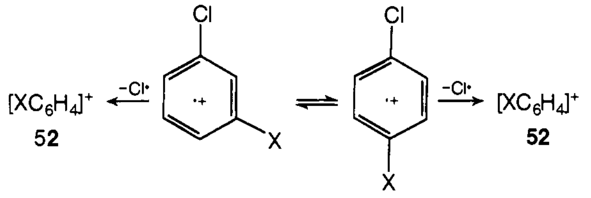
(286) P. D. Woodgate and C. Djerassi, *Tetrahedron Lett.*, 1875 (1970).

TABLE V. Energetic Data for Fragmentations of Aromatic Compounds

Compound	IP, eV	Fragment	AP, eV	AP − IP, eV	Substituent scrambling obsd?	Ref
Benzene	9.24	M − C_2H_2	14.95	5.71	100%	5, 202
Diphenyl ether	8.82	M − CO	12.56	3.74	50%	5, 278
Diphenyl sulfide	8.45	M − CS	12.57	4.12	80%	273, 278
Thiophene	9.20	M − CHS	12.80	3.60	Yes	5, 229, 230
Thiophenol	8.95	M − CS	12.18	3.23	Yes	5, 278, 279
Aniline	7.69	M − HCN	12.3	4.61	No	5, 280, 281
Phenol	9.09	M − CO	12.45	3.36	No	204, 278, 279

been termed "wide-range energy kinetics."[287-291] In brief, this involves measurement of the intensity of a fragment ion relative to the parent ion (a Z value). For both meta- and para-X-substituted chlorobenzenes, loss of halogen would occur to the same extent from both isomers if isomerization to a common structure(s) preceded fragmentation (Scheme XIII), and Z_p should be equal to Z_m. In the event, Z_p/Z_m values near unity were observed for several substituents X, including NH_2, F, Cl, and CN.[290] In spite of some theoretical problems with this approach,[292] the conclusion that isomerization to a common structure occurs in the chlorobenzenes appears to be a sound one.

SCHEME XIII



One aspect of skeletal reorganization and its accompanying hydrogen randomization which has not perhaps been emphasized sufficiently is the importance of experimental conditions in determining the extent of rearrangement and even whether rearrangement will occur. Thus the amount of skeletal rearrangement observed in styrene was found to increase as ions of longer lifetime and correspondingly lower energy were investigated,[257] a result in accord with the predictions of QET. A second important aspect of the problem is that the fragmentations used to investigate the occurrence of hydrogen scrambling and/or skeletal rearrangement will have different activation energies in the different compounds investigated. If the activation energy for isomerization is lower than that for the fragmentation studied, it is reasonable to assume that isomerization will be a significant reaction while the converse should also be true.[204] Experimental data do not support this rationalization entirely, however. Table V lists the ionization potentials of a number of aromatic compounds, with the appearance potentials of the fragment ion used to investigate the occurrence of skeletal rearrangement. Values were selected in which the measurement on both parent and fragment ion was carried out by the same method. The values for the difference, AP − IP, represent a crude measure of the activation energy for the fragmentation in question. These values represent maximum values, because the kinetic shift is neglected; for the $C_4H\cdot^+$ ion from benzene this represents at least 0.7 eV. It can be seen that there is little correlation between AP − IP for a given fragmentation and the occurrence of substituent scrambling in that fragmentation. Thus aniline, with an AP − IP of 4.61 eV, does not undergo scrambling, while both diphenyl sulfide (AP − IP, 4.12 eV) and thiophenol (AP − IP, 3.23 eV) do. Similarly, phenol (AP − IP, 3.36 eV) does not undergo substituent scrambling while diphenyl ether with an activation energy only slightly higher (3.74 eV) does. Clearly factors other than energetic considerations must be playing a part in these reactions, and it is suggested that the frequency factors for elimination of a neutral species are significantly larger in those species which do not undergo substituent scrambling (aniline, phenol) than in those which do. This conclusion is discussed more fully elsewhere.[278]

In summary, it is clear that both skeletal rearrangement and hydrogen scrambling do occur in many aromatic compounds. In some cases hydrogen scrambling occurs in the absence of significant skeletal rearrangement, and even when skeletal rearrangement accompanies hydrogen scrambling the extent of scrambling often exceeds the extent of skeletal reorganization. It would thus seem that scrambling occurs by at least two mechanisms: a mechanism involving skeletal rearrangement (mechanism 2 and/or 4), and a separate, independent mechanism not involving skeletal rearrangement (mechanism 1 or 3). Further definition of the nature of the scrambling processes will have to wait further experiments.

B. Hydrogen Rearrangements in Aromatic Compounds Involving Ring Expansion

The ring expansion of toluene and related compounds to form the tropylium ion on electron impact is a well studied reaction. It was reviewed in 1963,[293] and some aspects of this summary are therefore abbreviated.

Appearance potential data for benzylic compounds[294] indicate a particularly unusual value for the bond energy of the $C_6H_5CH_2$–H bond obtained by mass spectrometric data.[5,295] Thus the ionization potential of the benzyl free radical[296] differed by 0.7 eV or 16 kcal/mol from the earlier one[295] calculated from the AP of $C_7H_7^+$ from toluene and bibenzyl and appropriate thermochemical data. Examination of the spectra of deuterium-[297] and ^{13}C-la-

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(287) P. Brown, *J. Amer. Chem. Soc.*, **90**, 4459 (1968).

(288) P. Brown, *J. Amer. Chem. Soc.*, **90**, 4461 (1968).

(289) P. Brown, *Org. Mass Spectrom.*, **2**, 1317 (1969).

(290) P. Brown, *Org. Mass Spectrom.*, **3**, 639 (1970).

(291) P. Brown, *Org. Mass Spectrom.*, **2**, 1085 (1969).

(292) I. Howe, "Mass Spectrometry," Vol. I, D. H. Williams, Ed., The Chemical Society, London, 1971, p 71.

(293) H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 453.

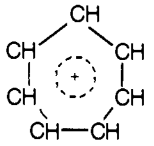
(294) F. H. Field and J. L. Franklin, *J. Chem. Phys.*, **22**, 1895 (1954).

(295) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **22**, 151 (1954).

(296) F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

(297) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Amer. Chem. Soc.*, **79**, 842 (1957).

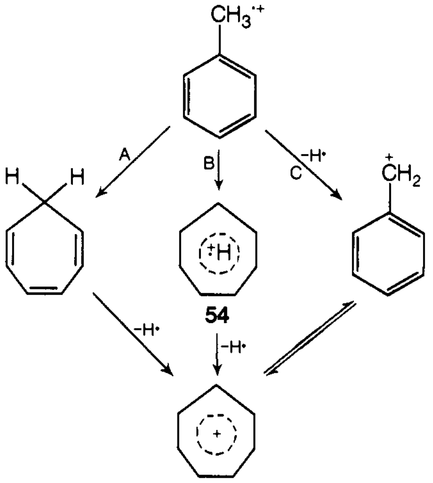
beled[298] toluene showed clearly that all the hydrogen atoms and carbon atoms in toluene became equivalent or nearly so in the $C_7H_7^+$ ion derived therefrom, and led directly to the postulation that the $C_7H_7^+$ ion has the tropylium structure (**53**). The exceptional stability of the tropylium ion in organic ground-state chemistry, as evidenced, for example, by the isolation of tropylium bromide as a stable high-melting solid,[299] lent theoretical and practical support to this formulation of the $C_7H_7^+$ ion, and, as a consequence, this formulation of the $C_7H_7^+$ ion has been widely accepted and taught, being included in the basic mass spectrometry taught in many chemistry courses at the college level.[300]



53

Recent double-labeling ^{13}C studies[274,275] indicate that in equilibrating among structures the carbon atoms lose all positional identity with respect to each other. This evidence, in addition to the earlier observations of *complete* hydrogen scrambling in decomposing $C_7H_7^+$ ions from toluene and various other C_7H_8 isomers including cycloheptatriene, may be explained in various ways. Three of these are illustrated in Scheme XIV. In pathway A, proposed initially by Harrison,[301] the toluene molecular ion isomerizes irreversibly to the molecular ion of cycloheptatriene (transfer of an α-hydrogen to the adjacent ring carbon atom, followed by insertion of the methylene group at random between any two ring carbon atoms). Scrambling of carbon as well as hydrogen atoms is accounted for by the random insertion, although it is possible that some carbon scrambling could have occurred independently by the valence tautomerism discussed in the previous section. PMO calculations[277] indicate that the stability of the toluene molecular ions may not be greatly different from that of the cycloheptatriene molecular ion, so this pathway is not unreasonable on energetic grounds. In pathway B, suggested by Meyerson,[302] the toluene molecular ion and the other isomers studied rearrange to a common $C_7H_8\cdot^+$ structure of high symmetry represented as **54**. In the third pathway C the toluene molecular ion retains its structural integrity, and the carbon scrambling results are accounted for by rapid equilibration between benzyl and cycloheptatriene forms of the $C_7H_7^+$ ion.

SCHEME XIV



A distinction between these pathways may be made in principle by an analysis of the extent of hydrogen scrambling with varying ion lifetimes. Both pathways A and C involve stepwise randomization processes, while pathway B, proceeding through a symmetrical intermediate, demands complete hydrogen randomization in all ions fragmenting by this route. Indeed, analysis of the relative losses of H and D from deuterium-labeled toluenes[303-305] has shown that the extent of hydrogen scrambling in deuterated toluenes decreases with increasing internal energy, indicating clearly that some, if not all, of the decompositions must proceed through a pathway that does not involve a symmetrical $C_7H_8\cdot^+$ ion. However, those $C_7H_7^+$ ions which are formed without scrambling must then scramble relatively rapidly by isomerization or during decomposition to form $C_5H_5^+$, since complete scrambling was observed prior to the formation of this ion.[305] These results are supported and extended by an icr study of toluene and various isomers.[306] In this study it was shown that the undecomposed toluene molecular ion retained its structural integrity and that no rearrangement, at least to cycloheptatriene, took place within the molecular ion in the ion–molecule reactions investigated. It thus appears that the scrambling reactions observed must take place in the $C_7H_7^+$ ion (or in its formation from the toluene molecular ion), rather than at the level of the $C_7H_8\cdot^+$ ion itself.

A study of the structure and formation process of the $C_7H_7^+$ ion generated by gas-phase radiolysis of toluene has recently appeared.[307] Studies of the methyldiphenylmethane products from irradiation of labeled toluenes indicated that only about a third of the $C_7H_7^+$ ions leading to the formation of these products were formed from a symmetrical intermediate. The difference between this result and the results for $C_7H_7^+$ ions formed on electron impact[304] may be explained by differing internal energies of the ions involved.

Other studies of hydrogen loss from toluene have appeared,[308-310] and the existence of two states of the toluene molecular ion decomposing to give $C_7H_7^+$ has been proposed[311-313] and challenged.[38] Studies of the spectra of various isomers of toluene have appeared; as previously mentioned, hydrogen scrambling occurs in cycloheptatriene,[302,306] and energetic studies on this compound were interpreted to support a formulation of the $C_7H_8\cdot^+$ ion as having a common structure from it and

(298) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

(299) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954).

(300) See, for example, R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Boston, Mass., 1966, p 451.

(301) F. Meyer and A. G. Harrison, *J. Amer. Chem. Soc.*, **86**, 4757 (1964).

(302) S. Meyerson, *J. Amer. Chem. Soc.*, **85**, 3340 (1963).

(303) F. W. McLafferty and H. D. R. Schuddemage, *J. Amer. Chem. Soc.*, 1866 (1969).

(304) I. Howe and F. W. McLafferty, *J. Amer. Chem. Soc.*, **92**, 3797 (1970); I. Howe and F. W. McLafferty, *ibid.*, **93**, 99 (1971).

(305) S. Meyerson, *J. Chem. Phys.*, **34**, 2046 (1961).

(306) M. K. Hoffman and M. M. Bursey, *Tetrahedron Lett.*, 2539 (1971).

(307) Y. Yamamoto, S. Takamuku, and H. Sakurai, *J. Amer. Chem. Soc.*, **94**, 661 (1972).

(308) J. G. Burr and R. A. Meyer, *J. Chem. Phys.*, **40**, 2046 (1964).

(309) M. Vestal and G. Lerner, "Fundamental Studies Relating to the Radiation Chemistry of Small Organic Molecules," Aerospace Research Laboratory Report 67-0114, U. S. Defense Documentation Center, Alexandria, Va., 1967.

(310) J. H. Beynon, J. E. Corn, W. E. Baitinger, R. M. Caprioli, and R. A. Benkeser, *Org. Mass Spectrom.*, **3**, 1371 (1970).

(311) F. Meyer and A. G. Harrison, *J. Chem. Phys.*, **43**, 1778 (1965).

(312) C. Lifshitz, *J. Chem. Phys.*, **47**, 1870 (1967).

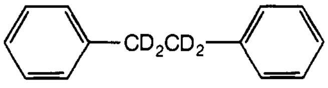
(313) A. G. Harrison, T. W. Shannon, and F. Meyer, *Advan. Mass Spectrom.*, **3**, 377 (1966).

from toluene,[298] although this conclusion needs to be evaluated in the light of the icr evidence previously discussed. Other compounds with similar spectra—which suggest scrambling to attain a common intermediate—include spiro[2,4]heptadiene-1,3,[314] norbornadiene,[315-317] 1-ethynylcyclopentene,[315,316] 3-ethynylcyclopentene,[315,316] hept-3-yne-1,5-diene,[318] quadricyclene,[319] methylfulvene,[320] and spiro[3,3]heptadiene-1,5.[321]

Other sources of $C_7H_7^+$ besides a C_7H_8 have been examined with the aid of labeling. Scrambling occurs in the $C_7H_7^+$ ion from benzyl chloride,[332,326] benzyl alcohol,[322,326,327] hepta-2,4-dien-6-yn-1-ol (**55**),[323] 1,1′-divinylferrocene,[324] the benzyl radical,[325] diphenylethane,[326] and hydrocinnamaldehyde.[271] In the case of diphenylethane, for example, isotopic distributions of $C_5H_5^+$ ions in the spectrum of diphenylethane-α,β-d_4 (**56**) imply complete loss of positional identity in the $C_7H_7^+$ ion, consistent with a tropylium structure.[326] A study of the energetics of formation of the $C_7H_7^+$ ion from benzyl chloride and 1-chlorohepta-2,4-dien-6-yne indicated that these ions have comparable energies and thus possibly similar structures.[328]

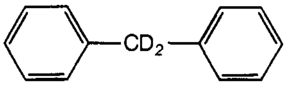
$CH{\equiv}CCH{=}CHCH{=}CHCH_2OH$

55

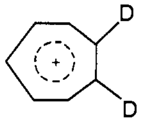


56

Not all ring expansions involve hydrogen scrambling subsequently, however. Thus data from the spectrum of diphenylmethane[326] indicate that ring expansion occurs from the α-d_2 species (**57**) to give a tropylium-*1,2*-d_2 intermediate (**58**). Similarly, the $C_7H_7^+$ ion from ethylbenzene-β-d_2 is formed without hydrogen rearrangement, although hydrogens are scrambled during subsequent decompositions of this ion.[293]

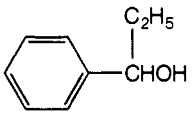


57

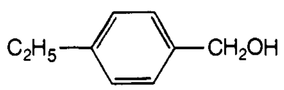


58

Ring expansion of hydroxyl-substituted toluenes presumably also occurs, since hydrogen scrambling precedes hydrogen loss from 1-phenylethanol.[328a] Not all $C_7H_7O^+$ ions necessarily have the hydroxytroplium structure, however, since studies of the energetics of ion formation have indicated that the $C_7H_7O^+$ ions from benzyl alcohol and hepta-2,4-dien-6-yn-1-ol are dissimilar.[328] Likewise the $C_7H_7O^+$ ions from **59**a and **59**b are dissimilar.[328]



59a



59b

Homologs of the tropylium ion also exist, as might be expected. Thus labeled xylenes have been shown to undergo scrambling of hydrogen consistent with a symmetrical structure,[329] while the complex loss of $CH_3\cdot$ from deuterated methylethylbenzenes can also be explained in terms of ring-expanded intermediates.[301] A number of substituted spiroheptadienes and methylcycloheptatriene gave very similar spectra to those of the xylene isomers and suggest that scrambling occurs in these species to attain a common structure.[330] Steric effects may affect the rearrangement, however, and it appears that such an effect operates in polymethylbenzenes to preclude rearrangement and hydrogen scrambling.[331] A methyl group flanked by two other methyls undergoes no hydrogen exchange before being lost. This result may be accommodated in terms of steric inhibition of the formation of a norcaradiene- or cycloheptatriene-type structure.

In spite of the seeming near-ubiquity with which ring expansion occurs in toluene and some other alkylated benzenes, there are many examples of substituted toluenes in which ring expansion does not occur. The first indication that this could be the case came from measurements of the ionization potentials of substituted benzyl radicals, which gave a Hammett correlation. This would be unlikely if isomerization occurred to a tropylium structure in which the effects of para and meta substituents would be the same.[332] The ionization of benzyl radicals, however, does not correspond to the situation in most studies of substituted toluenes, in which the compound must have an internal energy sufficient to break the CH-X bond. If the activation energy for CH_2-X bond cleavage is less than the internal energy required for rearrangement, then $YC_7H_6^+$ ions formed at the threshold should be formed by path A (Scheme XV) and should possess the benzyl structure. If, however, C-X bond cleavage requires a higher energy than the rearrangement, rearrangement will precede cleavage (path B) to give a tropylium ion. In either case, subsequent fragmentation by loss of C_2H_2 can involve rearrangement since this is a reaction requiring a fairly high internal energy.

The foregoing discussion suggests that rearrangement of substituted toluenes should be a sensitive function of both the energy required to break the C-X bond and the nature of any substituent Y. That the former factor is important is suggested by the previously mentioned observation that toluene yields a $C_7H_7^+$ ion in which the hydrogens are completely scrambled, while the $C_7H_7^+$ ion from ethylbenzene retains the identity of the hydro-

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(314) V. Hanuš, *Nature (London)*, **184**, 1796 (1959).

(315) V. Hanuš and Z. Dolejšek, *Jaderna Energie*, **6**, 350 (1956).

(316) V. Hanuš and Z. Dolejšek, *Kernenergie*, **3**, 836 (1960).

(317) S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Amer. Chem. Soc.*, **83**, 1401 (1961).

(318) A. A. Polyakova and A. A. Petrov, *Zh. Obshch. Khim.*, **31**, 3513 (1961).

(319) Z. Dolejsek, V. Hanus, and H. Prinzbach, *Angew. Chem.*, 74, 902 (1962).

(320) V. Hanus and Z. Dolejsek, *Collect. Czech. Chem. Commun.*, **28**, 652 (1963).

(321) J. P. M. Houbiers, L. A. Hulshof, and H. Wynberg, *Chem. Commun.*, 91 (1969).

(322) S. Meyerson, P. N. Rylander, E. L. Eliel, and J. D. McCollum, *J. Amer. Chem. Soc.*, **81**, 2606 (1959).

(323) R. T. Aplin and S. Safe, *Can. J. Chem.*, 47, 1599 (1969).

(324) D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, **90**, 973 (1968).

(325) R. F. Pottie and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 2634 (1961).

(326) S. Meyerson, H. Hart, and L. C. Leitch, *J. Amer. Chem. Soc.*, **90**, 3419 (1968).

(327) E. L. Eliel, J. D. McCollum, S. Meyerson, and P. N. Rylander, *J. Amer. Chem. Soc.*, **83**, 2481 (1961).

(328) H. Schwarz and F. Bohlmann, *Tetrahedron Lett.*, 1899 (1972).

(328a) N. M. M. Nibbering and T. J. de Boer, *Org. Mass. Spectrom.*, 1, 365 (1968).

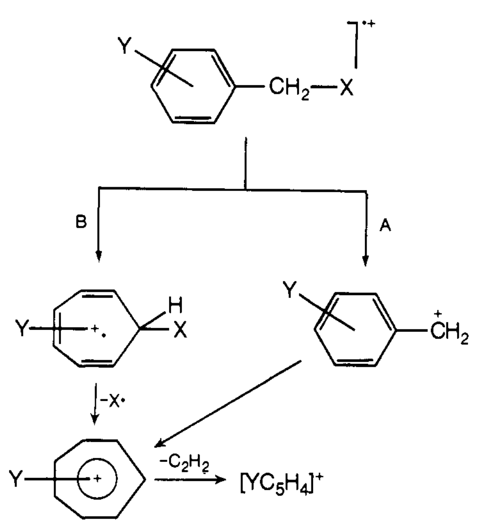
(329) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1968).

(330) F. Meyer, P. Haynes, S. McLean, and A. G. Harrison, *Can. J. Chem.*, **43**, 211 (1965).

(331) S. Meyerson and E. K. Fields, *Org. Mass Spectrom.*, **2**, 1309 (1969).

(332) A. G. Harrison, P. Kebarle, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 777 (1961).

SCHEME XV

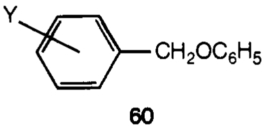


gens.[259] This is in line with expectations from the activation energy for the loss of hydrogen from toluene (2.8 eV) and the loss of methyl from ethylbenzene (2.3 eV), and suggests that the activation energy for rearrangement is within the range of 2.3–2.8 eV.[333] Further evidence along the same lines comes from a study of some fluoro *n*-alkylbenzenes.[334] In this study application of the appearance potential differences method to ions formed at the threshold from *m*- and *p*-fluoroalkylbenzenes led to the conclusion that the $FC_7H_6^+$ ion had the benzyl structure at threshold when generated from propyl, amyl, hexyl, and possibly ethyl isomers. In agreement with the earlier work cited, this method suggested a symmetrical structure for the $FC_7H_6^+$ ions from fluorotoluene and also, and as yet inexplicably, for this ion from fluoroheptylbenzene.

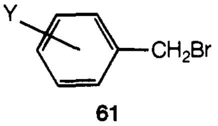
The importance of any substituent on the occurrence of ring enlargement is indicated by the fact that studies of appearance potentials,[266,335,336] and wide-range energy kinetics,[287,288] all indicate that ions formed at the threshold by loss of H· from substituted toluenes have benzylic structures in the case of methoxy,[335] methylthio,[336] ethoxy,[326] chloro,[289] and bromo[288] cases, but ring-expanded structures in the case of methyl, fluoro, and hydroxy substituents.[335] The situation is a little different when different routes of formation of the $YC_7H_6^+$ ion are employed, or when different techniques are used to examine the ion. Thus a study of the spectra of various halotoluenes indicated that loss of the halogen is preceded by ring expansion in the case of the fluoro and chloro compounds but not in the case of the bromo and iodo compounds.[333] Very recent work, however, involving a study of isotope effects on bromine *vs.* methyl loss from *p*-bromethylbenzene, suggests that this compound loses bromine from a rearranged (tropylium) structure.[336a] This result need not conflict with the situation in the halotoluenes, since these were studied by reactions occurring in ions of high internal energy, while *p*-bromoethylbenzene was studied by low-energy reactions occurring in the field-free region of the mass spectrometer, thus favoring rearrangement over simple bond cleavage. Be this as it may, it is possible to correlate the original results with the activation energy for halogen loss (Table VI), suggesting that the internal energy needed for ring expansion is actually in the range 2.5–2.8 eV. Similarly, studies of benzyl phenyl ethers (**60**), in which the $CH_2–OC_6H_5$ bond is more readily broken than the $CH_2–H$ bond of toluenes, were carried out by the wide-range electron energy kinetic approach. These studies implicated the formation of a substituted tropylium ion for the methyl, fluoro, chloro, bromo, and trifluoromethyl substituents, but benzyl for the methoxy and nitro groups.[287,291,337] Comparisons of further decomposition of the two amino compounds in this series,[338] and of the ion $O_2NC_7H_6^+$ from the phenyl ether (**60**) and bromide (**61**),[339] suggest that rearrangement has not occurred at the point of decomposition of these ions, contrary to an earlier suggestion in the case of the nitro compound,[337] but in agreement with later findings.[291] Similarly, nitroalkylbenzenes give evidence of being benzylic.[340]

TABLE VI. Activation Energy (AP − IP) for Loss of X from MeC_6H_4X

X	AP − IP, eV	Ring expansion
Cl	2.8	Yes
Br	2.4	No
I	2.4	No



60



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Wide-range electron energy studies have also been carried out on substituted ethylbenzenes,[289] with metastable characteristics of isomers included as well for diagnosis. In this case, benzyl structures were determined for the $[M - CH_3]^+$ ions formed from amino- and methoxy-substituted compounds, but tropylium structures from hydroxy, methyl, fluoro, chloro, bromo, and trifluoromethyl substituents. These results differ somewhat from conclusions drawn from comparing activation energies for the loss of methyl from ethylbenzenes;[341] the latter measurements implicated the cyano- and fluoro-substituted compounds as having different structures at the threshold, in addition to the amino- and methoxy-substituted derivatives. Some resolution of the discrepancy can be made on the basis of different structures at threshold and above threshold. In the same study,[341] retention of structural distinguishability was observed for all isomers of substituted *tert*-butylbenzenes.

Other studies of ring enlargement have been carried out on the butylbenzenes,[342,343] diphenylethanes,[344,345] π-substituted toluene,[346] and *p*-aminotoluene,[347] and the

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(333) A. N. H. Yeo and D. H. Williams, *Chem. Commun.*, 886 (1970).

(334) S. Majeti and D. A. Lightner, *Tetrahedron Lett.*, 1683 (1970).

(335) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *J. Amer. Chem. Soc.*, **84**, 4 (1962).

(336) F. Meyer and A. G. Harrison, *Can. J. Chem.*, **42**, 1762 (1964).

(336a) I. Howe, N. A. Uccella, and D. H. Williams, submitted for publication.

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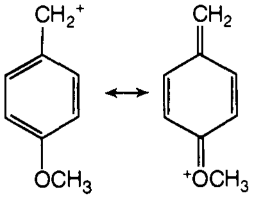
wide-range electron energy kinetic technique has been reviewed.[291]

In view of the accumulated evidence that methoxy- and nitro-substituted toluenes, at least, give benzylic $YC_7H_6^+$ ions, it is natural to inquire as to the reason for this. At the present time no satisfactory answer is available. For Y = OCH_3, resonance structures such as **62** undoubtedly stabilize the para isomer, but such resonance is not possible for the meta isomer (which also has the benzylic structure) nor for the nitro-substituted ions (unless they have rearranged (**63** → **64**)). The question must thus remain open until further studies have been made.



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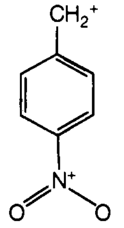

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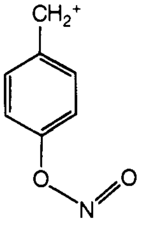
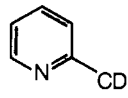


64

The formation of the tropylium ion in field-ionization mass spectrometry has recently been discussed.[348] In contrast to the situation commonly observed in electron-impact mass spectrometry, the authors propose that rearrangement to the tropylium ion proceeds *via* the benzyl cation in field-ionization fragmentation of ethylbenzene, *sec*-butylbenzene, and various other substituted toluenes, although toluene itself was not included in this study.

Returning to electron-impact studies, evidence is available that ring expansion occurs in various polycyclic and heterocyclic derivatives of toluene. Thus the spectra of 2- and 4-methylpyridines specifically deuterated in the methyl group (**65** and **66**) have been examined for evidence of scrambling between methyl and ring hydrogens.[224] Almost complete hydrogen scrambling occurs in the molecular ion before expulsion of HCN (DCN), although there may be a preference for loss of the 2-hydrogen in this reaction in 4-methylpyridine (**66**).[349] The possibility thus exists that the molecular ion of the methylpyridines ring-expands to a seven-membered ring azepinium ion (**67**), with subsequent hydrogen scrambling, at least prior to loss of H and/or HCN. CH_3 elimination, which proceeds with scrambling at low energies, may take place following ring contraction, or alternatively scrambling could take place over the whole molecule without destruction of the methylpyridine skeleton.



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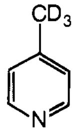

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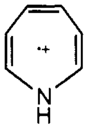
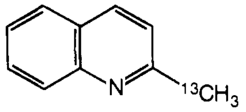


67

Evidence for both hydrogen scrambling over two rings and possible expansion to a seven-membered ring has been obtained from studies of methyl-[350,351] and dimethylquinolines.[352] Before loss of a hydrogen atom in the source, the hydrogens of the molecular ions of the monomethylquinolines had scrambled (partially or completely) over both rings. The spectrum of 2-methylquinoline-2-^{13}C (**68**) revealed an 85% retention of ^{13}C in the M − H_2CN ion, while a random insertion of ^{13}C between any carbon–carbon or carbon–nitrogen bond of the whole molecule predicts 86% ^{13}C retention in the M − H_2CN ion.[351] Similar studies with 1-methylisoquinoline-*1*-^{13}C (**69**) and related compounds suggest that ring expansion occurs extensively prior to the formation of the M − H_2CN ions in this series also.[353]



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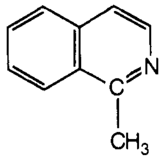

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Ring-expansion processes have been proposed, generally on an intuitive basis, for the fragmentations of various other alkylated heteroaromatic systems including furans,[354] benzofurans,[355] pyrroles,[353,356,357] indoles,[358] thiophenes,[359,360] and benzothiophenes.[361] A recent monograph lists further examples of heterocyclic compounds which are postulated to undergo ring expansion.[362]

Ring expansion to the azepinum ion (**66**) could also in principle take place during fragmentation of aniline. However, as outlined in the preceding section, ^{13}C-labeling evidence shows that the majority of decomposing molecular ions are unrearranged. There is evidence, however, for considerably greater rearrangement in the even-electron $(M - H)^+$ ion.[280] Ring expansion may also be important in the hydrogen scrambling of various other substituted benzenes, as discussed in the preceding section. Thus diphenyl ether,[278] diphenyl sulfide,[273] and thiophenol[279] all undergo carbon randomization which could be accounted for by ring expansion.

Returning to the question of the $C_7H_7^+$ ion and its homologs, it should be noted that in spite of the sensitive dependence of the ring-expansion process on energy content of the ion, substituents on the ring, and the nature of the group lost to form the benzyl or tropylium ion, it is frequently assumed that every ion capable of ex-

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panding to a substituted tropylium ion does in fact expand before further decomposition, in the absence of evidence one way or the other. Biemann summarized the situation in a review of analogous situations: "The justification for writing this ring expansion is the prettiness of the resulting ion."[363]

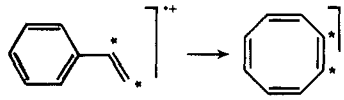
Perhaps the most likely of these untested cases are those in which unsubstituted $C_7H_7^+$ ions are formed. Intriguing examples of hydrocarbons which give prominent ions of the correct mass are 2,5,5-trimethylhex-1-en-3-yne,[364] several monoterpenes,[92] 1,4-diphenylbutadiene,[365] nona-1,5-diyne,[366] congressane,[367] and norbornadiene dimers.[368] The $C_7H_7^+$ ion is also formed from a number of functionally substituted compounds; again, there appears to be no evidence against ring expansion in cases of this type which have actually been studied by labeling. Some of these include the benzyl group in the original molecule: methyl phenylpentanoates,[369] phenylalanine,[370] benzylhydrazine,[371] phenylalkyloxazolidones,[372] *N*-benzyldihydropyridines,[373] glucosides,[374] steroidal amines,[375] alkaloids,[376] metal chelates,[377] and metal complexes such as $C_5H_5Fe(CO)_2CH_2C_6H_5$.[378] Other functionally substituted molecules which form $C_7H_7^+$ from other carbon skeletons include the 7-[379] and 2-substituted[380] norbornenes, nortricyclyl chloride,[380] phenyl ω-styrylalkyl ketones,[381] *p*-tolyltrifluoroacetamide,[382] monoterpene aldehydes and ketones,[383] a phenyldecalone and phenyldecalin,[384] diphenylcyanocyclopropane,[385] styrylpyrones,[386] glycidic esters and amides,[387] and *p*-toluenesulfonic acid;[388] examples where the carbon skeleton itself must be formed from isolated parts of the molecule are found in spectra of esters of phenylboronic acid,[389] silane derivatives such as $(CH_3)_3SiOC_6H_5$,[390] and phenyl-substituted cyclodisilazanes.[391]

In view of the effect of substituents on formation of tropylium, there is little security in postulating ring expansion to substituted tropylium ions. The risk is perhaps not quite as great in postulating alkylated tropylium ions, as has been done for ions in the spectra of some fulvene derivatives[392] and unsaturated secondary alcohols.[393] On the other hand, the formation of phenyltropylium,[394] phenylthio- and phenoxytropylium,[395] hydroxytropylium,[396-399] boranyltropylium,[400] alkyldimethoxytropylium,[401] isoxazolidinyltropylium,[402] tetrafluorotropylium,[403] and pentafluorotropylium ions[404] is very likely a function of the structure from which the substituted ions are formed. Tropylium ions ring-fused to other cycles of different sizes have been postulated, but there seems to be little evidence on their behalf other than the mass of the ion.[405-409]

Ring expansion was shown not to occur in the ion $C_6H_5SiH_2^+$,[157d] but it is possible that ring expansion may occur in some trialkylborazines, although detailed energetics data to substantiate this are not available.[409a]

C. Rearrangements in Phenyl-Substituted Alkenes and Alkynes

Hydrogen scrambling in styrene was mentioned in section III.C, where the results of both deuterium[256] and ^{13}C labeling[257] were cited. The ^{13}C evidence suggests that ring expansion to a cyclooctatetraene structure (eq 37) occurs only in ions of long lifetime and low energy, and even then the original side-chain atoms remain linked together. Scrambling in most of the molecular ions must



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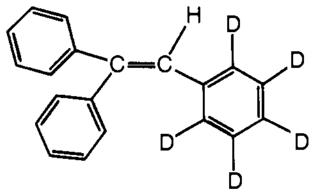
thus involve alternate pathways with hydrogen atoms migrating over a presumably intact carbon skeleton. Stilbene (**34**) likewise undergoes complete randomization of hydrogens before the $[M - H]^+$ ion is formed at 15 eV, and also undergoes a fragmentation involving the loss of a methyl group. This latter fragmentation has been the source of some controversy in the literature, with the scrambling of atoms before loss of $CH_3\cdot$ variously claimed to involve complete H and C scrambling[258] and the vinyl carbon with its hydrogen plus one ortho hydrogen of each phenyl ring.[259] Recent results[260-262] have extended these findings and have been interpreted in terms of two mechanisms for loss of $CH_3\cdot$, with the major loss occurring from a completely scrambled molecular ion and minor loss originating from the phenyl rings with participation of the hydrogens of the olefin unit. Two mechanisms are also indicated for loss of methyl from 1,1-diphenyl-2-(*phenyl*-d_5)ethylene (**70**), since losses of both $CH_3\cdot$ and $CH_2D\cdot$ are observed.[410] In the spectrum of 1,3-diphenylpropene (**71**), the loss of $CH_3\cdot$ involves the central carbon of the propylene chain plus rearranged hydrogens; the loss of C_2H_3 involves C-1, C-2, their hydrogen atoms, and one from the ortho position of the 3-phenyl group, after equilibration of the center double bond between positions; the loss of $C_2H_5\cdot$ involves C-2, C-3, their attached hydrogens, and (for some ions) both ortho hydrogens from the 3-phenyl ring or (for the remainder) one ortho hydrogen from each ring, two mechanisms being involved.[411] Hydrogen loss patterns of stilbene and other compounds have been analyzed in terms of the principles of the conservation of orbital symmetry.[412] These and related reactions will be discussed in section III.E.



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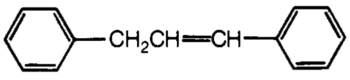


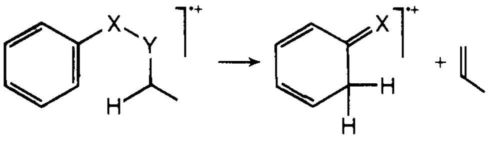
71

Not unexpectedly, hydrogen rearrangements occur commonly in the fragmentation of various 1-phenylheptenes.[413] Mechanisms postulated include 1,2-H shifts, 1,3-H shifts, and phenyl migration. Hydrogen randomization was also observed between the ortho position of the ring and the alkyl chain. Hydrogen scrambling also occurs in various phenylacetylenes,[263-265] as was observed previously in section III.A.

The $C_{12}H_8\cdot^+$ ions from phenanthrene, anthracene, and diphenylacetylene have been shown to give the same decomposition products.[413a] If these ions have the same structure (*e.g.*, biphenylene), then hydrogen rearrangement must be involved in their formation from at least some precursors.

D. Rearrangement of Side-Chain Hydrogens to an Aromatic Ring

Aromatic molecules substituted with a side chain of the general form shown below undergo a β-cleavage reaction with hydrogen transfer to the aromatic portion of the molecule. A number of pathways may be suggested for this reaction, for example, eq 38 and 39. While rearrangement by pathway 38 bears some formal similarities to the McLafferty rearrangement, to be discussed in the second part of this review, the possible duality of mechanism of the rearrangement makes it convenient to treat it separately at this point. We shall discuss the rearrangement by compound type, beginning with the alkylbenzenes.



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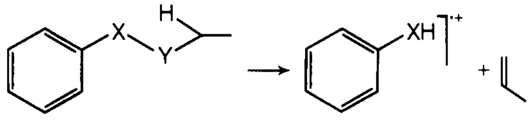

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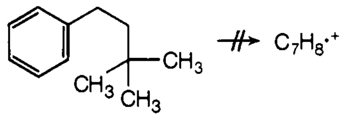
Rearrangement of alkylbenzenes involving β cleavage with return of a hydrogen atom to the aromatic portion of the molecule was observed in 1955.[414] Labeling studies on the reaction in 1-phenylbutane indicated that the $C_7H_8\cdot^+$ ion formed required transfer of H from the γ position, since the compound labeled in this position transferred 95% D.[415] The absence of significant rearrangement in 3,3-dimethyl-1-phenylbutane (eq 40) indicated that at least one γ hydrogen is required for rearrangement.[415]



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The mechanism of the hydrogen rearrangement has been the subject of considerable research. In the light of the labeling evidence reported, either pathway 38, yielding an ionized methylene cyclohexadiene ion, or pathway 39, yielding an ionized toluene molecular ion, could be correct. The weight of evidence is strongly in favor of the first mechanism, as the following discussion will show.

Studies of steric effects on the rearrangement showed that it does not proceed if both ortho positions are substituted. Thus 2,4-dimethyl-1-octadecylbenzene (**72**) gives an intense rearrangement ion, whereas no rearrangement ion is observed with the 2,4,6-trimethyl compound (**73**), suggesting that steric hindrance to hydrogen transfer effectively stops the reaction. Very little steric hindrance would be expected for rearrangement by path 39, of course.[416] Substituent effects on the rearrangement show a reasonably good correlation with Hammett substituent constants for substituents in the meta position, but those in the para position show a wide scatter.[417] The reaction is strongly favored by a *m*-amino group but suppressed

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(409a) P. Powell, P. J. Sherwood, M. Stephens, and E. F. H. Brittain, *J. Chem. Soc. A*, 2951 (1971).

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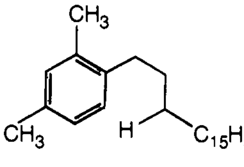
by a *p*-amino group and thus appears to be related by simple molecular orbital theory to the electron density provided by having the unpaired electron of the molecular ion in the highest occupied molecular orbital, *i.e.*, the ground electronic state of the ion.[343] These results have been interpreted to implicate reactivity of the ortho position as a "driving force" for the reaction, but it is not certain if substituent effects alter reactivity in a way which clarifies or obscures the reactivity of the unsubstituted compound.



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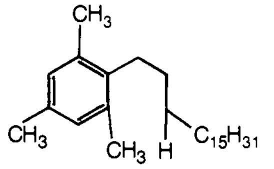


73

Evidence that the product of the rearrangement does not have the toluene structure is provided from two lines of work. In the first place, the energy requirements for the further decomposition of the $C_7H_8\cdot^+$ ion differ from those of toluene.[418] Secondly, and most compellingly, the $C_7H_8\cdot^+$ ion does not undergo an ion-molecule reaction characteristic of ionized toluene, the abstraction of NO_2 from neutral alkyl nitrites.[419] It thus seems clear that rearrangement proceeds *via* pathway 38, at least to the extent of 95% or greater. A recent detailed study of the specificity of the rearrangement[420] supports this conclusion and adds the interesting observation that extensive H–D exchange occurs between hydrogen (deuterium) atoms in the alkyl chain and the ortho ring hydrogen (deuterium) atoms.

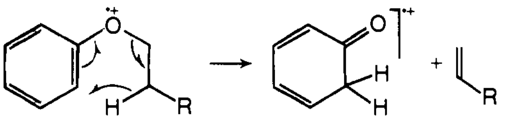
Entirely analogous rearrangements occur in the spectra of other alkylated aromatic compounds and also in the spectra of various aralkyl compounds with a functional group. Examples of compounds undergoing these rearrangements are summarized in Table VII. It should be mentioned that in some cases listed in the table rearrangement probably occurs to an atom of the aromatic ring other than carbon, thus strengthening the analogy to the McLafferty rearrangement.

TABLE VII. Side-Chain Rearrangements of Various Aralkyl Compounds

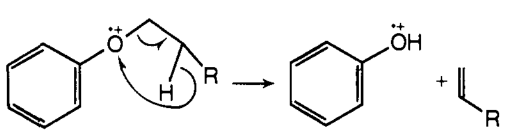
Compound	Ref	Compound	Ref
9-Alkylphenanthrenes	183	Alkylated 4-pyrimidones	*g*
Alkylphenols	*a*	Alkylated oxoquinazolines	*h*
4-Isobutylquinoline	*b*	Alkylated benzotriazinones	*i*
2-*n*-Butylquinoline	c	Alkylsydnones	*j*
Butylpyridines	*d*	2-Phenylethanol	*k*
Alkylbenzimidazoles	*e, f*		

[a] J. L. Occolowitz, *Anal. Chem.*, **36**, 2177 (1964). [b] T. S. Muraski and C. Djerassi, *J. Org. Chem.*, **33**, 2962 (1968). [c] F. R. Stermitz and C. C. Wei, *J. Amer. Chem. Soc.*, **91**, 3103 (1969). [d] D. A. Lightner, R. Nicoletti, G. B. Quistad, and E. Irwin, *Org. Mass Spectrom.*, **4**, 571 (1970). [e] S.-O. Lawesson, G. Schroll, J. H. Bowie, and R. G. Cooks, *Tetrahedron*, **24**, 1875 (1968). [f] T. Nishiwaki, *J. Chem. Soc. C*, 428 (1968). [g] T. Kato, H. Yamanaka, H. Ichikawa, T. Chiba, H. Abe, and S. Sasaki, *Org. Mass. Spectrom.*, **4**, 181 (1970). [h] C. Bogentoft and B. Danielsson, *Acta Pharm. Suecica*, **7**, 257 (1969). [i] J. C. Tou, L. A. Shadoff, and R. H. Rigterink, *Org. Mass. Spectrom.*, **2**, 355 (1969). [j] R. S. Goudie, P. N. Preston, and M. H. Palmer, *ibid.*, **2**, 953 (1969). [k] H. E. Audier, H. Felkin, M. Fetizon, and W. Vetter, *Bull. Soc. Chim. Fr.*, 3236 (1965).

Aryl alkyl ethers also show loss of the alkyl group with transfer of one hydrogen to either the aromatic ring or the oxygen atom (eq 41a and 41b).[68,421] In contrast to the situation with the aralkyl compounds just discussed, however, this rearrangement is not site specific. Thus in phenyl *n*-butyl ether the hydrogen transferred to the aromatic portion of the molecule was shown to originate in part from each position of the butyl chain.[422] In principle this observation could be explained either by postulating a certain amount of hydrogen scrambling in the alkyl chain prior to fragmentation, or by the occurrence of transition states of different ring sizes. A decision between these two possibilities was made on the basis of the fact that an increased specificity for rearrangement from the 3 position was observed in ions of low internal energy undergoing metastable decompositions, thus suggesting that the second explanation above is the correct one.[423]



(41a)



(41b)

The question of the mechanism of the rearrangement in aryl alkyl ethers (eq 41a or 41b) is obviously complicated by the lack of specificity noted above, and in fact both mechanisms have had support. Further complications are introduced by the possibility of substituent isomerization (section A), and in fact it was originally postulated on the basis of substituent effects that the loss of ethylene from phenyl ethyl ethers leads to the same ion whether the substituent is meta or para to the ethoxy group.[424] It was later noted that further decompositions of the ions are different,[425] and that in fact there are rather slight differences in the rates of formation of the ions thought to be formed from a common structure from the meta and para isomers.[426] It thus appears that the complication of substituent isomerization can safely be ignored, at least to a first approximation. An argument for rearrangement of phenyl alkyl ethers by pathway 41b that has been advanced is that the product ion behaves in the same way as phenol. Thus further decomposition of this ion is by loss of CO, as in the case of phenol, and decomposition both from phenol and the rearrangement ion yield flat-topped metastable peaks of identical width and abundance.[424] The decompositions of phenol and the rearrangement ion from phenetole by loss of CO have been compared at different ionizing energies and the results explained qualitatively in terms of the quasi-equilibrium theory, implicitly accepting the phenol structure for the decomposing ions.[427] In phenyl-1-^{13}C butyl ether, the ev-

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(418) Reference 259, pp 516–519.

(419) M. M. Bursey, M. K. Hoffman, and S. A. Benezra, *J. Chem. Soc. D*, 1417 (1971).

(420) D. A. Lightner, G. B. Quistad, and E. Irwin, *Appl. Spectrosc.*, **25**, 253 (1971).

(421) H. J. Jakobsen, G. Schroll, S.-O. Lawesson, D. A. Lightner, A. M. Duffield, and C. Djerassi, *Ark. Kemi*, **26**, 199 (1966).

(422) J. K. MacLeod and C. Djerassi, *J. Amer. Chem. Soc.*, **88**, 1840 (1966).

(423) A. N. H. Yeo and C. Djerassi, *J. Amer. Chem. Soc.*, **94**, 482 (1972).

(424) F. W. McLafferty, M. M. Bursey, and S. M. Kimball, *J. Amer. Chem. Soc.*, **88**, 5022 (1966).

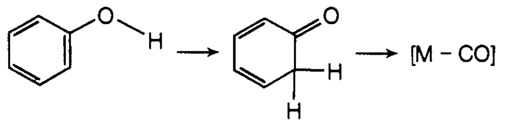
(425) R. H. Shapiro and K. B. Tomer, *Org. Mass. Spectrom.*, **2**, 579 (1969).

(426) F. W. McLafferty and L. J. Schiff, *Org. Mass Spectrom.*, **2**, 757 (1969).

(427) D. H. Williams, R. G. Cooks, and I. Howe, *J. Amer. Chem. Soc.*, **90**, 6759 (1968).

idence from labeling is that the $[M - C_4H_8]\cdot^+$ ion is structurally similar to the phenol molecular ion, since both decompose by loss of CO without carbon scrambling.[285]

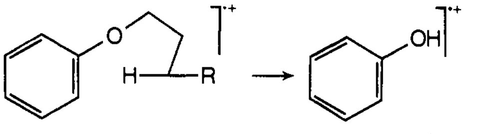
These arguments for the structure of the rearrangement ion all suffer from the defect that they relate only to ions decomposing by a further fragmentation. Since phenol itself is presumed to decompose by initial rearrangement to a cyclohexadienone structure (eq 42), it becomes a difficult but necessary task to distinguish between ions which rearranged to phenol *initially* and then decomposed *via* the cyclohexadienone pathway and ions which rearranged to a cyclohexadienone structure and decomposed further from this. This problem has been tackled in an ingenious way by a study of isotope effects on the fragmentation of phenol and the phenetole rearrangement product.[428] The observation of a similar isotope effect in the decompositions of the rearrangement ion from p-$BrC_6H_4OC_2D_5$ and of p-BrC_6H_4OD led to the conclusion that rearrangement does indeed yield the phenolic ion rather than the cyclohexadienone ion.



(42)

Precisely the opposite conclusion was reached in a study of the energetics of ion formation. A comparison of the measured heats of formation of the rearrangement ions from various alkoxybenzenes with that of the phenol molecular ion gave values for the former ions some 30 kcal/mol higher, suggesting that the rearrangement ions do not have the phenol structure.[429] However, the fragmentation reactions under consideration involved rearrangement, with elimination of a stable neutral, and these are conditions under which an appreciable kinetic shift and/or reverse activation energy might be anticipated. Hence this evidence does not necessarily exclude the phenolic structure for the rearrangement ion.

Further evidence for a six-membered transition state for the rearrangement, and therefore for a cyclohexadienone structure for the product ion, comes from a study of energy partitioning in phenetole and its fragment ions.[429a] This view finds some confirmation in the conclusions obtained by the study of the specificity of the rearrangement and subsequent fragmentation reactions at various internal energies previously mentioned.[423] The conclusion was drawn from this work that rearrangement involving hydrogen transfer from the 2 position of the butyl ether side chain probably proceeds by the mechanism indicated in eq 41a, while the low activation energy rearrangement from the 3 position probably proceeds by the pathway shown in eq 43.



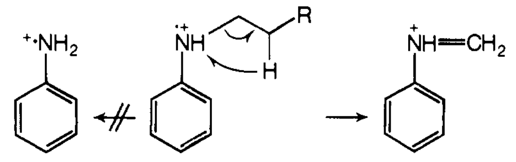
(43)

In conclusion, then, it appears that both pathways probably operate in the rearrangement of phenyl alkyl ethers, and the contribution of each pathway probably depends to a large extent on experimental conditions.

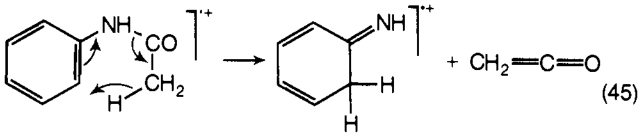
Rearrangements of a similar nature also occur, as might be expected, in the alkyl ethers of other aromatic compounds. A few examples will suffice to give the picture; rearrangement is observed in the alkyl ethers of thiophene,[421] anthracene,[429] quinazolines,[430] and naphthalene.[422]

Aryl alkyl sulfides also undergo a similar rearrangement[431] and the results of the limited studies that have been carried out on this system suggest that olefin elimination proceeds in a similar fashion to that in the ethers. Thus the spectrum of deuterium-labeled phenyl n-butyl sulfide indicated that site-specific deuterium transfer was not occurring in this compound either,[422] while energetic considerations suggest that the rearranged ion has the thioketone structure.[429] Examples of the rearrangement in various phenyl alkyl sulfides have been reported.[432]

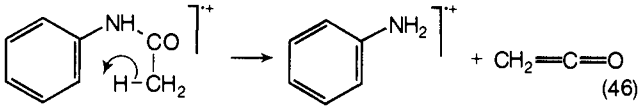
N-Alkylated aromatic amines, which might formally undergo an analogous rearrangement, in practice decompose almost exclusively by α-fission (eq 44), because of the effective stabilization of the positive charge by nitrogen. Rearrangement does occur, however, in various acylated anilines, such as acetanilide. This rearrangement (eq 45 and 46), leading to the loss of ketene, will be treated in more detail in Part III of this review.



(44)



(45)



(46)

At this point it will suffice to note that again two pathways (eq 45 and 46) are possible for this rearrangement, leading respectively to an ionized imine and ionized aniline as the product ions. Two lines of evidence suggest that the latter pathway is preferred. In the first place, a study of various methyl- and dimethylacetanilides showed that steric factors exert a negligible effect on the rate of the rearrangement, in contrast to the situation with the alkylbenzenes discussed previously.[433] In addition, substituent effects on the rearrangement are not greatly different for para- and meta-substituted acetanilides, a situation which would be surprising if rearrangement of a hydrogen atom took place to the benzene ring.[434,435] A novel substituent effect was observed with a highly electronegative substituent such as fluorine, however: the "frequency factor" for rearrangement became markedly smaller when the fluorine was moved from the para to the ortho position, although much smaller effects were observed for other halogens, and no effect was observed

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(428) I. Howe and D. H. Williams, *J. Chem. Soc. D*, 1195 (1971).

(429) R. G. Gillis, G. J. Long, A. G. Moritz, and J. L. Occolowitz, *Org. Mass Spectrom.*, 1, 527 (1968).

(429a) M. Bertrand, J. H. Beynon, and R. G. Cooks, 20th Annual Conference of the American Society for Mass Spectrometry, Dallas, Tex., 1972, Paper H3.

(430) T. J. Batterham, A. C. Triffett, and J. A. Wunderlich, *J. Chem. Soc. B*, 892 (1967).

(431) J. H. Bowie, S.-O. Lawesson, J. O. Madson, G. Schroll, and D. H. Williams, *J. Chem. Soc., B*, 951 (1966).

(432) L. R. Williams, *Aust. J. Chem.*, **21**, 2311 (1968).

(433) A. A. Gamble, J. R. Gilbert, and J. G. Tillett, *Org. Mass Spectrom.*, **3**, 1223 (1970).

(434) R. H. Shapiro and K. B. Tomer, *Org. Mass Spectrom.*, **2**, 279 (1969).

(435) A. A. Gamble, J. R. Gilbert, and J. G. Tillett, *J. Chem. Soc. B*, 1231 (1970).

(435a) S. A. Benezra and M. M. Bursey, *J. Chem. Soc. B*, 1515 (1971); M. M. Bursey and C. E. Parker, *Tetrahedron Lett.*, 2211 (1972).

TABLE VIII. Hydrogen Rearrangements in Miscellaneous Aromatic Compounds

Compound[a]	Fragment ion(s) formed[b] by rearrangement	Ref
Phenols, phenolic ethers		
Phenolic alkylamines	(M − CHO)	c
Methoxy naphthoquinones	(M − CHO)	*d*
Lignans	(M − CH_2O), (M − CO), (M − olefin)	*e*
Phenolic fusion products of Maesopsin	(M − CO), (M − CHO)	*f*
o-Hydroxybenzyl alcohol	(M − H), (M − H_3O)	509
Phenol	(M − CO), (M − CHO)	486
Thiophenols		
Thiophenols	(M − CH_3), (M − CS)	170, 492
Pentachlorothiophenol	(M − S)	*g*
Thioanisoles	(M − SH)	431, 482
Aromatic nitro compounds, etc.		
o-Nitroanisole	(M − CH_2O), (M − CH_2O − OH)	*h, i*
α,*N*-Diphenylnitrone	C_6H_5CO	*j*
Dinitronaphthalenes	(M − OH)	*k*
Nitrobenzenes	$^+$NOH	*l*
Nitroso compounds	(M − HCN)	*m*
Aromatic carbonyl derivatives	See text also	509
Benzyl phenyl ketoxime	(M − H_2O)	*n*
Benzophenone oxime	(M − O)	o
Aromatic ketones		
Benzyl phenyl ketone	(M − H_2O)	*l*
Aromatic amines, nitriles, etc.		
Aniline	(M − HCN)	*p*, 242
Phthalonitrile	(M − HCN)	*q*
Phthalocyanines	(M − HCN)	*q*
Aromatic amides, ureas, carbamates, etc.		
N,N-Dimethylbenzamide	(M − H)	*r*
Triphenylurea	(M − C_6H_5NCO)	s
Ethyl *N*-phenylcarbamate	(M − C_2H_4 − CO_2)	*t*
N-Phenylurea	C_6H_5NCO, $C_6H_5NH_2$	*u*
Sulfonylurea (tolbutamide)	$CH_3C_6H_4OH$	*v*
Sulfoxides and sulfones		
Diphenyl sulfoxide	(M − CHO)	*w*
Aromatic halides		
Fluorobenzene	Low mass hydrocarbon ions	*x*
Difluorobenzenes	Low mass hydrocarbon ions	*y*
Chlorobenzenes		290
Aromatic acids, esters	See text also	
Fluorophenylacetic acid	(M − CO_2)	*z*
Aryl trifluoroacetates	(M − CHO)	*aa*
Dibenzyl oxalate		*bb*
Heterocyclic compounds		
Carbazole	(M − C_2H_3), (M − H_2CN)	235
Dibenzothiophene	(M − CHS)	236
Dibenzo-*p*-dioxin	(M − CHO)	*cc*
Diphenylpyrazoles	$C_{13}H_9$	239
Diphenylisoxazoles	$C_{13}H_9$	239
Phenylpyrroles	$C_{13}H_9$	233
Thiazole, benzothiazole	(M − HCN)	213
Bis(aryl) compounds		
$C_6H_5SC_6H_5$	(M − CHS), (M − HS)	171
$C_6H_5N{=}NC_6H_5$		171
$C_6H_5OC_6H_5$	(M − CO), (M − CHO)	249
Azoxybenzenes	(M − CO)	*dd*
Miscellaneous compounds		
Benzalacetone	(M − H)	*ee*
Tropone	(M − OH)	*ff*
Phenoxarsines	(M − C_6H_5O)	*gg*

[a] Only one illustrative example of each class of compounds is given: the references cited should be consulted for detailed information on each class. [b] The major fragmentations involving hydrogen rearrangement are given, but other fragmentations may also involve hydrogen rearrangement. [c] J. Reisch, R. Pagnucco, H. Alfes, N. Jantos, and H. Mollman, *J. Pharm. Pharmacol.*, **20**, 81 (1968). [d] J. H. Bowie, D. W. Cameron, and D. H. Williams, *J. Amer. Chem. Soc.*, **87**, 5094 (1965). [e] A. Pelter, *J. Chem. Soc. C*, 1376 (1967). [f] J. H. Bowie and J. W. W. Morgan, *Aust. J. Chem.*, **20**, 117 (1967). [g] C. R. Lucas and M. E. Peach, *Can. J. Chem.*, **48**, 1869 (1970). [h] J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc. B*, 396 (1966). [i] O. A. Mamer, R. J. Kominar, and F. P. Lossing, *Org. Mass Spectrom.*, **3**, 1411 (1970). [j] T. H. Kinstle and J. G. Stam, *Chem. Commun.*, 185 (1968). [k] E. F. H. Brittain, C. H. J. Wells, H. M. Paisley, and D. J. Stickley, *J. Chem. Soc. B*, 1714 (1970). [l] J. Momigny, *Bull. Soc. Roy. Sci. Liege*, **25**, 93 (1956). [m] G. Schroll, R. G. Cooks, P. Klemmensen, and S.-O. Lawesson, *Ark. Kemi*, **28**, 413 (1968). [n] J. H. Bowie, B. K. Simons, P. F. Donaghue, and R. K. M. R. Kallury, *Tetrahedron*, **25**, 2969 (1969). [o] Reference 56, p 374. [p] P. N. Rylander, S. Meyerson, E. L. Eliel, and J. D. McCollum, *J. Amer. Chem. Soc.*, **85**, 2723 (1963).

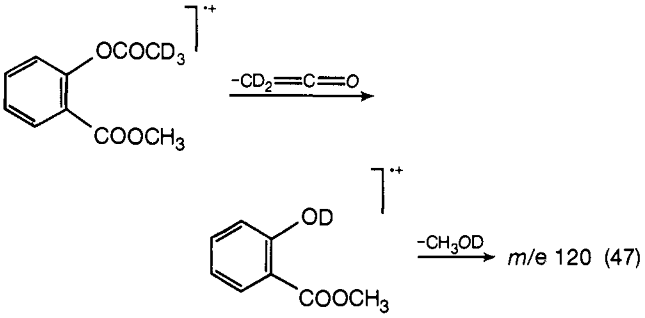
Table VIII *(Footnotes continued)*

[q] H. C. Hill and R. I. Reed, *Tetrahedron*, **20**, 1359 (1964). [r] J. F. Biellman and C. G. Hirth, *Org. Mass. Spectrom.*, **2**, 723 (1969). [s] R. G. Kostyanovskii, V. V. Yakshin, and S. L. Zimont, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 651 (1968). [t] C. P. Lewis, *Anal. Chem.*, **36**, 176 (1964). [u] M. A. Baldwin, A. Kirkien-Konasiewicz, A. G. Loudon, A. Maccoll, and D. Smith, *J. Chem. Soc. B*, 34 (1968). [v] M. F. Grostic, R. J. Wnuk, and F. A. Mackellar, *J. Amer. Chem. Soc.*, **88**, 4664 (1966). [w] J. H. Bowie, D. H. Williams, S.-O. Lawesson, J. Oe. Madsen, C. Nolde, and G. Schroll, *Tetrahedron*, **22**, 3515 (1966). [x] J. Momigny, *Ann. Soc. Sci. Bruxelles*, 71, 66 (1957). [y] L. D'Or, J. Momigny, and A. A. Wirtz-Cordier, *Bull. Cl. Sci., Acad. Roy. Belg.*, **47**, 811 (1961). [z] R. H. Shapiro, *Org. Mass Spectrom.*, 1, 907 (1968). [aa] M. J. Saxby, *ibid.*, 4, 133 (1970). [bb] T. H. Kinstle, and R. L. Muntz, *Tetrahedron Lett.*, 2613 (1967). [cc] I. C. Calder, R. B. Johns, and J. M. Desmarchelier, *Org. Mass Spectrom.*, 4, 121 (1970). [dd] J. H. Bowie, R. G. Cooks, and G. E. Lewis, *Aust. J. Chem.*, **20**, 1601 (1967). [ee] J. Ronayne, D. H. Williams, and J. H. Bowie, *J. Amer. Chem. Soc.*, **88**, 4980 (1966). [ff] O. L. Chapman, T. H. Kinstle, and M. T. Sung, *ibid.*, **88**, 2618 (1966). [gg] J. C. Tou and C. S. Wang, *Org. Mass Spectrom.*, **3**, 287 (1970).

in the rearrangement of the halogenated phenetoles.[435a] These results were explained by postulating differing charge distributions in the molecular ions of each type of compound and thus are not evidence against the four-membered transition state. In support of the evidence from substituent effects, deuterium isotope effects showed that the isotope effect observed for elimination of (HNC + DNC) from *p*-chloroaniline-*N*,*N*-d_2 is comparable to that observed for loss of the same fragments from the $[M - CH_2CO]\cdot^+$ ion from *p*-chloroacetanilide-α-d_3.[436]

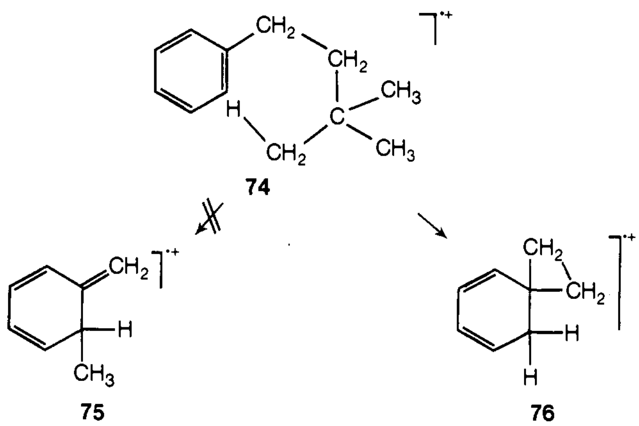
It may thus be concluded with reasonable assurance that rearrangement of acylated anilines proceeds by the mechanism of eq 46.

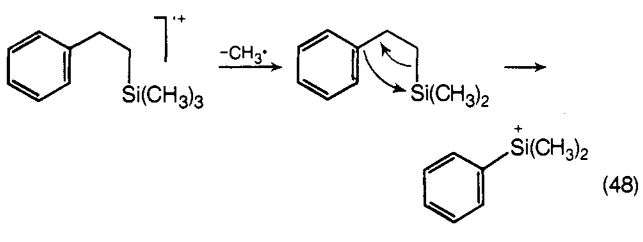
An analogous rearrangement occurs in the fragmentation of the phenyl esters of aliphatic acids. This reaction has not been studied in great detail, but a recent communication reports that hydrogen rearrangement in phenyl valerate involves mainly the hydrogens from the α position of the side chain.[437] No firm conclusions can be drawn from this evidence regarding the mechanism of the rearrangement (four- or six-membered transition state). However, two lines of evidence suggest that this rearrangement proceeds *via* a four-membered transition state. In the first place, substitution at the ortho positions in phenyl acetate failed to suppress the rearrangement, a result which parallels that with substituted acetanilides and is in sharp contrast to that for alkylbenzenes.[437a] Secondly, rearrangement of labeled methyl *O*-acetylsalicylate proceeded by ketene loss followed by methanol loss (an ortho effect, section III.G) (eq 47). The methanol lost was found to be completely methanol-*O*-d_1, with essentially no normal methanol, thus strongly suggesting that initial rearrangement occurs to give methyl salicylate-*O*-d_1.[437b]



(47)

Returning to the alkylbenzenes, various other fragmentations may include hydrogen transfer to an aromatic ring. Thus 3,3-dimethyl-1-phenylbutane (**74**) shows an intense peak due to an ion $C_8H_{10}\cdot^+$.[438] This ion could conceivably have been due to an alkyl migration (**74** → **75**), but deuterium labeling showed that transfer of only one of the nine δ-deuterium atoms of 3,3-dimethyl-1-phenylbutane-d_9 was retained in this ion. The pathway (**74** → **76**) was suggested for the rearrangement, along with alternate pathways in which the migrant hydrogen is deposited on the same carbon atom of the benzene ring as the residue of the alkyl group, or on a carbon of the alkyl chain.[438,439] There is no special evidence to support any of these postulates. The latter authors also observed a rearrangement of a siliconium ion analogous to the previously discussed hydrogen rearrangements (eq 48).[439,156b] Rearrangement did not occur, however, in benzyltrimethylsilane (eq 21, section II.F).[157]





(48)

E. Miscellaneous Rearrangement of Alkylbenzenes

In addition to the specific rearrangements undergone by alkylbenzenes discussed in the previous section, a number of other rearrangements occur in these compounds on electron impact. In this section we will attempt to summarize these miscellaneous reactions.

The spectra of *tert*-butylbenzene and 3-ethyl-3-phenylpentane show a loss of an alkyl group by the usual β cleavage and then a loss of an olefin to give $C_7H_7^+$. The hydrogen scrambling which occurs between these steps is consistent with the formation of a species with the symmetry of a cyclopropane ring with the phenyl group located at the center, or at least free to equilibrate on all positions, according to *d*-labeling results.[440] The results for 3-phenylpentane, after loss of the first ethyl group, are consistent with the operation of this mechanism for 90% of the ions (eq 49) and a simple γ-hydrogen cleav-

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(436) N. Uccella, I. Howe, and D. H. Williams, *Org. Mass Spectrom.*, **6**, 229 (1972).

(437) G. G. Smith and S. W. Cowley, *J. Chem. Soc. D*, 1066 (1961).

(437a) A. A. Gamble, J. R. Gilbert, and J. G. Tillett, *Org. Mass Spectrom.*, **5**, 1093 (1971).

(437b) H. Nakata and A. Tatematsu, *Org. Mass Spectrom.*, **5**, 1343 (1971).

(438) M. Fischer and C. Djerassi, *Chem. Ber.*, **99**, 750 (1966).

(439) W. P. Weber, R. A. Felix, and A. K. Willard, *Tetrahedron Lett.*, 907 (1970).

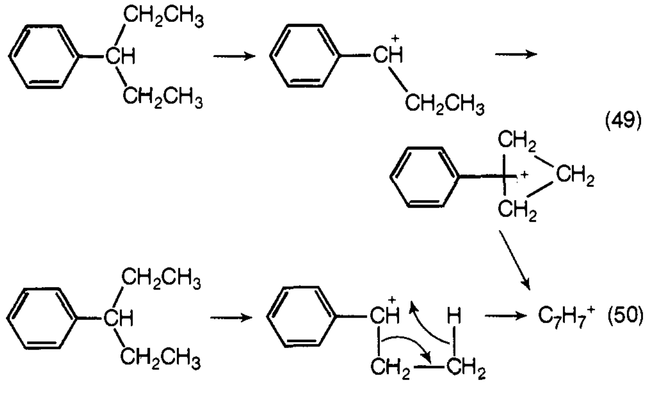
(440) P. N. Rylander and S. Meyerson, *J. Amer. Chem. Soc.*, **78**, 5799 (1956).

TABLE IX. Examples of Simple *Ortho* and *Peri* Effects Leading to Loss of Small Molecules

XH	YZ	Compound or aromatic ring system	Fragment eliminated	Ref
OH	COOH	Salicylic acids	H_2O	*a–c*
OH	COOH	8-Hydroxyl-1-naphthoic acid	H_2O	513
OH	COOH	Quinolinehydroxamic acids	H_2O	*f*
CH_3	COOH	*o*-Toluic acids	H_2O	*b*, *d*, 485
CH_3	COOH	2-Pyrones	H_2O	*e*
SH	COOH	*o*-Mercaptobenzoic acid	H_2O	492
NH_2	COOH	Quinolinehydroxamic acids	H_2O	*f*
NH_2	COOH	Anthranilic acids	H_2O	*g*
OCH_3	COOH	*o*-Methoxybenzoic acid	H_2O	*m*
OH	OH	Catechol	H_2O	486
OH	CH_2OH	*o*-Hydroxybenzyl alcohol	H_2O	508
CH_3	OH	*o*-Cresol	H_2O	486
CH_3	SH	2,3-Disubstituted pyridines	H_2S	*h*
OH	$COOCH_3$	Methyl salicylates	CH_3OH	*a–c*
OH, NH_2	$COOCH_3$	Amino salicylates	CH_3OH	*i*
OH	$COOC_2H_5$	Substituted coumarins	C_2H_5OH	*j*
OH	$COOC_2H_5$	Thiophenes	C_2H_5OH	*k*
OH	$COOC_2H_5$	Alkoxythiophenes	C_2H_5OH	421
OH	COOAr	Depsides, etc.	ArOH	*l*
OH	$COOC_2H_5$	Ethyl 8-hydroxyl-1-naphthoate	C_2H_5OH	513
CH_3	$COOCH_3$	*o*-Toluic esters	CH_3OH	*b*, *d*, *m*
CH_3	$COOCH_3$	*N*-Carbomethoxyazepines	CH_3OH	*n*
CH_3	$COOCH_3$	Furans	CH_3OH	*o*
CH_3	$COOC_2H_5$	Thiazoles	C_2H_5OH	*p*
CH_3	$COOC_2H_5$	Pyrroles	C_2H_5OH	*q*
C_2H_5	$COOC_2H_5$	Tetracyclines	C_2H_5OH	*x*, *y*
SH	CH_3O	*o*-Mercaptoanisole	CH_3OH	492
NH_2	$COOCH_3$	Phenazines	CH_3OH	*r*
NH_2	$COOCH_3$	Pyridines, pyridones	CH_3OH	*s*, *t*
NH_2	$COOC_2H_5$	Benzofurans	C_2H_5OH	*u*
CH_3	NH_2	Toluidines	NH_3	*v*
CH_3	NH_2	Pyridines	NH_3	*h*
NH_2	NH_2	*s*-Triazines	NH_3	*w*
OH	NHCOOR	Benzene	ROH	*z*
H	CN	Naphthalene	HCN	247

[a] W. M. Scott, M. E. Wacks, C. D. Eskelson, J. C. Towne, and C. Cazee, *Org. Mass Spectrom.*, 1, 847 (1968). [b] A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, **92**, 3984 (1970). [c] E. M. Emery, *Anal. Chem.*, **32**, 1495 (1960). [d] A. N. H. Yeo and D. H. Williams, *Chem. Commun.*, 956 (1969). [e] H. Nakata, Y. Hirata, and A. Tatematsu, *Tetrahedron Lett.*, 123 (1965). [f] R. T. Coults and K. W. Hindmarsh, *Org. Mass Spectrom.*, **2**, 681 (1969). [g] R. M. Teeter, *Anal. Chem.*, **38**, 1736 (1966). [h] G. H. Keller, L. Bauer, and C. L. Bell, *J. Heterocycl. Chem.*, **5**, 657 (1968). [i] A. Tatematsu, H. Nakata, Y. Nakajima, and H. Doi, *Shitsuryo Bunseki*, 14, 201 (1966). [j] R. A. W. Johnstone, B. J. Millard, F. M. Dean, and A. W. Hill, *J. Chem. Soc. C*, 1712 (1966). [k] R. Grigg, H. J. Jacobsen, S.-O. Lawesson, M. V. Sargent, G. Schroll, and D. H. Williams, *J. Chem. Soc. B*, 331 (1966). [l] S. Huneck, C. Djerassi, D. Becher, M. Barber, M. von Ardenne, K. Steinfelder, and R. Tummler, *Tetrahedron*, **24**, 2707 (1968). [m] T. Aczel and H. E. Lumpkin, *Anal. Chem.*, **33**, 386 (1961). [n] L. A. Paquette and D. E. Kuhla, *J. Org. Chem.*, **35**, 863 (1970). [o] R. Grigg, J. A. Knight, and M. V. Sargent, *J. Chem. Soc. C*, 976 (1966). [p] G. M. Clarke, R. Grigg, and D. H. Williams, *J. Chem. Soc. B*, 331 (1966). [q] H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman, and J. M. Wilson, *J. Chem. Soc.*, 1949 (1964). [r] F. G. Holliman, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc. C*, 2351 (1967). [s] H. Budzikiewicz, C. Horstmann, K. Pufahl, and K. Schreiber, *Chem. Ber.*, **100**, 2798 (1967). [t] A. M. Duffield, C. Djerassi, G. Schroll, and S.-O. Lawesson, *Acta Chem. Scand.*, **20**, 361 (1966). [u] G. Spiteller, *Monatsh. Chem.*, **92**, 1142 (1961). [v] V. E. Sahini, V. Constantin, and C. Podina, *Rev. Roum. Chim.*, **12**, 1405 (1967). [w] P. N. Preston, W. Steedman, M. H. Palmer, S. M. Mackenzie, and M. F. G. Stevens, *Org. Mass Spectrom.*, **3**, 863 (1970). [x] D. R. Hoffman, *J. Org. Chem.*, **31**, 792 (1966). [y] H. Brockmann, Jr., H. Budzikiewicz, C. Djerassi, H. Brockmann, and J. Niemeyer, *Chem. Ber.*, **98**, 1260 (1965). [z] G. G. Still, *Org. Mass Spectrom.*, **5**, 977 (1971).

age with β-hydrogen transfer in the phenylpropyl ion for the remaining 10% (eq 50).[441]



(49)

(50)

Hydrogen scrambling in the formation of trityl or benzhydryl carbonium ions from the labeled triphenylmethane $(C_6H_5)_3CD$ has already been mentioned,[217,252] as has the loss of $CH_3\cdot$ from triphenyl- and diphenylmethane molecular ions following hydrogen randomization.[217,253,254] Similarly, loss of CH_4 from the triphenylmethane molecular ion and of H and 2H from the doubly charged diphenylmethane ion likewise follow scrambling.[217] There is a peak corresponding to $C_7H_8\cdot^+$ in the spectrum of 2,2-diphenylpropane, but its mechanism of formation is not certain.[442] Loss of the elements of benzene from *o*-methyldiphenylmethane involves transfer of a methyl hydrogen to the departing phenyl group and is an example of an ortho effect, discussed in section III.G.

Rearrangements observed in the 1,2-diphenylethane system include the loss of $CH_3\cdot$ from the $[M - H]^+$ ion. Labeling studies indicate that the loss of the first hy-

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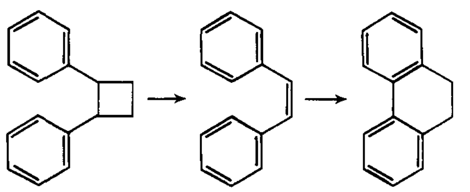
(441) S. Meyerson and H. Hart, *J. Amer. Chem. Soc.*, **85**, 2358 (1963).

(442) A. A. Polyakova, R. A. Khmel'nitskii, I. I. Grandberg, O. I. Doshlov, and O. R. Khrolova, *Zh. Org. Khim.*, **3**, 836 (1967).

drogen is from the two-carbon unit and that the methyl group is formed from two ortho hydrogens and the CH of the carbonium ion center.[259,443] The loss of ethylene from *cis*-1,2-diphenylcyclobutane may be accompanied by hydrogen migration to give 9,10-dihydrophenanthrene, which then loses a methyl group (eq 51).[444] This loss of $CH_3\cdot$ from 9,10-dihydrophenanthrene involves hydrogen atoms from the aromatic rings and the bridge, as a study with the *9,9,10,10-d*$_4$ compound showed.[233] Another study showed predominant loss of $CH_3\cdot$ and H_2 from the bridge, but as before scrambling was noted to some extent.[445]



(51)

Several other hydrogen rearrangements do not fit into any of the above divisions. Thus polymethylbenzenes lose $CH_3\cdot$ without hydrogen rearrangements if the methyl group is flanked by two other methyl groups, but with exchange of methyl H and ortho H through a methyl-methylene-methyl cycle if there is an unsubstituted position available adjacent to the methyl group.[446] This is an example of the operation of ortho effects, discussed in more detail in section III.G. Hydrogen rearrangements must also be involved in the loss of alkyl fragments from some phenylcyclohexadiene isomers,[447] 10-phenyldecalin,[375] and methylphenanthrenes,[448] while hydrogen rearrangements have also been implicated in the fragmentation of the 9-alkylphenanthrenes,[214] phenylcyclobutene,[255] steroids containing aromatic rings,[449] and an octahydrobenzofluoranthene.[450]

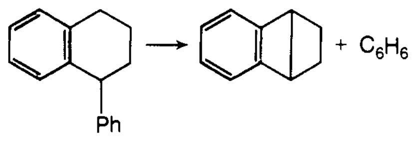
Several metastable transitions involving the decompositions of doubly charged ions from methyl aromatics have been observed: $C_7H_7^{2+}$ forms $C_4H_4^+$ and $C_3H_3^+$ with the release of 3.5 eV energy, and $C_5H_5^+$ plus $C_2H_2^+$ with 2.8 eV; the former requires significant rearrangement, the latter need not.[210] In addition to these ions from toluene, doubly charged molecular ions of methylphenanthrenes and methylanthracenes split out a number of fragments which call for rearrangement.[451] Toluene doubly charged molecular ion does not scramble completely before loss of H but does before loss of H_2.[302,452]

One interesting rearrangement of 1-phenyltetralin involves the 1,4 elimination of benzene (eq 52).[453,454] It has been pointed out that this reaction is simply a specific instance of the 1,4 elimination of arenes in molecules of type **77**.[455] Reactions of this type will be discussed in the section on ortho effects (III.G).

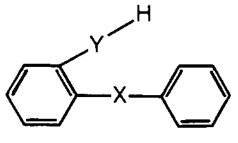
TABLE X. Elimination of a Neutral Arene from Bis(aryl) Compounds (Eq 57)

YH	X	Compound type	Ref
CH_3	O	*o*-Methyldiaryl ethers	*a*
CH_3	CH_2	*o*-Methyldiarylmethanes	*b–e*
OH	O	*o*-Hydroxydiphenyl ethers	*f*
OH	CO	*o*-Hydroxybenzophenones	520
CH_3	CO	*o*-Methylbenzophenones	520
OH	CH_2	2,2′-Methylenebisphenols	*g*
CH_2R	CHR	1-Phenyltetralin	*h, i*
OH	Se	2,2′-Selenobisphenols	*j*
OH	S	*o*-Hydroxydiaryl sulfides	*g*
CH_3	CH_2	*o*-Methyldipyrrolylmethane	*k*

[a] R. I. Reed and J. M. Wilson, *Chem. Ind.* (*London*), 1428 (1962). [b] S. Meyerson, H. Drews, and E. K. Fields, *J. Amer. Chem. Soc.*, **86**, 4964 (1964). [c] H. Budzikiewicz and J. S. Swoboda, *Chem. Ber.*, **98**, 3264 (1965). [d] H. Hart, C. A. Buehler, A. J. Waring, and S. Meyerson, *J. Org. Chem.*, **30**, 331 (1965). [e] W. M. Scott, M. E. Wacks, C. Steelink, and J. D. Fitzpatrick, *Org. Mass Spectrom.*, **3**, 657 (1970). [f] J. A. Ballantine and C. T. Pillinger, *ibid.*, 1, 447 (1968). [g] J. Lesko, V. Vesely, and S. Korcek, *Collect. Czech. Chem. Commun.*, **34**, 2836 (1969). [h] M. L. Gross, C. L. Wilkins, and T. G. Regulski, *Org. Mass Spectrom.*, **5**, 99 (1971). [i] C. L. Wilkins and M. L. Gross, *J. Amer. Chem. Soc.*, **93**, 895 (1971). [j] S. Korcek, S. Holotik, J. Lesko, and V. Vesely, *Chem. Zvesti*, **23**, 281 (1969). [k] A. H. Jackson, G. W. Kenner, H. Budzikiewicz, C. Djerassi, and J. M. Wilson, *Tetrahedron*, **23**, 603 (1967).



(52)



77

Tetralin itself loses ethylene, and it has been shown that this does not occur by a simple "reverse Diels–Alder" reaction. Thermochemical measurements suggested that the product ion is actually formed by loss of ethylene from a tetrahydroazulene precursor formed from tetralin by hydrogen and skeletal rearrangement.[455a]

F. Typical Rearrangements in Other Aromatic Ions

In this section a number of miscellaneous hydrogen rearrangements of substituted aromatic compounds will be summarized. As far as possible they are grouped together according to the functional group(s) involved in the rearrangement. In view of the frequent lack of deuterium labeling and other data in many of the examples cited, the mechanisms proposed must be regarded as very tentative in most cases. Readers are referred to the full papers cited for a fuller treatment of individual rearrangements.

The fragmentations of aralkyl compounds of general formula **78** on electron impact have attracted much recent attention, and some interesting rearrangements

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(443) R. A. W. Johnstone and B. J. Millard, *Z. Naturforsch. A*, **21**, 604 (1966).

(444) M. L. Gross and C. L. Wilkins, *Tetrahedron Lett.*, 3875 (1969).

(445) A. Maguestian, Y. Van Haverbeke, and F. Delalieu, *Bull. Soc. Chim. Belg.*, **78**, 589 (1969).

(446) S. Meyerson and E. K. Fields, *Org. Mass Spectrom.*, **2**, 1309 (1959).

(447) A. M. Braun, *Org. Mass Spectrom.*, **3**, 1479 (1970).

(448) P. Nounou, *J. Chim. Phys.*, **65**, 700 (1968).

(449) C. Djerassi, J. M. Wilson, H. Budzikiewicz, and J. W. Chamberlin, *J. Amer. Chem. Soc.*, **84**, 4544 (1962).

(450) M. C.*Hamming and G. W. Keen, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 1-APP (1969).

(451) P. Nounou, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 219 (1970).

(452) T. Ast, J. H. Beynon, and R. G. Cooks, *J. Amer. Chem. Soc.*, **94**, 1834 (1972).

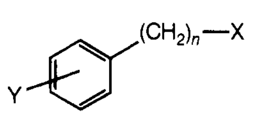
(453) M. L. Gross, C. L. Wilkins, and T. G. Regulski, *Org. Mass Spectrom.*, **5**, 99 (1971).

(454) C. L. Wilkins and M. L. Gross, *J. Amer. Chem. Soc.*, **93**, 895 (1971).

(455) S. Meyerson and E. K. Fields, *Org. Mass Spectrom.*, **5**, 1227 (1971).

(455a) H.-F. Grützmacher and M. Puschmann, *Chem. Ber.*, **104**, 2079 (1971).

(both hydrogen and skeletal) have been uncovered. The formation of $C_8H_9^+$ ions from $C_6H_5CH_2CH_2X$ compounds have received the most attention, and substituent effects have been interpreted variously as indicative of phenonium (**79**)[456] or classical[457] structures for this ion type. Labeling evidence, however, shows that complete scrambling of hydrogen precedes loss of acetylene from the $C_8H_9^+$ ion,[214,458] and a methyl tropylium or cyclooctatrienyl structure was proposed for it.[458] Later results with ^{13}C-labeled β-phenylethyl bromide showed that it was not necessary to assume eight-membered ring structures to explain the hydrogen randomization.[257] Since all these results apply to decomposing $C_8H_9^+$ ions, it is still possible and indeed likely that the $C_8H_9^+$ ion initially formed has the phenonium structure, and this then may rearrange to the cyclooctatrienyl structure prior to decomposition. Further evidence in support of anchimeric assistance in the expulsion of bromine from substituted phenethyl bromides was adduced from a study of the kinetics of bromine loss; similar studies suggested that no aryl participation occurs in the γ-phenylpropyl bromides (**78**, $n = 3$, X = Br), but weak participation occurs in the δ-phenylbutyl bromides (**78**, $n = 4$, X = Br).[456]



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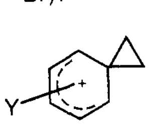
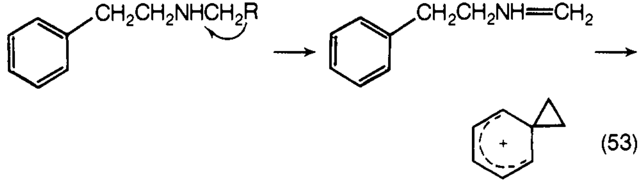


79

Other examples of anchimeric assistance in the fragmentation of aromatic compounds, involving hydrogen rearrangements in most cases, have been proposed in studies of β-phenethylamines (eq 53),[459] 5-bromo-2-phenyl-2-pentene (**80**),[460] the trimethylsilyl ether of β-phenylethanol (**81**),[461] the phenoxyethyl halides (**82**),[462] β-bromoethyl benzoate (**83**),[463] and various 4-substituted azulene derivatives, including 2-(4-azulyl)ethyl tosylate (**84**).[464] In the case of 2-(1-azulyl)ethyl tosylate, however, the observed hydrogen scrambling was found to be due to a metal-catalyzed reaction of the neutral molecule, rather than in a reaction of the ionized molecule.[465]



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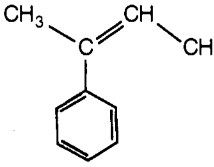

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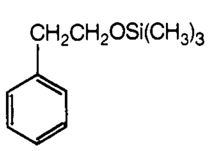

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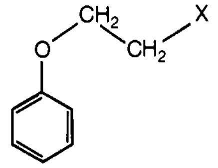

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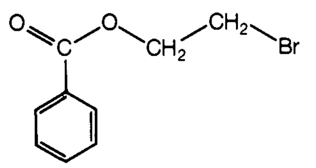

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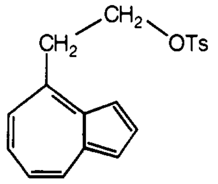

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Hydrogen rearrangements have also been observed in aralkyl compounds in which anchimeric assistance is not involved. Thus mutual exchange of 1- and ortho hydrogens before loss of C_2H_3Br from γ-phenylpropyl bromide was observed,[466] while extensive hydrogen rearrangement is also found in ions of benzyl cyanide decomposing in the second field-free region of a double-focusing mass spectrometer, where ^{13}C labeling showed that *both* side-chain carbons are involved in the loss of HCN after complete hydrogen randomization![467] Other aralkyl compounds studied include phenylnitroalkanes,[458,468,469] 3-phenylpropyl nitrite,[469] 3-phenyl-propylamine,[470] hydrocinnamaldehyde,[271] and substituted phenyl butyrates.[471,472]

A widespread reaction of methoxylated aromatic compounds is the loss of CH_2O from the molecular ion. This reaction is observed, for example, from both the positively[473] and negatively[474] charged molecular ion of anisole and has been the subject of some mechanistic study. In $C_6H_5OCD_3$ loss of formaldehyde occurs to the extent of 88% as loss of CD_2O, although the accompanying minor loss of a formyl radical involves complete hydrogen scrambling.[266] A similar loss of formaldehyde occurs in $CH_3OC_6H_4^+$ ions to give $C_6H_5^+$ ions,[475] and the reaction also has an analogy in the thermal decomposition of methoxy aromatics.[476] It is observed in more complex cases in heterocyclic compounds,[477,478] in natural products,[479,480] and in 2-methoxynaphthalene, although cur-

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(456) R. H. Shapiro and T. F. Jenkins, *Org. Mass Spectrom.*, **2**, 771 (1969).

(457) H.-F. Grützmacher, *Org. Mass Spectrom.*, **3**, 131 (1970).

(458) N. M. M. Nibbering and Th. J. de Boer, *Org. Mass Spectrom.*, **2**, 157 (1969).

(459) W. J. Richter and W. Vetter, *Org. Mass Spectrom.*, **2**, 781 (1969).

(460) K. B. Tomer, J. Turk, and R. H. Shapiro, *Org. Mass Spectrom.*, **6**, 235 (1972).

(461) J. Diekman, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, **32**, 3904 (1967).

(462) C. B. Theissling, N. M. M. Nibbering, and Th. J. de Boer, *Advan. Mass Spectrom.*, **5**, 642 (1970).

(463) R. H. Shapiro and K. B. Tomer, *Org. Mass Spectrom.*, **3**, 333 (1970).

(464) R. G. Cooks, N. L. Wolfe, J. R. Curtis, H. E. Petty, and R. N. McDonald, *J. Org. Chem.*, **35**, 4048 (1970).

(465) R. G. Cooks, R. N. McDonald, J. R. Curtis, and H. E. Petty, *Org. Mass Spectrom.*, **5**, 785 (1971).

(466) N. M. M. Nibbering and Th. J. de Boer, *Tetrahedron*, **24**, 1427 (1968).

(467) T. A. Molenaar-Langeveld, N. M. M. Nibbering, and Th. J. de Boer, *Org. Mass Spectrom.*, **5**, 725 (1971).

(468) N. M. M. Nibbering and Th. J. de Boer in ref 259, p 47.

(469) N. M. M. Nibbering and Th. J. de Boer, *Org. Mass Spectrom.*, **3**, 487 (1970).

(470) D. A. Lightner, F. W. Sunderman, L. Hurtado, and E. Thommen, *Org. Mass Spectrom.*, **3**, 1325 (1970).

(471) I. Howe, D. H. Williams, D. G. I. Kingston, and H. P. Tannenbaum, *J. Chem. Soc. B*, 439 (1969).

(472) I. Howe and D. H. Williams, *J. Amer. Chem. Soc.*, **90**, 5461 (1968).

(473) C. S. Barnes and J. L. Occolowitz, *Aust. J. Chem.*, **16**, 219 (1963).

(474) C. Nolde, J. Oe. Madsen, S.-O. Lawesson, and J. H. Bowie, *Ark. Kemi*, **31**, 481 (1970).

(475) D. Lednicer and M. F. Grostic, *J. Org. Chem.*, **32**, 3251 (1967).

(476) L. K. Freiden, A. A. Balandin, and N. M. Nazarova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 102 (1949).

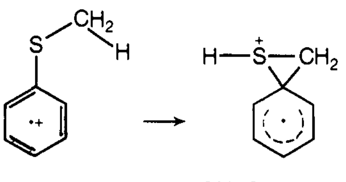
(477) L. Paolini, G. Nencini, M. L. Tosato, and T. Salvatori, *Gazz. Chim. Ital.*, **97**, 635 (1967).

(478) J. H. Bowie, G. E. Lewis, and J. A. Reiss, *Aust. J. Chem.*, **21**, 1233 (1968).

(479) R. I. Reed and J. M. Wilson, *J. Chem. Soc.*, 5949 (1963).

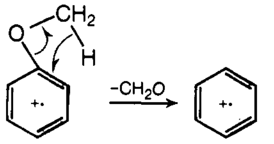
(480) I. R. C. Bick, J. H. Bowie, and G. K. Douglas, *Aust. J. Chem.*, **20**, 1403 (1967).

iously not in 1-methoxynaphthalene.[481] In 1,7-dimethoxynaphthalene, initial loss of CH_3, then CO, and ultimately CH_2O is observed, but in phenanthrene and tolan methoxy ethers, no loss of CH_2O is observed.[481] Thioanisoles show analogous loss of CH_2S, in addition to fragmentation involving loss of SH. Labeling studies on this latter reaction with thioanisole trideuterated in the methyl group showed loss of SD dominating over loss of SH to the extent of about 2:1,[431,482] and the mechanism of eq 54 was proposed,[482] in which the hydrogen attached to sulfur may come from the ring or the methyl group.



(54)

Returning to the loss of CH_2O from anisoles, the mechanism originally proposed for the rearrangement involved a four-centered transition state to yield a product which is formally ionized benzene (eq 55).[473] Substituent effects on the decomposition have been studied,[483,484] and were interpreted to suggest the retention of site identity during the decomposition. However, very recent results[429a] using energy partitioning as an ion structure probe indicate that the anisoles lose CH_2O by two mechanisms; apparently H transfer occurs through both a four- and a five-centered transition state. In agreement with this result, a study of labeled anisole molecular ions decomposing in the second field-free region showed that in these ions at least some hydrogen exchange between the methyl group and the ortho position of anisole preceded loss of CH_2O;[485] if the hydrogen exchange is stepwise and reversible, then Scheme XVI harmonizes this result and the results of the energy partitioning study.



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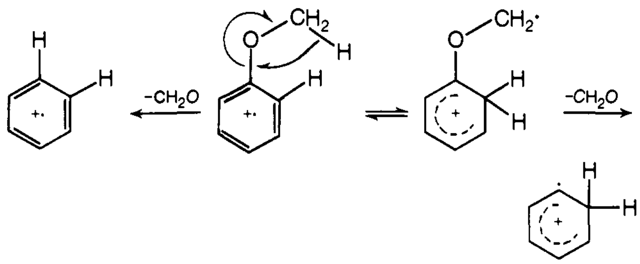
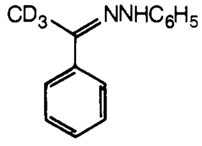
SCHEME XVI



It has long been known that phenol and phenolic systems show loss of CO and CHO.[486] Among phenolic systems which display these losses are phenolic phenazines and quinoxalines,[487] halogenophenols (where loss of X or HX competes with loss of CO or HCO),[488] flavones,[489] flavylium compounds,[490] and lichens.[491] It has been postulated that phenol rearranges to a cyclohexadienone structure in order to facilitate the loss of CO.[243] Analogous losses occur from thiophenol[492] and aniline and must of course proceed with rearrangement of one hydrogen attached to the heteroatom, as has been demonstrated experimentally.[242] Skeletal rearrangements accompanying these losses have been previously discussed (section III.A).

Hydrogen rearrangements have been observed in the fragmentations of several aromatic carbonyl derivatives. Thus benzaldehyde[493,496-498] and acetophenone azines[494,495] have been extensively investigated, and evidence for both hydrogen and carbon rearrangements was found in their fragmentations on electron impact. Similarly, the anils of substituted benzaldehydes show hydrogen rearrangement in the formation of "amine" decomposition products.[499] Phenylhydrazones also form "amine" product ions, and deuterium labeling indicated a 1:1 ratio for hydrogen *vs.* deuterium transfer in **85** to form $C_6H_5NH^{\cdot +}$.[500] Other studies of rearrangements in phenylhydrazones have appeared.[501-504] Certain rearrangements of nitrophenylhydrazones and of phenylhydrazones of ortho-substituted aromatic aldehydes or ketones involve ortho effects and will be discussed in section III.G. Oximes also show hydrogen rearrangement, as indicated by a study of benzylphenyl ketoxime, where losses of H_2O, H_2CH, and HCN are observed with some hydrogen randomization occurring in the HCN loss.[505] Hydrogen rearrangements have also been observed in the spectra of aryl sulfonylhydrazones[506] and various aroyl hydrazones (**86**).[507] In the latter case the rearrangement of the methine hydrogen with elimination of neutral PhCN was shown not to be a McLafferty rearrangement but to proceed *via* a four-centered mechanism.[507]



85

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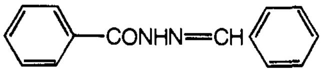
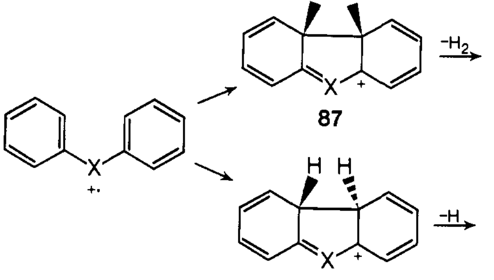


86

Some intriguing hydrogen rearrangements are observed in the spectra of benzyl alcohol and its derivatives. Thus there is almost complete randomization of hydrogens in benzyl alcohol before loss of hydrogen, but not before various other fragmentations;[327] ring expansion to a substituted tropylium ion was inferred from this result. A study of the three isomers of hydroxybenzyl alcohol showed that the ortho isomer differed from the other two isomers in giving $(M - H_2O)$ and $(M - H_2O - H_2)$ ions; the $(M - 2)$ ion could be stabilized by hydrogen bonding. In the other isomers loss of HCO followed by expulsion of H_2 was the favored fragmentation pathway.[508] Recent detailed ^{18}O- and deuterium-labeling studies have shown that the benzylic and ring hydrogen atoms of *m*-hydroxybenzyl alcohol equilibrate their hydrogen atoms without expansion to a seven-membered ring.[509] A rationalization is also proposed[509] for the observation that meta- and para-OD-substituted deuterated benzyl alcohols show loss of D_2O.

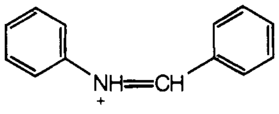
A final example of hydrogen rearrangements in aromatic systems is provided by the rearrangements of various bis(aryl) systems to yield (M − H) or (M − 2H) ions. Application of orbital symmetry arguments to the reaction (Scheme XVII) suggested that in those cases where X is a two-electron system bringing the phenyl rings into conjugation (*e.g.*, NH), then thermal closure to **87** and photochemical closure to **88** would be allowed. In those cases where X is a zero-electron system (*e.g.*, CH), the converse would be the case. In practice it was found that loss of molecular H_2 only occurred from the latter type of ion (X = CH, arising by loss of Br from diphenylmethyl bromide), and then it was concluded that photochemical rules were being followed, since only **87** should be able to lose hydrogen directly as a molecule.[510] Similar results were obtained for hydrogen loss from 1,4-diphenylbutadiene, and an excited-state cyclization was invoked here also.[511]

SCHEME XVII



88

More recent work, however, has cast some doubt on this interpretation, and it was suggested that the results merely reflect the tendency of radical cations to lose radicals and even-electron species to lose molecules.[512] This contention was supported by a study of the system **89**, where the group X (CH=NH) provides two electrons to the conjugated system but does so in an even-electron fragment. The ion **89** eliminates a hydrogen molecule more readily than a hydrogen atom, leading to the conclusion that ions of general formula $ArXAr^{+}$ can close to yield ion **87** (*i.e.*, by a disrotatory path) whether the conjugated system has 4*n* or 4*n* + 2 electrons. Clearly then, the application of orbital symmetry rules to mass spectrometric fragmentations can provide only ambiguous answers with our present knowledge of the energy levels of organic ions.



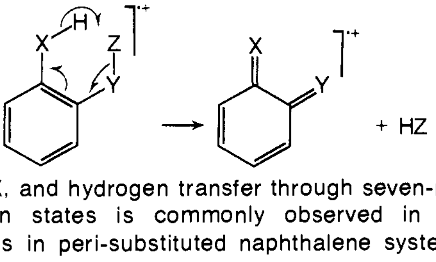
89

In conclusion, many miscellaneous hydrogen rearrangements are undergone by various other classes of aromatic compounds. There is not space to discuss these in detail, but a representative selection has been assembled in Table VIII; the references cited should be consulted for fuller details of specific cases.

G. Proximity Effects in Aromatic Systems. Ortho and Peri Effects

In any ionized molecule possessing sufficient energy to form fragment ions, the likelihood of the fragmentation process involving a hydrogen rearrangement reaction will be related not only to the energy of activation for such a process but also to the so-called "frequency factor" for the process. In aromatic systems a receptor site and a suitably located itinerant hydrogen atom are frequently favorably located for interaction to occur, and it is thus not surprising that fragmentations resulting from such interactions are often significant processes in the mass spectra of aromatic compounds. The interactions involved are called "ortho effects" when the itinerant hydrogen is located ortho to the functional group with which it interacts, and "peri effects" when these two groups are peri to each other. Since the basic fact of interaction between adjacent groups in unchanged by the exact location of the groups, no attempt to discuss these effects separately will be made in this review.

The commonest interactions of adjacent groups in aromatic compounds are those in which a small molecule such as H_2O, CH_3OH, or NH_3 is eliminated. Such interactions usually occur when a functional group containing a suitable hydrogen atom (*e.g.*, CH_3, OH, NH_2) is either ortho or peri to a second functional group containing an OH, OCH_3, or NH_2 group. The general reaction is illustrated in eq 56, and Table IX lists the various possible sources of the itinerant hydrogen and receptor sites, together with examples of each reaction type. It should be noted that the reaction as written (eq 53) indicates that hydrogen transfer is occurring *via* a six-membered state. However, hydrogen transfer *via* a five-membered transition state must be occurring in some of the examples of Table IX, and hydrogen transfer through seven-membered transition states is commonly observed in analogous reactions in peri-substituted naphthalene systems.[513] An



(56)

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(508) J. S. Shannon, *Aust. J. Chem.*, **15**, 265 (1962).

(509) T. A. Molenaar-Langeveld and N. M. M. Nibbering, *Tetrahedron*, **28**, 1043 (1972).

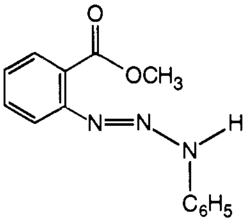
(510) R. A. W. Johnstone and S. D. Ward, *J. Chem. Soc. C*, 1805 (1968).

(511) R. A. W. Johnstone and S. D. Ward, *J. Chem. Soc. C*, 2542 (1968).

(512) M. J. Bishop and I. Fleming, *J. Chem. Soc. C*, 1712 (1969).

(513) R. J. Packer and D. C. C. Smith, *J. Chem. Soc. C*, 2194 (1967).

attempt to observe transfer of hydrogen through an eight-membered transition state was unsuccessful, however. No loss of methanol was observed from compound **90**, even though it occurred readily from the similar compound **91**.[514] Although this experiment does not prove that eight-membered transition states never occur for hydrogen transfer, they are certainly likely to be very rare.



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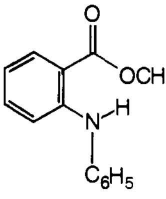
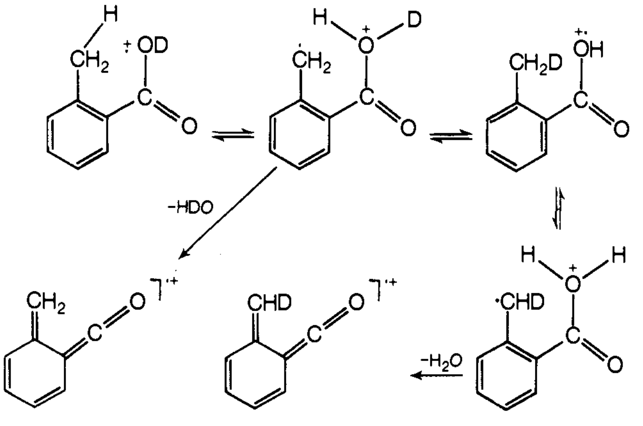


91

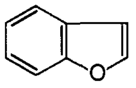
It should also be noted that the mere observance of the loss of a small neutral molecule such as water or methanol from an aromatic system does not prove the existence of an ortho effect. Such losses are often observed even in simple compounds where ortho substitution does not exist as, for example, in the loss of water from both *m*- and *p*-cresol and, also, to a limited extent from resorcinol and hydroquinol.[486] In all these examples the ortho isomer loses water more readily than the other isomers, so a genuine ortho effect probably does operate, but it is clearly not the only pathway for water loss. This fact unfortunately reduces the utility of ortho effects as a tool for structure elucidation, although they are still valuable in distinguishing between isomers when both isomers are available. A recent paper makes the same point in respect of variously substituted diphenylmethane derivatives.[515]

The mechanism of water loss from *o*-toluic acid has been studied with deuterium-labeling techniques, and evidence is presented that the reaction proceeds in a stepwise fashion (Scheme XVIII), rather than in the concerted manner of eq 53.[485] Thus loss of *both* HDO and H_2O is found from *o*-toluic acid-*O*-d, rather than the simple loss of HDO predicted by the concerted mechanism.

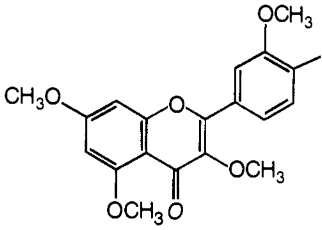
SCHEME XVIII



A number of other structural groupings give rise to loss of water by an ortho effect, but in these cases the mechanism of the reactions is more complex than the simple examples in Table IX. Probably the most important of these "complex ortho effects" are those in which a carbonyl group is adjacent to a methoxy group on an aromatic ring, a situation which is commonly seen in natural products such as flavonoids,[489,516] anthraquinones,[517,518] naphthoquinones,[517] and coumarins[519] as well as benzophenones[520] and simpler compounds such as *o*-methoxybenzaldehyde.[517] The reaction in o-methoxybenzaldehyde has been investigated by deuterium and ^{18}O labeling, and it was found that the carbonyl oxygen atom is eliminated together with either one hydrogen from the methoxy group and the aldehydic hydrogen, or two hydrogens from the methoxy group.[517] The benzofuran structure **92** was proposed for at least a part of the ions formed by this loss. It was also observed in this study that compounds without ortho substituents showed weak ions due to loss of water, so that again it appears that the utility of this effect for structural elucidation is limited.



92

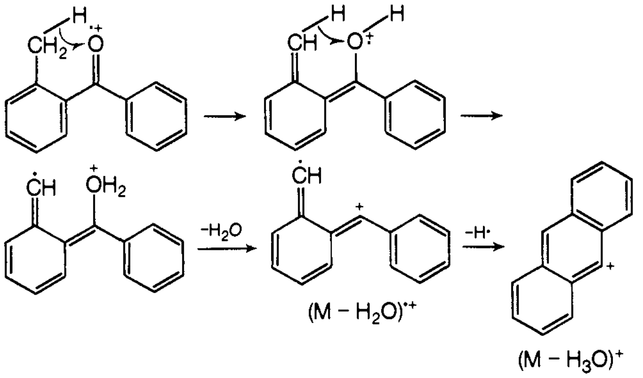


93

Certain flavones containing two methoxy groups adjacent to a carbonyl group as, for example, **93**[489] and also some ethoxyanthraquinones,[519] give intense ions corresponding to loss of H_3O in their mass spectra. The formation of these ions has been investigated by deuterium labeling,[519] and again it has been found that at least two pathways must operate in their formation. The loss of OH from acridones with an ethoxy group peri to the carbonyl group has also been investigated.[520a]

Other losses of water occur from 2-methylbenzophenones,[520] where the pathway indicated in Scheme XIX

SCHEME XIX



has been suggested for this complex rearrangement. Ions corresponding to $(M - H_3O)^+$ are observed in this type of compound also, and Scheme XIX gives one possible pathway for their formation. In the absence of deuterium labeling, however, such pathways must be regarded as only tentative.

The second major type of fragmentation in which proximity effects are important is that represented by the loss

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(514) C. Wunsche, G. Ege, E. Beisiegel, and F. Pasedach, *Tetrahedron*, **25**, 5869 (1969).

(515) H. Budzikiewicz, J. Rullkotter, and H. M. Schiebel, *Org. Mass Spectrom.*, **6**, 251 (1972).

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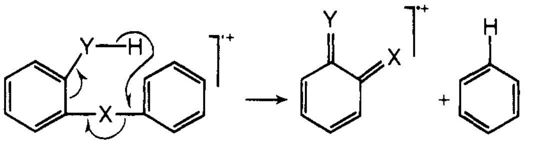
(519) M. M. Badami, M. B. E. Fayez, T. A. Bryce, and R. I. Reed, *Chem. Ind. (London)*, 498 (1966).

(520) J. A. Ballantine and C. T. Pillinger, *Org. Mass Spectrom.*, **1**, 425 (1968).

(520a) J. H. Bowie, R. G. Cooks, R. H. Prager, and H. H. Thredgold, *Aust. J. Chem.*, **20**, 1179 (1967).

of a neutral aromatic molecule from ortho-substituted bis(aryl) compounds, as illustrated in eq 57.[455] Examples of this type of reaction are collected in Table X.



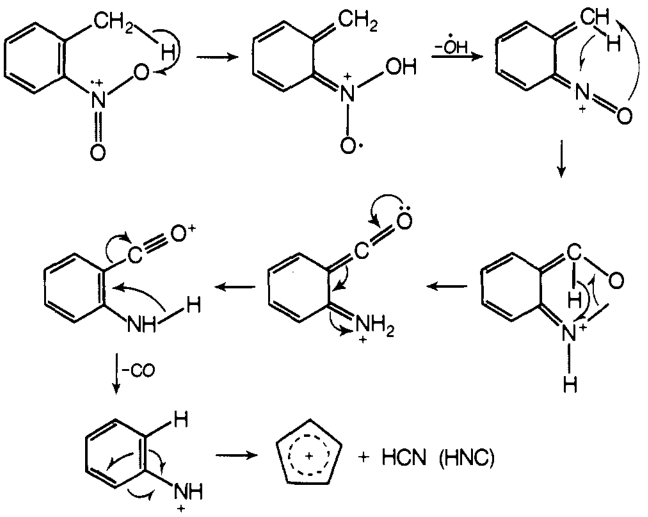
(57)

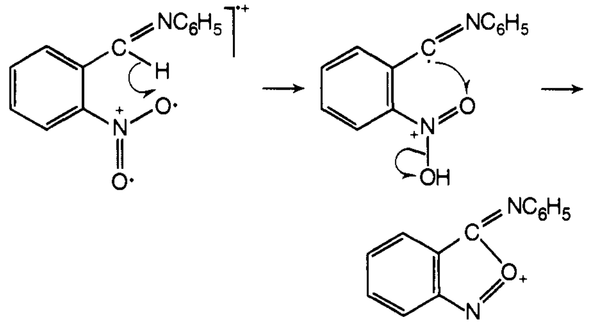
This reaction would appear to be useful for structure elucidation, although the absence of rearrangement by eq 57 should not be taken alone as evidence against an ortho orientation. To take one example, both *o*- and *p*-hydroxymethyldiphenylmethane show very weak peaks corresponding to loss of benzene, but the former gives an intense ion at $(M - H_2O)^+$, whereas the latter only produces a weak ion at this mass.[515] The latter reaction is thus more useful in this instance although even in this case ambiguity can arise.

Other losses of neutral arene molecules, although by mechanisms that differ from eq 54, are shown by various diphenic acid derivatives[521] and metal–Schiff base complexes.[522]

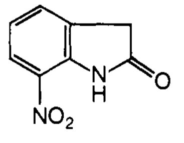
One functional group which frequently participates in ortho effects is the nitro group; the bulk of this group makes the formation of cyclic transition states of favorable size with neighboring groups quite easy. This interaction has been studied in some detail in *o*-nitrotoluene,[523-526] where it results initially in the loss of a hydroxyl radical, followed by the loss of CO and HNC (or HCN). A mechanism has been proposed (Scheme XX) to account for these losses,[523] in harmony with the observation[526] that the carbon of the methyl group is the carbon lost as CO. Similar losses are also observed from 1-nitro-2-methylnaphthalene,[527] o-nitrodiphenylmethane,[527a] and nitromethylphenothiazines.[528] Loss of hydroxyl is also shown by a number of other o-nitro derivatives including o-nitroaniline,[243] anils of o-nitrobenzaldehyde (eq 58),[529] and 7-nitrooxindole (**94**).[530]

SCHEME XX



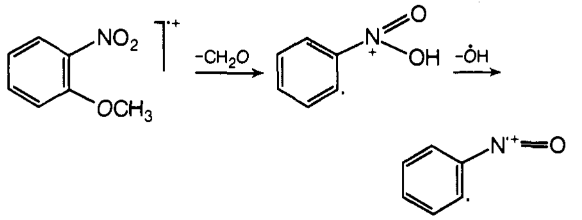


(58)



94

Not all *o*-nitro derivatives manifest an ortho effect by the loss of hydroxyl. In the case of *o*-nitroanisole, for example, this initial loss from the molecular ion is of CH_2O, as expected for an aromatic methyl ether. Subsequent to this loss, however, a hydroxyl group is eliminated and the inference is that this is due to prior hydrogen migration to the nitro group (eq 59).[531-533] The thermal fragmentation of o-nitroanisole was found to be significantly different from its mass spectrometric decomposition. Other simple *o*-nitro compounds have also been investigated including o-nitrobenzoic acid $(M - CO_2)$,[533] o-nitrobenzaldehyde $(M - NOOH - CO)$,[533] o-nitrobenzyl alcohol $(M - H - NOOH)$,[533] and o-nitrobenzaldehyde dimethyl acetal $(M - CH_3OH)$.[534] The conclusion was made from a study of such compounds that ortho effects in nitroarenes are of two basic types.[533] The first is the transfer of H from the ortho substituent to the nitro group followed usually by complex rearrangements that result in the elimination of a small molecule. The process of eq 56 is an example of this first type of effect, although it should be emphasized that *o*-nitroanisole also shows other, more complex, fragmentation pathways. The second ortho effect concerns the migration of an atom or group of atoms from a substituent to the vacated (probably charge-carrying) ortho site. The loss of CO from the $(M - NO_2)$ ion of o-nitrobenzoic acid has been inferred to be of this type of process (eq 60).



(59)

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(524) J. H. Beynon, B. E. Job, and A. E. Williams, *Z. Naturforsch. A*, **21**, 210 (1966).

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(526) J. H. Beynon, R. A. Saunders, A. Topham, and A. E. Williams, *J. Chem. Soc.*, 6403 (1965).

(527) J. H. Beynon in "Mass Spectrometry," R. I. Reed, Ed., Academic Press, New York, N. Y., 1965, p 359.

(527a) G. E. Robinson, C. B. Thomas, and J. M. Vernon, *J. Chem. Soc. B*, 1273 (1971).

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(529) J. H. Bowie, R. G. Cooks, J. W. Fisher, and T. M. Spotswood, *Aust. J. Chem.*, **21**, 2021 (1968).

(530) R. T. Coutts, K. W. Hindmarsh, and E. Mah, *Can. J. Chem.*, **48**, 3747 (1970).

(531) J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc. B*, 396 (1966).

(532) O. A. Mamer, R. J. Kominar, and F. P. Lossing, *Org. Mass Spectrom.*, **3**, 1411 (1970).

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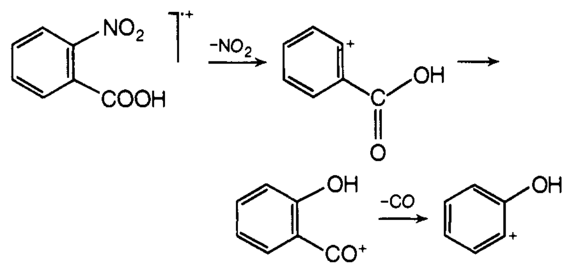
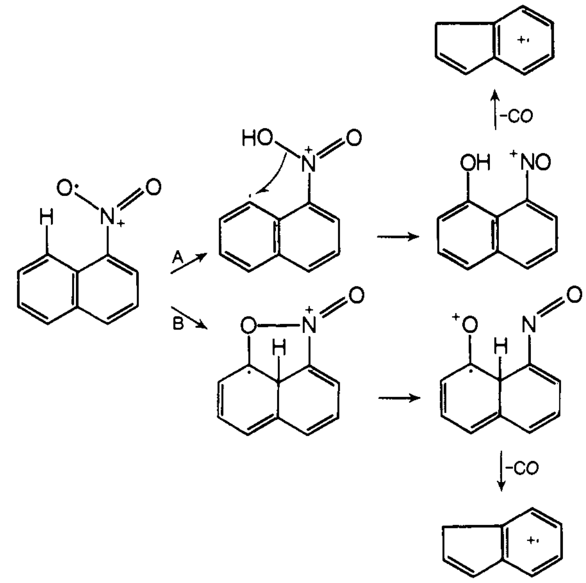
(534) M. M. Bursey, *Tetrahedron Lett.*, 981 (1968).



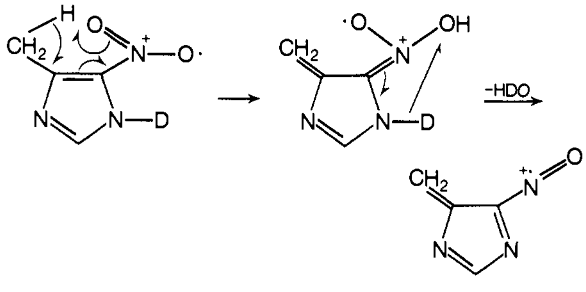
(60)

In 1-nitronaphthalene the loss of CO is observed from the molecular ion, and the mechanisms of Scheme XXI have been suggested to account for this observation.[524,531] These mechanisms are supported by the observation[524] that 1-nitronaphthalenes bearing an 8 substituent (NH_2, NO_2) do not eliminate carbon monoxide, but a distinction between paths A and B is not easy to make. In the original proposal[524] path A was favored on the basis of calculations of electron density at the 8 position, but more recent work[535] suggests that path B is favored in most cases, at least in the dinitronaphthalene series. In this series, only 1,3-dinitronaphthalene appears to fragment *via* pathway A, although the interesting failure of 1,2-dinitronaphthalene to lose CO may be explained by steric hindrance to a step such as the second step of path A. Other dinitro derivatives appear to fragment normally: 2,6-dinitrotoluene, for example, losing two hydroxyl groups.[525] 2-Nitrobiphenyl, however, also loses CO analogously to 1-nitronaphthalene.[523] Ortho effects are also found in the spectra of nitro- and dinitrophenylhydrazines[535] and hydrazones.[535-541] The prominent loss of H_2O from the parent ion of o-nitrophenylhydrazines must be due to the operation of an ortho effect[535] and so also must the loss of H_2O and OH (apparently in one step!) from various *o*-nitrophenylhydrazones.[537] Other fragmentations which are proposed to proceed *via* ortho interactions include the formation of protonated cyclohexanone from cyclohexanone 2,4-dinitrophenylhydrazone[535] and a pathway involving oxygen migration in the dinitrophenylhydrazones of aromatic aldehydes.[538]

SCHEME XXI



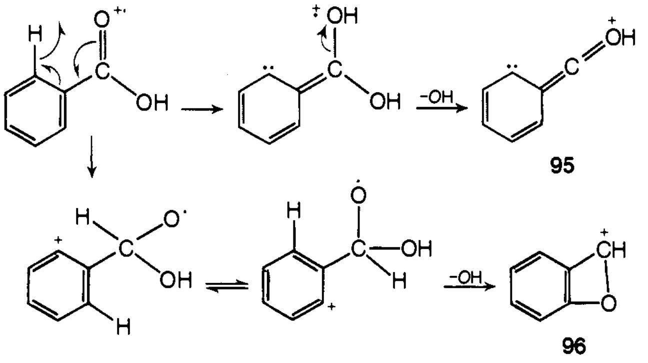
Ortho effects are also proposed to account for certain ions in the spectra of β-nitrostyrenes[541] and 4-methyl-5-nitroimidazole[542] where deuterium labeling has been used to establish the interaction of the nitro group with both ortho substituents (eq 61).



(61)

Another interesting example of the ortho effect is that involving the loss of a hydroxyl group from aromatic carboxylic acids. On the face of it, this reaction might appear to be merely a simple cleavage reaction, but studies of benzoic acid-*O*-*d*[304,543-546] have shown unambiguously that at least two pathways must be involved in this fragmentation. Thus benzoic acid-*O*-*d*, loses both OD and OH as shown by fragment ions[543,545,546] and metastable ions.[304,544] The loss of OH has been variously estimated as 18[545] and 5%[304] in normal ions and reaches a maximum of 66[544] or 60%[304] in low-energy ions decomposing in the field-free regions of the mass spectrometer. These results are readily explained by the postulate that fragmentation can occur both by a normal cleavage to yield the benzoyl cation, and by a rearrangement process represented in Scheme XXII which yields either the ion **95**[545] or **96**.[546]

SCHEME XXII



Similar rearrangements are not observed to any great extent in salicylic acid,[547] where the alternate ortho effect leading to loss of water provides the predominant fragmentation pathway, but loss of OH is observed from the molecular ion of *o*-toluic acid-*O*-*d*, in addition to a more intense loss of HOD and H_2O.[485] Phthalic acid shows no loss of OH, indicating strong intramolecular bonding of the carboxyl groups, but the (M − CO_2) ion does lose either OH or H_2O.[548] A study of phthalic acid-

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(536) F. Benoit and J. L. Holmes, *Can. J. Chem.*, **47**, 3611 (1969).

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(544) J. H. Beynon, B. E. Job, and A. E. Williams, *Z. Naturforsch. A*, **20**, 883 (1965).

(545) S. Meyerson and J. L. Corbin, *J. Amer. Chem. Soc.*, **87**, 3045 (1969).

(546) J. L. Holmes and F. Benoit, *Org. Mass Spectrom.*, **4**, 97 (1970).

(547) S. A. Benezra and M. M. Bursey, *Org. Mass Spectrom.*, **6**, 463 (1972).

(548) F. Benoit, J. L. Holmes, and N. S. Isaacs, *Org. Mass Spectrom.*, **2**, 591 (1969).

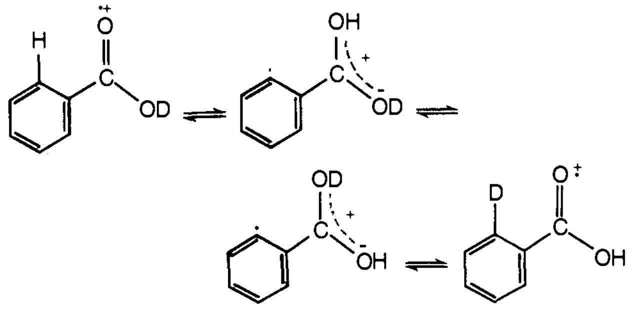
TABLE XI. Miscellaneous Ortho Effects

Ortho groups		Compound or aromatic ring system	Fragment ion formed	Ref
CH	H	Triphenylmethane	$(M - CH_3)$	*a*
CH_2	H	Diphenylmethanes	$(M - CH_3)$	*a*
$OCOCH_3$	COOH	Acetylsalicylic acid	$(M - CH_3COOH)$	*b*
COOR	COOR	Phthalates	$C_8H_5O_3$	*c*
CH_2Br	OCH_3	*o*-Methoxybenzyl bromide	$(M - Br - CH_2O)$	*d*
OCH_3	OCH_3	Meconine	$(M - H_2O)$	*e*
$NRCOCH_3$	H	*N,N*-Diphenylacetamide	$(M - CH_2CO)$	*f*
COOH	$C_6H_5OCH_3$	2-Methoxy-2′-diphenic acid	$CH_3C_6H_4COO$	*g*
CH_3	SO_2	*o*-Tolyl phenyl sulfone	$(M - H_2O - OH)$	*h*
OH	$COCH_2Cl$	2-Hydroxy-ω-chloroacetophenone	$(M - HCl)$	*i*
OC_2H_5	$CONH_2$	*o*-Ethoxybenzamide	$(M - NH_3)$	*j*
XH	NHCSH	Thioformanilides	$(M - SH)$	*k*
CH_3	X	*o*-Methylphenyl halides	$(M - HX)$	*l*
CH_3	$N{=}CHC_6H_5$	*o*-Methyl anils	$(M - C_6H_5)$	*m*
OH	$COCH{=}CHC_6H_5$	2′-Hydroxychalcone	$(M - C_6H_5)$	*n*
N-O	H	Quinoline *N*-oxide	$(M - CHO)$	*o*
N-O	CH_3	2-Methylquinoline *N*-oxide	$(M - OH)$	*o*
N-O	CH_3	1-Methylisoquinoline *N*-oxide	$(M - OH)$	*p*
N-O	CH_3	2-Methylpyridine	$(M - OH)$	*q–s*
N-O	CH_3	Aromatic *N*-oxides	$(M - OH)$	*t*
NC_5H_{10}	N=	2-Piperidylpyrimidine	$(M - C_5H_9N)$	*u*
CH_2COCH_2COOR	CH_3	Furan	$(M - CH_3COCH_2COOR)$	*v*
$COOCH_3$	Ferrocene	*o*-Carbomethoxyferrocenylbenzenes	$(M - CH_2O)$	*w*
OCH_3	OCH_3	2,2′-Dimethoxybiphenyl	$(M - C_6H_5O)$	*x*
$NHSiMe_3$	$NHSiMe_3$	Naphthalene	$(M - SiMe_4)$	*y*
OCH_2Ph	CH_2R	Tetrahydroisoquinoline	$(M - PhCH_3)$	*z*
CO	OCH_3	Tropolone methyl ether	$(M - CHO)$	*aa*
OH	OH	Perylenequinone	$(M - O)$	*bb*

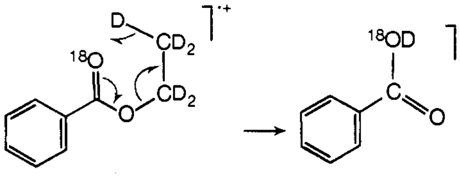
[a] K. D. Berlin and R. D. Shupe, *Org. Mass Spectrom.*, **2**, 447 (1969). [b] A. Tatematsu and T. Goto, *Yakugaku Zasshi*, **85**, 624 (1965). [c] F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959). [d] Z. Pelah, J. M. Wilson, M. Ohashi, H. Budzikiewicz, and C. Djerassi, *Tetrahedron*, **19**, 2233 (1963). [e] B. M. King, D. A. Evans, and K. Biemann, *Org. Mass Spectrom.*, **3**, 1049 (1970). [f] H.-W. Fehlhaber and P. Welzel, *ibid.*, 4, 545 (1970). [g] C. Wunsche, A. Sachs, A. Einwiller, and W. Mayer, *Tetrahedron*, **24**, 3407 (1968). [h] S. Meyerson, H. Drews, and E. K. Fields, *Anal. Chem.*, **36**, 1294 (1964). [i] B. Willhalm, A. F. Thomas, and F. Gautschi, *Tetrahedron*, **20**, 1185 (1964). [j] G. Spiteller, *Monatsh. Chem.*, **92**, 1142, 1147 (1961). [k] W. Walter, R. F. Becker, and H.-F. Grützmacher, *Tetrahedron Lett.*, 3515 (1968). [l] F. W. McLafferty, *Anal. Chem.*, **34**, 16 (1962). [m] D. J. Elias and R. G. Gillis, *Aust. J. Chem.*, **19**, 251 (1966). [n] S. Sasaki, Y. Itagaki, T. Kurokawa, E. Watanabe, and T. Aoyama, *Shitsuryo Bunseki*, 14, 82 (1966). [o] D. Buchardt, A. M. Duffield, and R. H. Shapiro, *Tetrahedron*, **24**, 3139 (1968). [p] D. R. Hoffman, *J. Org. Chem.*, **31**, 792 (1966). [q] R. Grigg and B. G. Odell, *J. Chem. Soc. B*, 218 (1966). [r] D. A. Lightner, R. Nicoletti, G. B. Quistad, and E. Irwin, *Org. Mass Spectrom.*, 4, 571 (1970). [s] N. Bild and M. Hesse, *Helv. Chim. Acta*, **50**, 1885 (1967). [t] A. Tatematsu, H. Yoshizumi, E. Hayashi, and H. Nakata, *Tetrahedron Lett.*, 2985 (1967). [u] T. Nishiwaki, *Tetrahedron*, **23**, 1153 (1967). [v] R. Grigg, M. V. Sargent, D. H. Williams, and J. A. Knight, *Ibid.*, **21**, 3441 (1965). [w] D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, **89**, 4917 (1967). [x] U. Rapp, A. Sachs, C. Wunsche, and W. Mayer, *Chem. Ber.*, 105, 217 (1972). [y] W. J. A. Vandenheuvel, J. L. Smith, R. A. Firestone, and J. L. Beck, 20th Annual Conference, of the American Society for Mass Spectrometry, Dallas, Tex., 1972, Paper A6. [z] G. A. Charnock and A. H. Jackson, *J. Chem. Soc., Perkin Trans. 2*, 856 (1972). [aa] J. L. C. Wright, W. D. Jamieson, S. Safe, and L. C. Vining, *Can. J. Chem.*, **50**, 821 (1972). [bb] K. H. Weisgraber and U. Weiss, *J. Chem. Soc., Perkin Trans. 2*, 83 (1972).

O-d_2[546] again implicated ortho effects in the loss of these fragments. Thiobenzoic acid, on the other hand, loses SH with no interaction with ortho hydrogen atoms.[546]

SCHEME XXIII



The ortho effect just discussed has been used as a tool to investigate the structure and reactivity of the ion formed by loss of ethylene from β-bromoethyl benzoate, and by implication the structure of the molecular ion of benzoic acid. Thus it was shown that the oxygen atoms of the product ion become equivalent either during or after the McLafferty rearrangement producing them.[549] This, taken in conjunction with the results just discussed, is consistent with a structure for the benzoic acid molecular ions in which, in a time of the order of 10^{-5} sec, the oxygen atoms become equivalent and there is complete scrambling between the acid hydrogen and the ortho hydrogen (Scheme XXIII). A detailed study of the product ion formed by loss of C_2D_4 from $C_6H_5C^{18}OOC_2D_5$ was made by ion kinetic energy spectroscopy[550] and revealed the interesting information that initial transfer of deuterium is to the carbonyl group of the ester (eq 62), but that equilibration eventually occurs, presumably by a succession of steps similar to those outlined in Scheme XXII, so that eventually the deuterium is equally distributed over both oxygen atoms. In addition, it was possible to estimate the hindered rate of rotation of the side chain as indicated in Scheme XXII as about one-fourth of the time taken by the ions to reach the center of the first field-free re-

 (62)

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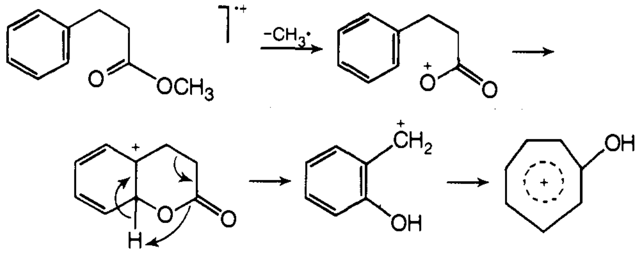
(549) R. H. Shapiro and K. B. Tomer, *Org. Mass Spectrom.*, **2**, 1175 (1969).

(550) R. H. Shapiro, K. B. Tomer, R. M. Caprioli, and J. H. Beynon, *Org. Mass Spectrom.*, **3**, 1333 (1970).

gion of the mass spectrometer. Studies with ring-deuterated compounds further showed that scrambling of the ring hydrogens does not precede the loss of OH from benzoic acid or the (M − C_2H_4) ion of ethyl benzoate.[551]

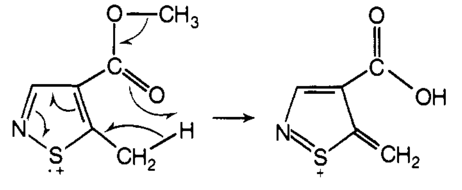
Finally, there are a number of fragmentation reactions of aromatic molecules which are obviously the result of ortho effects, and yet which defy simple classification. These reactions are summarized in Table XI. Some interesting ortho effects involve what appears to be an aromatic substitution reaction at the ortho position. Thus the loss of ketene from methyl 3-phenylpropionate is proposed to occur *via* the pathway outlined in Scheme XXIV.[552,553] Similarly, a number of compounds of the general formula $C_6H_5CH{=}CHCOR$ show intense (M − H) peaks, which largely arise through the loss of a hydrogen atom from the aromatic ring, probably *via* an intramolecular aromatic substitution reaction which results in the relatively stable benzopyrylium cation.[554] The loss of halogen from dinitrophenylhydrazine derivatives of o-halobenzaldehydes is also probably a result of an internal displacement reaction.[539]

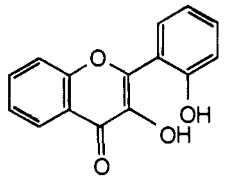
SCHEME XXIV



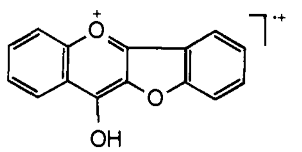
A unique loss of CH_3 (rather than OCH_3) from 4-carbomethoxy-5-methylisothiazole has been attributed to interaction of the two adjacent substituents, as indicated in Scheme XXV.[555] Loss of OH is also particularly prominent in 2′,3-dihydroxyflavones (**97**) probably with the formation of the ion **98**.[556] An analogous reaction in 2′,3-dimethoxyflavones leads to the elimination of CH_3O.[489]

SCHEME XXV





97



98

IV. Addendum

A further study of the ion-molecule reactivity of cycloalkanes with ammonia has appeared.[557] In contrast with the conclusions made from an earlier study,[82] these authors conclude that ring opening does occur in some ionized cyclopropane and cyclobutane molecules, and that the fraction of $C_3H_6^+$ ions which transfer a proton to NH_3 can be considered an accurate measure of the fraction of ions which exhibit an acyclic structure under the particular conditions of the experiment.

A study of hydrogen rearrangements in 2,4-dimethyl-1-pentene indicates that specific rearrangements occur in this compound both with respect to the loss of propylene (McLafferty rearrangement) and also for the loss of ethylene (skeletal rearrangement).[558]

A study of the structure of the benzene molecular ion by measurement of the kinetic energy released by the $[C_6H_6]\cdot^+$ ion generated by direct ionization of benzene and by charge exchange of $[C_6H_6]^{2+}$ indicated that the reactive form of the ion has an acyclic structure.[559] Hydrogen scrambling does not occur to a significant extent before loss of HCN from ionized 1,2,4-triazole,[560] and the *p*-fluoro labeling technique has been used to study the extent of skeletal rearrangement in various five-membered heterocycles containing nitrogen.[561] No obvious correlation with the results of photochemical studies was found in this latter study.

Interest in the ring-expansion reactions of aromatic compounds continues. 2,6-Dichlorotoluene shows similar decompositions to 3,4-dichlorocycloheptatriene, losing C_2H_2, C_2HCl, and C_2Cl_2 from its $(M - H)^+$ ion, and suggesting skeletal rearrangement of this ion.[562] Hydrogen scrambling processes in ions derived from diphenylmethane derivatives have been investigated,[563] while ring expansion and hydrogen scrambling have been studied in the molecular ion of 3-methylthiophene[564] and the $[M - CH_3]^+$ ion from tri- and tetramethylbenzenes.[565] The benzotropylium structure is proposed for the ion resulting from loss of chlorine from ionized 1- and 2-chloromethylnaphthalene and 1-chloro-5-phenyl-2-penten-4-yne.[566]

The side-chain rearrangements of phenetole and acetanilide have also been investigated. In the former case, icr studies showed that the hydrogen transferred is generated predominantly from the terminal position of the side chain, but some transfer from the position next to oxygen also occurs. The ion–molecule reactions of the product $C_6H_6O\cdot^+$ ion indicate that it has the phenolic structure.[567] In the case of acetanilide, examination of metastable peak abundance ratios for the elimination of HNC *vs.* DNC from the $[M - \text{ketene}]\cdot^+$ ion of various deuterium-labeled acetanilides shows that this ion resembles aniline rather than cyclohexadienimine.[568] It has

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(551) R. H. Shapiro, K. Tomer, J. H. Beynon, and R. M. Caprioli, *Org. Mass Spectrom.*, **3**, 1593 (1970).

(552) J. K. MacLeod, *Org. Mass Spectrom.*, **2**, 791 (1969).

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(568) S. Hammerum and K. B. Tomer, *Org. Mass Spectrom.*, **6**, 1369 (1972).

been shown that hydrogen bonding is *not* significant in affecting the preexponential factor for rearrangement of chlorinated acetanilides,[569] contrary to an earlier report.[435a]

Finally, a novel ortho effect has been uncovered in the mass spectra of several 1-alkyl-2-substituted-5-nitroimidazoles,[570] and ortho effects in various aromatic nitro compounds have been studied.[571]

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(569) S. A. Benezra and M. M. Bursey, *J. Chem. Soc., Perkin, Trans. 2*, 1537 (1972).

(570) G. E. Van Lear, *Org. Mass Spectrom.*, **6**, 1117 (1972).

(571) K. B. Tomer, T. Gebreyesus, and C. Djerassi, *Org. Mass Spectrom.*, **7**, 383 (1973).