Intramolecular Hydrogen Transfer in Mass Spectra. III. Rearrangements Involving the Loss of Small Neutral Molecules

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Contents

I. Introduction

Parts I[3] and II[4] of this series dealt respectively with the hydrogen transfers involved in the fragmentation of aliphatic hydrocarbons and aromatic compounds on electron impact, and with the McLafferty rearrangement and related reactions. In this third and final part we take up the subject of the hydrogen transfer reactions involved in the loss of small neutral species from the molecular ion or certain fragment ions formed on ionization of organic compounds in the mass spectrometer. While most of the examples cited will be electron-impact-induced fragmentations, some examples of field ionization and photoionization studies will be included where appropriate.

The literature for this article has been covered through December 1973. As an indication of the growth of work in this area, our initial set of approximately 1000 references, which was complete to mid-1971, has been updated by the addition of approximately 600 new references covering the period mid-1971 to 1973. Only a fraction of these references can be discussed in the text, and the more important examples are therefore grouped into tables corresponding to the main sections of the article.

Throughout this review a number of mechanistic schemes will be proposed to account for the observed hydrogen transfer processes. Unless otherwise stated, these schemes are derived from the references cited, and not from the authors of this review. It should be borne in mind that in many cases the ion structures proposed do not have a firm experimental basis and are presented therefore more as convenient ways of rationalizing the evidence from labeling and other studies than as firmly established structures.

II. Loss of Water

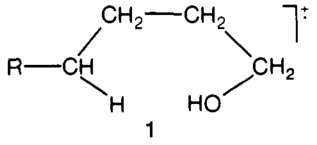
Undoubtedly the commonest loss of a small neutral fragment in mass spectrometry involves the loss of a water molecule. This loss occurs not only from alcohols, but also from carboxylic acids, aldehydes and ketones, amides, and many other classes of organic compound. The loss of water from certain aromatic compounds involving ortho and peri effects has already been discussed in Part I of this review[3] and will not be dealt with any further. We shall discuss first water loss from various alcohols and then proceed to the case of water loss from molecules containing other functional groups.

A. Loss of Water from Alcohols

The fact that alcohols are known to eliminate water in a thermal reaction indicates that thermal elimination of water may be competitive with or even completely dominate electron-induced fragmentation. In some particular cases this is indeed the situation, and it has been suggested that an alcohol such as cortisol, which undergoes ready thermal dehydration, can be used to test the efficiency of sample introduction systems.[5,6] For most alcohols, however, thermal dehydration plays a relatively small role compared with electron-impact-induced water elimination, particularly when a good direct sample introduction system is used. We shall thus discuss water elimination from alcohols only in terms of the latter mechanism, although it should be realized that thermal processes may on occasion be competitive with it.

1. Loss of Water from Alkanols

Deuterium-labeling studies in butanol[7-9] and in higher alcohols[10-12] indicate that elimination of water occurs predominantly (80–90%) by 1,4-elimination through a six-membered intermediate (1). This is in marked contrast to the thermal process which occurs by 1,2-elimination, and this fact, taken in conjunction with the observation of metastable peaks for the formation of the $(M - 18)^{\cdot +}$ ion directly from the molecular ion, establishes the eliminations described as being electron impact induced. In the case of 1-hexanol, label retentions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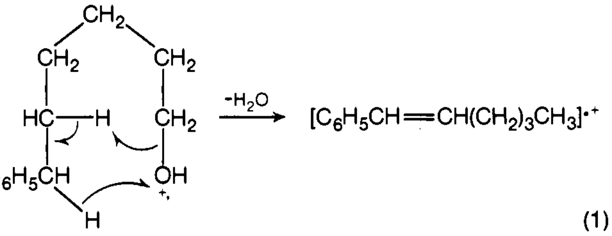
in secondary decompositions of the (M − 18)$\cdot^+$ ions suggested that the loss of water in this compound is accompanied by formation of a new bond between C-1 and C-4.[11] On the other hand, it has been suggested that elimination of water is coupled with the expulsion of ethylene in a concerted process.[13] While this may be correct for some $(M - H_2O - C_2H_4)\cdot^+$ ions, the observation of metastable peaks for the formation of these ions from $(M - H_2O)\cdot^+$ ions in the spectra of primary straight-chain alkanols[13] indicates that the process must also proceed in a stepwise fashion. It thus appears that the predominant mechanism for loss of water from primary straight-chain alkanols involves a six-membered activated complex and at least in some cases requires bond formation between the 1- and 4-carbon atoms. There is no evidence to support either a stepwise or a concerted mechanism. The minor pathways for loss of water could be explained either by a different activated complex requiring a smaller ring (for example, 1,3-elimination) or by the same six-membered activated complex preceded by exchange of hydrogens on the 3- and 4-carbons. In the case of hexanol, which loses hydrogen from the 3-position but not from the 5-position, this latter argument demands exchange between C-3 and C-4, but not between C-4 and C-5, and thus it seems less satisfactory than the former for this case. The occurrence of hydrogen scrambling preceding the loss of water from cyclohexanol has been shown not to occur, at least for normal ions,[14] and so it seems probable that hydrogen exchange is unimportant in acyclic alcohols also.

Although water elimination from alcohols usually proceeds by the 1,4-elimination pathway, structural features in the parent molecule may act to direct fragmentation into alternate pathways. A striking example of this effect is found in the spectra of 6-phenylhexanol and 5-phenylpentanol, where the hydrogen lost with the hydroxyl group comes largely (75–80%) from the 6- and 5-carbon atoms, respectively.[15] The mechanism of eq 1 is suggested as an explanation for this unusual behavior, where the formation of a stable conjugated alkene provides a significant driving force for the reaction. Similar results are reported in studies of the loss of water from deuterated ω-benzyloxyalkan-1-ols, $C_6H_5CD_2O(CH_2)_nOH$,[16] from 26-hydroxy-5α-furostan (**2**),[17] and from various α,ω-diols.[18] The operation of these "remote-group" interactions in mass spectrometry has been explained by the tendency of ions to coil in the gas phase, possibly as a means of attaining internal solvation.[15] In addition to studies of large-ring transition states for water loss, studies have been made of water loss from shorter chain aralkyl alcohols such as 2-phenylethanol and 3-phenylpropanol-1. In the former case the second hydrogen lost with the hydroxyl group arises, not unexpectedly, from the β position,[19] but in 3-phenylpropanol-1, hydrogen exchange occurs prior to water loss and involves the ortho, 3-, and hydroxyl hydrogens.[20]



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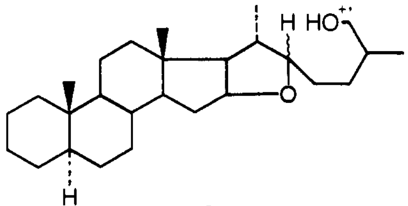

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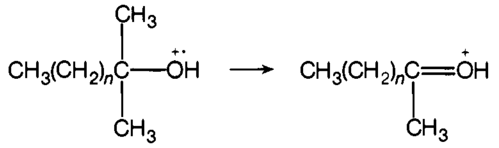
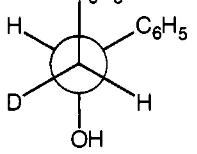
Dehydration of fragment ions may also occur, and this appears not to proceed in as specific a fashion as that observed in the molecular ions; this result is perhaps not surprising, since dehydration of fragment ions involves an even-electron species while the molecular ion is of course an odd-electron species. In addition, the greater internal energy required for reaction of fragment ions may be a factor in the lower specificity of these reactions. Elimination of water from the $(M - CH_3)^+$ ions **3b** derived from 2-methyl-2-pentanol and 2-methyl-2-hexanol (**3a**) arises to the extent of about 30% each by 1,3- and 1,4-eliminations.[10] Similarly, loss of water from the α-cleavage product of 7-tridecanol occurs by 1,4-elimination only to the extent of 40% of the total elimination pathway.[12]



$$CH_3(CH_2)_nC(CH_3)_2\overset{+\cdot}{O}H \longrightarrow CH_3(CH_2)_nC(CH_3)\!=\!\overset{+}{O}H$$

3a, *n* = 3 or 4 **3b**

The stereochemical requirements for water elimination have been explored in some recent papers. In 1,2-diphenylethanol, which loses water by a 1,2-elimination process, the isomers **4** and **5** show 36:64 and 48:52 ratios for loss of HOD:HOH.[21] These data, combined with those for the corresponding methyl ethers, and after a correction for an isotope effect of 1.87 atoms of protium transferred per atom of deuterium, indicate the stereoselectivity in the reaction is about 55:45. In the case of (*S*)-2-pentanol, the small amount of 1,3-elimination observed occurs preferentially (55%) with abstraction of the pro-*R* hydrogen, suggesting that the activated complex **6** is favored over **7** by a few hundred calories; in this study the isotope effect for elimination of water was assumed to be close to unity.[22]



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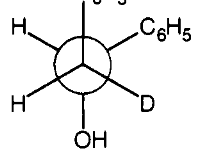

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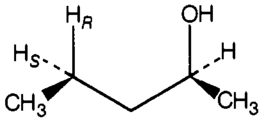

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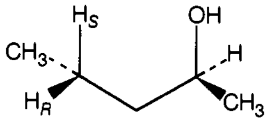

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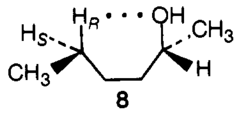
In the case of the 1,4-elimination of water from (*R*)-2-hexanol, however, the pro-*R* hydrogen is again preferentially abstracted (pro-*R*:pro-*S* hydrogen abstraction ratio 1.10:1).[23] This result indicates that the activated complex **8** is favored over **9** by a few hundred calories and parallels a similar specificity in the Barton reaction.



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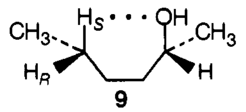

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Two theoretical studies of water loss from alkanols have appeared. The first one used a simplified form of the quasi-equilibrium theory to predict the extent of water loss from ethanol and the propanols,[24] while the second compared the effect of temperature on the (M − 18)$\cdot^+$ ion with predictions from the same theory.[25] Further examples of water loss from alkanols will be found in Table I. It should be noted that this and subsequent tables are not intended to be exhaustive summaries of the literature: the intention is rather to include in them only detailed studies and representative examples of the fragmentation in question from various structural types. There seems little point, for example, in recording every single reported instance of water elimination from alcohols.

2. Loss of Water from Alkenols and Alkynols

The mass spectral decompositions of alkenols and alkynols have not been investigated as thoroughly as those of the corresponding alkanols, but loss of water is not unexpectedly a ubiquitous fragmentation process in those molecules that have been studied.[26-29] In the case of the loss of water from the 2-buten-1-ols, $CH_3CH{=}CHCH_2OH$, the process was found to involve specifically the loss of a hydrogen from the terminal methyl group together with the hydroxyl group; in other words, loss occurred by the expected six-membered transition state.[29] Further examples are included in Table II.

3. Loss of Water from Cycloalkanols

Water loss occurs readily from the molecular ion of cycloalkanols, and this reaction has been studied extensively. This section will deal first with water loss from cyclohexanol and will then proceed to bicyclic alcohols and finally to polycyclic alcohols such as the steroids.

The fragmentations of cyclohexanol on electron impact have been studied several times: work up to 1967 is reviewed by Budzikiewicz, Djerassi, and Williams,[30] while more recent results are summarized by Bowie.[31] Loss of water from the molecular ion occurs readily, providing the second largest peak in the spectrum at 70 eV. The site specificity of this loss has been the subject of some debate. The facts are that water loss from cyclohexanol involves predominantly the hydroxyl hydrogen (85%) and a hydrogen from just about every other position on the ring, with the most important contribution (50%) coming from the 4-position.[14,32,33] Two major theories have been advanced to explain these observations. In one hypothesis, loss of water occurs predominantly if not exclusively by a 1,4-elimination process, and the involvement of other hydrogens is explained by partial hydrogen scrambling preceding water elimination. The extent of scrambling is held to increase in the ions of long lifetime undergoing metastable decompositions, thus providing an explanation for the lower specificity observed for these fragmentations.[33] In the other hypothesis, the observed losses of hydrogen from ring positions other than the 4-position are explained by a 1,3(1,5)-elimination of water from the α-cleaved ion.[22] More recent work has elaborated on this hypothesis, and it is proposed that exchange of the C-2 hydrogen of the α-cleaved ion with the hydroxyl hydrogen and isomerization to a hexanal-type ion followed by 1,3(1,5)-elimination from this ion also contributes to the observed water loss.[14] Although this explanation lacks the simplicity of the first explanation, it does give data in good agreement with the experimental observations. In particular, the involvement of the α-cleaved ion seems reasonable and offers a satisfying explanation for the relative complexity of the cyclohexanol case when compared with acyclic alcohols, since, of course, the α-cleaved ion in the latter would have a different *m/e* value from the molecular ion and would thus yield fragment ions of different *m/e* values from corresponding fragments of the molecular ion. Hydrogen scrambling appears not to be significant in water loss from cyclohexanol.[22] On balance, therefore, the evidence favors the latter hypothesis, although the reviewers would not exclude the possibility that some hydrogen scrambling may occur in the long lifetime ions giving rise to metastable peaks. The 1,4-elimination observed from the uncleaved molecular ion occurs with essentially complete cis stereospecificity, as would be expected on geometric grounds,[14,22] while the 1,3 elimination is nonstereospecific.[22] The mechanisms proposed for water elimination from cyclohexanol are summarized in Scheme I; the percentage total reaction occurring by each of the proposed pathways at 70 eV is indicated alongside the pathway.

TABLE I. Water Loss from Alkanols[a]

Aliphatic Alcohols	
General	24, 25, 81, 82, 84, 240
Simple primary alcohols	
Ethanol	241 (E)
1-Butanol	7, 10, 85
1-Pentanol	8, 10, 82b
Hexanol	10, 11, 83
1-Heptanol	10
Neopentyl alcohol	242 (D, L)
Branched long-chain aliphatic alcohols	243 (D)
$C_nH_{2n+1}O^+$ ions derived from alcohols	244 (E), 245 (E)
Secondary and tertiary alcohols	
General	12
2-Propanol, ions from	87
tert-Butyl alcohol	246 (L)
2-Pentanol	22
2-Hexanol	23
Substituted primary alcohols	
Benzyl alcohols	88, 247 (M), 248(D), 249 (M)
2-Phenylethanol	250 (D)
1,2-Diphenylethanol	21
ω-Phenylalkanols	15
Pyridoxol and analogs	251 (D), 252 (D, M)
Hydroxyethylphenothiazines	253
Hydroxyethylaminopurines	254 (M)
Tetrahydrofurfuryl alcohol	255
Diterpene alcohols	256 (M)
Selenodiethanol	257 (M)
26-Hydroxy-5α-furostan	17
Substituted secondary and tertiary alcohols	
Diacetone alcohol	258
Cyanohydrins	259 (M)
Terpene alcohols	260 (M)
Cyclohexyl-3-furylcarbinol	261
Monosaccharide dithioacetals	262 (M)
Hydroxywilfordic acid	263
Coumarin derivatives	264 (M)
Oxydihydrocarpesin	265
Marmesin	266
Columbianetin	267 (M)

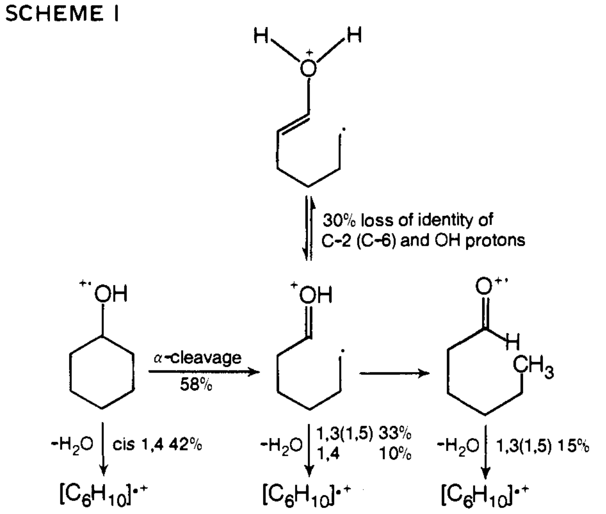
[a] Letters after references indicate: (M) mechanism postulation; (E) energetics; (D) deuterium labeling; (L) labeling with other elements. The information is given at the first listing of each new reference.

TABLE II. Water Loss from Alkenols

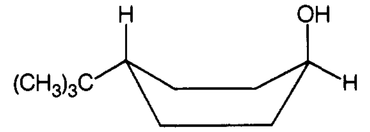
Crotyl alcohol	29
α,β-Unsaturated secondary alcohols	26
Acetylenic alcohols	28
Retinol	268

In addition to cyclohexanol itself, various alkyl cyclohexanols have been investigated. In the case of 4-*tert*-butylcyclohexanol, loss of water occurs readily from the trans isomer (**10**) but to a much smaller extent from the cis isomer (**11**).[34-37] This of course is expected in the light of the results

SCHEME I



from cyclohexanol itself, since only *trans*-1,4-*tert*-butylcyclohexanol (**10**) could undergo a cis 1,4-elimination of water. It has been shown that the hydrogen eliminated with the hydroxyl group is indeed the cis 4-hydrogen. The greater relative abundance of the $(M - H_2O)\cdot^+$ ion in the spectrum of **10** compared with cyclohexanol, and the relative absence of water loss by pathways other than 1,4-elimination, may be rationalized by noting that 1,4-elimination from **10** requires only the abstraction of a tertiary hydrogen atom. In the case of the 4-isopropylcyclohexanols, however, ready elimination of water was observed from both the cis and the trans isomers.[38] This may be explained by a normal cis 1,4-elimination from the trans isomer and by a cis 1,5-elimination from the cis isomer, and deuterium labeling evidence supports this rationalization.[38] The specificity of water loss has also been studied from menthol and its isomers[39,40] and from the 2-, 3-, and 4-methylcyclohexanols,[37] in addition to other isomers of *tert*-butylcyclohexanol.[35,41]



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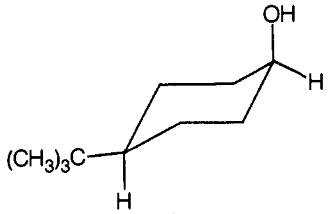

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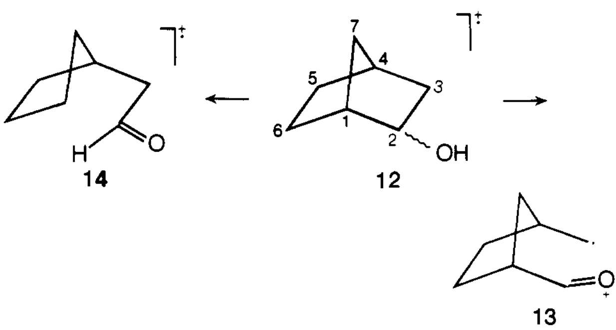
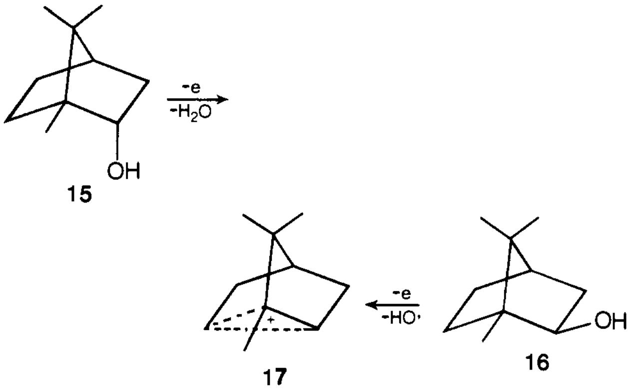
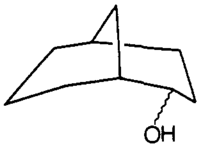
In summary, water loss from cyclohexanol and its derivatives occurs predominantly by a stereospecific cis 1,4-elimination process, and stereoisomers of substituted cyclohexanols consequently differ in the extent to which they lose water on electron impact. This fragmentation could thus in principle be used to define the relative stereochemistry of cyclohexanol isomers, and possibly also of the isomers of larger ring alcohols. More work is required on larger ring alcohols before this latter possibility becomes a reality, however.

The losses of water from the bicyclic compounds norborneol and borneol have been the subject of some recent studies which extend and modify the conclusions of earlier studies. In the case of the norborneols (**12**) it is proposed that the loss of water from the molecular ion consists of two processes, one involving and one not involving the hydroxyl hydrogen atom.[42] Approximately half the water loss is proposed to arise from an α-cleaved ion **13** which then loses the hydroxyl group and a hydrogen atom from either the 6- or the 7-position. The other half of the water loss involves the alternate α-cleavage followed by rearrangement to a cyclopentylacetaldehyde cation **14** and water loss from this ion with the hydrogen atoms coming randomly from the 5- and 7-positions. These mechanisms agree with those of earlier studies[43,44] in the absence of any loss of hydrogen from the C-3 position (i.e., in the absence of 1,2-elimination) but differ in other respects from them. In the case of borneol itself and its isomers, however, elimination of water involves a 1,2-process at least to the extent of 50% of the total elimination.[45,46] The 3-hydrogen lost with the hydroxyl group comes almost exclusively from the exo position regardless of whether borneol (**15**) or isoborneol (**16**) is studied,[46] and this result is explained in terms of a stepwise elimination of HO to give the ion **17** which then loses the 3-exo hydrogen preferentially to yield camphene and/or bornene cation radicals. This conclusion has been questioned,[45] but as yet no satisfactory alternate explanation has appeared.





The stereochemistry of water loss from the bicyclo[3.3.1]nonanols has also been studied recently.[47-49] The 2-bicyclo[3.3.1]nonanols (**18**) show nonstereospecific water loss, but the isomeric *exo*- and *endo*-3-bicyclo[3.3.1]nonanols (**19**) undergo stereoselective water elimination, with up to 80% of water loss from the exo isomer occurring by a cis 1,4-elimination.[49] The observation of significant differences in the fragmentation pathways of stereoisomers led to the suggestion that these differences could be exploited for the purposes of making stereochemical assignments.[47,49]



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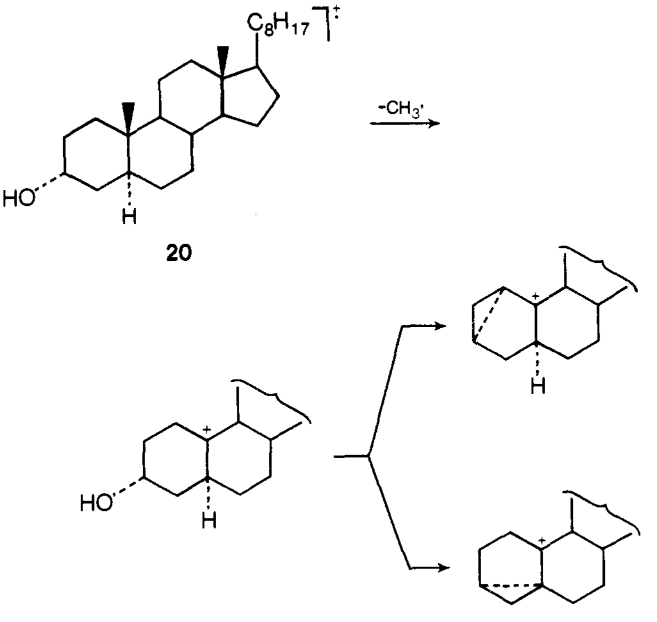
Among polycyclic systems, there has been interest in the comparison of epimeric pairs of steroid alcohols in order to use water elimination as a measure of hydroxyl group orientation. The initial observation in this area was made by Biem-

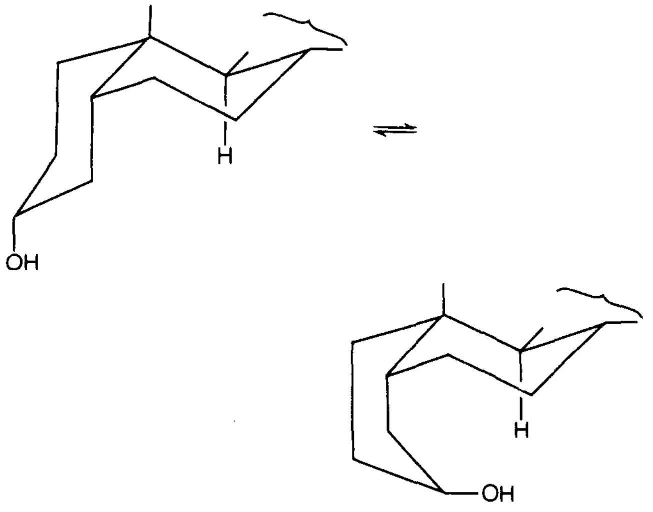
SCHEME II



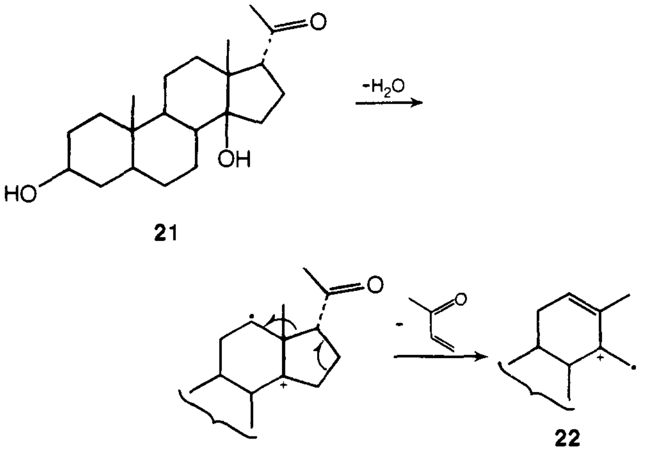
ann, who noted that the more crowded isomer of an epimeric pair of alcohols lost water to the greatest extent.[50] Several other groups have reported similar findings[51-62] on various sterols, and it has been proposed that for equatorial hydroxyl groups the [M − 18]/[M] intensity ratio is less than one, while for axial groups it exceeds one.[57] This rule has been shown not to hold in all cases, however.[61]

The site-specificity of water loss from various sterols and related compounds has been investigated less extensively than its stereochemical dependence, but enough work has been done to indicate that water loss from sterols often follows somewhat different lines from that from simple cyclohexanols. Thus in the case of the 5α-cholestan-3-ols, water loss from the 3α alcohol (**20**) proceeds by the pathway of Scheme II, with water elimination following loss of a methyl group. Loss of water from the 3β alcohol takes a more random pathway, and is suggested to occur after ring fission.[63] In the case of the 5β-cholestan-3-ols, however, fragmentation takes a different course, and the 3α isomer loses the C-9 hydrogen together with the hydroxyl group in the loss of water directly from the molecular ion.[64] This loss presumably occurs via a boat form of the A ring (Scheme III): the 3β isomer, which cannot place its hydroxyl group into proximity with the tertiary 9α hydrogen even by a ring flip, again undergoes a nonspecific water loss.

SCHEME III



Although these results differ from those obtained on the simple cyclohexanols, not all polycyclic alcohols undergo unusual fragmentations. Thus both substituted steroid sapogenins[65] and certain podocarpotriene derivatives[66] undergo water loss by the usual 1,4- and 1,3-elimination pathways, while water loss from various bufadienolides also appears to proceed normally.[67] Loss of water from the 17βH isomer of 14β-pregnane-3β,14-diol-20-one (**21**) proceeds largely (54%) by a 1,3-elimination of the 14β-OH group to give an ion which then eliminates a methyl vinyl ketone fragment (**21** → **22**); the 17 αOH-isomer does not show this fragmentation.[68] Further examples of water loss from cyclic alcohols are given in Table III.



4. Loss of water from Diols and Polyols

Loss of water from diols and polyols is naturally a more complex process than loss from cycloalkanols or simple alkanols. Some studies have been carried out on acyclic systems,[69] but most workers have concentrated on cyclic systems. In the case of *trans*-cyclopentane-1,2-diol, three mechanisms are proposed for water elimination, including the expected 1,4-elimination pathway.[70] With the cyclohexane-1,2-diols, there have been three reports with somewhat different conclusions. In the first investigation Buchs suggested four routes for the loss of water, involving the loss of hydrogen from both hydroxyl groups, or from one hydroxyl group and either the C-4 or C-5 position, and finally from neither hydroxyl group.[71] In spite of this detailed study, however, the author candidly admits that he is unable to formulate a mechanism consistent with all his results. In the second paper, published independently of the first, Strong and Djerassi propose essentially the same four pathways, and in addition suggest structures for the various ions formed.[72] In the third paper, however, Benoit and Holmes arrive at rather different conclusions.[73] Although their data for deuterium loss from various deuterium labeled cyclohexane-1,2-diols agree well with that reported by the previous investigators, their analysis of the data and of data derived from the metastable peaks for H_2O, HDO, and D_2O loss from these compounds led them to conclude that essentially complete scrambling of the OH and the C-4 and C-5 hydrogens was taking place. The ring-opened structure of Scheme IV was suggested as the intermediate in

SCHEME IV

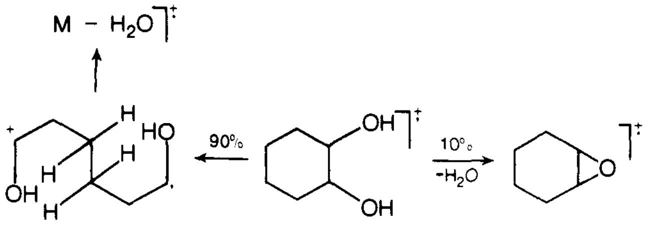
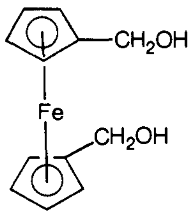


TABLE III. Water Loss from Cyclic Alcohols

Cycloalkanols	
Cyclohexanol	14, 32, 33, 269 (D)
2-Halocyclohexanol	270 (E), 271
4-Isopropylcyclohexanol	38
4-*tert*-Butylcyclohexanol	34–37, 41
Silacyclopentanols	272
Germacyclopentanols	272, 273 (M)
General cyclic alcohols	274, 275
Polycyclic alcohols	
Norborneols	42–44
Borneols	45, 46
Cyclohexylnorbornanols	276 (D)
Aminoborneols	277
Bicyclo[3.3.1]nonanols	47–49
Decanols	51
Adamantanols	278, 279
Polycyclic alcohols	280, 281 (D), 282, 283
1-Hydroxychlordene	284
Terpenes	
Menthols	39, 40
Carols	285, 286
Borneols	45, 46
Monoterpene alcohols	287, 288
Sclareol	53, 289
Manool, larixol	289
Caucalol	290
Carotenoids	291 (D), 292
Other terpenols	66, 293–296, 297 (M), 298 (M), 299, 300, 301 (M)
Alkaloids	
Ajmaline and related alkaloids	302, 303
Amaryllidaceae alkaloids	304 (M), 305, 306 (D, M), 307 (D, M)
Aspidospermine alkaloids	308, 309
Berberine alkaloids	310 (D)
Burnamicine alkaloids	311
Lycopodium alkaloids	312
Lycorine alkaloids	313
Indole alkaloids	314 (M)
Indolinocodeine	315 (M)
Sarpagine, akuammidine	316
Tetrahydroquinolylimidazole	317
Yohimbine	318
Hippeastrine alkaloids	319
Steroids	
General	50, 54, 62, 320, 321
Inlet system tests	5, 6, 322
3-Hydroxy steroids	63, 64, 323–328
6-Hydroxy steroids	329
10-Hydroxy steroids	330
11-Hydroxy steroids	51, 61, 331
14-Hydroxy steroids	52, 55, 68
15-Hydroxy steroids	51, 331
16-Hydroxy steroids	51, 331
17-Hydroxy steroids	58, 59, 332, 333, 334 (M), 335, 336
17a-Hydroxy steroids	58, 60, 337
21-Hydroxy steroids	338
Cardenolides	339, 340
Sapogenins	65, 341, 342
Bufadienolides	67
Cyprinol and ranol	343
Ecdysone	344
Holadysone	345
Plant sterols	346
Withaferin	347 (M)
Ergosterol	348
Kondurangogenin A	349
Other hydroxy steroids	56, 350–352
Polyfunctional hydroxy steroids	
Bile acids	342
Amino alcohols	86
Azasteroids	352
Spirodithian derivatives of 3-oxo steroids	354
Other natural products	
Carcinolepin	355
Chromones	356 (M)
Flavonoids	357 (M), 358 (M), 359 (M)
Gibberellins	360 (M)
Gliotoxins	361
Juglone derivatives	362
Moenosinol	363 (M)
Monensin and related compounds	364
Phorbol derivatives	365
Pyrethroids	366
Tetracyclines	367, 368
Usnic acid derivatives	369 (M)
Aromatic compounds	
1-Naphthol	370 (D, M)
Ortho-substituted phenols	89, 371 (M), 372 (M), 373 (M), 374 (M)
Coumarins	375, 376
Isopropylidenediphenyl carbonates	377
Heterocycles	
Piperidine derivatives	378
Pyridine derivatives	379, 380 (D)
Vitamin B_6 and related compounds	251, 252
Pyrimidine derivatives	381 (M)
Uracil and thymine derivatives	382 (L, M)
11*H*-Dibenzo[*o,f*][1,2]diazepin system	383
Indole derivatives	384–386
Indolinols	387 (M)
Quinoline derivatives	388 (M), 389 (D, M)
Quinoxalines	390
Riboflavin metabolite	391
Butenolides	392

this process; this scheme also indicates the 10% of reaction which goes via direct hydroxyl group interaction in ions decomposing in the source.

As might be expected, elimination of water is observed for various other diols, including cyclohexane-1,3- and -1,4-diol,[74] decalin-2,3- and -1,4-diol,[74] bicyclo[2.2.1]heptanediols,[75] tetralin-1,2-diols,[76] and various steroid diols.[77] The mechanisms proposed for water loss from these compounds are basically similar to those proposed for loss from cyclohexane-1,2-diol, and thus will not be discussed individually. On the other hand, the stereochemical requirements for water loss from several different diols are of some interest. Perhaps the most straightforward case is that of water loss involving hydrogen atoms from *both* hydroxyl groups, which can readily be differentiated from other modes of water loss by analysis of the spectrum of the di-O-deuterated compound. For this loss it is found that the two hydroxyl groups have to be in a location such that the shortest OH···OH distance is less than about 3.2 Å.[77] In practice this means that only steroidal 1,2- or 1,3-diols eliminate water by this pathway, although a *cis*-cyclohexane-1,4-diol could also eliminate water via a chair–boat interconversion. Similar steric arguments undoubtedly account for the fact that the ferrocene **23** loses water readily,[78] and may also account for part of the stereospecificity observed in water loss from bicyclo[2.2.1]heptanediols. Thus of all the bicycloheptanediols examined, of which **24** and **25** are examples, only **25** failed to show a significant peak due to loss of water from the molecular ion.[75]



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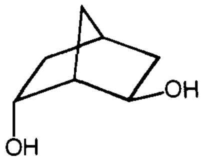

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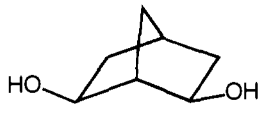

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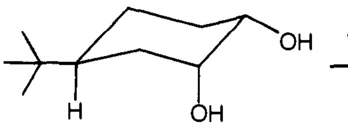
Stereospecificity in the loss of water from the four possible stereoisomers of 4-*tert*-butylcyclohexane-1,2-diol is partially explicable in terms of a stereospecific cis 1,4-elimination in the isomer **26**.[79] This process is particularly favorable because the hydrogen abstracted is tertiary, but it is hard to see why the isomer **27** should not undergo elimination almost as readily, and detailed labeling studies are required before eliminations in this system are fully understood.



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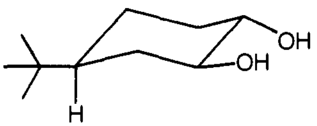

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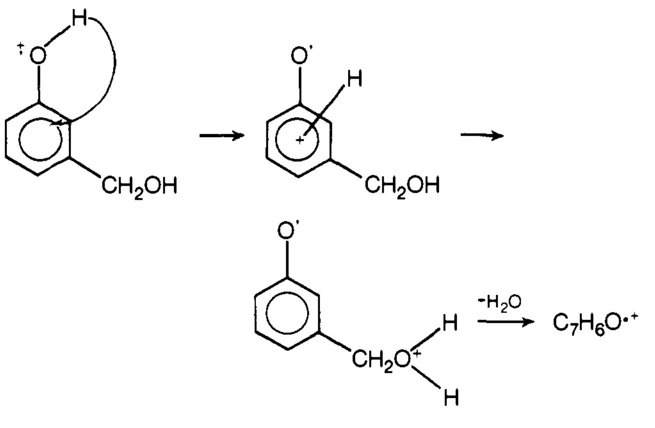
Water loss from *m*-hydroxybenzyl alcohol has been the subject of a recent detailed study; evidence from both deuterium and ^{18}O-labeling supports the mechanism of Scheme V for this reaction.[80] Further examples of water loss from diols and polyols are given in Table IV.

SCHEME V



5. *Loss of Water from Alcohols under Ionization Conditions Other Than Electron Impact*

As might be expected, the elimination of water from ionized alcohols is not confined to ions produced by electron impact. Water loss is observed from the excited states of alcohols produced by field ionization,[81-83] by photoionization,[84] and by radiolysis.[85] The loss of water from hexanol following field ionization has been carefully investigated, and it was established that hydrogen abstraction involves C-3 as well as C-4.[83] This result of course parallels the corresponding fragmentation following electron impact but the two results differ quantitatively. In the case of electron-impact-induced decomposition, we have seen that approximately 91% of the hydrogens lost come from C-4.[10-11] On field ionization, however, the relative extent of hydrogen abstraction from C-3 and C-4 depends on the internal energy of the ions with abstraction from C-3 via a five-membered transition state being the preferred process at high internal energies. This finding raises the question of the meaning of the electron-impact results, since it is entirely possible that the sample of fragment $C_6H_{12}{\cdot}^+$ ions used to assess the extent of hydrogen abstraction from different positions could be an anomalous low-energy sample, the "normal" higher energy ions having decomposed to other fragment ions before collection. If this is indeed the case, then the electron-impact measurements have been made on a sample of low-energy ions weighted in favor of the lower energy fragmentation pathway proceeding via a six-membered transition state, and the true picture might well include a much larger fraction of abstraction via a five-membered transition state. At the present time there seems no good way to test this hypothesis, but clearly there is need for caution in interpreting the relative extent of different pathways of electron-impact-induced fragmentations based on the intensities of ions which are not a representative sample of the ions produced in that fragmentation. This caution is a general one and applies whenever the ion used to monitor a fragmentation process is undergoing further fragmentation on the mass spectrometer time scale.

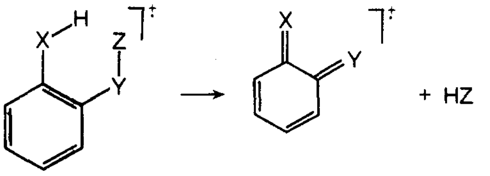
Water loss from alcohols is also observed under conditions of chemical ionization, but in this situation no rearrangement process is involved. The hydroxyl group simply acts as a base and forms an oxonium ion with a proton from some acid in the reactant gas plasma; this protonated species can then lose water to form a carbonium ion.[86] On the other hand, rearrangement processes can be involved in the loss of water from ions produced by ion–molecule reactions, as shown by a study of water loss from the species produced by reaction of protonated acetaldehyde with 2-propanol.[87]

B. Loss of Water from Other Functional Groups

The loss of water from organic compounds on electron impact is not confined to alcohols but embraces a wide range of other functional groups. Perhaps the most useful generalization is that water can be lost in either of two situations. In the first situation an oxygen-containing functional group located either ortho or peri to, or (in aliphatic systems) adjacent to, a hydrogen-containing functional group can interact with the latter group and excise a molecule of water, methanol, or some other small species. In the second general case, a carbonyl-containing functional group can lose water, usually via its enol form. There are, of course, many exceptions to these generalizations, but they can at least serve as the basis for our classification of reactions.

1. *Water Loss Involving Vicinal Interactions*

As mentioned at the beginning of this section, the subject of ortho and peri effects has already been discussed in Part I of this review,[3] and this section will thus only summarize the results reviewed there. Briefly, water loss commonly occurs by the pathway indicated in eq 2, although the transition state

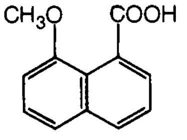


(2)

TABLE IV. Loss of Water from Polyols

Acyclic polyols	18, 69, 393, 394 (M)
Monoglycerides	395
Cyclic polyols	
Cyclobutaneoctaol	396
Cyclopentane-1,2-diol	70
Cyclopentenediolone	397
Cyclohexane-1,2-diols	71–73, 79, 398, 399
Cyclohexane-1,3- and -1,4-diols	74a
Cyclohexanetriols, -tetraols, -pentaols, and -hexaols	400 (D), 401
Cyclohexanedodecaols	396
m-Hydroxybenzyl alcohol	80
Tetrahydroxyquinone	396
Glycoaldehyde	401
Diphenic acid derivatives	402
Bicyclic polyols	
Caranediol	403
Bicycloheptanediols	75
Bicyclooctanepolyols	404
Tetralin-1,2-diol	76
Decalin-2,3-diol	74b
Sugars	
1,6-Anhydro-2,3-*O*-isopropylidene-β-D-talopyranose	405 (D, M)
Methyl glycosides	
Xylofuranosides	406, (D, M)
Glucopyranosides	407–409
Deoxyfluoroglucose phosphate	410
Aminocyclitol antibiotics	411
Kanamycin A derivatives	412 (D)
Nucleosides	
General	413 (D, M), 414, 415, 416 (D, M), 417
Pyrazomycin	418 (D, M)
Substituted ureidopurines	419
Substituted sugars	
Dianhydrohexitols	420
Unsaturated carbohydrates	421
Amino sugars	422, 423
Azido sugars	424
Thio sugars	425
Lincomycin	426
β-Hydroxy ester	427
Steroid polyols	
General steroid diols	77, 428 (M), 429, 430 (D, M), 431, 432
Cholic acid derivatives	433, 434
Steroid pentaol	435
Ecdysterones	344, 436, 437
Dihydroxycalciferol	438 (D)
Dihydroxycardenolide	439
Dihydroxybufadienolides	440 (M)
Terpene polyols	
Bryodulcosigenin	441
Desglycoescin	442
Gratiogenin	443
Humulinic acids	444, 445 (M)
Kaurandiols	446
Priverogenin A monoacetate	447
Siphonaxanthin and its ester	448
Siphonein and derivatives	448
Alkaloid polyols	
Ajaconine	449
Quinolizidine alkaloids	450 (D)
Spirobenzylisoquinoline alkaloids	451 (D)
Other natural products	
Aphin derivatives	452
Bilobalide	453
Cannabidiol and -triol	454
Coniferaldehyde dimer	455
Dimethylchromene dimer	456
Flavan diols	457
Ginkgolides	453
Herqueinone and derivatives	458
Lignans	459
Megalomycins	460 (M)
Heterocycles	
Alloxazine derivatives	461 (M)
Diazepine derivative	462 (M)
Imidazolylbutanetriols	463 (M)
2-Methylpentane-2,4-diol sulfite	464
Tetrahydrobenzoxazepine derivatives	465 (M)
Miscellaneous	
Ferrocene polyols	78, 466
Neuroleptics	467
Carbaryl metabolite	468

need not be six-membered in all cases. A recent example of this reaction is found in the substituted naphthoic acid **28**, which loses water readily although other isomers lose water either less readily or not at all.[88] This effect is also found in dipositive ions studied free of interference from monopositive ions; anthranilic acid (**29**), for example, loses water from M^{2+}, while the meta isomer loses only HO· followed by other species.[89]



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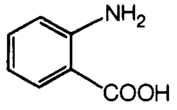

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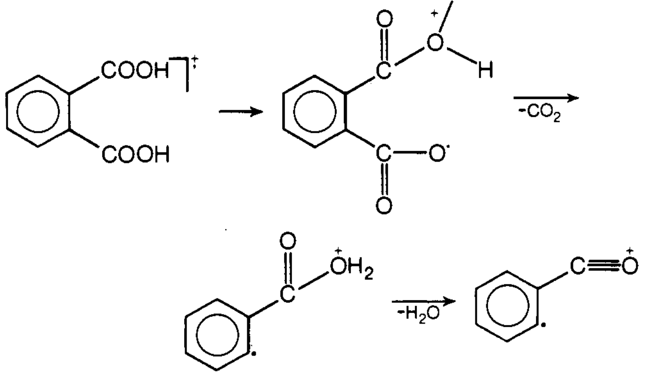
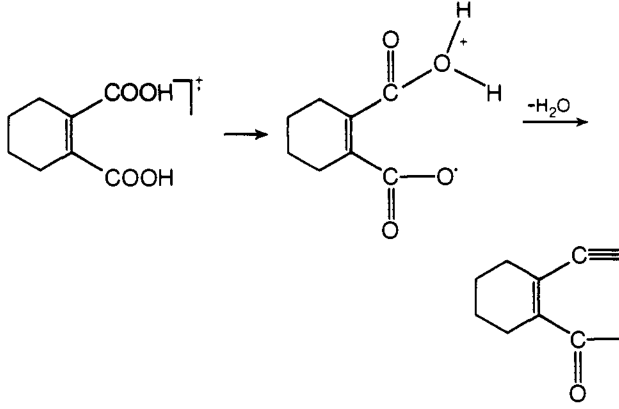
In addition to the elimination of water between ortho and peri substituents, water loss is also observed from interactions between the carboxyl groups of aliphatic and alicyclic dicarboxylic acids. In the case of vicinal acids such as maleic acid,[90] succinic acid,[91] cyclohexane-1,2-dicarboxylic acids,[92,93] and phthalic acid,[94] the carboxyl groups are located "ortho" to each other and a strong interaction between them would be expected. In the event, however, it turns out that these acids fragment by different fragmentation pathways. In the case of maleic acid[90] and phthalic acid,[94] the major loss of water follows expulsion of a molecule of carbon dioxide: the mechanism of Scheme VI is proposed for these processes. On the other hand, 1-cyclohexene-1,2-dicarboxy-

SCHEME VI



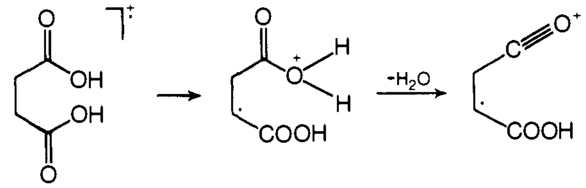
SCHEME VII



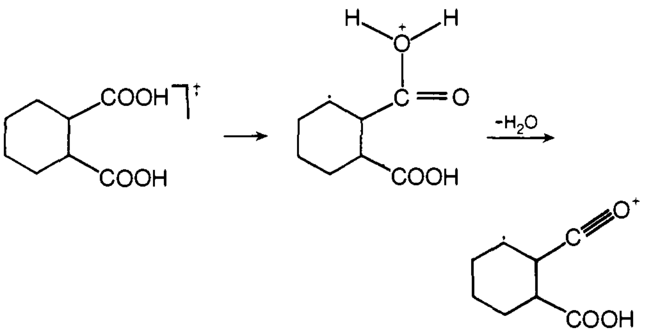
lic acid, which might be expected to undergo an identical fragmentation, expels water *first*, followed by a molecule of carbon dioxide (Scheme VII).[93]

Saturated dicarboxylic acids undergo yet another fragmentation leading to water loss. Thus succinic acid, in addition to losing water by a pathway analogous to that of Scheme VII, also loses water via a hydrogen abstraction from the methylene carbons (Scheme VIII);[91] the pathway of Scheme VII accounts for approximately 33% of the total water loss and that of Scheme VIII for the remainder. In the case of *cis*-cyclohexane-1,2-dicarboxylic acid, however, water loss by the pathway of Scheme VII has shrunk to 15% of the total, with the remainder lost by the new pathway of Scheme IX.[92] It may thus be seen that the mode of water loss is strongly dependent on the precise structure and also stereochemistry of the diacid in question, and even seemingly similar acids undergo loss by different mechanisms. This fact is strikingly illustrated by a comparison of the *cis*- and *trans*-cyclohexane-1,2-dicarboxylic acids.[92] Although these acids both have the same geometric relationship between their carboxyl groups, the trans acid shows a much stronger carboxyl–carboxyl interaction than the cis acid. This may be explained by the greater ease with which the axial carboxyl group of the cis acid can interact with the cyclohexane ring.

SCHEME VIII



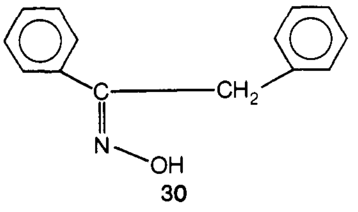
SCHEME IX



Other α,ω-dicarboxylic acids undergo water loss by mechanisms which reflect to a large extent the relative ease of interaction of the carboxyl groups. Oxalic acid, for example loses water to a very minor extent, presumably by a pathway analogous to that of Scheme VII, while at the other end of the scale adipic acid loses water predominantly by interaction between the carboxyl group and γ-hydrogens of the alkyl chain.[91] Although the loss of H_2O from the molecular ion virtually ceases for acids from suberic to dodecanedicarboxylic acid, the loss of *two* water molecules becomes prominent for these same acids, suggesting a bicyclic transition state involving both carboxylic groups and, presumably, the γ-hydrogens of the alkyl chain. Alternatively, a stepwise mechanism for loss of the two water molecules is possible: on this hypothesis, the low stability of the ion formed by the loss of the first water molecule could account for the abundance of the $(M - 2H_2O)\cdot^+$ ion.

Water loss has also been observed from the negatively charged molecular ion of several dicarboxylic acids, including phthalic and maleic acids.[95]

Finally, the loss of water from benzyl phenyl ketoxime (**30**) can be regarded as an example of a vicinal interaction.[96,96a]



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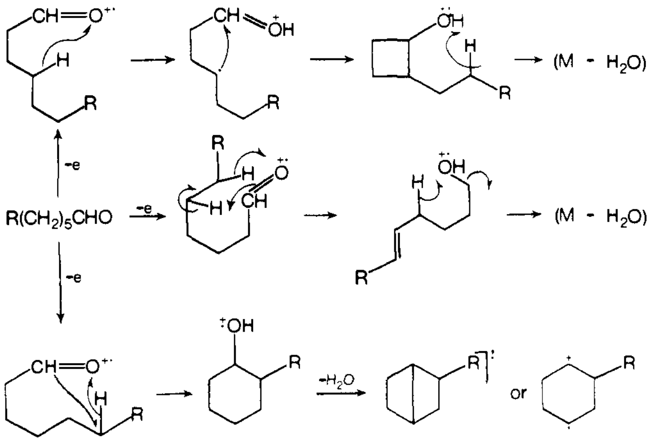
2. *Water Loss from Carbonyl Compounds*

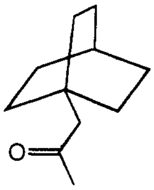
The dominant features of the mass spectrometry of aliphatic aldehydes were defined in a 1957 correlation study,[97] and include the loss of water from the molecular ion when the aldehyde contains six or more carbon atoms. The mechanism of the reaction has been studied more recently[98-100] and shown to involve largely the hydrogens on C-3 to C-6 of the original chain, with the greatest involvement of C-3, C-4, and C-5 in hexanal and C-3, C-4, C-5, and C-6 in heptanal.[100] Three possible pathways for this water loss are suggested (Scheme X).[100]

SCHEME X



The field ionization spectrum of heptanal[101] has been studied, and it has been found not to undergo loss of water to any appreciable extent.

While the loss of water from aldehydes is a prominent process on electron impact, water loss from simple ketones is of minor importance. In ketones with at least a chain of seven carbon atoms attached to the carbonyl group, however, loss of water from the molecular ion becomes a significant fragmentation pathway.[102] In certain cases water loss from the molecular ion may become important; this is the case, for example, with certain bridgehead acetone derivatives such as **31**,[103] and with various cyclic ketones, of which cyclohexanone and *D*-homoandrostan-17a-one (**32**) can serve as examples.[104,105] The reasons for enhanced water loss from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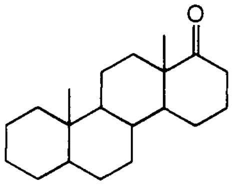
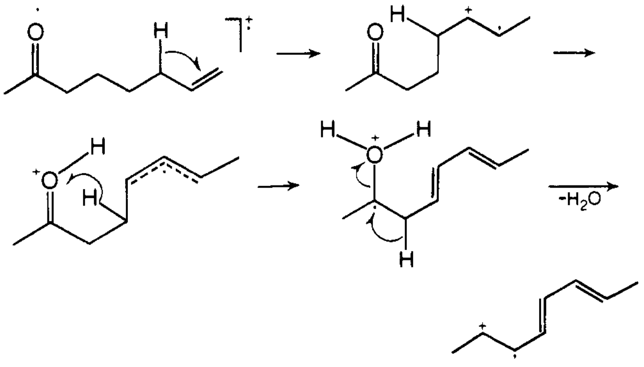
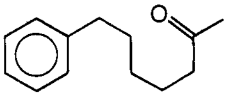

32

these compounds are not fully understood, and where the reaction has been investigated by deuterium labeling,[104-107] it has been found that an essentially random incorporation of hydrogen atoms into the elided water molecule occurs, so presumably several different pathways are involved. Enhanced water loss is also observed from certain unsaturated ketones such as 7-octen-2-one, but in this case the loss appears to be more specific and the mechanism of Scheme XI is suggested to account for it.[108]

SCHEME XI



Water loss also occurs from phenyl-substituted ketones, although here again the process is not ubiquitous. Ketone **33**, for example, loses water readily, while in its lower homolog **34** this reaction is suppressed.[109] On the other hand, the ketone **35** does lose water quite readily,[26] and so there is no clearcut correlation between chain length and water loss in this series.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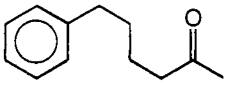
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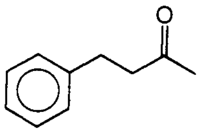
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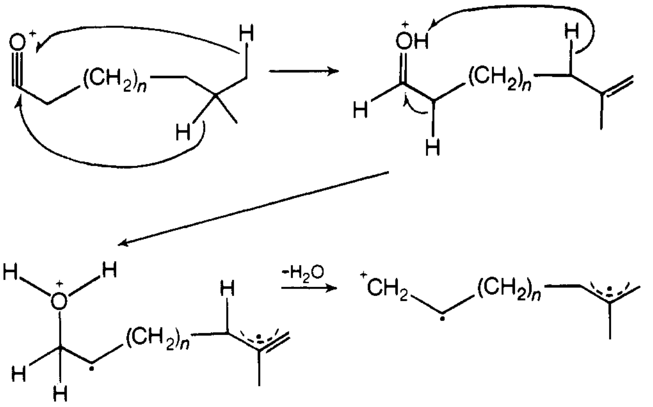
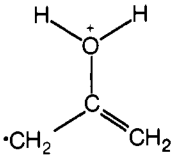
SCHEME XII



In addition to water loss from the molecular ions of ketones, water is often lost from various fragment ions. One such process involves loss of water from the α-cleavage ions of aliphatic ketones, and can generate a prominent ion in certain cases.[110,111] Deuterium-labeling studies support the pathway of Scheme XII for this remarkable rearrangement.[111]

A somewhat similar series of hydrogen transfers down a carbon chain is postulated to account for the loss of water from the cleavage products of keto esters.[112] It is interesting to note also that the *failure* of the ionic product of the double hydrogen rearrangement of ketones to lose water to any significant extent is taken as evidence against the structure **36** for this ion,[113] providing further support for its formulation as **37**, which had been proposed earlier on the basis of ICR experiments.[4]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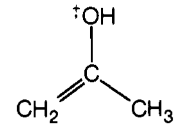
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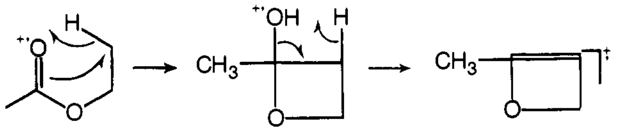
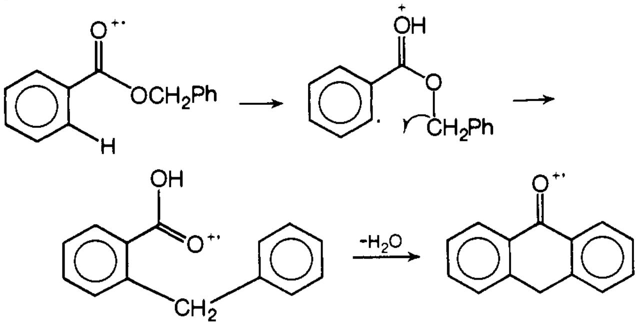
Finally, the loss of water on field ionization of some aliphatic ketones has been investigated.[114] Although ketones, like aldehydes, show either small fragment ion peaks due to water loss or none at all under field ionization conditions, the metastable peaks for this loss can readily be observed. In the study quoted, the intensity of the metastable peak for water loss was found to vary systematically with the degrees of freedom of the parent ketone, but no ready explanation for this phenomenon has been forthcoming, other than the general comment that the loss of water "probably goes via a specific type of reaction."

In view of the similarity between esters and ketones in many reactions involving enol formation, it might be expected that esters would lose water in a similar fashion to ketones. It turns out, however, that the additional oxygen atom of esters modifies the available pathways so that esters behave rather differently from simple ketones. In some cases, for example, they can fragment like aldehydes, and the pathway of Scheme XIII has been proposed to account for the loss of water from ethyl acetate.[115] On the other hand, a thorough study of the mechanism of water loss from benzyl benzoate, including deuterium and ^{18}O labeling and ion kinetic energy (IKE) studies, led to the conclusion that the loss takes place by the pathway of Scheme XIV.[116]

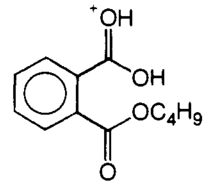
SCHEME XIII



SCHEME XIV



In the case of di- and higher esters, the possibility exists of interaction between two or more ester groups. This possibility is realized in the case of dialkyl phthalates with a butyl or longer group as the alkyl group, and one of the pathways to the formation of the prominent *m/e* 149 ion in these compounds involves the elimination of water from the intermediate ion **39** formed by rearrangement of the precursor ion **38**.[117] A similarly complicated rearrangement involving multiple hydrogen transfer from remote sites is found in the fragmentation of various 4-*n*-alkyl esters of trimellitic anhydride (**40**) and also in related compounds including triglycerides of long-chain fatty acids.[118,119] An unusual fragmentation in the case of the former compounds is loss of an alkene residue with hydrogen transfer to a carbonyl oxygen of the anhydride group, followed by a second hydrogen transfer from the remaining portion of the alkyl chain and elimination of a water molecule.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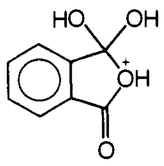
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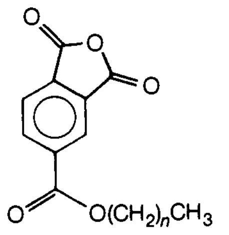
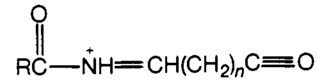
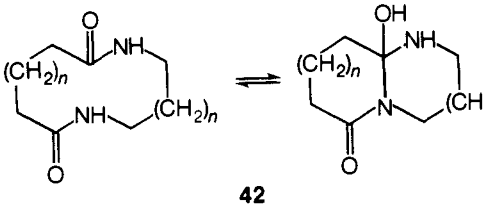

40

Loss of water from simple amides is an unfavorable process, and peaks corresponding to water loss from the parent ion are undetectable in most such compounds.[120] Low intensity ions arising from the loss of water are detectable in benzamide and thiobenzamide, however,[121] and one process for the fragmentation of *N*-ethylphthalimide involves loss of C_2H_3 followed by H_2O.[122] As with esters, structural features in the amide may promote water elimination; thus a series of *N*-acyl-ω-amino acids was found to lose water readily to give the ion **41**.[123] Perhaps the most striking example of the enhancement of water loss by structural features in the parent molecule comes from studies of the fragmentation of amides of the general structure **42**.[124,125] In this case, however, the mechanism for water elimination probably incorporates a thermal cyclization to a cyclol, so it is a moot point whether it is fair to regard this as an example of water elimination from amides.



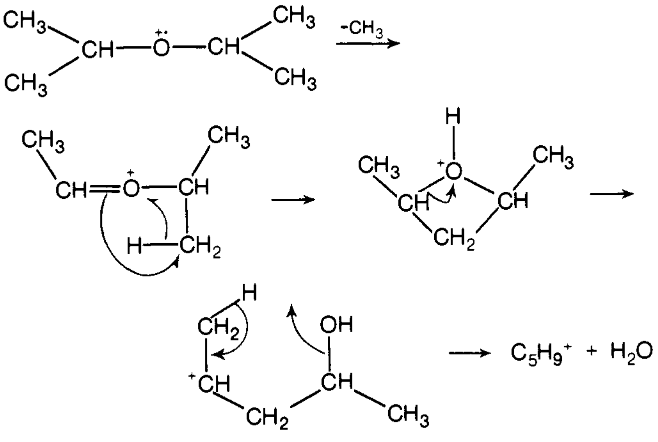
$\mathrm{R}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}—\overset{+}{\mathrm{N}}\mathrm{H}{=}\mathrm{CH(CH_2)_nC{\equiv}O}$

41

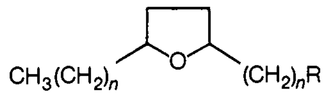

42

Although lower aliphatic ethers do not show any loss of water from the molecular ion, higher molecular weight ethers do lose water on electron impact to give peaks which, although not very abundant, are the most important in the high mass region of the spectrum.[125a] Water loss is also common from the important α-cleavage ion. This reaction has been shown to proceed by a pathway involving only the hydrogens of the butyl chain in the fragmentation of the $(M - 15)^+$ ion from isopropyl *n*-butyl ether, and it becomes increasingly important as the ionizing voltage is lowered.[126] The use of ion–molecule reactions to generate the precursor ion in a low energy state enabled the dehydration reaction alone of diisopropyl ether to be studied, and the mechanism of Scheme XV has been proposed to account for this complex rearrangement.[87] Cyclic ethers do not have to undergo quite such complicated rearrangements in order to lose water, and this fact probably accounts for the observation that the loss of water from the α-cleavage product of compounds of general formula **43** is a relatively favorable process, amounting to 25% of the total ionization in the case where $n = 2$ and $R = CH_3$.[127]

SCHEME XV



Water may also be eliminated from a number of other compounds, including such unlikely candidates as the oxazole **44**.[128] Further examples of water loss from various compound types are given in Table V.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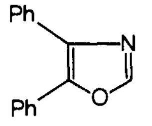

44

III. Loss of Alcohols

A. Loss of Alcohols from Ethers

The loss of alcohol from ethers is analogous to the loss of water from alcohols, but has been much less studied. For small α-branched ethers (for example, ethyl *sec*-butyl ether) the loss of an alcohol is essentially precluded by facile formation of the α-cleavage ions followed by further fragmentations of these ions.[129] In straight-chain ethers, loss of an alcohol fragment may be a significant reaction pathway, and indeed the $(M - 46)\cdot^+$ ion amounts to 50% of the base peak intensity in the spectrum of ethyl *n*-hexyl ether. It is not clear how much of this ion is formed by a concerted elimination, however, since a metastable peak is observed for the process $(M - C_2H_5O)^+ \rightarrow (M - C_2H_5OH)\cdot^+$. In any event, the reaction is certainly not specific in a structural sense, since hydrogen abstraction in the elimination of ethanol from the molecular ion occurs from C-3 (41%), C-4 (35%), and C-5 (18%), with no detectable loss from other positions of the hexyl chain.[130] The elimination of ethanol from aliphatic ethers is thus dissimilar to the loss of water from aliphatic alcohols, which occurs to the extent of about 90% through a six-membered intermediate.[7-12]

Stereochemical requirements for the loss of methanol by a 1,2-elimination process from the methyl ethers of the 1,2-diphenylethanols (**4** and **5**) have been studied.[21] The results parallel those for the loss of water from the alcohols with the ratio of CH_3OD to CH_3OH loss for the methyl ethers of **4** and **5** being 31:69 and 35:65, respectively. Apparently in this reaction stereochemical effects are playing a relatively minor role, and the major factor influencing transition state energies

TABLE V. Water Loss from Compounds Other Than Alcohols

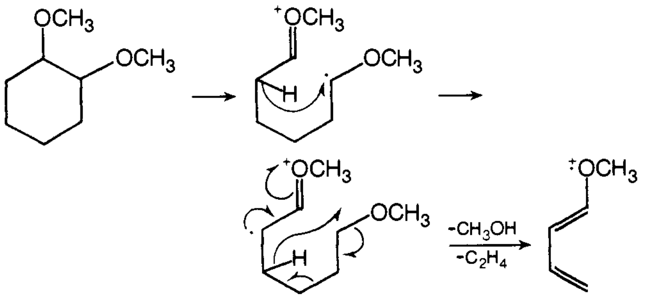
Acids	
Amino acids	469 (D, M), 470, 471 (D), 472, 473
Cyclopropanecarboxylic acids	474 (M), 475 (M), 476 (D, M)
Dicarboxylic acids	91, 95, 477, 478, 479 (D, M), 480, 481
Ortho effects in aromatic rings	94, 482 (M), 483 (M), 484 (M), 485 (M), 486
ω-Bromoalkanoic acids	487 (M)
β,γ-Unsaturated alkanoic acids	488 (M)
Diphenylmethane derivatives	489 (D, M)
Azulene derivatives	490 (M)
Flavone derivatives	491
A-seco steroid acid	492
Tetronic acid and derivatives	493 (D, M), 494 (D, M)
Amides	
Aliphatic amides	495, 496, 497 (M), 498, 499
Aromatic amides	121, 498, 499
Peptides	500–509
Cyclic peptides and cyclodepsipeptides	124, 125, 510 (M), 511 (M)
Imides	122, 123, 512 (D, M), 513, 514
Carbamates	515 (D, M), 516 (d, M)
Esters	
Aliphatic esters	115, 517–519 (M), 519
Aromatic esters	116, 118, 520 (D, M), 521 (D, M), 522 (D, M)
β-Keto esters	523, 524 (M)
Fatty acid esters	525, 526 (M), 527, 528
Other natural product esters	529–532
Simple lactones	533, 534 (M)
Natural product lactones	535 (M), 536 (M), 537 (M), 538 (M), 539
Cyclic carbonates	540
Ethers	
Aliphatic ethers	126, 541 (D, M), 542, 543 (M)
Cyclic ethers	544, 545 (D, M), 546 (D, M), 547 (M), 548 (M)
Di- and polyethers	549, 550 (M)
Trimethylsilyl ethers	551, 552 (D, M)
Ketals and hemiketals	553, 554 (M), 555 (M), 556 (M), 557 (D, M)
Hydroperoxides and peroxides	558, 559 (M), 560 (M)
Ketones and aldehydes	
Aldehydes	97, 98, 101, 561 (M)
Saturated aliphatic ketones	81, 102, 103, 109, 111–113, 562 (D, M)
Unsaturated aliphatic ketones	108–111, 563 (D, M), 564 (M), 565
Cyclic ketones	104, 556 (M), 567 (M), 568 (M), 569, 570 (D, M)
Cyclopentanediones	571 (M)
Quinones	572 (M), 573, 574
Steroidal ketones	106, 107, 575–578
Aromatic ketones	579, 580, 581 (D, M), 582 (D, M), 583 (D, M)
Nitrogen-containing compounds	
Oximes and oxime ethers	96, 96a, 584 (M), 585 (D, M), 586 (M), 587, 588 (M)
Substituted hydrazones	589, 590
Nitroaromatics	591 (M), 592, 593 (D, M)
Substituted pyridines	251, 252, 594 (D, M), 595 (M), 596, 597 (D)
Pyrazines and pyrimidines	598, 599 (D, L, M)
Triazines	600 (M)
Isatin derivatives	601 (D, M)
Quinoline, isoquinoline derivatives	602, 603 (M)
Oxazole, thiazole, and isoxazole derivatives	128, 596, 604, 605 (M) 606 (D, M), 607, 608
Bridgehead nitrogen heterocycles	609 (M), 610 (D, M)
Thiadiazole derivatives	611 (M)
Sulfur-containing compounds	
Thioesters	612
Sulfides	613 (E)
Sulfones and sulfoxides	81, 614 (M), 615 (D, M), 616
Sulfonic acid derivatives	617 (D, M)
Derivatives of other elements	
Triphenylboroxine	618 (M)
Organophosphorus acids, esters, and amides	619, 620 (M), 621, 622 (M), 623, 624 (M)
Silanes	625
Germyl ethers	626
Organoarsenic acids	627 (M), 628 (D, M)
Selenium compounds	203, 613, 629 (M)
Metal chelates	603 (M), 631 (M), 632 (D, M), 633 (M), 634 (M), 635
Organomanganese derivatives	636

appears to be the isotope effect for breaking a C–D rather than a C–H bond.

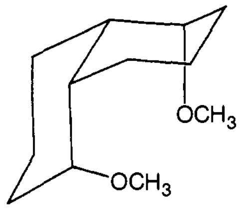
Methyl cycloalkyl ethers lose methanol in a similarly random fashion to acyclic ethers. Methyl cyclohexyl ether, for example, undergoes hydrogen abstraction to the extent of 8% from C-2 and C-6, 66% from C-3 and C-5, 23% from C-4, and 84% from C-3, C-4, and C-5 combined; the assumption of an isotope effect of K_D/K_H = 0.9 removes the discrepancy between these last two values.[131]

The loss of methanol from the methyl ethers of various diols and polyols has been investigated.[74,75,132-134] Loss of methanol occurs readily from the dimethyl ether of propane-1,3-diol, but the extent of methanol loss decreases as the separation between the methoxy groups increases. Tri- and tetramethoxy alkanes also lose methanol quite readily, as might be expected.[132] In the case of the various dimethoxycyclohexanes, methanol loss is least significant for the 1,2-isomer, presumably because of a more favorable pathway in the case of this isomer to the ion at *m/e* 84 (Scheme XVI).[133] On this hypothesis, initial α-cleavage triggers hydrogen rearrangement and a concerted elimination of methanol and ethylene to yield a stabilized butadiene radical cation. In the case of 1,4-dimethoxycyclohexane, methanol elimination occurs by

SCHEME XVI



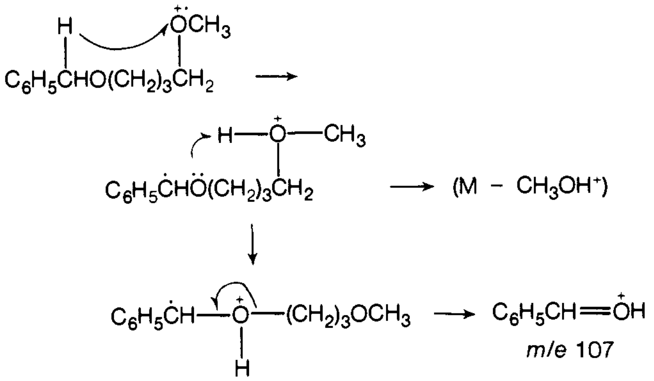
a 1,4-process, since the 1,4-dideuterio compound loses CH_3OD almost exclusively. The elimination of methanol from dimethoxycyclohexanes and related compounds is therefore dependent to some extent on the stereochemistry of the compound in question; *trans*-1,3-dimethoxycyclohexane, for example, eliminates methanol over twice as readily as the cis isomer. It is postulated that reaction is initiated by hydrogen transfer from a carbinol carbon to a methoxy oxygen, and that the occurrence of the reaction depends on the closeness of approach of these two sites in possible conformations of the molecular ion.[134] In the case of the bicyclo[2.2.1]heptanediol dimethyl ethers, however, the occurrence of fast ring fragmentations precluded any stereochemical effect, and the mass spectra of these compounds resembled each other closely.[75] A recent study of the various isomers of the decalin-1,5-diols also failed to find any significant effect of stereochemistry on methanol loss from these compounds. The *cis*-1,5-dimethoxy isomer of *cis*-decalin (**45**) did, however, show a loss of CH_2O which was not shown by the other isomers; this loss was attributed to initial abstraction of a hydrogen of one OCH_3 group by the other group.[134a]



45

Support for the formulation of the mechanism of methanol loss via hydrogen transfer of a carbinol hydrogen to the alkoxy group comes from studies on various benzyloxy ethers. Thus 4-benzyloxybutyl methyl ether shows a strong peak at *m/e* 107, corresponding to the reaction indicated in Scheme XVII; loss of methanol probably also occurs via the same intermediate as that leading to the *m/e* 107 ion.[135]

SCHEME XVII



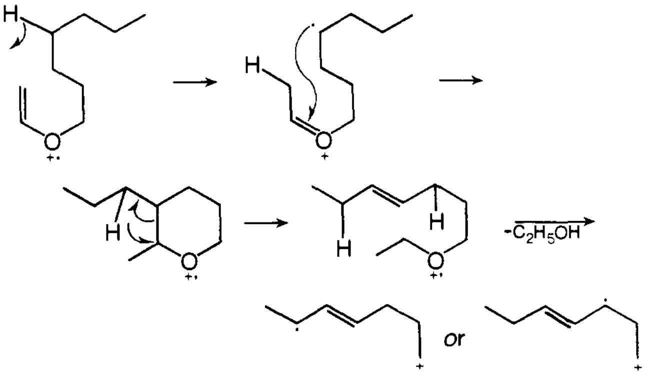
The mass spectra of unsaturated ethers are enlivened by the occurrence of multiple hydrogen transfer processes preceding the loss of alcohol fragments. In the case of alkyl vinyl ethers such as *n*-heptyl vinyl ether, a triple hydrogen migration occurs that results in the elimination of a molecule of ethanol from the molecular ion; this fragmentation is relatively insignificant at 70 eV but becomes important at 15 eV.[136] The pathway of Scheme XVIII has been suggested for this unusual rearrangement.

Allylic ethers, not to be outdone, undergo a quadruple hydrogen transfer prior to expulsion of a propanol fragment, provided that the saturated chain contains at least seven carbons.[137] The mechanism proposed is essentially that of Scheme XVIII, with the addition of a hydrogen migration to convert the initial allyl ether into a vinyl ether.

TABLE VI. Alcohol Loss from Ethers and Related Compounds

Simple ethers	
Alkyl ethers	21, 129, 130, 637 (M), 638, 639 (M)
$C_nH_{2n+1}O^+$ ions derived from alkyl ethers	245
Vinyl ethers	136, 640 (D, M)
Cycloalkyl ethers	131, 210, 641, 642 (M), 643 (D, M), 644 (D, M), 645 (D, M)
Linear polyethers	132, 550, 646 (M), 647
Cyclic polyethers	74b, 75, 133, 134, 404, 571
Oxime ethers	155
Aromatic ethers	88, 402, 455, 625, 648 (M), 649 (M), 650–652
Unsaturated ethers	541, 542
Sugars	
Methyl glycosides	339, 406, 408, 425, 653, 654 (D, M), 655, 656 (D), 657–659, 660 (D), 661–664, 665 (D), 666 (D)
Amino sugars	412, 667–670, 671 (D), 672, 673
Other derivatives	674–676
Alkaloids	306, 307, 313, 316, 450, 677–679 (D)
Steroid ethers	322, 347, 440, 543, 680 (D), 681
Other natural products	
Humulinic acids	444
Lignans	296
Gibberellins	682
Flavonoids	683 (D, M)
Prostaglandin derivatives	684
Ginseng terpenes	299
Metal complexes	633
Acetals	112, 510, 553, 681, 685, 686 (M), 687 (M)
β-Branched alcohols	240, 394

SCHEME XVIII

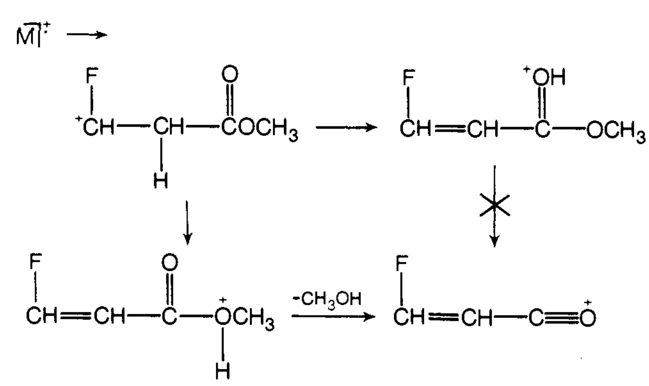


Further examples of the loss of alcohols from ethers and related compounds are given in Table VI.

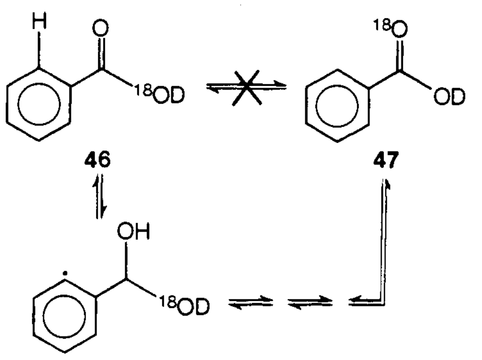
B. Alcohol Loss from Esters

The mechanism of the loss of methanol from methyl esters on electron impact has been the subject of a recent review,[138] and this section will therefore be somewhat abbreviated. In this review, Winnik proposes two classes of mechanisms to account for the observations that saturated esters never show loss of methanol from the molecular ion, while methanol loss is commonly encountered from unsaturated esters and from heteroatom substituted esters. In the first class

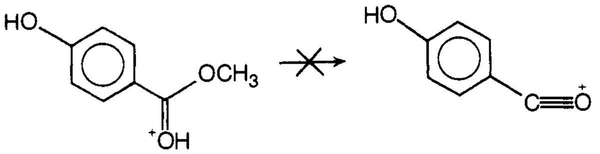
SCHEME XIX



of mechanisms (Scheme XIX), a group F stabilizes formation of a carbocation remote from the ester group. Proton transfer can then occur either to the carbonyl oxygen or the ether oxygen; if the former occurs methanol elimination cannot take place, since a (1,3) hydrogen migration is symmetry forbidden, but the latter process allows methanol elimination to transpire. In support of this contention that (1,3) hydrogen migrations are unfavorable processes on the mass spectrometric time scale, we may note that the isomeric acids **46** and **47** do not interconvert directly but only via abstraction of the ortho hydrogen by the carbonyl oxygen.[13] Also, the ion **48**, generated by hydrogen transfer from the corresponding *n*-hexadecyl ether, did not undergo loss of methanol.[138]



46 **47**



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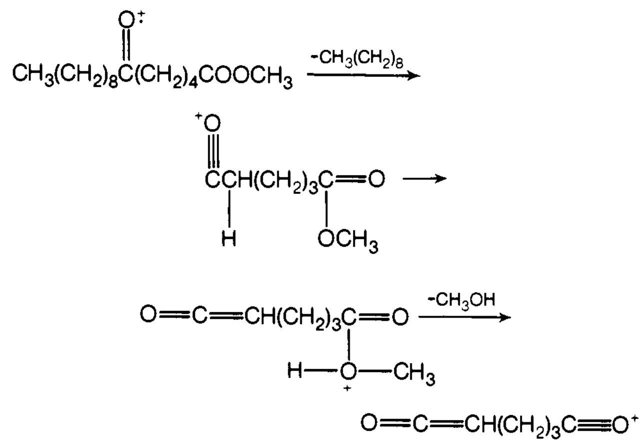
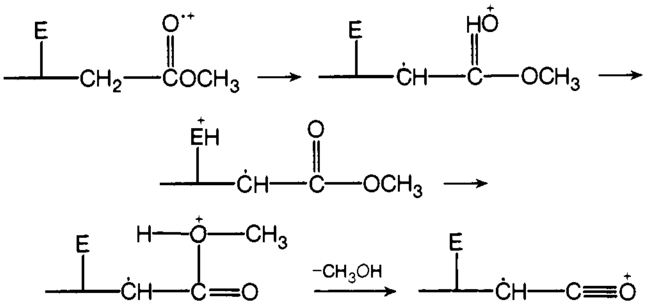
The first mechanism explains the observed methanol loss from the fragment ions of amino-, keto-, hydroxy-, and alkoxy-substituted esters, as well as branched, long-chain methyl esters. The best studied case is probably that of methyl 6-ketopentadecanoate, which shows a peak corresponding to methanol loss from the α-cleavage ion at *m/e* 143.[140] Deuterium labeling supports formation of part of the yield of this ion by the pathway of Scheme XX, but another part must be formed by a more complex scheme, since there is some involvement of the C-2 hydrogens in the process and a simple 1,2-elimination of methanol is known not to occur. Ethyl 6-methoxypentadecanoate has also been investigated and found to lose ethanol by the pathway of Scheme XIX,[141] and various nonterminal amino esters yield similar fragments.[142] The fragment ions RC$^+$H(CH$_2$)$_n$COOCH$_3$ of alkyl-substituted fatty acid methyl esters formed by cleavage α to the alkyl substituent show loss of methanol, while no methanol is lost from their molecular ions,[143] and this finding may also be explained on the basis of the mechanism of Scheme XIX. Other compounds whose fragmentation may be explained in part on the basis of this scheme include diesters[144-146] and unsaturated methyl esters.[146]

SCHEME XX

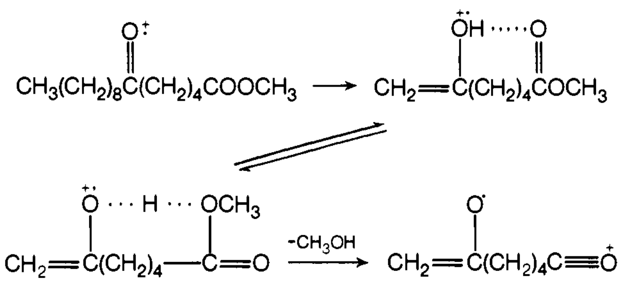


The second mechanism proposed by Winnik is illustrated in Scheme XXI. In this mechanism a group E, capable of forming hydrogen bonds, catalyzes the transfer of a proton on the carbonyl group to the ether oxygen, which can then be lost as a methanol fragment. This process is responsible for most of the loss of methanol from the McLafferty rearrangement product ion of methyl 6-ketopentadecanoate (Scheme XXII), although a small amount of methanol loss from this ion occurs by a pathway of Scheme XIX. A similar pathway, but with an initial α-cleavage instead of McLafferty rearrangement, can explain methanol loss from methyl 6-hydroxypentadecanoate.[147] An elegant experiment by Wolff and his coworkers shows that the source of the additional hydrogen lost with the methoxy group in certain methyl benzoates substituted with a hydroxyl-bearing alkyl chain in the para position is the benzylic carbon to the extent of 50%.[148] The mechanism of Scheme XXIII nicely rationalizes this finding and provides further support for the importance of the general mechanism of Scheme XXI in methanol loss. Similar mechanisms may be written for methanol loss from various nonterminal amino esters[142] and from methyl 6-phenylhexanoate.[15] Further examples and apparent exceptions to the mechanisms of

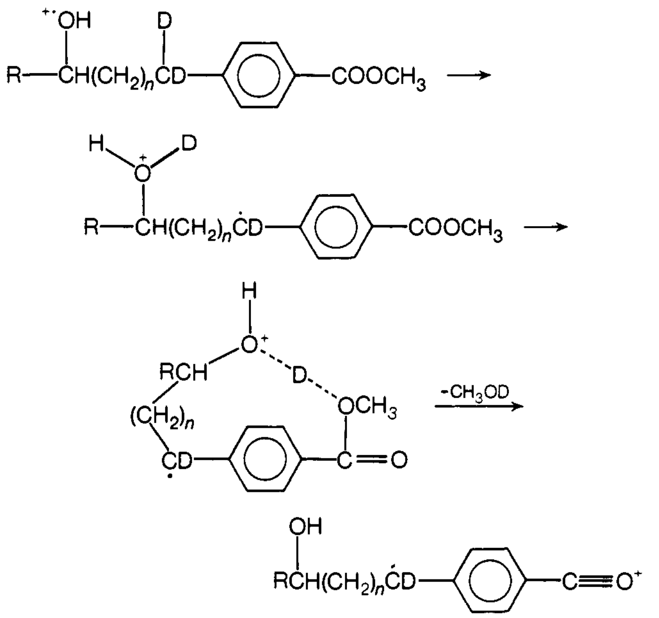
SCHEME XXI



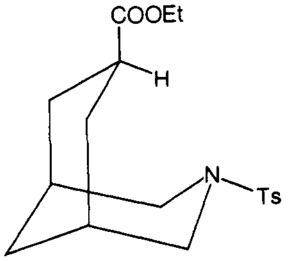
SCHEME XXII



SCHEME XXIII



Schemes XIX and XXI are given in the original reference cited;[138] mention may be made here in addition of the possibility that ethanol elimination from the tosylate **49**[149] and methanol loss from 4-*n*-alkyl trimellitic esters (**50**)[118,119] occur by similar mechanisms.



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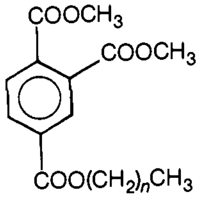
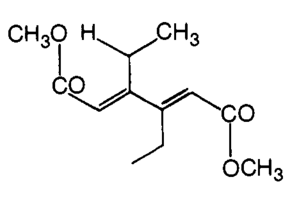
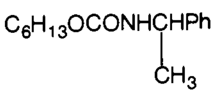


50

Not all alcohol eliminations from alkyl esters can be subsumed under the headings of Schemes XIX and XXI, however. Thus loss of alcohols from various α,β-unsaturated esters appears to involve a concerted six-membered transition state,[150,151] as does methanol loss from methyl 3,4-diethylmuconates (**51**),[152] while the loss of hexanol from *n*-hexyl *N*-(1-phenylethyl)carbamate (**52**) is apparently a simple 1,2-loss.[153] An interesting stereochemical effect on fragmentation pathways is found in the spectra of the diesters **53** and **54**: the cis-endo isomer **53** loses methanol with a specific abstraction of a hydrogen from C-1 or C-8, via a seven-membered transition state, while the cis-exo isomer **54** loses only a methoxy radical.[154]

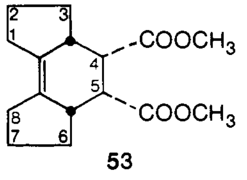


51



$C_6H_{13}OCONHCH(CH_3)Ph$

52



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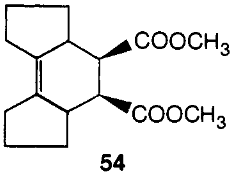

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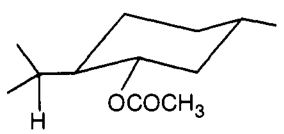
The loss of alcohol fragments is also occasionally encountered from compounds other than simple ethers and esters. Oxime methyl ethers, for example, lose methanol quite readily,[155] and further examples of alcohol loss both from esters and miscellaneous compounds are gathered together in Table VII. Even the loss of an enol fragment in the McLafferty rearrangement with charge retention on the olefin can be regarded as an alcohol elimination.[108]

IV. Loss of Carboxylic Acids

Carboxylic acid esters of alcohols larger than methanol undergo both a McLafferty rearrangement and a McLafferty rearrangement in which an additional hydrogen atom is transferred to the acid moiety. In both these rearrangements, which were discussed in Part II of this review,[4] the charge is retained on the carboxylic acid fragment; these reactions will not be discussed any further. In addition, however, the loss of a neutral acid fragment from the ester with the formation of a charged alkene is also a common process. This reaction is seen most commonly in the loss of acetic acid from acetates, and the following discussion refers largely to this example.

It turns out that the loss of acetic acid from an acetate is not simply an example of the McLafferty rearrangement with charge retention of the olefin fragment. The major piece of evidence for this statement is the observation that the specificity of the reaction is quite different from that of the McLafferty rearrangement; in the case of various *n*-alkyl acetates hydrogen was abstracted from C-2 on the average 55% of the time, with C-3 supplying a hydrogen atom the remaining 45% of the time.[10] The mechanism may thus involve either two discrete ring processes or else (less probably) hydrogen scrambling preceding hydrogen transfer to oxygen.

In the case of cycloalkyl acetates, the site-specificity of the reaction depends to a large extent on the structure of the substrate. In the case of cyclohexyl acetate elimination occurred by a 1,2 process 83% of the time, with 1,3 and 1,4 processes making up the remaining 17%. Menthyl acetate (**55**), on the other hand, loses acetic acid by a 1,2 process only 66% of the time, with 1,3 elimination involving the tertiary hydrogen of the isopropyl side chain making up much of the remainder,[157] while the bornyl acetate **56** loses acetic acid exclusively by a 1,2-process.[45] Since, however, the loss of a carboxylic acid can involve hydrogen transfer to either oxygen atom of the ester, it is entirely possible that the process formally described as a 1,2-elimination is in fact occurring by a pathway involving a six-membered transition state.



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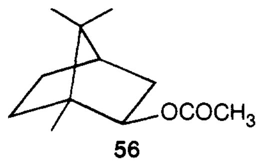

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The stereochemistry of acetic acid loss has also been investigated. In the case of the 1,2-diphenyl acetates and 2-butyl acetate, a cis elimination is favored, with a preference for an anti relationship between the phenyl rings or methyl groups of the substrates.[158] A preference for a cis elimination is also suggested from a study of the elimination of acetic

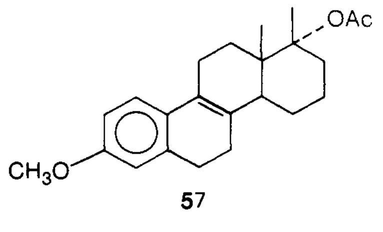

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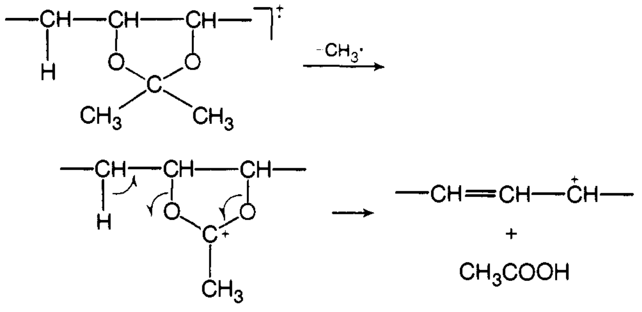
TABLE VII. Alcohol Loss from Esters and Miscellaneous Compounds

Simple esters	135, 141, 487, 518, 688 (M)
Unsaturated esters	150, 151, 268, 497, 689, 690 (M), 691 (D, M)
β-Keto esters	523, 524
Long-chain fatty acid esters	
Saturated fatty acid esters	517, 542, 692 (D), 693 (D), 694
Unsaturated fatty acid esters	695, 696
Cyclic fatty acid esters	528
Cyclopropane fatty acid esters	526, 695
Allenic and acetylenic esters	697 (D, M)
Hydroxy esters	147, 698
Unsaturated hydroxy esters	527
Epoxy esters	699
Aldehyde esters	519
Keto esters	140, 700, 701 (D, M)
Diketo fatty acid esters	702 (M)
gem-Diesters	703 (D, M), 704 (D, M), 705 (M)
vic-Diesters	154, 706 (D, M), 707 (M)
Other diesters	152, 496, 567, 708
Aromatic esters	
m-Carbomethoxydiphenylmethane	489
Ortho effects in trimellitates	118, 119
Ortho effect in carbanilates	709 (M)
Other ortho effects in benzene systems	89, 371–373, 484, 521, 710 (M), 711 (M), 712, 714 (M, D), 715 (D, M)
Neighboring group effect in azulene	716 (M)
Ortho effects in pyridines and pyrazoles	717, 718 (M)
Ortho effects in thiophene	375
Ortho effects in furans	719, 720 (M), 721 (M)
Indoles and benzindoles	722–725
Azepine derivatives	726–728
Porphyrin derivatives	729
Amino acid esters	
Small acid esters	730 (M), 731, 732 (D, M), 733 (D)
Peptide derivatives	501, 503, 734, 735, 736 (M), 737, 738, 739 (M)
Other natural products	
Methyl abietate	740
Cholesterol derivative	741
Methyl chrysanthemate	475
Methyl commate	742
Gibberellins	360, 743 (D)
Iridoid terpenes	288
Methyl penillate	744
Prostaglandin derivatives	745
Tetracycline derivatives	368, 572
Hippeastrine alkaloid derivatives	319
Other esters	
3-Azabicyclononane derivatives	149
Coumarin derivatives	746
Tetronic acids	494
Other functional groups	
Trifluoroacetamides	747 (M)
Triphenyl arsenite	627
Carbamates	748 (M), 749 (D, M), 750
Ortho esters	751 (M)
Ketones	108
Sulfonyl carbamates	752
Wittig reagents	753

acid from *cis*- and *trans*-2-methylcyclohexyl acetates, but the interpretation here is not so clearcut because of the conformational mobility of the system.[156] Elimination is almost exclusively cis in the case of the bornyl acetates, however.[45] Stereochemistry can also affect the relative ease of acetic acid loss; the steroid **57** with an axial acetate group loses acetic acid more readily than its epimer with an equatorial acetate.[159]

In summary, the available evidence suggests that the elimination of acetic acid from acetates on electron impact does *not* occur by a simple McLafferty rearrangement. In particular, the occurrence of two pathways for elimination (1,2 and 1,3) and the close similarity of acetic acid elimination and water elimination in the bornyl acetates[45] suggests that elimination is occurring to a large extent via a four-centered transition state rather than the six-centered transition state of the McLafferty rearrangement. This conclusion only applies with full force to the bornyl acetates, however, and it is possible that elimination in the case of other acetates proceeds via both four- and six-centered transition states.

SCHEME XXIV



Loss of the elements of acetic acid has also been observed from acetonides, and the mechanism of Scheme XXIV has been suggested to account for this observation.[160]

Further examples of the loss of acetic acid from various molecules are given in Table VIII.

V. Loss of Other Carbonyl Fragments

The loss of small carbonyl fragments such as CO, CHO, and CH_2O from various molecules is a common electron-impact-induced process. The loss of CO and CHO, for example, is commonly encountered in the spectra of phenols and other aromatic compounds; this reaction was discussed briefly in Part I of this review[3] and will not be discussed any further here.

The loss of CH_2O is also a common reaction on electron impact, particularly from aryl methyl ethers. Here again, this reaction was discussed in Part I of this review,[3] and so it will not be discussed further. Formaldehyde may also be eliminated, however, from a number of other systems, and it is of some interest to discuss some of these reactions.

The loss of formaldehyde from benzyl methyl ether has been investigated by ion kinetic energy spectroscopy, leading to the conclusion that hydrogen transfer in the nonisomerized

SCHEME XXV

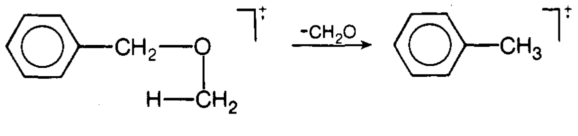
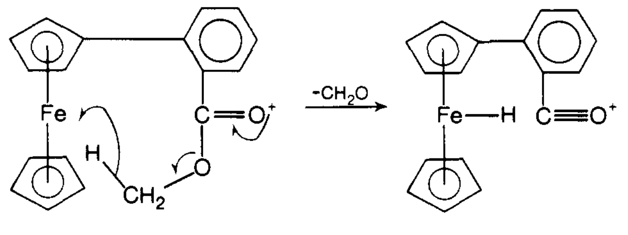


TABLE VIII. Carboxylic Acid Losses

Esters of acyclic alcohols	
Alkyl acetates	10, 84, 117, 156, 158, 754–756
Substituted alkyl acetates	700, 757 (M), 758
Acetoxymaleic anhydride	759
Esters of cyclic alcohols	
Monocyclic alcohols	157, 643, 760 (M), 761
Bornyl acetates	45
Adamantyl acetates	279, 496
Azepinoindole acetates	762
Esters of acyclic polyols	69, 395, 420, 665, 666, 675, 763, 764 (D), 765, 766
Aromatic esters	
Phenyl esters	767–769
Azulyl esters	490
Saccharide esters	
Monosaccharides	405, 421, 664, 770, 771 (D), 772, 773 (D, M), 774 (D, M), 775 (D), 776, 777
Aminomonosaccharides	658, 670–671, 778–782, 783 (D, M), 784, 785 (M)
Thiomonosaccharides	425
Halogenated monosaccharides	786–788 (M)
Glycoside esters	
Methyl glycosides	424, 789 (D, M)
Other glycosides	427, 530, 739, 790 (M), 791 (D, M)
Cerebrosides	792
Nucleosides	415, 417, 793
N-Phenylosatriazole derivatives	794, 795 (M)
Glucuronic acid conjugates	741, 796 (D, M)
Polysaccharide esters	780, 797 (D, M), 798–801
Steroid esters	
General	50, 321, 346, 802, 803 (M), 804, 805 (M), 806 (D, M), 807
3-Acetoxy steroids	320, 323, 327, 330, 428, 431, 808 (M), 809, 810 (D, M), 811 (M), 812–814
17-Acetoxy steroids	159, 538, 576
26-Acetoxy steroids	17
Bile acids	342, 815
Cardenolides	340, 816 (D)
Bufadienolides	67, 347, 440, 817
Other	343, 344, 442, 447, 818
Other natural product esters	
Alkaloids	305, 312–314
Acyl peptides	819, 820 (M), 821
Terpenes	290, 293, 295, 297, 822, 823, 824 (M), 825 (M)
Flavonoids	357, 457
Carotenoids	268, 291, 826
Alloxazines	461
Cephalosphorin	827 (M)
Chainin	828
Coumarins	376
Gibberellins	682
Megalomycins	460
Mycosides	676
Myxinol	829
Phorbol	365
Trileucofisetinidin	830
Catechin condensation product	549
Losses from functional groups other than esters	
Acetals	160, 555, 760, 831, 832 (D, M), 833 (M)
Carboxylic acids	
Diphenic acid	402
Free amino acids	473
β-Aroyl-α-methylpropionic acids	834 (M)
Selenocarboxylic acids	629, 835, 836
Lactones	533
Dibenzoylmethane–metal complexes	632
γ-Bromo-γ-phenylbutyric acid	487
Nitrogen derivatives	
O-Acyl cyanohydrins	259
Acyl hydrazines	837 (D, M)
O-Acyl oximes	155
O-Acyl nitroxides	378
Phenyl thiohydantoins	838, 839

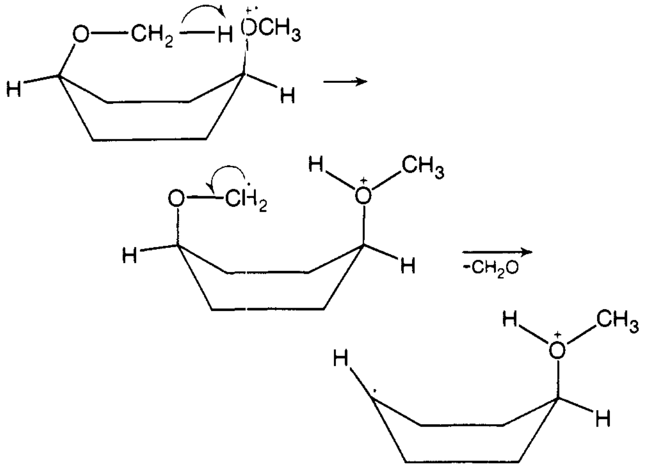
SCHEME XXVI



molecular ion occurs via a four-membered cyclic transition state to yield the toluene molecular ion at threshold (Scheme XXV).[161] Loss of formaldehyde also occurs in an unusual fragmentation of various ortho-substituted ferrocenyl benzenes[162] and ferrocenes substituted with a methyl acrylate residue.[163] The mechanisms suggested incorporate hydrogen transfer to the iron atom (Scheme XXVI).

The loss of formaldehyde from various dimethyl ethers has been observed where the methoxy groups can interact with each other.[134,134a] The mechanism of Scheme XXVIA has been suggested for this reaction. Finally, the loss of formaldehyde from butyl propionate has been suggested to proceed by the mechanism of Scheme XXVIB to yield an ethyl propyl

SCHEME XXVIA



SCHEME XXVIB

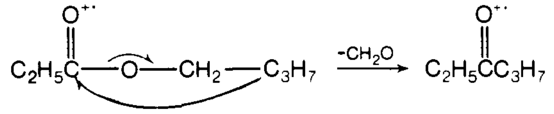


TABLE IX. Losses of Small Carbonyl Fragments

Losses of CO	
From aldehydes	304, 562, 579, 840 (D, M)
From acids	715, 841 (M)
From formamides	495, 842
From alcohols	
Benzyl alcohols	248, 648, 843 (M)
α,β-Unsaturated alcohols	26
2-Hydroxybenzothiazole	844 (D, M)
Cyclobutaneoctaol	396
Phenols	371, 375, 380, 384, 635, 649, 845, 846 (M)
From acetals	555
From lactones	535
From ortho esters	751
From isoxazoles	847 (M)
From nitro and nitroso compounds	247, 848 (M), 849 (M)
From *N*-oxides	850 (M), 851 (M)
From benzoxazepines	852 (M)
From thionylanilines	853 (M), 854 (M)
From phenyl sulfoxides	855 (M)
From organophosphorus esters	856
Losses of CHO	
From alcohols	304, 366, 607, 679, 857 (D, M)
From phenols	80, 371, 375, 396, 649, 858
From ethers	356, 358, 859 (D, M), 860 (M), 861 (M)
From carboxylic acids	842
From lactones	392, 524
From ketones	566, 748
From nitrogen derivatives	
Hydroxamic acids	389, 862 (D, M)
N-oxides	851
Substituted pyrimidines	598
From sulfur-containing compounds	863 (M)
Loss of CH_2O	
From alcohols	394, 428, 490, 510, 675, 863a, 864 (E), 865 (M), 866 (D, M)
From polyols	74b, 75, 134, 421, 425, 646, 664, 775
From $C_nH_{2n+1}O^+$ ions from alcohols	244, 245
From ethers	
Benzyl ethers	161
Methyl phenyl ethers	247, 265, 356, 375, 459, 599, 648, 649, 677, 686, 843, 861, 867 (E), 868 (M), 869 (E), 870 (M), 871 (D, M), 872 (M), 873–874, 875 (M), 875a (D, M), 876 (M), 877, 878 (M), 879 (M), 880 (M), 881 (D, M)
From carboxylic acids	203, 882
From amides	122, 883, 884 (D, M)
From methyl esters	162, 163, 636, 720, 729, 733, 885 (D, M)
From esters of larger primary alcohols	134b, 885a (D, L) 134b, 885a (D, L)
From hydroxamate esters	886 (M)
From organophosphorus esters	619, 624, 856, 887, 888
From methyl sulfinates	889
From methyl seleninates	890
From niobium and tantalum complexes	633
From oxysilyl compounds	634
Losses of CO_2	
From carboxylic acids	488
From dicarboxylic acids	91, 94, 481
From esters	360, 891 (M)
In peptide sequencing	502, 503
From lactones	536
From carotenoids	448
From polyols	396
Loss of aldehydes	
From alcohols	465, 892 (D, M)
From amides	497
From ethers	210, 550, 721, 893 (D, M), 894 (D, M)
From ketones	267, 895 (M)
From organophosphorus esters	624
From lignans	843
Loss of ketones	
From alcohols	266, 267
From ketones	164, 165
From ethers	545
From dithiocarbonate esters	896 (D, M)
Loss of methyl formate	
From methyl carboxylates	360, 428, 475, 567, 740, 743, 744, 897 (D, M)
Loss of methyl acetate	
From a β-keto ester	720
Loss of other fragments	
$C_2H_2O_2$ from a substituted methylcyclopropanecarboxylate	474
$C_3H_3O_2$ from costunolide	599

ketone ion.[117,163a] Further reactions involving the loss of formaldehyde are given in Table IX.

Other losses of carbonyl fragments include the elimination of acetone from various α,β-unsaturated methyl ketones via an isomerization followed by a McLafferty rearrangement,[164] and the loss of acetone from various β-decalones and 2-oxo steroids.[165] In both cases the actual fragment eliminated is presumably the enol of acetone.

Further examples of the elimination of small carbonyl fragments are given in Table IX.

VI. Loss of Hydrogen Halides

In the case of simple alkyl halides, the loss of hydrogen halide is most important in fluorides and chlorides, where it competes effectively against the simple loss of a halogen atom. The specificity of halide loss varies, however, with the nature of the halogen. In the case of hydrogen fluoride elimination from *n*-butyl and *n*-hexyl fluoride, elimination involved principally the 3- and 4-positions in the former and the 5-position in the latter, although other positions are also involved.[166] In *n*-butyl chloride, however, elimination is predominantly (93%) a 1,3-process, while even in *n*-pentyl chloride the 1,3-process still contributes 72% of the total HCl loss, with a 1,4-elimination making up the bulk of the remainder.[167] The increase in 1,4-elimination in *n*-pentyl chloride is consistent with the observation that abstraction of a secondary hydrogen is generally easier than abstraction of a primary hydrogen; 1,4-elimination in *n*-butyl chloride would of course require primary hydrogen abstraction.

TABLE X. Loss of Hydrogen Halides

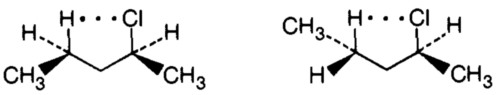
Loss of HF	
From aliphatic fluorides	166, 898, 899
From cyclic and polycyclic compounds	279, 398, 538
From amides	171, 732, 901 (M)
From fluoro alcohols	410, 902, 903 (D, M)
From trifluoromethyl ketones	904, 905 (M), 906 (M)
From CF_3PH_2	907
From trifluoromethyl heterocyclics	894, 908 (D, M), 909 (D, M), 910 (L)
From monofluoro aromatic compounds	911 (M), 912 (M), 913 (D, M)
From polyfluoro and perfluoro aromatic compounds	579, 914–919
From organoboron difluorides	920
Loss of HCl	
From aliphatic chlorides	22, 167, 242, 616, 921, 922, 923 (E, L), 924–926, 927 (D, M), 928, 929
From alicyclic chlorides	269, 271, 398, 930, 931 (D, M), 932, 933
From polycyclic chlorides	279, 284, 431, 496, 810, 814, 880, 934–936
From chloro alcohols	18, 336, 788
From acyl chlorides	937 (M)
From chlorophenyl derivatives	586, 650, 846, 858, 913, 938 (M), 939 (M), 940 (M), 941, 942 (E), 943–945, 946 (D, M), 947 (E), 948
From chlorinated heterocycles	379, 949
From chloroferrocenes	950
From ionic chlorides	951–954 (M)
From *N*-chloroamines	955 (D)
From a chlorophosphine	956
From silicon and germanium chlorides	626, 634, 957, 958
From a platinum chloride	959
From mercuric chlorides	642
From niobium and tantalum chlorides	634
From trivalent metal complexes	635
From rhodium chlorides	960, 961
Loss of HBr	
From aliphatic bromides	168, 170, 242, 921, 928, 962 (E)
From cyclic bromides	270, 929
From polycyclic bromides	279, 496, 814
From bromo alcohols	18, 336, 394, 788
From bromophenyl compounds	88, 650, 913, 940, 946
From ionic bromides	954, 963
From *N*-bromoamines	955
From bromoarsines	964 (D, M)
From silicon bromides	957
From trivalent metal complexes	635
From rhodium bromides	961
Loss of HI	
From aliphatic iodides	921, 928, 965
From polycyclic iodides	279, 496
From iodophenyl compounds	913, 966
From ionic iodides	967 (D, M)
From trivalent metal complexes	635

The loss of HBr from alkyl bromides is a less favorable process than loss of a bromine atom, and it has proved difficult to analyze the specificity of this reaction. However, an analysis of the spectra of variously deuterated 2-bromobutanes indicated that predominant 1,3-elimination occurred in this compound; a 1,4-process is, of course, impossible because of the nature of the compound investigated.[168] In the case of isohexyl bromide, where a 1,4-elimination is not only possible but even favored by the fact that it would involve a tertiary hydrogen atom, this elimination process predominates.[169]

Loss of H_2X is quite an important fragmentation process by lower molecular weight bromides and iodides, but becomes less important as the molecular weight of the halide increases.[170]

The stereochemical requirements of HCl elimination from both cyclic and acyclic chlorides have been studied. In the case of HCl loss from 2-chloropentane, which proceeds predominantly by the 1,3-pathway, the relative ease of abstraction of the diastereotopic hydrogens on C-4 is about the same as for the corresponding alcohol, and may be summarized by Scheme XXVII.[22] In cyclohexyl chloride, both 1,3- and 1,4-eliminations are observed; unlike the corresponding alcohol, in the chloride *both* eliminations are stereospecifically cis.[22]

SCHEME XXVII

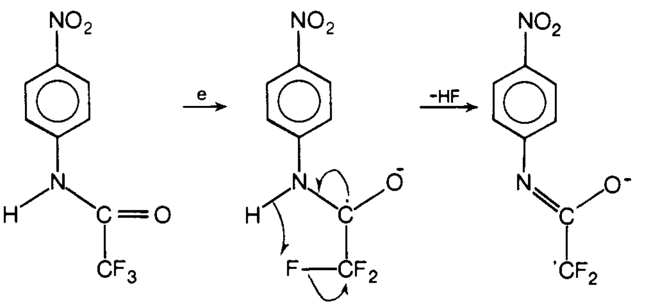


55%

45%

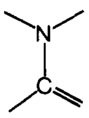
Loss of hydrogen halide is also observed from many other types of compound, and some of the most important examples are collected in Table X. Loss of hydrogen halides has been observed also in negative ion mass spectra; in the case of HF loss from *p*-nitrophenyl trifluoroacetamide, the mechanism of Scheme XXVIII is indicated by deuterium labeling.[171]

SCHEME XXVIII



VII. Loss of Hydrogen Cyanide

Elimination of HCN is an important mass spectrometric fragmentation process. It is particularly prevalent in the spectra of nitrogen-containing heterocyclic compounds, but almost any nitrogen-containing organic compound which contains either an enamine (**58**) or an imine (**59**) structural element shows some loss of HCN.


58

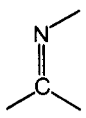

59

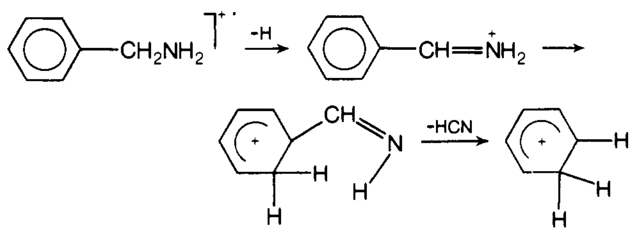
TABLE XI. Loss of HCN

From aromatic nitriles	177, 177a, 968 (M), 969 (E)
From aromatic isocyanides	172, 176, 881
From anilines	178, 188, 861, 970 (D, M), 971 (L, M), 972 (L, M), 973 (L, M), 974 (E), 875
From anilides	179, 180, 976 (D, M), 977 (D, M)
From *N*-nitrosoanilines	848
From phenyl azides	978 (L, M), 979 (D, M), 980 (M)
From other aromatic nitrogen compounds	848, 853, 854, 981 (M), 982 (D, M)
Heterocycles	
From pyridines	380, 983 (D, M), 984 (D, M), 985 (M), 986 (M), 987 (D, M), 988 (D, L, M)
From other six-membered rings containing nitrogen	989 (D, E), 990 (M), 991 (M), 992
From condensed six-membered rings containing nitrogen	388–390, 851, 862, 993 (M), 994, 995 (M), 996 (D, M), 997, 998, 999 (D, M), 1000
From five-membered rings containing nitrogen	847, 1001 (D, M)
From five-membered rings containing two nitrogens	183, 611, 885, 1002–1004, 1005 (M), 1006 (M), 1007 (D, M)
From condensed five-membered rings containing nitrogen	384, 849, 1008 (M), 1009 (D, M), 1010 (D, M), 1011 (D, M), 1012 (M), 1013 (M), 1014 (M), 1015 (M)
From five-membered rings containing three nitrogens	182, 1016, (D, E, M), 1017 (D, L)
From five-membered rings containing four nitrogens	1018 (M), 1019 (D)
From purines and pteridines	894, 1020, 1021 (M), 1022
From other nitrogen heterocycles	850, 852, 910, 1023 (D, M), 1024, 1025, 1026 (M), 1027 (M)
From benzyl nitriles	174, 175, 1028 (M), 1029 (M)
From anils	1030 (M), 1031 (M), 1032 (M)
From azines	184, 1033
From oximes	96, 96a, 588
From hydrazine derivatives	185, 190
From amides	121, 189, 897
From other nitrogen-containing compounds	828, 954, 955, 1034 (M), 1035 (M), 1036 (M), 1037 (D, M), 1038 (M), 1039, 1040

The simplest compounds containing the structural element **59** are the alkyl cyanides, and isopropyl cyanide does indeed show a strong peak corresponding to the loss of HCN from the molecular ion.[172] Larger cyanides are less prone to eliminate HCN directly,[172a] but isohexyl cyanide does form a moderately intense ion corresponding to $(M - CH_3 - HCN)^+$.[173] More pronounced losses of HCN are observed from the molecular ions of the isocyanides, and here even quite large molecules undergo this fragmentation pathway.[172] Labeling studies on ethyl cyanide[173a,b] indicate that the loss of HCN is a 1,1-elimination, at least nominally. It has been suggested that a hydrogen shift from the α carbon to the cyanide carbon precedes HCN loss.[173b]

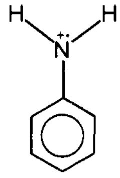
The loss of HCN from some benzyl cyanides has been studied recently.[174,175] In the case of benzyl cyanide itself, ions decomposing in the source lose specifically the cyano group together with a hydrogen atom derived randomly from the original seven hydrogens. Low internal energy ions decomposing in the second field-free region, however, do so with participation of *both* side-chain carbons (22% benzylic carbon and 78% cyano carbon), again after a complete randomization of all hydrogens.[174] In the case of *o*-nitrobenzyl cyanide a 1,1-elimination of HCN was proposed.[175]

SCHEME XXIX

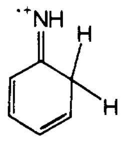


Various other aromatic compounds with a nitrogen-containing side chain also show the elimination of HCN on electron impact. Random loss of HCN and DCN is observed from phenyl-*2,4,6*-d_3 isocyanide[176] and phenyl cyanide.[177] HCN elimination is also observed from the $(M - H)^+$ ion of benzylamine, where the mechanism of Scheme XXIX is suggested for HCN loss on the basis of deuterium-labeling experiments.[178]

Hydrogen randomization often accompanies HCN loss from aromatic nitrogen derivatives such as aniline and phenyl azide, and since this area was discussed in Part I of this review[3] it will not be dealt with here. It has, however, proved possible to make use of the loss of HCN to distinguish between isomeric ion structures, and on this basis the structure **60**, rather than the isomeric structure **61**, has been assigned to the ion resulting from the expulsion of ketene from acetanilide.[179-181]

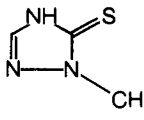


60



61

The loss of HCN from nitrogen heterocycles is a common reaction, as has already been noted. Here again, randomization of the available ring hydrogens is often, but not always, observed prior to HCN expulsion, and several examples of this reaction were discussed in Part I. It should be noted that although simple heterocycles such as pyridine undergo hydrogen randomization prior to elimination of HCN,[3] more complex heterocycles such as 1-methyl-1,2,4,-triazoline-5-thione (**62**)[182] or 1-methylpyrazole (**63**)[183] appear to undergo specific fragmentation processes leading to HCN loss.



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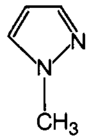


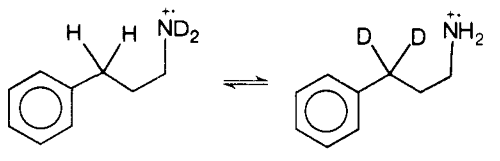
63

Loss of HCN is also noted from various carbonyl derivatives such as oximes,[96] azines,[184] and sulfonylhydrazones.[185] In conclusion, therefore, HCN loss is a common fragmentation process of relatively low specificity, and is therefore of relatively little use as a structural probe in mass spectometry.

Further examples of HCN loss from various compounds are given in Table XI.

VIII. Loss of Other Nitrogen-Containing Fragments

The simplest loss of a nitrogen-containing fragment on electron impact is the loss of ammonia from various primary alkyl amines, which is of course analogous to the loss of water from alcohols. The process is much less important in amines than in alcohols, however, because amines undergo very facile α-cleavage. Thus the spectrum of *n*-butylamine is dominated by the α-cleavage ion at *m/e* 30, and shows only a low (1% of base peak) intensity peak at *m/e* 56, corresponding to $(M - NH_3)\cdot^{+}$.[186] The elimination of ammonia becomes more important in phenylalkylamines, particularly in 3-phenylpropylamine (**64**); in this compound the hydrogen lost with the NH_2 group comes from the benzylic position, and there appears to be exchange between the hydrogens at this position and those attached to nitrogen (**64** $\rightleftarrows$ **64a**) prior to elimination of ammonia.[187]



64 **64a**

Loss of ammonia from aromatic amines is also a relatively unimportant reaction, although it becomes more important in certain amines bearing an ortho methyl group, presumably through the operation of an ortho effect.[188] Ammonia loss is also observed from the diamides of various dicarboxylic acids,[189] together with various miscellaneous compound types. Thus various hydrazine derivatives eliminate not only NH_3 but also NH and NH_2,[190] and N_2H_2,[191] while certain diacyl-α,ω-diaminoalkanes lose NH_3 after a prior elimination of CH_3CO (Scheme XXX).[192]

SCHEME XXX

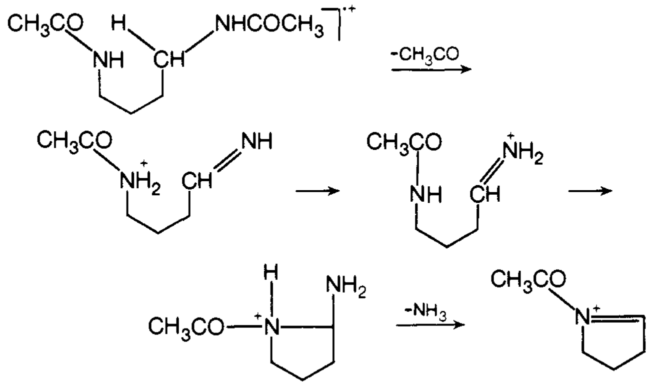
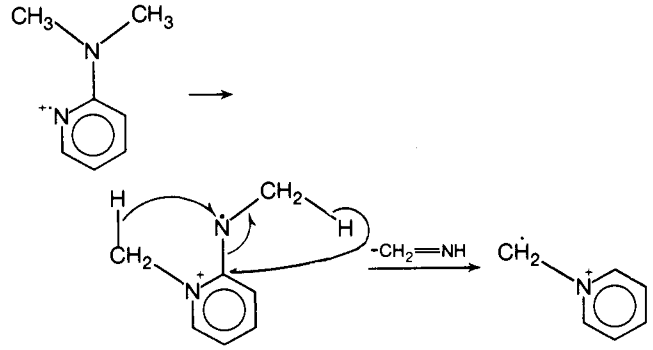


TABLE XII. Loss of Miscellaneous Nitrogen Containing Fragments

Loss of NH_3	
From aliphatic amines	187, 241, 471, 582, 1041
From amino acids and amino esters	469, 472, 730, 1042–1044
From polycyclic amines	278, 279
From steroidal amines	866, 1045 (D, M), 1046 (D, M)
From benzylamines	388, 652
From cyclic amines	1047
From aromatic amines	188, 367, 372, 379, 591, 861, 1021
From amides	189, 192, 418, 476, 573, 880, 1048, 1049 (M), 1050 (D, M), 1051, 1052 (M)
From hydrazine derivatives	190
From other compounds	1032, 1053 (M)
Losses of amines	315, 367, 512, 516, 609, 1054 (D, M)
Losses of amides	
From acetylated amino sugars	412, 423, 667, 673, 778
From other amides	197, 359, 750, 838, 857, 1055 (M), 1056 (D, M), 1057
Loss of diimide	
From hydrazines	191, 910
Loss of hyponitrous acid	
From *N*-nitrosamines	1058, 1059 (D, M)
Loss of nitrous acid	
From nitro compounds	171, 227, 650, 810, 842, 1060 (D), 1061 (M), 1062, 1063 (M), 1064 (D, M)
Loss of imines	
From aromatic amines	193, 254, 483
From metal chelates	1065 (M), 1066
From aliphatic amines	1035
Loss of acetonitrile	1067
Loss of cyanic acid	
From amides	611, 1022, 1068 (D, M), 1069
From a carbamate	1070 (D, M)
From other compounds	195, 590, 1071 (M)
Loss of alkyl isocyanates	
From carbamates	468, 515, 748, 749, 1072 (M)
Loss of thiocyanic acid	196, 1073
Loss of NO	389, 886
Loss of other small nitrogen-containing fragments	182, 381, 474, 608, 686, 846, 1074 (E), 1075 (D, M)

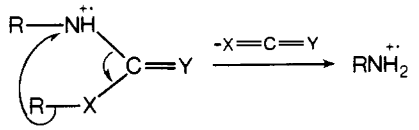
In addition to ammonia and other nitrogen hydrides, amines can expel other nitrogen-containing fragments. Some of these are included in Table XII, but the loss of CH_2NH from various dimethylamino heteroaromatic compounds appears to be a new reaction and is outlined in Scheme XXXI.[193]

SCHEME XXXI



Elimination of the unit HN=C=O occurs from ureas,[194] semicarbazones,[195] and related compounds, while loss of HN=C=S occurs from thiosemicarbazones.[196] These eliminations are formally analogous to the elimination of ketene from amides, and the general mechanism of Scheme XXXII can be written for this reaction. More complex rearrangements must, however, be involved in the loss of $HCONH_2$

SCHEME XXXII



X = NH or CH_2
Y = O or S

TABLE XIII. Loss of Sulfur-Containing Fragments

Loss of SH	
From sulfides	199, 380, 381, 597, 744, 751, 757, 840, 1076–1078, 1079 (D, M), 1080 (M), 1081 (M), 1082, 1083 (E), 1084 (M), 1085, 1086 (M)
From sulfur heterocycles	595, 840, 844, 863, 963, 1087, 1088 (D, M), 1089 (M), 1090–1092, 1093 (D, M), 1094 (D, M)
From thione compounds	121, 888, 896, 976, 1095 (M), 1096, 1097
From a sulfoxide	614
From a thioamide	1098
Loss of H_2S	
From thiols and related compounds	114, 121, 198, 241, 278, 1099 (M)
From sulfides and related compounds	205, 206, 379, 595, 599, 1076, 1078–1082, 1095, 1100 (M), 1101 (D, M), 1102
From sulfur heterocyclics	650, 1027, 1103 (M)
From metal complexes	1104
From a thioamide	1098
Loss of thiols	
From sulfides	136, 613, 674, 1044, 1100, 1105
From thione compounds	838, 1106
From other compounds	627, 650, 1107, 1108
Loss of sulfides	905, 1109 (M)
Loss of thiocarbonyl fragments	
Loss of HCS	859, 1081, 1086
Loss of H_2CS	855, 1084, 1110 (M), 1111 (M)
Loss of $CH_2{=}C{=}S$	595
Loss of organic thioacids	156, 202, 338, 490, 808, 1112, 1113
Loss of HSO, HSO_2, and HSO_3	464, 615, 1079, 1114 (M), 1115 (M)
Loss of HS_2 and H_2S_2	840, 963, 1080, 1093, 1116, 1117 (D, M)
Loss of CS and CS_2	773, 844, 1118 (D, M)
Other losses	182, 524, 1044

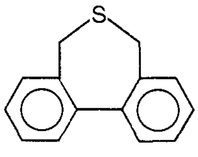
from steroids containing a γ-lactam functionality;[197] other losses of this type are included in Table XII.

Finally, various nitro and nitroso compounds undergo the loss of HNO, H_2NO, or HNO_2 fragments, either before or after the loss of alkyl radicals. These reactions are generally rather complex, and have not been extensively investigated; some examples are included in Table XII.

IX. Loss of Sulfur- and Selenium-Containing Fragments

Elimination of H_2S from aliphatic thiols is analogous to the elimination of water from alcohols and occurs about as readily. In the case of 1-pentanethiol, deuterium labeling indicated that reaction occurs by both 1,3 (40%) and 1,4 (60%) pathways at 70 eV; at 12 eV, in distinction to results for the alcohols and chlorides, there is a fairly significant alteration in the relative importance of the two paths to 44 and 51%, respectively.[198]

In the case of thioethers, whether acyclic or cyclic, the loss of HS becomes an important fragmentation process in addition to or instead of the loss of H_2S. The relative extent of HS and H_2S loss appears to be quite heavily dependent on the structure of the sulfide; thus the cyclic thioether **65** shows an intense (M − HS) peak (55% of the molecular ion intensity), while the similar compound **66** has an (M − HS) peak only 2% of the parent ion intensity.[199] The elimination of H_2S and/or HS is also a common process from sulfur-containing heterocycles, and examples of this reaction and other H_nS eliminations are given in Table XIII.



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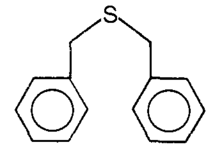
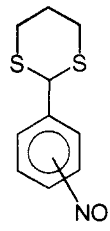


66

Loss of CH_2S is observed from aryl methyl thioethers, analogous to the loss of CH_2O from anisoles;[200,201] these compounds also show the loss of SH to yield an ion formally analogous to the tropylium ion.[200] Elimination of fragments such as CH_3SOH is noted from sulfoxides and related compounds.[202]

Loss of selenium-containing fragments closely parallels the loss of sulfur fragments. Thus dibenzyl selenides lose HSe,[203] while selenoureas eliminate H_2Se;[204] further examples are given in Table XIII.

Negative ion studies have been carried out on nitro-2-aryl-1,3-dithianes (**67**)[205] and -oxathianes (**68**).[206] In most cases loss of H_2S was noted, although not all isomers of the oxathiane **68** showed this loss.



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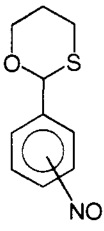


68

X. Loss of Trimethylsilanol

The loss of $(CH_3)_3SiOH$ from trimethylsilyl ethers is formally analogous to the loss of alcohol fragments from simple ethers (section III.A). This fragmentation process is a very minor one in the spectra of simple trimethylsilyl ethers such as *n*-pentyl trimethylsilyl ether, but it yields the base peak in the spectrum of dihydrocinnamyl trimethylsilyl ether. Deuterium labeling indicated that the elimination proceeded by the 1,3 pathway of Scheme XXXIII, as might have been expected from the observed structural specificity of the reaction.[207] The mass spectrometry of trimethylsilyl ethers has been studied quite extensively in connection with the spectral analysis of natural products, particularly steroids and carbohydrates, and Table XIV gives examples of the losses of trimethylsilanol which have been observed from these compounds. Mechanistic studies of this rearrangement have been made, and it has been shown that the loss of trimethylsilanol from various steroid trimethylsilyl ethers is dependent on the position of the ether group on the steroid skeleton. Thus a 17β ether is elimi-

SCHEME XXXIII

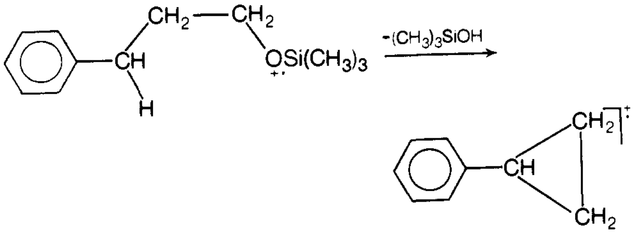
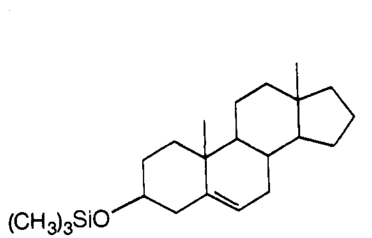


TABLE XIV. Loss of Trimethylsilanol

From straight-chain and monocyclic trimethylsilyl ethers	207, 210–213, 527, 698, 1119–1126 (M)
From prostaglandin trimethylsilyl ethers	532, 552, 755
From trimethylsilyl derivatives of saccharides	417, 1127–1130, 1131 (D, M), 1132–1135
From trimethylsilyl derivatives of steroids	208, 209, 237, 335, 437, 1136–1148
From other natural product trimethylsilyl ethers	449, 1149, 1150
From trimethylsilyl esters	213, 1122

nated more readily than either a 3β or a 3α ether, and in the absence of other factors the elimination of trimethylsilanol from the 3β position is the least likely of the eliminations examined.[208] In the case of 5-en-3β-ol derivatives, however, such as androst-5-en-3β-ol TMS ether (**69**), elimination of trimethylsilanol occurs readily and involves mainly the hydrogen(s) on C-4, presumably yielding a stable conjugated diene ion.[209]



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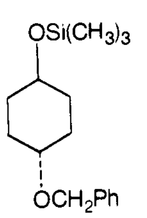
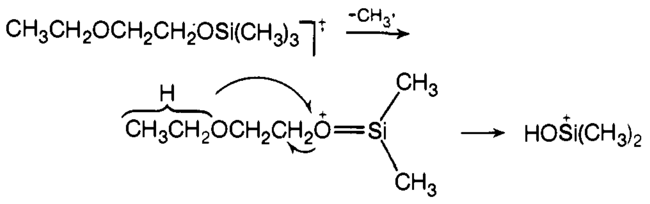


70

Loss of trimethylsilanol from the benzyl ether **70** does not yield an abundant fragment ion at 70 eV, but at low voltage (12 eV) it yields the base peak in the spectrum.[210] Deuterium labeling confirmed that the hydrogen on the 4-position was lost with the trimethylsilyl group. In the case of acyclic alkoxy trimethylsilyl ethers and bis(trimethylsilyl) ethers, a peak at *m/e* 75 is frequently observed due to the species $(CH_3)_2SiOH^+$, and the pathway of Scheme XXXIV has been suggested for the formation of this ion from 2-ethoxyethyl trimethylsilyl ether.[211] Studies have also been made of various alkoxycyclohexanol trimethylsilyl ethers; in these cases both loss of $(CH_3)_3SiOH$ and formation of $(CH_3)_2SiOH^+$ are observed.[212]

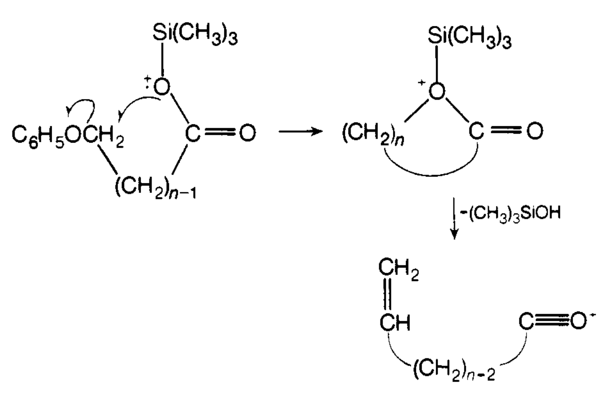
SCHEME XXXIV



The spectra of the trimethylsilyl esters of ω-phenoxyalkanoic acids have also been investigated. Although the elimination of trimethylsilanol from the molecular ion is not observed for those compounds investigated, this loss was noted from one of the abundant fragment ions, and the mechanism of Scheme XXXV was postulated to account for this, although it was noted that other formulations are possible.[213]

In summary, it can be noted that elimination of $(CH_3)_3SiOH$ from trimethylsilyl ethers is a process which occurs readily provided that there is available an activated hydrogen suitably placed for abstraction by the trimethylsiloxy group. In other situations trimethylsilanol elimination may take place following initial formation of a fragment ion, but there are too few examples of this reaction available to enable any generalizations to be made concerning it at the present time. Examples of the loss of trimethylsilanol from various compounds are given in Table XIV.

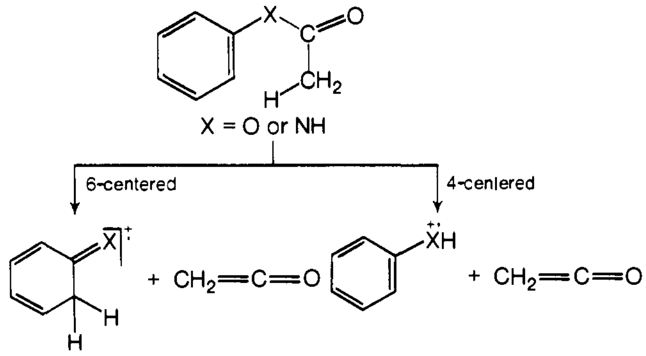
SCHEME XXXV



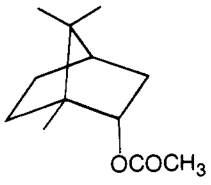
XI. Loss of Ketene

Unlike the losses that have been described in the preceding sections, the loss of ketene from an organic molecule on electron impact usually involves the transfer of a proton *from* the group eliminated *to* the remainder of the molecule. The reaction is commonly observed in aryl acetates and *N*-arylacetamides, and can proceed in principle via either a four-centered or a six-centered rearrangement (Scheme XXXVI). This reaction was discussed in Part I, section III.D, and it was seen that the rearrangement proceeds via the four-centered transition state in both acetates and acetamides.[3] This conclusion has been unchanged by any more recent studies, and consequently this reaction need not be discussed any further.

SCHEME XXXVI



Loss of ketene also occurs from a variety of compound types other than aryl acetates and acetamides. Thus while ketene loss is not observed from the acetate esters of simple alkanols, more complex acetates such as **71**[215] do show significant ketene loss. Expulsion of ketene is also observed from enol acetates[216] (**72**, again postulated to be via a four-membered transition state), the $(M - H)^+$ ion of the acetylenic alcohols (Scheme XXXVII)[217] and β-keto esters (Scheme XXXVIII);[218] this latter process is, in fact, an example of the McLafferty rearrangement. Losses of ketene are also observed from various cycloalkanones and cycloalkenones; in the case of cycloalkanones either a five-membered ring[219] or



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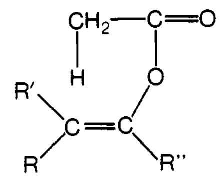

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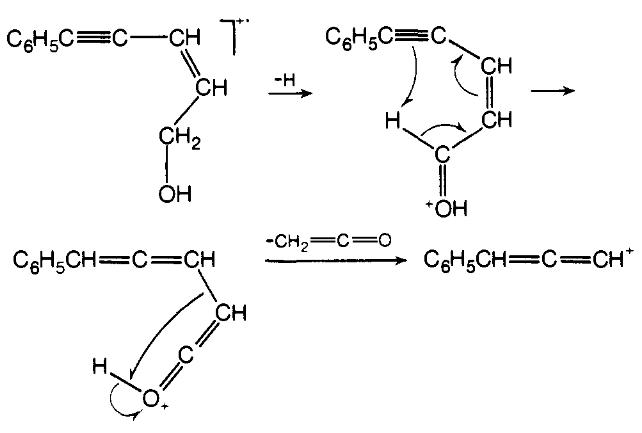
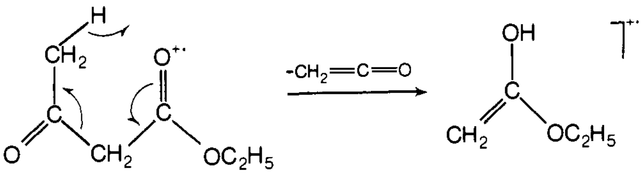
SCHEME XXXVII



SCHEME XXXVIII



a second carbonyl group[220] appears to be necessary for the reaction to take place easily. For cyclohexenones it has been shown that the mechanisms for ketene loss shown in Scheme XXXIX are consistent with the experimental data for this reaction.[221]

SCHEME XXXIX

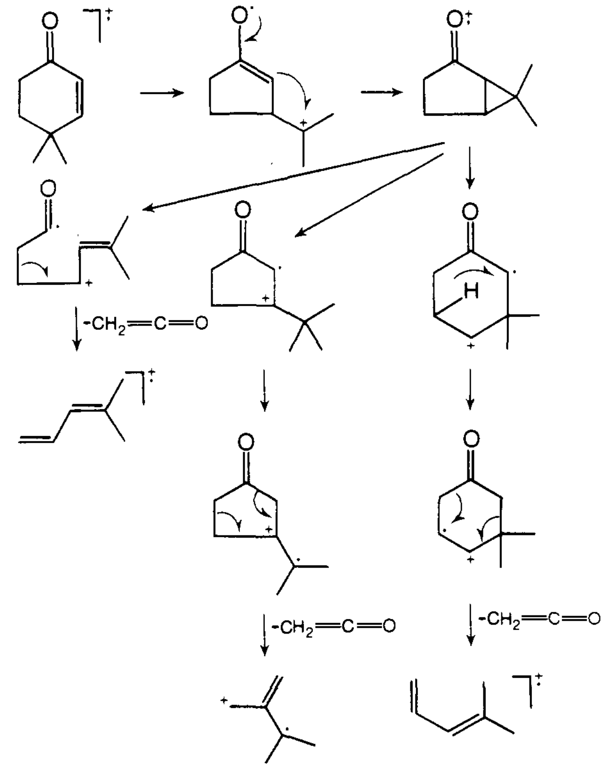
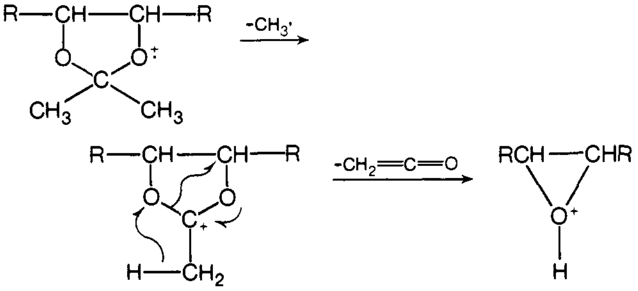


TABLE XV. Loss of Ketene

From alkyl acetates and polyacetates	69, 260, 531, 765, 1151 (D, M), 1152
From simple cyclic and polycyclic acetates	215, 28, 460, 761, 762
From saccharide acetates	225, 422, 424, 425, 530, 658, 664–666, 670, 672, 675, 739, 763, 770–772, 775, 779, 780–782, 784–787, 789, 791–800, 801, 825, 1127, 1131, 1152–1155, 1155a
From steroid acetates and polyacetates	67, 327, 338, 340, 349, 435, 440, 538, 576, 803
From aromatic acetates	226, 358, 373, 649, 714, 767, 768, 790, 1156–1160, 1161 (D), 1162, 1163 (E), 1164, 1165 (E), 1166 (D, M), 1167 (M), 1168–1170, 1171 (E), 1172, 1173
From heterocyclic acetates	1089, 1174–1177
From enol acetates	216, 217, 362, 457, 529, 549, 759, 1178, 1179 (D, M), 1180 (M), 1181
From amides	
Aliphatic amides	192, 901, 1049, 1182 (D, M), 1183–1185, 1186 (M), 1187 (D, M)
Acylated cyclic amines	303, 497, 883, 884, 892, 1039, 1188 (M), 1189 (M), 1090 (D, M), 1091 (D, M)
N-Acylated amino-saccharides	423, 658, 667, 668, 670, 673, 1127, 1131, 1192
N-Acylated aromatic amines	179, 180, 227, 372, 498, 499, 652, 767, 871, 977, 1067, 1193 (D, M), 1194 (M), 1195 (E), 1196 (E)
N-Acylated aromatic heterocycles	486, 600, 611, 844, 872, 995, 1009, 1197 (M), 1198, 1199
From ketones	219, 221, 568, 571, 577, 581, 805, 840, 1200, 1201 (M), 1202 (D, M), 1203 (L, M)
From metal β-diketonates	223, 224, 630, 631
From alcohols	248, 572, 1202
From carboxylic acids	835, 1204
From methyl esters	518, 535, 636, 967, 1205 (M), 1206 (D, M), 1207 (M)
From acetonides	160, 222, 557
From other compounds	185, 886, 1185, 1208, 1209 (D, M)

SCHEME XL



Ketene loss is also observed from the $(M - CH_3)^+$ ion of acetonides, and the pathway of Scheme XL has been suggested to account for this.[222] It is worth noting that the loss of acetic acid also occurs from acetonides (Scheme XXIV), and in general the loss of ketene and acetic acid often accompany each other in the mass spectra of compounds with the appropriate structural features. Ketene loss has also been noted from various metal complexes of β-diketones and related ligands,[223,224] in the field ionization mass spectra of carbohydrate acetates,[225] and in the negative-ion mass spectra of various aryl acetates[226] and acetamides.[227]

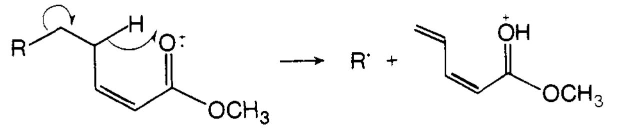
Further examples of ketene loss from various compound types are included in Table XV.

XII. Loss of Hydrocarbon Fragments

A. Loss of Alkyl Fragments

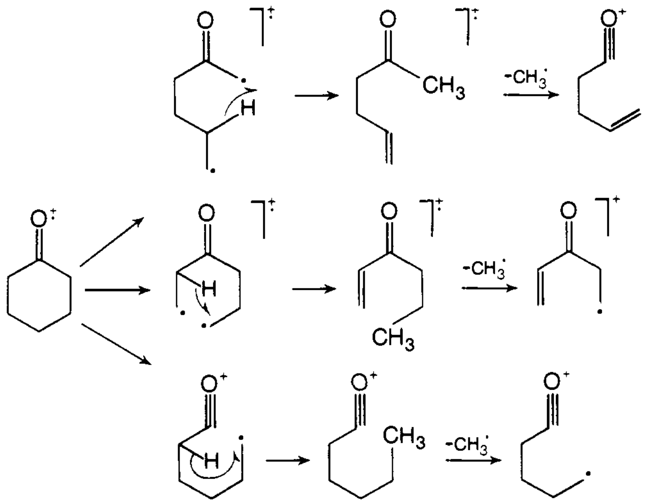
The loss of alkyl fragments from various hydrocarbons has already been discussed in Part I of this review.[3] In particular, the common loss of a methyl radical from cycloalkanes may be mentioned as an example of a process where hydrogen migration is required prior to the completion of the fragmentation. Hydrogen transfer processes may also be involved in some apparently simple cleavages; thus it has been suggested that the abundant ϵ-cleavage ion in α,β-unsaturated esters is produced by the pathway of Scheme XLA.[227a–c]

SCHEME XLA



One of the most intriguing mass spectrometric fragmentations is that involving the elimination of an alkyl fragment from molecules where this group is not present as such. Saturated cyclic ketones, which contain only methylene units, yet often manage to show the loss of a methyl fragment, and this process obviously requires ring cleavage and hydrogen transfer from some available site in the course of fragmentation. In the case of cyclopentanone, deuterium labeling established that the hydrogens of the β-carbon are both lost in the elimination of $CH_3\cdot$.,[228] while in cyclohexanone deuterium labeling established that several pathways must be involved in the loss of $CH_3\cdot$: the most important of these are shown in Scheme XLI.[104,229]

SCHEME XLI

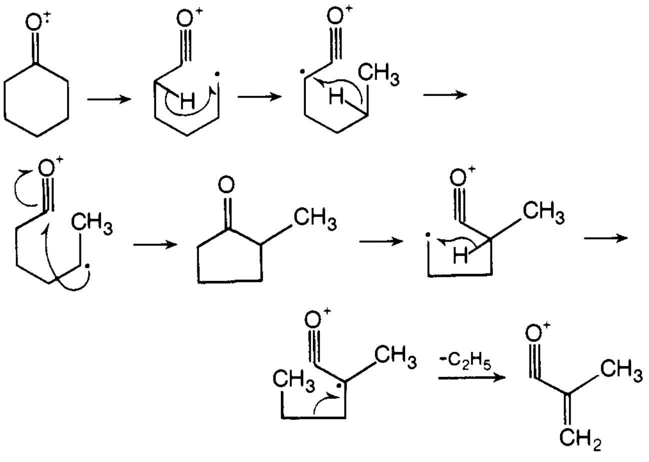


Cyclohexanone also loses an ethyl group by a mechanism complex enough to give mass spectrometry a bad name as black magic rather than a scientific discipline![104,229] The mechanism proposed[229] is shown in Scheme XLII; the crucial step involves the formation of a five-membered ring from the original six-membered ring. While other mechanisms could conceivably be written for this reaction, this one has the merit of accounting for the labeling results by a chemically reasonable pathway.

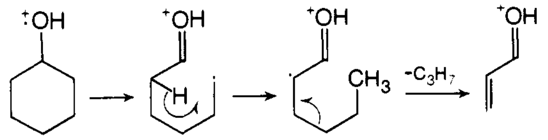
Loss of alkyl fragments is also observed from cyclic unsaturated ketones,[230] cyclic β-diketones,[231] and bicyclic ketones such as the β-hydrindanones.[219]

Cyclic alcohols such as cyclohexanol also lose alkyl fragments; in the particular case of cyclohexanol the mechanism of Scheme XLIII has been proposed on the basis of deuterium-labeling evidence.[32]

SCHEME XLII

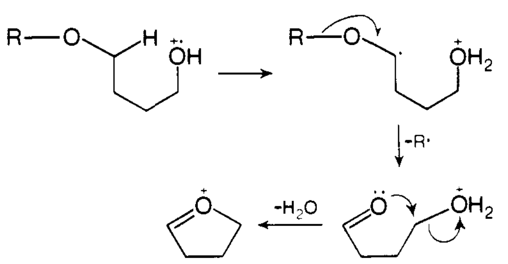


SCHEME XLIII



Even the loss of alkyl fragments from molecules already containing these fragments can be the result of intramolecular hydrogen transfer processes. Thus the formation of abundant $(M - R)^+$ and $(M - R - H_2O)^+$ ions in the spectra of compounds of the general formula $RO(CH_2)_4OH$ has been explained by the mechanism of Scheme XLIV, where an initial intramolecular hydrogen transfer is involved in "activating" the ether cleavage leading to loss of R.[135]

SCHEME XLIV



Similarly, in the case of ethyl *n*-butyl ether, deuterium labeling has demonstrated that loss of the ethyl radical is not a simple cleavage process: a double hydrogen transfer is required for loss of C-1 and C-2 of the butyl group, together with another hydrogen probably from C-4 of this group (Scheme XLV).[232]

Loss of a methyl radical surprisingly also takes place from various aromatic systems such as phenylthiophenes,[233] quinoline and related compounds,[234] and diphenyl sulfide.[235] In

SCHEME XLV

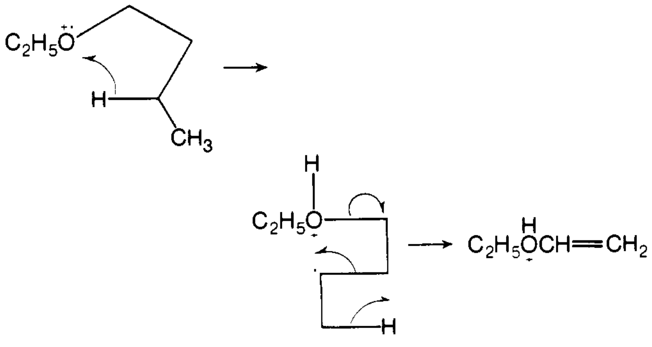


TABLE XVI. Loss of Hydrocarbon Fragments

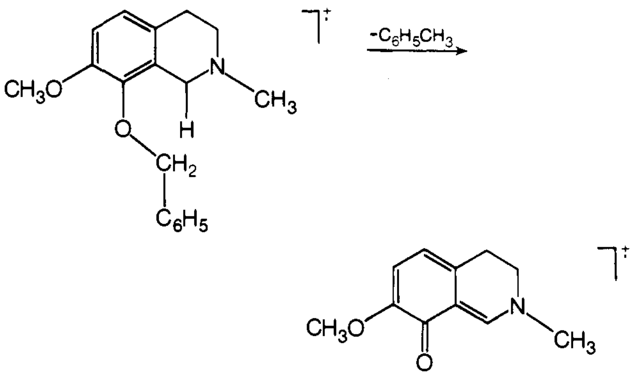
Loss of CH_3	
From cyclic hydrocarbons	591
From alcohols	26, 70, 74a
From ethers	546, 640, 652, 877
From aldehydes and ketones	104, 562, 566
From cyclic amines	1043, 1189
Loss of CH_4	
From alcohols	24, 238, 245, 246, 864
From cyclic ethers	546
From carboxylic acids	488
From amines	188, 306, 883, 964, 1040
From heterocycles	1052
From silicon ethers	237, 634, 1134, 1210
From phosphorus compounds	856, 964
From sulfur compounds	1180
Loss of C_2H_2	516, 597, 838, 864
Loss of C_2H_3	188
Loss of C_2H_4	
From alcohols	244, 245, 246
From ethers	380, 637, 648, 767, 1211 (E)
From peroxides	1212
From carboxylic acids	477
From esters	239, 724, 750, 891, 1042, 1213 (M)
From orthoesters	751
From esters of inorganic acids	856, 1214 (M), 1215
From aldehydes	98
From amines	848, 1030
From heterocycles	584, 1015, 1216
From sulfur and silicon compounds	774, 1217 (M)
Loss of C_2H_5	
From aldehydes and ketones	98, 104, 566, 1189
From quinuclidines	1189
Loss of C_2H_6	123, 864, 961
Loss of larger acetylenes	
From carotenoids	548
Loss of larger alkyl radicals	
From aldehydes and ketones	98, 219
From alcohols	260, 286, 403
From ethers	546
From Schiff bases	1030
Loss of larger alkenes	
From alcohols	325
From ethers	126, 374, 458, 544, 1218 (D, M)
From ketones	895
From amines	848, 1035
From amides	504, 603, 820
From esters	117, 483, 749
From silicon compounds	751
From metal complexes	960, 1104
Loss of cyclopropane	
From metal complexes	905
Loss of aromatic hydrocarbons	
From diarylmethanes	1219 (M)
From carotenoids	292, 544, 1220 (D, M), 1221
From ketones	905
From nitrogen compounds	236, 583, 718
From silicon compounds	625, 1222
From phosphorus compounds	1069
From arsenic compounds	627, 1223
From transition metal complexes	1207

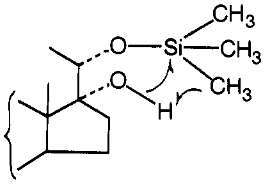
the latter case a ^{13}C labeling study indicated that the C-1 carbon is lost preferentially as CH_3,[235] while deuterium labeling studies of both of the other cases indicate a multiplicity of pathways leading to methyl loss.[233,234]

B. Loss of Hydrocarbon Molecules

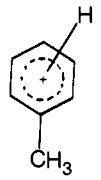
The loss of a hydrocarbon molecule from any organic compound must involve a hydrogen transfer process, provided that it occurs in a single-step process and not as the consecutive loss of a hydrogen atom and an alkyl or aryl group. The loss of alkane molecules from both aliphatic and alicyclic hydrocarbons is an important fragmentation process which has been discussed in section II of Part I of this review.[3] Other examples of this type of process include the elimination of benzene from bis(aryl) compounds, discussed in section 111.G of Part I of this review,[3] and the loss of toluene from a benzyloxytetrahydroquinoline (Scheme XLVI).[236] Both types of process are attested to by the appropriate metastable peaks, and, although it has been shown that the observation of metastable peaks is not always indicative of a concerted process,[3] the likelihood is that these particular eliminations do proceed by a concerted pathway. The loss of methane is observed from various compounds, including the trimethylsilyl ether of a steroid diol (**73**, arrows)[237] and the (M − CH_3 − CO)$^+$ ion (**74**) generated from *p*-methyl-1-phenylethanol-1.[238]

SCHEME XLVI





73



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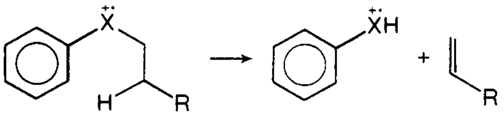
The loss of alkene fragments from organic molecules is another example of a reaction necessarily involving intramolecular hydrogen transfer. Examples of this type of rearrangement already discussed include elimination of an alkene from an aromatic side chain (Scheme XLVII, discussed in Part I, section III.D),[3] and the McLafferty rearrangement (Scheme XLVIII, discussed in Part II).[4] The loss of ethylene from ethyl

SCHEME XLVII



SCHEME XLVIII

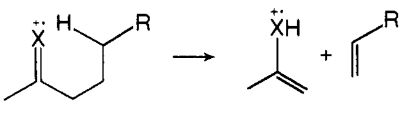


TABLE XVII. Loss of Miscellaneous Fragments

Loss of other fragments containing carbon and oxygen	132, 644, 857, 860, 1095
Loss of fragments containing carbon and fluorine	747, 906, 1224
Loss of OH·	
From carbon/hydrogen/oxygen-containing compounds	367, 845
From nitro compounds	247, 591–593, 842, 849, 1031
From other nitrogen compounds	249, 747, 848, 886, 991
From phosphorus-containing compounds	1185
From sulfur-containing compounds	614, 615, 853, 870, 1083
From metal complexes	1207
Loss of HOOH and HO_2	558, 560, 1115
Loss of boron-containing fragments	618, 1225, 1226 (M), 1227 (M)
Loss of other silicon-containing fragments	1228, 1229
Loss of phosphorus-containing fragments	620, 964
Loss of arsine	1231
Loss of selenium-containing fragments	203, 204, 257, 836, 1038, 1091, 1232, 1233
Loss of CuH	1065

benzoate has also been discussed (Part 1, section III.G).[3] Further examples of alkane and alkene loss from various systems are given in Table XVI.

XIII. Loss of Miscellaneous Fragments

The losses of various miscellaneous fragments on electron impact are listed in Table XVII. From the variety of losses collected in this category, there obviously can be no central mechanism. Two especially well-represented types of loss stand out, however: the tendency for nitro compounds, particularly aromatic compounds, to lose OH under certain conditions; and the loss of selenium-containing fragments analogous to sulfur-containing fragments from selenides. The loss of H_2O_2 from hydroperoxides may resemble loss of water from alcohols, though little work has been done to confirm or disprove this point.

XIV. Addendum

The flood of papers dealing with aspects of hydrogen transfer in mass spectrometry has continued unabated since the completion of the manuscript. Space limitations preclude anything more than a brief mention of some of the more significant ones available in our libraries as of June 1975.

Three detailed studies of water loss from alicyclic alcohols have appeared. In two of these studies various epimeric diterpene alcohols were utilized as substrates, and it was concluded that both cis 1,3- and cis 1,4-eliminations occurred stereospecifically provided that the hydrogen abstracted was tertiary.[1233] In the other study, water elimination from some adamantane derivatives was investigated.[1234] Water loss has also been noted from various other molecular structures, including acetylated 2,2′-diaminodiphenylmethanes,[1235] phthalazinone derivatives,[1236] the *m/e* 99 fragment ion of dialkyl phosphates,[1237] a fragment ion from certain 4,6-dialkyl-1,3-dioxanes,[1238] and the $(M - CH_3)^+$ fragment ion of ethyl 2-ethoxybenzoate.[1239] In addition, the unusual loss of HO· from various bipiperidyl alkaloids containing an amide function has been studed in detail.[1240]

The loss of methanol from 4-*tert*-butylcyclohexyl methyl ether under photoionization conditions occurs more readily from the trans isomer which also has the more abundant molecular ion; a 1,4-mechanism is proposed for this elimination.[1241] The loss of methanol from dimethyl ethers of the type $CH_3O(CH_2)_nOCH_3$ has been studied by ion cyclotron resonance.[1241a] In congruence with the studies discussed earlier, this loss involves nearly specific abstraction of a methylene hydrogen adjacent to the methoxy group that is not being lost. The loss of alcohols from various esters proceeds more or less as expected: in the case of the dimethyl esters of the cyclobut-3-ene-1,2-dicarboxylic acids, loss of methanol from the trans acid is greater than that from the cis acid,[1242] while the loss of methanol or phenol from the negatively charged molecular ions of the methyl or phenyl esters of 4- and 5-nitrosalicylic acid shows that ortho effects are important in negative ion spectra. Loss of methanol is also observed from the $(M - C_2H_4)^{\cdot+}$ ion of ethyl 2-ethoxybenzoate[1239] and a fragment ion of certain 4,6-dialkyl-1,3-dioxanes.[1238]

As in the case of the electron-impact-induced reaction, the loss of acetic acid from the 4-*tert*-butylcyclohexyl acetates on photoionization occurs by a combination of pathways involving 1,2-, 1,3-, and 1,4-eliminations.[1241]

The loss of formaldehyde has been noted from the 1,3-dioxanes previously mentioned,[1238] and also from the molecular ion of arylsulfonylmethyl sulfonates.[1244] Formaldehyde loss is also significant in the spectrum of 1,2-dimethoxyethane, and a six-centered transition state is proposed to account for this.[1241a]

The methylfluorosilanes $(CH_3)_nSiF_{4-n}$ show a characteristic loss of HF from the parent ion minus a hydrogen atom in their negative ion spectra.[1245]

The loss of amine fragments from N,N,N′,N′-tetrasubstituted 1,3-diaminopropanes has been shown to involve the loss of the amine group from C-1 together with a hydrogen from C-3; an azetidine ring is postulated as the product of this reaction.[1246] The loss of nitrous acid from the molecular ion of the methyl ester of γ-nitrobutyric acid occurs to the extent of about 85% by a 1,1-elimination, providing the third example of an elimination of this type.[1247] Previous examples of this type of elimination have been the elimination of HCN from alkyl cyanides[173b] and from *o*-nitrobenzyl cyanide.[175] The loss of HO· from γ-nitrobutyric acid also involves a 1,1-elimination.[1247]

Although the triaryl-*s*-trithianes do not undergo loss of H_2S and similar fragments on electron-impact when the aryl groups are phenyl, the chloro- and methoxy-substituted trithianes do show the loss of HS· and H_2S.[1248]

The loss of ketene continues to be a common occurrence in the spectra of carbonyl compounds, particularly those with additional unsaturation. Ketene loss is, thus, observed from the $(M - H_2NO)^+$ ion of α-aminooxy-β-phenylpropionic acid[1249] and from various vinylogous amides.[1250] Ketene loss from acyclic 1,3-diketones has been shown to yield an ion with an enolic structure,[1251] while that from acetanilidetricarbonylchromium occurs via a six-membered transition state.[1252] This latter result contrasts with that for elimination of ketene from uncomplexed acetanilide, where a four-membered transition state has been implicated.[3] One example where ketene is *not* eliminated is found in the mass spectrum of hexananilide; the molecular ion loses C_4H_8 in a McLafferty rearrangement to give an ion at *m/e* 135 which loses C_2H_2O, but labeling evidence and metastable analysis showed that the fragment lost was ethynyl alcohol rather than ketene.[1253]

A number of unusual eliminations of HX were observed in the mass spectra of various alkyl borates. The original paper should be consulted for details of these reactions.[1254]

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