Organic Mass Spectrometry, 1969, Vol. 2, pp. 81 to 103. Heyden & Son Limited. Printed in Northern Ireland

THE MASS SPECTRA OF SOME METHYL NORBORNYL CHLORIDES

C. A. Bunton and T. W. Del Pesco*
Department of Chemistry, University of California at
Santa Barbara, Santa Barbara, California 93106

(*Received* 9 *September* 1968; *accepted* 14 *October* 1968)

Abstract—The mass spectra of *exo*-2-norbornyl chloride, 1- and 2-methyl *exo*-2-norbornyl, *exo*-camphenilyl, apoisobornyl, bornyl and isobornyl chloride, and camphene hydrochloride, α- and β-fenchyl chloride and fenchene hydrochloride, and *exo*-isofenchyl chloride and 2,5,5-trimethyl *exo*-2-norbornyl chloride, and camphene and α-fenchene have been examined at 12 to 16 and 80 eV and at 30 to 49 and 80°, or higher temperatures. Wagner-Meerwein rearrangements occur very readily in the ion source and compounds related by these rearrangements give very similar fragmentation patterns. Thermal decompositions are important with the tertiary chlorides especially at higher source temperatures. The rates of methanolysis of some of these chlorides were measured.

Many workers have discussed the mechanism of reactions in ion sources of mass spectrometers[1] and the relation between gas phase elimination of hydrogen halides from alkyl halides and S_N1 and E1 solvolytic reactions.[2a,2b,3] Many of these gas phase eliminations involve rearrangement of the carbon skeleton, as in the corresponding solvolyses[4a,4b] and relative rate sequences are similar in both sets of chemical reactions.

Our interest in this problem was stimulated by the analogy drawn by DeJongh and Shrader between the relative intensities of the peak due to the molecular ion, $C_7H_{11}Br^+$ and the base peak, $C_7H_{11}^+$ and the rates of solvolysis of *exo*- and *endo*-2-norbornyl bromides.[5] According to the kinetic approach to mass spectra using the steady state treatment,[6] the rate of formation of $C_7H_{11}^+$ from $C_7H_{11}Br^+$ should be proportional to the ratio of the recorded intensities and the relative rates were in fact similar to those found for the solvolyses, provided that allowance was made for the temperature difference between the two sets of experiments. (This treatment also ignores solvent effects and ion pair return.) Recent work, however, has shown that the ratio of daughter peak to parent depends on the accelerating voltage[7] and that the simple treatment is only approximate.

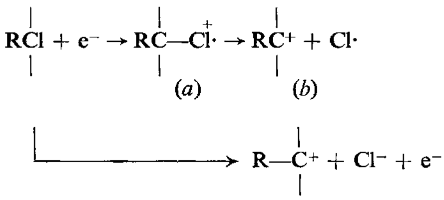
There has been considerable work done on the fragmentation of bicyclic terpenoids,[8 to 11] but for the most part the terpenes themselves or their oxygenated derivatives have been studied. The study of the norbornyl bromides has been mentioned[5] and it has also been shown that the mass-spectral fragmentation pattern of *endo*- and *exo*-2-norbornenyl chloride is dominated by the retro-Diels-Alder reaction.[11]

We have examined the mass-spectral fragmentation patterns of a number of methyl substituted *endo*- and *exo*-2-norbornyl chlorides, using an MS-902 double focusing

---

* NDEA Title IV Fellow 1965 to 1968.

spectrometer with a cooled ion source to minimize thermal decompositions which may complicate the spectra[12] and varying the electron voltage in order to simplify the fragmentation pattern. So far as was possible we chose compounds which generated ions which could be related by Wagner-Meerwein rearrangements, so that we could compare the reactions in the ion source with solvolyses. We used chlorides, because loss of Cl· from the parent ion (*a*) generates the carbonium ion, (*b*), by either of two reactions:[13]



$$\mathrm{RCl} + e^- \rightarrow \underset{(a)}{\mathrm{RC{-}\overset{+}{Cl}}\cdot} \rightarrow \underset{(b)}{\mathrm{RC^+}} + \mathrm{Cl}\cdot$$

$$\mathrm{RCl} \longrightarrow \mathrm{R{-}C^+} + \mathrm{Cl^-} + e^-$$

Alcohols, ketones and olefins generally fragment to give radical cations.[12,14]

An additional advantage of using chlorides is that any chlorine-containing fragment will show isotopic peaks due to the presence of ^{35}Cl and ^{37}Cl.

The mass spectra of these norbornyl chlorides are not rich in metastable ions, at least under the conditions which we used; however we were able to support some of the postulated reactions by observation of metastable ions. When metastable peaks are generated in the decomposition of the molecular ion to a daughter ion with loss of chlorine we should observe two metastable peaks due to the presence of both ^{35}Cl and ^{37}Cl. However the metastable peaks were generally very small and hence the smaller of the two was not observed.

RESULTS

The mass spectra were examined to determine (i) the mechanism of fragmentation to the major ions; (ii) the degree to which isomers related by Wagner-Meerwein rearrangement give the same spectra; (iii) the relative ion intensities for *endo*- *exo*-isomers; (iv) the effects of changes in electron voltage and source temperature upon the mass spectra. We could not study all these questions because we could not make some of the *endo*-chlorides.

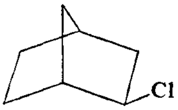
Where m/e values are given for ions which contain chlorine, those in parentheses relate to the ion which contains ^{37}Cl. The mass spectra are shown in either figures or tables. We have generally used figures for the mass spectra obtained at 80 eV and 30° and tables are used for those obtained at low electron voltages and at higher temperatures. The mass spectra for camphene (XIV) and α-fenchene (XV) are very similar to those observed by Ryhage and von Sydow using a single focusing mass spectrometer at 20 eV and 250°.[8]

We give the peak sizes as percentages of that of the base peak and in the tables we have omitted those peaks which are less than 5% of the base peak, except for the molecular ion peaks (for some of the more complex spectra we omit those which are less than 10%). A few spectra were run at 170°, but these have not been tabulated, because they are similar to those obtained at 70 to 80°, with the exceptions noted.

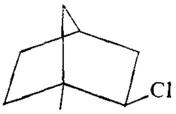
In our discussion of reaction schemes we do not consider the ions of low m/e ($<$*ca.* 60), because Dimmel and Wolinsky have discussed this problem in detail.[10]

The following 2-norbonyl chlorides were examined:

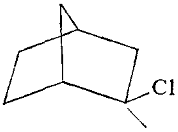
exo-2-norbornyl chloride (I)



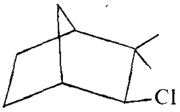
1-methyl-*exo*-2-norbornyl chloride (II)



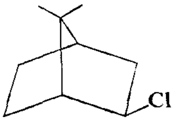
2-methyl-*exo*-2-norbornyl chloride (III)



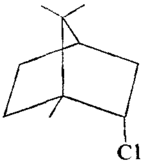
exo-camphenilyl chloride (IV)



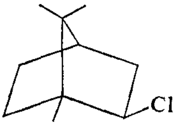
apoisobornyl chloride (V)



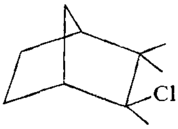
bornyl chloride (VI)



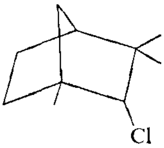
isobornyl chloride (VII)



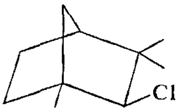
camphene hydrochloride (VIII)



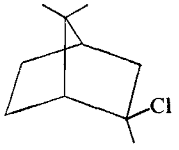
α-fenchyl chloride (IX)



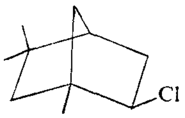
β-fenchyl chloride (X)



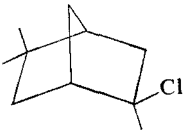
α-fenchene hydrochloride (XI)



exo-isofenchyl chloride (XII)

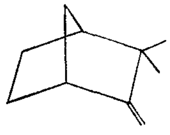


2,5,5-trimethyl-*exo*-2-norbornyl chloride (XIII)

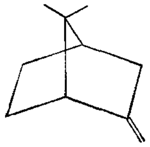


Two olefins were also examined:

camphene (XIV)



α-fenchene (XV)



exo-2-Norbornyl chloride (I) *at m/e*

(i) There are major peaks at *m/e* 130 (132), 95, 68 and 67 (Table 1). Reactions by which these ions could be formed are shown in Scheme 1.

TABLE 1. PRINCIPAL PEAKS IN MASS SPECTRA OF *exo*-2-NORBORNYL CHLORIDE*

Electron voltage	*m/e* 39	41	53	54	55	66	67	68	69	79	81	88	95	130	132
16	—	—	—	—	—	—	47	100	—	—	6	—	23	46	13
80	14	9	7	8	5	8	77	100	5	6	6	5	18	31	9

* At 30°.

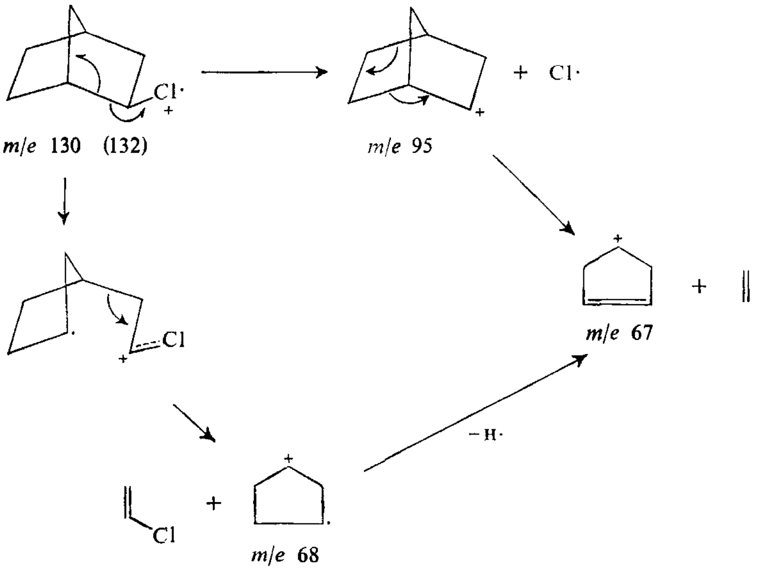
1-*Methyl and* 2-*methyl-exo-2-norbornyl chloride* (II) *and* (III)

(i) The major peaks are at *m/e* 144, (146), 129, (131), 109, 108, 81, 68 and 67 (Table 2* and Fig. 1) and could be formed as in Scheme 2 for the tertiary 2-methyl-2-*exo*-2-norbornyl chloride.

(ii) The mass spectra of secondary and tertiary chlorides are almost identical.

(iii) When the electron voltage is decreased to 16 eV the spectra are simplified. The base peaks are still at *m/e* 81, but the relative intensities are changed and the parent peak at *m/e* 144 (146) is larger for the tertiary than the secondary chloride, as are those due to C_5 ions.

* See Appendix.



SCHEME 1

An increase in source temperature from 30 to 71° increases the peak at *m/e* 67 of the cyclopentenyl cation more for the tertiary than the secondary chloride and for both isomers the molecular peak is decreased and the spectra contain more minor peaks. An increase in source temperature to 170° decreases the intensities of peaks due to ions of high *m/e*, but in other respects the spectra are very similar to those obtained at 71°.

(iv) There are metastable peaks at *m/e ca.* 45·5 and 45 in the mass spectra of both 1- and 2-methyl norbornyl chlorides which could be generated in the decomposition of molecular ion at *m/e* 144 to the ion of *m/e* 81, suggesting that loss of chlorine and elimination of ethylene can occur simultaneously rather than stepwise as shown in Scheme 2.

exo-Camphenilyl chloride (IV) *and apoisobornyl chloride* (V)

(i) The major peaks are at *m/e* 158 (160), 123, 122, 109 and 67; in addition there are several moderately sized peaks in the range *m/e* 78 to 81, which are probably C_6 fragments, which could be formed for example from *m/e* 109 by loss of methyl groups (Table 3* and Fig. 2). Reactions by which the ions could be formed are shown in Scheme 3.

(ii) The mass spectra of the Wagner-Meerwein related isomers are very similar for the high masses.

(iii) Lowering the electron voltage to 16 eV leads to a decrease in fragmentation as does a decrease of ion source temperature. The mass spectra of these chlorides were also obtained at 16 and 80 eV and 79°. The spectra are very similar to those obtained at 30°, except that the peaks at lower *m/e* values are favored relative to those at high. However, with *exo*-camphenilyl chloride (IV) the peak at *m/e* 123 increases slightly relative to the adjacent peaks with an increase in temperature.

---

* See Appendix.

In Scheme 3 we show a stepwise scheme for decomposition of the molecular ion to the ion at *m/e* 109. We observed metastable ion at *m/e* 75·2 in the mass spectrum of apoisobornyl chloride (V), which however, could be formed by the direct decomposition of the molecular ion in which these various steps are concerted. In this scheme and in others where we show the elimination of a methylene residue from a substituted methyl cation it is possible that ring fission and loss of 14 mass units are concerted processes.

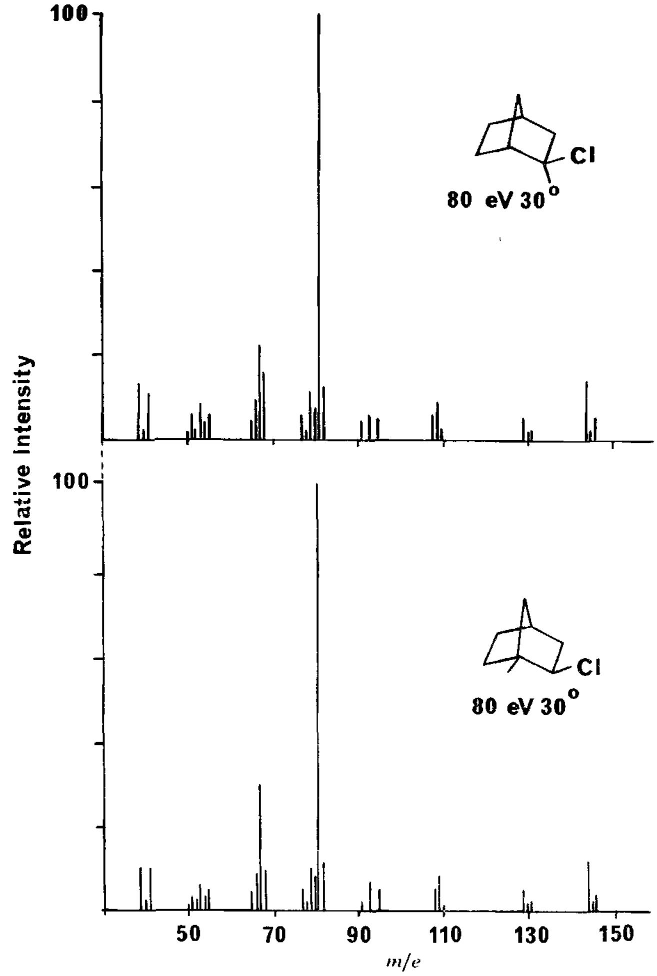
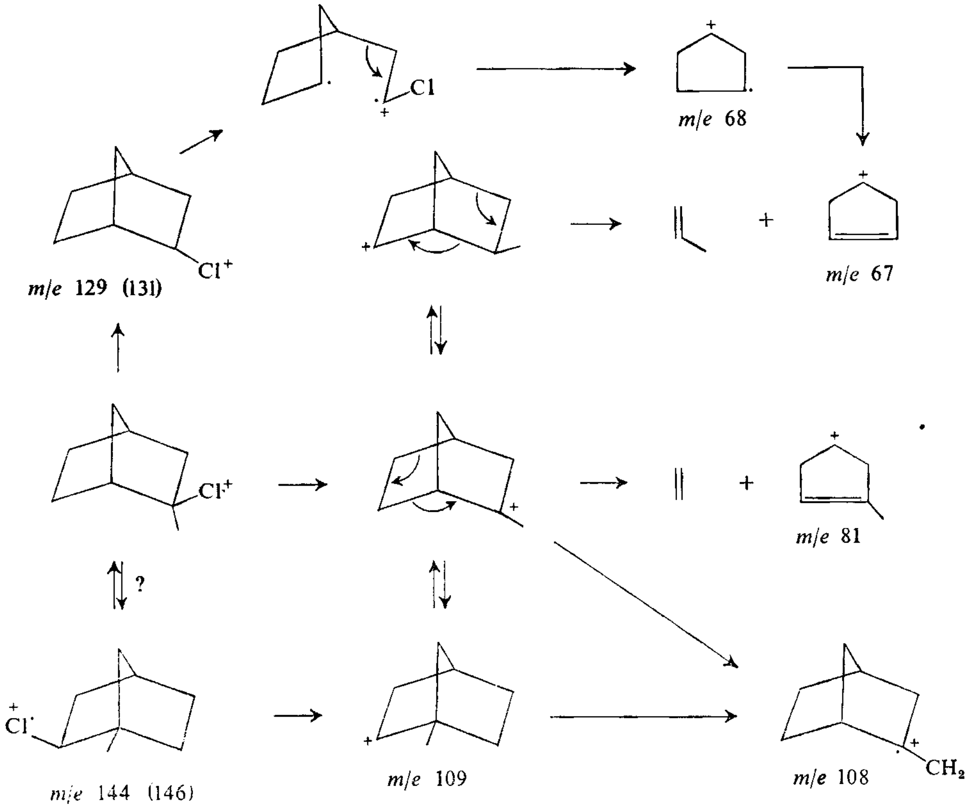


Fig. 1. Mass spectra of 1- and 2-methyl norbornyl chloride (II) and (III).

Although the mass spectra of these two chlorides are very similar, there are differences in the intensities of the peaks at [M — 35] (*m/e* 123) due to loss of a chloride atom from the parent ion. This loss is greater with *exo*-camphenilyl chloride (IV) than with apoisobornyl chloride (V) with 16 eV electrons, but less with 80 eV electrons. This difference may reflect a tendency for greater fragmentation of the [M — Cl]$^+$ peak with higher electron voltages, or a change in the dissociative process with changing



Scheme 2

electron voltage,[13] e.g. we could have

at 80 eV
$$RCl + e^- \rightarrow R\overset{+\cdot}{Cl} \rightarrow \overset{+}{R} + \overset{\cdot}{Cl}$$
at 16 eV
$$RCl + e^- \rightarrow R^+ + \overline{Cl} + e^-$$

For solvolysis apoisobornyl chloride is the more reactive, by a factor of *ca.* 200 at 25° in methanol. These differences illustrate the problems in relating the rates of ionization of norbornyl halides in solution to the fragmentation pattern in a mass spectrometer ion source.[5]

Bornyl and isobornyl chloride, (VI) *and* (VII) *and camphene hydrochloride* (VIII)

(i) The major peaks in the spectra are at *m/e* 172, (174), 157 (159), 137, $\underline{136}$, $\underline{121}$, 110, $\underline{107}$, 95, $\underline{93}$. (Table 4* and Figs. 3 and 4). The underlined peaks are also found in the mass spectrum of camphene, (Table 4 and Ref. 8).

The reactions by which they could be formed, are shown in Scheme 3. It should be noted that certain ions, e.g. that at 136 and those derived from it could be formed by thermal decomposition to camphene, followed by its ionization.

(ii) The mass spectra of isobornyl chloride (VII) and camphene hydrochloride (VIII) are almost identical, suggesting either that a common non-classical ion is

---

* See Appendix.

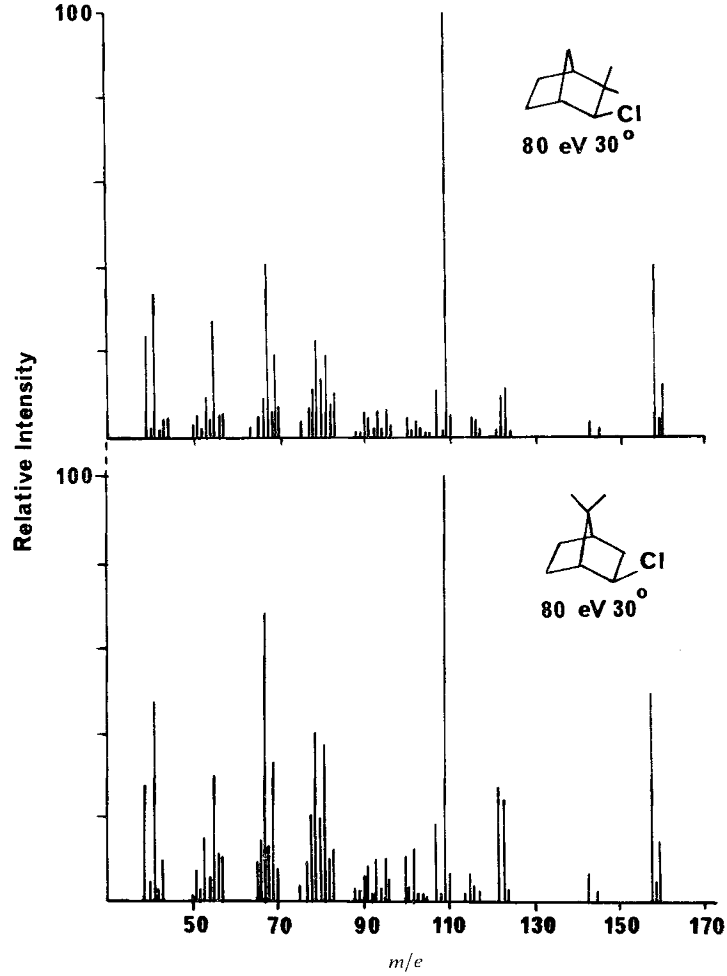


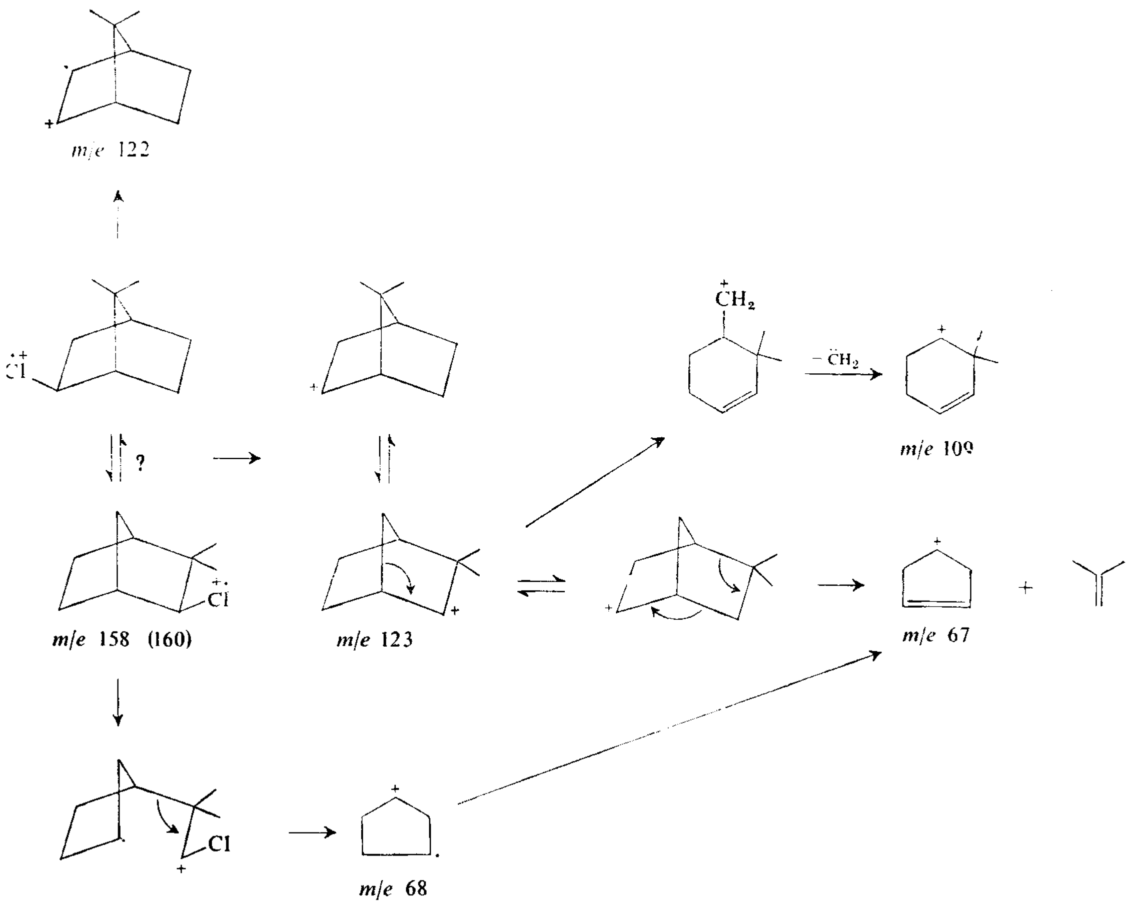
Fig. 2. Mass spectra of *exo*-camphenilyl and *apo*-isobornyl chloride (IV) and (5).

formed, or that the ions are rapidly equilibrating. The differences probably arise because of the greater thermal instability of camphene hydrochloride.

(iii) The spectra of isobornyl (VII) and bornyl (VI) chlorides contain the same peaks, but with different intensities. The major differences are in the ions *m/e* 136, 121 and 93, which are more prominent in the spectrum of isobornyl chloride and are also found in the mass spectrum of camphene. These differences correspond to the faster thermal decomposition of isobornyl as compared with bornyl chloride.[2a,2b]

(iv) Increasing the temperature of the ion source increases the intensity of those ions which could be formed from camphene, suggesting that thermal eliminations may be very important in determining the appearance of the mass spectrum. Decreasing the electron voltage has the same effect and could be caused by changes in the competition between direct ionization of the chlorides and thermal elimination to camphene (XIV).

(v) The base peak in the mass spectrum of isobornyl chloride (VII) has *m/e* 136



Scheme 3

and there is a metastable ion at m/e 107·8 which could be generated in the decomposition of the molecular ion at m/e 172 to the base peak at m/e 136.

In Scheme 4 we show the ion at m/e 136 decomposing to the ion at m/e 121 and then losing : CH_2; clearly direct decomposition of the ion at m/e 136 to that at m/e 107 with loss of C_2H_5 is an attractive alternative.

We can compare these reactions in the ion source with those in the gas phase by using the relative intensities of the ions $[M - HCl]^+/[M]^+$ as a measure of the relative rates of loss of HCl from isobornyl and bornyl chloride (VI) and (VII). The relative rate in the mass spectrometer is *ca.* 4, while in the gas phase elimination it is 10 at 350° and the relative reactivities should decrease with increasing temperature.[2a] We can also compare our values for the relative rates of loss of Cl· for isobornyl and bornyl chloride, on the assumption that they are given by the relative values of $[M - Cl]^+/[M]^+$. For isobornyl and bornyl chloride the relative rate is 2, as compared with 10 for *exo*- and *endo*-norbornyl bromide.[5] For solvolyses the relative reactivity of the *exo*-isomer is very much greater for isobornyl-bornyl chlorides as compared with the norbornyl compounds.[15]

These differences in relative rates point out the weakness of these analogies between

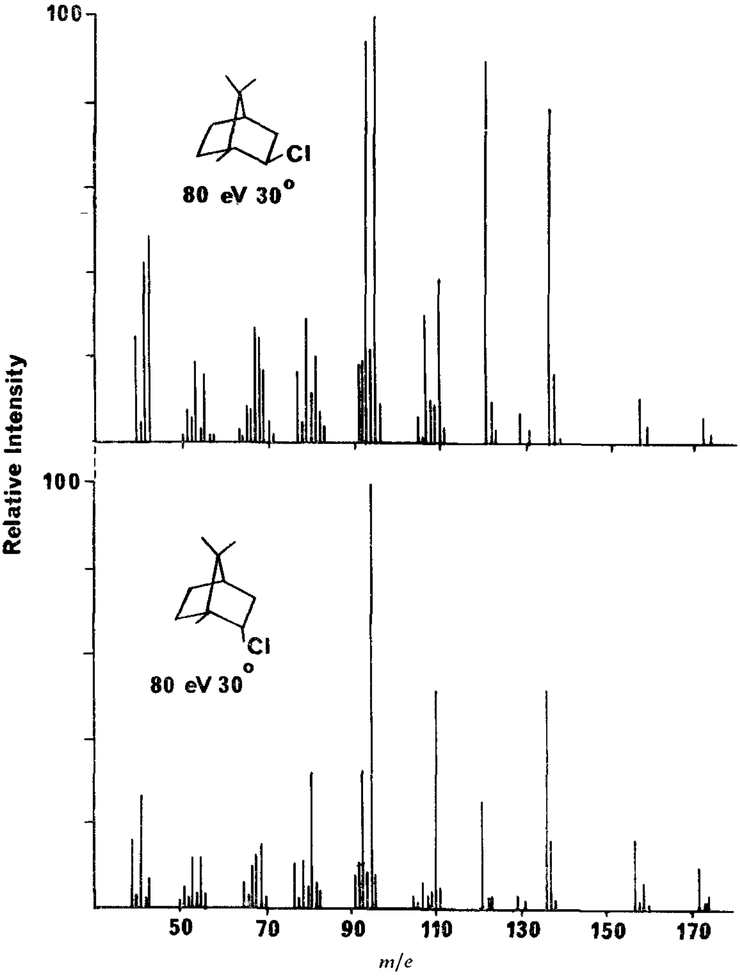


FIG. 3. Mass spectra of bornyl and isobornyl chloride (VI) and (VIII).

relative rates in an ion source and in thermal gas or solution phase reactions. These weaknesses may stem from the inherent errors in the determination of relative rates in an ion source[7] and from neglect of thermal decompositions which may precede ionization.

α- and β-Fenchyl chloride, (IX) *and* (X), *and α-Fenchene hydrochloride* (XI)

(i) The major peaks are at *m/e* 172 (174), 157 (159), 137, 136, 123, 121, 93, 81, 80, 79. The underlined peaks are also formed in the mass spectrum of α-fenchene (XV). The results for these chlorides and α-fenchene are given in Table 5* and Figs. 5 and 6. Reactions by which these ions could be formed are shown in Scheme 5.

(ii) The spectra of α-fenchene hydrochloride (XI) and β-fenchyl chloride (X) are similar except that those ions which could be formed by a thermal elimination to

---

* See Appendix.

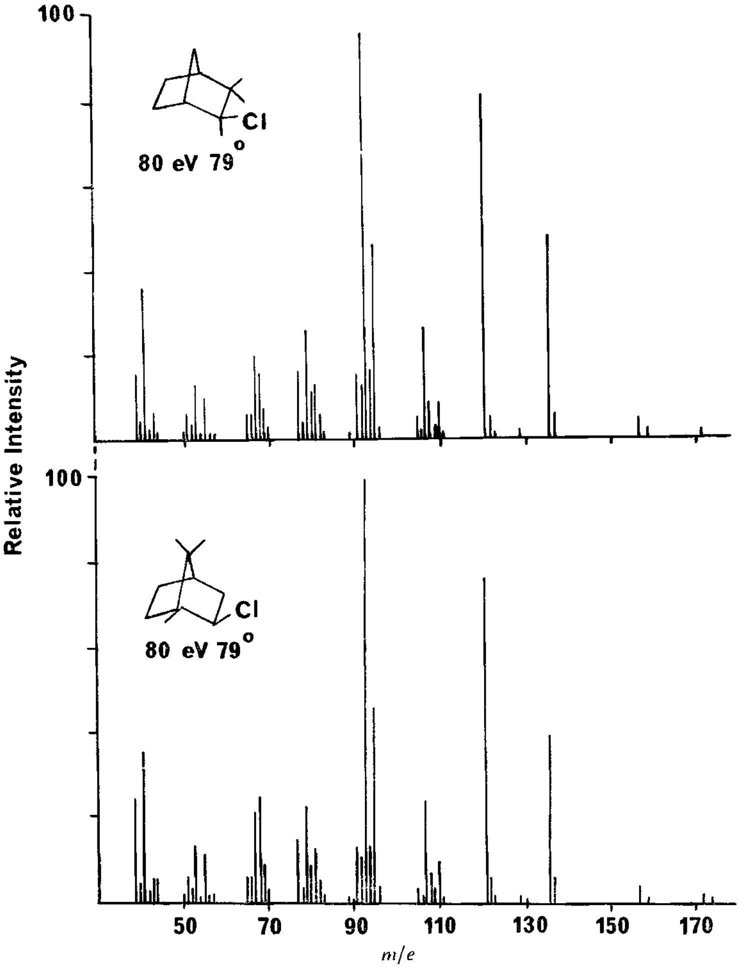


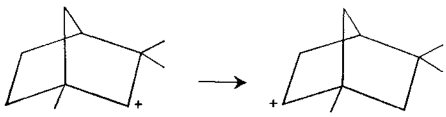
FIG. 4. Mass spectra of isobornyl chloride and camphene hydrochloride (VII) and (VIII).

α-fenchene (XV), followed by its ionization, are much larger with α-fenchene hydrochloride (Figs. 5 and 6).

(iii) The mass spectra of α- and β-fenchyl chlorides (IX) and (X) are very similar, except for the ion at *m/e* 157, unlike the situation for bornyl and isobornyl chloride (VI) and (VII).

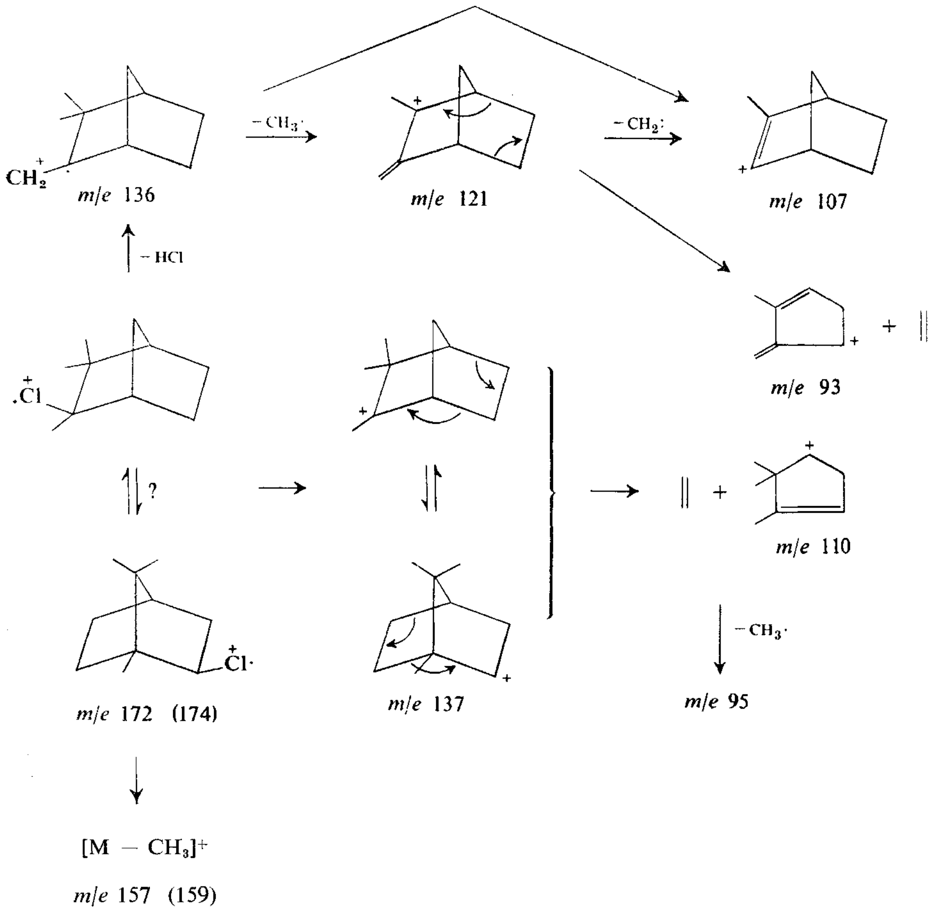
(iv) With decrease of the electron voltage from 80 eV to 16 eV the mass spectra of α-fenchene (XV) and α-fenchene hydrochloride (XI) became very similar suggesting that thermal elimination now gives considerable amounts of α-fenchene which is then ionized.

The presence of the peak at *m/e* 81 in the spectra of these fenchyl chlorides suggests that the fenchyl cation (c) readily undergoes a hydride shift to generate the isofenchyl cation (*d*). This migration is very common in carbonium ion reactions of bicyclic compounds.[4]



(*c*) (*d*)

One important feature of these spectra is that the ion *m*/*e* 157 [M — 15] is formed by the ionization of both fenchene hydrochloride (XI) and β-fenchyl chloride (X), where the Wagner-Meerwein rearrangements can readily occur, but not with the *endo*-secondary compound α-fenchyl chloride (IX).



Scheme 4

The peak at *m*/*e* 123 is moderately important in some of these spectra and could be formed by loss of : CH_2 from *m*/*e* 137. This reaction, like the formation of the ion of *m*/*e* 79 from *m*/*e* 93, could involve transfer of hydrogen from a methyl group to the residual ion, or elimination of a carbene at C_3, C_5 or C_6. Another possibility is that the molecular ion at *m*/*e* 172 decomposes directly to the ion of *m*/*e* 123, because in the mass spectrum of α-fenchene hydrochloride (XI) we observe a small metastable of

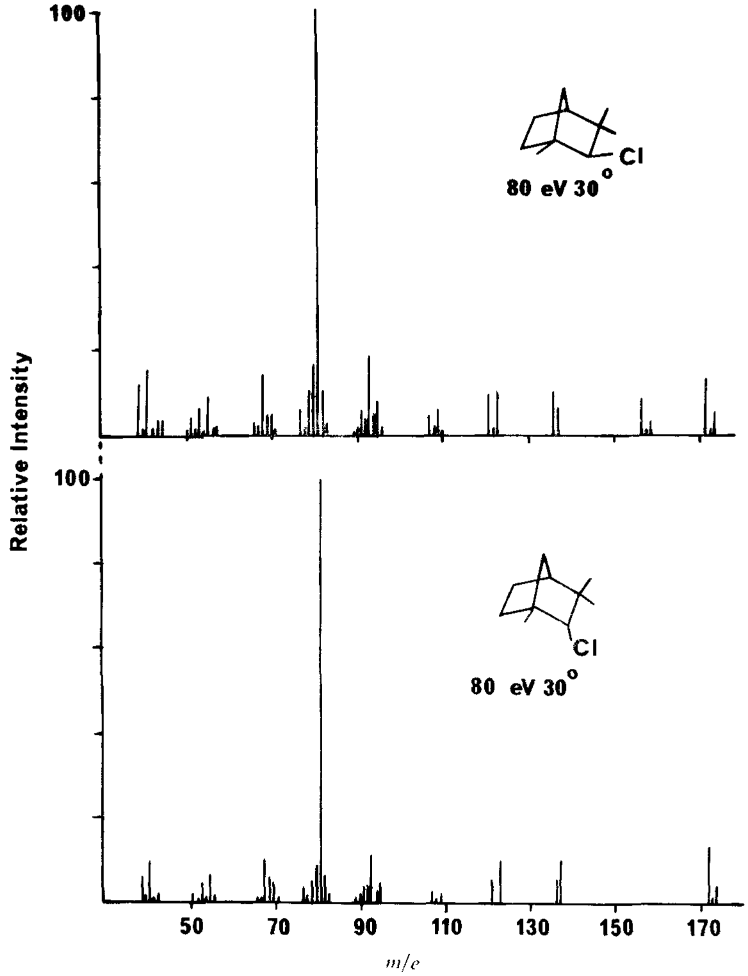


FIG. 5. Mass spectra of α- and β-fenchyl chloride (IX) and (X).

m/e ~89, and the transition *m/e* 172 → *m/e* 123 could give a metastable ion at *m/e* 88·3. Somewhat similarly the ion at *m/e* 79 could be formed by loss of a C_3H_7 residue from the ion at *m/e* 136 rather than by the stepwise process shown.

exo-Isofenchyl chloride (XII) *and 2,5,5-trimethyl-exo-2-norbornyl chloride* (XIII)

(i) There are major peaks at *m/e* 157 (159), 137, 136, 121, 109, 95 to 93, 81 to 79, (Table 6* and Fig. 7). Reactions by which these ions could be formed are shown in Scheme 6.

(ii) The mass spectra of these Wagner-Meerwein related isomers are very similar.

(iii) Lowering the electron voltage to 16 eV decreases the extent of fragmentation for both isomers.

The unusual feature about the mass spectra of these isomers is that the base peak is that of the [M — 15] ion formed by loss of a methyl group. We assume that it is the 2-methyl group which is lost, but isotopic labeling is needed to test this assumption.

---

* See Appendix.

As an additional feature of the spectra is the ion at *m/e* 79 which is formed from the tertiary chloride (XIII), but is relatively unimportant with the secondary chloride. The peak at *m/e* 79 is present in the mass spectra of both camphene and α-fenchene and some of the other chlorides but isotopic labeling is necessary to determine how it is formed. Loss of hydrogen atoms from the ions *m/e* 81 and 80 is a possibility, but thermal elimination of HCl from (XIII) would give an isofenchene whose mass spectra would include a peak at *m/e* 79.

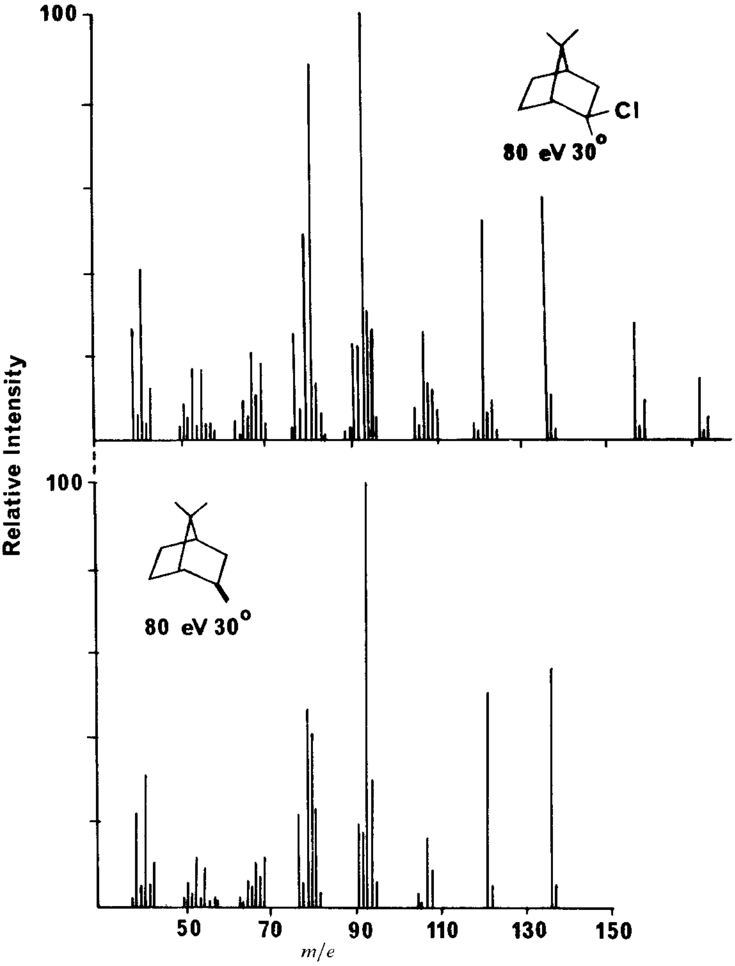
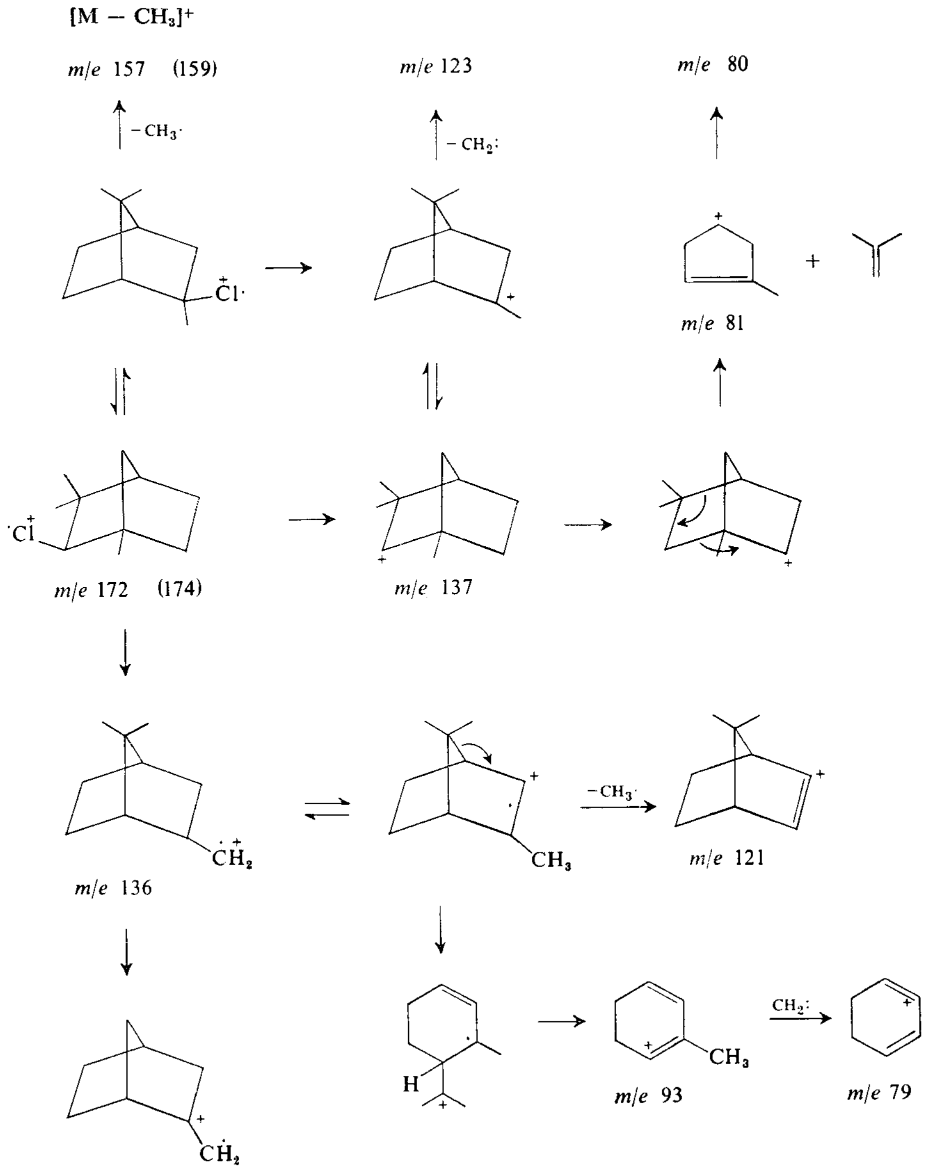


FIG. 6. Mass spectra of α-fenchene hydrochloride and α-fenchene (XI) and (XV).

(iv) The carbonium ions derived from β-fenchyl chloride (X) and *exo*-isofenchyl chloride (XII) are interconvertible by 2,6-hydride shifts and the mass spectra of these two compounds show considerable similarities (Figs. 5 and 7), except that the peaks at *m/e* 157 and 159 due to methyl loss are very large for isofenchyl chloride, but much smaller for β-fenchyl chloride (X) and α-fenchene hydrochloride (XI) which are interconvertible by Wagner-Meerwein rearrangements.



SCHEME 5

The peaks at *m/e* 157 and 159 were *not* detected in the mass spectra of the *endo*-isomer α-fenchyl chloride (IX).

DISCUSSION

In all the examples examined we obtain very similar mass spectra for Wagner-Meerwein related isomers and some of the differences can be accounted for by assuming that the more reactive tertiary isomer undergoes some thermal decomposition to the olefin before ionization occurs and that part of its mass spectrum is really that of the olefin and in accord with this supposition the differences are greater the higher the

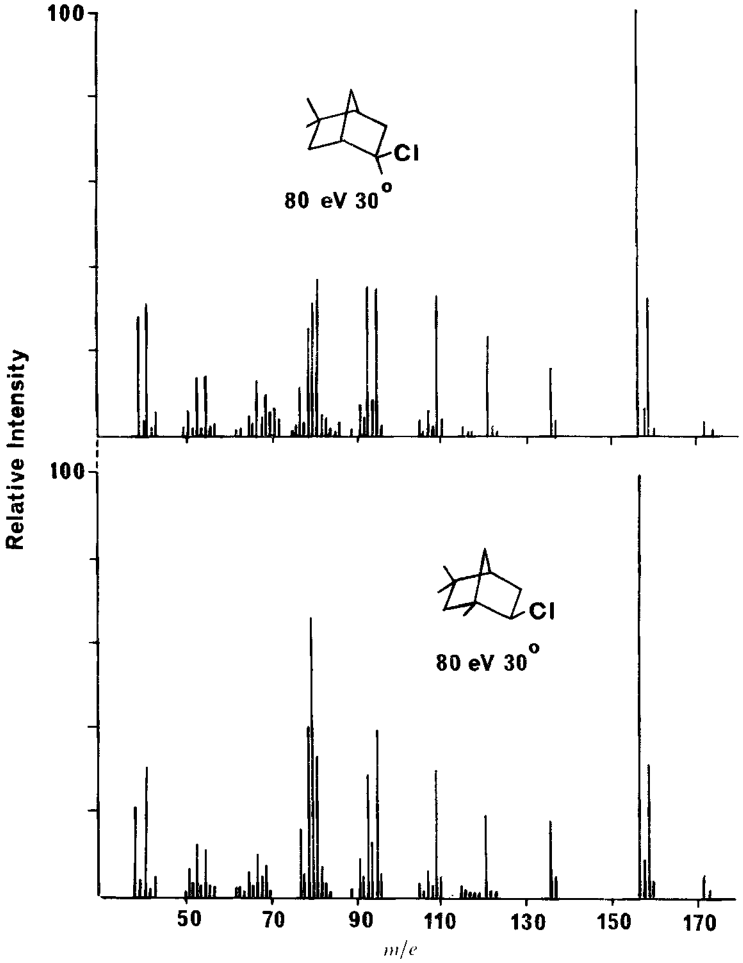
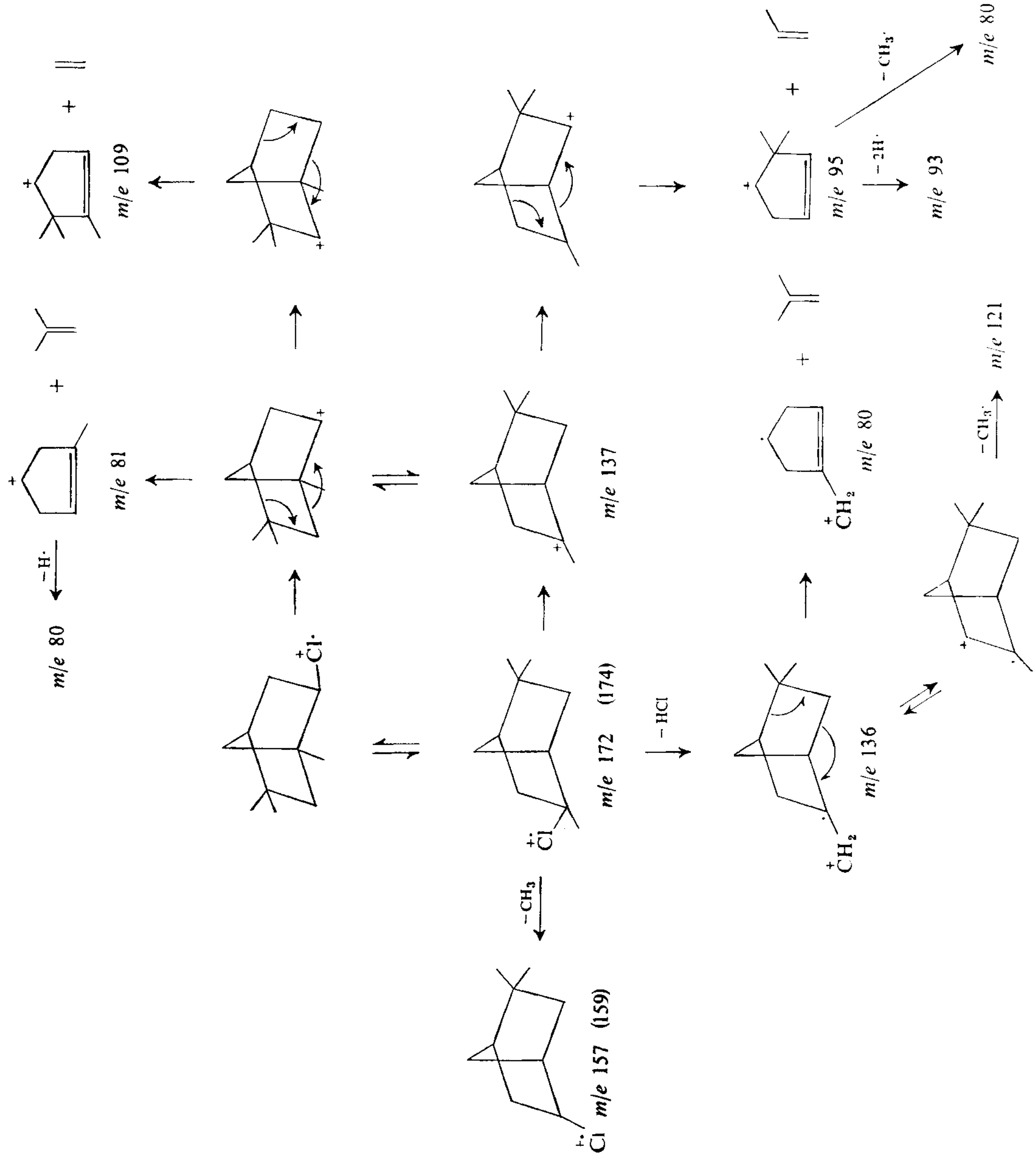


FIG. 7. Mass spectra of *exo*-isofenchyl and 2,5,5-trimethyl-*exo*-norbornyl chloride (XII) and (XIII).

source temperature. These observations suggest that the mass spectra of thermally labile materials may be very dependent upon the source temperature and geometry. Our results do not fit the supposition that the rates of solvolysis can be related to the rate of carbonium ion formation in the ion source for a series of structurally related norbornyl halides, although this fact may be related to the problem of determining the relative rates of formation of ions from measurements of ion intensities.[6]

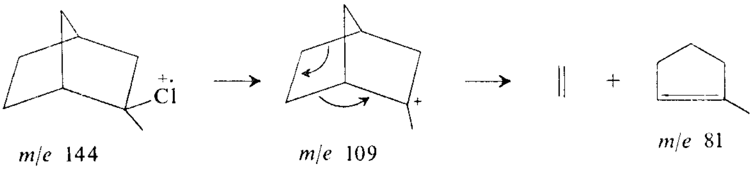
One can, however, draw analogies between the similarity of solvolytic products from norbornyl halides and related compounds which can generate a common carbonium ion, or a series of equilibrating ions and the similarity of the mass spectrum. The lifetime of an ion in the ion source of a mass spectrometer is long by comparison with the lifetime of an organic cation in solution.[16] Howe and Williams quote 1 to 5 μsec for residence in the ion source and 15 μsec for travel from the source to collector slit for an ion of m/e 100 in the AEI MS-9 spectrometer at 8 kV accelerating voltage.[7]


m/e 80
−H·
m/e 81
m/e 109
+Cl·
m/e 137
+:Cl
m/e 172 (174)
−CH₃
−HCl
+:Cl
m/e 157 (159)
+CH₂
m/e 136
+CH₂
m/e 80
m/e 95
−2H·
m/e 93
−CH₃·
m/e 80
−CH₃·
m/e 121

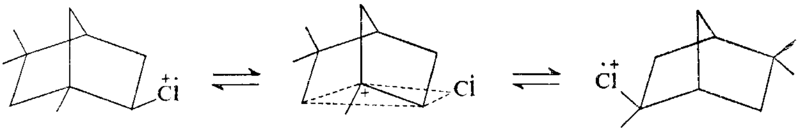
SCHEME 6

There is is therefore ample time for a variety of structural rearrangements to occur, particularly in view of the high energy of the ions.

It seems probable that equilibration of these ions is completed before they reach the magnetic analyzer. For example 1- and 2-methyl-*exo*-2-norbornyl chloride both give metastable peaks of equal intensity at *m/e* 44·9 and these peaks would be formed as a result of a $[M]^+ \rightarrow \text{base}^+$ fragmentation involving loss of a chlorine atom followed by the retro-Diels-Alder decomposition:



In the fragmentation schemes we have left open the question as to whether there is a rapid equilibration of the parent radical ions formed from isomeric starting materials, or whether equilibration occurs after formation of a carbonium ion by loss of a chlorine atom or a methyl radical. For most of the compounds which we examined it is reasonable to assume that equilibration occurs after loss of Cl. or CH_3., but with *exo*-isofenchyl and 2,5,5-trimethyl-*exo*-2-norbornyl chlorides (XII) and (XIII) the amounts of methyl loss, as judged by the size of the [M − 15] peaks at *m/e* 157, are very similar. It would seem improbable that two distinct parent ions, one derived from a secondary and the other from a tertiary chloride, would lose a methyl radical at the same rate and this result provides support for the assumption that the parent radical ions undergo a Wagner-Meerwein type of rearrangement.*



In addition we note the possibility that in some cases the molecule may fragment directly to a carbonium ion, rather than undergo ionization followed by loss of a chlorine atom,[13] although for the most part our results can be explained without postulating these two paths to the carbonium ion.

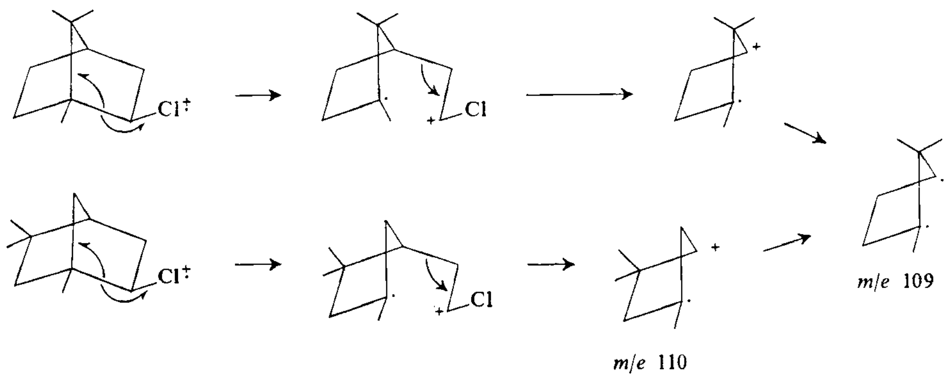
In many of our experiments, particularly with low electron voltages, the ion currents were small and metastable ions were not detected, because of their low abundance.

Another series of reactions could generate the ion of *m/e* 109 from some of the trimethylnorbornyl chlorides.

These reactions do not seem to be of major importance because the ion at *m/e* 110 is not a strong contributor to many of the mass spectra. A similar fragmentation, however, probably leads to the ion of *m/e* 68 in the mass spectrum of *exo*-2-norbornyl chloride (Scheme 1).

---

* This argument has been phrased in terms of loss of methyl from C_1 of C_2, but it should also be valid if one of the *gem*-methyl groups was lost.



Our results show that fragmentation patterns are unlikely to help in structural investigations of methyl substituted compounds which are related by Wagner-Meerwein rearrangements and strengthen the conclusion of Dimmel and Wolinsky that it is difficult to distinguish between *exo*- and *endo*-isomers mass spectrometrically.[10]

We can only guess at the structures and charge distributions of many of the ions which are formed in the ion source, in particular with the di- and trimethyl substituted compounds, because hydride and methyl shifts occur readily in the cations formed in the ion source and in solvolytic reactions.[1,4,10,12]

Many of the ions which are formed by ionization of these norbornyl chlorides are also generated by ionization of the alcohols, but the pattern is affected by the ease of generation of the carbonium ion from the chloride, as compared with the greater possibilities for the initial fragmentation of the parent ion of the alcohols.[1,10]

Dimmel and Wolinsky noted that a large peak at *m/e* 41 appears to be characteristic of compounds which contain *gem*-dimethyl groups.[10] Our evidence supports this conclusion, although the peak at *m/e* 41 decreases sharply if the ionizing voltage is decreased to 16 eV, suggesting that it would be unwise to use low electron voltages in determinations of the structure of monoterpenoids by mass spectrometry.

EXPERIMENTAL

Materials. The chlorides were prepared from precursors, olefins or alcohols, which were commercial materials or had been prepared by standard methods and which were purified by preparative g.l.c. All the secondary chlorides except isobornyl chlorides were themselves purified by preparative g.l.c.

As evidence of structure and purity the rates of methanolysis of each of these chlorides were also measured conductimetrically for the more reactive compounds and titrimetrically for the less. Good first order rate constants were obtained for at least 3 half-lives, and their values fitted nicely with the known rate constants for the methanolyses of bornyl and isobornyl chloride and camphene hydrochloride.[15] *exo*-2-Norbornyl chloride (I) was prepared by the addition of HCl at −78° to norbornene in pentane.[17] Analysis of the chloride by g.l.c. using Carbowax 4000, showed that it contained $<1\%$ impurity.

2-Methyl-*exo*-2-norbornyl chloride (III) was prepared from 2-methyl-*endo*-2-norbornanol (5·55 g) by converting it into the alkoxide with potassium metal (1·72 g) in stirred refluxing hexane (500 ml) under N_2, removing excess potassium and slowly adding thionyl chloride (5·11 g) under N_2. When SO_2 evolution had stopped the solid KCl (3·2 g) was filtered off and the hexane pumped off. The oil was distilled at 32° and 0·2 mm to give 2-methyl-*exo*-2-norbornyl chloride, m.p. 32°. The methanolysis at 25° gave a linear first order rate plot for 7 half-lives, with $k_\psi = 4{\cdot}70 \times 10^{-4}$ sec^{-1}.

The compound was also made from the *endo*-tertiary alcohol with conc. HCl in ether[18,19] but this material contained some secondary chloride (II) as shown by the i.r. peak at 895 cm^{-1}, and the curvature of the first order rate plot after 3 half-lives. Another sample prepared by treating the olefin with HCl in dry ether also contained small amounts of the secondary chloride (II). 1-Methyl-*exo*-2-norbornyl chloride (II) was prepared by stirring 2-methyl-*endo*-2-norbornyl with conc. HCl in ether for 4 hrs. The product was isolated as an oil by standard methods, and had b.p. 40° at 0·2 mm. The first order rate constant of solvolysis in methanol at 25° was $6{\cdot}8 \times 10^{-7}$ sec^{-1} (calc. from runs at higher temperatures).

Apoisobornyl chloride (V) and *exo*-camphenilyl chloride (IV) were prepared from *endo*-camphenilol and PCl_5 by the method of Komppa and Nyman.[20] The product contained three chlorides (V), 62%; (IV) 32%; and 5,5-dimethyl-*exo*-2-norbornyl chloride 6%, which were separated by g.l.c. on Carbowax 4000. The preparations of bornyl and isobornyl chloride (VI) and (VII) and camphene hydrochloride (VIII) have been described.[15]

α-Fenchene hydrochloride (XI) was prepared from α-fenchene (XV) and ethereal HCl and from α-fenchol (10 g) in pentane (100 ml) and PCl_5 at 0°. The infrared spectrum of both products were identical and they had an n.m.r. spectrum in agreement with that reported by Brown and Liu.[21] The first order rate constant in methanol at 25·0° was 6×10^{-3} sec^{-1}, the reported value in ethanol is $8{\cdot}5 \times 10^{-4}$ sec^{-1} at 25°.[21]

α-Fenchyl chloride (IX) was obtained with bornyl chloride (VI) by treating β-pinene with dry HCl in ether for 6 hrs. at 30°. The product contained (VI) 75% and (IX) 25% which were separated by g.l.c. using a Carbowax 4000 column at 120°.

β-Fenchyl chloride (X) and isofenchyl chloride (XII) were prepared by rearranging α-fenchene hydrochloride (24 g) in conc. HCl (300 ml) and ether (50 ml) for 2 hrs. at 30° with stirring. Work up of this material with extraction into pentane and washing with water and aq. $NaHCO_3$ and drying over K_2CO_3 gave an oil which contained β-fenchyl (72%) and isofenchyl chloride (21%) and an unidentified compound (7%) which were separated by g.l.c. using an SE 30 on Chromosorb G column at 60°. The amount of isofenchyl chloride could be increased by using longer reaction times.

2,5,5-Trimethyl-*exo*-2-norbornyl chloride (XIII), was prepared from *endo*-isofenchol (5 g) and PCl_5 (9·5 g) in pentane (50 ml) at 0° with stirring for 3 hrs. The reaction mixture was washed with aq. $NaHCO_3$ and the pentane layer dried over K_2CO_3, and the pentane distilled off. The oil (5 g) had no absorption in the infrared corresponding to an alcohol or olefin, but its n.m.r. spectrum, and its first order rate constant in methanol, $5{\cdot}43 \times 10^{-4}$ sec^{-1} at 25·0°, were consistent with it being a tertiary chloride. When it was treated with HCl in ether it rearranged to β-fenchyl chloride (10%) and *exo*-isofenchyl chloride (85%) and an unidentified chloride (5%).

Mass spectra. The chlorides are sufficiently volatile to be introduced into the ion source using a cold inlet system and the ion source temperature could be kept at ambient temperature (28° ± 3°) by circulating cold water through the ion source. Despite these precautions it seems that thermal decomposition to camphene or α-fenchene occurred with some of the tertiary chlorides, probably because the area around the filament is hotter than the rest of the ion source. The temperatures in the ion source could be measured to ±3°. A rhenium filament was used in all the experiments and the accelerating voltage was 8 kV. The pressure in the analyzer was *ca.* 3×10^{-7} mm, and in the ion source *ca.* 2×10^{-6} mm (measured with an ionization gauge adjacent to the ion source).

Acknowledgements—Support of this work by the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged. We thank Mr T. Stanfield for carrying out some of the mass spectral analyses, and we are happy to acknowledge helpful discussions with Professor A. Maccoll.

APPENDIX

TABLE 2. PRINCIPAL PEAKS IN MASS SPECTRA OF 1- AND 2-METHYL-*exo*-2-NORBORNYL CHLORIDE

Compound	Electron voltage	Temp.	*m/e*	39	41	53	55	66	67	68	77	79	80	81	82	93	108	109	144	146
1-Me-(II)	16	30°		—	—	—	—	10	9	6	—	—	6	100	10	—	13	7	15	5
2-Me-(III)	16	30°		—	—	—	—	8	13	12	—	—	6	100	12	—	14	8	24	8
1-Me-(II)	80	71°		13	12	8	6	13	33	13	5	14	13	100	13	8	7	6	8	3
2-Me-(III)	80	71°		12	11	8	6	15	42	24	5	13	10	100	9	7	7	8	8	3
1-Me-(II)	12	71°		—	—	—	—	14	—	—	—	—	13	100	9	5	12	9	17	6
2-Me-(III)	12	71°		—	—	—	—	25	13	17	—	6	17	100	10	5	15	13	22	7

TABLE 3. PRINCIPAL PEAKS IN MASS SPECTRA OF *exo*-CAMPHENILYL CHLORIDE (IV) AND APOISOBORNYL CHLORIDE (V)*

Compound	*m/e*	57	67	69	78	79	80	81	82	83	100	102	107	109	122	123	158	160
exo-camphenilyl (IV)		—	14	10	20	12	15	34	14	16	—	—	—	100	35	25	45	21
apoisobornyl (V)		10	19	11	15	11	15	15	—	—	16	11	10	100	34	25	80	23

* At 16 eV and 30°; peaks less than 10% of base are omitted.

TABLE 4. PRINCIPAL PEAKS IN THE MASS SPECTRA OF BORNYL CHLORIDE (VI), ISOBORNYL CHLORIDE (VII), AND CAMPHENE (XIV)*

Compound	*m/e*	39	41	43	53	55	66	67	68	69	77	78	79	80	81	82	91	92
Bornyl (VI)		—	—	—	—	—	—	—	5	—	—	—	—	6	15	5	—	13
Isobornyl (VII)		—	—	—	—	—	—	—	—	—	—	5	5	5	6	—	—	16
Camphene (XIV)		—	—	—	—	—	—	—	—	—	—	—	—	7	—	—	—	13
Camphene (XIV)†		13	18	5	7	6	5	13	10	5	11	—	20	10	6	—	14	12
Compound	*m/e*	93	94	95	96	107	108	110	111	121	122	136	137	157	159	172	174	
Bornyl (VI)		24	7	55	5	5	—	77	8	21	5	100	28	24	8	20	4	
Isobornyl (VII)		47	14	45	—	22	10	26	—	79	6	100	12	9	—	3	—	
Camphene (XIV)		50	11	10	—	16	5	—	—	85	7	100	9					
Camphene (XIV)†		100	13	14	—	22	6	—	—	77	6	38	5					

* At 16 eV and 30° unless specified; † at 80 eV.

TABLE 5. PRINCIPAL PEAKS IN MASS SPECTRA OF α- AND β-FENCHYL CHLORIDE, (IX) AND (X), α-FENCHENE HYDROCHLORIDE (XI) AND α-FENCHENE (XV)*

Compound	*m/e*	68	69	79	80	81	82	92	93	94	95	107	108	109	110	121	122	123	136	137	157	159	172	174
α-fenchyl (IX)		—	—	—	14	100	9	8	16	—	—	—	—	—	—	12	—	27	28	10	—	—	24	8
β-fenchyl (X)		—	—	—	23	100	15	6	17	—	6	—	—	6	—	5	—	16	40	10	19	6	32	10
α-fenchene hydro (XV)		5	7	15	50	73	12	19	73	27	18	21	12	12	9	50	5	10	100	16	36	12	17	5
α-fenchene (XV)		—	—	10	37	14	—	25	75	30	5	25	11	—	—	50	—	—	100	9				

* At 16 eV and 30°.

TABLE 6. PRINCIPAL PEAKS IN MASS SPECTRA OF EXO-ISOFENCHYL CHLORIDE (XII) AND 2,5,5-TRIMETHYL-EXO-2-NORBORNYL CHLORIDE (XIII)*

Compound	*m/e*	79	80	81	93	94	95	96	109	110	121	136	137	157	158	159	172	174
exo-isofenchyl (XII)		—	42	10	—	9	8	6	20	—	8	36	5	100	9	32	5	2
2,5,5-trimethyl-exo-2-(XIII)		20	9	5	14	8	7	—	21	5	18	40	5	100	7	31	6	2

* At 16 eV and 30°.

REFERENCES

1. A. Maccoll, 'Some Aspects of Carbonium Ion Chemistry, in R. I. Reed (Ed.) *Mass Spectrometry*, Academic Press, New York, 1965.
2. (a) A. Maccoll, in *Theoretical Organic Chemistry*, Kekulé Symposium, London, 1957, p. 230; (b) A. Maccoll, in *The Transition State*, Chem. Soc., London, Spec. Publ. No. 16, 1962.
3. S. W. Benson and G. R. Maugen, *J. Am. Chem. Soc.* **87**, 4036 (1965); M. E. O'Neal and S. W. Benson, *J. Phys. Chem.* **71**, 2903 (1967) and references cited.
4. (a) P. D. Bartlett, *Non Classical Ions*, Benjamin, New York, 1965, and references cited. (b) J. Berson, in P. de Mayo (Ed.) *Molecular Rearrangements*, Wiley, New York, 1963 Chap. III.
5. D. C. DeJongh and S. R. Shrader, *J. Am. Chem. Soc.* **88**, 3881 (1966).
6. M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.* **88**, 529 (1966).
7. I. Howe and D. H. Williams, *Chem. Commun.* 270 (1968).
8. R. Rhyage and E. von Sydow, *Acta Chem. Scand.* **17**, 2025 (1963).
9. D. S. Weinberg and C. Djerassi, *J. Org. Chem.* **31**, 115 (1966).
10. D. R. Dimmel and J. Wolinsky, *J. Org. Chem.* **32**, 410, 2735 (1967), and references cited.
11. W. C. Steele, B. H. Jennings, G. L. Botyos and G. O. Dudek, *J. Org. Chem.* **30**, 3886 (1965).
12. M. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco, 1967, p. 440.
13. K. Biemann, *Mass Spectrometry*, McGraw-Hill, New York, 1962, p. 434.
14. K. Biemann, *Mass Spectrometry*, McGraw-Hill, New York, 1962, Chap. III.
15. P. Beltramé, C. A. Bunton, A. Dunlop and D. Whittaker, *J. Chem. Soc.* 658 (1964).
16. B. M. Benjamin, H. J. Schaeffer and C. J. Collins, *J. Amer. Chem. Soc.* **79**, 6160 (1957); S. Winstein, *J. Am. Chem. Soc.* **87**, 381 (1965); G. Solladié, M. Muskatirovic and H. S. Mosher, *Chem. Commun.* 809 (1968).
17. J. D. Roberts, E. R. Trumbull, W. Bennett and R. Armstrong, *J. Am. Chem. Soc.* **72**, 3116 (1950).
18. N. J. Toivonen, E. Siltamen and K. Ojala, *Ann. Acad. Sci. Fennicae*, Ser A II, No. 64 (1955).
19. S. Beckmann, R. Schaker and R. Bamberger, *Chem. Ber.* **87**, 997 (1954).
20. G. Kommpa and G. A. Nyman, *Chem. Ber.* **69**, 1813 (1936).
21. H. C. Brown and K. T. Liu, *J. Am. Chem. Soc.* **89**, 466 (1967).