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PENTACYCLODECANE CHEMISTRY—III

FRAGMENTATION PATTERNS OF PENTACYCLODECANE DERIVATIVES ON ELECTRON IMPACT[1]

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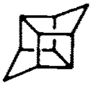
Abstract—The fragmentation patterns on electron impact of 10 derivatives of pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$] decane and 5 derivatives of pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane were investigated. The predominant mode of fragmentation was cleavage of the pentacyclodecane nuclei in half except for the ketone derivatives. Other major fragmentation routes are discussed.

CONSIDERABLE interest has been shown recently in the synthesis and chemistry of derivatives of pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane (I) and pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane (XI).[1,2] The purpose of this paper is to present data on the major fragmentation pathways of some of these compounds when bombarded by 75 eV. electrons in the gas phase in a mass spectrometer.



I

XI

EXPERIMENTAL

Mass Spectra. The mass spectra of all compounds except the hydrocarbon I were obtained with a magnetically scanning 90° sector spectrometer with an electron ionizing voltage of 75 eV. The ion source temp was ~250°. The samples were vaporized from a 5, 1, or 0·5 l. glass reservoir through a molecular leak into the ion-source. The inlet temp was 200° for compounds IX and XI–XV; 250° for II–VI, VIII and X; and 270° for VII. The mass spectrum of I was obtained at room temp in a Bendix Time-of-Flight mass spectrometer.[1] Evidence that the compounds were thermally stable under the experimental conditions was based on the high m.ps (>240°) of all the chlorinated derivatives except IX, and the established thermal stability of I at 300°,[1] XI at 450°,[3] XII at 250°, and XIII at 425°.[4] The relative ion peak-intensities in the mass spectra of IX were the same when the spectrometer inlet temps were 200° and 250°. Compound XI gave identical spectra at 150° and 200°. The spectra of XII were the same at 100° and 200°.

Compounds. References to the syntheses and structure proofs of all the compounds except the alcohol XII are given in Table 1.

Pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]*decan*-4-ol (XII). A solution of the ketone XIII[4] (14·6 g, 0·100 mole) in 100 ml dry ether was added dropwise over a period of 1·3 hr to a stirred LAH slurry (2·0 g, 0·05

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[1] Part II, Wendell. L. Dilling, H. P. Braendlin and E. T. McBee, *Tetrahedron*, 23, 1211 (1967). Part I, E. T. McBee, Wendell. L. Dilling and H. P. Braendlin, *J. Org. Chem.* 27, 2704 (1962).

[2] See also references cited in Ref. 1, Part II. Alternate names, used in *Chem. Abstr.*, for I and XI are octahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalene and octahydro-1,2,4-metheno-3H-cyclobuta[cd]pentalene respectively.

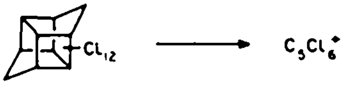
[3] G. O. Schenck and R. Steinmetz, *Chem. Ber.* 96, 520 (1963).

[4] R. C. Cookson, J. Hudec and R. O. Williams, *Tetrahedron Letters*, No. 22, 29 (1960).

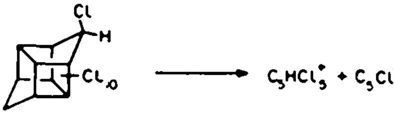
mole) in 100 ml ether under N_2 at room temp. After stirring for *ca.* 20 hr the mixture was hydrolysed with 10 ml of conc. H_2SO_4 in 200 ml. water. The ether layer was separated and combined with two ether extracts of the aqueous layer. After washing with water and drying, the solvent was evaporated leaving 8·4 g (57%) of nearly pure XII. Recrystallization from heptane and sublimation at 100° (40 mm) gave white crystalline XII, m.p. 173–174°; $\nu_{max}^{CCl_4}$ 3630, ~3330, 2970, 2860, 1450, 1078, 1045 cm^{-1}; essentially no UV absorption, $\epsilon_{210m\mu}$ ~15; NMR spectrum (CCl_4): a singlet at −4·21 ppm (from internal Me_4Si) (relative area 0·2), a singlet at −3·92 (1·8), a multiplet at −3·15 to −2·15 (7·9) for the tertiary protons, and two unsymmetrical doublets centered at −1·65 and −1·39 (2·1) (J ≈ 11·5 c/s.) for the methylene protons. Shaking the NMR sample with D_2O decreased the relative intensity of the peak at −3·92 to 0·8 and produced a peak at ~ −4·6 for HOD. The two singlets at −4·21 and −3·92 probably represent the protons on the hydroxyl-bearing carbon atom for the two stereoisomers of XII. Gas chromatographic analysis on 17 different columns showed only one peak. (Found: C, 81·07; H, 7·82. Calc. for $C_{10}H_{12}O$: C, 81·04; H, 8·16%.)

RESULTS AND DISCUSSION

The data presented in Table 1 show that in most cases the predominant mode of fragmentation was cleavage of the pentacyclodecane nucleus in half, unaccompanied by major amounts of the random fragmentation and rearrangements often observed with hydrocarbons and halocarbons. For symmetrical molecules, e.g. VII, these two fragments were the same, $C_5Cl_6^+$, while an unsymmetrical molecule such as V gave two different fragments, $C_5HCl_5^+$ and $C_5Cl_6^+$. Usually the assignment of the empirical formulas of the ions was unambiguous due to the observation of distinct Cl^{35}/Cl^{37} ratios[5] and the m/e values. Typical spectra are shown in Figs. 1–4.[6]



VII



V

In the fragmentation patterns of IV, VIII, IX and X the most abundant ions were not those formed solely from cleavage of the pentacyclodecane nucleus in half (Table 1). However, the majority of the other more abundant ions arose from this type of cleavage accompanied by the loss of a chlorine atom. For example the four most abundant fragments from VIII (Fig. 2) were $C_5Cl_4HOH^+$, $C_5Cl_3HOH^+$, $C_5Cl_6^+$ and $C_5Cl_5^+$.

Other exceptions to the predominant mode of cleavage noted above are readily explained as being due to the nature of a functional group. The acetate IX fragmented preferentially to give CH_3CO^+ (m/e 43) as the most abundant ion.[7] However, cleavage of the pentacyclodecane nucleus in half was still a major fragmentation route. The ketone XIII gave none or very little $C_5H_4O^+$ while the chlorinated ketones X and XV gave only small amounts of $C_5Cl_4O^+$. These oxygenated ions may be

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[5] J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry* p. 299. Elsevier, New York (1960).

[6] The m/e values listed in Figs. 1 and 2 are calculated using only the Cl^{35} isotope.

[7] For the mass spectra of acetates, cf. Ref. 5, p. 383.

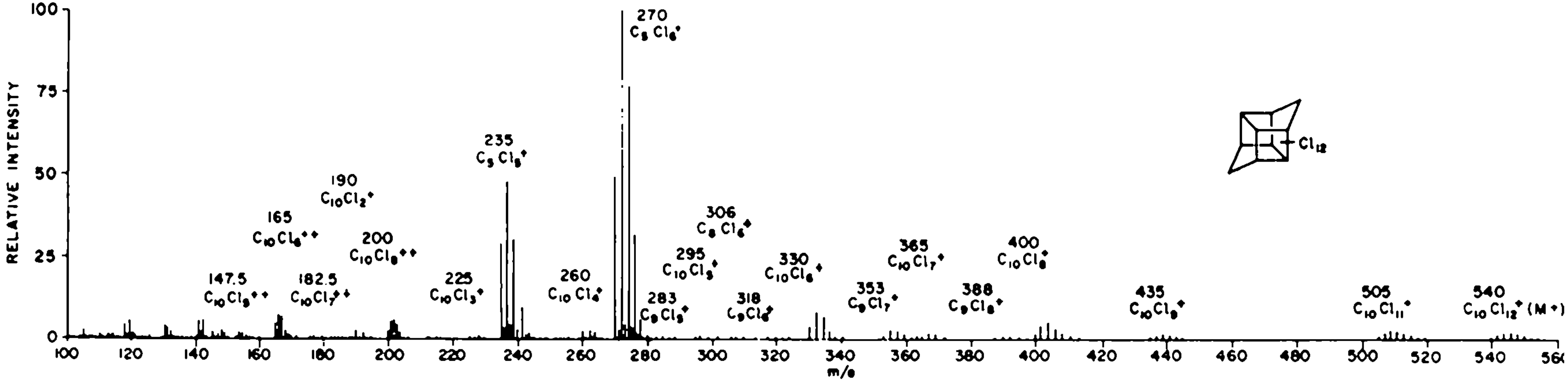


FIG. 1. Mass spectrum of dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (VII)

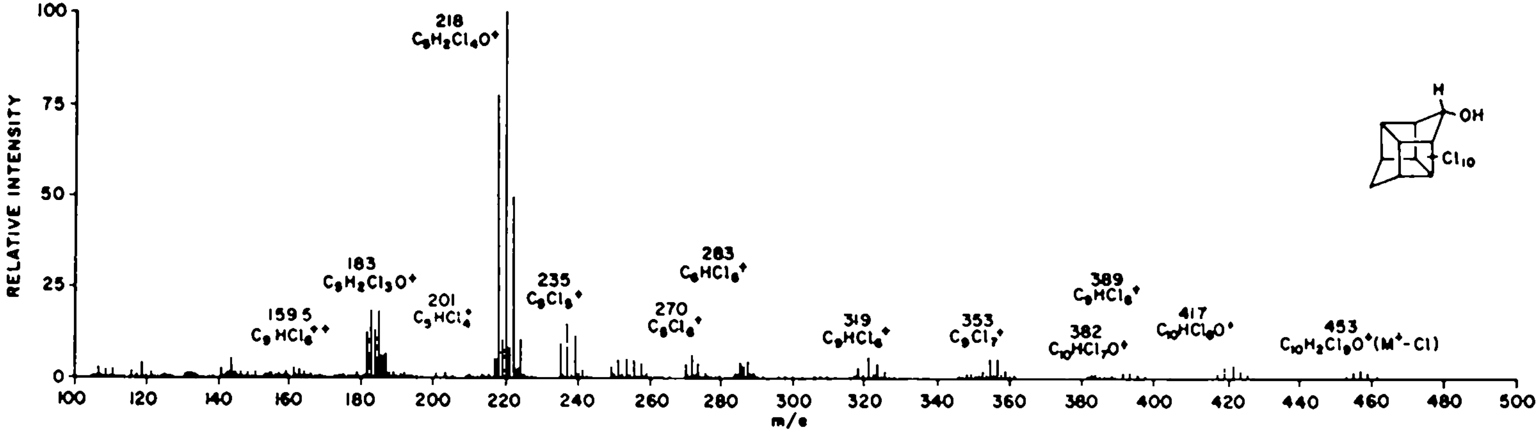
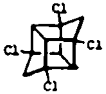
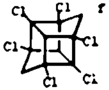
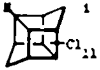
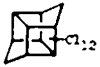
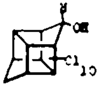
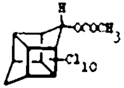
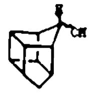
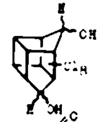


FIG. 2. Mass spectrum of 1,2,3,4,5,5,6,7,8,9-decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]-10-decanol (VIII)

TABLE 1. MAJOR FRAGMENT IONS OBTAINED BY ELECTRON IMPACT ON PENTACYCLODECANE DERIVATIVES

Compound Number	Structural Formula	Molecular Formula	Molecular Ion (M^+) or Largest m/e Fragment Observed	m/e Observed[a]	C_5 Fragments	m/e Observed[a]	% Total Ionization[b,c]	References[d]
I[e]		$C_{10}H_{12}$	$C_{10}H_{12}^+(M^+)$	132	$C_5H_6^+$	66	58·4	1
II		$C_{10}H_8Cl_4$	$C_{10}H_8Cl_3^+$	233–239	$C_5H_4Cl_2^+$	134–139	67·1	1
III	 [f]	$C_{10}H_6Cl_6$	$C_{10}H_6Cl_5^+$	301–309	$C_5H_3Cl_3^+$	168–175	56·4	1
IV		$C_{10}H_2Cl_{10}$	$C_{10}H_2Cl_9^+$	437–447[g]	$C_5H_2Cl_4^+$ $C_5Cl_6^+$	202–210 270–278	65·4 3·3[h]	1
V		$C_{10}HCl_{11}$	$C_{10}HCl_{10}^+$	471–483[g]	$C_5HCl_5^+$ $C_5Cl_6^+$	236–244 270–280	38.2 11·9	1
VI	 [i]	$C_{10}HCl_{11}$	$C_{10}HCl_{11}^+(M^+)$	506–518[g]	$C_5HCl_5^+$ $C_5Cl_6^+$	236–244 270–280	27·1 19·0	1
VII		$C_{10}Cl_{12}$	$C_{10}Cl_{12}^+(M^+)$	540–554	$C_5Cl_6^+$	270–280	44·8	8,9,10
VIII		$C_{10}H_2Cl_{10}O$	$C_{10}Cl_9HOH^+$	453–461[g]	$C_5Cl_4HOH^+$ $C_5Cl_6^+$	218–226 270–278	37·7[j] 4·0	1
IX		$C_{12}H_4Cl_{10}O_2$	$C_{10}Cl_{10}HOCOCH_3^+(M^+)$	530–538[g]	$C_5Cl_4HOCOCH_3^+$ $C_5Cl_6^+$	260–266 270–278	4·8[k] 2·1	1
X		$C_{10}Cl_{10}O$	$C_{10}Cl_{10}O^+(M^+)$	486–496	$C_5Cl_6^+$ $C_5Cl_4O^+$	270–280 216–222	35·7[l] 5·1	10,11

XI[e]		$C_{10}H_{12}$	$C_{10}H_{12}^+(M^+)$	132	$C_5H_6^+$	66	51·1	1,3
XII		$C_{10}H_{12}O$	$C_{10}H_{11}OH^+(M^+)$	148	$C_5H_6^{+}$[m] $C_5H_5OH^+$[n]	66 82	18·6 8·1	
XIII		$C_{10}H_{10}O$	$C_{10}H_{10}O^+(M^+)$	146	$C_5H_6^+$[m]	66	4·6[o]	1,4
XIV		$C_{10}H_4Cl_8O_2$	$C_{10}Cl_7(HOH)_2^+$	401–407[g]	$C_5Cl_4HOH^+$	218–226	34·7	1
XV		$C_{10}Cl_8O_2$	$C_{10}Cl_7O_2^+$	397–405	$C_5Cl_4O^+$	216–224	12·7[p]	1,11,12

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[a] The ranges of m/e values of the Cl isotopes were those actually visible in the spectra. [b] The percent total ionization was determined from the equation: % total ionization = 100 (peak intensity/$\sum$ peak intensities). The C^{13} isotope peaks for I, XI, XII and XIII were not included in the calculated percent of total ionization due to overlapping of peaks of other fragment ions. [c] Unless otherwise noted these fragment percentages represent the most intense peaks in the spectra. [d] References to synthesis and structure proof of compounds. [e] The mass spectra of I and XI were nearly identical. [f] The structure of III could also be the isomers IIIa or IIIb based on n.m.r. data.[1] IIIb is unlikely based on the mass spectrum observed. [g] Instrumental accuracy for m/e values >~450 for ions containing H was ±2 m/e units. [h] $C_5Cl_5^+$ and $C_5H_2Cl_3^+$ were more abundant than $C_5Cl_6^+$. [i] The structure of VI could also be the isomer VIa based on n.m.r data.[1] [j] $C_5Cl_4HOH^+$ was the most abundant fragment; $C_5Cl_3HOH^+$ and $C_5Cl_5^+$ were more abundant than $C_5Cl_6^+$. [k] CH_3CO^+ (44·2% of the total ionization) was the most abundant fragment; $C_{10}Cl_8HOCOCH_3^+$ and $C_5Cl_4HOCOCH_3^+$ were the second and third most abundant fragments. $C_5Cl_5^+$, $C_5Cl_4HOH^+$, and $C_5HCl_4^+$ were more abundant than $C_5Cl_6^+$. [l] C_5Cl_6 was the most abundant; $C_5Cl_5^+$ and $C_5Cl_7^+$ were more abundant than $C_5Cl_4O^+$. [m] Although unlikely, this fragment could be $C_4H_2O^+$. [n] This fragment could also be $C_6H_{10}^+$. [o] $C_9H_9^+$ (or $C_8H_5O^+$), $C_9H_{10}^+$ (or $C_8H_6O^+$), and $C_7H_7^+$ (or $C_6H_3O^+$) were more abundant than $C_5H_6^+$ (or $C_4H_2O^+$) (see Figure 4). No detectable $C_5H_4O^+$ (m/e 80) fragment was observed. [p] $C_5Cl_5O^+$ was more abundant than $C_5Cl_4O^+$.


IIIa


IIIb


VIa

[8] H. J. Prins, *Rec. trav. chim.* **65**, 455 (1946).

[9] J. S. Newcomer and E. T. McBee, *J. Amer. Chem. Soc.* **71**, 952 (1949).

[10] E. T. McBee, C. W. Roberts, J. D. Idol, Jr. and R. H. Earle, Jr., *J. Amer. Chem. Soc.* **78**, 1511 (1956).

[11] G. W. Griffin and A. K. Price, *J. Org. Chem.* **29**, 3192 (1964).

[12] P. E. Eaton, *Ph.D. Thesis*, Harvard University (1960).

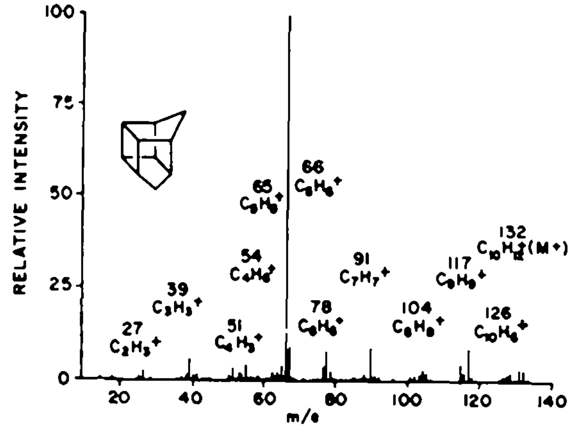

Fig. 3. Mass spectrum of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (XI)

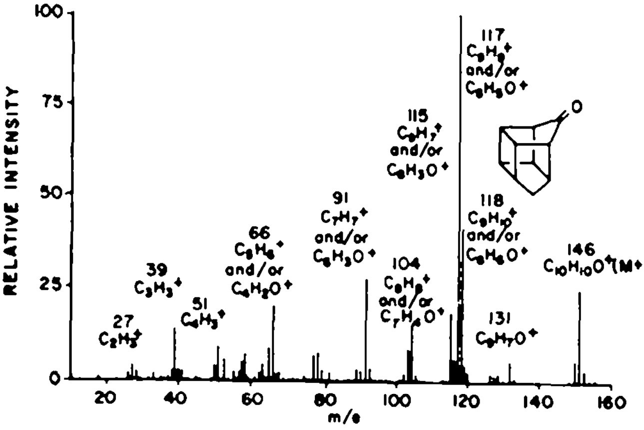

Fig. 4. Mass spectrum of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-4-one (XIII)

cyclopentadienones which arise as outlined below. The low relative abundance of these ions may reflect the known instability of these cyclopentadienones.[13]

We are suggesting that a likely fragmentation route for the ready formation of the C_5 ions is cleavage of two cyclobutane and two cyclopentane rings to give a cyclopentadiene ion and neutral molecule. The cleavage of four-membered rings into two two-carbon containing moieties on electron impact is a common occurrence[14] and would explain reaction (1). On the other hand, reaction (2) involves a slightly different mode of electron rearrangement. The relief of strain in these molecules would provide a driving force for the observed cleavage.

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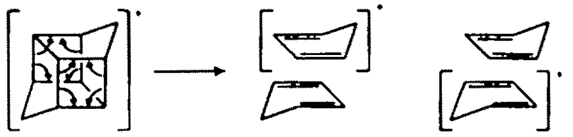
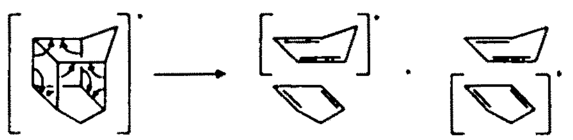
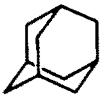
[13] For a review of cyclopentadienones cf. M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker *Chem. Revs.* **65**, 261 (1965).

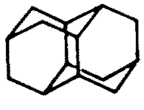
[14] [a] American Petroleum Institute Research Project 44, *Catalog of Mass Spectral Data*, National Bureau of Standards, Washington, D.C., 1949, Serial No. 416; [b] G. W. Griffin and L. I. Peterson, *J. Amer. Chem. Soc.* **84**, 3398 (1962); [c] J. J. Beereboom and M. S. von Wittenau, *J. Org. Chem.* **30**, 1231 (1965).

At this point it is of interest to contrast the major type of fragmentation found for these pentacyclodecane derivatives with the mass spectra reported for the caged compounds adamantane (XVI)[15] and congressane (XVII).[16] The latter two hydrocarbons have no easy mode of skeletal fragmentation; consequently the molecular ion peak is the most intense in the mass spectrum of each compound.[15,16] An ion of m/e 91 was the second most abundant ion formed from congressane. It was suggested that this ion resulted from a symmetrical cleavage of the molecular ion in half, followed by skeletal rearrangement and loss of three hydrogen atoms to give the tropylium ion.[16] In contrast the spectra reported in this paper show that the pentacyclodecane derivatives have a relatively low energy path for cleavage in half. As a result the molecular ions have low stabilities, and intense peaks are observed for the C_5 fragments. The fused cyclohexane derivatives XVI and XVII are unstrained, a factor also contributing to their lack of fragmentation. The mechanisms shown above for the pentacyclodecanes have not been proven, but appear reasonable from the data presented.


(1)


(2)


XVI


XVII

In the spectra of IV–VI, VIII and IX, percent total ionization measurements showed the molecular ion decomposed more often to fragments in which the positive change resided with the C_5 portion of the molecule containing hydrogen and/or oxygen, and decomposed less often to $C_5Cl_6^+$. This is presumably due to the destabilizing inductive effect of the six chlorine atoms in $C_5Cl_6^+$.

Of the compounds studied only the acetate IX and the diol XIV did not fragment to give numerous doubly charged ions. The peaks for some doubly charged ions were more intense than those for their corresponding singly charged analogs. For example the hexachloride III gave a larger peak for $C_{10}H_6Cl_3^{2+}$ than for $C_{10}H_6Cl_3^+$. In general these compounds gave more abundant doubly charged ions than are normally

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[15] R. C. Fort, Jr. and P. v. R. Schleyer, *Chem. Revs.* 64, 286 (1964).

[16] C. Cupas, P. v. R. Schleyer and D. J. Trecker, *J. Amer. Chem. Soc.* 87, 917 (1965).

observed in the mass spectra of organic compounds.[17] Beynon has discussed the formation of doubly charged ions from strongly bonded ring compounds.[18]

The most numerous ions formed from fragmentation of the chlorinated derivatives were those containing five and ten carbon atoms. C_{1-4} and C_{6-9} ions were of low abundance or not detected at all. For example III fragmented to give $C_{10}H_5Cl_4^+$, $C_{10}H_5Cl_3^+$, and various other combinations of $C_{10}H_xCl_y$, with lesser amounts of ions containing $C \neq 5$ or 10. Of the non-C_5 and C_{10} ions, the C_9 ions were generally detected to a greater extent than C_{6-8} and C_{1-4} ions, e.g., the alcohol VIII gave significant ion-currents due to $C_9HCl_8^+$, $C_9Cl_7^+$ and $C_9HCl_6^+$. Probably these C_9 ions arise from expulsion of one of the methylene bridges since only two carbon–carbon bonds would have to be broken while loss of any of the other eight carbon atoms would require the breaking of three carbon–carbon bonds.

In the spectrum of the perchlorocarbon VII (Fig. 1) it is interesting to note the presence of peaks for $C_{10}Cl_{12}^+$, $C_{10}Cl_{11}^+$, $C_{10}Cl_9^+$, $C_{10}Cl_8^+$, $C_{10}Cl_7^+$, $C_{10}Cl_6^+$, $C_{10}Cl_5^+$, $C_{10}Cl_4^+$, $C_{10}Cl_3^+$ and $C_{10}Cl_2^+$, and the absence of peaks for $C_{10}Cl_{10}^+$. Although the predominant mode of fragmentation of VII was cleavage to give the half-molecular ion, the majority of other peaks arose from ions formed by successive losses of chlorine atoms from the molecular ion. The ten-carbon atom framework was retained although not necessarily in the same arrangement. The data show that if the molecular ion does not fragment in half, the next most likely decomposition route is the loss of chlorine atoms without loss of carbon atoms to give both abundant $C_{10}Cl_x^+$ and $C_{10}Cl_x^{2+}$. At present we have no explanation for the absence of $C_{10}Cl_{10}^+$. The only other appreciable number of ions from VII were those containing nine carbon atoms which likely arose from expulsion of one of the methylene bridges.

The mass spectra of the $C_{10}H_{12}$ isomers I and XI were quite similar, and although both showed molecular ion peaks at m/e 132, the intensities of the M^+—H peaks were greater. In addition peaks corresponding to the loss of up to six hydrogen atoms from the parent ion were detectable. Peaks for C_2 through C_{10} ions were observed, and $C_7H_7^+$ at m/e 91 may be the tropylium ion. A possible mode of its formation from I is outlined in reaction sequence (3). A similar mechanism can be drawn in the case of XI with only a slight modification in the first step. Ion *a* is the same as that proposed for the first step of the rearrangement of the toluene molecular ion to give the tropylium ion.[19] There are a limited number of references in which it is postulated that tropylium ions are formed from non-benzenoid molecules on fragmentation under electron impact.[16,20]

The alcohol XII gave a measurable molecular ion with M^+—H being more abundant than M^+ as was observed with the hydrocarbons I and XI. Expected molecular ion decompositions occurred to give M^+—2H, 3H, CH_3, OH, H_2O, H_3O, CO and $CH_{1-5}O$. M/e 91 could again arise from tropylium ion formation as outlined above.

The ketone XIII gave a more intense molecular ion peak than an M^+—H peak

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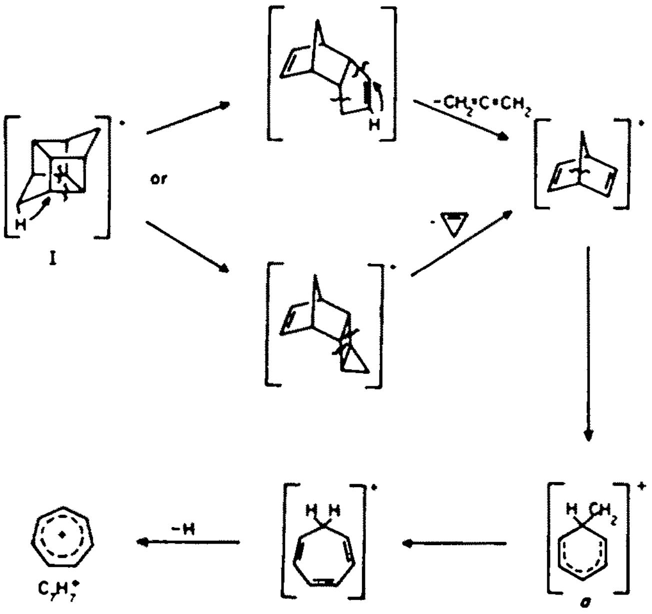
[17] F. H. Field and J. L. Franklin, *Electron Impact Phenomena and the Properties of Gaseous Ions* p. 184. Academic Press, New York (1957).

[18] Beynon, Ref. 5, p. 282.

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

[20] H. Budzikiewicz, C. Djerassi and D. Williams, *Interpretation of Mass Spectra of Organic Compounds* p. 155. Holden-Day, San Francisco (1964).

indicating that the first hydrogen atom lost from XII was a part of the >CHOH group. Losses of CO and CHO appeared to be the favored types of fragmentation, and m/e 91, $C_7H_7^+$, was also significant (Fig. 4). The CO loss is again an example of the expulsion of one of the methylene bridges from these caged structures.



(3)

Most of the spectrum of XIV appeared to arise from C_{10}, C_9 and C_8 ions, a similarity noted above with the other compounds of this series. M^+—Cl,CO in the spectrum of XV gave rise to a large ion contribution for $C_8Cl_7CO^+$; elimination of one and two neutral CO molecules may provide a driving force for the formation of significant amounts of other C_9 ions as well as C_8 and C_4 ions. Again abundant doubly charged ions were produced.

The loss of CO from the ketones X, XIII and XV under electron impact is similar to that observed for other cyclic ketones.[21] The similarity between the cracking pattern under electron impact and the photochemical breakdown of cyclic ketones[21] seems to be borne out to some extent with these compounds.[22]

In conclusion we would like to point out the novel mode of cleavage of the pentacyclodecane nucleus in half and the similarity of the fragments from the isomeric structures. These compounds do not in general undergo the random fragmentation and rearrangement often observed with hydrocarbons and halocarbons. A knowledge of the major fragmentation route for these compounds will be of aid in assigning structures of unknown derivatives of these systems such as compound III (Table 1). We intend to study other derivatives of these series to determine if fragmentation occurs in the same manner as shown above, and also to extend the study to related caged structures.

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[21] N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D. Angelo, *J. Amer. Chem. Soc.* 87, 4097 (1965).

[22] G. W. Griffin and A. K. Price, private communication.