v, m/e 236 (M−5)   w, m/e 84   x, m/e 165

The one acetate examined, 5-hydroxynaphthoquinone acetate (XVIII) behaves unexceptionally, exhibiting the anticipated loss of ketene (M − 42) in its spectrum, subsequent cleavages being identical with those observed for 5-hydroxynaphthoquinone (juglone, VIII). The most interesting feature of the tetrahydroanthraquinone (XXII) spectrum is the appearance of an m/e 165 ion, corresponding to x which must be formed by extensive rearrangement.

In summary, mass spectrometry is of considerable utility in locating a naphthoquinone substituent in the benzenoid or quinonoid ring. Moreover, the O—C=CH—C—O unit is indicated by the presence of an appreciable $C_3HO_2^+$ ion (m/e 69); quinonoid hydroxyl groups lead to highly characteristic rearrangement ions. Therefore, this method, applied in conjunction with nuclear magnetic resonance, infrared, and ultraviolet spectroscopic techniques, should greatly assist structure elucidation in this class of compounds.

Experimental Section

All spectra were determined using an A.E.I. MS 9 mass spectrometer operating at 70 e.v. With the exception of 5,7-dihydroxynaphthoquinone (X) and 5,8-dihydroxynaphthoquinone (XVI), samples were introduced through a heated inlet system at a temperature of approximately 200°. The direct insertion technique was employed to obtain the spectra of X and XVI.

The Mass Spectra of Methyl-Substituted Cyclopentadienes

A. G. Harrison,[1] P. Haynes,[2] Stewart McLean, and F. Meyer

Contribution from the Department of Chemistry, University of Toronto, Toronto 5, Ontario, Canada. Received April 17, 1965

The mass spectra of a series of methyl-substituted cyclopentadienes have been obtained and the major fragmentation paths upon electron impact elucidated. The spectra of the cyclopentadienes are shown to be very similar to the spectra of isomeric cyclohexadienes. From comparison of spectra and from appearance potential data, it is concluded that the major fragment ions from the methylcyclopentadienes do not retain the cyclopentadienyl structure but undergo rearrangement, probably to form a cyclic benzenium-type ion.

Introduction

As part of a study of the chemistry of cyclopentadiene, a series of methyl-substituted cyclopentadienes has been prepared recently in this laboratory.[3] As an aid to identification, the mass spectra were determined, and it was observed that the spectra showed practically no features attributable to positional isomerism involving the methyl groups. A similar lack of positional isomerism effects is observed in the mass spectra of alkyl-substituted benzenes and has been explained[4] by postulating that the major fragment ions are tropylium or substituted tropylium ions in which differences of arrangement of substituents do not have an important effect. Experimental evidence for the formation of a tropylium structure has been presented for toluene and related isomers,[5] C_8H_{10} alkylbenzenes,[6,7] and higher alkylbenzenes.[8] On the other hand it has been suggested[9] that the major fragment ions from benzene itself are acyclic.

The lack of positional effects in the spectra of the methylcyclopentadienes coupled with the observation[10] that the effect of methyl substitution on the ionization potential of cyclopentadiene is similar to that observed in the benzene series suggested that rearrangements might be occurring in the fragmentation of the methylcyclopentadienes similar to those observed for the alkylbenzenes. This has led us to undertake a detailed investigation of the mass spectra of the methylcyclopentadienes and a comparison, where possible, of the spectra of the methylcyclopentadienes with the spectra of cyclic and acyclic isomers. The mass spectral data have been supplemented by appearance potential data for the major fragment ions.

(1) Alfred P. Sloan Fellow, 1962–1964.
(2) Holder of National Research Council (Canada) Studentship, 1963–1964.
(3) S. McLean and P. Haynes, *Tetrahedron*, 21, 2313, 2343 (1965).
(4) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10.

(5) (a) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, 27, 901 (1957); (b) Z. Dolejsek, V. Hanus, and H. Prinzbach, *Angew. Chem.*, 34, 902 (1962); (c) C. Lifshitz and S. H. Bauer, *J. Phys. Chem.*, 67, 1629 (1963); (d) S. Meyerson, *J. Am. Chem. Soc.*, 85, 3340 (1963).
(6) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *ibid.*, 84, 4 (1962).
(7) F. Meyer, P. Haynes, S. McLean, and A. G. Harrison, *Can. J. Chem.*, 43, 211 (1965).
(8) F. Meyer and A. G. Harrison, *J. Am. Chem. Soc.*, 86, 4757 (1964).
(9) J. Momigny, L. Brakier, and L. D'Or, *Bull. Classe Sci. Acad. Roy. Belg.*, 48, 1002 (1962).
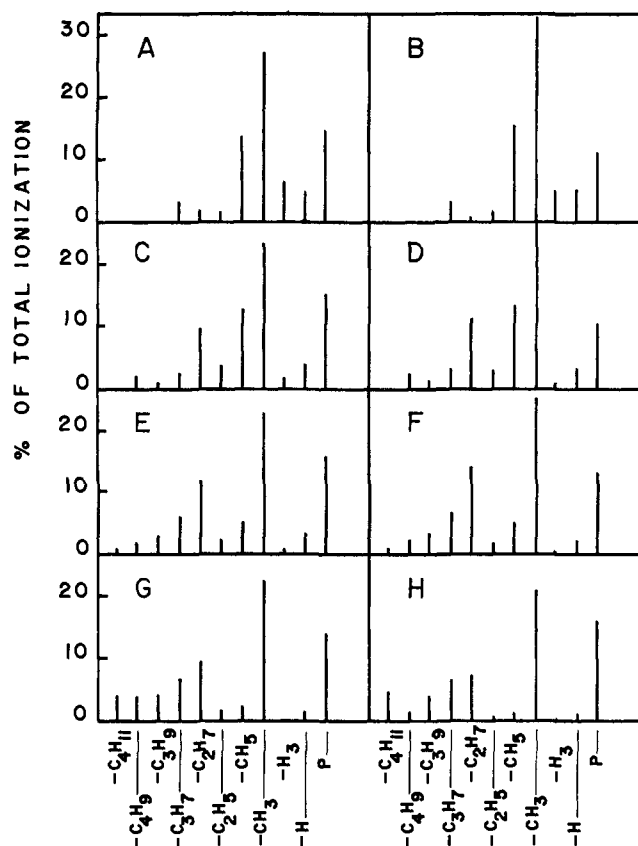(10) F. Meyer and A. G. Harrison, *Can. J. Chem.*, 42, 2256 (1964).

Figure 1. Partial mass spectra of methylcyclopentadienes: A, 1,2-dimethyl; B, 5,5-dimethyl; C, 1,2,3-trimethyl; D, 1,5,5-trimethyl; E, 1,2,3,4-tetramethyl; F, 1,4,5,5-tetramethyl, G, 1,2,4,5,5-pentamethyl; H, hexamethyl.

Figure 2. General fragmentation scheme for methylcyclopentadienes.

Experimental Section

Mass spectra were measured with an A.E.I. MS-2 spectrometer[6] at 50 v. electron energy and 3 v. (7 v./cm.) repeller field using magnetic scanning. Appearance potentials were determined in the usual manner[11] using xenon to calibrate the voltage scale.

The synthesis and proof of structure of the methylcyclopentadienes have been described elsewhere.[3] All samples were purified by gas–liquid partition chromatography (g.l.p.c.) and stored at Dry Ice temperatures until used. Hex-3-en-1-yne and 3-methylpent-3-en-1-yne were prepared by dehydration of hex-1-yn-3-ol and 3-methylpent-1-yn-3-ol, respectively, using $KHSO_4$ as dehydrating agent with final purification by g.l.p.c. All other samples were commercially available.

We are indebted to the Air Reduction Chemical and Carbide Company for the samples of isopropenylacetylene, hexynol, and methylpentynol.

Results and Discussion

The mass spectra of the methylcyclopentadienes show many aspects in which they are similar to the mass spectra of the methylbenzenes. Thus, as in the benzene series, the spectrum of the parent cyclopentadiene shows the largest peak for the parent ion, the monomethyl compound shows the largest peak for loss of H as the neutral fragment, while all higher members of the series show the largest peak for loss of CH_3. The fragmentations of the dimethyl to hexamethyl

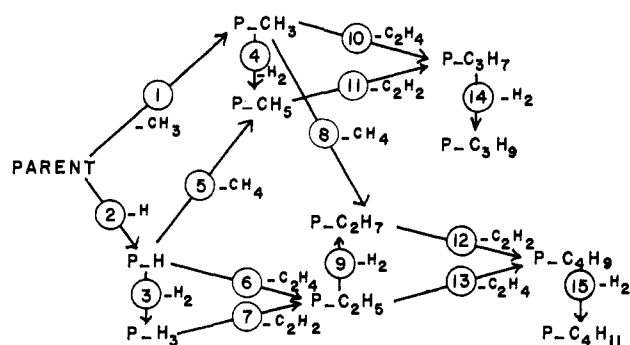(11) A. G. Harrison and T. W. Shannon, Can. J. Chem., 40, 1730 (1962).

compounds are very similar as shown by the partial spectra of a number of methylcyclopentadienes presented in Figure 1. To focus on the similarity of the spectra, the intensities in Figure 1 are expressed as a percentage of the total ionization and are plotted as a function of the empirical formulas of the neutral fragment or fragments lost rather than as a function of the ionic mass. The similarity of the spectra when plotted in this fashion is striking and, when combined with the abundant metastable peaks observed in the spectra, permits the formulation of a general fragmentation scheme presented in Figure 2. The observed metastable peaks are listed in Table I and, where possible, have been identified by the reaction numbers used in Figure 2.

The major fragmentation path for the polymethylcyclopentadienes proceeds by initial loss of CH_3 with subsequent further fragmentation of the $(P - CH_3)^+$ ion. A minor fragmentation path produced initially the $(P - H)^+$ ion followed by further fragmentation. For monomethylcyclopentadiene, whose partial spectrum is given in Table II, this second fragmentation path becomes the major decomposition route. The absence of CH_3 groups causes a profound change in the extent and type of fragmentation in cyclopentadiene itself (Table III). As shown by the spectrum in Table III and the metastable peaks listed in Table I, the major fragmentation paths for cyclopentadiene involve loss of C_2H_2 from the parent to form $C_3H_4^+$ (m/e 40) and loss of H from the parent to form $C_5H_5^+$ followed by loss of C_2H_2 to form the $C_3H_3^+$ (m/e 39) fragment ion. Comparison of the spectra of methylcyclopentadiene and cyclopentadiene with the spectra of the isomers shown in Tables II and III will be made in detail below.

The spectra of Figure 1 and the fragmentation scheme of Figure 2 show that abundant fragment ions are formed in the methylcyclopentadienes where the neutral fragments taken together contain the elements of an alkyl group. A similar pattern of fragmentation is observed in the spectra of the methylbenzenes. Thus abundant ions found in the spectra of cyclopentadienes are of formula $C_nH^+_{2n-5}$, two mass units higher than the $C_nH^+_{2n-7}$ ions which are the major fragments in the mass spectra of the methylbenzenes. The fragmentation scheme of Figure 2 shows that the $C_nH^+_{2n-5}$ ions, formed by loss of alkyl, subsequently lose H_2 to give ions which have the same empirical formulas as the major ions in the benzene series. As an illustration, the loss of CH_3 from trimethylcyclopentadiene (C_8H_{12}) gives $C_7H_9^+$ and this is followed by loss of H_2 to give the

Table I. Metastable Transitions in Cyclopentadienes

m/e	Transition	C5H6	C6H8	C7H10	C8H12	C9H14	C10H16	C11H18
120.0	$C_9H_{14}^+ \rightarrow C_9H_{13}^+ + H$					2		
117.0	$C_9H_{13}^+ \rightarrow C_9H_{11}^+ + H_2$						4	
107.6	$C_{10}H_{16}^+ \rightarrow C_9H_{13}^+ + CH_3$						1	
103.0	$C_8H_{11}^+ \rightarrow C_8H_9^+ + H_2$				3	4		
101.0	$C_8H_9^+ \rightarrow C_8H_7^+ + H_2$					X	X	
93.8	$C_9H_{14}^+ \rightarrow C_8H_{11}^+ + CH_3$					1		
92.0	$C_7H_{10}^+ \rightarrow C_7H_9^+ + H$			2				
91.0	$C_9H_{13}^+ \rightarrow C_8H_9^+ + CH_4$						8	X
89.1	$C_7H_9^+ \rightarrow C_7H_7^+ + H_2$			3	4	9	14	X
85.1	$C_{10}H_{15}^+ \rightarrow C_8H_{11}^+ + C_2H_4$						6	10
84.4	$C_{10}H_{16}^+ \rightarrow C_8H_{11}^+ + C_2H_5$						X	
80.1	$C_8H_{12}^+ \rightarrow C_7H_9^+ + CH_3$					1		
78.0	$C_6H_8^+ \rightarrow C_6H_7^+ + H$		2					
77.3	$C_8H_{11}^+ \rightarrow C_7H_7^+ + CH_4$						8	X
75.0	$C_6H_7^+ \rightarrow C_6H_5^+ + H_2$		3	4	9	14	15	
71.5	$C_9H_{13}^+ \rightarrow C_7H_9^+ + C_2H_4$					6	10	13
66.3	$C_7H_{10}^+ \rightarrow C_6H_7^+ + CH_3$			1				
64.0	$C_5H_6^+ \rightarrow C_5H_5^+ + H$	2						
63.9	$C_7H_9^+ \rightarrow C_6H_5^+ + CH_4$			5	8		X	X
59.3	$C_8H_9^+ \rightarrow C_6H_7^+ + C_2H_2$				7	11	12	X
58.3	$C_8H_{11}^+ \rightarrow C_6H_7^+ + C_2H_4$				6	10	13	X
46.4	$C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$			7	11	12	X	X
36.1	$C_3H_4^+ \rightarrow C_3H_2^+ + H_2$	X						
35.0	$C_3H_3^+ \rightarrow C_3H^+ + H_2$	X						
24.3	$C_5H_6^+ \rightarrow C_3H_4^+ + C_2H_2$	X						
23.5	$C_5H_5^+ \rightarrow C_3H_3^+ + C_2H_2$	X	X					

Table II. Partial Mass Spectra of C6H8 Isomers[a]

m/e	Methyl-cyclo-penta-diene	1,4-Cyclo-hexa-diene	1,3-Cyclo-hexa-diene	Hex-3-en-1-yne	3-Methyl-pent-3-en-1-yne	Hex-1-en-3-yne
80	20.4	23.3	18.2	15.1	19.4	12.9
79	32.0	28.0	30.7	20.9	20.3	15.5
78	3.03	4.65	5.94	1.76	1.75	2.87
77	11.7	15.5	11.7	7.96	10.2	10.6
65	2.89	1.86	1.93	6.35	5.29	6.65
63	1.36	0.75	0.77	2.05	2.05	2.87
54	0.89	0.81	1.75	1.03	0.95	0.85
53	2.55	1.86	2.14	2.64	3.36	2.55
52	4.26	3.98	4.31	6.18	5.33	4.20
51	5.44	5.64	6.03	5.17	5.94	4.30
50	3.71	3.58	3.97	3.75	4.05	3.20
39	7.77	5.84	7.14	11.7	10.3	9.26

[a] Intensities as per cent of total ionization.

Table III. Partial Mass Spectra of C5H6 Isomers[a]

m/e	Cyclo-pentadiene	Iso-propenyl-acetylene	Propenyl-acetylene	Pent-1-en-3-yne
66	35.71	31.85	26.39	28.01
65	16.81	14.95	12.85	10.64
64	1.61	0.98	1.17	...
63	3.62	3.43	4.93	6.13
62	2.60	2.23	3.14	4.20
61	1.65	1.35	2.42	3.36
51	1.13	7.35	3.01	4.76
50	0.83	4.09	2.62	2.80
40	10.82	11.54	12.11	...
39	15.23	14.21	18.39	25.63
38	4.57	2.87	5.33	4.76
37	2.18	1.40	3.33	2.66

[a] Intensities as per cent of total ionization.

$C_7H_7^+$ fragment which is the major ion in the spectra of the xylenes (C_8H_{10}). Alternatively, loss of CH_4 from the $C_nH^+_{2n-5}$ ion also leads to ions of the same empirical formula as those found in the methylbenzenes. Thus it is not particularly surprising that the mass spectra of methylcyclopentadienes and methylbenzenes of the same carbon number should be similar in the lower mass regions. This similarity is shown (in Figure 3) by the comparison of the spectrum of trimethylcyclopentadiene with that of the xylenes and the spectrum of tetramethylcyclopentadiene with that of trimethylbenzene.

A further aspect in which the cyclopentadienes resemble the benzenes is the small effect of positional isomerism on the mass spectra. Cyclopentadiene isomers differing only in the positions of substitution on carbons 1 to 4 showed mass spectra which were identical within experimental reproducibility. The positional isomers examined included: 1-methyl- and 2-methylcyclopentadiene, 1,2-dimethyl- and 2,3-dimethylcyclopentadiene, 1,2,3-trimethyl- and 1,2,4-trimethylcyclopentadiene, 1,4,5,5-tetramethyl- and a mixture of 1,2,5,5- and 1,3,5,5-tetramethylcyclopentadiene. On the other hand the spectra of compounds disubstituted in the 5-position (geminal compounds) showed small but significant differences from isomers not geminally substituted. This is shown by the spectra of Figure 1 and is also shown by the intensities listed for selected ions in Table IV. Geminally substituted isomers show a lower parent ion intensity, a lower $(P - H)^+$ intensity, and an increased $(P - CH_3)^+$ intensity, although the effect is much smaller than that observed for similar substitution in acyclic systems.

The small effect of positional isomerism on the mass spectra cannot be attributed to thermal isomerization prior to ionization. Although the methylcyclopentadienes are known to undergo isomerization in both the liquid phase[12] and the gas phase[13] the rate is slow, with

(12) S. McLean and P. Haynes, *Tetrahedron Letters* 2385 (1964); *Tetrahedron*, 21, 2329 (1965).

(13) (a) W. R. Roth, *Tetrahedron Letters*, 1009 (1964); (b) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, 19, 1939 (1963).

Table IV. Comparison of Spectra of Geminal and Nongeminal Methylcyclopentadienes

No. of methyls	Intensity[a]					
	Parent+		(Parent − H)+		(Parent − CH₃)+	
	Geminal	Nongeminal	Geminal	Nongeminal	Geminal	Nongeminal
0		35.7		16.8		1.1
1		20.4		32.0		2.9
2	11.3	14.7	5.23	4.71	32.7	27.0
3	10.2	15.0	3.09	3.64	26.9	22.8
4	13.0	15.6	2.01	2.99	24.8	22.5
5	13.9		1.12		22.3	
6	16.3		0.76		22.3	

[a] Per cent of total ionizations.

the exception of 5-methylcyclopentadiene, compared to the residence time of the molecules in the ionization chamber. In addition, no rearrangement of the compounds studied was observed in the gas chromatograph with an inlet temperature of 200° and a column temperature of 75°. The temperature of the mass spectrometer ionization chamber was found to be 40–50°
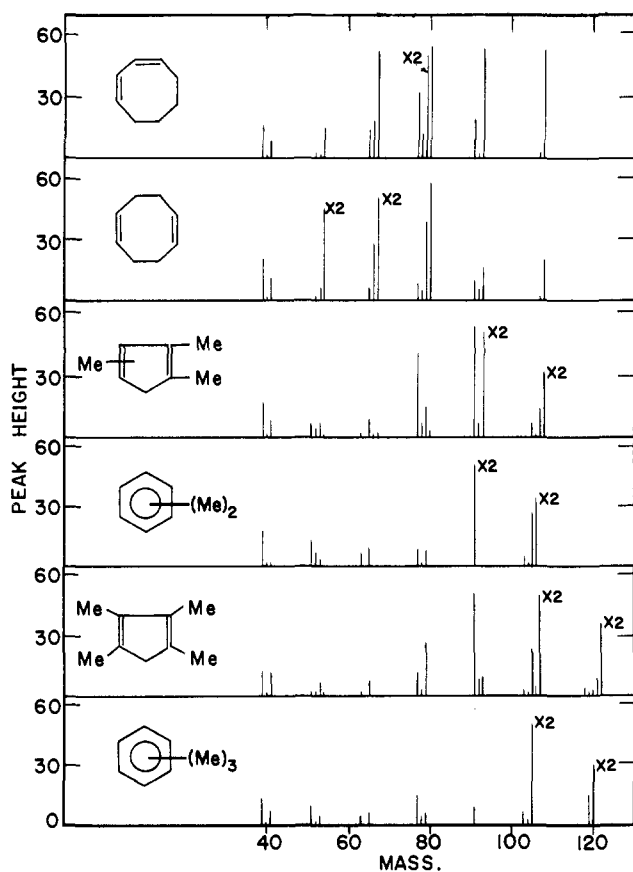

Figure 3. Comparison of mass spectra of methylcyclopentadienes with methylbenzenes and cyclooctadienes.

under operating conditions. On the other hand, 5-methylcyclopentadiene undergoes a rapid rearrangement at room temperature[12] and consequently no cyclopentadienes monosubstituted in the 5-position were studied.

The major fragment ions formed by loss of CH_3 from the methylcyclopentadienes would have a methylcyclopentadienyl structure in the absence of rearrangement. An ion of such structure would not be expected to have the stability implied by the large relative

abundances in the spectra. Indeed, the low abundance of the $C_5H_5^+$ ion (nominally cyclopentadienyl ion structure) in the mass spectra of cyclopentadiene and methylcyclopentadiene suggests that this cation is of low stability and methyl substitution would not be expected to stabilize the ion appreciably. Therefore we suggest that the fragmentation to form the $C_nH^+_{2n-5}$ ions in the methylcyclopentadienes proceeds with rearrangement to yield a more stable ion. The evidence presented below suggests that this rearrangement proceeds by a ring expansion to form a six-membered cyclic ion which can be regarded as a protonated benzene (benzenium ion).
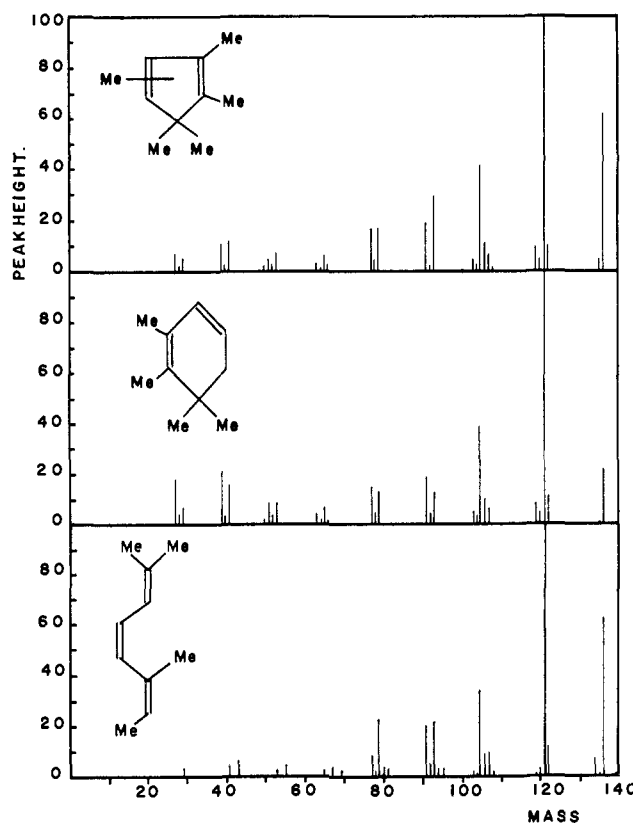

Figure 4. Mass spectra of pentamethylcyclopentadiene and two isomers.

This suggestion receives support from the close similarity of the spectra of the methylcyclopentadienes to the spectra of the isomeric cyclohexadienes. Table II compares partial mass spectra of methylcyclopenta-

Table V. Partial Mass Spectra of C_7H_{10} Isomers[a]

m/e	5,5-Dimethyl-cyclopentadiene	1,2-Dimethyl-cyclopentadiene	1-Methyl-1,4-cyclohexadiene	1,3-Cyclo-heptadiene	Bicyclo-[3.2.0]-heptene
94	11.27	14.68	16.65	10.5	3.8
93	5.23	4.71	3.65	4.0	4.7
92	0.54	0.76	1.00	0.5	1.5
91	5.10	6.35	7.86	4.4	6.3
79	32.68	27.03	24.95	28.4	31.6
78	2.91	2.35	2.25	...	...
77	15.10	13.60	14.35	10.2	8.3
66	0.64	1.0	1.04	5.6	5.8
65	1.39	1.59	2.58	2.5	2.5
53	2.01	2.06	1.59	2.0	2.2
52	1.63	1.41	1.11	...	...
51	3.21	3.08	2.51	...	...
41	1.22	1.47	1.34	2.2	2.4
39	4.17	7.37	5.20	5.9	6.2
27	2.45	3.01	2.63	2.6	2.7

[a] Intensities as per cent of total ionization.

diene, 1,4-cyclohexadiene, and 1,3-cyclohexadiene,[14] while Table V compares partial spectra of two dimethylcyclopentadienes and the isomeric 1-methyl-1,4-cyclohexadiene. Figure 4 compares the spectrum of pentamethylcyclopentadiene with that of 1,2,6,6-tetramethyl-1,4-cyclohexadiene.[15] In all cases the spectra of the substituted cyclopentadienes are very similar to the spectra of the corresponding isomeric cyclohexadiene. Obviously the cyclopentadienes and cyclohexadienes are undergoing fragmentation by the same nominal paths while the close similarity of the spectra suggests that the intermediate ions may have the same structure.

The spectra of two C_7H_{10} isomers, 1,3-cycloheptadiene and bicyclo[3.2.0]hept-6-ene, reported recently,[5c] are also very similar to the spectra of the dimethylcyclopentadienes (Table V). The formation of $C_6H_7^+$ (m/e 79) from these isomers must involve extensive rearrangement, indicating that the driving force for the reaction must be the stability of the $C_6H_7^+$ ion. These results show that the cyclopentadienes have mass spectra similar to the spectra of the isomeric cyclohexadienes and cycloheptadienes. Such similarity does not extend to the cyclooctadiene system. The mass spectra of 1,3- and 1,5-cyclooctadiene differ markedly from that of the isomeric trimethylcyclopentadiene (Figure 3), indicating different fragmentation modes for the two classes of compounds. The mass spectra of a number of $C_{10}H_{16}$ terpenes, isomeric with pentamethylcyclopentadiene, have been reported recently.[16] Of these only the spectrum of alloocimene, also shown in Figure 4, is similar to the spectrum of pentamethylcyclopentadiene. It is obvious that similar fragmentation reactions are occurring; however, the identity of structure of the fragment ions is not established.

The similarity of mass spectra of the isomeric cyclopentadienes is consistent with, but does not prove, the suggestion that fragmentation forms ions of the same structure. Further support for this suggestion is obtained from an examination of the energetics of

formation of the $C_7H_9^+$ and $C_6H_7^+$ fragment ions, primarily from the C_7H_{10} and C_6H_8 compounds. The relevant data are summarized in Table VI. The heats of formation of the neutral molecules necessary for the thermochemical calculations of Table VI are summarized in the Appendix.

The appearance potentials of $C_7H_9^+$ from 1,2-dimethylcyclopentadiene, 1-methyl-1,4-cyclohexadiene, 1,2,3-trimethylcyclopentadiene, and bicycloheptene[5c] are in agreement and lead to an average value, $\Delta H_f(C_7H_9^+) = 224$ kcal./mole, while the appearance potential from 1,3-cycloheptadiene leads to a value which is only slightly higher. This heat of formation appears to be too low to be attributed to the dimethylcyclopentadienyl cation. Assuming the C–H bond dissociation energy in cyclopentadienes to be approximately 90 kcal./mole one estimates from I (c-C_5H_5) = 8.72 e.v.[17] and I (c-$C_5H_4CH_3$) = 8.54 e.v.[18] heats of formation of $\sim$270 and $\sim$260 kcal./mole for the cyclopentadienyl and methylcyclopentadienyl cations, respectively. This suggests that the heat of formation of the dimethylcyclopentadienyl cation should be in the range 240–260 kcal./mole. The experimental value of 224 kcal./mole is much lower than this estimate. The problems associated with the interpretation of appearance potential measurements have been extensively discussed[19–21] and it appears, in general, that heats of formation calculated from appearance potential measurements tend to be higher than those derived from thermochemical measurements and directly measured ionization potentials. The observation, in the present case, of a lower ionic heat of formation from the appearance potential measurement therefore suggests that the ion has rearranged to a more stable structure. Since the $C_7H_9^+$ ion from all molecules studied has the same heat of formation, it is reasonable to assume that the structure is the same in all cases. Whether this structure is best represented as a methylbenzenium ion, a protonated cycloheptatriene, or an acyclic ion cannot be decided from the present data.

(14) Catalogue of Mass Spectral Data, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh 13, Pa., spectrum no. 436.

(15) Catalogue of Mass Spectral Data, Manufacturing Chemists Association Project, Carnegie Institute of Technology, Pittsburgh 13, Pa., spectrum no. 55.

(16) R. Ryhage and E. Von Sydow, Acta Chem. Scand., 17, 2025 (1963).

(17) A. G. Harrison, L. Honnen, H. J. Dauben, and F. P. Lossing, J. Am. Chem. Soc., 82, 5593 (1960).

(18) R. F. Pottie and F. P. Lossing, ibid., 85, 269 (1963).

(19) M. Wallenstein and M. Krauss, J. Chem. Phys., 34, 929 (1961).

(20) H. M. Rosenstock and M. Krauss, ref. 4, Chapter 1.

(21) M. Krauss and V. H. Dibeler, ref. 4, Chapter 3.

Table VI. Appearance Potentials and Ionic Heats of Formation in Cyclopentadienes and Related Compounds

Compd.	Neutral fragments	Ion	A (ion), e.v.	$\Delta H°_{298}$ (ion), kcal./mole
1,2-Dimethylcyclopentadiene	H	$C_7H_9^+$	11.05	221
1-Methyl-1,4-cyclohexadiene	H	$C_7H_9^+$	11.03	222
m-Methylanisole	H + CO	$C_7H_9^+$	11.7	219
1,2,3-Trimethylcyclopentadiene	CH_3	$C_7H_9^+$	10.8	227
1,3-Cycloheptadiene	H	$C_7H_9^+$	11.30	230
Bicyclo[3.2.0]hept-6-ene	H	$C_7H_9^+$	10.7	224
1,3-Cycloheptadiene	CH_3	$C_6H_7^+$	10.1	224
Bicyclo[3.2.0]hept-6-ene	CH_3	$C_6H_7^+$	9.8	224
1,3-Cyclohexadiene	H	$C_6H_7^+$	11.32	235
5-Methyl-1,3-cyclohexadiene	CH_3	$C_6H_7^+$	10.6	233
4-Methyl-1,4-cyclohexadiene	CH_3	$C_6H_7^+$	10.61	232
5,5-Dimethylcyclopentadiene	CH_3	$C_6H_7^+$	10.75	233
1,2-Dimethylcyclopentadiene	CH_3	$C_6H_7^+$	10.7	233
Methylcyclopentadiene	H	$C_6H_7^+$	11.3	232
Anisole	H + CO	$C_6H_7^+$	12.1	235
Benzyl alcohol	HCO	$C_6H_7^+$	10.9	228
Butenylacetylene	H	$C_6H_7^+$	10.7	252
Isobutenylacetylene	H	$C_6H_7^+$	10.7	249
7-Methoxycycloheptatriene	CH_3 + CO	$C_6H_7^+$	11.1	255
m- and p-methylanisole	CH_3 + CO	$C_6H_7^+$	12.9	266
p-Ethyltoluene	CH_3 + C_2H_2	$C_6H_7^+$	15.3	266
Methylcyclopentadiene	H_2 + H	$C_6H_5^+$	14.0	296
Butenylacetylene	H_2 + H	$C_6H_5^+$	12.7	298
Isobutenylacetylene	H_2 + H	$C_6H_5^+$	12.7	295
Cyclopentadiene	H	$C_5H_5^+$	12.9	280
Anisole	CO + CH_3	$C_5H_5^+$	13.5	288
Isopropenylacetylene	H	$C_5H_5^+$	11.6	278
Isoprene	H_2 + H	$C_5H_5^+$	13.9	286
Toluene	H + C_2H_2	$C_5H_5^+$	16.7	290
Butenylacetylene	CH_3	$C_5H_5^+$	12.2	307
Isobutenylacetylene	CH_3	$C_5H_5^+$	12.4	308
Methylcyclopentadiene	CH_3	$C_5H_5^+$	13.5	306
1,4-Cyclohexadiene	CH_3	$C_5H_5^+$	13.6	309
Cycloheptatriene	H + C_2H_2	$C_5H_5^+$	16.66	305
Bicyclo[3.2.0]heptadiene	H + C_2H_2	$C_5H_5^+$	14.9	299

The appearance potentials of the $C_6H_7^+$ ion from the C_7H_{10} isomers, 1,2-dimethylcyclopentadiene, 5,5-dimethylcyclopentadiene, 5-methyl-1,3-cyclohexadiene,[22] and 1-methyl-1,4-cyclohexadiene lead to ionic heats of formation in agreement with those obtained for the $C_6H_7^+$ ion from 1,3-cyclohexadiene,[22] methylcyclopentadiene. anisole, and benzyl alcohol. The evidence for the neutral fragments in the case of anisole[23] and benzyl alcohol[24] has been discussed previously. The average value $\Delta H_f(C_6H_7^+) = 232 \pm 3$ kcal./mole is considerably higher than the value of 224 kcal./mole obtained by Lifshitz and Bauer[5c] for the $C_6H_7^+$ ion from 1,3-cycloheptadiene and bicycloheptene.

The $C_6H_7^+$ ion from the methylcyclopentadienes cannot be the methylcyclopentadienyl cation, since, as discussed above, this ion should have a heat of formation of about 260 kcal./mole. The low value derived from appearance potential measurements must be taken to indicate that rearrangement to an ionic structure of lower heat of formation has occurred in formation of the $C_6H_7^+$ ion. Since the ionic heats of formation derived from the cyclopentadienes and cyclohexadienes are identical we suggest that the same ion is formed from both types of compounds and that this ion is probably the benzenium ion. The appearance potentials of $C_6H_7^+$ from the two acyclic C_6H_8 isomers,

hex-3-en-1-yne and 3-methylpent-3-en-1-yne, lead to $\Delta H_f(C_6H_7^+) = 251$ kcal./mole, a value considerably higher than that obtained from the cyclic isomers and probably can be attributed to an acyclic ion. The appearance potentials of $C_6H_7^+$ from 7-methoxycycloheptatriene, the methylanisoles, and p-ethyltoluene lead to $\Delta H_f(C_6H_7^+)$ in the range 255–265 kcal./mole assuming the neutral fragments listed. These fragmentation paths are supported by metastable evidence. The higher apparent heats of formation are not surprising in view of the rather extensive rearrangements involved.

It might be noted that although the appearance potential data suggest a different structure for the $C_6H_7^+$ ions from the cyclic and acyclic C_6H_8 isomers the mass spectra, including that of hex-1-en-3-yne,[25] show only very small differences (Table III). This may be partially explained by the observation that the $C_6H_5^+$ ion formed as the major fragment from $C_6H_7^+$ has the same apparent ionic heat of formation for both the cyclic and acyclic isomers. The average value from Table VI, $\Delta H_f(C_6H_5^+) = 296 \pm 4$ kcal./mole, is not significantly lower than the range 302–312 kcal./mole reported[9] for the $C_6H_5^+$ ion from benzene and isomeric acyclic C_6H_6 isomers. In these cases the ion was considered to be acyclic.

Although the energetics data for the $C_7H_9^+$ and $C_6H_7^+$ ions from the methylcyclopentadienes can be

(22) J. L. Franklin, F. W. Lampe, and H. E. Lumpkin, J. Am. Chem. Soc., 81, 3152 (1959).
(23) F. Meyer and A. G. Harrison, Can. J. Chem., 42, 2008 (1964).
(24) E. L. Eliel, J. D. McCollum, S. Meyerson, and P. N. Rylander, J. Am. Chem. Soc., 83, 2481 (1961).
(25) A. A. Polyakova, K. I. Zimina, A. A. Petrov, and R. A. Kheml'-nitskii, Zh. Obshch. Khim., 30, 912 (1960).

interpreted to indicate that the ions do not have the cyclopentadienyl structure no simple interpretation can be made for the $C_5H_5^+$ ion. As shown in Table VI a number of cyclic and acyclic compounds, including cyclopentadiene, yield $\Delta H_f(C_5H_5^+) = 280$–290 kcal./mole while a further group, including methylcyclopentadiene, yield $\Delta H_f(C_5H_5^+) = 300$–310 kcal./mole. These values are all higher than the estimate of 270 kcal./mole for the cyclopentadienyl cation given above and it is not possible to reach any definitive conclusions from these data. If the $C_5H_5^+$ ion from cyclopentadiene has the cyclopentadienyl structure it is obviously formed in a process involving excess energy. The appearance potential, $A(C_5H_5^+) = 12.9$ e.v. from cyclopentadiene, is in reasonable agreement with the recent value of 12.6 e.v.[17] but much higher than the value of 10.7 e.v. reported[26] some years ago. Again it can be noted that the cyclic and acyclic C_5H_6 isomers have similar mass spectra (Table III).

In summary the data for $C_7H_9^+$ and $C_6H_7^+$ ions show quite clearly that these ions, as formed in the mass spectra of methyl-substituted cyclopentadienes, cannot have the cyclopentadienyl structure but must have undergone rearrangement to a more stable form. The numerous similarities between the cyclopentadienes and cyclohexadienes suggest that the structure is most probably a six-membered cyclic benzenium ion.

Appendix

The heats of formation of the neutral molecules used in the thermochemical calculations of the previous section are tabulated in Table VII along with the source of the data.[27-30]

As indicated, the heats of formation of the olefinic acetylenes were estimated by the group equivalent method of Franklin[29] while the heats of formation of methylanisole and 7-methoxycycloheptatriene were estimated by the bond energy scheme of Cox.[30]

The heats of formation of the methyl-substituted cyclopentadienes were estimated by assuming that the heat of hydrogenation to the corresponding substituted cyclopentane was the same as that of cyclopentadiene. The heats of formation of the methylcyclopentanes are given by Rossini, et. al.[27] Essentially the same values

(26) J. Hissel, Bull. Soc. Roy. Sci. Liege, 21, 457 (1952).

Table VII. Heats of Formation of Neutral Molecules

Molecule	ΔH°_{298}, kcal./mole	Source
Cyclopentadiene	31.84	Ref. 17
Methylcyclopentadiene	24.8	
1,2-Dimethylcyclopentadiene	18.3	Estimated, see text
5,5-Dimethylcyclopentadiene	17.3	
1,2,3-Trimethylcyclopentadiene	10	
1,3-Cycloheptadiene	22.1	Ref. 5c
Bicyclo[3.2.0]hept-6-ene	30.0	Ref. 5c
1,3-Cyclohexadiene	26.1	Ref. 22
5-Methyl-1,3-cyclohexadiene	21.0	Ref. 22
1,4-Cyclohexadiene	27.4	Estimated, see text
1-Methyl-1,4-cyclohexadiene	19.4	
Toluene	11.95	Ref. 27
Ethyltoluene	−0.78	Ref. 27
Isoprene	18.1	Ref. 27
1,3,5-Cycloheptatriene	43.5	Ref. 28
Isopropenylacetylene	61.2	Estimated by group equivalent method, ref. 29
Butenylacetylene	57.2	
Isobutenylacetylene	54.4	
Anisole	−18.5	Ref. 30
Benzyl alcohol	−23.8	Ref. 30
Methylanisole	−25.5	Estimated by bond energy scheme, ref. 30
7-Methoxycycloheptatriene	4.9	

were obtained by using the heats of formation of butadiene and methyl-substituted butadienes to calculate the increment for replacement of H by CH_3.

The heat of formation of 1,4-cyclohexadiene was estimated to be 27.4 kcal./mole on the assumption that the heat of hydrogenation of each double bond was identical and using ΔH°_{298} (cyclohexane) $= -29.43$ kcal./mole[27] and ΔH°_{298} (cyclohexene) $= -1$ kcal./mole.[31] Consideration of the increment for replacing H by CH_3 at an isolated double bond led to ΔH°_{298} (1-methyl-1,4-cyclohexadiene) $= 19.4$ kcal./mole.

(27) F. D. Rossini, et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.
(28) H. L. Finke, P. W. Scott, M. E. Gross, J. E. Messerly, and G. Waddington, J. Am. Chem. Soc., 78, 5469 (1956).
(29) J. L. Franklin, Ind. Eng. Chem., 41, 1070 (1949).
(30) J. D. Cox, Tetrahedron, 18, 1337 (1962).
(31) J. D. Cox, ibid., 19, 1175 (1963).