AN ELECTRON IMPACT STUDY OF SOME C_8H_{10} ISOMERS

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Received August 4, 1964

ABSTRACT

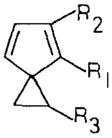
The mass spectra of 1-, 2-, and 6-methylspiro[2.4]hepta-1,3-diene have been measured and found to be very similar to the spectra of 7-methylcycloheptatriene and the isomeric alkyl benzenes. It is concluded that in all cases the major part of the fragmentation occurs by identical paths involving identical intermediates. This conclusion is supported by deuterium labelling and appearance potential data. On the other hand the mass spectrum of 2,5-dimethyl-1,5-hexadien-3-yne, an acyclic C_8H_{10} isomer, shows a number of significant differences in its fragmentation pattern. These differences are reflected in the energetics of ion formation and it is concluded that in this case the fragmentation proceeds through different intermediates.

INTRODUCTION

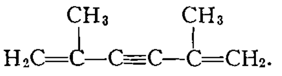
It was pointed out recently (1, 2) that the mass spectra of a number of C_7H_8 isomers are very similar and this was explained by the assumption that all compounds decompose largely via a common intermediate, probably a seven-membered ring. The C_7H_8 isomers included toluene and cycloheptatriene (1), bicyclo[2.2.1]hepta-2,5-diene, spiro[2.4]hepta-1,3-diene, 1- and 3-ethinylcyclopentene, and quadricyclene (3). More recently the mass spectrum of bicyclo[3.2.0]hepta-2,6-diene has been recorded (4) and is again very similar. Extensive deuterium labelling has supported the assumption of a symmetrical seven-membered ring intermediate, presumably the tropylium ion (5).

We report now the mass spectra of a number of methyl-substituted analogues of these compounds, the C_8H_{10} isomers. The mass spectra of 1-, 2-, and 6-methylspiro[2.4]hepta-1,3-diene (I, II, III) have been compared with three other C_8H_{10} compounds: 7-methylcycloheptatriene, *m*-xylene, and an acyclic compound 2,5-dimethylhexa-1,5-dien-3-yne (IV). The spectra of the 1- and 2-methyl spiro compounds are identical while the 6-methyl compound shows only minor differences. The spectra of the methyl-substituted spiroheptadienes are very similar to the spectra of the xylenes and methylcycloheptatriene. Furthermore the spectra of the deuterium-labelled methylspiroheptadienes show extensive hydrogen-deuterium scrambling in the formation of $C_8H_9^+$ and $C_7H_7^+$, similar to the results reported previously for *p*-xylene (6). On the other hand the spectrum of the acyclic isomer, 2,5-dimethyl-1,5-hexadien-3-yne, differs significantly from the spectra of the other C_8H_{10} isomers and these differences are reflected in the energetics of formation of the $C_8H_9^+$ and $C_7H_7^+$ fragments.

The further decomposition of the $C_8H_9^+$ ion is shown from deuterium labelling in the methylspiroheptadienes and methylethylbenzene to involve complete scrambling of all hydrogens.



I. R_1 = Me; R_2 = R_3 = H.
II. R_2 = Me; R_1 = R_3 = H.
III. R_3 = Me; R_1 = R_2 = H.

IV. 

$$H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}C{\equiv}C{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2.$$

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Canadian Journal of Chemistry. Volume 43 (1965)

EXPERIMENTAL

All mass spectra were obtained with an A.E.I. MS-2 mass spectrometer which has been described previously (7). Mass spectra were recorded at 50 V electron energy, 20 μA ionizing current, and a repeller voltage of 3 V (7 V/cm). Appearance potentials were measured as described previously (8) using xenon to calibrate the voltage scale.

1-(I) and 2-(II)Methylspiro[2.4]hepta-1,3-diene

The synthesis of these compounds by the reaction of 1,2-dibromoethane with sodium methylcyclopentadienide in the presence of sodium amide in liquid ammonia is described elsewhere (9).

1- and 2-Methylspiro[2.4]hepta-1,3-diene-6,6,7,7-d_4

These were synthesized in the same way using 1,2-dibromoethane-d_4.

1- and 2-Methyl-d_3-spiro[2.4]hepta-1,3-diene

These were prepared by the reaction in liquid ammonia of 1,2-dibromoethane with sodium methyl-d_3-cyclopentadienide which had been prepared *in situ* by treatment of sodium cyclopentadienide with bromomethane-d_3 and then sodium amide.

6-Methylspiro[2.4]hepta-1,3-diene (III)

6-Methylspiro[2.4]hepta-1,3-diene (III) was synthesized from sodium cyclopentadienide and 1,2-dibromopropane by the procedure described for I and II (9). The product, retention time 1.65 (relative to spiroheptadiene = 1.00 (9)), $\lambda\lambda_{\max}^{\mathrm{MeOH}}$ 257, 227 mμ, formed an N-phenylmaleimide adduct, m.p. 170–171 (sealed tube). (Found: C, 77.31; H, 6.03; N, 5.13. $C_{18}H_{17}O_2N$ requires C, 77.39; H, 6.13; N, 5.01.)

2,5-Dimethyl-1,5-hexadien-3-yne(IV)

2,5-Dimethyl-1,5-hexadien-3-yne(IV) was prepared from 2,5-dihydroxy-2,5-dimethyl-3-hexyne by Nazarov's method (10). Purification of the yellow product by gas–liquid chromatography led to the isolation of its principal component as a *colorless* liquid, $\lambda\lambda_{\max}^{\mathrm{heptane}}$ 250 mμ (ϵ 14 250), 233 mμ (shoulder, ϵ 11 800), 262 mμ (shoulder, ϵ 12 100), which showed absorption at 1 613 and 895 cm^{-1} in the infrared and a complex multiplet (at least 10 narrowly spaced lines) centered at 4.78 τ (area 2) and a narrowly spaced multiplet (at least 3 lines) at 8.12 τ (area 3) in the nuclear magnetic resonance (n.m.r.) spectrum. The material rapidly became an intensely yellow oil on standing in air.

7-Methylcyclohepta-1,3,5-triene

7-Methylcyclohepta-1,3,5-triene was very kindly supplied by Mr. R. B. Medz and Professor H. J. Dauben, Jr. of the University of Washington.

Compounds used in the present study were purified by gas–liquid chromatography using a 9 ft. × $\frac{1}{4}$ in. column of 20% MEEE(($MeOCH_2CH_2OCH_2CH_2)_2O$) on Chromosorb P (60–80 mesh), typically at 75 °C with 80 ml/min helium as carrier gas.

RESULTS AND DISCUSSION

Table I shows the major peaks in the spectra of six C_8H_{10} isomers expressed as percentage of total ionization. The peaks shown account for approximately 85% of the total ionization.

TABLE I

Partial mass spectra of C_8H_{10} compounds

m/e	1- and 2-Methyl-spiroheptadiene	6-Methyl-spiroheptadiene	7-Methyl-cycloheptatriene	*m*-Xylene	2,5-Dimethyl-1,5-hexadien-3-yne
106	11.66	10.09	10.88	18.30	19.71
105	6.57	5.05	4.48	7.96	4.40
103	2.24	1.51	1.66	1.89	1.42
91	31.10	31.20	37.84	31.40	17.01
79	4.11	3.84	3.04	2.39	4.22
78	2.67	6.34	3.58	2.16	6.43
77	4.85	4.22	4.39	4.18	3.73
65	4.10	4.28	4.64	2.49	8.99
63	1.86	2.42	1.91	1.98	3.67
52	1.92	2.41	1.66	1.83	2.07
51	4.42	4.26	3.86	3.57	3.59
50	1.93	1.86	1.48	1.21	1.83
41	0.88	1.35	0.67	0.63	1.46
39	5.06	6.41	4.56	4.24	6.43

The mass spectrum of 1-methylspiro[2.4]hepta-1,3-diene was found to be identical with the spectrum of the 2-methyl isomer, while the only significant difference in the spectrum of the 6-methyl isomer is the higher intensity for m/e = 78 (parent-28). This higher intensity may correspond to the simple loss of $CH_3CH\langle$ from the 6-methyl isomer, a fragmentation which is not possible for the other isomers without rearrangement. The spectra of the spiro compounds bear a very close resemblance to the spectra of 7-methylcycloheptatriene and the C_8H_{10} alkylbenzene isomers, of which *m*-xylene has been chosen as representative. On the other hand the spectrum of the acyclic isomer shows a greatly reduced parent-CH_3 (m/e = 91) intensity and an increased $C_5H_5^+$ (m/e = 65) intensity. The close similarity of the spectra of the monocyclic and spiro isomers suggests that for these isomers fragmentation occurs by common paths involving common intermediates. The same fragmentation paths undoubtedly apply for the acyclic isomer as well; however, the intermediates formed in this case have different structures.

For all compounds the same metastable transitions were observed (Table II), indicating the same fragmentation paths. The major decomposition path is the sequence [1]:

$$C_8H_{10}^+ \rightarrow CH_3 + C_7H_7^+ \rightarrow C_2H_2 + C_5H_5^+ \rightarrow C_2H_2 + C_3H_3^+ \qquad [1]$$

TABLE II

Metastables in C_8H_{10} compounds

Reaction	Metastable
$105^+ \rightarrow 103^+ + 2$	101.0
$106^+ \rightarrow 91^+ + 15$	78.1
$105^+ \rightarrow 79^+ + 26$	59.4
$105^+ \rightarrow 78^+ + 27$	57.9*
$106^+ \rightarrow 78^+ + 28$	57.4
$91^+ \rightarrow 65^+ + 26$	46.4
$65^+ \rightarrow 39^+ + 26$	23.5

*Only one metastable observed.

A second minor path proceeds through the $C_8H_9^+$ ion to form ions in the C_6 and C_4 region. In addition several other minor paths are possible, such as that suggested above for formation of m/e = 78 in 6-methylspiroheptadiene.

Table III records the appearance potentials of the $C_8H_{10}^+$, $C_8H_9^+$, and $C_7H_7^+$ ions from seven C_8H_{10} isomers in addition to the appearance potential of $C_8H_9^+$ from *p*-ethyl

TABLE III

Appearance potentials and heats of formation of $C_8H_{10}^+$, $C_8H_9^+$, and $C_7H_7^+$

	Appearance potential (±0.1 eV)			ΔH_f (kcal/mole)		
Compound	$C_8H_{10}^+$	$C_8H_9^+$	$C_7H_7^+$	$C_8H_{10}^+$	$C_8H_9^+$	$C_7H_7^+$
1-Methylspiroheptadiene	8.02	9.9	9.8	229	220	237
2-Methylspiroheptadiene	8.07	9.9		230	220	
6-Methylspiroheptadiene	8.40	10.65	9.7	240	239	238
7-Methylcycloheptatriene	8.39	11.0	10.0	231	240	235
m-Xylene	8.85	11.85*	11.6	208	225	240
2,5-Dimethyl-1,5-hexadien-3-yne	8.95	10.4	10.5	275	252	278
Spiroheptadiene			10.45			241
Ethylbenzene	9.17†	11.4	11.2	218	223	234
p-Methylethylbenzene		11.2			225	

*Reference 7.
†Tables of ionization potentials by R. W. Kiser, U.S. Atomic Energy Commission TID-6142.

toluene. The last three columns show the ionic heats of formation calculated from these data. The heats of formation for several of the isomers are not known and were estimated as outlined in a later section. For the cyclic isomers the appearance potential data are consistent with the spectral intensities given in Table I. Thus *m*-xylene has the highest parent ion intensity, as would be predicted since the activation energy (A(fragment) − A(molecule ion)) for further fragmentation is highest in this case. The high parent ion intensity for 2,5-dimethyl-1,5-hexadien-3-yne cannot be explained in this fashion since the activation energy for further fragmentation is lower than for any other compound studied. If fragmentation occurred through the same intermediates, one might well expect the lowest parent ion intensity for the acyclic isomer.

The $\Delta H_f(C_7H_7^+)$ from the spiroheptadienes, methylcycloheptatriene, xylene, and ethylbenzene all lead to a value of 237 ± 3 kcal/mole, suggesting that in all cases the same ion is formed through the same intermediate. For ethylbenzene, deuterium labelling (11) strongly suggests a tropylium ion structure for the $C_7H_7^+$ ion. The identity of the heat of formation suggests a tropylium structure for the $C_7H_7^+$ ion from the other isomers as well. However, in all cases the ion must be formed with excess energy, since the true heat of formation for a tropylium ion is probably considerably lower (12). The excess energy may be viewed as the energy required to raise the molecule to an excited ionized state capable of dissociating to give the cyclic $C_7H_7^+$. For 2,5-dimethyl-1,5-hexadien-3-yne a much higher value for $\Delta H_f(C_7H_7^+) = 278$ kcal/mole is obtained. This suggests either a different (acyclic) structure or a more complicated rearrangement to form the cyclic $C_7H_7^+$ ion which requires a greater excess energy. In the absence of labelling evidence a definite conclusion cannot be reached although the former appears more likely. In any event it is evident that the fragmentation does not proceed through the same intermediate ionic state in this case.

Although the appearance potential data for the $C_7H_7^+$ ion serve to point out the similar behavior of the cyclic compounds and the rather striking difference for the acyclic isomer, the data for the $C_8H_9^+$ ion are much less clear-cut. As shown by the data in Table III the appearance potential of $C_8H_9^+$ from 1- and 2-methylspiroheptadiene, ethylbenzene, and *m*-xylene lead to $\Delta H_f(C_8H_9^+) = 220$–$225$ kcal/mole, in agreement with values in this same range obtained from appearance potential measurements in the xylenes (7), the diethylbenzenes (13), the methyl-*n*-propylbenzenes (13), and *p*-ethyltoluene. On the other hand $A(C_8H_9^+)$ from 6-methylspiroheptadiene and 7-methylcycloheptatriene give a $\Delta H_f(C_8H_9^+) = 239$–$240$ kcal/mole, in agreement with a value of 236 kcal/mole reported for $C_8H_9^+$ from mesitylene (13). Both these sets are much higher than the value of 202 ± 3 kcal/mole derived from the directly measured ionization potentials of the xylyl radicals (14) and from the appearance potential of $C_8H_9^+$ from the xylylbromides (7). In the latter case it was suggested, from the absence of observable substituent orientation effects, that the $C_8H_9^+$ ion had the methyltropylium structure. If such is the case the $C_8H_9^+$ formed by dissociation of the alkylbenzenes and spiroheptadienes must be formed with excess energy which, in contrast with the results for $C_7H_7^+$ formation, varies with the compound studied.

The appearance potential of $C_8H_9^+$ from 2,5-dimethyl-1,5-hexadien-3-yne leads to $\Delta H_f(C_8H_9^+) = 252$ kcal/mole. One would expect this to correspond to an acyclic ion and the heat of formation is indeed considerably higher than that obtained from any of the cyclic isomers. However, since the total spread in values for $\Delta H_f(C_8H_9^+)$ is rather large it is probably premature to reach any definite conclusions in the absence of more conclusive evidence.

The similarity in behavior of the spiro compounds and the alkylbenzenes upon electron impact is shown further by comparison of the spectra of deuterium labelled methylspiroheptadienes and labelled alkylbenzenes (particularly *p*-xylene (6)). Two deuterium-labelled spiro compounds methyl-d_3-spiroheptadiene and methylspiroheptadiene-6,6,7,7-d_4 were studied. In both cases spectra were obtained for mixtures of the 1- and 2-methyl-substituted isomers. Partial mass spectra in the C_8 and C_7 region are given in Table IV. The spectra are corrected for naturally occurring ^{13}C.

TABLE IV

Partial mass sepctra of 1- and 2-methylspiroheptadienes

	Methylspiroheptadiene				Methylspiroheptadiene		
m/e	d_0	Methyl-d_3	6,6,7,7-d_4	*m/e*	d_0	Methyl-d_3	6,6,7,7-d_4
110			36.26	102	1.06		
109		36.10	13.93	95			43.88
108		15.82	7.06	94		30.57	12.50
107		6.16	2.97	93		10.52	22.58
106	35.64	2.96	3.00	92		11.30	12.56
105	21.02	3.96	1.80	91	100.0	51.12	2.39
104	1.34	1.28		90	0.57	0.69	0.46
103	7.10			89	2.00	0.99	

The C_8 region is formed from the parent ion with essentially complete scrambling of the deuterium and hydrogen just as in *p*-xylene (6). There is a preference for loss of H over loss of D, probably due to an isotope effect. The loss of D compared with the total loss of hydrogen and deuterium from the parent is 26% and 32% in the d_3- and the d_4-compound respectively compared with calculated percentages of 30% and 40% assuming complete scrambling and no isotope effect. The ratios are corrected for a small contribution for loss of H_2 which gives a peak at the same mass as loss of deuterium.

As is the case for *p*-xylene (6), the loss of methyl from the methylspiroheptadienes is a very complicated process as shown by the large intensities at *m/e* 91 to 94 in the d_3-compound and 92 to 95 in the d_4-compound. The labelling results clearly are not in accord with a simple loss of the CH_3 group and indeed they cannot be explained by any simple fragmentation scheme. Low energy scans in the C_7 region for the methylspiroheptadiene-d_4 suggested that there is more than one process for the loss of methyl from the parent ion. With lower energy the intensity at $m/e = 95$ ($C_7H_3D_4^+$) decreases with respect to 92, 93, and 94. It is interesting to note that although the 95 peak corresponds to straight loss of the original methyl group and is the biggest peak in the spectrum; it is energetically the least favored process for loss of methyl. Combining the data at 50 V for the two deuterated spectra the percentages given in Table V can be assigned to the loss of CH_3 containing hydrogen from different parts of the molecule. H_m stands for hydrogen from the original methyl group, H_r for hydrogen from the five-membered ring, and H_s for hydrogen from the three-membered ring. The solution is given between two limiting values because it was not possible to solve the equations completely. $CH_mH_rH_s + CH_rH_rH_s = 2.56\%$ and this gives the limits $CH_mH_rH_s = 2.56\%$ and $CH_rH_rH_s = 2.56\%$. Because there are probably different processes with slightly different energy requirements it is not possible to propose any general reaction mechanism but it might be noted that the results indicate a high degree of mixing of the methyl hydrogens and three-membered ring hydrogens ($CH_mH_sH_s$ and $CH_mH_mH_s$).

As mentioned previously the structure of the $C_8H_9^+$ ion is not certain. A methyl-substituted tropylium structure has been proposed for the $C_8H_9^+$ ion formed by dissociative

TABLE V

Loss of methyl from 1- and 2-methylspiroheptadiene between two limiting values

Methyl group	% loss	Methyl group	% loss
$CH_mH_mH_m$	49.40–49.40	$CH_mH_rH_s$	0–2.56
$CH_mH_sH_s$	10.15–7.60	$CH_rH_rH_s$	2.56–0
$CH_rH_sH_s$	13.45–16.00	$CH_mH_rH_r$	0–0
$CH_mH_mH_s$	10.91–10.91	$CH_mH_mH_r$	0–0
$CH_sH_sH_s$	13.53–13.53	$CH_rH_rH_r$	0–0

ionization of the xylylbromides (7), based on the lack of effects due to substituent orientation. Labelling studies (15) on the loss of methyl from *p*-methylethylbenzene are also best explained on the assumption of a methyltropylium structure for the $C_8H_9^+$ ion. However, the results obtained for the further decomposition of the $C_8H_9^+$ ion, both in this work and in previous studies (5), cannot be reconciled with a simple methyltropylium structure for those $C_8H_9^+$ ions which undergo further frgamentation.

The $C_8H_9^+$ ion loses C_2H_2 to form the $C_6H_7^+$ ion which further loses H_2 to form $C_6H_5^+$ as shown from the metastable peaks at 59.4 and 75.1 corresponding to reactions [2] and [3] respectively.

$$C_8H_9^+ \rightarrow C_6H_7^+ + C_2H_2 \tag{2}$$

$$C_6H_7^+ \rightarrow C_6H_5^+ + H_2. \tag{3}$$

These decomposition paths have been observed previously for *p*-xylene (6) and ethylbenzene (16) and it was observed that essentially complete scrambling of the hydrogens in $C_8H_9^+$ occurred in the formation of the C_6 ions. Similar results have been obtained for the labelled methylspiroheptadienes in the present work. Table VI compares the measured intensities in the C_6 region of the labelled methylspiroheptadienes with the intensities calculated assuming complete loss of identity in the precursor $C_8H_9^+$ ion (or deuterated equivalent). The reasonable agreement between measured and calculated intensities indicates that the assumption of complete scrambling is valid and further indicates the similarity of behavior upon electron impact of the spiro compounds and the isomeric alkyl benzenes.

TABLE VI

Mass spectra in the C_6 region for methylspiroheptadienes

		Methyl-d_3		6,6,7,7-d_4				Methyl-d_3		6,6,7,7-d_4	
m/e	d_0	Meas.	Calcd.	Meas.	Calcd.	*m/e*	d_0	Meas.	Calcd.	Meas.	Calcd.
83		0.18	—	1.93	2.40	79	12.72	8.13	8.95	9.31	8.10
82		4.21	3.93	5.24	7.10	78	7.58	6.35	6.89	4.43	3.56
81		8.29	7.99	4.95	6.93	77	15.52	2.00	1.64	1.50	0.58
80	0.14	6.79	7.30	6.04	7.42	76	1.06	1.05	—	0.65	—

In the spectrum of *p*-methylethylbenzene, $C_8H_9^+$ forms the base peak. In the fragmentation forming this ion, loss of both the α-methyl and the β-methyl occurs in the ratio 1:5 as was shown from the spectra of methylethylbenzene-α-methyl-d_3 and -β-methyl-d_3 (15). Both reactions have the same energy requirements and it was concluded that the $C_8H_9^+$ has the same structure in both cases. The mechanism for this reaction is discussed elsewhere (15).

In the spectra of the two deuterated methylethylbenzenes, $C_8H_9^+$ and $C_8H_6D_3^+$ ions are formed which further fragment to form the C_6 ions. In *p*-methyl-d_3-ethylbenzene, metastable peaks for reactions [4], [5], and [6] are observed.

[4] $C_8H_6D_3^+ \rightarrow C_6H_4D_3^+ + C_2H_2$, metastable 62.3

[5] $C_8H_6D_3^+ \rightarrow C_6H_5D_2^+ + C_2HD$, metastable 60.8

[6] $C_8H_6D_3^+ \rightarrow C_6H_6D^+ + C_2D_2$, metastable 59.4.

The metastable peak at mass 59.4 also corresponds to reaction [2]. In *p*-methylethyl-β,β,β-d_3-benzene only the metastable peak at 59.4 was observed because of the much lower intensity of the $C_8H_6D_3^+$ ion. Calculations based on complete scrambling of the hydrogen and deuterium atoms in $C_8H_6D_3^+$ in forming the C_6 region are in reasonable agreement with the measured intensities as shown in Table VII. In Table VII are given also the major peaks in the spectra of the two deuterated methylethylbenzenes and the corresponding intensities in methylethylbenzene-d_0.

TABLE VII

Partial mass spectra of *p*-methylethylbenzenes

		Methylethylbenzene						Methylethylbenzene			
		Methyl-d_3		Ethyl-β,β,β-d_3				Methyl-d_3		Ethyl-β,β,β-d_3	
Mass	d_0	Meas.	Calcd.	Meas.	Calcd.	Mass	d_0	Meas.	Calcd.	Meas.	Calcd.
123		38.8		35.5		80		3.25	3.52	1.35	0.68
120	36.9					79	10.50	7.86	7.12	8.47	8.45
108		100.0		20.0		78	4.23	4.66	4.58	4.51	3.70
105	120.0	18.9		100.0		77	14.49	3.74	2.78	9.04	10.27
82		2.90	3.16	0.70	0.61	76	0.83	0.48	0.18	0.68	0.58
81		4.13	4.53	1.20	0.87						

The above evidence indicates that, for those $C_8H_9^+$ ions which have sufficient internal energy to undergo further decomposition, a simple methyltropylium structure is not adequate since all hydrogens and also all carbons (6) become equivalent. It is possible to accommodate the results by postulating a number of isomerizations from a tropylium to a benzyl structure accompanied by hydrogen shifts or alternatively by expansion to an eight-membered ring with a number of intramolecular hydrogen shifts before decomposition.

Estimation of Heats of Formation

ΔH_f(7-mecylcoheptatriene) has been previously estimated (12) to be 37.2 kcal/mole using Franklin's group equivalent method (17). By the same method ΔH_f(spiro[2.4]-heptal,3-diene) can be calculated as follows using $\Delta H_f(\text{cyclo-}C_5H_6) = 31.9$ kcal/mole (18). $\Delta H_f(\text{spiroheptadiene}) = \Delta H_f(\text{cyclo-}C_5H_6) - \Delta H_f(\text{—}CH_2\text{—}) + \Delta H_f(\text{—}\overset{|}{\underset{|}{C}}\text{—}) + 2\Delta H_f(\text{—}CH_2\text{—}) + (\text{correction for cyclopropane ring}) = 52.0$ kcal/mole. In a similar manner values of 44.1 kcal/mole and 45.4 kcal/mole for the 1- and 2-methyl- and the 6-methylspiroheptadienes were obtained. By Franklin's method ΔH_f(2,5-dimethyl-1,5-hexadien-3-yne) = 68.2 kcal/mole. The heats of formation of *m*-xylene, ethylbenzene, and *p*-methylethylbenzene necessary for the calculations of Table III were taken from the literature (18).

ACKNOWLEDGMENTS

The authors are indebted to the National Research Council and to the Alfred P. Sloan Foundation for financial support.

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