

Studies in Mass Spectrometry. I. Mass Spectra of Substituted Naphthoquinones

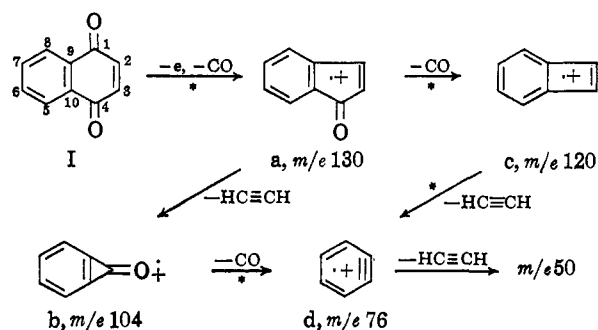
J. H. Bowie, D. W. Cameron, and D. H. Williams

Contribution from the University Chemical Laboratory, Cambridge University, Cambridge, England. Received May 28, 1965

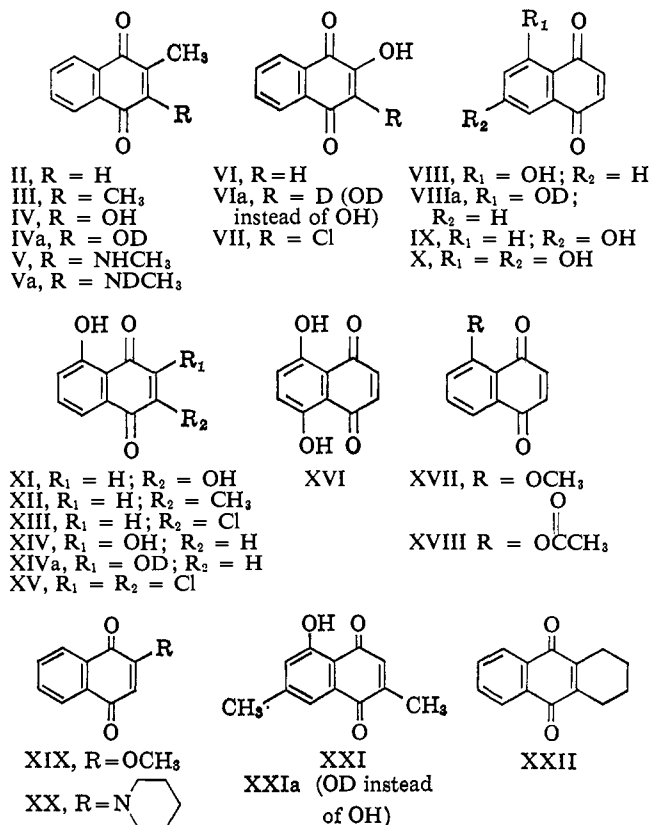
The mass spectra of 21 substituted naphthoquinones are reported and discussed. The characteristic fragmentation and rearrangement processes, substantiated in most cases by appropriate metastable peaks and/or deuterium labeling, greatly facilitate the location of substituents in the bicyclic system.

Naphthoquinone (I) breaks down in a well-defined manner upon electron impact,¹ and plausible struc-

Scheme I^a



^a Transitions indicated by an asterisk are supported by the presence of an appropriate metastable peak.

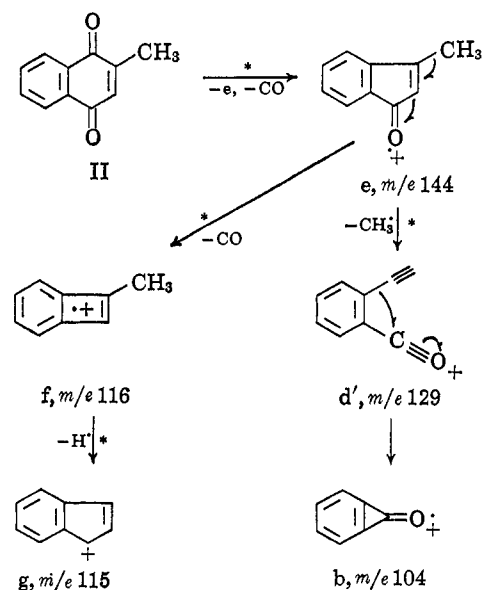


(1) J. H. Beynon and A. E. Williams, *Appl. Spectry.*, **14**, 156 (1960).

tures can be assigned to the most abundant fragment ions (see Scheme I and also Table I). The mass spectra of 21 substituted naphthoquinones (II-XXII), reported by us in this paper, indicate that the essential features of the breakdown of I are preserved in the spectra of the substituted derivatives. Details of the spectra are summarized in Figures 1 and 2 and Table I; in the table all ions having an abundance greater than 5% of that of the base peak (arbitrarily taken as 100%) are recorded.

The mass spectra of 2-methylnaphthoquinone (II) and 2,3-dimethylnaphthoquinone (III) are much as expected. In the case of the 2-methyl derivative (II), the loss of a methyl radical is more pronounced from the $M - CO$ fragment (e , m/e 144) than from the molecular ion, and may be represented by $e \rightarrow d'$ (m/e 129).² Most important, the presence of the abundant m/e 104 ion (b), and its decomposition products m/e 76 (d) and m/e 50, substantiates the location of the methyl group at C-2 rather than on the benzene ring. An abundant species f (m/e 116) is formed by elision of two carbon monoxide molecules from the molecular ion. As expected, the odd-electron species f decomposes by loss of a hydrogen radical to afford m/e 115, most plausibly represented as the benzocyclopentadienyl cation g formed by ring expansion (Scheme II).

Scheme II

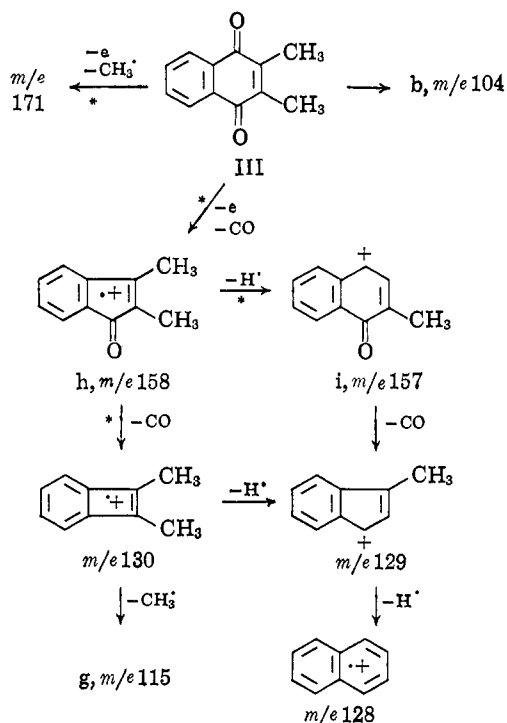


In the spectrum of the 2,3-dimethyl compound (III), in addition to the loss of a methyl radical both from the $M - CO$ ion (h , m/e 158) and directly from the molecular ion, to furnish m/e 143 and m/e 171, respectively, there is appreciable expulsion of a hydrogen

(2) In the plausible fragmentation sequences given for asymmetric quinones, the choice of CO group which is expelled is purely arbitrary.

radical from h to afford m/e 157. This last process obviously reflects the presence of two methyl groups in h from which a hydrogen radical may be lost to give an even-electron ion (e.g., i). Some of the decomposition processes, many of which are supported by the presence of metastable peaks, are summarized in Scheme III; exact mass measurements substantiate the composition of all these fragment ions. Once more the appearance of an abundant m/e 104 ion (b) and its characteristic decomposition products establishes the absence of 5-, 6-, 7-, or 8-substituents.

Scheme III

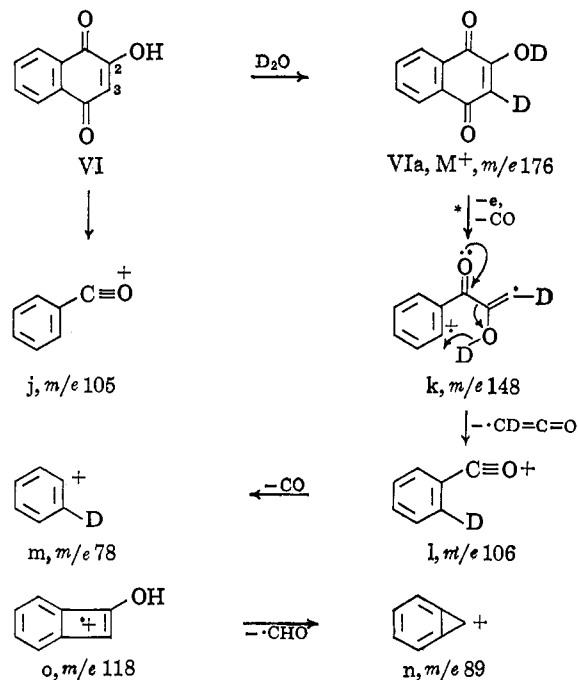


The spectra of naphthoquinones containing a C-2 or C-3 hydroxyl substituent (e.g., IV, VI, VII, and XIV) are noteworthy for a highly characteristic hydrogen rearrangement which results in a partial or almost total shift of the m/e 104 ion b, encountered in the spectra hitherto discussed, to m/e 105, corresponding to the benzoyl ion j. If the spectrum of 2-hydroxynaphthoquinone (lawsone, VI) is determined after introduction of a small quantity of deuterium oxide into the heated inlet system of the spectrometer,³ the molecular ion then occurs at m/e 176, corresponding to the predominant d_2 -species VIa. Evidently the C-3 hydrogen atom is activated towards replacement by deuterium through equilibration with the tautomeric trione. As may be anticipated, m/e 105 shifts to m/e 106 in the spectrum of VIa, but this compound cannot be utilized to distinguish between hydrogen rearrangement from the C-2 hydroxyl group and rearrangement of the C-3 hydrogen, even though the former seems *a priori* more likely. However, in the spectrum of O- d_1 -2-hydroxy-3-methylnaphthoquinone (O- d_1 -phthiocol, IVa), obtained by introducing IV into the inlet system with deuterium oxide, the m/e 105 ion of IV is shifted almost quantitatively to m/e 106, establishing the hydroxyl group as the principal source of the rearranged hydrogen. We conclude therefore that the

(3) J. S. Shannon, *Australian J. Chem.*, 15, 265 (1962).

benzoyl ion (j, m/e 105) may in general be formed by rearrangement of the hydroxyl hydrogen in the spectra of various 2-hydroxy- or 3-hydroxynaphthoquinones. A number of appropriate metastable ions indicate that the hydrogen rearrangement occurs in the $M - CO$ ion; a plausible mechanism involving a six-membered cyclic transition state ($k \rightarrow l$) is indicated for d_2 -lawsone (VIa) in Scheme IV. The structures proposed for j and l are strongly supported by their decomposition to the phenyl cation (m/e 77) and d_1 -phenyl cation (m, m/e 78), respectively. In other respects, the decomposition of lawsone (VI) is analogous to that of naphthoquinone (I), except for the formation of a $C_7H_5^+$ ion (m/e 89), which may be formulated as the benzocyclopropenyl cation (n) arising via the elimination of a formyl radical from the $M - 2CO$ ion (o, m/e 118). Finally, before leaving our discussion of the rearrangement typified by $k \rightarrow l$, it should be noted that the increasing ratio of m/e 105 to m/e 104 on progressive substitution of C-2 and C-3 by a methyl group (see spectra of II and III in Table I) is evidence that an analogous but less preponderant rearrangement of a methyl hydrogen may operate in these cases.

Scheme IV^a



^a The composition of all fragment ions which are considered have been established by exact mass measurements.

The isomeric compounds 2-hydroxy-3-methylnaphthoquinone (phthiocol, IV) and 2-methyl-5-hydroxynaphthoquinone (plumbagin, XII) may of course be readily differentiated by the presence of the abundant m/e 105 ion present only in the spectrum of the former. The far more abundant $M - CH_3$ ion (m/e 173) derived from XII relative to IV (22% and <1% of molecular ion base peak, respectively) also serves to differentiate these isomers, although the cause of this difference in behavior is not readily apparent. In general, the presence of a hydroxyl group in the benzenoid ring of XII, VIII, IX, XI, XIII, XIV, and XV is indicated by the presence of a prominent m/e 120 ion (p) in their spectra which breaks down to the hydroxybenzyl

Table I. Mass Spectra of Naphthoquinone (I) and Substituted Naphthoquinones (II-XXII)^a

Compd.																				
I	<i>m/e</i>	50	51	66	74	75	76	77	102	104	105	130	131	158 (M)	159					
	<i>I, %</i>	23	12	6	12	14	40	6	39	46	7	40	6	100	11					
II	<i>m/e</i>	39	50	51	63	74	75	76	77	104	105	115	116	129	144	145				
	<i>I, %</i>	15	21	8	7	13	15	48	12	60	16	41	40	6	54	6				
		172 (M)	173	14																
III	<i>m/e</i>	50	51	75	76	77	104	105	115	128	129	130	143	157	158	171				
	<i>I, %</i>	8	6	5	20	7	27	12	12	9	13	8	6	13	20	5				
		186 (M)	187	16																
IV	<i>m/e</i>	50	51	55	76	77	78	103	104	105	115	131	132	133	159	160				
	<i>I, %</i>	11	8	7	13	15	6	6	10	18	6	20	18	8	6	16				
		161	188 (M)	189																
IVa	<i>m/e</i>	76	77	78	103	104	105	106	131	132	133	134	160	161	188					
	<i>I, %</i>	18	16	14	6	14	18	21	8	28	21	6	9	15	34					
		189	190	$(d_0 = 25, d_1 = 73, d_2 = 2\%)$																
V	<i>m/e</i>	50	51	52	74	75	76	77	90	103	104	105	115	116	128	130				
	<i>I, %</i>	10	7	6	6	8	24	20	7	9	13	13	29	14	6	8				
		131	132	143	144	145	158	159	160	161	172	186	199	200	201 (M)					
Va ^b	<i>m/e</i>	50	51	76	77	78	104	105	115	116	131	132	133	144	145	160				
	<i>I, %</i>	6	5	9	7	5	8	10	8	11	7	11	6	6	28	20				
		161	173	187	200	201	202 (M)	203												
VI	<i>m/e</i>	50	51	59	63	69	73	74	75	76	77	89	90	104	105	106	118			
	<i>I, %</i>	18	8	8	6	11	7	10	10	20	27	18	12	11	82	11	11			
		146	174 (M)	175																
VIa	<i>m/e</i>	50	51	52	60	63	64	70	74	75	76	77	78	90	91	104	105			
	<i>I, %</i>	8	8	8	6	6	6	8	10	8	29	14	22	8	7	11	37			
		106	107	147	148	174	175	176	177	$(d_0 = 7, d_1 = 38, d_2 = 55\%)$										
VII	<i>m/e</i>	76	77	104	105	145	173	180	181	182	208 (M)			209	210	211				
	<i>I, %</i>	21	13	16	12	24	30	41	11	19	100	21	40	10						
VIII	<i>m/e</i>	37	38	39	45	50	51	53	54	59	61	62	63	64	65	74	75	77		
	<i>I, %</i>	12	16	21	14	20	19	22	8	13	19	34	66	31	8	14	10	10		
		83	85	89	90	91	92	102	118	119	120	121	146	147	173	174 (M)				
VIIIa	<i>m/e</i>	18	13	33	25	10	67	7	89	15	60	7	37	7	35	100				
	<i>I, %</i>	62	63	64	65	89	90	91	92	93	118	119	120	121	122	146	147			
		14	25	18	7	8	9	8	26	18	32	21	34	28	6	14	10			
IX	<i>m/e</i>	50	51	63	64	91	92	118	120	146	174 (M)			175	176					
	<i>I, %</i>	7	6	13	11	7	19	24	30	18	100	17	17							
		148	173	174	175	176	177	178	179	$(d_0 = 52, d_1 = 28, d_2 = 10, d_3 = 7; d_4 = 3\%)$										
X	<i>m/e</i>	50	51	53	61	62	63	69	77	78	79	105	108	134	135	136	161			
	<i>I, %</i>	12	31	12	7	12	13	36	11	10	7	9	34	52	6	44	6			
		162	189	190 (M)																
XI	<i>m/e</i>	36	7	100	13															
	<i>I, %</i>	92	105	106	120	121	122	134	162	188	190 (M)			191	192					
		8	24	8	14	42	11	12	18	10	100	29	6							
XII	<i>m/e</i>	39	51	63	64	77	92	120	121	131	132	145	160	173	174	188 (M)				
	<i>I, %</i>	8	6	10	6	8	14	18	14	18	13	6	18	22	6	100				
		189																		
XIII	<i>m/e</i>	53	62	63	74	89	92	95	145	146	152	173	174	180	208 (M)					
	<i>I, %</i>	12	12	18	8	17	17	11	58	6	14	48	39	22	100					
		209	210	211																
XIV	<i>m/e</i>	39	43	51	53	57	60	62	63	64	65	69	73	78	87	92	93	105		
	<i>I, %</i>	8	8	9	7	7	9	10	14	9	9	13	8	7	7	18	14	14		
		106	120	121	134	162	163	190 (M)	191											
XIVa	<i>m/e</i>	6	40	65	15	29	6	100	33	68	69	70	71	73	74	75	76	77		
	<i>I, %</i>	19	21	17	22	21	16	10	21	12	34	18	27	22	27	15	22	52		
		78	79	80	81	82	83	84	85	87	89	91	92	93	94	95	96	97		
	22	16	10	20	13	22	11	16	11	11	21	18	26	18	15	10	12			
	98	104	105	106	107	120	121	122	123	135	136	137	163	164						
	11	10	66	28	11	31	54	69	64	10	14	11	18	23						
	165	190	191	192	193	194	195	196	$(d_0 = 7, d_1 = 25, d_2 = 36, d_3 = 23, d_4 = 5, d_5 = 3\%)$											
	18	20	61	100	69	21	11	7												

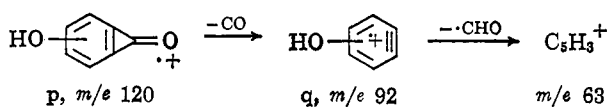
Table I (Continued)

Compd.																		
XV	<i>m/e</i>	36	40	53	54	61	62	63	73	74	87	92	97	116	120	123	125	
	<i>I, %</i>	19	16	9	9	15	18	24	7	14	15	14	8	9	8	18	6	
XVI	<i>m/e</i>	179	180	181	207	208	209	242 (M)		243	244	245	246					
	<i>I, %</i>	45	10	15	100	13	34	100		15	60	9	10					
XVII	<i>m/e</i>	108	134	136	189	190 (M)		191										
	<i>I, %</i>	11	8	6	34	100		12										
XVIII	<i>m/e</i>	39	44	50	51	62	63	74	75	76	77	89	91	102	103			
	<i>I, %</i>	9	6	9	6	12	16	9	19	38	7	7	8	37	9			
XIX	<i>m/e</i>	104	105	114	130	131	132	133	142	159	160	170	171					
	<i>I, %</i>	35	9	16	27	20	8	7	7	19	9	11	7					
XX	<i>m/e</i>	188 (M)		189	190													
	<i>I, %</i>	100		16	7													
XXI	<i>m/e</i>	42	43	44	63	92	118	120	146	173	174	175	216 (M)					
	<i>I, %</i>	12	14	18	6	7	12	10	7	15	100	13	6					
XXII	<i>m/e</i>	50	51	63	69	74	75	76	77	89	101	102	104	105	130	131		
	<i>I, %</i>	15	7	7	15	8	10	22	7	46	7	38	10	6	9	7		
XXIII	<i>m/e</i>	158	159	173	188 (M)		189	190										
	<i>I, %</i>	36	20	39	100		15	7										
XXIV	<i>m/e</i>	41	42	50	51	52	53	54	55	56	57	63	67	68	69	74	75	76
	<i>I, %</i>	15	8	20	18	10	8	6	16	10	6	6	6	7	6	14	20	40
XXV	<i>m/e</i>	77	78	79	80	82	83	84	85	89	101	102	103	104	105	115	128	
	<i>I, %</i>	16	14	8	6	7	10	34	6	12	19	44	9	36	15	10	6	
XXVI	<i>m/e</i>	129	130	131	146	156	157	158	159	172	184	185	186	198	200			
	<i>I, %</i>	11	16	8	8	6	8	28	6	11	14	12	13	10	6			
XXVII	<i>m/e</i>	212	224	236	239	240	241 (M)		242									
	<i>I, %</i>	16	6	8	17	26	100		21									
XXVIII	<i>m/e</i>	50	51	52	63	77	105	106	131	134	135	145	146	159	174			
	<i>I, %</i>	6	8	6	6	12	6	12	10	14	12	12	10	5	24			
XXIX	<i>m/e</i>	187	202 (M)		203													
	<i>I, %</i>	23	100		15													
XXX	<i>m/e</i>	50	51	52	69	77	78	79	106	107	132	134	135	136	145	146		
	<i>I, %</i>	6	9	7	6	9	11	6	9	10	9	10	24	14	7	12		
XXXI	<i>m/e</i>	147	174	175	176	187	188	189	202	203	204	205	206					
	<i>I, %</i>	11	11	20	6	11	24	10	53	100	44	19	7					
XXXII	<i>m/e</i>	(<i>d</i> ₀ = 24, <i>d</i> ₁ = 48, <i>d</i> ₂ = 17, <i>d</i> ₃ = 8, <i>d</i> ₄ = 3%)																
	<i>I, %</i>	50	51	76	77	104	105	115	128	133	141	152	165	180	183	194		
XXXIII	<i>m/e</i>	6	6	12	11	8	17	6	6	6	5	9	9	8	8	7		
	<i>I, %</i>	195	197	208	211	212 (M)		213										
XXXIV	<i>m/e</i>	9	32	11	14	100		17										
	<i>I, %</i>																	

^a All ions having an abundance greater than 5% of that of the base peak (arbitrarily taken as 100%) are recorded. ^b This spectrum corresponds to the N-d₁ derivative; the spectrum of unlabeled material has been removed by subtraction.

ion radical (q, *m/e* 92, Scheme V). The latter fragment appears to decompose consistently by expulsion of a formyl radical to give the C₅H₃⁺ cation (*m/e* 63). Except for the formation of *m/e* 63, 5-hydroxynaphthoquinone (juglone, VIII) and 6-hydroxynaphthoquinone (IX) fragment analogously to naphthoquinone (I) itself.

Scheme V



Of the isomeric dihydroxynaphthoquinones X, XI, XIV, and XVI, naphthazarin (XVI) is unusual, its spectrum exhibiting an abundant molecular ion and very little fragmentation (Table I); this behavior reflects the stabilization of the naphthazarin system by hydrogen bonding and resonance. However, the fragmentation which does occur is of the expected type leading to the dihydroxybenzyne ion r (*m/e* 108). The qualitatively similar, but quantitatively much more pronounced decomposition of 5,7-dihydroxynaphthoquinone (X) is illustrated in Figure 1. Comparison of this spectrum with that (Figure 2) of 2,5-dihydroxynaphthoquinone (XI) clearly illustrates the useful generalization that a "doublet" at M - 54 and M - 56

is characteristic of a 2,3-unsubstituted naphthoquinone; in these cases, the nature and number of substituents on the benzene ring can readily be inferred from the M - 82 peak (M - 2CO - HC≡CH) and its decomposition products. It is noteworthy that although the M -

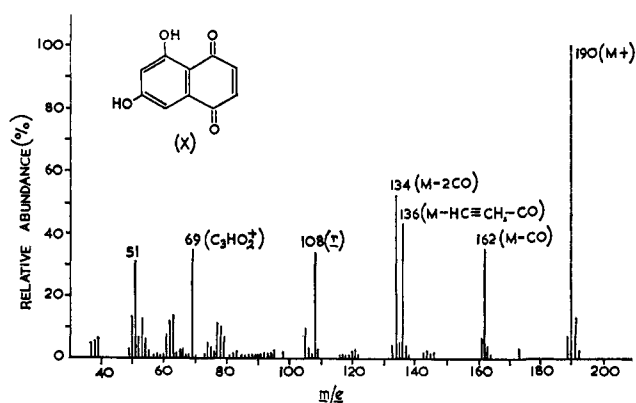


Figure 1. Mass spectrum of 5,7-dihydroxynaphthoquinone (X).

CO and M - 2CO peaks in the spectra of naphthoquinones containing phenolic hydroxyl groups could in principle arise in part *via* expulsion of a carbon monox-

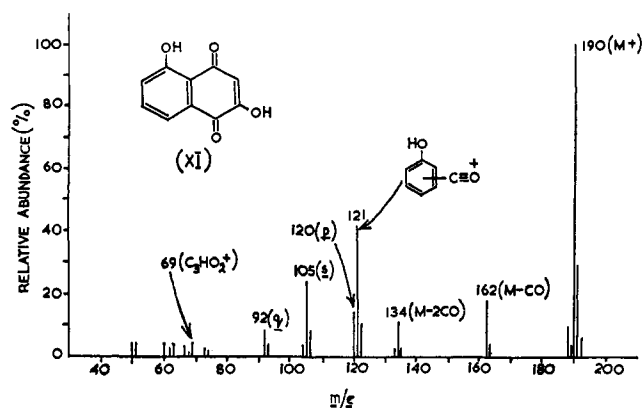
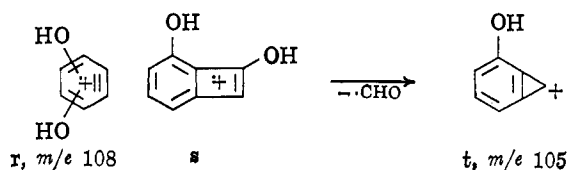


Figure 2. Mass spectrum of 2,5-dihydroxynaphthoquinone (XI).

ide molecule from the phenolic ring,⁴ such processes do not appear important. For example, the m/e 134 ion in the spectrum (Figure 2) of XI is preferably formulated as s, since it decomposes to t (m/e 105) in a manner analogous to the fragmentation of its deoxy analog (see $o \rightarrow n$). The formulation of m/e 105 as t rather than as the isobaric benzoyl ion j seems secure in the absence of an m/e 77 ion (phenyl cation) in the spectrum (Figure 2) of XI.

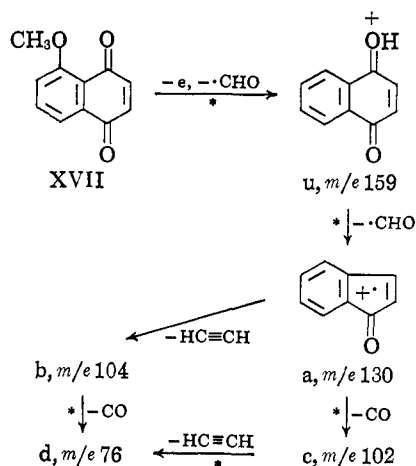


The spectra of the three chloronaphthoquinones (VII, XIII, and XV) are particularly amenable to analysis due to the characteristic abundances of the two chlorine isotopes (^{35}Cl : $^{37}\text{Cl} \approx 3:1$). In all cases loss of a chlorine radical from the molecular ion or the $M - \text{CO}$ ion is pronounced (see Table I). Conversely a carbon monoxide molecule may be expelled from the molecular ion or the $M - \text{Cl}$ species, but ions corresponding to $M - 2\text{CO} - \text{Cl}$ are negligible in all three chloro compounds. $M - 2\text{CO}$ species are not detectable except in the spectrum of 2-chloro-5-hydroxynaphthoquinone (XIII) in which this species constitutes 14% of the base peak [m/e 152 ion (see Table I) corresponding to ^{35}Cl isotope]. All these processes are confirmed by appropriate metastable ions.

5-Methoxynaphthoquinone (XVII) was prepared by methylation of the hydroxy compound (VIII) with methyl iodide and silver oxide. The product contained traces of a dihydrojuglone methyl ether (as evidenced by peaks at m/e 190 and m/e 175 in its mass spectrum) which could be removed by column chromatography under nitrogen in the dark and crystallization of the purest fraction from carbon tetrachloride. In the mass spectrum of XVII, the expulsion of a formyl radical from the molecular ion is observed to afford m/e 159, represented as the protonated naphthoquinone u (Scheme VI). Elimination of a second formyl radical furnishes m/e 130, the representation of which as a is consistent with its usual breakdown to m/e 104 (b), m/e 102 (c), and m/e 76 (d).

(4) Cf. behavior of simple phenols: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1964, pp. 167, 168.

Scheme VI

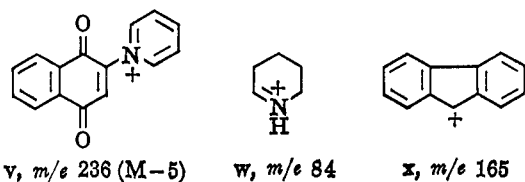


The isomeric 2-methoxynaphthoquinone (XIX) behaves very differently. The spectrum contains abundant $M - \text{CH}_3$ (m/e 173) and $M - \text{CH}_2\text{O}$ (m/e 158) ions. The latter decomposition occurs in part with formation of the naphthoquinone molecular ion as evidenced by the characteristic $a \rightarrow b \rightarrow d$ and $a \rightarrow c \rightarrow d$ sequences which are apparent in the spectrum of XIX and supported by appropriate metastable ions. Thus in the methyl ethers XVII and XIX, the initial fragmentation involves the methoxyl groups and the naphthoquinone skeleton is only broken subsequently. An additional noteworthy feature of the spectrum of XIX is the presence of an m/e 69 ion (C_3HO_2^+), which appears in the spectra of all the naphthoquinones (VI, X, XI, XIV, and XIX) containing the (O—C—C—O) unit. A plausible structure for this fragment is $\text{O}=\text{C}=\text{CH}-\text{C}\equiv\text{O}^+$.

The spectra of the aminonaphthoquinones which have been examined show some interesting features. The relatively abundant $M - 5$ species (6% of base peak) in the spectrum of 2-piperidinonaphthoquinone (XX) corresponds to the pyridinium ion v; similar behavior is exhibited by a number of simpler pyrrolidine and piperidine enamines.⁵ The $M - 29$ (m/e 212) and $M - 43$ (m/e 198) fragments are associated with the well-studied breakdown⁶ of the piperidine ring system upon electron impact. Elimination of the C-2 substituent occurs with concomitant hydrogen rearrangement to the quinone ring and the naphthoquinone molecular ion so formed breaks down as usual. The m/e 84 ion is due to the immonium ion w. Interpretation of the spectrum of 2-methyl-3-methylaminonaphthoquinone (V) has been aided by the spectrum of the $N-d_1$ derivative Va. The $M - \text{CHO}$ ion (m/e 172), whose composition has been determined by high resolution measurements, retains deuterium in the spectrum of Va and therefore the hydrogen atom lost in this process is almost certainly one of those from the methyl groups. The $M - \text{C}_2\text{H}_3\text{N}$ ion (m/e 160) in the spectrum of V does not retain the deuterium atom in the spectrum of Va. The cleavage must involve therefore a hydrogen transfer from the N-methyl group to the ring system, but the process must be rather complex.

(5) J. T. B. Marshall and D. H. Williams, unpublished work.

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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.

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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 explained⁴ 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 suggested⁹ that the major fragment ions from benzene itself are acyclic.

The lack of positional effects in the spectra of the methylcyclopentadienes coupled with the observation¹⁰ 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.

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(1) Alfred P. Sloan Fellow, 1962-1964.
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