Electron Impact-induced Rearrangements of Natural Polyacetylenes

By R. T. APLIN and S. SAFE
(*The Dyson Perrins Laboratory, Oxford University*)

DURING the past two years mass spectrometry has found useful application in the elucidation of the structures of natural polyacetylenes. However, in general the information obtained from the mass spectra of polyacetylenes concerns only the molecular ion and the fragmentation of the non-acetylenic portion of the molecule.[1,2] Current work in this laboratory and earlier results have confirmed that cleavage between triple bonds is an unfavourable process. The mass spectra† of a number of straight chain and terminal phenyl polyacetylenes (I—XIII) have revealed structurally significant fragmentation patterns.

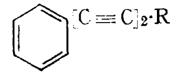
$CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}[CH\overset{t}{=}CH)_2{\cdot}R$ (I) R = CH_2OH; (II) R = CHO;

(III) R = $[CH_2]_2{\cdot}CH_2OH$; (IV) R = $CH{:}CH_2$

$CH_3{\cdot}[C{\equiv}C]_3{\cdot}[CH\overset{t,t}{=}CH]_2{\cdot}R$ (V) R = CH_2OH; (VI) R = $[CH_2]_2{\cdot}CH_2OH$

$CH_3{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}CH\overset{t}{=}CH{\cdot}R$ (VII) R = CH_2OH

$CH_3{\cdot}[C{\equiv}C]_3{\cdot}CH\overset{t}{=}CH{\cdot}R$ (VIII) R = CH_2OH



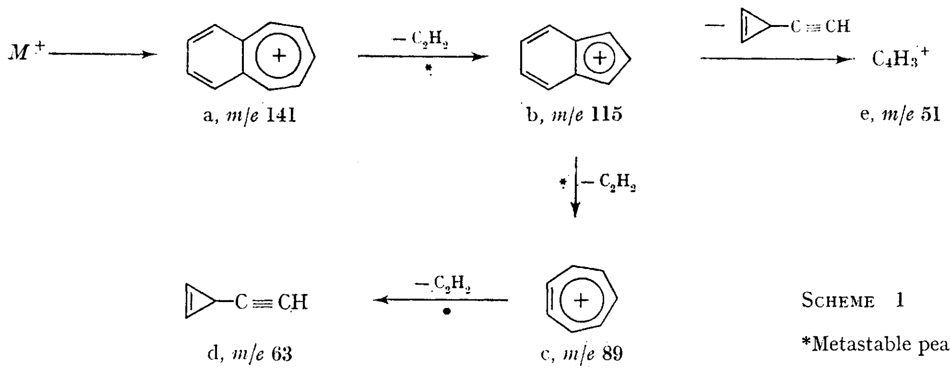
$[C{\equiv}C]_2{\cdot}R$ (IX) R = $CH\overset{t}{=}CH{\cdot}CH_2OH$; (X) R = $CHOH{\cdot}CHOH{\cdot}CH_2OH$;

(XI) R = $CHOH{\cdot}CHOH{\cdot}CH_3$*

$HC{\equiv}C{\cdot}[CH\overset{t,t}{=}CH]_2{\cdot}R$ (XII) R = CH_2OH; (XIII) R = CHO

* *threo*- and *erythro*-Isomers.

The compounds (I—VI) containing either the ene-diyne-diene or triynediene chromophores typical of many natural polyacetylenes[3] exhibit a common fragmentation pathway (Table 1). A possible rationalisation of these fragments is shown in Scheme 1.



SCHEME 1

*Metastable peak observed

The fragment (a) is formed by cleavage at the C–R bond (I—VI). This process is accompanied by an intense metastable ion for the lower-molecular-weight compounds (I, II, and V). For both the triyne-diene and ene-diyne-diene alcohols (I and V) hydrogen transfer occurs from the R portion indicated by the formation of the fragment (b) at *m/e* 116 in the mass spectra of the deuterated (CHDOH) compounds. The type of fragmentation depicted in Scheme 1 is reminiscent of that of α- and β-methylnaphthalenes (Table 1), which are known to be fragmented with loss of a proton and rearrangement to give the species (a) which then eliminates acetylene to give the species (b).[4,5] The fragments observed below *m/e* 115 from the compounds (I—VI) are virtually identical to those observed in the spectra of α- and β-methylnaphthalenes, although some differences in the relative intensities are observed (Table 1).

The fragmentation of the C_{10} polyacetylenes (VII, VIII, Scheme 2) bears a similar relationship to that of indene (Table 2).

$$\begin{tikzcd}
M^+ \arrow[r, "*"'] & \text{b}, m/e\ 115 \arrow[r, "-C_5H_4", "*"'] \arrow[d, "*"', "-C_2H_2"] & \text{e}, m/e\ 51 \\
 & \text{c}, m/e\ 89 \arrow[r, "-C_2H_2", "*"'] & \text{d}, m/e\ 63
\end{tikzcd}$$

SCHEME 2

---

† The spectra were determined on an A.E.I. MS9 mass spectrometer using a direct insertion probe with a source block temperature of 60—110°. The elemental compositions of the ions discussed were determined by high-resolution measurements.

TABLE 1

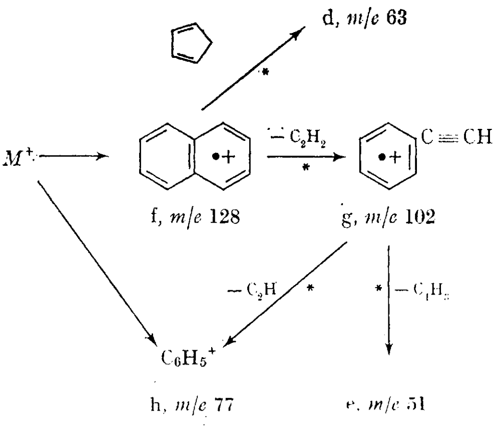
	M^+	%	a m/e 141	b m/e 115	c m/e 89	d m/e 63	e m/e 51
			%	%	%	%	%
α-Methylnaphthalene ..	142	100	52	25	5	6	4
β-Methylnaphthalene ..	142	100	62	25	2	6	4
(I)	172	95	29	86	15	21	18
(II)	170	29	100	100	27	55	32
(III)	200	79	82	100	20	30	27
(IV)	168	100	10	32	10	7	15
(V)	170	100	62	67	10	16	10
(VI)	198	82	37	48	18	5	15

TABLE 2

	M^+	%	b m/e 115	c m/e 89	d m/e 63	e m/e 51
			%	%	%	%
Indene	116	100	78	13	17	6
(VII)	146	100	35	14	17	14
(VIII)	144	100	83	12	13	6

TABLE 3

	M^+	%	f m/e 128	g m/e 102	h m/e 77	d m/e 63	e m/e 51
			%	%	%	%	%
Naphthalene	128	100	100	12	4	6	9
(IX)	182	35	45	12	24	24	27
(X)	216	12	51	16	25	6	5
(XI) *threo*	200	15	81	28	27	5	10



SCHEME 3

The phenyl compounds (IX, X, and XI) fragment as shown in Scheme 3 (Table 3), the fragments below *m/e* 128 resembling those of naphthalene.

The most striking similarity of acetylene and aromatic compound fragmentation pattern is provided by the mass spectrum of (XII) which is virtually identical to that of benzyl alcohol.[5]

The remarkable correspondence between the mass-spectral fragmentation patterns of the compounds (I—XIII) and other related acetylenes‡ to those of various aromatic compounds strongly supports the suggestion that, under electron impact, rearrangement occurs to stable aromatic species of the type depicted in Schemes 1—3.§

These very characteristic fragmentations are currently being used in the elucidation of the structures of natural polyacetylenes.

(*Received, December 16th,* 1966; *Com.* 1004.)

---

‡ Unpublished results.

§ Detailed discussion of the fragmentations will be the subject of a further publication.

[1] S. C. Cascon, W. B. Mors, B. M. Tursch, R. T. Aplin, and L. J. Durham, *J. Amer. Chem. Soc.*, 1965, **87**, 5237.

[2] Sir Ewart R. H. Jones, S. Safe, and V. Thaller, *J. Chem. Soc.* (*C*), 1966, 1220.

[3] F. Bohlmann, *Fortschr. chem. Forsch.*, 1966, **6**, 65; J. D. Bu'Lock, *Progr. Org. Chem.*, 1964, **6**, 86.

[4] H. Heitman, Ph.D. Thesis, University of Amsterdam, 1965.

[5] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, 1964.