THE BEHAVIOUR OF PERCHLORO-3,4-DIMETHYLENE-CYCLOBUTENE, -PENTAFULVENE AND -PENTAFULV-ALENE UNDER ELECTRON-IMPACT*

ISRAEL AGRANAT, RUTH M. J. LOEWENSTEIN and ERNST D. BERGMANN Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

(Received 1 September 1970; accepted 22 November 1970)

Abstract—The mass spectra of 1,2-dichloro-3,4-bis(dichloromethylene)cyclobutene (IV) and of hexachloropentafulvene (II) have been studied. Compound IV cannot be an intermediate in the formation of II from octachloro-1,2-dimethylenecyclobutane (III) under electron-impact, as previously suggested. In the mass spectra of II and IV the species $[C_6]^{+\cdot}$ and $[C_5]^{+\cdot}$ occur, obviously through cleavage of the semicyclic C—C bond.

The mass spectrum of pentachlorofulvalene (VI) shows strikingly that successive elimination of an even number of Cl atoms is preferred over that of an odd number of Cl atoms; probably corresponding C—Cl bonds in the two rings are broken simultaneously. Amongst the fragments, the species $[C_{10}]^{+\cdot}$ and $[C_7]^{+\cdot}$ and possibly also $[C_8]^{+\cdot}$ and $[C_9]^{+\cdot}$ have been observed.

RECENTLY, Meyerson and Fields have studied the behaviour of several C_6Cl_8 and C_6Cl_6 isomers upon pyrolysis and under electron-impact in a mass spectrometer.² In particular, they pointed out the differences between the fragmentation patterns of hexachlorobenzene (I) and hexachloropentafulvene (II). On the strength of the similarity in the intensity distributions of $[C_6Cl_6]^{+}: [C_6Cl_5]^{+}: [C_6Cl_4]^{+}$ in the fragmentation pattern of hexachloropentafulvene (II) and octachloro-1,2-dimethylene-cyclobutane $C_6Cl_8(III)$, and the dissimilarity between hexachlorobenzene (I) and III, Meyerson and Fields proposed the following mechanism for the fragmentation of III:



An intermediate in this mechanism is the molecular ion derived from a third C_6Cl_6 isomer, 1,2-dichloro-3,4-bis(dichloromethylene)cyclobutene (IV). It seemed, therefore, that the study of the mass spectrum of IV would shed light on this mechanism; for comparison we have also studied the mass spectrum of II; the results are summarized in Table 1.

The ratio $[C_6Cl_6]^+$: $[C_6Cl_5]^+$: $[C_6Cl_4]^+$ in the mass spectrum of II was very * See Ref. 1.

m e	Relative intensities		1-	Relative intensities		
	(11)	(IV)	m/e	(II)	(IV)	
35	5.7	6.1	146	3.7	4.6	
36	7.3	18.4	153	1.1	3.0	
37	1.8	2.4	155	1.1	3.0	
47	13.1	20.9	165	3.7	6.5	
48	1.5	3.4	167	3.6	6.3	
49	4.4	6.9	169	1.2		
59	1.2	2.8	177	12.7	17.0	
60	6.7	14.2	178		1.4	
61		1.7	179	12.2	16.7	
71	19.2	21.0	180		1.4	
72	7.7	13.0	181	3.9	5.9	
73	6.2	15.5	188	1.4	2.3	
82	4.1	3.9	190	1.9	2.9	
83	5.7	16.5	192		1.4	
84	3.0	3.0	212	20.7	40.3	
85	1.9	3.0	213	1.3	2.8	
88	2.5	4.4	214	24.6	52.7	
89	2.4	4.4	215	1.7	3.9	
94	5.2	4.3	216	11.2	22.8	
95	13.3	23.6	217		3.0	
96	3.8	3.8	218	2.8	6.5	
97	5.3	7.0	219		2.0	
106	16.8	22.3	220		1.9	
107	29.2	40.8	247	23.9	56.5	
108	12.9	14.0	248	1.7	3.8	
109	7.7	11.5	249	36.6	94.4	
110	1.9	1.9	250	2.6	6.4	
118	13.0	16.4	251	24.2	57.5	
119	1.1	1.2	252	1.7	4.0	
120	7.4	12.6	253	7.1	17.9	
122	1.4	2.0	254		1.4	
123.5	1.3		255	1.3	3.3	
124		1.4	282	60.0	55.4	
124.5	2.1		283	3.3	3.9	
125.5	1.3		284	100.0	100.0	
130	7.4	12.3	285	6.0	6.9	
132	5.6	7.3	286	80.0	83.8	
141	7.4	16.9	287	4.8	5.4	
142	39.9	53.4	288	31.7	32.2	
143	12.0	20.8	289	2.1	2.4	
144	24.8	29.9	290	7.3	8.4	
145	3.4	6.9	292	1.1	1.1	

 TABLE 1. THE MASS SPECTRUM OF HEXACHLOROPENTAFULVENE (II) AND 1,2-DICHLORO-3,4-BIS(DICHLOROMETHYLENE)CYCLOBUTENE (IV) (peaks having an abundance less than 1 % are not recorded)

similar to that obtained by Meyerson and Fields:² 100:36.6:24.6. This ratio was different, however, (100:94.4:52.6) in the spectrum of IV; nor was it similar to the ratio obtained in the case of I. These observations rule out the above mechanism for the fragmentation of III. Apparently, there exist at least three different fragmentation patterns of cyclic C₆Cl₆ compounds, as regards the relative intensities of the fragment peaks. In the fragmentation of III, II⁺ might be an intermediate, but if

this is so, III passes into II^+ not through IV⁺. It seems more likely that the resemblance in the mass spectra of II and IV 'may be fortuitous.'²



Another aspect of the fragmentation patterns of II and IV is of some more general interest. In a recent study of the mass spectrum of hexachlorocyclopentadiene (V), Schäfer has observed a fragmentation pattern involving a successive elimination of chlorine atoms leading finally to a $[C_5]^{+}$ species $(m/e \ 60)$.³ Its intensity was $22 \cdot 1 \, {}_0^{\circ}$ of $[C_5 Cl_5]^{+}$ $(m/e \ 237)$; the intensity of the molecular ion $[C_5 Cl_6]^{+}$. $(m/e \ 272)$ was $17 \cdot 9 \, {}_0^{\circ}$. Analogously, the signals $m/e \ 72$ in the spectra of II and IV (intensities of 7 \cdot 7 and 13 \cdot 0 relative to the respective molecular ions), may be attributed to a $[C_6]^{+}$ species. Some contributions of the $m/e \ 71$ signal due to carbon isotopes from $[C_3 Cl]^{+}$ are probably included in the $m/e \ 72$ signals; however, these contributions cannot be significant, since there is no signal at $m/e \ 74$. The signals at $m/e \ 73$ (relative intensities of 6 $\cdot 2$ (in II) and 15 $\cdot 5$ (in IV) are derived mainly from $[C_3^{37}Cl]^{+}$, and only marginally from the carbon isotopes of $[C_6]^{+}$. These conclusions are somewhat speculative, as these signals may originate from the doubly charged $[C_6Cl_2]^{++}$.

In the spectra of II and IV, there appears also the species $[C_5]^{+}$ (*m/e* 60) with intensities (6.7 and 14.2% of the molecular ion) which are very similar to those of $[C_6]^{+}$. Obviously, the semicyclic carbon-carbon bond is cleaved (C_5 — C_6 in the case of II, C_3 — C_5 or C_4 — C_6 in the case of IV). These *m/e* 60 signals cannot be attributed to a doubly charged ion, e.g. $[C_4^{35}Cl^{37}Cl]^{++}$ for the following reason: whilst the species $[C_4Cl_2]^{+}$ is represented by the signals *m/e* 118, 120 and 122, with relative intensities of 13.0, 7.4 and 1.4 (in II) and 16.4, 12.6 and 2.0 (in IV), the relative intensities of the *m/e* 59 signals are only 1.2 (in II) and 2.8 (in IV). Thus *m/e* 60 is not likely to represent $[C_4^{35}Cl^{37}Cl]^{++}$.

The identification of doubly charged ions in the mass spectra of II and IV is rather complicated. A detailed analysis shows that they are most probably not a major feature in these spectra, however. In this context, we have also studied the mass spectrum of octachloropentafulvalene $C_{10}Cl_8$ (VI) (Table 2). The observed ratio of the intensities of the $[C_{10}Cl_n]^+$ ions $(n = 0, 1, 2 \cdots 8)$ shows a striking feature:

Species	:	$C_{10}Cl_8$	$C_{10}Cl_7$	$C_{10}Cl_6$	$C_{10}Cl_5$	$C_{10}Cl_4$	$C_{10}Cl_{3}$	$C_{10}Cl_2$	C10Cl	C_{10}
m/e	:	404	369	332	297	262	225	190	155	120
Rel. int.	:	100	6.7	89.9	12.8	28.7	10.1	28.1	11.1	22·0

Successive [or simultaneous (?)] elimination of an even number of chlorine atoms is generally preferred over the successive elimination of an odd number of chlorine atoms. Such a preferred process is not found in the spectra of II and IV. This difference in behaviour between VI and II or IV may be rationalized by the hypothesis that the breakage of a given C—Cl bond in one of the rings of VI is always accompanied by the breakage of the corresponding C—Cl bond in the second ring.

A second interesting feature in the spectrum of VI is the formation of a $[C_{10}]^+$ $(m/e \ 120)$ species with a relative intensity of 22.0. Whilst the $m/e \ 119$ and 121 signals (relative intensities 15.0 and 7.0) represent predominantly the species $[C_7^{35}Cl]^+$ and $[C_7^{37}Cl]^+$, respectively, the $m/e \ 120$ signal cannot be assigned to a chlorine containing fragment, since the relative intensities of the peaks at $m/e \ 118$ and 122 are only 2.1 and 2.0 respectively.*

No direct evidence exists as to the structure of the $[C_{10}]^{+}$ species. If the above hypothesis on the sequence of the cleavage of the chlorine atoms is accepted, however, it is likely that the $[C_{10}]^{+}$ species is the carbon backbone of the pentafulvalene molecule.

The occurrence of the $[C_{10}]^{+}$ species in the spectrum of VI prompted a search for lower $[C]^{+}$ species. The most conspicuous possible representative of this type of fragment is m/e 84 ($[C_7]^{+}$) with a relative intensity of 32·1. *Prima facie*, this signal may correspond to $[C^{35}Cl^{37}Cl]^{+}$; however, the low intensity of the signal at m/e 82 and the absence of any signal at m/e 86, rule out this possibility. The assignment of m/e 84 to $[C_7]^{+}$ is also in accord with the occurrence of $[C_7Cl]^{+}$ (see above). On the other hand, the identification of the analogous $[C_8]^{+}$ and $[C_9]^{+}$ species is doubtful since the signals at m/e 96 and 108 (with relative intensities of 16·4 and 12·8) may be ascribed to chlorine containing species (e.g. $[C_2Cl_2]^{+}$, $[C_{10}Cl_2]^{++}$ in the former signal, and $[C_3Cl_2]^{+}$ in the latter).

Finally, it should be noted that the mass spectrum of VI is remarkably rich in doubly charged ions. Each $[C_{10}Cl_n]^{+\cdot}$ $(n = 0, 1, 2 \cdots 8)$ fragment is accompanied by a $[C_{10}Cl_n]^{++\cdot}$ species (Table 3) [except in the case of n = 7, in which, however, the relative intensity of the *singly* charged ion is low (viz. 6.8)]. The assignments are based on the existence of 'half-masses' corresponding to $C_{10}Cl_n$ for n = 1,2,3,4,5 and on the high intensities of the signals corresponding to $[C_{10}Cl_n]^{+\cdot}$ for even n.

The high abundance of doubly charged $[C_{10}Cl_n]^{++}$ species in the spectrum of VI is consistent with the above hypothesis and might suggest that the double charge is distributed equally over the two rings. The two halves of the molecule of VI are thus not independent of each other. The driving force for this surprising phenomenon may be the symmetry inherent in the process and its products.

292

^{*} As pointed out by the referee, the—formally possible—assignment of the fragments 119 and 121 to $C^{35}Cl_2^{37}Cl_1$ and $C^{35}Cl_3^{37}Cl_2$, respectively, is not acceptable in view of the low abundance (2.7%) of the corresponding $C^{35}Cl_3$ species $(m/e \ 117)$.

m/e	Rel. int.	m e	Rel. int.	m/e	Rel. int.
35	4.5	114	4.5	200	4.8
36	6.7	117	2.7	201	13.0
37	1.6	118	6.9	202	11.4
38	2.2	119	15.0	203	3.4
39	3.3	120	22.0	205	1.8
40	1.5	121	7.0	213	2.1
41	13.2	122	2.0	215	2.1
42	3.3	123	2.2	225	10.1
43	12.1	130	19.3	226	1.8
44	1.7	130.5	1.8	227	9.8
45	3.9	131	22.6	228	1.8
47	7.9	131.5	2.0	229	3.9
49	2.8	132	13.2	236	2.4
50	1.8	133	5.7	238	3.2
51	4.9	141	15.5	260	25.0
53	1.5	142	12.7	261	5-1
55	7.9	143	21.1	262	28.7
56	6.3	144	9.1	263	5.9
57	9.4	145	7.8	264	16.1
60	6.8	146	2.1	265	3.3
67	2.1	147.5	11.5	266	4.9
69	7.8	148.5	17.4	274	1.6
70	2.1	149	2.7	285	1.9
71	9.0	149.5	11-2	295	8.3
72	3.5	150	1.8	297	12.8
73	4.5	150.5	4.4	299	9.4
77	4.8	154	11.2	301	3.6
77.5	2.7	155	11.1	306	2.7
81	2.1	156	7.0	308	4.5
82	2.6	157	3.6	310	4.0
83	4.5	158	1.7	330	50.3
84	32.1	165	18·2	331	6.3
85	3.4	166	48·0	332	89·9
89	1.8	167	29.4	333	11.2
91	1.9	168	18.3	334	66.1
94	5.0	169	5.8	335	9.4
95	30.9	170	2.2	336	29.4
95.5	2.1	177	1.8	337	4.9
96	16.3	178	6.2	338	8.2
96.5	1.8	179	2.1	365	3.3
97	7.8	180	3.9	367	6.8
105	2.8	182	2.6	369	6.4
106	10.6	183	5.0	371	4.4
107	6.3	184	4⋅8	400	38.0
108	12.8	185	2.8	402	92.4
109	3.3	189	4.5	404	100.0
110	2.3	190	28.1	406	67.8
112	11.4	191	6.9	408	29.4
112.5	1.8	192	16.4	410	13.7
113	10.3	193	3.9		
113.5	1.7	194	3.5		

TABLE 2. THE MASS SPECTRUM OF OCTACHLOROPENTAFULVALENE (VI) (peaks having an abundance less than 1% are not recorded)

e

Species	m e	Rel. int.	Species	m e	Rel. int.
[C ₁₀ Cl ₈]+•	404	100.0	$[C_{10}Cl_3]^+$.	225	10.1
[C ₁₀ Cl ₈] ⁺⁺ ·	202	11.4	$[C_{10}C]_3]^{++}$	112.5	1.8
[C10Cl2]+•	367	6.8	$[C_{10}Cl_2]^+$	190	28.1
[C ₁₀ Cl ₇]++·	183.5		$[C_{10}Cl_2]^+$	191	6.9
			$[C_{10}Cl_2]^+$	192	16.4
$[C_{10}Cl_6]^+$	332	89.9			
[C ₁₀ Cl ₆] ⁺⁺ ·	166	48 ⋅ 0	$[C_{10}Cl_2]^{++}$	95	30.9
			$[C_{10}Cl_2]^{++}$	95.5	2.1
			$[C_{10}Cl_2]^{++}$	96	16.3
[C ₁₀ Cl ₅]+·	297	12.8			
$[C_{10}Cl_5]^{++}$	148.5	17.4			
			$[C_{10}Cl_1]^+$	155	11.1
			$[C_{10}Cl_1]^{++}$	75.5	2.7
[C ₁₀ Cl ₄]+·	262	28.7	10° 100		
$[C_{10}Cl_4]^+$	263	5.9	[C ₁₀]+·	120	22.0
$[C_{10}Cl_4]^{++}$	131	22.6	$[C_{10}]^{++}(?)$	60	2.8
[C ₁₀ Cl ₄]++•	131.5	2.0			

TABLE 3. $[C_{10}Cl_n]^{++}$ and $[C_{10}Cl_n]^{+++}$ species in the mass spectrum of octachloropentafulvalene (VI)

The fragmentation pathway of VI may then be described in the following manner:



EXPERIMENTAL

Hexachloropentafulvene (II) was prepared by partial dechlorination of 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)cyclobutene according to Dinbergs,⁴ and was obtained as red needles, m.p. $152 \cdot 5^{\circ}$ (from hexane) (lit. $152^{\circ},^4$ 153 to 154^5).

1,2-Dichloro-3,4-bis(dichloromethylene)cyclobutene (IV) was prepared from hexachloropropene and aluminium amalgam according to Fujino and co-workers.⁶ It formed colorless prisms, m.p. 147° (from ether) (lit. 147 to $148^{\circ 6}$).

Octachloropentafulvalene (VI) was prepared by partial dechlorination of decachloro-bis-(1-cyclopentadienyl) with triethyl phosphite according to Mark⁷ and was obtained as violet-blue cubes, m.p. 200° (dec.) (from cyclohexane) (lit. 200° (dec.)^{7.8}).

The mass spectra were measured on a CH-4 instrument (MAT) operating at 70 V The direct insertion technique was employed. The most intense peak was taken as a base peak (relative intensity 100%).

REFERENCES

- 1. Fulvenes and Thermochromic Ethylenes—Part 62. For Part 61 see H. Weiler-Feilchenfeld and A. Solomonovici, J. Chem. Soc. in press.
- 2. S. Meyerson and E. K. Fields, J. Chem. Soc. (B) 1001 (1966).
- 3. L. Schäfer, Chem. Commun. 1622 (1968).
- 4. K. Dinbergs, Ph.D. Thesis, Purdue University, 1956; Dissertation Abstr. 16, 1063 (1956).
- 5. A. Roedig, Annalen, 569, 161 (1950).
- 6. A. Fujino, Y. Nagata, and T. Sakan, Bull. Chem. Soc. Japan 38, 295 (1965).
- 7. V. Mark, Org. Syn. 46, 93 (1966).
- 8. D. C. F. Law, Ph.D. Thesis, University of Wisconsin, 1967. Dissertation Abstr. 28, 585-B (1967).