determined correction factors for differences in relative thermal conductivities.

In order to determine the yields of the more volatile products, the work-up for some runs was changed. The organic layer that had been separated after the addition of 5 ml of saturated NaCl solution to the reaction mixture was washed once with 5 ml of saturated NaCl solution and once with 5 ml of 1 *M* $NaHCO_3$ solution. This organic layer was then dissolved in an equal volume of $CDCl_3$, dried ($MgSO_4$), and analyzed by nmr. The identification of some of the compounds was completed by addition of authentic samples to this solution.

The specific conditions and methods of analysis for each alkylphenylcarbinol are as follows.

Methylphenylcarbinol.—The reaction times were 6–8 min, the standard was methyl benzoate, and the TCEP column at 150° and the SE-30 column at 110° were used. In the run in which equal molar amounts of the alcohol and CAN were used, a solution of 10 mmol of CAN in 5 ml of water was added to 10 mmol of the alcohol in 5 ml of acetonitrile. The homogeneous dark reddish brown solution was heated on the steam bath until the color disappeared which took 5.5 min. The organic layer which formed was separated and the aqueous layer was extracted four times with 5-ml portions of ether. The combined organic layers were treated as described above and the ratio of recovered starting material to acetophenone was analyzed by nmr.

Ethylphenylcarbinol.—The reaction times were 4–5 min, the standard was acetophenone, and the TCEP column at 150° was used. In the nmr analysis for volatile products, the triplet at δ 1.30 increased and no new lines appeared when ethyl nitrate was added to the solution.

Isopropylphenylcarbinol.—The reaction times were 2–2.5 min, the standard in the analysis of the nonvolatile products was methyl benzoate, and the TCEP column at 125° was used. In the nmr analysis of the volatile products, the standard was acetophenone and the addition of isopropyl nitrate to the solution increased the intensity of the doublet at δ 1.32, but the addition of *N*-isopropylacetamide to the solution gave rise to a new doublet at δ 1.03.

***tert*-Butylphenylcarbinol.**—The reaction times were 1.5 to 2 min, the standard was acetophenone, and the TCEP column at 135° and the SE-30 column at 150° were used. In the nmr analysis of the volatile products, the addition of *tert*-butyl alcohol to the solution enhanced the singlet at δ 1.20, the addition of *N*-*tert*-butylacetamide to the solution enhanced the singlet at δ 1.31, but the addition of *tert*-butyl nitrate to the solution gave rise to a new singlet at δ 1.47.

Registry No.—Ceric ammonium nitrate, 16774-21-3; methylphenylcarbinol, 98-85-1; ethylphenylcarbinol, 93-54-9; isopropylphenylcarbinol, 611-69-8; *tert*-butylphenylcarbinol, 3835-64-1.

Fragmentation of Organic Compounds on Electron Impact. VII.[1a] Migration of Chlorine during Fragmentation of Chlorinated Norbornenes

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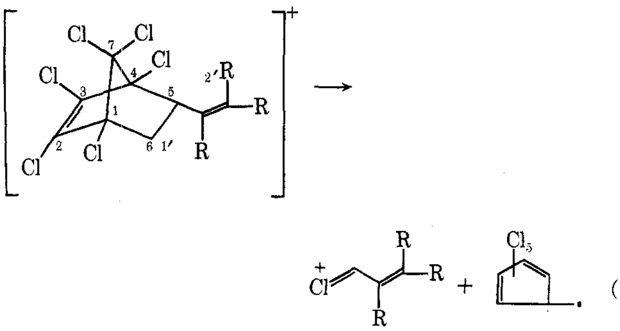
The mass spectral fragmentation patterns of a series of chlorinated norbornenes have been investigated. The compounds were prepared by the Diels–Alder reaction of chlorinated cyclopentadiene derivatives (diene component) and various monoolefins, diolefins, and aromatic olefins (dienophile component); in all cases the adduct formed in high yield and only the least hindered double bond of the dienophile entered into the reaction. Several of the compounds undergo a novel electron-impact induced rearrangement involving the migration of chlorine (eq 1). The rearranged ion is the most abundant ion in the spectrum of the styrene adduct and is present in high abundance in the spectra of various acyclic 1,3-diene adducts. The rearrangement is suppressed when a heteroatom is not attached to C-7, a methyl group is attached to C-6, or a double bond is not present at C-1′. Other fragmentations of particular interest include the elimination of the elements of the rearranged ion from the molecular ion, the formation of a trichloromethyl ion, and the retro-Diels–Alder reaction.

In recent years much effort has been devoted to the study of rearrangements of organic compounds in the mass spectrometer.[2] Most of the rearrangements involve the migration of hydrogen atoms or alkyl groups, but a number of examples are now known in which the migrating group contains a heteroatom. However, only rarely has the rearrangement of a halogen atom been detected[3] and little is known about the steric and electronic requirements of the process. We have discovered that migration of chlorine occurs with ease in certain appropriately constituted norbornenes and the fragmentation reactions of these compounds constitute the subject of this paper.



(1)

Results and Discussion

The chlorinated norbornenes shown in Table I were prepared by the Diels–Alder reaction of chlorinated cyclopentadiene derivatives (diene component) and appropriate monoolefins, diolefins, and aromatic olefins (dieneophile component); double bond isomerization does not occur; and the least hindered double bond of the dienophile reacts exclusively.

Molecular Ions.—Inspection of the partial mass spectra of the norbornenes listed in Tables II and III reveals that all of the compounds exhibit molecular ions. The relative abundance of the molecular ions, listed in Table IV, varies from 0.2 to 2.0% of Σ_{31}, with all but two of the values falling between 0.6 and 1.6% of Σ_{31}. This variation is relatively small in view of the gross structural differences of the substituent groups and reflects the moderating influence

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[1] (a) Paper VI: D. S. Weinberg and M. W. Scoggins, *Org. Mass Spectrom.*, **2**, 553 (1969). (b) Glidden-Durkee, Jacksonville, Fla.

[2] R. T. Gray, R. J. Spangler, and C. Djerassi, *J. Org. Chem.*, **35**, 1525 (1970), and references cited therein.

[3] L. R. Williams, *Org. Mass Spectrom.*, **1**, 613 (1968).

TABLE I
IDENTIFICATION OF CHLORINATED NORBORNENES

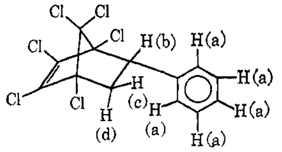
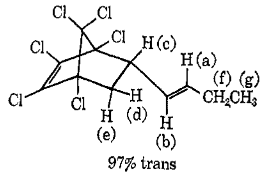
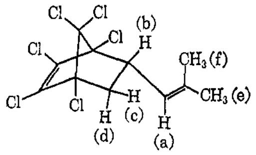
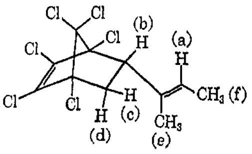
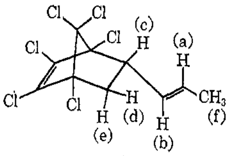
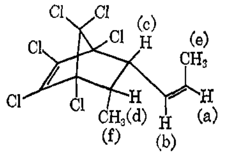
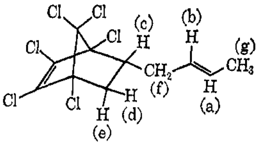
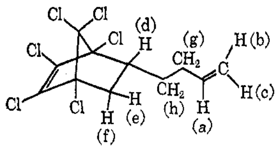
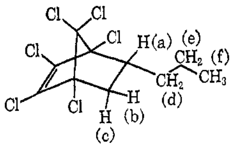
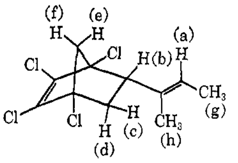
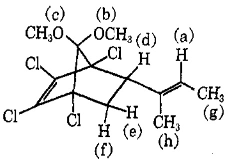
No.	Compd	Yield, %	Bp (mm), mp, °C	Analytical data
I		37	72.5–73.0	*Anal.* Calcd for $C_{13}H_8Cl_6$: C, 41.43; H, 2.14; Cl, 56.43; mol wt, 374. Found: C, 41.5; H, 2.1; Cl, 56.9; mol wt, 374. Nmr: a, τ 2.8 (5 H); b, 6.0 (1 H); c,d, 7.3, 7.4 (2 H)
II	 97% trans	80	97 (0.03)	*Anal.* Calcd for $C_{11}H_{10}Cl_6$: C, 37.23; H, 2.84; Cl, 59.43; mol wt, 352. Found: C, 37.1; H, 2.9; Cl, 59.7; mol wt, 352. Nmr: a, τ 4.3 (1 H); b, 5.0 (1 H); c, 6.7 (1 H); d, 7.3 (1 H); e,f, 8.0 (3 H); g, 9.0 (3 H)
III		61	98 (0.09)	*Anal.* Calcd for $C_{11}H_{10}Cl_6$: C, 37.23; H, 2.84; Cl, 59.93; mol wt, 352. Found: C, 36.6; H, 2.8; Cl, 60.2; mol wt, 352. Nmr: a, τ 5.3 (1 H); b, 6.3 (1 H); c, 7.3 (1 H); d,e,f, 8.2 (7 H)
IV	 90% cis	57	93 (0.03)	*Anal.* Calcd for $C_{11}H_{10}Cl_6$: C, 37.23; H, 2.84; Cl, 59.33; mol wt, 352. Found: C, 37.1; H, 2.8, Cl, 59.2; mol wt, 352. Nmr: a, τ 4.7 (1 H); b, 6.6 (1 H); c,d, 7.6, 7.7 (2 H); e,f, 8.3 (6 H)
V	 85% trans	88	78 (0.04)	*Anal.* Calcd for $C_{10}H_8Cl_6$; C, 35.23; H, 2.36; Cl, 62.48; mol wt, 338. Found: C, 35.2; H, 2.4; Cl, . . . ; mol wt, 338. Nmr: a, τ 4.3 (1 H); b, 5.0 (1 H); c, 6.7 (1 H); d, 7.4 (1 H); e,f 8.0, 8.3 (4 H) (distribution of peaks between τ 8.0 and 8.3 reflects presence of cis and trans isomers)
VI	 100% cis	62	92 (0.04)	*Anal.* Calcd for $C_{11}H_{10}Cl_6$: C, 37.23; H, 2.84; Cl, 59.93; mol wt, 352. Found: C, 36.9; H, 2.9; Cl, 60.0; mol wt, 352. Nmr: a, τ 4.2 (1 H); b, 5.0 (1 H); c, 6.2 (1 H); d, 7.0 (1 H); e, 8.3 (3 H); f, 9.1 (3 H)
VII		77	91 (0.03)	*Anal.* Calcd for $C_{11}H_{10}Cl_6$: C, 37.23; H, 2.84; Cl, 59.93; mol wt, 352. Found: C, 36.9; H, 2.9; Cl, 59.9; mol wt, 352. Nmr: a,b, τ 4.2–4.8 (2 H); c,d,e, 7.2–7.8 (3 H); f,g, 8.1–8.5 (5 H)
VIII		80	93 (0.05)	*Anal.* Calcd for $C_{11}H_{10}Cl_6$: C, 37.23; H, 2.84; Cl, 59.93; mol wt, 352. Found: C, 36.9; H, 2.6; Cl, 59.8; mol wt, 352. Nmr: a, τ 4.3 (1 H); b,c, 5.0 (2 H); d,e, 7.3 (2 H); f,g,h, 7.8–8.5 (5 H)
IX		96	94 (0.08)	*Anal.* Calcd for $C_{10}H_{10}Cl_6$: C, 35.02; H, 2.94; Cl, 62.03; mol wt, 340. Found: C, 34.96; H, 3.04; Cl, 60.6; mol wt, 340. Nmr: a,b, τ 7.3 (2 H); c,d,e,f, 8.0–9.0 (8 H)
X	 100% trans	72	75 (0.07)	*Anal.* Calcd for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.23; Cl, 49.58; mol wt, 284. Found: C, 46.08; H, 4.19; Cl, 49.8; mol wt, 284. Nmr: a, τ 4.7 (1 H); b, 6.8 (1 H); c,d,e,f, 7.3–8.0 (4 H); g,h, 8.4 (6 H)
XI	 100% trans	85	100 (0.05)	*Anal.* Calcd for $C_{13}H_{16}Cl_4O_2$: C 45.12; H, 4.66; Cl, 40.98; mol wt, 344. Found: C, 47.7; H, 4.5, Cl, 41.8; mol wt, 344 Nmr: a, τ 4.8 (1 H); b,c, 6.4, 6.5 (6 H); d, 6.8 (1 H); e, 7.6 (1 H); f, 8.1 (1 H); g,h, 8.3 (6 H)

TABLE II

PARTIAL[a] MASS SPECTRA OF CHLORINATED NORBORNENES

	Number of chlorine atoms	Peak intensities					
m/e	in ion	I	II	III	IV	V	VI
36	1	8	6	4	4	4	1
39	0	3	13	7	7	9	5
41	0		20	12	11	9	6
53	0		8	5	7	15	5
67	0		100	43	76	26	38
68	0		5	2	4	100	2
81	0	1	2	10	13		
82	0	1	88	88	82		100
89	0					78	6
91	0	2					
103	1	10	94	100	100		
104	0	89	2	5	4		
117	3	2	1	2		1	
125	1	100					
214	4	4	3	28	11	24	
227	4		7	3	6	3	1
235	5	8	27	21	25	18	10
249	5					3	
267	3	3					
270	6	2	6	3	4	5	1
275	5		13	4		6	
281	4		11		3		
289	5				12		2
303	4	0.7				4	
316	5		5	1			
317	5		8	1	12		2
338	5	0.5				3	
339	5	0.5					
352	6		5	6	4		2
374	6	5					

[a] Only those peaks are listed which are at least 10% as intense as the base peaks or are of special interest. The latter consist of the parent peaks, various low intensity peaks relevant to the discussion of fragmentation mechanisms, and peaks of moderate intensities included for comparison. The number of chlorine atoms in each ion was determined by high resolution mass measurements or by the distribution of isotope peaks; the intensities of all the chlorine isotope peaks representing a particular chlorine-containing ion were summed and listed as a single value at the *m/e* value for the ^{35}Cl species in order to reduce the complexity of the table.

TABLE III

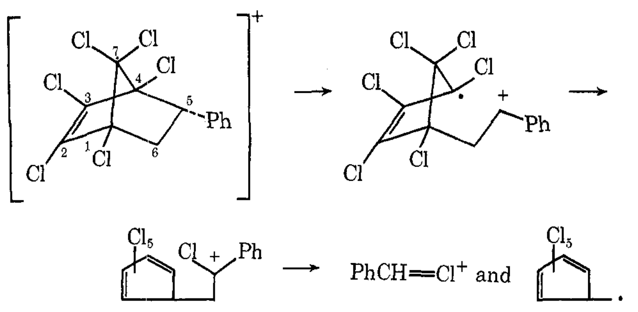
PARTIAL[a] MASS SPECTRA OF CHLORINATED NORBORNENES

	Number of chlorine atoms	Peak intensities				
m/e	in ion	VII	VIII	IX	X	XI
36	1	15	1	12	4	1
39	0	15	6	16	5	1
41	0	30	11	54	5	1
43	0			49	1	
53	0	12	4	5	4	2
55	0	100	7	46	2	4
59	0					9
67	0	28	15		46	7
69	0	3	1	57	2	
70	0			3	2	
81	0	28	15		7	1
82	0	8	1		100	5
83	0	3	3	7	8	
91	1			14		
99	1					23
103	1	17	3	15	12	5
117	3	14	13	23		
177	1				66	
202	4				26	
210	3					5
212	2				22	
214	4	13	33	68		
227	4	16	43	44		
235	5	15	70	77		
237	1					20
241	2					29
245	4					2
248	3				5	
249	5 (3)		19	31	(5)	
262	5 (4)		23	19		(7)
270	6	6	100	100		
272	2					7
273	2					14
277	3					16
281	4	6	35			
284	4				6	
305	5			80		
308	3					40
309	3					100
317	5	7	45			
340	6			21		
344	4					5
352	6	1	13			

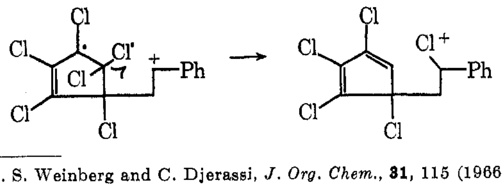
[a] See Table II for criteria used to select data included in this table.

of the remainder of the molecule on the ionization and fragmentation processes.

Ions Formed by Rearrangement Processes.—The most abundant and significant ion in the mass spectrum of I occurs at *m/e* 125. It represents 28.1% of Σ_{31} and has the composition C_7H_6Cl; consequently it must be produced by a novel rearrangement. Initial fragmentation probably involves cleavage of the C-4–C-5 bond. Earlier studies of bicyclic systems have suggested that cleavage of bonds attached to the bridgehead carbon atoms are facile[4,5] and in this system such a reaction is particularly favored since both an allylic radical and allylic carbonium ion are generated in the process.[6] Migration of chlorine to C-5 then occurs followed by cleavage of the C-5–C-6 bond.



In view of the propensity of chlorine atoms to take part in five-membered transition states[7] and the op-



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(4) D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

(5) D. S. Weinberg and C. Djerassi, *ibid.*, **31**, 3832 (1966).

(6) F. W. McLafferty, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 7.

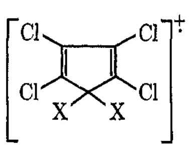
(7) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 12.

TABLE IV

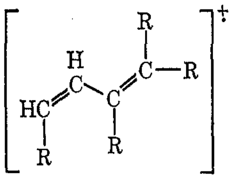
PER CENT OF Σ_{31} REPRESENTED BY SELECTED IONS

Compd no.	Per cent of Σ_{31} ions[a] A	B	C	D	E	F	G
I	2.0	28.1	1.1	0.6	0.6	25.0	2.2
II	0.6	11.0	0.2	0.1	0.7	11.2	3.2
III	1.0	17.1	4.3	0.3	0.7	15.1	3.6
IV	0.6	14.8	1.6		0.6	12.3	3.7
V	0.6	15.9	5.5	0.2	1.0	20.4	3.7
VI	0.6	1.9			0.3	32.0	3.2
VII	0.2	2.8	2.1	2.3	1.0	1.3	2.5
VIII	1.5	0.3	5.7	1.5	11.3	0.1	7.9
IX	1.6	0.1	7.5	1.7	7.5	0.2	5.8
X	1.1	2.2			4.9	18.7	4.8
XI	0.8	3.6 (OCH_3) 0.8 (Cl)	1.0		1.1	0.8	1.1

[a] Identification of ions: A = molecular ion; B = rearranged ion ($RCHX^+$ where X = Cl, H, or OCH_3); C = ion A minus rearranged radical and ion A minus rearranged radical minus chlorine (A − RCHX· and A − RCHX· − Cl·); D = trichloromethyl ion; E = compound i below where X = Cl, H, OCH_3; F = compound ii below (note in compound I, this ion is $[C_6H_5\text{-}CH{=}CH_2]^{+\cdot}$); G = ion E minus one X radical, where X = Cl, H, or OCH_3.



i



ii

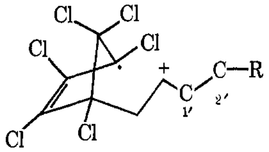
portunity for double bond formation to occur,[6] one of the chlorine atoms attached to C-7 is probably involved in the rearrangement. Evidence will be presented later that this in fact is the case.

The ion produced in the rearrangement may be a chlorotropylium ion[8] rather than a benzylic ion, but no information on this point was obtained and the behavior of compounds II to V (*vide infra*) demonstrates that the formation of a tropylium ion is not a requirement for the rearrangement.

Compounds II to IV produce rearranged ions at *m/e* 103 which represent 11.0, 17.1, and 14.8% of Σ_{31}, respectively. Compound V gives the corresponding ion at *m/e* 89 and it represents 15.9% of Σ_{31}. Hence substitution of an alkenyl group containing a double bond at C-1′ for the phenyl group does not suppress the rearrangement. The relative abundance of the rearranged ions is lower than that of the corresponding ion in the spectrum of I, but, in view of the other ions produced, this results from the cleavage of the alkyl groups before and after rearrangement rather than to a reduced tendency of the rearrangement to occur. The abundance of rearranged ions is high and indicates that the rearrangement occurs with great facility in all of these compounds.

Compound VI, which differs from compound V only by the presence of a methyl group at C-6, gives a rearranged ion at *m/e* 89 which represents only 1.9% of Σ_{31}. The low abundance of this ion underscores the extreme sensitivity of the rearrangement to the molecular structure of the compound. In this case the presence of the methyl substituent favors the retro-Diels–Alder reaction and the acylic diolefin ion at *m/e* 82 is generated which carries 32.0% of the ion current.

The rearrangement produces ions in low abundance when the alkyl substituent contains a double bond at a position other than C-1′ or when a double bond is not present. Thus, compounds VII and VIII produce rearranged ions at *m/e* 103 which represent only 2.8 and 0.3% of Σ_{31} and compound IX produces an ion at *m/e* 91 which represents only 0.1% of Σ_{31}. This behavior shows unequivocally that the double bond, although frequently mobile under electron impact conditions,[4] does not migrate sufficiently rapidly in these compounds for the isomers to lose their identity before fragmentation occurs. The fragmentation reactions which do occur produce many abundant ions and hence, unlike the situation for compound V, the rearrangement is not overshadowed by a single energetically favored competing reaction. The low abundance of rearranged ions may reflect in part the lower stability of the initial intermediate. When a C-1′ double bond is not present, the lifetime of the intermediate may not be long enough to permit the molecule to assume the proper conformation for the transfer of chlorine, and random fragmentation of the molecule may occur instead.



Compound X, which contains two hydrogen atoms attached to C-7, produces a chlorine-containing rearranged ion at *m/e* 103 which represents only 2.2% of Σ_{31}. This species is less abundant than ten other ions produced in the fragmentation process and hence is not produced by an energetically favored process. A hydrogen-containing rearranged ion appears at *m/e* 69; it represents 0.4% of Σ_{31} but may not be produced by the specific rearrangement under consideration (a deuterium-labeled compound would have to be studied to settle this point). In addition, compound XI, which contains methoxy groups attached to C-7, produces a chlorine-containing rearranged ion at *m/e* 103 which represents 0.8% of Σ_{31} and a methoxy-containing rearranged ion at *m/e* 99 which represents 3.6% of Σ_{31}. In this case the low abundances are somewhat misleading, because a competing reaction involving the loss of chlorine dominates the fragmentation process. Thus the ion at *m/e* 99 is one of only three ions more than 20% as abundant as the ion produced in greatest yield (*m/e* 309, M − Cl). The point of importance is that a methoxy group migrates 4.5 times as often as a chlorine atom in spite of the fact that there is twice as much chlorine present in the molecule. Thus, the behavior of compounds X and XI, taken together, clearly demonstrate that the predominant rearrangement involves the migration of a heteroatom attached to C-7.

The rearrangement strikingly resembles an electron impact induced rearrangement of 4-methoxycyclohexanone disclosed several years ago.[9] In both cases, a

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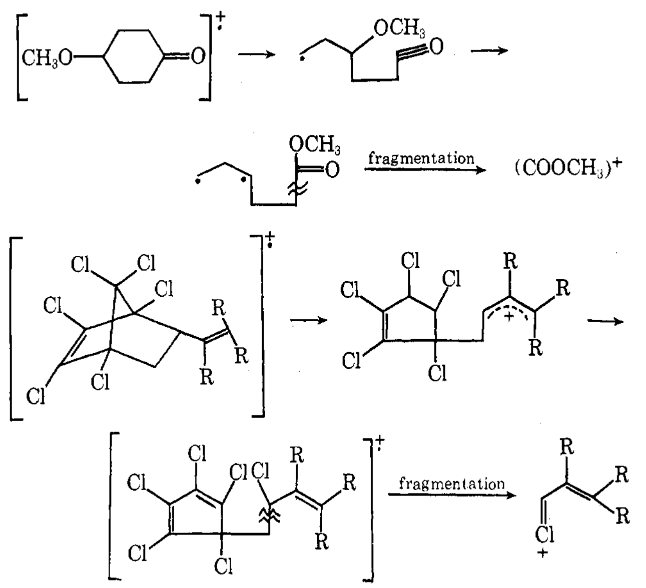
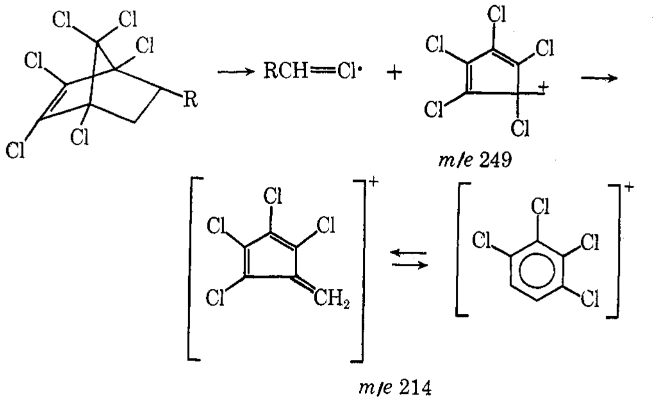
[8] S. Meyerson, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10.

[9] M. M. Green, D. S. Weinberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **88**, 3883 (1966).

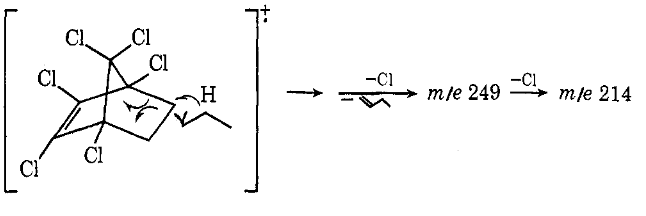


heteroatom migrates from the γ position to a stabilized carbonium ion generated by cleavage of an α-carbon bond. It is interesting that a chlorine-containing rearranged ion could not be detected in the spectrum of 4-chlorocyclohexanone studied recently in an extension of the earlier work.[2] This may reflect the instability of the rearranged acid halide rather than the poor migrating ability of chlorine. Ionized acid chlorides give molecular ions in very low abundance due to the loss of chlorine, and 4-chlorocyclohexanone produces a strong M − Cl ion.

Ions Formed by the Apparent Elimination of Rearranged Radicals and Chlorine Atoms.—All of the compounds which produce rearranged ions containing one atom of chlorine (*vide supra*) also yield ions which result from the elimination of the elements of a rearranged, chlorine-containing radical or this species plus a chlorine atom. Compound XI yields analogous ions at m/e 245 and 210, respectively, the different m/e values resulting from the presence of a methoxy group in the ion. The abundance of the ions is low, ranging from 1 to 8% of Σ_{31}. This is at most one-third of the abundance of the ions produced by chlorine migration in compounds I to V, but 1 to 70 times higher than the abundance of these same ions in compounds VII–IV. The result for the latter series of compounds suggests that the migration of chlorine may occur to a moderate extent even when the abundance of the chlorine containing ion is low, due to charge retention by the more highly chlorinated bicyclic species.



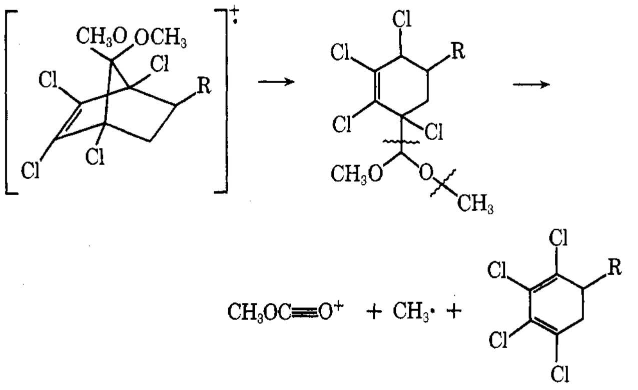
However, it is also possible that the ions under discussion may be generated by an entirely different fragmentation reaction, such as the following. An appropriate metastable peak could not be detected in support of the former mechanism and hence either mechanism may be operative.



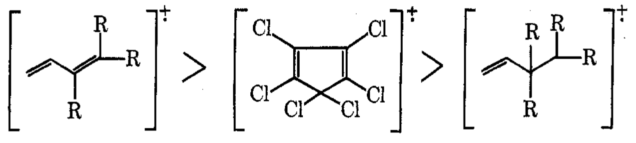
Trichloromethyl Ion.—Another rearranged ion produced by the migration of chlorine is the trichloromethyl ion. It appears in the spectra of most of the compounds at m/e 117 but is most abundant in the spectra of compounds VII–IX.

Since these compounds do not produce the chlorine-rearranged ion in high abundance, the dichloromethylene bridge may play an important role in this reaction, but the mechanism may be somewhat complex, since hexachlorocyclopentadiene also yields a trichloromethyl ion in low abundance.

Methoxycarbonyl Ion.—Compound XI gives an ion at m/e 59 which has the composition $C_2H_3O_2$ and represents 1.4% of Σ_{31}. It probably has the structure $CH_3OC{\equiv}O^+$ and may be produced as follows.

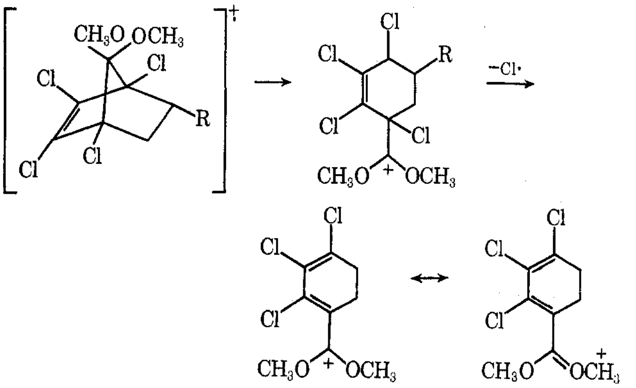


Ions Produced in the Retro-Diels–Alder Reaction.—All of the compounds included in this study undergo the retro-Diels–Alder reaction, with each fragment carrying a portion of the ion current. Acyclic conjugated olefins are produced in high abundance by compound I (m/e 104; 25.0% Σ_{31}), compounds II, III, IV, VI, and X (m/e 82; 11.2, 15.1, 12.3, 32.0, and 18.7% Σ_{31}, respectively), and compound V (m/e 68; 20.4% Σ_{31}), while ionized hexachlorocyclopentadiene (m/e 270) is produced in low abundance. The situation changes abruptly when the side chain in the molecule does not contain a double bond at C-1′. Compounds VII, VIII, and IX produce olefin fragments in low abundance at m/e 82 (1.3% Σ_{31}), m/e 82 (0.1% Σ_{31}), and m/e 70 (0.2% Σ_{31}), respectively, while the compounds produce hexachlorocyclopentadiene ions in moderate abundance at m/e 270 (1.0, 11.3, and 7.5% Σ_{31}). Since the nonconjugated olefin ions are not substantially more labile than the diolefin ions, the retro-Diels–Alder reaction generates ionized fragments in the following order of abundance.



Compound XI is capable of generating an ionized conjugated diolefin in this reaction, but it fails to produce such an ion in high abundance. This is probably due to the existence of a competing reaction which is mentioned in the next section.

Ions Formed by the Elimination of Chlorine and Hydrogen Chloride.—All of the compounds eject various combinations of chlorine and hydrogen chloride on electron impact, but only compound XI produces such ions which represent more than 9% of Σ_{31}. In the spectrum of this compound, the ion formed by the loss of a chlorine atom is the most abundant ion and the sum of the abundance of the M − Cl, M − HCl, and M − Cl − HCl ions represent 23.6% of Σ_{31}. It is apparent that special mechanisms are operative in this system, such as the following.



Experimental Section

General.—The olefins were obtained from Chemical Samples Co. or Phillips Petroleum Co. in high purity. Hexachlorocyclopentadiene was obtained from the Aldrich Chemical Co. and used without further purification. All boiling points and melting points are uncorrected. Molecular weight values were obtained from the mass spectra and are corrected for the presence of isotopic species. Nmr spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. The mass spectra were obtained on a Consolidated Electrodynamics Corp. 21-110 high-resolution mass spectrometer at 70 eV. Samples were introduced through a heated inlet system at 200° into an ion source which was also maintained at 200°.

1,2,4,4-Tetrachlorocyclopentadiene-1,3.—This compound was prepared according to the procedure described by Donish[10] and was obtained in 39% yield, mp 62–63° (lit.[10] mp 61°).

1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene.—The procedure of McBee[11] was employed to obtain this product in 89% yield, mp 27° (lit.[11] mp 27–28°).

Diels–Alder Adducts of Hexachlorocyclopentadiene, 1,2,3,4-Tetrachlorocyclopentadiene-1,3, and 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadine.—The chlorinated norbornenes were prepared by heating equivalent amounts of chlorinated cyclopentadiene and the appropriate olefin in a sealed glass tube for 18 hr at 95°. The yields and analyses are listed in Table I. No peaks produced by impurities could be detected in the mass spectra. The nmr spectra indicated that reaction occurs excessively between the chlorinated diene and the least hindered double bond of the acyclic olefin and that no double bond isomerization occurs.

Registry No.—I, 15584-72-2; *trans*-II, 28861-40-7; III, 28861-43-0; *cis*-IV, 28861-37-2; *trans*-V, 28861-35-0; *cis*-V, 28861-36-1; *cis*-VI, 28861-44-1; *trans*-VII, 29005-85-4; VIII, 29005-86-5; IX, 29005-87-6; *trans*-X, 29005-88-7; *trans*-XI, 29005-89-8.

[10] A. A. Donish, M. Silverman, and Y. A. Tajima, *J. Amer. Chem. Soc.*, **76**, 6144 (1954).

[11] E. T. McBee, D. L. Crain, R. D. Crain, L. R. Beloholv, and H. P. Braendlin, *ibid.*, **84**, 3557 (1962).

Electronic Effects in E2 Reactions. III. Base-Induced Eliminations of Some Phenyl 2-Pentyl Sulfones[1]

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Products of elimination have been determined for reaction of a series of 2-pentyl aryl sulfones with sodium ethylene glycolate in refluxing ethylene glycol and potassium *tert*-butoxide in refluxing pyridine. Compounds studied were *p*-nitrophenyl, *p*-bromophenyl, phenyl, *p*-methylphenyl, *p*-methoxyphenyl, 2,4,6-trimethylphenyl, and *p*-dimethylaminophenyl 2-pentyl sulfones. With a single exception (*p*-NO_2 sulfone in ethylene glycol) the proportion of 1-pentene from the base-induced eliminations was constant within the estimated limits of experimental error. In both media the ratio of *trans*- to *cis*-2-pentene from the mesityl sulfone was significantly different from that from the other sulfones. Several compounds failed to undergo base-induced elimination under these conditions. The *p*-bromophenyl sulfone was converted to *p*-hydroxyphenyl 2-pentyl sulfone in ethylene glycol and was recovered unchanged from the pyridine medium. The *p*-nitrophenyl sulfone yielded no volatile products in pyridine. The *p*-dimethylaminophenyl sulfone underwent elimination in the absence of base in both media. The results are discussed.

In recent years, the concept of a continuous spectrum of transition states for E2 reactions, differing in the extent to which the $C_\beta H$ and $C_\alpha X$ bonds are broken in the transition state, has found widespread acceptance.[2] The model has been used to account for a wide variety of structural and environmental influences on the rates and products of E2 reactions. The proposal[3] that the direction of elimination can be strongly influenced by steric factors has met with less general acceptance,

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[1] (a) Abstracted from the Ph.D. Thesis of R. E. Miller, Jr., Carnegie-Mellon University, June 1967. (b) Parts I and II of this series: A. K. Colter and R. D. Johnson, *J. Amer. Chem. Soc.*, **84**, 3289 (1962); A. K. Colter and D. R. McKelvey, *Can. J. Chem.*, **43**, 1282 (1965).

[2] Recent reviews: (a) W. H. Saunders, Jr., in "The Chemistry of the Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, Chapter 2; (b) D. V. Banthorpe in "Studies on Chemical Structure and Reactivity," J. H. Ridd, Ed., Wiley, New York, N. Y., 1966, Chapter 3; (c) J. F. Bunnett, *Surv. Progr. Chem.*, **5**, 53 (1969).

[3] H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, **78**, 2203 (1956).