TABLE I
TEST OF MOLECULAR WEIGHT DETERMINATION BY N.M.R.

Unknown	M, calcd.	M, found	Peaks used for integration
Acenaphthene	154.20	155.3[a]	C_2H_4
		148.3	
		152.9	
		152.4	Aromatic hydro-
		150.6	gens
		153.6	
4-t-Butylcyclo- hexanol			
cis and trans	156.26	150.3	t-Butyl group
mixture		150.1	H–C–O–
Dehydroabietonitrile	281.42	271.3	Four methyls
		267.5	Aromatic H_3
2,4-Bispentamethyl- enespiro-5-carboxy- methylene-1,3-di- oxacyclopentane in form of methyl ester	266.33	272.4	Methyl ester
2-p-Anisoylpropionic	222.23	214.5	Lower aromatic H_2
acid Me ester		223.0	Higher aromatic H_2
		217.7	Aromatic methoxy
		211.0	Methyl ester
		217.3	2-Methylene
		226.0	H_{10} of Me's and C_2H_4
		221.6	Aromatic H_4
Anisaldehyde	136.14	138.7	Methoxy
		141.7	Aromatic H_4
Iodoform	393.78	392.5	Single peak
Benzoquinone	108.09	110.9	
p-Dinitrobenzene	168.11	174.1	
1,3,5-Trinitrobenzene	213.11	221.9	
Diphenylacetic acid	212.24	211.7	Tertiary H
Cholesterol	386.64	374.8[b]	Olefinic H
1,2-Diacetoxy-4-p-	278.29	280.1	Lower aromatic H_2
anisylbutene-3		271.0	Higher aromatic H_2, lower olefinic H
		290.8	Acetates
		288.8	
		283.6	
		270.5	Aromatic H_4, lower olefinic H
		268.0	Higher olefinic H–C–O–
		281.9	Aromatic H_4, olefinic C_2H_2, H–C–O–
p-Anisylacetic acid	166.18	163.0	Methylene,
		167.1	methoxy
		162.4	Lower aromatic H_2
p-t-Butylacetanilide	191.26	198.8	Acetyl
		196.8[b]	
		187.0	t-Butyl

[a] Different values based on the same peaks were determined using different R_f field strength and sweep time. [b] 1,3,5-Trinitrobenzene used as standard. Hexamethylcyclotrisiloxane served as standard in all other determinations.

tracing about five times in both directions. Substitute the average intensities and the weights into the formula. Note that for the purposes of the determination any solvent can be used whose absorption lies outside the standard and region of interest.

Possible Sources of Error.—Inhomogeneity might cause standard and unknown to be exposed to different field strength inside the probe. Hydroxyl groups exchange with moisture in the solvent and should not be used in the determination. Overlap of peaks can seriously reduce the accuracy of the integration. Note that if two peaks of unequal intensity and/or shape overlap, it is erroneous to cut the region by a vertical line at the lowest

TABLE II
EXAMPLES OF CONDITIONS FOR MEASUREMENTS ON THE VARIAN A 60 SPECTROMETER

Filt. bandwidth	1	1	1	1
R_f field	0.02	0.12	0.6	0.14
Sw. time	500	500	50	500
Sw. width	500	1000	500	1000
Sw. offset	0	0	0	0
Spect. amplitude	1.6	10	32	4
Int. amplitude	20	50	20	8
Spin	Yes	Yes	No	Yes
Standard	Sil[d]	Sil[d]	Sil[d]	Sil[d]
Mg.	110.8	11.852	51.6	35.7
Meq.	8.99	0.961	4.18	2.89
Unknown	[a]	CHI_3	[b]	[c]
Mg.	254.8	64.383	101.5	87.4
Obsd. peaks	C_2H_4	CHI_3	Arom.	Ac
Meq. peaks	6.608	0.1636	1.083	1.372
No. traces	5 + 5	1 + 1	5 + 5	1 + 1
Solvent	$CDCl_3$	$CDCl_3$	CCl_4	$CDCl_3$
Ml.	0.5	0.5	0.6	0.9

[a] Acenaphthene. [b] Dehydroabietonitrile. [c] p-t-Butylacetanilide. [d] Sil, hexamethylcyclotrisiloxane.

point of the spectrum between the peaks. Errors from impurities, inaccurate weighing or reading of the integral are self-evident.

Procedures for precise integration are discussed in operating manuals; we mention only a few crucial points here. Saturation must be avoided. Errors from saturation are greatest if sample and unknown peak are of unequal shape or size. Fluctuations due to instability (noise) are corrected by averaging several traces. If overlap is not produced by peak broadening, the sample spinning can be stopped, much higher R_f field used without saturation, and noise greatly reduced.

Tables I and II illustrate the usefulness of the new method and give the relevant information on the conditions of some of the measurements.

Preparation and Mass Spectrum of Hexachlorocyclopropane

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Although hexafluorocyclopropane has been known for some time,[1] hexachlorocyclopropane has not been reported previously.[2] We have prepared this compound

(1) A. F. Benning, F. B. Downing, and J. D. Park, to Kinetic Chemicals, Inc., U. S. Patent 2,394,581 (February 12, 1946).

(2) As this communication was being prepared to go to press, an abstract by S. W. Tobey and R. C. West reported the synthesis of hexachlorocyclopropane from tetrachloroethylene, chloroform, and potassium hydroxide. Their work was presented before the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962. More recently we learned through a referee that W. R. Moore, S. E. Krikorian, and J. E. LaPrade also have prepared this compound and measured its mass spectrum.

$$Cl_2C=CCl_2 + CCl_2 \longrightarrow Cl_2C\underset{\underset{Cl_2}{C}}{\diagup\diagdown}CCl_2$$
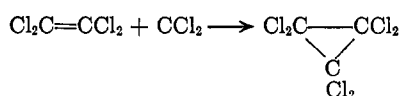
by the reaction of dichlorocarbene with tetrachloroethylene.

Experimental

A mixture of 204 ml. (2 moles) of tetrachloroethylene, 25 ml. of dimethoxyethane, and 185 g. (1 mole) of sodium trichloroacetate was stirred and refluxed until no more carbon dioxide was evolved (about 20 hr.). The cooled mixture was filtered, the sodium chloride was washed with three 50-ml. portions of n-hexane, and the combined filtrate and washings were distilled at 150 torr. to a final flask temperature of 115°. The residue solidified on cooling. It was dissolved in 100 ml. of n-pentane; the solution was filtered and chilled to −60°. The crystals (31 g.) were recrystallized from absolute ethanol with a little charcoal to give 26 g. of hexachlorocyclopropane melting at 106°. (Found: C, 14.4; Cl, 85.3. C_3Cl_6 requires: C, 14.5; Cl, 85.5.)

Results

Hexachlorocyclopropane is a white, crystalline solid with a terpene odor. It volatilizes readily at room temperature if left in the open; it is stable at 30° to acid, base, and permanganate. The low yield—10.4%, based on sodium trichloroacetate—might have been anticipated. Dichlorocarbene as a strong electrophile adds readily to olefins with electron-donating substituents, but would not be expected to give good yields with a highly chlorinated olefin. The composition of the other reaction products is being investigated.

The mass spectrum of hexachlorocyclopropane shows a progression of ions of well defined identity. Peaks occur in groups, the profiles of which correspond to statistical distributions of Cl^{35} and Cl^{37} atoms in natural abundance[3] and hence define clearly the number of chlorine atoms contained. Thus, the spectrum shows: $C_3Cl_5^+$, $C_3Cl_4^+$, $C_3Cl_3^+$, $C_3Cl_2^+$, C_3Cl^+, C_3^+; $C_2Cl_4^+$, $C_2Cl_3^+$, $C_2Cl_2^+$, C_2Cl^+; CCl_3^+, CCl_2^+, CCl^+; Cl_2^+, and Cl^+. This spectrum was compared with that of the open-chain isomer, hexachloropropene, and the spectra of the chlorinated isomers, in turn, were compared with those of cyclopropane and propene.

The four spectra are shown in Table I, with intensities expressed as per cents of total ion current. In the interest of simplicity, intensities of the isotopic variants of each ionic species have been summed; thus, the yield of each ion in the spectrum is measured by a single intensity value. Agreement between our spectrum of hexachloropropene and that reported earlier[4] is only fair; however, the earlier report gave no information either on the source and purity of the sample or on experimental conditions used in measuring the spectrum. The samples used in our work included commercial material and that made in our laboratories by dehydrochlorinating both symmetrical and asymmetrical heptachloropropanes with potassium hydroxide in methanol.[5] They all contained appreciable amounts of impurities, of which methyl trichloroacrylate was a major component; these impurities were not reduced below about 5% by gas chromatography.

TABLE I

MASS SPECTRA OF C_3Cl_6 AND C_3H_6 ISOMERS

Ion, X = Cl or H	Hexachlorocyclopropane[a]	Hexachloropropene[a,b]	Cyclopropane	Propene
$C_3X_6^+$	...	2.39	24.8	16.2
$C_3X_5^+$	37.6	32.5	23.2	25.9
$C_3X_4^+$	0.35	1.68	7.67	6.97
$C_3X_3^+$	6.68	11.2	18.1	20.1
$C_3X_2^+$	4.74	9.56	3.82	5.52
C_3X^+	5.84	7.32	2.92	4.20
C_3^+	2.41	3.41	0.55	0.84
$C_2X_4^+$	4.72	0.24	0.54	...
$C_2X_3^+$	1.84	0.98	9.45	10.7
$C_2X_2^+$	3.92	2.95	3.54	3.51
C_2X^+	1.13	0.86	0.65	0.85
CX_3^+	9.83	9.43	1.38	1.91
CX_2^+	5.62	1.71	1.80	1.39
CX^+	6.27	4.19	0.74	0.74
C^+	b	b	0.46	0.55
X_2^+	0.21	0.24	0.12	0.55
X^+	5.75	6.83	c	e
$C_3X_6^{+2}$	...	2.13	...	...
$C_3X_5^{+2}$	1.16	...	...	...
$C_3X_4^{+2}$	0.39	...	...	...
$C_3X_3^{+2}$	...	0.12	...	...
$C_3X_2^{+2}$	0.97	...	...	...
C_3X^{+2}	...	0.01	...	...
X_2^{+2}	0.52	...	c	e
Species containing 4, 5, and 6 carbons	...	2.24[d]	...	...

[a] Corrected for HCl, presumably formed by a wall reaction in the ionization chamber. HCl accounted for 0.76% of total ion intensity in the spectrum of hexachlorocyclopropane and 1.20% in that of hexachloropropene. [b] Corrected for 3.6 vol. % methyl trichloroacrylate. [c] Not measured. [d] Due to unknown impurities.

Spectra of the chlorinated compounds were measured on a Consolidated Model 21–103 instrument with the inlet system at a temperature of 140° for the cyclic isomer and 250° for the olefin. Those of the hydrocarbons were measured on another 21–103 instrument with the inlet system at room temperature. All measurements were made with 70-v. electrons.

The spectra of the C_3Cl_6 isomers are generally similar, showing pronounced differences in relative intensity for only three singly charged ions: $C_3Cl_6^+$, $C_2Cl_4^+$, and CCl_2^+. Respective intensities of these ions in the spectrum of hexachlorocyclopropane are zero[6] and greater by factors of 20 and 3 than in that of the olefinic isomer. Spectra of the hydrocarbon analogs resemble each other even more closely. The parent peak of cyclopropane is the more intense by a factor of 1.5 and is, indeed, the most intense peak in the spectrum of this compound. Intensity of $C_2H_4^+$ in the spectrum of cyclopropane is only one-ninth that of $C_2Cl_4^+$ in the spectrum of hexachlorocyclopropane; the spectrum of propene shows no measurable yield of $C_2H_4^+$. Intensities of CH_2^+ in the two spectra differ but little. Distributions of doubly charged ions in the spectra of the chlorinated compounds differ sharply but, at present, inexplicably.

(6) We are indebted to the referee for calling attention to a discrepancy between the spectrum of W. R. Moore, et al., and an earlier spectrum of ours, measured with the inlet system at 250°, which contained small $C_3Cl_6^+$ peaks. Reducing the temperature to 140° removed these peaks, substantiating Dr. Moore's suggestion that the higher temperature causes pyrolysis of hexachlorocyclopropane even at the low sample pressure, 20 to 30 torr., in the inlet system. About 15% conversion to hexachloropropene had occurred; no other products were apparent.

(3) J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," D. Van Nostrand Company, Princeton, N. J., 1960.

(4) H. R. Harless, presented before A.S.T.M. Committee E-14 on Mass Spectrometry, Chicago, Ill., June, 1961.

(5) F. Bergmann and L. Haskelberg, J. Am. Chem. Soc., 63, 1437 (1941).

The close similarity of the spectra of C_3X_6 (X = H or Cl) isomer pairs, like that of C_7H_8 isomers,[7,8] suggests that the isomers decompose under electron impact largely through common intermediates. In the case of the hydrocarbons, support for this suggestion can be drawn from evidence, based on appearance–potential measurements, that the $C_3H_5^+$ ion derived from cyclopropane does not have the cyclopropyl structure and is, in fact, the same chemical species as $C_3H_5^+$ ions derived from acyclic compounds.[9,10]

The differences between the spectra of isomers suggest that all or most of the $C_2X_4^+$ and part of the CX_2^+ are formed directly from parent ions with the original cyclopropane structure. The reactions involved presumably resemble the reverse of that by which hexachlorocyclopropane was synthesized. The differences between the spectra of chlorinated and unchlorinated species apparently reflect the greater difficulty of formation of C_3Cl_6 from, and lower stability with respect to, C_2Cl_4 and CCl_2 than of C_3H_6 with respect to C_2H_4 and CH_2. Such a view is in accord with the poor yield obtained by us in the synthesis of hexachlorocyclopropane and with chemical evidence indicating that CCl_2 is more stable than CH_2. For example, dichlorocarbene is easily generated by low-energy processes such as the reaction of base with chloroform[11] or thermal decomposition of sodium trichloroacetate[12]; preparation of methylene, on the other hand, requires photolysis of ketene or diazomethane.[13]

(7) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).
(8) S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961).
(9) F. H. Field, *J. Chem. Phys.*, **20**, 1734 (1952).
(10) R. F. Pottie, A. G. Harrison, and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 3204 (1961).
(11) W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).
(12) W. M. Wagner, *Proc. Chem. Soc.* (London), 229 (1959).
(13) W. Kirmse, *Angew. Chem.*, **73**, 161 (1961).

Intramolecular Nucleophilic Participation. III. Transition State Geometry in the Hydrolysis of o- and p-Carbomethoxycumyl Chlorides

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The solvolysis of o-carbophenoxybenzhydryl bromide takes place much more rapidly than does that of its *para* isomer.[1] The relatively high reactivity of the *ortho* isomer has been explained on the assumption that its carbophenoxy group can participate electronically in the activation process by releasing electrons to the vacant p-orbital developing at the reaction center. The o- and p-carbomethoxybenzyl bromides, on the other hand, solvolyze at comparable rates. Failure of the carbomethoxy group to participate effectively in the reaction of the o-substituted benzyl bromide has been explained[1,2] on the assumption that it is highly critical energetically for the development of positive charge on

(1) A. Singh, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 1179 (1962).
(2) R. E. Lovins, L. J. Andrews, and R. M. Keefer, *ibid.*, **84**, 3959 (1962).

carbon at the reaction center that the p-orbital which is being vacated overlap the π electrons of the aromatic nucleus. For maximum overlap of this type the trigonal valences of the carbon atom in question must lie in the ring plane, an arrangement which is not favorable for effective participation by the carbomethoxy group.

The present investigation, in which the hydrolysis rates of cumyl chloride and its o- and p-carbomethoxy derivatives have been determined, has been conducted to ascertain whether or not it is also important for stabilization of the cumyl cation (I), which is tertiary in character, that the vacant p-orbital on the exocyclic carbon overlap the π molecular orbital of the ring.

I
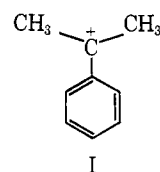
A summary of the results of the rate runs is given in Table I. As should be characteristic of a solvolysis in which bond breaking, rather than bond making, is the dominant feature of the activation process,[3] the electron-withdrawing carbomethoxy substituent has been found to have a strong deactivating influence in cumyl chlo-

TABLE I
RATE CONSTANTS FOR HYDROLYSIS OF THE SUBSTITUTED CUMYL CHLORIDES

$10^2[RCl]_i$ mole/l.	Solvent, % aqueous acetone[a]	Temp., °C.	$10^5 k_s$, sec.$^{-1}$
Cumyl chloride [$C_6H_5C(CH_3)_2Cl$]			
5.00	80	25.0	103
9.56	85	25.0	68.8
1.76	90	25.0	15.0
11.3	90	25.0	14.4
16.6	90	25.0	14.5
Av. k_s (90% aq. acetone)			14.6
p-Carbomethoxycumyl chloride[b]			
3.69	70	25.0	4.68
8.06	70	25.0	4.65
10.8	70	25.0	3.68
Av. k_s (25.0°)			4.34
3.86	70	36.0	19.0
7.66	70	36.0	14.8
8.36	70	36.0	14.9
Av. k_s (36.0°)			16.2
o-Carbomethoxycumyl chloride[c]			
3.04	70	25.0	11.3
3.94	70	25.0	11.0
6.65	70	25.0	9.2
Av. k_s (25.0°)			10.5
4.04	70	36.0	36.8
4.45	70	36.0	33.6
Av. k_s (36.0°)			35.2

[a] Prepared by mixing $100 - x$ volumes of acetone with x volumes of water to give $(100 - x)\%$ of aqueous acetone. [b] Values of E_a = 22 kcal./mole and ΔS^* = -7 e.u. have been calculated for p-carbomethoxycumyl chloride using the average k_s values at 25.0° and 36.0°. [c] Values of E_a = 19 kcal./mole and ΔS^* = -16 e.u. have been calculated for o-carbomethoxycumyl chloride using the average k_s values at 25.0° and 36.0°.

(3) C. G. Swain and W. P. Langsdorf, Jr., *ibid.*, **73**, 2813 (1951).