Mass Spectra of Dihalogenocycloalkanes

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The mass spectra of the dichloro- and bromochloro-cyclobutanes, the dichlorocyclopentanes, and the dichloro-, chlorofluoro-, and stable dibromo-cyclohexanes are reported. Four major breakdown pathways can be distinguished, the favoured fragmentation route depending on the ring size, the type of halogen substitution, the the relative position, and *cis–trans*-relationships of the two substituents. Within one set of isomers, the 1,1-isomer and the *cis*-1,2-isomer had clearly distinguishable spectra, but the spectra of the other isomers were similar.

No reports of the mass spectra of dihalogenocycloalkanes have appeared in the literature, and the present study was undertaken to examine the usefulness of mass spectra in the identification of dihalogenocycloalkane stereoisomers, and to observe the behaviour of these dihalides on electron impact. Mass spectra of norbornyl bromides have been examined by de Jongh and Shrader,[1] and some electron impact studies with isomeric substituted cyclobutanes and cyclohexenes have been reported.[2,3]

Mass Spectra of Dichloro-cyclohexanes, -cyclopentanes, and -cyclobutanes.—The mass spectral data are in Tables 1, 2, and 3. The peak intensities of the ions are given as percentages of the intensity of the base peak, and the compounds are listed in the order of their retention times on Silicone oil, starting with the 1,1-isomer which was eluted first. The final peak in each case is the *cis*-1,2-isomer, and the other isomers occurring between these two are hereinafter referred to as the ' central isomers.' The cracking patterns of the central isomers of dichlorocyclohexane are similar having a base peak at *m/e* 81 corresponding to $C_6H_9^+$, and the same metastable ion positions. Loss of an HCl molecule followed by loss of a Cl· atom appears to be the favoured

[1] D. C. De Jongh and S. R. Shrader, *J. Amer. Chem. Soc.*, 1966, **88**, 3881.

[2] E. F. H. Brittain, C. H. J. Wells, and H. M. Paisley, *J. Chem. Soc.* (*B*), 1968, 304.

[3] E. F. H. Brittain, C. H. J. Wells, and H. M. Paisley, *J. Chem. Soc.* (*B*), 1969, 503.

TABLE 1

Mass spectra of dichlorocyclohexane isomers at 22 eV. Ions of ⩾1% base peak only are given except for the parent ions and halogen isotope ions

m/e	1,1	*t*-1,2	*t*-1,3	*t*-1,4	*c*-1,3	*c*-1,4	*c*-1,2
39	2	2	1	1	1	1	1
41	9	9	5	6	5	5	13
53	12	3	2	2	2	2	3
54	7	10	5	6	6	5	14
62	—	2	1	1	1	1	3
65	3	1	1	1	—	1	1
67	8	12	6	10	4	4	13
75	4	5	3	4	3	3	5
76	—	2	1	1	1	1	1
77	4	3	2	3	2	2	4
78	2	4	4	4	3	3	3
79	14	7	8	8	7	7	7
80	19	59	31	44	33	31	100
81	100	100	100	100	100	100	46
82	7	11	7	8	7	7	5
88	20	4	3	3	2	1	7
90	7	1	1	1	1	1	3
101	4	—	—	—	—	—	—
103	1	—	—	—	—	—	—
116	68	7	9	9	7	7	6
117	6	2	2	3	6	6	2
118	22	3	4	3	3	3	2
119	2	—	—	1	2	2	1
151	—	—	—	—	—	—	3·3
152	—	2·9	1·3	1·6	1·5	1·6	—
153	—	—	—	—	—	—	2·3
154	—	2·2	0·9	1·1	1·1	1·0	—
155	—	—	—	—	—	—	0·3
156	—	0·4	0·1	0·2	0·2	0·2	—

TABLE 2

Mass spectra of dichlorocyclopentane isomers at 20 eV

m/e	1,1	*t*-1,2	*t*-1,3	*c*-1,3	*c*-1,2
39	4	14	2	4	2
40	13	12	2	3	—
41	54	24	11	23	3
42	—	—	3	3	—
62	1	—	3	4	2
63	—	—	1	2	—
64	6	3	1	2	1
65	3	25	13	17	13
66	100	22	6	6	4
67	8	100	100	71	5
68	1	11	6	5	—
75	2	8	3	10	29
76	2	6	5	12	2
77	—	3	1	4	9
78	—	—	2	5	—
96	2	3	—	8	3
98	2	2	1	5	2
100	2	5	6	5	9
101	9	45	14	100	100
102	43	25	5	17	9
103	6	21	6	42	33
104	15	8	1	6	2
108	4	—	—	—	—
110	4	—	—	—	5
112	—	—	—	—	4
114	—	—	—	—	1
136	—	—	—	—	20
137	—	—	—	39·4	7
138	—	11·2	4·8	—	13·5
139	—	—	—	24·6	4
140	—	8·1	3·4	—	2·3
141	—	—	—	4·8	0·7
142	—	1·4	0·5	—	—

process, although loss of two HCl molecules is also important. The fragment at *m/e* 81 then breaks up further by ring opening and loss of a CH_2 fragment or loss of an ethylene molecule. This is also the major breakdown route for the 1,1-, *trans*-1,2-, and *trans*-1,3-dichlorocyclopentane isomers and the base peak is at *m/e* 67 corresponding to $C_5H_7^+$.

TABLE 3

Mass spectra of dichlorocyclobutane isomers at 20 eV

m/e	1,1	*t*-1,2	*t*-1,3	*c*-1,3	*c*-1,2
39	4	3	3	4	4
41	3	3	4	2	3
53	17	12	11	9	10
62	15	100	100	100	100
64	6	33	38	39	36
63	—	—	—	—	35
65	—	—	—	—	12
75	2	9	13	7	7
77	1	3	5	3	3
88	—	14	17	13	—
90	—	5	6	4	—
89	31	7	7	4	63
91	12	2	3	2	21
96	100	5	2	8	3
98	77	3	1	6	2
100	14	1	—	2	1
109	4	—	1	1	—
111	3	—	—	—	—
113	1	—	—	—	—
124	0·8	0·7	1·0	0·9	5·6
126	0·7	0·4	0·8	0·6	3·7
128	0·1	0·1	0·1	0·1	0·6

The 1,1-isomers, having lost HCl, appear to be more stable and loss of ethylene (*e.g.*, with 1,1-dichlorocyclohexane *m/e* 116, 118 ⟶ 88, 90) and methyl (*m/e* 116, 118 ⟶ 101, 103) compete with loss of Cl· (*m/e* 116, 118 ⟶ 81). The *cis*-1,2-isomer loses a hydrogen atom from the parent and this is followed by loss of a chlorine atom and then an HCl molecule. Loss of ethylene by ring fission (*m/e* 116, 118 ⟶ 88, 90) is also appreciable for the *cis*-1,2-dichlorocyclohexane. *cis*-1,2-Dichlorocyclopentane loses a hydrogen atom or a hydrogen molecule, and this is followed by loss of two HCl molecules. The *cis*-1,3-isomer also shows the hydrogen atom loss sequence. With the cyclopentane isomers a further ring-fission process of the parent leading to fragments of masses 75, 77 and 62, 64 can also be distinguished.

With all the dichlorocyclobutane isomers the main fragmentation route was ring cleavage leading to two chloroethylene fragments, *e.g.*, with the *trans*-1,2-isomer *m/e* 124, 126, 128 ⟶ 62, 64.

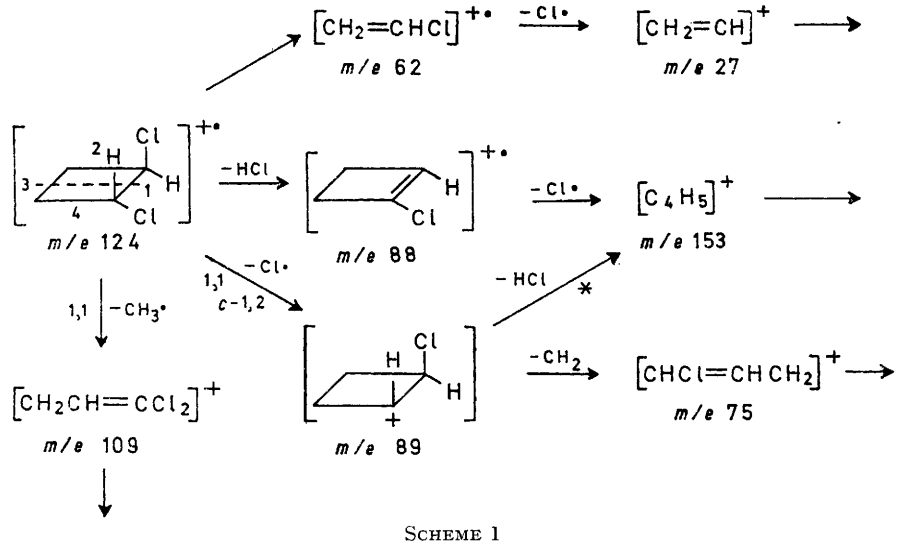
The central isomers again showed the loss of HCl followed by Cl· sequence, and the 1,1- and *cis*-1,2-isomers broke up by loss of Cl· followed by HCl (see Scheme 1).

Variation of Ionising Voltage.—The mass spectrum of *trans*-1,2-dichlorocyclohexane was recorded at various ionising voltages between 20 and 80 eV. The variation in abundance of some important ions, expressed as $100I/\Sigma I$, with ionising potential is shown in the Figure.

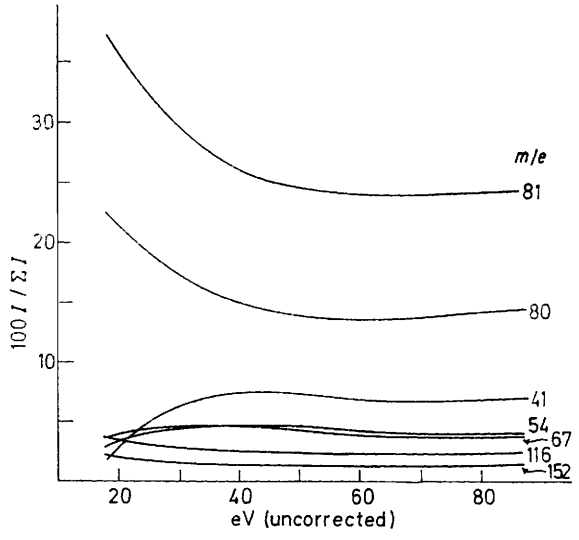
The abundance of the C_6 fragments, *i.e.*, *m/e* 152, 116, 81, *etc.*, increases slightly towards lower ionising energies and the abundance of the smaller fragments decreases. However, with the exception of the ion at *m/e* 41 ($C_3H_5^+$) the percentage changes are quite small, and little

change in the mass spectrum with ionising potential is observed. Small changes only are therefore expected with other dihalogenocycloalkanes.

Mass Spectra of Chlorofluorocyclohexanes, Bromochlorocyclobutanes, and Dibromocyclohexanes.—The mass spectral data of six of the seven chlorofluorocyclohexanes, four of the five bromochlorocyclobutanes, and five of the dibromocyclohexanes are in Tables 4, 5, and 6. The compounds are listed in order of their retention times on Silicone oil. The major fragmentation routes



SCHEME 1



Variation in ion abundances from *trans*-1,2-dichlorocyclohexane with ionising potential

of the chlorofluorocyclohexanes are depicted in Scheme 2. All the isomers except the *cis*-1,2 lost HCl from the parent followed by loss of a fluorine atom and loss of an HF molecule, or ring cleavage and loss of methyl. The *cis*-1,2-isomer first lost a hydrogen atom or hydrogen molecule in the same way as *cis*-1,2-dichlorocyclohexane and *cis*-1,2-dichlorocyclopentane.

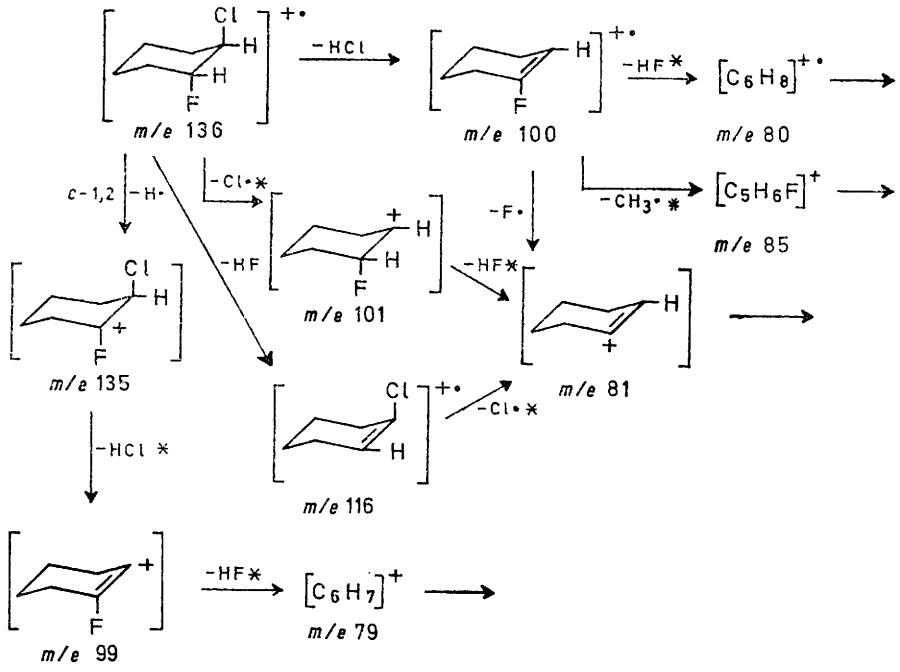
In contrast to the dichlorocyclobutanes, all four bromochlorocyclobutanes broke up by loss of a bromine atom to give the ion at *m/e* 89 as the base peak. This ion then decomposed by HCl elimination. Ring cleavage occurred only to a small extent for all isomers *m/e* 168, 170, 172 ⟶ 62, 64.

TABLE 4

Mass spectra of chlorofluorocyclohexane isomers at 22 eV

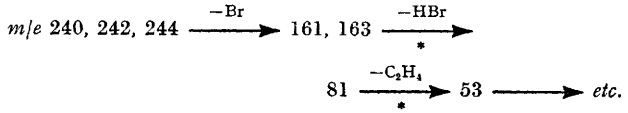
m/e	1,1-	*t*-1,2	*c*-1,3	*t*-1,4	*c*-1,4	*c*-1,2
39	8	6	18	13	10	6
41	25	10	33	39	44	6
53	10	7	17	13	6	9
54	17	30	50	49	46	8
55	23	13	24	27	28	7
59	19	17	28	28	38	10
67	15	13	18	16	32	7
69	8	5	6	4	8	—
72	62	17	40	32	54	8
73	12	8	16	13	13	9
77	—	—	—	—	—	14
79	21	40	55	48	21	31
80	35	100	100	95	100	8
81	100	47	100	100	48	7
82	12	6	13	11	6	—
85	42	20	29	32	58	18
97	—	—	—	—	—	13
98	—	—	—	—	—	19
99	19	11	20	9	14	100
100	67	17	51	50	50	11
101	81	7	52	49	7	—
116	10	6	—	4	7	—
118	4	3	—	1	2	—
134	—	—	—	—	—	9
135	—	—	—	—	—	28
136	2·0	2·5	3·0	4·4	2·4	5·4
137	—	—	—	—	—	11
138	0·7	0·8	1·0	1·6	0·8	0·6

The main fragmentation route for all the dibromocyclohexane isomers was loss of a bromine atom from the parent, followed by HBr elimination to give the base peak at *m/e* 81. This ion then further decomposed by



SCHEME 2 Major fragmentation routes for chlorofluorocyclohexanes; starred processes confirmed by the presence of a metastable ion. The lowest molecular weight ion only of the chlorine isotope cluster is given in each case. The processes marked *c*-1,2 *etc.* occurred for that isomer only

ring opening and loss of an ethylene molecule or a CH_2 fragment as in Scheme 3.



SCHEME 3

TABLE 5

Mass spectra of bromochlorocyclobutane isomers at 20 eV

m/e	1,1-	*t*-1,2	*t*-1,3	*c*-1,3
39	4	18	8	7
41	2	14	3	3
51	1	2	2	1
52	1	3	2	1
53	24	70	74	67
54	6	18	7	8
61	12	4	2	2
62	3	30	5	5
63	5	4	2	2
64	2	9	2	2
75	1	59	6	9
77	—	19	2	3
88	—	42	7	6
89	100	100	100	100
90	—	18	7	8
91	34	33	31	32
106	—	—	2	6
108	—	—	2	6
132	1	—	11	6
134	1	—	10	6
140	46	7	—	—
142	60	9	—	—
144	14	1	—	—
154	2	—	—	—
156	1	—	—	—
158	—	—	—	—
168	0·3	—	15·5	2·0
170	0·4	—	19·4	2·6
172	0·1	—	3·5	0·7

TABLE 6

Mass spectra of dibromocyclohexane isomers at 20 eV

m/e	*t*-1,2	*t*-1,3	*t*-1,4	*c*-1,3	*c*-1,4
39	1	1	1	1	1
41	4	3	4	3	3
53	3	2	3	2	2
54	5	2	2	2	2
55	2	2	2	2	2
67	7	3	3	4	2
77	1	2	3	2	2
78	2	3	3	2	2
79	4	19	17	9	9
80	2	11	14	9	14
81	100	100	100	100	100
82	10	8	8	8	7
119	1	1	1	1	1
121	1	1	1	1	1
161	16	13	15	12	15
163	16	12	15	11	15
240	1·0	0·9	1·0	0·9	0·3
242	1·7	1·4	1·5	2·0	0·5
244	0·9	0·8	0·7	1·0	0·3

DISCUSSION

Elimination of hydrogen halide from the molecular ion is the most wide spread route to decomposition, occurring to some extent for nearly all of the compounds studied. In the thermal elimination of hydrogen halide when alkyl halides are pyrolysed, it is believed that elimination often involves a quasi-ionic activated complex which requires the hydrogen and halogen to be *cis* to each other.[4] The present electron-impact data are also most simply understood in terms of a similar quasi-ionic *cis*-elimination. Thus all the *trans*-1,2-dichloro-compounds where the hydrogen and chlorine

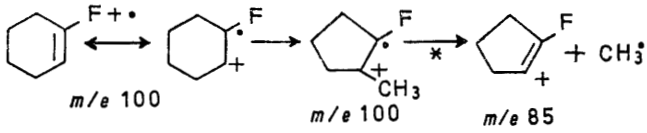
[4] A. Maccoll and P. J. Thomas, *Progr. Reaction Kinetics*, 1967, **4**, 119.

are *cis* give strong peaks corresponding to loss of HCl or loss of two HCl molecules. In the same way *trans*-1,2-chlorofluorocyclohexane also gives a strong peak corresponding to loss of HCl followed by loss of HF. In the dichlorocyclobutane ring system the hydrogen and chlorine atoms are held rigidly in the *cis*-configuration for the *trans*-1,2-isomer, whereas in the corresponding dichlorocyclopentane the hydrogen and chlorine atoms have some freedom of movement and the *cis*-configuration is not rigidly maintained. Similarly greater freedom of movement is possible for the *trans*-1,2-dichlorocyclohexane. Thus HCl elimination is particularly favoured in the *trans*-1,2-dichlorocyclobutane, and absent for the *cis*-1,2-dichlorocyclobutane. HCl elimination from *trans*-1,2-dichlorocyclopentane occurs much more readily than from the *cis*-1,2-isomer, and the same is true of the corresponding dichlorocyclohexanes. For the *trans*-1,3-, *trans*-1,4-, *cis*-1,3-, and *cis*-1,4-dichlorocyclohexanes the chlorine atom can become *cis* to a hydrogen of an adjacent methylene group, so that little difference in ease of HCl elimination would be expected. In the same way HBr elimination only occurs to any great extent with the *trans*-1,2-bromochlorocyclobutane where the bromine is *cis* to the hydrogen on the neighbouring chlorine-substituted, carbon atom. For the *trans*-1,3-, and *cis*-1,3-isomers HBr elimination is much diminished, and little difference between the two isomers is observed. In the comparatively less rigid dibromocyclohexane system, no HBr elimination was observed.

Loss of a hydrogen atom or a halogen atom from the parent occurs when hydrogen halide elimination is not favoured. Thus *cis*-1,2-chlorofluorocyclohexane loses H· predominantly, *cis*-1,2-dichorocyclohexane loses H· and Cl·, *cis*-1,2-dichlorocyclopentane loses H· and H_2, and *cis*-1,2-dichlorocyclobutane loses Cl·. The loss of halogen becomes more important as the carbon–halogen bond dissociation energy decreases and with the bromine-containing compounds loss of a bromine atom predominates for all the isomers.

Ring cleavage predominates in the strained dichlorocyclobutane series. The 1,1-isomer cleaves to give $[CCl_2{=}CH_2]^{+\bullet}$ and all the other isomers yield $[CH_2{=}CHCl]^{+\bullet}$. For the bromochlorocyclobutanes loss of bromine predominates, but some ring cleavage also occurs, the 1,1-isomer giving $[C_2H_2ClBr]^{+\bullet}$ and the other isomers $[CH_2{=}CHCl]^{+\bullet}$. Ring cleavage evidently mostly occurs at bonds 1 and 3, since little of the $[C_2H_2Cl_2]^{+\bullet}$ ion is observed for the *trans*-1,2- or *cis*-1,2-dichloro-isomers. This also holds for the bromochlorocyclobutanes, although the *trans*-1,2-isomer does give rise to some of the $[C_2H_2ClBr]^{+\bullet}$, so that cleavage is not confined exclusively to the 1,2- and 3,4-bonds. In the dichlorocyclopentane system, the presence of the ions $[C_2H_3Cl]^{+\bullet}$ (*m/e* 62, 64) and $[C_3H_5Cl]^{+\bullet}$ (*m/e* 76, 78) for all isomers (except 1,1), suggests that some ring cleavage also occurs here, although in the absence of a metastable peak this could not be confirmed. In the least strained dichlorocyclohexane and chlorofluorocyclohexane systems, there is very little evidence for ring cleavage.

In the chlorofluorocyclohexane system the parent ion first eliminated HCl giving the ion at *m/e* 100. This ion then decomposed by three main routes; loss of HF, loss of F·, or loss of a methyl fragment. The latter process gives rise to the ion at *m/e* 85, and probably occurs *via* ring contraction. A metastable fragment confirms the



connection between the two ions. A similar loss of methyl is observed for the 1,1-dichlorocyclohexane isomer, *m/e* 116, 118 ⟶ 101, 103, and for the 1,1-dichlorocyclopentane isomer (not shown in Table 2) *m/e* 102, 104 ⟶ 87, 89, although the ions are very weak, and no metastable peak confirming the process could be found. The methyl loss in the chlorofluoro-system is presumably favoured because loss of F· or HF is so much less easy.

In every series of dihalogeno-isomers the mass spectra of the 1,1- and *cis*-1,2-dihalogenocycloalkanes were clearly distinguishable from each other and from the other dihalogeno-isomers, and could be used for characterisation. In general the mass spectra of the other isomers within any particular series were all similar and not easily distinguishable from each other. However the *trans*-1,2-bromochlorocyclobutane could be identified by the moderately strong ions at *m/e* 140, 142, and 144 due to $[C_2H_2ClBr]^{+\bullet}$, which were absent for the *trans*-1,3- and *cis*-1,3-isomers. In the dichlorocyclopentane series the *cis*-1,3-isomer could be identified by the strong peaks at *m/e* 137, 139, and 141 corresponding to $[C_5H_7Cl_2]^+$.

EXPERIMENTAL

Mass spectra were recorded on an AEI MS 12 instrument. The electron beam energy was 20 eV, unless otherwise stated. Compounds were introduced from a Perkin-Elmer F11 gas chromatograph, coupled *via* a single stage Bieman separator directly into the mass spectrometer source. A 150 m Silicone oil capillary column at 60 °C was used, the Bieman separator and coupling line were maintained at 100 °C, and the ion source at *ca.* 200 °C.

Materials.—1,1-Dichlorocyclohexane was prepared from cyclohexanone and phosphorus pentachloride.[5] *trans*-1,2-Dichlorocyclohexane was prepared from cyclohexene and chlorine, and *cis*-1,2-dichlorocyclohexane from 2-chlorocyclohexanol.[6] *cis*- and *trans*-1,3-Dichlorocyclohexane were obtained by preparative g.l.c. of a mixture of dichlorocyclohexanes, and *cis*- and *trans*-1,4-dichlorocyclohexane were prepared and separated by 'spinning band' distillation.[7] The compounds were purified by preparative g.l.c. and characterised by n.m.r. spectroscopy.[8]

[5] B. Caroll, D. G. Kubler, H. W. Davis, and A. M. Whaley, *J. Amer. Chem. Soc.*, 1951, **73**, 5382.
[6] M. S. Newman and C. A. Van der Werf, *J. Amer. Chem. Soc.*, 1945, **67**, 233.
[7] W. Kwestroo, F. A. Meijer, and E. Havinga, *Rec. Trav. chim.*, 1954, **78**, 717.
[8] G. A. Russell, I. Akiluho, and R. Konaka, *J. Amer. Chem. Soc.*, 1963, **85**, 2988.

1,1-Dichlorocyclopentane, *trans*-1,2-dichlorocyclopentane, and *cis*-1,2-dichlorocyclopentane were prepared by methods analogous to those for the corresponding dichlorocyclohexanes. *cis*- and *trans*-1,3-Dichlorocyclopentanes were prepared by chlorination of chlorocyclopentane followed by spinning band distillation. All the compounds were purified by g.l.c. and characterised by their n.m.r. spectra.

Pure 1,1-, *cis*-1,3-, *trans*-1,4-, *cis*-1,4-, and *cis*-1,2-chlorofluorocyclohexanes were prepared by chlorination of fluorocyclohexane, and preparative g.l.c. on the resulting mixture of chlorofluorocyclohexanes. *trans*-1,2-Chlorofluorocyclohexane was prepared by addition of HF to 1-chlorocyclohexene, followed by preparative g.l.c. of the resulting mixture. All compounds were characterised by ^{19}F and ^{1}H n.m.r. spectroscopy. Pure *trans*-1,3-chlorofluorocyclohexane could not be obtained. The order of elution of dihalogenocycloalkanes on Silicone oil being clearly established from the foregoing, and other [9] preparations, the dichlorocyclobutanes, bromochlorocyclobutanes, and dibromocyclohexanes were prepared by gas-phase chlorination of chlorocyclobutane, bromination of chlorocyclobutane, and bromination of bromocyclohexane respectively. The isomers were then characterised from their retention times.

[9] D. S. Ashton and J. M. Tedder, unpublished work.

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