Free-radical Substitution in Aliphatic Compounds. Part XXV.† The Gas-phase Chlorination of Chlorocyclobutane and Methylcyclobutane

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The chlorination of chlorocyclobutane and methylcyclobutane has been studied in the gas phase over a wide temperature range. Competitive experiments with 1-chlorobutane have shown that unlike unsubstituted cyclobutane, chloro- and methyl-cyclobutane are more reactive than the corresponding cyclopentyl and cyclohexyl derivatives. This difference between substituted and unsubstituted cyclobutanes is attributed to release of strain in the formation of the substituted cyclobutyl radical. The *trans* to *cis* ratio of the 1,2-dichlorocyclobutane and the 2-chloro-1-methylcyclobutane products at 100° were 6·8 : 1 and 1·2 : 1 respectively. These results are consistent with ideas concerning the *trans*:*cis* ratios discussed in previous papers.

THE present paper describes the extension to the cyclobutane ring system of a halogenation study with substituted cycloalkanes.[1] The chlorination[2] and bromination[3] of cyclobutane has been investigated previously but there have been no attempts to study quantitatively the chlorination of chlorocyclobutane or of methylcyclobutane. The present work is intended to fill this omission and to provide further evidence of radical/substituent interaction leading to high *trans*:*cis* ratios in the 1,2-dichlorocycloalkane products.

EXPERIMENTAL

The gas-phase reactions were carried out in a conventional vacuum line as described previously.[4] N.m.r. spectra were recorded at 100 MHz on a Varian H.A. 100 instrument. G.c.–mass spectroscopy of the chloromethylcyclobutanes was carried out on an F11 gas chromatograph coupled *via* a Biemann separator to an A.E.I. MS12 mass spectrometer. Analysis was carried out on a Griffen and George D6 chromatograph (using a gas density balance as detector). The R.S. (relative selectivity) values tabulated are expressed as arithmetic means and the errors as standard deviations.

Reagents.—Methylcyclobutane was prepared by (atmospheric) hydrogenation of methylenecyclobutane using palladium/charcoal catalyst. Chlorocyclobutane was commercial material. Both were purified by preparative gas chromatography to give material boiling at 36°/760 mmHg and 82°/760 mmHg respectively. Each showed only one peak by analytical gas chromatography.

Identification of Isomeric Dichlorocyclobutanes.—Chlorination of chlorocyclobutane gave five isomeric dichlorocyclobutanes. The order of elution was assumed to be in the order observed for other dichlorocycloalkane systems.[5] The dichlorocyclobutanes were prepared by overchlorination, separated by preparative gas chromatography and identified by n.m.r. spectroscopy; the data are recorded in Table 1.

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† Part XXIV, D. E. Copp and J. M. Tedder, *Internat. J. Chem. Kinetics*, 1972, **4**, 69.

[1] D. S. Ashton and J. M. Tedder, *J. Chem. Soc.* (*B*), 1971, 1723.

[2] J. L. Knox and R. L. Nelson, *Trans. Faraday Soc.*, 1959, **55**, 943.

[3] K. C. Ferguson and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2618.

[4] H. Singh and J. M. Tedder, *J. Chem. Soc.*, 1964, 4737.

[5] D. S. Ashton, J. M. Tedder, and J. C. Walton, *J. Chromatog.*, 1471, **55**, 231.

TABLE 1

N.m.r. spectral data of the isomeric dichlorocyclobutanes

Isomer	Signal	No. of H nuclei	Multiplicity
1,1-Dichloro	7·06	4	Triplet $J = 7$ Hz
	7·86	2	C
trans-1,2	5·80	2	C
	7·46	2	C
	8·00	2	C
cis-1,2	5·46	2	C
	7·56	4	C
trans-1,3	5·38	2	Triplet of triplets $J = 6$ Hz
	7·19	4	Triplet A_2X_2 $J = 6$ Hz
cis-1,3	6·00	2	Triplet of triplets $J = 8$ Hz
	6·84	2	C } AB
	7·40	2	C

All signals expressed relative to Me_4Si. C denotes complex.

TABLE 2

Gas-phase chlorination of chlorocyclobutane

			R.S.$^{1x}_{1,1}$		
Temp.	1,1-Dichloro	*trans*-1,2	*cis*-1,2	*trans*-1,3	*cis*-1,3
35°	1	0·77 ± 0·01	0·07 ± 0·006	1·03 ± 0·01	0·68 ± 0·01
52	1	0·75 ± 0·02	0·09 ± 0·004	1·02 ± 0·01	0·67 ± 0·01
78	1	0·78 ± 0·01	0·08 ± 0·004	1·02 ± 0·01	0·74 ± 0·01
104	1	0·75 ± 0·01	0·11 ± 0·004	1·02 ± 0·01	0·70 ± 0·01
127	1	0·71 ± 0·04	0·14 ± 0·100	1·03 ± 0·04	0·70 ± 0·01
150	1	0·74 ± 0·01	0·11 ± 0·004	1·02 ± 0·03	0·69 ± 0·01
175	1	0·69 ± 0·01	0·11 ± 0·007	1·04 ± 0·03	0·69 ± 0·02
195	1	0·59 ± 0·01	0·14 ± 0·006	0·98 ± 0·01	0·80 ± 0·02

TABLE 3

Competitive gas-phase chlorination of 1-chlorobutane and chlorocyclobutane

Temp.	R.S.$^{\text{1,1-dichlorocyclobutane}}_{\text{1,4-dichlorobutane}}$
28°	5·98 ± 0·18
70	6·05 ± 0·18
110	4·88 ± 0·18
140	4·50 ± 0·10

TABLE 4

Gas-phase chlorination of methylcyclobutane

			R.S.$^{1x}_{1,1}$		
Temp.	1,1-	*trans*-1,2	*cis*-1,2	*trans*-1,3 + *cis*-1,3	1-Chloromethyl
74°	1	0·55 ± 0·02	0·46 ± 0·02	1·27 ± 0·04	0·26 ± 0·01
104	1	0·64 ± 0·03	0·52 ± 0·03	1·34 ± 0·06	0·31 ± 0·01
122	1	0·58 ± 0·01	0·53 ± 0·01	1·36 ± 0·06	0·27 ± 0·02
150	1	0·59 ± 0·02	0·57 ± 0·01	1·35 ± 0·03	0·29 ± 0·01

1,1-Dichlorocyclobutane was identified by the absence of a methine absorption; in this respect it is unique among the other four isomeric dichlorocyclobutanes. *trans*-1,2-Dichlorocyclobutane was confirmed by retention time; a sample being prepared from cyclobutene and chlorine. In *trans*-1,3-dichlorocyclobutane the two methine protons in the positions-1 and 3 will form an A_2X_2 system with the methylene protons on carbon atom 2. Thus the triplet at τ 7·19 is consistent only with the *trans*-1,3-isomer. Similar triplets have been observed in the n.m.r. spectra of all the *trans*-1,3-dichlorocycloalkanes.[6,7] The two methylene protons on carbon atom 2 in the *cis*-1,3-isomer would produce with the methine protons on carbon atoms 1 and 3 an AB system. The absorptions centred at τ 6·84 and 7·40 represent such a system. The *cis*-1,2-dichlorocyclobutane was identified from its mass spectrum; the loss of a hydrogen atom before loss of HCl is characteristic of *cis*-1,2-dichlorocycloalkanes (in this case *cis*-1,2-dichlorocyclobutane).

Identification of Isomeric Chloromethylcyclobutanes.—Chlorination of methylcyclobutane gave six isomeric chloromethylcyclobutanes (as shown by g.c.–mass spectroscopy of the reaction mixture). The order of elution was assumed to be the same as that observed for the chloromethylcyclopentanes:[7] 1-chloro-1-methyl; *trans*-1,2-; *trans*-1,3- + *cis*-1,3-; *cis*-1,2-; 1-chloromethylcyclobutane.

Gas-phase Chlorination of Chlorocyclobutane.—A mixture of chlorocyclobutane (10 parts) and chlorine (1 part) at a total pressure of *ca*. 58 mmHg was illuminated with a 150 W tungsten lamp for 90 min. The products were condensed into a trap from which injections were made directly into the chromatography apparatus, the column of which was maintained at 90°. The results in Table 2 are tabulated as relative selectivities.

Competitive Chlorination.—A mixture of 1-chlorobutane (5 parts), chlorocyclobutane (5 parts), and chlorine (1 part) at a total pressure of *ca*. 110 mmHg was illuminated with a tungsten lamp for 90 min. The reaction products were, in this case, analysed at 75° to obtain a better separation of components.

Gas-phase Chlorination of Methylcyclobutane.—This reaction was carried out in a similar manner to the chlorination of chlorocyclobutane. The same analytical conditions were employed except that in this case the reaction products were analysed at 65°. The results are shown in Table 4.

Competitive Chlorination.—A mixture of 1-chlorobutane (10 parts), methylcyclobutane (5 parts), and chlorine (2

TABLE 5

Competitive gas-phase chlorination of 1-chlorobutane and methylcyclobutane

Temp.	R.S.$^{\text{1-chloro-1-methylcyclobutane}}_{\text{1,3-dichlorobutane}}$
70°	0·51 ± 0·04
104	0·54 ± 0·03

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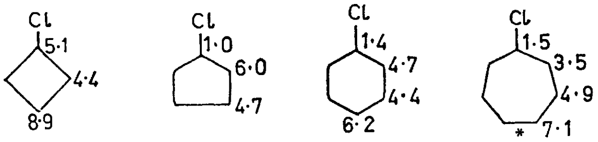
[6] D. S. Ashton and J. M. Tedder, *J. Chem. Soc.* (*B*), 1970, 1031.

[7] D. S. Ashton and J. M. Tedder, *J. Chem. Soc.* (*B*), 1971, 1719.

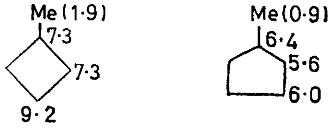
parts) at a total pressure of *ca.* 160 mmHg was illuminated with a 150-W tungsten lamp for 90 min. The analytical conditions were the same as for methylcyclobutane and chlorine.

DISCUSSION

By combining the data in Tables 2 and 3 it is possible to compare the relative rates of chlorination for the complete series of chlorocycloalkanes (cyclo-$C_nH_{2n-1}Cl$; $n = 4$—7) at 80 °C. Combination of Tables 4 and 5 enables a similar diagram for methylcyclobutane and methylcyclopentane to be drawn. Previous investigations[3] have shown the unsubstituted cycloalkanes C_nH_{2n} ($n = 4$—7) to exhibit a reactivity to radical attack in the order $C_4 \ll C_5 > C_6 > C_7$. It will be seen at once that the substituted cyclobutanes do not fit into this sequence at all. The high reactivity at the 1-position in chlorocyclobutane is particularly striking. Chlorination of the 3-position in 1-chlorobutane is unaffected by the substituent chlorine atom, the reaction proceeding exactly at the same rate as the secondary positions in butane itself. Attack at the 3-position in chlorocycloheptane, chlorocyclohexane, and chlorocyclopentane follows the relative reactivity observed for radical attack in the corresponding cycloalkanes. However the 3-position in chlorocyclobutane instead of being the least reactive is the most reactive 3-position in all the chlorocycloalkanes studied. The explanation of the high reactivity of the substituted cyclobutanes may possibly be found in the release of steric strain associated with the formation of the substituted cyclobutyl radical. The radical will quickly assume the planar, sp^2 configuration, no matter which position is attacked; this will greatly reduce the non-bond repulsions between the substituent and hydrogen atoms on the same side of the ring. The greatest release will occur when the radical is formed at the 1-position and this probably accounts for the very high rate of attack at the 1-position in chlorocyclobutane which on polar grounds would be expected to be rather unreactive. Competitive experiments with 1-chlorobutane (Table 3) have enabled an activation energy *ca.* 0·2 kcal mol^{-1} to be calculated for position-1 in chlorocyclobutane. The small temperature variation in relative selectivity (R.S.) for the various dichlorocyclobutanes suggests low activation energies of this order for all isomers. Low activation energies are consistent with relief of steric strain in the formation of the substituted cyclobutyl radical.



Relative rates of chlorination at 80° (1°-position in n-butane = 1). * Temp. = 100°



Relative rates of chlorination at 100° (1°-position in n-butane = 1)

The high reactivity of chlorocyclobutane could also be attributed to interaction between a 3*p*-atomic orbital of the chlorine and a delocalised π-orbital encompassing the ring. Such orbitals have long been proposed for cyclopropane and more recently the concept has been extended to cyclobutane.[8] The high reactivity of methylcyclobutane argues against this explanation since it would be necessary to invoke a major contribution from methyl hyperconjugation. The concept of released steric strain is however applicable to both methyl- and chloro-cyclobutanes, the slightly lower reactivity of the latter being attributable to a polar effect. On the other hand the high reactivity of the methyl group in methyl cyclobutane (nearly twice as reactive as the primary position in n-butane) can possibly be attributed to a stabilising interaction between the half-filled *p*-orbital of the methylene radical ($\dot{C}H_2$–) group and the appropriate ring orbital.

The high *trans*: *cis* ratio observed for the 1,2-dichlorocyclobutanes is in contrast with the value of almost unity for 1-chloro-2-methylcyclobutane. When we compare the *trans*: *cis* ratio for the 1,2-dichlorocycloalkanes we find this reaches a maximum for the cyclopentane ring system. This is entirely consistent with the picture of interaction between the half-filled π-orbital at the 2-position with a 3*p*-atomic orbital of the substituent as we have proposed to account for the *trans*: *cis* ratio observed in chlorination of the other chlorocycloalkanes.[1,6,7] The relative rigidity of the cyclobutane ring would mean that the difference between the conformation leading to the *trans*-isomer and that leading to the *cis*-isomer was small. Thus the decline in selectivity between *cis* and *trans* is accounted for. The *trans* : *cis* ratio is also greater than unity for the 1,3-dichlorocyclobutane though again the ratio is less than for the C_5 and C_6 ring systems. This change in the *trans* : *cis* ratio for the 1,3-dichlorocycloalkanes with ring size is consistent neither with the steric hinderance, nor with the polar theories (see Parts XXII and XXIII) but is consistent with the orbital-interaction picture.

TABLE 6

trans : *cis* Ratios for 1,2-isomers and 1,3-isomers at 100°

	1,2-Isomer	1,3-Isomer
Cyclo-Cl-C_4H_7	6·8	1·4
Cyclo-Cl-C_5H_9	15·5	1·7
Cyclo-Cl-C_6H_{11}	10·5	2·0
Cyclo-Cl-C_7H_{13}	5·2	1·1
Cyclo-Me-C_4H_7	1·2	
Cyclo-Me-C_5H_9	1·3	

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[8] P. Bischof, E. Haselbach, and E. Heilbronner, *Angew. Chem.*, 1970, **9**, 953.