Free Radical Substitution in Aliphatic Compounds. Part XXVI.† The Gas-phase Bromination of Halogenocycloalkanes

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The gas-phase bromination of halogenocyclohexanes gave the expected isomeric bromohalogenocyclohexanes, together with cyclohexene, bromocyclohexane, and traces of *trans*-1,2-dibromocyclohexane. These latter products were formed as a result of elimination of hydrogen halide from the starting material. The initial halogenocyclohexanes were shown to undergo elimination of hydrogen halide in the presence of hydrogen bromide. Variation of the surface : volume ratio had a pronounced effect on the elimination which suggested that this reaction had a large heterogeneous component. Bromination of chloro- and fluoro-cyclopentane also produced elimination products which were formed as a result of the reaction of hydrogen bromide with the halogenocyclopentane.

THE gas-phase bromination of alkanes containing electron-attracting substituents shows a polar deactivation to attack at positions β to the substituent.[1] The bromination of *cis*-4-bromo-t-butylcyclohexane by Skell and Readio [2] and *trans*-1-bromomethyl-4-methylcyclohexane by Traynham and Hines [3] each yielded a large preponderance of the 1,2-disubstituted isomer. Earlier, Thaler [4] showed *trans*-1,2-dibromocyclohexane to be 94% of the total products in the bromination of bromocyclohexane. All of these studies were made in the liquid phase and in each case the authors attributed the preponderance of ' 1,2-dibromocycloalkane ' to anchimeric assistance by a bridging bromine atom.

Tanner *et al.*[5] have made an extensive reinvestigation of the bromination of 1-bromobutane and other bromoalkanes in the liquid phase. They concluded at first that the preponderence of 1,2-dibromobutane in the products was due to initial formation of but-1-ene followed by addition of bromine. The loss of bromine atoms from β-bromoalkyl radicals has long been known,[6] but their work showed that added hydrogen bromide accelerated apparent attack at the 2-position.

The present paper reports an investigation of the gas-phase bromination of fluoro-, chloro-, and bromocyclohexane and of fluoro- and chloro-cyclopentane. Complications due to olefinic intermediates were not unexpected in the case of bromocyclohexane, but they were not anticipated in the case of fluoro-cyclohexane and -cyclopentane. In the event, olefinic products were observed, involving the loss of the substituent halogen as hydrogen halide with all the halogenocycloalkanes.

EXPERIMENTAL

The gas-phase reactions were carried out in a conventional vacuum line as described.[7] Normally spherical Pyrex reaction vessels were used for the brominations. In the experiments involving variation of the surface : volume ratio a cylindrical reaction vessel, packed with Pyrex tubes, was employed. Photobromination was allowed to proceed for a specific time and then the total reaction mixture was distilled under vacuum from the vessel to a small tube cooled in liquid nitrogen. During this distillation the mixture passed through a tube containing carefully dried Carbosorb (soda lime). Experiments with and without Carbosorb established that its sole function was to remove hydrogen bromide and bromine, the total amount of ' olefin ' and 'abstraction ' products was unchanged by the presence or absence of Carbosorb and no decomposition of the cycloalkyl halides was observed. Samples of the reaction mixture were taken from the small tube for analysis by g.l.c. A Griffin and George D6 gas density balance was used for the experiments with fluoro- and bromo-cyclohexane and fluorocyclopentane. A Pye 104 flame ionisation chromatograph, calibrated against a gas density balance, was used for the experiments with chlorocyclohexane and -cyclopentane. The products were separated using columns packed with 15% tritolyl phosphate on ' Embacel '. Each reaction mixture was analysed several times and the figures given in the Tables represent the average of about five analytical runs. The accuracy of the analytical method is better than ±10% and results, even at low conversions, are reproducible.

Reactant halogenocycloalkanes were purified by spinning-band column distillation, or by preparative g.l.c. until chromatographically pure (>99·5%). Hydrogen bromide was prepared by addition of bromine to tetrahydronaphthalene and purified by trap to trap distillation.

Products were separated and estimated by g.l.c. analysis of each reaction mixture. Cyclohexene, bromocyclohexane, 3-bromocyclohexene, and *trans*-1,2-dibromocyclohexane were identified by comparison of the retention times of the unknown peaks in the product chromatograms with those of authentic materials run under exactly the same conditions. These identifications were confirmed by g.l.c.–m.s. analysis and comparison of the resulting mass spectra with those of authentic samples. The isomeric dihalogenocycloalkanes were also identified from their retention times, and by coupled g.l.c.–m.s. analysis. The mass spectra showed unambiguously which peaks in a given mixture were dihalogenocycloalkanes and helped to identify some of the isomers.[8] Where stereospecific syn-

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[1] J. M. Tedder, *Quart. Rev.*, 1960, **14**, 336.
[2] P. S. Skell and P. D. Readio, *J. Amer. Chem. Soc.*, 1964, **86**, 3334.
[3] J. G. Traynham and W. G. Hines, *J. Amer. Chem. Soc.*, 1968, **90**, 5208.
[4] W. Thaler, *J. Amer. Chem. Soc.*, 1963, **85**, 2607.
[5] D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Amer. Chem. Soc.*, 1969, **91**, 7398; D. D. Tanner, H. Yabuuchi, and E. V. Blackburn, *ibid.*, 1971, **93**, 4802; D. D. Tanner, M. W. Mosher, N. C. Das, and E. V. Blackburn, *ibid.*, p. 5846.
[6] P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 1960, 144.
[7] P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 1961, 3520.
[8] D. S. Ashton, J. M. Tedder, and J. C. Walton, *J. Chem. Soc.* (*B*), 1970, 1775.

theses were available the isomers were synthesised. Some of the isomers were separated by preparative g.l.c. and identified from their n.m.r. spectra. The methods used for each isomer are shown in Table 1. The relative retention volumes on a tritolyl phosphate column of the isomers of bromofluorocyclohexane, bromochlorocyclohexane, dibromocyclohexane, bromofluorocyclopentane, and bromochlorocyclopentane are known.[9] Our reaction mixtures were run under similar chromatographic conditions and the isomers could therefore be identified since we have shown that the relative retention volumes of dihalogenocycloalkanes can be used to distinguish the various isomers.

RESULTS AND DISCUSSION

Fluorocyclohexane.—Photobromination of fluorocyclohexane produced all the isomeric fluorobromocyclohexanes except for *cis*-1-bromo-2-fluorocyclohexane which was not detected. In addition, cyclohexene is formed first. These products are referred to as ' olefin products ' throughout this paper. The sum total of their concentrations gives a measure of the amount of cyclohexene formed. It was found that when the products were collected by distillation through Carbosorb, which removes HBr and bromine, the amount of cyclohexene increased and the amount of bromocyclohexane, 3-bromocyclohexene, and *trans*-1,2-dibromocyclohexane decreased by a corresponding amount. It is clear therefore that these three products are formed partly in the gas phase and partly in solution at the end of the reaction by non-radical processes.

Table 2 shows that the proportions of the products are dependent on the time of reaction. At longer times the proportion of ' olefin products ' was increased; variations in the amounts of the isomeric fluorobromocyclohexanes were also noted. This suggested that the

TABLE 1

Methods of identifying products

Product	C_6Br_2	C_6BrCl	C_6BrF	C_5BrCl	C_5BrF
Isomer					
1,1	M.s.	M.s.	M.s.	M.s., n.m.r.	M.s.
trans-1,2	Synth.,[a] m.s., n.m.r.	Synth.,[c] m.s., n.m.r.	Synth.,[d] m.s.	Synth.,[c] m.s., n.m.r.	M.s. of *trans*-1,2 + *trans*-1,3
cis-1,2				M.s., n.m.r.	
trans-1,3	M.s.	M.s.	M.s. of mixture	M.s., n.m.r.	M.s. of *trans*-1,2 + *trans*-1,3
cis-1,3	M.s.	M.s.		M.s., n.m.r.	M.s.
trans-1,4	Synth.,[b] m.s., n.m.r.	M.s.	Synth.,[e] m.s. of mixture		
cis-1,4	Synth.,[b] m.s., n.m.r.	M.s.			

[a] By addition of bromine to cyclohexene. [b] By reaction of hydrogen bromide with cyclohexane-1,4-diol (E. Havinga, W. Kwestroo, and F. A. Meijer, *Rec. Trav. chim.*, 1954, **73**, 721). [c] By reaction of the cycloalkene with hydrogen chloride and *N*-bromosuccinimide (H. L. Goering and L. L. Sims, *J. Amer. Chem. Soc.*, 1955, **77**, 3465). [d] By treatment of *trans*-1,2-dibromocyclohexane with KF in digol. [e] Mixture of the two isomers prepared by treatment with KF in digol.

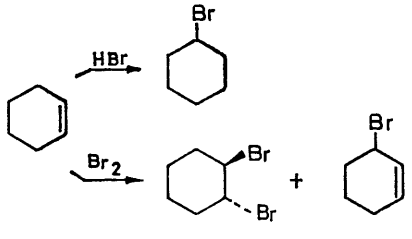
TABLE 2

Photobromination of fluorocyclohexane at 100 °C. Relative proportions of products are expressed as a percentage of the total products, for various photolysis times. Fluorocyclohexane 3·5 parts to bromine 1 part

Time (min)	C_6H_{10} (%)	$C_6H_{11}Br$ (%)	1,1-$C_6H_{10}FBr$ (%)	*t*-1,2 + *t*-1,3 (%)	*c*-1,3 (%)	*c*-1,4 + *t*-1,4 (%)	Reaction (%)[a]
1	2·0	10·8	72·6	14·6			11
3	1·5	4·7	17·2	35·2	24·6	18·2	12
8	3·4	45·8	4·2	32·0	7·3	7·3	21
15	1·3	51·0	3·8	31·5	7·8	4·4	33
30	10·2	41·3	6·3	28·2	9·3	4·7	47
60	20·8	32·5	6·8	23·0	12·0	5·0	52
120	10·7	34·3	5·0	23·0	19·3	7·6	76

[a] Based on the amount of bromine consumed.

and bromocyclohexane were produced together with traces of *trans*-1,2-dibromocyclohexane and 3-bromocyclohexene. The relative proportions of the products are shown, for photolyses lasting 1—120 min, in Table 2.



Bromocyclohexane, 3-bromocyclohexene, and *trans*-1,2-dibromocyclohexane were formed by reaction of hydrogen bromide and bromine with cyclohexene which cyclohexene was formed by reaction of the starting material with a product of the abstraction reaction, and the most likely candidate was HBr. Mixtures of fluorocyclohexane and hydrogen bromide were made up, and considerable reaction was observed in the dark even at room temperature. The products were cyclohexene and bromocyclohexane, and the relative amounts formed are shown in Table 3. In a photobromination experiment hydrogen bromide formed in the abstraction step will obviously decompose the starting material in a similar way. The amount of ' olefin products ' will increase as the hydrogen bromide builds up in the system, thus accounting for the preponderance of ' olefin products ' at longer times.

[9] D. S. Ashton, J. M. Tedder, and J. C. Walton, *J. Chromatog.*, 1971, **55**, 231; 1972, **72**, 269.

TABLE 3

Reaction of fluorocyclohexane with hydrogen bromide at 25 °C. Products are expressed as a percentage of the fluorocyclohexane remaining at the end of the reaction

	Reactants		Products	
Time (min)	$C_6H_{11}F$ (parts)	HBr (part)	$\frac{[C_6H_{10}]_f}{[C_6H_{11}F]_f} \times 100$	$\frac{[C_6H_{11}Br]_f}{[C_6H_{11}F]_f} \times 100$
35	11·5	1	5·5	
35	5·0	1	13·0	5·0
35	2·3	1	13·3	3·4
35	1·3	1	8·2	10·7
35	0·5	1	19·2	9·4
35	0·25	1	33·4	5·3
600 *	0·92	1	759	230

* Reaction at 70 °C.

TABLE 4

Effect of surface : volume ratio on the reaction of fluorocyclohexane with hydrogen bromide at 25 °C. Products are expressed as a percentage of the $C_6H_{11}F$ unconsumed. Reaction time 90 min.

Reactants			
HBr (parts)	$C_6H_{11}F$ (parts)	$S : V$ (cm^{-1})	$\frac{[\text{Olefin products}]_f}{[C_6H_{11}F]_f} \times 100$
1	1	0·7	14·5
1	1	9·1	32·7
2	1	0·7	167
2	1	9·1	1310

Elimination of hydrogen fluoride from fluorocyclohexane is energetically unfavourable. Homolytic reactions in which HBr attacks fluorocyclohexane with surface component. Once hydrogen fluoride is produced, this is known to cause catalytic decomposition of fluorocyclohexane.[10]

Chlorocyclohexane.—Photobromination of chlorocyclohexane produced all the isomeric chlorobromocyclohexanes, except for *cis*-1-bromo-2-chlorocyclohexane, together with substantial amounts of the 'olefin products' cyclohexene, bromocyclohexane, 3-bromocyclohexene, and *trans*-1,2-dibromocyclohexane. The relative proportions of the products are shown in Table 5. No obvious trend emerges from these results, although it is clear that considerable variations in the relative proportions do occur. Chlorocyclohexane was also found to react with hydrogen bromide in the dark. The products were cyclohexene and bromocyclohexane and the amount of these products was also considerably increased by using a larger surface : volume ratio.

The elimination reaction occurs to much less extent with chlorocyclohexane, presumably because the HCl liberated in the reaction does not catalyse further decomposition of the starting material as does the HF from fluorocyclohexane.

Bromocyclohexane.—Photobromination of bromocyclohexane produced all the dibromocyclohexanes, together with large amounts of the 'olefin products' cyclohexene and 3-bromocyclohexene. The relative proportions of the products formed during different photolysis times are shown in Table 6. Addition of hydrogen bromide to the product cyclohexene gives

TABLE 5

Photobromination of chlorocyclohexane at 100 °C. Relative proportions of the products are expressed as a percentage of the total products for various photolysis times. Chlorocyclohexane 9·6 parts to bromine 1 part

Time (min)	C_6H_{10} (%)	C_6H_9Br (%)	$C_6H_{11}Br$ (%)	*t*-1,2-$C_6H_{10}Br_2$ (%)	1,1-$C_6H_{10}ClBr$ (%)	*t*-1,2 (%)	*t*-1,3 (%)	*t*-1,4 (%)	*c*-1,3 (%)	*c*-1,4 (%)
1	6·2	16·8	2·2	9·1	52·8	6·4	1·8	1·9	2·0	0·7
2	0·7	4·7	0·1	14·2	63·3	7·3	2·8	2·8	2·2	1·8
5	0·8	9·9		6·7	69·1	8·9	1·4	0·5	1·9	0·6
120	4·0	1·6		1·8	84·9	4·2	1·2	1·0	0·6	0·7

TABLE 6

Photobromination of bromocyclohexane at 100 °C. Products are expressed as a percentage of the total products. Bromocyclohexane 10 parts to bromine 1 part

Time (min)	C_6H_{10} (%)	C_6H_9Br (%)	*t*-1,2-$C_6H_{10}Br_2$ (%)	1,1 (%)	*t*-1,3 (%)	*c*-1,3 (%)	*t*-1,4 (%)	*c*-1,4 (%)	Reaction (%) [a]
10	58·8		41·2						0·7
20	55·4		44·6						0·9
30	68·8		29·3		2·0				1·5
60	34·5	10·1	25·4	3·8	9·2	6·3	5·6	5·1	1·1
120	33·2	5·7	47·3	1·7	3·7	3·0	2·7	2·7	3·0

[a] Based on bromocyclohexane consumed. A trace of *cis*-1,2-dibromocyclohexane was also detected.

the elimination of HF are also energetically unfavourable. It was suspected therefore that the reaction between hydrogen bromide and fluorocyclohexane might be a process occurring at the reaction vessel walls. Table 4 shows the effect on the reaction products of using vessels of differing surface : volume ratios. Increasing the surface area caused a big increase in the amount of olefin formation from the fluorocyclohexane. It is clear that the elimination reaction has a substantial back the starting material bromocyclohexane, so it is not possible to assess the full extent of elimination in this case. *trans*-1,2-Dibromocyclohexane can be formed by the straightforward abstraction process, or by addition of bromine to cyclohexene. It is an inescapable conclusion that the preponderance of the *trans*-1,2-isomer is due to this addition step. The amount of

[10] S. M. McElvain and J. W. Langston, *J. Amer. Chem. Soc.*, 1944, **66**, 1769.

3-bromocyclohexene formed from the bromocyclohexane and chlorocyclohexane was considerably more than from the fluorocyclohexane. This was probably because the concentration of bromine was lower in the two former reactions, thus favouring allylic attack on the cyclohexene.

Bromocyclohexane also reacts with hydrogen bromide in the dark, giving cyclohexene as the only detectable product. Table 7 shows the amounts of this product

TABLE 7

Reaction of bromocyclohexane with hydrogen bromide at 100 °C. Product expressed as a percentage of the unconsumed bromocyclohexane

Time (min)	Reactants: $C_6H_{11}Br$ (parts)	Reactants: HBr (parts)	Product $\frac{[C_6H_{10}]_t}{[C_6H_{11}Br]_t} \times 100$
35 *	5·0	1	0·1
90	7·0	1	0·9
600	0·9	1	47·1

* At 25 °C.

formed in various times. Undoubtedly a considerable proportion of the cyclohexene reacts with HBr to give back the starting material, so that the figures in Table 7 do not give a true picture of the total extent of elimination.

pentane 6·7%, and *cis*-1-bromo-3-fluorocyclopentane 2·4%.

The present results show that hydrogen bromide attacks fluoro-, chloro-, and bromo-cycloalkanes in the gas phase producing a cycloalkene. We can also expect that the hydrogen bromide will attack the dihalogenocycloalkanes which are the products of the abstraction reaction. The present work was initiated with the intention of continuing the studies on directive effects already described.[11] However, since the product dihalogenocycloalkanes may be decomposed at different rates by hydrogen bromide, quantitative results for the rate of attack of the bromine atom at particular positions in the ring can only be obtained if the concentration of hydrogen bromide is relatively very small. The runs lasting the shortest length of time come closest to meeting this criterion. The results reported are useful for identifying some overall trends, but the quantitative detail is obscured.

In the first place, our results with bromocyclohexane suggest that the predominance of the *trans*-1,2-dibromocyclohexane in the products is due to addition of reactant bromine to the elimination product cyclohexene. The cyclohexene can be formed by attack of HBr on bromocyclohexane; alternatively the β-bromocyclohexyl radical may also lose bromine, since this is energetically

TABLE 8

Photobromination of chlorocyclopentane at 100 °C. Products are expressed as a percentage of the total products. Chlorocyclopentane 10 parts to bromine 1 part

Time (min)	C_5H_7Br (%)	C_5H_9Br (%)	*t*-1,2-$C_5H_8Br_2$ (%)	1,1-C_5H_8ClBr (%)	*t*-1,2 (%)	*t*-1,3 (%)	*c*-1,3 (%)
1	2·2	2·0	1·4	77·2	16·5	0·6	0·1
2	2·4	3·2	3·9	72·5	15·9	1·7	2·7
5	5·1	3·0	4·6	71·3	15·2	0·6	0·1
10	6·4	2·4	2·3	62·8	25·8	0·2	
150	2·0	3·3	3·6	63·7	21·6	4·2	1·6

A trace of cyclopentene was also detected.

Chlorocyclopentane and Fluorocyclopentane.—Photobromination of chlorocyclopentane gave all the bromochlorocyclopentane isomers, except for *cis*-1-bromo-2-chlorocyclopentane. The 'olefin products' cyclopentene, bromocyclopentane, 3-bromocyclopentene, and *trans*-1,2-dibromocyclopentane were also identified. Table 8 shows the relative amounts of the products. Chlorocyclopentane also reacted with hydrogen bromide in the dark giving cyclopentene and bromocyclopentane as the products. This reaction was also favoured by an increased surface : volume ratio.

In the photobromination of fluorocyclopentane all the isomeric fluorobromocyclopentanes were identified, except for *cis*-1-bromo-2-fluorocyclopentane. The 'olefin products' formed a very substantial proportion of the products under all conditions. The following amounts of product were found from a run at 100 °C lasting 60 min: cyclopentene 65·4%, bromocyclopentane 15·3%, *trans*-1,2-dibromocyclopentane 8·8%, 1-bromo-1-fluorocyclopentane 1·4%, *trans*-1-bromo-2-fluorocyclopentane + *trans*-1-bromo-3-fluorocyclo-

favourable. Although care must be taken in comparing gas-phase work with that in solution, the conclusion of Tanner *et al.*, that there is no need to invoke anchimeric assistance by the bromine substituent [5] certainly applies to the present results. Secondly, the attack by bromine atoms on all the halogenocycloalkanes leads to a small predominance of *trans*-bromohalogeno-isomers over the *cis*-isomers. A similar preference for *trans*-attack was found in the chlorination of halogenocycloalkanes.[11] This is in accord with Skell's picture of 'bridging' although we have, as discussed in previous papers, preferred to regard this as an orbital interaction leading to stabilisation of a particular conformation of the radical. Finally the large amounts of 1-bromo-1-halogenoisomers may also be noted. A similar preference for attack at the site bearing the substituent was also observed in the bromination of 2-halogenoalkanes.[6]

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[11] D. S. Ashton and J. M. Tedder, *J. Chem. Soc.* (*B*), 1971, 1719, 1723.