Free-radical Substitution in Aliphatic Compounds. Part XXVII.[1] Chlorination and Bromination of 1-Cyanobutane and Cyanocyclobutane

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1-Cyanobutane and cyanocyclobutane have been chlorinated and brominated in the gas phase over a wide range of temperatures. The results for 1-cyanobutane are compared with previous halogenations of 1-substituted n-butanes. The chlorination of cyanocyclobutane gives a very high *trans/cis* ratio for the 1-cyano-2-chlorocyclobutane and quite a high *trans/cis* ratio for the 1,3-product. This is interpreted in terms of an interaction between the π-orbitals of the cyano-group and the half-filled $2p_z$ atomic orbital of the radical site. The bromination of cyanocyclobutane is accompanied by a small amount of elimination of HCN; this reaction is increased by addition of HBr or by an increase in the surface area.

RECENT studies from this laboratory have been concerned with the halogenation of cyclic systems;[2,3] the chlorination and bromination of cyanocyclobutane was undertaken as an extension of this work. Previously we had studied the halogenation of 1-cyanobutane, but the work had remained unpublished.[4] We now report this earlier work since it provides a useful basis on which the present results can be discussed. The chlorination of 1-cyanobutane in the liquid phase has been studied by Bruylants and Rouchard.[5]

EXPERIMENTAL

The gas-phase reactions were carried out in a conventional vacuum line as described previously.[6] N.m.r. spectra were recorded at 100 MHz on a Varian H.A. 100 instrument. G.c.-mass spectroscopy of the reaction mixtures was carried out on a Perkin-Elmer F11, coupled *via* a Biemann separator to an A.E.I. MS 12 mass spectrometer. Analysis was carried out on a Griffin and George D6 chromatograph (using a gas-density balance as detector). The isomeric bromo- and chloro-cyanobutanes were analysed on a 6 ft × $\frac{3}{16}$ in stainless-steel column packed with tritolyl phosphate (40%) on Embacel (60—100 mesh). The isomeric chlorocyanocyclobutanes were analysed on a 6 ft × $\frac{3}{16}$ in column packed with silicone oil (20%) on Embacel (60—100 mesh). Preparative gas chromatography was carried out with a Pye-Unicam Series 105 instrument, using a 15 ft column packed with tritolyl phosphate (15%) on Embacel (60—100 mesh).

Reagents.—Both 1-cyanobutane and cyanocyclobutane were commercial materials and were purified by distillation to give material boiling at 148°/755 and 139°/751 mmHg respectively. Each showed only one peak by analytical gas chromatography.

1-Bromo-1-cyanocyclobutane was prepared by over-bromination of cyanocyclobutane; it was separated and purified by preparative gas chromatography and showed only one peak by analytical gas chromatography.

Identification of Isomeric Bromo- and Chloro-cyanobutanes.—Chlorination of 1-cyanobutane gave four isomeric chlorocyanobutanes. The order of elution was assumed to be 1-chloro-, 2-chloro-, 3-chloro-, and 4-chloro-1-cyanobutane as observed with other chlorobutane derivatives studied previously.[6-8] An authentic sample of 4-chloro-1-cyanobutane, prepared from 1-bromo-4-chlorobutane [9] confirmed the last peak on the chromatogram. A similar order of elution was proposed for the isomeric bromocyanobutanes. Authentic samples confirmed the first and fourth peaks on the chromatogram as 1-bromo- and 4-bromo-1-cyanobutane; the former was prepared from 1-cyanobutane and bromine,[10] the latter from 1,4-dibromobutane and potassium cyanide.[11]

Identification of Isomeric Bromo- and Chloro-cyanocyclobutanes.—Chlorination of cyanocyclobutane gave five isomeric chlorocyanocyclobutanes. The order of elution was expected to be the same as the order observed for the dichlorocyclobutanes. All five chlorocyanocyclobutanes

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[3] D. S. Ashton and J. M. Tedder, *J. Chem. Soc.* (*B*), 1971, 1723.
[4] H. Singh, Ph.D. Thesis, University of Sheffield 1965.
[5] J. Rouchaud and A. Bruylants, *Bull. Soc. chim. belges*, 1966, **75**, 783.
[6] H. Singh and J. M. Tedder, *J. Chem. Soc.*, 1964, 4737.
[7] P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 1960, **144**.
[8] I. Galiba, J. M. Tedder, and R. A. Watson, *J. Chem. Soc.*, 1964, 1321.
[9] R. M. Hixon and D. Starr, *J. Amer. Chem. Soc.*, 1921, **43**, 660.
[10] C. L. Stevens and W. Holland, *J. Org. Chem.*, 1953, **18**, 1112.
[11] N. J. Leonard and W. C. Wildman, *J. Amer. Chem. Soc.*, 1949, **71**, 3100.

were prepared by overchlorination and were separated by preparative gas chromatography; their n.m.r. spectra were determined. The *trans*-1,2-, *trans*-1,3-, and *cis*-1,3-chlorocyano-compounds were prepared by treating the corresponding *trans*-1,2-, *trans*-1,3-, and *cis*-1,3-dichlorocyclobutanes with cuprous cyanide in dimethylformamide.[12] In practice, a mixture of the unchanged dichlorocyclobutane, *cis*- and *trans*-chlorocyanocyclobutanes, and *cis*- and *trans*-dicyanocyclobutanes resulted, which was in turn separated by preparative gas chromatography; the n.m.r. spectra of the components were determined. This supported the order of elution: 1-chloro-1-cyano-, *trans*-1,2-, *trans*-1,3-, *cis*-1,3-, and *cis*-1,2-chlorocyanocyclobutane. A detailed analysis of these spectra (Table 1) is the subject of a

TABLE 1

^{1}H 100 MHz Spectra of the isomeric bromo- and chlorocyclobutanes

Isomer	Signal	Nuclei	Multiplicity *
1,1-Chlorocyano-	7·24	4	c
	7·72	2	c
trans-1,2-	5·50	1	q J 8 Hz
	6·83	1	qt J 8 Hz (J 3 Hz)
	7·63	4	c
trans-1,3-	5·39	1	tt J 7 Hz
	6·66	1	tt J 5 Hz
	7·20	4	c
cis-1,3-	5·74	1	c
	7·24	5	c
1,1-Bromocyano-	7·32	4	c
	7·88	2	c

All signals expressed relative to Me_4Si. * q = Quartet, t = triplet, c = complex.

separate investigation from this laboratory. Bromination of cyanocyclobutane produced cyclobutene, bromocyclobutane, 1-bromo-1-cyanocyclobutane, and *trans*-1,2-dibromocyclobutane. The 1-bromo-1-cyanocyclobutane was separated by preparative gas chromatography and identified by the absence of any methine absorption in its n.m.r. spectrum. *trans*-1,2-Dibromocyclobutane was prepared from cyclobutene and bromine. Bromocyclobutane was commercial material used only for identification.

Gas-phase Chlorination of 1-*Cyanobutane*.—A mixture of 1-cyanobutane (10 parts) and chlorine (1 part) at a total pressure of *ca.* 15 mmHg was illuminated with a 200-W tungsten lamp for 90 min. The products were condensed into a trap from which injections were made directly into the chromatography apparatus, the tritolyl phosphate column being used at 140°. The results are given in Table 2, tabulated as relative selectivities [R.S.].

TABLE 2

Chlorination of 1-cyanobutane

	$RS^{1,x}_{1,1}$			
	(4)	(3)	(2)	(1)
Temp.	CH_3	CH_2	CH_2	CH_2CN
110°	0·26 ± 0·01	1·0	0·44 ± 0·04	0·06 ± 0·01
206	0·31 ± 0·01	1·0	0·48 ± 0·01	0·09 ± 0·01
300	0·42 ± 0·01	1·0	0·61 ± 0·01	0·19 ± 0·01

Gas-phase Bromination of 1-*Cyanobutane*.—A mixture of 1-cyanobutane (10 parts) and bromine (1 part) at a total pressure of *ca.* 10 mmHg was illuminated with a 200-W tungsten lamp for 90 min. The reaction products were analysed as described for the chlorination.

TABLE 3

Bromination of 1-cyanobutane

	$RS^{1,x}_{1,1}$			
	(4)	(3)	(2)	(1)
Temp.	CH_3	CH_2	CH_2	CH_2CN
150°	0·012 ± 0·001	1·0	0·100 ± 0·005	0·287 ± 0·008
300	0·030 ± 0·016	1·0	0·204 ± 0·017	0·097 ± 0·010

Gas-phase Chlorination of Cyanocyclobutane.—A mixture of cyanocyclobutane (5 parts) and chlorine (1 part) at a total pressure of *ca.* 35 mmHg was illuminated with a 150-W tungsten lamp for 90 min. The reaction products were analysed on a silicone oil column at a temperature of 115°.

TABLE 4

Chlorination of cyanocyclobutane

		$RS^{1,x}_{1,1}$			
Temp.	1-Chloro-1-cyano	*trans*-1,2-	*cis*-1,2-	*trans*-1,3-	*cis*-1,3-
76°	1	1·69 ±0·11	0·16 ±0·07	1·77 ±0·07	0·72 ±0·01
106	1	2·19 ±0·05	0·23 ±0·03	2·12 ±0·02	1·23 ±0·06
126	1	1·92 ±0·01	Traces	2·41 ±0·03	1·47 ±0·04
166	1	1·86 ±0·19	Traces	3·21 ±0·08	1·66 ±0·11
200	1	2·28 ±0·01		3·64 ±0·01	1·73 ±0·01

Competitive Chlorination of 1-*Chlorobutane and Cyanocyclobutane*.—A mixture of cyanocyclobutane (10 parts), 1-chlorobutane (5 parts), and chlorine (2 parts) at a total pressure of 50 mmHg was illuminated with a 150-W tungsten lamp for 90 min. The analytical conditions were the same as those for the chlorination of cyanocyclobutane.

TABLE 5

Competitive chlorination of 1-chlorobutane and cyanocyclobutane

Temp.	R.S. 1-Chloro-1-cyanocyclobutane 1,4-dichlorobutane
78°	2·01 ± 0·04
102	1·86 ± 0·02
141	1·92 ± 0·03
168	1·71 ± 0·03

Gas-phase Bromination of Cyanocyclobutane.—A mixture of cyanocyclobutane (5 parts) and bromine (1 part) at a pressure of 20 mmHg was illuminated with a 150-W tungsten lamp for selected times between 2 and 180 min. In the experiment at 60 min, the products were distilled through Carbosorb; this prevented addition of HBr and bromine in solution to the cyclobutene formed in the gas-phase reaction. The tritolyl phosphate column, at a temperature of 115° was used for analysis.

Reaction of Cyanocyclobutane and 1-*Bromo*-1-*cyanocyclobutane with Hydrogen Bromide*.—Mixtures of cyanocyclobutane and hydrogen bromide, and mixtures of 1-bromo-1-cyanocyclobutane and hydrogen bromide were allowed to react at room temperature, in the dark, in reaction vessels with different surface to volume ratios. Distillation

[12] (*a*) L. Friedman and H. Schechter, *J. Org. Chem.*, 1961, **26**, 2522; (*b*) M. S. Newman and H. Boden, *J. Org. Chem.*, 1961, **26**, 2525.

through Carbosorb was followed by analysis on a tritolyl phosphate column at a temperature of 105°.

TABLE 6

Bromination of cyanocyclobutane at 100°, with variation of time

$[C_4H_7CN]_i = 2{\cdot}37 \times 10^{-4}$ mol l^{-1}
$[Br_2]_i = 5{\cdot}5 \times 10^{-5}$ mol l^{-1}

Time (min)	$\frac{[\text{Total olefin product}]_f}{[C_4H_7CN]_f}$	$\frac{[1,1\text{-BrCN}\square]_f}{[C_4H_7CN]_f}$
2	$0{\cdot}38 \times 10^{-2}$	$0{\cdot}65 \times 10^{-2}$
3	$1{\cdot}12 \times 10^{-2}$	$1{\cdot}99 \times 10^{-2}$
5	$1{\cdot}11 \times 10^{-2}$	$5{\cdot}99 \times 10^{-2}$
30	$1{\cdot}32 \times 10^{-2}$	$9{\cdot}64 \times 10^{-2}$
60	$1{\cdot}35 \times 10^{-2}$	$10{\cdot}52 \times 10^{-2}$
135	$1{\cdot}56 \times 10^{-2}$	$7{\cdot}27 \times 10^{-2}$
180	$2{\cdot}63 \times 10^{-2}$	$4{\cdot}42 \times 10^{-2}$

TABLE 7

Reaction of cyanocyclobutane with HBr at 100°, with variation of surface to volume ratio

$[C_4H_7CN]_i = 2{\cdot}37 \times 10^{-4}$ mol l^{-1}
$[HBr]_i = 3{\cdot}75 \times 10^{-4}$ mol l^{-1}

S/V (cm^{-1})	Time (min)	$\frac{[\text{Total olefin product}]_f}{[C_4H_7CN]_f}$
0·7	120	$0{\cdot}79 \times 10^{-2}$
0·7	240	$1{\cdot}59 \times 10^{-2}$
9·1	120	$2{\cdot}68 \times 10^{-2}$
9·1	240	$4{\cdot}17 \times 10^{-2}$

TABLE 8

Reaction of 1-bromo-1-cyanocyclobutane with HBr at 100°, with variation of time

$[C_4H_6CNBr]_i = 1{\cdot}03 \times 10^{-4}$ mol l^{-1}
$[HBr]_i = 3{\cdot}75 \times 10^{-4}$ mol l^{-1}

S/V (cm^{-1})	Time (min)	$\frac{[\text{Total olefin product}]_f}{[C_4H_7CNBr]_f}$
0·7	30	$0{\cdot}47 \times 10^{-2}$
0·7	60	$0{\cdot}81 \times 10^{-2}$
0·7	90	$1{\cdot}39 \times 10^{-2}$
0·7	180	$2{\cdot}51 \times 10^{-2}$
9·1	180	$8{\cdot}64 \times 10^{-2}$

DISCUSSION

The present data for the gas-phase chlorination of 1-cyanobutane agrees extremely well with the liquid-phase data of Rouchard and Bruylants.[2] In Table 9 the

TABLE 9

Chlorination of substituted n-butane derivatives in the gas phase at *ca.* 90°

RS_4^x

4 CH_3	3 CH_2	2 CH_2	1 CH_2	X	Ref.
1	3·6	3·6	1	H	13
1	3·7	2·1	0·8	Cl	7
1	4·3	1·2	0·04	CF_3	8
1	3·9	2·1	0·2	COCl	6
1	3·9	1·7	0·2	CN	This work

present results for 1-cyanobutane are compared with some of our earlier data.

There are no existing data for the bromination of nitriles with which the present results can be compared, but in Table 10 they are compared with some of our previous data.

The data for bromine atom attack at the 2-position show that the cyano-group is nearly as deactivating as the trifluoromethyl group. In the chlorination of 1-cyanobutane the 1-position is slightly deactivated, but

TABLE 10

Bromination of substituted n-butane derivatives in the gas phase at *ca.* 150°

RS_4^x

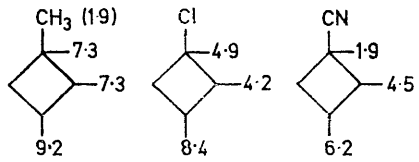
4 CH_3	3 CH_2	2 CH_2	1 CH_2	X	Ref.
1	80	80	1	H	13
1	80	32	34	Cl	7
1	80	7	1	CF_3	8
1	80	30	30	COCl	6
1	80	8	25	CN	This work

in the corresponding bromination it is activated. This is a common situation as Tables 9 and 10 show. It indicates that although the cyano-group exerts a powerful electron-attracting effect, resonance stabilization of the incipient α-cyano-radical is also important.

$$[R\text{-}\dot{C}H\text{-}C{\equiv}\ddot{N} \longleftrightarrow R\text{-}CH{=}C{=}\dot{N}{:}]$$

The chlorination results at these temperatures are not sufficient to justify the calculation at Arrhenius parameters, and with the bromination results (Table 3) there appears to have been some breakdown of the α-radical at 300°.

Competitive studies between 1-chlorobutane and cyanocyclobutane (Table 5) have enabled a comparison to be effected with chlorocyclobutane and methylcyclobutane, studied previously.[1] The high rate of chlorine atom attack, particularly at the 1-position occurring in



Gas-phase chlorination at 100°

both chlorocyclobutane and methylcyclobutane was largely attributed to relief of steric strain in the resultant substituted cyclobutyl radical. Such an explanation may also be invoked for chlorine atom attack on cyanocyclobutane where the 1-position, although the least reactive site in the three substituted cyclobutanes studied, is still quite reactive when compared with the 1-position in 1-cyanobutane.

In previous papers[3,4] we have attributed the high *trans*/*cis* ratio (especially for the 1,2-isomers of dihalogenocycloalkanes) to an interaction between the half-filled π-orbital of the radical site and the *p*-orbital of the substituent. An interaction of this type, between one of the π-orbitals of the nitrile groups and the half-filled 2*p* atomic orbital of the radical site, would lead to preferential *trans* attack. This is observed at both the

[13] P. C. Anson, P. S. Fredricks, and J. M. Tedder, *J. Chem. Soc.*, 1959, 918.

2- and 3-positions (only trace amounts of the *cis*-1,2-isomer were observed in some experiments—Table 4).

The bromination of cyanocyclobutane gave 1-bromo-1-cyanocyclobutane as the only product of abstraction.

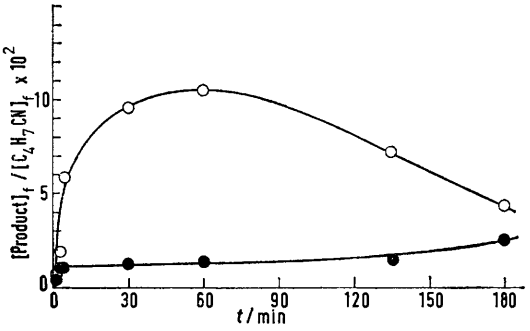


FIGURE Bromination of cyanocyclobutane at 100°:

$$\circ = \frac{[1,1\text{-BrCN}\square]_t}{[C_4H_7CN]_t}; \quad \bullet = \frac{[\text{Total olefin product}]_t}{[C_4H_7CN]_t}$$

However, small amounts of bromocyclobutane and *trans*-1,2-dibromocyclobutane were formed, together with traces of cyclobutene. No trace of bromobutane, 1,2-dibromobutane, or but-1-ene was observed in the bromination of 1-cyanobutane. Cyclohexene, bromocyclohexane, and *trans*-1,2-dibromocyclohexane have been observed in the gas phase bromination of bromo-, chloro-, and fluoro-cyclohexane;[14] the cyclohexene was formed by a surface elimination of hydrogen halide, catalysed by HBr. Distillation of the reaction products through Carbosorb decreased the amount of bromocyclobutane and *trans*-1,2-dibromocyclobutane but increased the amount of cyclobutene; this pointed to the derivation of bromocyclobutane and *trans*-1,2-dibromocyclobutane from cyclobutene by reaction with HBr and bromine respectively.

Since cyanocyclobutane gave only one ' abstraction product ' under the experimental conditions employed, a study was made of its reaction with both bromine and HBr. Variation of time in the bromination of cyanocyclobutane (Table 6 and Figure) showed a steady increase in 1-bromo-1-cyanocyclobutane, reaching a maximum at *ca.* 60 min followed by a steady decrease. The graph of ' olefin ' products (cyclobutene, bromocyclobutane, and *trans*-1,2-dibromocyclobutane) shows a steady increase. In the Figure the maximum in 1-bromo-1-cyanocyclobutane at *ca.* 60 min represents the termination of the abstraction reaction due to complete

$$RH + Br\cdot \longrightarrow R\cdot + HBr$$

consumption of bromine. From 60 min onwards the reaction of the HBr formed in the abstraction step with 1-bromo-1-cyanocyclobutane and cyanocyclobutane will predominate and the amount of 1-bromo-1-cyanocyclobutane will decrease.

Reaction of cyanocyclobutane with HBr, with a varying surface/volume ratio (Table 7), shows the heterogeneous nature of the elimination. Since cyanocyclobutane is in excess in all of the bromination experiments, its reaction with HBr will constitute the main effect of the heterogeneous component. However, as the concentration of 1-bromo-1-cyanocyclobutane increases, its reaction with HBr will become detectable.

The reaction of 1-bromo-1-cyanocyclobutane with HBr was studied in a separate series of experiments (Table 8). The products were 1-bromocyclobutene and 1-cyanocyclobutene. Variation of time showed, over the 120 min reaction period, a steady increase in the production of these two compounds, while variation of the surface/volume ratio accentuated again the heterogeneous nature of the reaction.

[2/1564 *Received*, 4*th July*, 1972]

[14] D. S. Ashton, A. Nechvatal, I. K. Stoddart, J. M. Tedder, and J. C. Walton, unpublished work.