

## Free Radical Substitution. Part 34.<sup>1</sup> The Chlorination of 1- and 2-Nitrobutanes in the Gas and Liquid Phases

By Saeed-y-Atto, Alan Potter, Hari Singh, and John M. Tedder,\* Department of Chemistry, The University, St. Andrews KY16 9ST, Scotland

1- and 2-nitrobutanes have been chlorinated in the gas phase and in solution. The intermediate nitrobutyl radicals with the nitro-group in a  $\beta$ -position are unstable and in the gas phase lose  $\text{NO}_2$  to yield the corresponding butene. The relative rates of attack at the various sites have been determined. The nitro-group proves to be the most deactivating non-ionic substituent studied so far.

In this series we have reported the directive effect of different substituents on the halogenation of 1-substituted butanes ( $\text{XCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  where  $\text{X} = \text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$ ,<sup>2</sup>  $\text{CF}_3$ ,<sup>3</sup>  $\text{COF}$ ,  $\text{COCl}$ , and  $\text{CO}_2\text{CH}_3$ ;<sup>4</sup>  $\text{CH}_3\text{CO-O}$ ,  $\text{CF}_3\text{CO-O}$ ,<sup>5</sup>  $\text{N}\equiv\text{C}$ ,<sup>6</sup>  $\text{C}_6\text{H}_5$ ,<sup>7</sup> and  $\text{CH}_3\text{O}$ <sup>8</sup>). A similar but much less intensive study has been made of 2-substituted butanes.<sup>9,10</sup> In the course of these investigations the effect of solvents on the course of liquid-phase chlorinations has been studied.<sup>11,12</sup> The present paper describes a study of the directive effects of the nitro-group in both the 1- and the 2-positions in butane. The only previous report of the chlorination of a nitroalkane under controlled conditions is that of Walling and Jacknow who chlorinated 1-nitropropane with *t*-butyl hypochlorite.<sup>13</sup>

### EXPERIMENTAL

The gas-phase reactions were studied in a conventional vacuum line, and the liquid phase ones in a small Pyrex flask fitted with a long capillary through which hydrogen chloride could escape.<sup>11</sup> Chlorination was initiated photochemically using a 100 W tungsten lamp. The products were analysed quantitatively by g.l.c. using a density balance as detector. The identity of each eluted peak was established by preparative g.l.c. followed by n.m.r. spectroscopy using a Bruker WP80 spectrometer.

1-Nitrobutane was prepared from 1-bromobutane by the action of dry silver nitrite. 2-Nitrobutane was prepared from 2-iodobutane by treatment with sodium nitrite in dimethyl sulphoxide. The redistilled compounds were further purified by preparative g.l.c. To assist identification 1-chloro-1-nitrobutane and 2-chloro-2-nitrobutane

nitrobutane,  $\delta(\text{CCl}_3\text{D})$  0.9 (3 H, t,  $J$  14 Hz), 1.2—1.6 (2 H, m), 2.1—2.4 (2 H, m), and 5.9 (1 H, quint,  $J$  14 Hz). The second product peak (only present in the solution phase experiments) was identified as 2-chloro-1-nitrobutane,  $\delta(\text{CCl}_3\text{D})$  1.1 (3 H, t,  $J$  16 Hz), 1.8 (2 H, m), and 4.4—4.6 (3 H, m). The third and largest product peak was identified as 3-chloro-1-nitrobutane,  $\delta(\text{CCl}_3\text{D})$  1.5 (3 H, d,  $J$  7 Hz), 2.0—2.6 (2 H, m), 3.9—4.3 (1 H, m), and 4.5 (2 H, t,  $J$  14 Hz). The fourth peak was identified as 1-chloro-4-nitrobutane,  $\delta(\text{CCl}_3\text{D})$  1.6—2.3 (4 H, m), 3.6 (2 H, t,  $J$  11 Hz), and 4.4 (2 H, t,  $J$  12 Hz).

The chlorination products of 2-nitrobutane were identified similarly. The first peak to be eluted was 2-chloro-2-nitrobutane which had identical retention time and properties to an authentic sample. The next two peaks were the *erythro*- and *threo*-isomers of 2-chloro-3-nitrobutane,  $\delta$  1.6 (3 H, d,  $J$  7 Hz), 1.7 (3 H, d,  $J$  7 Hz), and 4.36—4.8 (2 H, m), and  $\delta$  1.55 (3 H, d,  $J$  7 Hz), 1.63 (3 H, d,  $J$  7 Hz), and 4.26—4.9 (2 H, m). The fourth product peak was too small to be collected but by process of elimination must be 1-chloro-2-nitrobutane. The fifth and final product peak

TABLE 1

Chlorination of 1-nitrobutane in the gas phase:  $\text{RS}_4^3$

| $T/^\circ\text{C}$ <sup>a</sup> | $\text{RS}_4^3$ | $T/^\circ\text{C}$ | $\text{RS}_4^3$ |
|---------------------------------|-----------------|--------------------|-----------------|
| 78                              | 3.9             | 175                | 3.4             |
| 100                             | 3.6             | 200                | 2.8             |
| 150                             | 3.6             |                    |                 |

<sup>a</sup>  $^\circ\text{C} = \text{K} - 273.15$ .

was 1-chloro-3-nitrobutane,  $\delta(\text{CCl}_3\text{D})$  1.58 (3 H, d,  $J$  7 Hz), 2.32—2.78 (2 H, m), 3.6 (2 H, t,  $J$  7 Hz), and 4.85 (1 H, sextet,  $J$  7,  $J'$  7 Hz).

TABLE 2

Chlorination of 1-nitrobutane in benzene and carbon tetrachloride and in the gas phase:  $\text{RS}_4^2$

| Solvent                | Solvent: 1-nitrobutane | $T/^\circ\text{C}$ | No. of runs | $\text{CH}_2\text{NO}_2$ | $\text{CH}_2$   | $\text{CH}_3$ | $\text{CH}_3$ |
|------------------------|------------------------|--------------------|-------------|--------------------------|-----------------|---------------|---------------|
| $\text{CCl}_4$         | 7:1                    | 25                 | 5           | 0.01                     | $0.37 \pm 0.04$ | $2.3 \pm 0.1$ | 1.00          |
| $\text{C}_6\text{H}_6$ | 7:1                    | 25                 | 5           | 0.00                     | $0.44 \pm 0.02$ | $4.8 \pm 0.2$ | 1.00          |
| Gas †                  |                        | 75                 | 3           | 0.00                     |                 | $3.9 \pm 0.3$ | 1.00          |

† Dichlorobutane and butene also formed.

were prepared by the reaction of molecular chlorine with the sodium salts of the nitro-compounds.

The chlorination of 1-nitrobutane was carried out in the liquid phase on a relatively large scale and five chloro-nitrobutane peaks were observed on the chromatogram. The first product peak was very small indeed but had a retention time identical to that of authentic 1-chloro-1-

The gas-phase chlorination of 1-nitrobutane only yielded two chloronitrobutanes, 3-chloro-1-nitrobutane and 1-chloro-4-nitrobutane. The chlorination was carried out over a range of temperatures and the relative selectivity  $\text{RS}_4^3$  determined.

The logarithm of  $\text{RS}_4^3$  was plotted against the inverse of the temperature and the resultant straight line had a slope

TABLE 3  
Chlorination of 2-nitrobutane in various solvents and in the gas phase:  $RS_4^z$

| Solvent                | Solvent: 2-nitrobutane | $T/^\circ\text{C}$ | No. of runs | $\text{CH}_3$   | $\text{CHNO}_2$ | $\text{CH}_2$ *   | $\text{CH}_3$ |
|------------------------|------------------------|--------------------|-------------|-----------------|-----------------|---|---------------|
| Neat                   |                        | 25                 | 5           | $0.06 \pm 0.00$ | $0.05 \pm 0.02$ | $\left\{ \begin{array}{l} 0.74 \pm 0.07 \\ 0.53 \pm 0.02 \end{array} \right.$ | 1.00          |
| $\text{CCl}_4$         | 1:1                    | 25                 | 5           | $0.06 \pm 0.01$ | $0.06 \pm 0.02$ | $\left\{ \begin{array}{l} 0.87 \pm 0.04 \\ 0.56 \pm 0.01 \end{array} \right.$ | 1.00          |
| $\text{C}_6\text{H}_6$ | 1:1                    | 25                 | 4           | $0.08 \pm 0.05$ | $0.67 \pm 0.07$ | $\left\{ \begin{array}{l} 0.67 \pm 0.03 \\ 0.67 \pm 0.04 \end{array} \right.$ | 1.00          |
| $\text{CS}_2$          | 1:1                    | 25                 | 4           | $0.07 \pm 0.05$ | $0.54 \pm 0.07$ | $\left\{ \begin{array}{l} 1.01 \pm 0.05 \\ 0.95 \pm 0.04 \end{array} \right.$ | 1.00          |
| Gas †                  |                        | 30                 | 5           | $0.04 \pm 0.02$ | $0.15 \pm 0.05$ | $\left\{ \begin{array}{l} 0.90 \pm 0.03 \\ 0.45 \pm 0.24 \end{array} \right.$ | 1.00          |

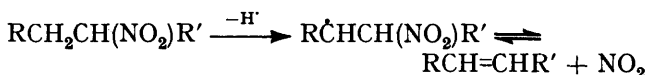
\* *threo*- and *erythro*-isomers. † Dichlorobutanes were also formed and estimated.

$E_4 - E_3 = 630 \pm 260 \text{ cal mol}^{-1}$  \* and an intercept  $\ln(A_3/A_4) = 0.05 \pm 0.3$ .

The chlorination of 1-nitrobutane was investigated in the solution phase using carbon tetrachloride and benzene as solvents; concentrations are presented as volume ratios. The chlorination of 2-nitrobutane was investigated in the gas phase and in solution. 1-Nitrobutane was brominated in the gas phase. The experimental was difficult because of the low vapour pressure of the products. However, the observed relative selectivities at  $170^\circ\text{C}$  were  $RS_4^1 2.3 \pm 1.3$ ,  $RS_4^2$  trace, and  $RS_4^3 69 \pm 7.3$ .

#### DISCUSSION

The abstraction of a hydrogen atom from the  $\beta$ -position in a nitroalkane yields an unstable radical which can decompose unimolecularly. The loss of  $\text{NO}_2$  is apparently a reversible process since in the solution-



phase experiments the 1,2-chloronitrobutanes were isolated, while in the gas-phase experiments the 1,2-chloronitrobutanes were missing and the corresponding dichloro-compounds and butenes were isolated instead.

and -attracting properties, the nitro-group has a negligible influence on hydrogen abstraction by halogen atoms beyond the  $\beta$ -position in the gas phase. A similar conclusion arises from the qualitative bromination results where again the ratio of attack at the 3- and 4-positions is within error the same as for all other substituents studied. In bromination the relative selectivity for hydrogen abstraction at the  $\alpha$ -position appears slightly higher than that for the 2-position in 1,1,1-trifluoropentane.<sup>3</sup>

The ratio of *erythro*- to *threo*-2-chloro-3-nitrobutanes is greater in the gas phase than in solution, but further discussion of this steric effect will await a study of the chlorination of more 2-substituted butanes.

Table 4 clearly shows that the nitro-group is more deactivating at the  $\alpha$ - and  $\beta$ -positions in chlorination than is the chlorocarbonyl group. The most unexpected result is however the relatively high rate of attack at the substituted 2-position in 2-nitrobutane. In the chlorination of 1-nitrobutane the least reactive site is the substituted 1-position, but in the chlorination of 2-nitrobutane the least reactive site is the *unsubstituted* 1-position. The same is true for the two acid chlorides. A possible explanation of the high reactivity of the sub-

TABLE 4

Comparison of the chlorination of 1- and 2-nitrobutanes with the chlorination of pentanoyl and 2-methylbutanoyl chlorides. Relative selectivities  $RS_4^z$

|                          | Solvent                | $\text{XCH}_2$ | $\text{CH}_2$ | $\text{CH}_2$ | $\text{CH}_3$ | $\text{CH}_3$ | $\text{CHX}$ | $\text{CH}_2$ | $\text{CH}_3$ |
|--------------------------|------------------------|----------------|---------------|---------------|---------------|---------------|--------------|---------------|---------------|
| $\text{X} = \text{NO}_2$ | $\text{CCl}_4$         | 0.01           | 0.37          | 2.3           | 1             | 0.06          | 0.06         | 1.4           | 1             |
|                          | $\text{C}_6\text{H}_6$ | 0.00           | 0.44          | 4.8           | 1             | 0.08          | 0.67         | 1.3           | 1             |
|                          | Gas                    | 0.00           |               | 3.9           | 1             | 0.04          | 0.13         | 1.8 *         | 1             |
| $\text{X} = \text{COCl}$ | $\text{CCl}_4$         | 0.08           | 1.2           | 2.5           | 1             | 0.18          | 0.74         | 2.1           | 1             |
|                          | $\text{C}_6\text{H}_6$ | 0.04           | 1.3           | 6.1           | 1             | 0.26          | 1.8          | 3.2           | 1             |
|                          | Gas                    | 0.16           | 2.3           | 3.9           | 1             | 0.22          | 1.3          | 3.7           | 1             |

\* Calculated from the observed yield of 2-chloro-3-nitrobutanes plus the combined yields of *meso*- and ( $\pm$ )-2,3-dichlorobutanes.

The loss of  $\text{NO}_2$  from 1-methyl-1-nitropropyl radical makes it impossible to estimate the rate of hydrogen abstraction from the 2-position. Table 1 shows that the ratio of attack at the 3- and 4-positions is, within experimental error, the same as that for all the other 1-substituted butanes (*cf.* ref. 2—8) and the activation energy difference and  $A$  factor ratio are well within the range of values obtained for other molecules. This suggests that in spite of its extreme electron-accepting

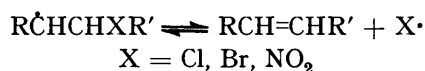
\* 1 cal = 4.184 J.

substituted position in 2-nitrobutane (and in 2-methylbutanoyl chloride) is release of steric compression occurring when the radical is formed. Hydrogen abstraction from the 1-position in 1-nitrobutane would not result in a significant release of steric strain.

The effect of the medium varies. In the chlorination of the 1-substituted butanes the 3-position is invariably the most reactive site, and the *relative* reactivity of this site is greatest in benzene and least in carbon tetrachloride. The other factor coinciding with the change of

solvent is the *erythro*:*threo* ratio found in the chlorination of 2-nitrobutane. In the reactions believed to involve a complexed atom, e.g. benzene and carbon disulphide, the *erythro*:*threo* ratio is nearly unity, while in the gas phase it is 2:1; reaction in the non-complexing solvents falls in between. These results could be consistent with our previous conclusions.<sup>9</sup> In the gas phase the reaction is very fast and the 1-methyl-2-nitropropyl radical will have a preferred conformation which favours formation of the *threo*-isomer. In the complexing solvent the 1-methyl-2-nitropropyl radical itself will be weakly complexed preferentially in the '*erythro*' conformation. This will favour the interaction with the chlorine molecule to yield the *threo*-isomer by default. The net effect could be that both diastereoisomers are formed at approximately the same rate.

There is an alternative explanation.<sup>10</sup> The substituents which lead to large *erythro*:*threo* ratios are those which, in the gas phase, tend to dissociate to yield an olefin and an atom or radical. The substituents



which yield large *erythro*:*threo* ratios are those which dissociate readily while those with small *erythro*:*threo* ratios (X = F, CN, CH<sub>3</sub>CO·O, CF<sub>3</sub>CO·O, etc.) are those

which are unlikely to dissociate. The chlorocarbonyl group falls in between. This proposal does not necessarily imply partial 'bridging' but it would be consistent with it.<sup>14,15</sup>

We thank Dr. J. C. Walton for his interest and advice and one of us (S. A.) is indebted to the Iraqi Government for a research scholarship.

[1/843 Received, 27th May, 1981]

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