Polar Effects in Radical Reactions: a New Selective Type of Radical Bromination

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CHLORINATION and bromination of saturated aliphatic compounds are known to have a different course owing to their different energetics, so that bromine atoms are more selective than chlorine atoms.[1]

We now report a new type of bromination, characterized by the same high selectivity as already found in the corresponding chlorination. The reaction involves the use of the *N*-bromodimethylamine and ferrous sulphate in concentrated sulphuric acid under the same experimental conditions as for the chlorination of saturated compounds.[2]

The results (as per cent of isomers), for methyl hexanoate and 1-chlorohexane are summarized in Table 1, which also records the results of the chlorination of the methyl hexanoate with *N*-chlorodimethylamine under the same experimental conditions. Table 2 shows the results of the bromination of the methyl valerate with *N*-bromodimethylamine as compared with the known values for the chlorination and bromination with molecular chlorine and bromine.

From these results the following conclusions may be drawn:

(*a*) The isomer distribution, practically identical

TABLE 1

Bromination with N-*bromodimethylamine*

Cl	CH_2	CH_2	CH_2	CH_2	CH_2	CH_3
	—	2·5	7·5	19·7	67·6	2·7

CH_3OCO	CH_2	CH_2	CH_2	CH_2	CH_3
	—	0·41	5·9	87	6·88

Chlorination with N-*chlorodimethylamine*[2]

CH_3OCO	CH_2	CH_2	CH_2	CH_2	CH_3
	—	0·7	6·3	87·3	5·7

TABLE 2

	CH_3OCO	CH_2	CH_2	CH_2	CH_3
Cl_2 (55—60°)[3]	1·3	5·4	30·1	44·5	18·7
Br_2 (50°)[3]	—	35	19·6	45·4	traces
$Me_2\overset{+}{N}HBr$ (20—30°)	—	0·47	6	81·3	12·2

for the bromination and chlorination of the methyl hexanoate, is strong evidence that in both cases the same hydrogen-abstracting species is operating, *i.e.*, an amminium radical according to the radical chain, previously suggested by us:[2]

$$R_2\overset{+}{\underset{\cdot}{N}}H + RH \rightarrow R_2\overset{+}{N}H_2 + R\cdot$$

$$R\cdot + R_2\overset{+}{N}HX \rightarrow RX + R_2\overset{+}{\underset{\cdot}{N}}H \qquad (X = Cl,Br)$$

(*b*) This new bromination is more selective towards the influence of a polar substituent. This high selectivity, the easy availability of the *N*-bromodimethylamine,[4] the simple experimental conditions and the greater versatility of the bromo-derivatives in comparison with the chloro-derivatives gives this reaction great synthetic possibilities, especially for saturated aliphatic compounds.

(*c*) The amminium radicals again show the highest selectivity in terms of electron availability of any known radical because the electrophilic character of the amino-radical is strongly increased by the positive charge obtained by the protonation. This strong influence of the inductive effect of a polar substituent was also observed in the homolytic aromatic amination, carried out under the same conditions.[4]

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[1] C. Walling, "Free radicals in solution", John Wiley, New York, 1957, p. 369; J. M. Tedder, *Quart. Rev.*, 1960, **14**, 336.

[2] F. Minisci, R. Galli, A. Galli, and R. Bernardi, *Tetrahedron Letters*, 1967, 2207; *Chimica e Industria*, 1967, **49**, 594.

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

[4] F. Minisci, R. Galli, A. Galli, and R. Bernardi, *Chimica e Industria*, 1967, **49**, 252; F. Minisci, *Chimica e Industria*, in the press.

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