

## 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.<sup>1</sup>

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.<sup>2</sup>

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 <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>					
—	2.5	7.5	19.7	67.6	2.7

CH <sub>3</sub> OCO—CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>					
—	0.41	5.9	87	6.88	

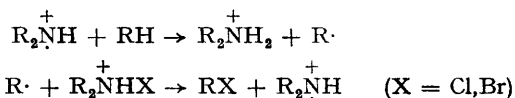
*Chlorination with N-chlorodimethylamine<sup>2</sup>*

CH <sub>3</sub> OCO—CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>					
—	0.7	6.3	87.3	5.7	

TABLE 2

	CH <sub>3</sub> OCO—CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>				
Cl <sub>2</sub> (55—60°) <sup>a</sup>	1.3	5.4	30.1	44.5	18.7
Br <sub>2</sub> (50°) <sup>a</sup>	—	35	19.6	45.4	traces
Me <sub>2</sub> NHBr (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 aminium radical according to the radical chain, previously suggested by us:<sup>2</sup>



(b) This new bromination is more selective towards the influence of a polar substituent. This high selectivity, the easy availability of the *N*-bromodimethylamine,<sup>4</sup> 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 aminium 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.<sup>4</sup>

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

<sup>2</sup> F. Minisci, R. Galli, A. Galli, and R. Bernardi, *Tetrahedron Letters*, 1967, 2207; *Chimica e Industria*, 1967, **49**, 594.

<sup>3</sup> H. Singh and J. M. Tedder, *J. Chem. Soc.*, 1964, 4737.

<sup>4</sup> 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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