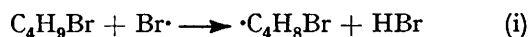


Liquid-phase Bromination of Bromobutane: Variation of the Ratio of 1,2- to 1,3-Dibromobutanes Produced

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The liquid-phase bromination of 1-bromo- and 1-chloro-butane has been studied using *t*-butyl hypobromite and bromine oxide as brominating agents. These reagents give a mixture of all four dibromobutanes from 1-bromobutane with less 1,2- than 1,3-dibromobutane, in contrast to bromination with molecular bromine which gives mainly 1,2-dibromobutane. The significance of these observations, taken together with the data obtained from the halogenation of 1-chlorobutane is discussed with respect to anchimeric assistance and the effect of hydrogen bromide on the course of bromination.

THE bromination of 1-bromobutane with elemental bromine has been the subject of a number of investigations.¹⁻⁴ In solution, the main product of the reaction is 1,2-dibromobutane.² In the gas-phase, the composition of the mixture of dibromides formed is affected by the presence of hydrogen bromide formed during the hydrogen abstraction step (i). It has been suggested that



hydrogen bromide is responsible for the formation of the high proportion of 1,2-dibromobutane both in the gas- and liquid-phase bromination of 1-bromobutane,^{3,5} and attempts have been made in liquid-phase brominations to suppress the effect of hydrogen bromide by using

other brominating agents such as *N*-bromosuccinimide,³ or bromotrichloromethane,⁶ or by using a large excess of bromine.⁴ In these cases the main product is still 1,2-dibromobutane.

Bunce⁷ has shown that a mixture of mercury(II) oxide and bromine will brominate 1-bromobutane to give more 1,3- than 1,2-dibromobutane and he suggested that the radicals responsible for the bromination were $\text{BrO}\cdot$ and $\text{Br}\cdot$. This present paper reports an investigation into the bromination of 1-bromobutane with *t*-butyl hypobromite and with bromine oxide.

The results obtained show that, with these reagents,

⁴ D. D. Tanner, J. E. Rowe, T. Pace, and Y. Kosugi, *J. Amer. Chem. Soc.*, 1973, **95**, 4705.

⁵ D. S. Ashton, J. M. Tedder, and J. C. Walton, *Chem. Comm.*, 1971, 1487.

⁶ J. H. Hargis, *J. Org. Chem.*, 1973, **38**, 346.

⁷ N. J. Bunce, *Canad. J. Chem.*, 1972, **50**, 3109.

¹ P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 1960, 144.

² W. Thaler, *J. Amer. Chem. Soc.*, 1963, **85**, 2607.

³ D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Amer. Chem. Soc.*, 1969, **91**, 7398.

position 2, adjacent to the terminal carbon atom carrying the bromine substituent, is less reactive than position 3 and that there is no anchimeric assistance at position 2 by the bromine atom at C-1.

EXPERIMENTAL

Apparatus.—Halogenation reactions, carried out in homogenous solution were run in sealed Pyrex tubes having first been degassed by two freeze-thaw cycles. The tubes contained halogenobutane in excess and halogenating agent either neat or in CCl_4 as solvent. The reactions were initiated by a 150 W tungsten-halogen projector lamp, and were considered complete when the contents of the tube were colourless. Reaction temperatures were maintained to $\pm 0.1^\circ$ by a thermostatted water-bath.

Bromine oxide reactions were carried out by mixing trichlorofluoromethane solutions (10 ml) of bromine (1M) with mercury(II) oxide (10 g, 40 mmol) in the dark for 3 min. The resulting mixture was filtered directly on to 1-bromobutane (1 ml, 10 mmol). Samples were taken at intervals and quenched with aqueous sodium hydrogen sulphite prior to analysis.

Products were analysed directly from the reaction mixtures by g.l.c. at 100°C on a $2\text{ m} \times 6\text{ mm}$ column containing 10% tritoyl phosphate on 60–80 mesh Embacel support, using a flame ionisation detector. The response of this detector to the various reaction products was calibrated for a standard mixture against a gas chromatograph equipped with a gas density balance detector, and the relative proportions of isomers were calculated from peak areas measured by an integrator, and are corrected for the response factor unless otherwise stated.

Reagents.—1-Bromobutane. Commercial 1-bromobutane was purified by distillation in a Büchi spinning band fractionating column at atmospheric pressure. The fraction, b.p. 102° (lit.,⁸ 101.26°), was shown by g.l.c. to contain not more than 0.1% impurity.

t-Butyl hypobromite. This reagent was prepared in 25% yield by the method of Walling and Padwa,⁹ except that mercury(II) oxide was used instead of silver sulphate to generate the hypobromous acid.¹⁰ It was found to be 92% pure by iodimetric titration.

Bromine. Commercial samples were used unpurified.

Bromine oxide. This reagent was prepared in trichlorofluoromethane solution, according to the method of Bunce.⁷

t-Butyl hypochlorite. This reagent, prepared according to the method of Katz,¹¹ was stored cold over solid sodium hydroxide and used without further purification.

1-Chlorobutane. This compound was commercial reagent grade and used without further purification.

Identification of Products.—The isomeric dibromobutanes were eluted from the g.l.c. column in the order 1,1-, 1,2-, 1,3-, and 1,4-dibromobutane. The 1,2-, 1,3-, and 1,4-peaks were identified by comparing retention times with those of authentic samples. A sample of 1,1-dibromobutane was isolated by preparative g.l.c. from a reaction mixture, and identified by its n.m.r. spectrum.⁶ The two sets of isomeric bromochlorobutanes have been shown to be eluted in the same order as the dibromobutanes.²

⁸ I. H. Heilbron, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, 4th edn., vol. 1, p. 424.

⁹ C. Walling and A. Padwa, *J. Org. Chem.*, 1962, **27**, 2976.

¹⁰ Mellor's 'Comprehensive Treatise on Inorganic and Theoretical Chemistry,' Supplement II, Part I, Longman, London, 1956, p. 750.

DISCUSSION

Bromination of 1-bromobutane with molecular bromine in the liquid phase leads to the formation of an isomeric mixture of dibromobutanes containing nearly six times more 1,2- than 1,3-dibromobutane² (Table 4, reaction 1). In contrast, Bunce⁷ has shown that bromination by

TABLE 1*

Bromination of 1-bromobutane with t-butyl hypobromite

| Conditions | | | Isomer distribution | | | |
|---|-------------|----------------------------|---------------------|-----------------|-----------------|------------------------|
| Solvent | Molar ratio | Temp. ($^\circ\text{C}$) | CH_3 — | CH_2 — | CH_2 — | CH_2Br |
| Neat | 6 : 1 | 40 | 0.15 | 1.00 | 0.72 | 0.69 |
| Neat | 6 : 1 | 25 | 0.14 | 1.00 | 0.72 | 0.56 |
| Neat | 12 : 1 | 25 | 0.17 | 1.00 | 0.75 | 0.58 |
| Neat | 3 : 1 | 25 | 0.19 | 1.00 | 0.71 | 0.59 |
| CCl_4 | 12 : 1 | 25 | 0.14 | 1.00 | 0.76 | 0.59 |
| CCl_4 | 6 : 1 | 25 | 0.15 | 1.00 | 0.76 | 0.62 |
| CCl_4 | 3 : 1 | 25 | 0.13 | 1.00 | 0.72 | 0.55 |
| Neat with added $\text{Cl}_2\text{C}=\text{CHCl}$ | 12 : 1 | 25 | 0.13 | 1.00 | 0.73 | 0.57 |
| | | | Mean 0.15 | 1.00 | 0.73 | 0.59 |
| | | | ± 0.02 | | ± 0.02 | ± 0.04 |

* Errors quoted are standard deviations.

TABLE 2

Bromination of 1-bromobutane with bromine oxide in trichlorofluoromethane solution

| Reaction time (h) | Isomer distribution | | | |
|-------------------|---------------------|-----------------|-----------------|------------------------|
| | CH_3 — | CH_2 — | CH_2 — | CH_2Br |
| 0.75 | 0.09 | 1.00 | 0.68 | 0.77 |
| 2 | 0.08 | 1.00 | 0.82 | 0.84 |
| 3 | 0.13 | 1.00 | 0.97 | 0.87 |
| 5 | 0.08 | 1.00 | 1.14 | 0.84 |
| 6 | 0.08 | 1.00 | 1.30 | 0.78 |
| 7 | 0.12 | 1.00 | 1.38 | 0.78 |
| 20 | 0.03 | 1.00 | 2.80 | 0.71 |

TABLE 3

Bromination of 1-bromobutane in the presence of bromine and t-butyl hypobromite at 45°

| Molar ratio | | | Isomer distribution | | | |
|---------------------------------|---------------|--------------------------------|---------------------|-----------------|-----------------|------------------------|
| $\text{C}_4\text{H}_9\text{Br}$ | Br_2 | $\text{Bu}^\text{t}\text{OBr}$ | CH_3 — | CH_2 — | CH_2 — | CH_2Br |
| 12 | 0.1 | 1 | 0.16 | 1.00 | 0.73 | 0.56 |
| 12 | 0.2 | 1 | 0.15 | 1.00 | 0.80 | 0.56 |
| 12 | 0.5 | 1 | 0.17 | 1.00 | 0.74 | 0.68 |
| 12 | 1 | 1 | 0.15 | 1.00 | 0.82 | 0.60 |
| 12 | 2 | 1 | 0.59 | 1.00 | 1.02 | 0.53 |
| 12 | 0 | 1 | 0.17 | 1.00 | 0.76 | 0.64 |

bromine in the presence of mercury(II) oxide produces *ca.* 1.6 times more 1,3- than 1,2-dibromobutane and noticeably more of the 1,1- and 1,4-isomers than is obtained by bromination with bromine alone.

A similar ratio of dibromobutanes is obtained in the initial stages of the reaction of bromine oxide with 1-bromobutane. However, if the reaction is allowed to go to completion, hydrogen bromide accumulates and 1,2-dibromobutane becomes the predominant isomer in the product mixture (Table 2).

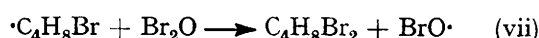
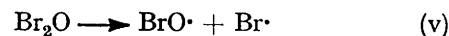
We have found the light-initiated reaction of 1-bromo-

¹¹ I. Katz, U.S.P. 2,694,722 (1954) (*Chem. Abs.*, 1955, **49**, 12,528b).

butane with *t*-butyl hypobromite also leads to the formation of more 1,3- than 1,2-dibromobutane (Table 1). The results in Table 4, reaction 5, are averaged from Table 1 since varying reactant ratio, solvent, and temperature did not significantly affect the product ratio.

Nature of the Chain Reaction.—Examination of the relative selectivities per hydrogen for C-3 relative to C-4 ($RS^{3:4}$), for the bromination of 1-bromobutane by the various reagents shown in Table 4, indicate that $RS^{3:4}$ for bromine atoms (reaction 1) is immeasurably high. On the other hand, the $RS^{3:4}$ values for *t*-butyl hypobromite

that the chain carrier is the $BrO\cdot$ radical [reactions (v)–(vii)].



The $RS^{3:4}$ value for bromination of 1-chlorobutane with *t*-butyl hypobromite (12.0) is, within experimental error, the same as for 1-bromobutane, and the $RS^{3:4}$

TABLE 4
Halogenation of 1-bromobutane

| Reaction | Reagent | Solvent | Reaction time (h) | Temp. (°C) | Reference | Relative ratio of isomers formed. Not corrected for number of hydrogen atoms at each site | | | | $RS^{3:4}$ ^a |
|----------|--|-------------------------------|-------------------|------------|-----------|---|---|---|---|-------------------------|
| | | | | | | CH ₃ —CH ₂ —CH ₂ —CH ₂ Br | CH ₃ —CH ₂ —CH ₂ —CH ₂ Br | CH ₃ —CH ₂ —CH ₂ —CH ₂ Br | CH ₃ —CH ₂ —CH ₂ —CH ₂ Br | |
| 1 | Br ₂ | None | 6 | 60 | 2 | * | 1.00 | 5.78 | 0.09 | ∞ |
| 2 | HgO—Br ₂ | None | | 25 | 7 | 0.11 | 1.00 | 0.63 | 0.59 | 13.6 |
| 3 | Br ₂ O | CCl ₄ ^a | 0.75 | 25 | This work | 0.09 | 1.00 | 0.68 | 0.77 | 16.67 |
| 4 | Br ₂ O | CCl ₄ | 20 | 25 | This work | 0.03 | 1.00 | 2.80 | 0.71 | 50.0 |
| 5 | (CH ₃) ₃ COBr | None or CCl ₄ | 1.5 | 25 | This work | 0.15 | 1.00 | 0.73 | 0.59 | 10.0 |
| 6 | (CH ₃) ₃ COBr and Br ₂ | None | 50 | 45 | This work | 0.17 | 1.00 | 0.74 | 0.68 | 8.8 |
| 7 | BrCCl ₃ | None | | 20 | 6 | * | 1.00 | 2.16 | * | ∞ |
| 8 | (CH ₃) ₃ COCl | None | 1 | 25 | This work | 0.25 | 1.00 | 0.58 | 0.38 | 6.0 |
| 9 | (CH ₃) ₃ COCl with Cl ₂ C=CHCl | None | 1 | 25 | This work | 0.17 | 1.00 | 0.62 | 0.49 | 8.8 |
| 10 | Cl ₂ | | | 60 | 2 | 0.46 | 1.00 | 0.43 | 0.09 | 3.3 |

^a Incomplete reaction. ^b $RS^{2:3}$ for this and Table 5 is the quoted figure for the 1,2 isomer.

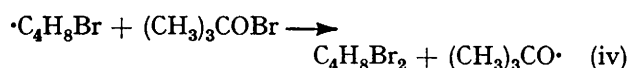
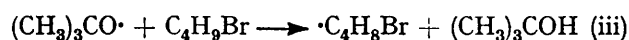
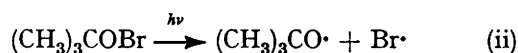
* None detected.

TABLE 5
Bromination of 1-chlorobutane

| Reaction | Reagent | Reaction time (h) | Temp. (°C) | Reference | Relative ratio of isomers formed. Not corrected for number of hydrogen atoms at each site | | | | $RS^{3:4}$ |
|----------|--------------------------------------|-------------------|------------|-----------|---|---|---|---|------------|
| | | | | | CH ₃ —CH ₂ —CH ₂ —CH ₂ Cl | CH ₃ —CH ₂ —CH ₂ —CH ₂ Cl | CH ₃ —CH ₂ —CH ₂ —CH ₂ Cl | CH ₃ —CH ₂ —CH ₂ —CH ₂ Cl | |
| 11 | (CH ₃) ₃ COBr | 1.5 | 25 | This work | 0.12 | 1.00 | 0.46 | 0.75 | 12.0 |
| 12 | HgO—Br ₂ | | 25 | 7 | 0.11 | 1.00 | 0.35 | 0.56 | 13.6 |
| 13 | Br ₂ | | 60 | 2 | * | 1.00 | 0.49 | 0.44 | ∞ |

* None detected.

and bromine oxide are 10.0 and 16.7 respectively. This would indicate that hydrogen abstraction is performed by some chain carrier other than bromine atoms. In the case of *t*-butyl hypobromite the chain carrier is most probably the *t*-butoxyl radical [reactions (ii)–(iv)].



Similarly in the reaction where bromine oxide is the brominating agent, the low $RS^{3:4}$ value of 16.7 suggests

value (8.8) for chlorination of 1-bromobutane with *t*-butyl hypochlorite in the presence of a chlorine atom trap indicates the intervention of the same chain carrier, since it has been shown that chlorine atom chains can compete with *t*-butoxyl radical chains in this chlorination reaction to reduce the $RS^{3:4}$ value.¹² The very large $RS^{3:4}$ values observed in the photolytic bromination of 1-bromobutane with bromotrichloromethane,⁶ suggests that in this reaction, bromine atoms and not trichloromethyl radicals are the main chain carriers. It is unlikely that a trichloromethyl radical chain can be sustained during this bromination since reaction (viii) has been shown to be fast.¹³



Recently it has been shown that bromination of the

¹² C. Walling and J. A. McGuinness, *J. Amer. Chem. Soc.*, 1969, **91**, 2053.

¹³ I. A. Matheson, H. W. Sidebottom, and J. M. Tedder, *Internat. J. Chem. Kinetics*, 1974, **6**, 493.

side chain of some arenes by bromotrichloromethane in solution does indeed involve a bromine atom chain.¹⁴

Evidence for Lack of Anchimeric Assistance.—The formation of more 1,2- than 1,3-dibromobutane has been interpreted in terms of extensive participation of the adjacent bromine atom on C-1 in the C-H bond-breaking step.² Table 4 shows that the RS^{2:3} value for bromination of 1-bromobutane with molecular bromine is *ca.* 6, whereas for bromination with bromine oxide and *t*-butyl hypobromite (Table 4, reactions 3 and 5) it is *ca.* 0.7. Thus there is no evidence for participation of the bromine substituent at C-1, in the C-H bond breaking at C-2 in the abstraction step, when these two reagents are being used for the bromination. This is confirmed by the fact that chlorination of 1-bromobutane with chlorine or *t*-butyl hypochlorite (Table 4, reactions 9 and 10) and bromination of 1-chlorobutane (Table 5, reaction 13) all show RS^{2:3} values of <1.

In the case of bromination of 1-bromobutane with molecular bromine the high RS^{2:3} values observed may be more satisfactorily explained by the reversibility of the hydrogen abstraction step for all positions except C-2 where orbital interaction between the half-filled orbital at C-2 and the bromine substituent at C-1 stabilises the

radical.^{3,15} To test whether the effect of hydrogen bromide could be suppressed when using molecular bromine, various mixtures of bromine, *t*-butyl hypobromite, and 1-bromobutane were irradiated. A similar ratio of isomeric dibromobutanes was produced as was obtained when *t*-butyl hypobromite was used alone provided that the molar concentration of bromine does not exceed the *t*-butyl hypobromite concentration (Table 3). This observation suggests that any hydrogen bromide produced as a result of bromine atom chains is removed immediately by reaction with *t*-butyl hypobromite [reaction (ix)], as is the case for the reaction of hydrogen chloride with *t*-butyl hypochlorite.¹⁶



Our results therefore suggest that when bromination of 1-bromobutane is effected by *t*-butyl hypobromite or by bromine oxide where the hydrogen abstraction step is unlikely from bond energy considerations to be reversible, the bromine substituent at C-1 in 1-bromobutane does not exhibit anchimeric assistance to hydrogen abstraction at position 2.

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¹⁴ D. D. Tanner and N. Wada, *J. Amer. Chem. Soc.*, 1975, **97**, 2190.

¹⁵ D. S. Ashton, J. M. Tedder, M. D. Walker, and J. C. Walton, *J.C.S. Perkin II*, 1973, 1346.

¹⁶ J. L. Brokenshire, A. Nechvatal, and J. M. Tedder, *Trans. Faraday Soc.*, 1970, **66**, 2029.