

Rearrangements of *N*-Bromo-amines

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THE rearrangement of *N*-bromo- α -halogeno-amides¹ or *N*-bromoperhalogeno-amides² in aqueous sodium hydroxide yields alkyl bromides and sodium isocyanate.

brought about rearrangement within a few minutes in 95–99% yields. (Reaction 1, R = C₃F₇). Unless an excess of alkali was present, no rearrangement took place. The failure of the



Stevens and his co-workers investigated the mechanisms proposed for the reaction. An optically active *N*-bromo- α -chloro-amide was rearranged to an alkyl bromide with retention of configuration.³ *N*-Bromo- α -chloro-amides were rearranged in solutions containing isotopically labelled bromide ion; no external bromide was found in the alkyl bromide product.⁴ They concluded that the *N*-bromo-amide conjugate base underwent intramolecular rearrangement *via* a cyclic transition state.

N-bromo-amide conjugate base to undergo rearrangement in the absence of hydroxide ion invalidates the intramolecular rearrangement mechanism.

Progress of rearrangements at 15–45° was followed by iodometric analysis. The first-order kinetics expected for intramolecular rearrangement were not observed. When the percentage reaction was plotted against time, sigmoidal curves resulted and lengthy induction periods became apparent. Exclusion of oxygen from the reactions shortened the induction periods. Reaction rates increased with increasing alkali or initial *N*-bromo-amide concentrations. Ammonia catalysed rearrangement, and oxygen, hypobromite, iodide, iodine, and isobutyramide each inhibited rearrangement. The effects of small proportions of inhibitors showed that a chain reaction was involved in the reaction mechanism.



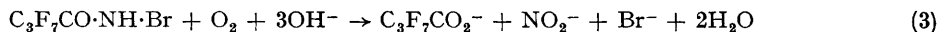
This communication reports experiments which are incompatible with the intramolecular rearrangement mechanism.

Equimolar amounts of *N*-bromoheptafluorobutyramide and sodium hydroxide in water formed the *N*-bromo-amide conjugate base. At 45°, the *N*-bromo-amide conjugate base was stable, but the addition of alkali to the solution

When oxygen was passed into solutions of alkali and *N*-bromo-amide, rearrangement ceased instantly and new products slowly formed according to the stoichiometry of Reaction 3. The reaction

was inhibited by hypobromite and catalysed by ammonia.

Mandelamide and sodium hypochlorite in alkaline solution gave benzaldehyde and sodium



N-Bromo- α -chloroisobutyramide and an excess of alkali reacted at 15–30° according to the stoichiometry of Reaction 1. Complex kinetics and induction periods were observed. In the presence of oxygen or hypobromite, no 2-bromo-2-chloropropane was formed and the *N*-bromo-amide slowly decomposed to other products. Reactions of *N*-bromotrihalogenoacetamides followed a similar pattern.

After long periods of inhibition, the rearrangements revived if the inhibitors were removed or consumed in side reactions. Intermediates which react with the inhibitors have not been identified.

Other amide rearrangements were studied. Hofmann rearrangement of *N*-bromoisobutyramide (0.025M) in aqueous sodium hydroxide (1.0M) at 15° gave isopropylamine in a first-order reaction ($k = 7.27 \times 10^{-4} \text{ sec.}^{-1}$) which was not inhibited by oxygen, iodide, or hypobromite.

isocyanate⁵ in a reaction which was first-order in both mandelamide and hypochlorite. The rate decreased with increasing alkali concentration but increased greatly in the presence of iodide ion. For reaction of aqueous mandelamide, sodium hypochlorite, and sodium hydroxide, each 0.025M, the second-order rate constant at 9.1° was 0.051 l. mole⁻¹ sec.⁻¹ The experiments showed chlorination of the amide was the rate-determining step. Mandelamide and sodium hypobromite or hypoiodite reacted much faster than mandelamide and sodium hypochlorite. None of the reactions was inhibited by oxygen or an excess of hypohalite and except for aspects of the stoichiometry, no similarities to rearrangements of *N*-bromo- α -chloro-amides were observed.

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¹ C. L. Stevens, T. K. Mukherjee, and V. J. Traynelis, *J. Amer. Chem. Soc.*, 1956, **78**, 2264.

² D. R. Husted and W. L. Kohlhase, *J. Amer. Chem. Soc.*, 1954, **76**, 5141; D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1957, **30**; J. M. Patterson, D. D. Wilson, and D. Trimnell, *J. Org. Chem.*, 1962, **27**, 3148.

³ C. L. Stevens, H. Dittmer, and J. Kovacs, *J. Amer. Chem. Soc.*, 1963, **85**, 3394.

⁴ C. L. Stevens, M. E. Munk, A. B. Ash, and R. D. Elliott, *J. Amer. Chem. Soc.*, 1963, **85**, 3390.

⁵ R. A. Weerman, *Rec. Trav. chim.*, 1918, **37**, 16.