# Dehydrohalogenation of Primary Alkyl Halides in Hexamethylphosphoric Triamide

By RICHARD S. MONSON

(*Department of Chemistry, California State College, Hayward, California* 94542)

*Summary* Normal alkyl bromides are found to undergo ready dehydrobromination in hexamethylphosphoric triamide at 180—210°, affording unrearranged alk-1-enes in good yield.

BASE-CATALYSED dehydrohalogenations have been reported to proceed smoothly in hexamethylphosphoric triamide (HMPT).[1,2] Nucleophilic substitution reactions in this solvent, where the nucleophilic anions are considered to act as strong bases, are usually accompanied by elimination.[3] Recently, dehydrobromination of α-bromo-ketones has been observed in HMPT with no basic agent present.[4]

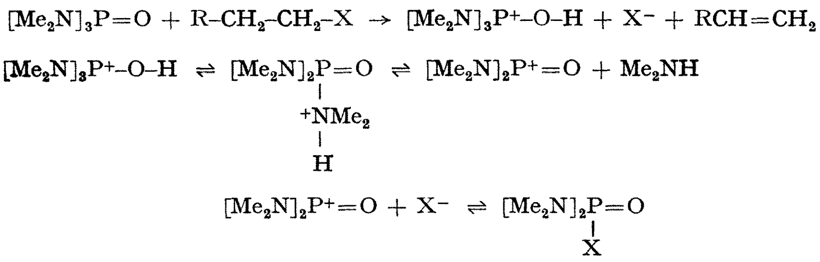
We report dehydrohalogenation of primary alkyl bromides and chlorides in pure HMPT. When normal alkyl bromides are heated at 180—210° in HMPT, dehydrohalogenation occurs at a moderate rate with some solvent decomposition. The olefin distils from the reaction mixture and the distillate is worked-up to remove the dimethylamine present. After drying, unrearranged alk-1-enes are obtained in greater than 99% purity as determined by i.r. and g.l.p.c. (Aerograph Model 600 HyFi with flame ionization detector, column 15% SE-30 on acid-washed Chromosorb, 1/8 in × 2 m). 1-Bromohexane (16·5 g, 0·1 mol) in 65 ml of HMPT required *ca.* 1 h. for completion of reaction. The product distilled from the reaction mixture initially at 65°, but the distillation temperature fell as dimethylamine began to come over. After work-up, the product had a retention time at 110°, flow rate 20 ml min$^{-1}$, of 1·12 min, identical to that of an authentic sample. Yields of this and other products similarly obtained are given in the Table.

With 1-chloroheptane the rate of formation of olefin was considerably slower. In a typical run the reaction was discontinued after *ca.* 3 h when the pot temperature reached 220°. The purity of the product was comparable to that obtained from the bromides, but the yield was only 15%.

When the reaction was applied to cyclohexylmethyl bromide, a mixture of methylenecyclohexane and 1-methylcyclohexene (verified by n.m.r.) was obtained in a ratio of 52:48; retention times were 2·25 min and 2·53 min, respectively, identical to those of authentic samples. This suggests that at the high temperature required for dehydrohalogenation, sensitive terminal olefins undergo rearrangement.

*Products of dehydrohalogenation of primary alkyl halides in HMPT*

| Halide | Product | Yield | $n_D^{20}$ of Product | $n_D^{20}$ of Authentic specimen |
|---|---|---|---|---|
| 1-Bromohexane | Hex-1-ene | 61% | 1·3891 | 1·3878 |
| 1-Bromoheptane | Hept-1-ene | 65% | 1·3994 | 1·3995 |
| 1-Bromo-octane | Oct-1-ene | 68% | 1·4086 | 1·4088 |
| 1-Chloroheptane | Hept-1-ene | 15% | 1·3989 | 1·3995 |
| Cyclohexylmethyl bromide | Methylenecyclohexane (52%)<br>1-Methylcyclohexene (48%) | 64% | | |



$$[Me_2N]_3P{=}O + R{-}CH_2{-}CH_2{-}X \rightarrow [Me_2N]_3P^+{-}O{-}H + X^- + RCH{=}CH_2$$

$$[Me_2N]_3P^+{-}O{-}H \rightleftharpoons \underset{\substack{|\\ {}^+NMe_2\\ |\\ H}}{[Me_2N]_2P{=}O} \rightleftharpoons [Me_2N]_2P^+{=}O + Me_2NH$$

$$[Me_2N]_2P^+{=}O + X^- \rightleftharpoons \underset{\substack{|\\ X}}{[Me_2N]_2P{=}O}$$

SCHEME

Cyclohexanol was found to be unreactive under the reaction conditions. It should therefore be possible to carry out dehydrobromination of appropriate bromo-alcohols.

A possible mechanism for the reaction, based on the behaviour of HMPT in related systems,[1] is shown in the Scheme.

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[1] J. F. Normant, *Bull. Soc. chim. France*, 1965, 859, and preceding papers.
[2] H. Normant, *Angew. Chem. Internat. Edn.*, 1967, **6**, 1046.
[3] J. F. Normant and H. Deshayes, *Bull. Soc. chim. France*, 1967, 2455.
[4] R. Hanna, *Tetrahedron Letters*, 1968, 2105.