

## Dehydrohalogenation of Primary Alkyl Halides in Hexamethylphosphoric Triamide

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**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).<sup>1,2</sup> Nucleophilic substitution reactions in this solvent, where the nucleophilic anions are considered to act as strong bases, are usually accompanied by elimination.<sup>3</sup> Recently, dehydrobromination of  $\alpha$ -bromo-ketones has been observed in HMPT with no basic agent present.<sup>4</sup>

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

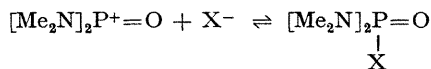
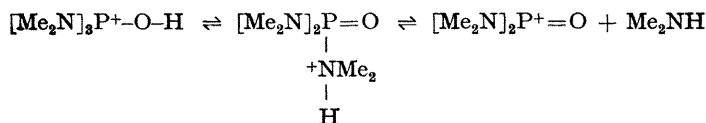
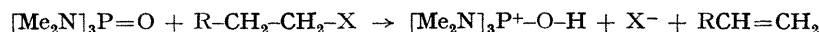
65°, but the distillation temperature fell as dimethylamine began to come over. After work-up, the product had a retention time at 110°, flow rate 20 ml min<sup>-1</sup>, of 1.12 min, identical to that of an authentic sample. Yields of this and other products similarly obtained are given in the Table.

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%) 1-Methylcyclohexene (48%)	64%		



SCHEME

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  $\times$  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

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

A possible mechanism for the reaction, based on the behaviour of HMPT in related systems,<sup>1</sup> is shown in the Scheme.

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<sup>1</sup> J. F. Normant, *Bull. Soc. chim. France*, 1965, 859, and preceding papers.

<sup>2</sup> H. Normant, *Angew. Chem. Internat. Edn.*, 1967, 6, 1046.

<sup>3</sup> J. F. Normant and H. Deshayes, *Bull. Soc. chim. France*, 1967, 2455.

<sup>4</sup> R. Hanna, *Tetrahedron Letters*, 1968, 2105.