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Reaction of Benzylic Chlorides with Hexamethylphosphoric Triamide

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Synopsis. Benzyl chloride was converted into benzyldimethylamine (**1**), dibenzylmethylamine (**2**), and benzylpentamethylphosphoric triamide (**3**), when it was heated in hexamethylphosphoric triamide (HMPT). Diphenylmethane (**4**), benzhydrylmethylamine (**5**), and benzophenone methylamine (**6**) were obtained when benzhydryl chloride was used in place of benzyl chloride. Triphenylmethyl chloride afforded triphenylmethane (**7**) as the sole isolable product.

Monson reported that primary and secondary alcohols possessing β-hydrogen atom are readily transformed into the unrearranged olefins in hexamethylphosphoric triamide (HMPT) at 230—240 °C *via* the corresponding alkyl tetramethylphosphorodiamidates,[1] and that primary alkyl halides having β-hydrogen atom afford in HMPT unrearranged 1-alkenes in good yields.[2] In the case of alcohols having no β-hydrogen atom, we found that the reaction proceeds in different ways to give reduction products, substituted products and phosphorodiamidated products.[3] In the reaction of benzyl alcohol with HMPT, we isolated benzyl tetramethylphosphorodiamidate which Monson suggested as an intermediates, and showed that bis(*N*,*N*-dimethylamino) phosphoryl group could behave as a leaving group to give the substituted compounds.

Benzyl chloride has no β-hydrogen atom, but has a chlorine atom which is thought to be a better leaving group than bis(*N*,*N*-dimethylamino)phosphoryl group. We wish to report results (see Table) obtained by the thermal treatment of benzylic chlorides with HMPT.

The results are similar to those of the reaction of benzylic alcohols with HMPT except for two points: i) An additional product was produced—benzylpentamethylphosphoric triamide (**3**) in the case of benzyl chloride, and benzophenone methylimine (**6**) in the case of benzhydryl chloride. ii) The yields of the products were higher than in the case of benzylic alcohols. Triphenylmethyl chloride and triphenylmethanol gave triphenyl methane (**7**) in 83% and 44% yields,[3] respectively. This might be ascribed to the nature of chlorine atom as a better leaving group than that of the bis(*N*,*N*-dimethylamino)phosphoryl group.[5]

TABLE 1. REACTION OF BENZYLIC CHLORIDES WITH HMPT

Substrate	Isolated products (%)
$PhCH_2Cl$	$PhCH_2NMe_2$ (39), $(PhCH_2)_2NMe$ (27), (**1**) (**2**) $PhCH_2NMeP(O)(NMe_2)_2$ (23) (**3**)
Ph_2CHCl	Ph_2CH_2 (13), Ph_2CHNMe_2 (40), (**4**) (**5**) $Ph_2C{=}NMe$ (6) (**6**)
Ph_3CCl	Ph_3CH (83) (**7**)

Experimental

All the temperatures are uncorrected. The IR and MS spectra were obtained on a Shimadzu IR-27 spectrometer and Hitachi RMS-4 mass spectrometer, respectively. The NMR spectra were obtained on a Varian EM-360 spectrometer, TMS being chosen as an internal standard.

Hexamethylphosphoric Triamide (HMPT). Commercial HMPT was refluxed for 5 hr under N_2 with calcium hydride, and then distilled, bp 110 °C/15 mmHg.

Starting Materials. Commercial benzyl chloride was distilled before use. Benzhydryl chloride and triphenylmethyl chloride were prepared according to the published methods.[6,7]

General Procedure for the Reaction with HMPT. The substrate (0.01 mol) was dissolved in HMPT and heated at 230—240 °C under N_2 for 1 hr. After HMPT had been removed by distillation under diminished pressure, the residue was separated by a combination of vacuum distillation, column chromatography and preparative glc. Each reaction product was identified by comparison with the authentic specimen.[3b,8]

References

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3) (a) M. Kawanisi, S. Arimatsu, R. Yamaguchi, and K. Kimoto, *Chem. Lett.*, **1972**, 881 (b) S. Arimatsu, R. Yamaguchi, and M. Kawanisi, This Bulletin, **47**, 1693 (1974).

4) R. S. Monson and D. N. Priest, *Chem. Commun.*, **1971**, 1018.

5) Since 1- and 2-chloroadamantane did not react with HMPT under similar reaction conditions, the enhanced cationic nature of the benzylic carbon atom can be the driving force for the reactions. (S. Arimatsu, unpublished results.)

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