Conversion of Benzyl Alcohols into Benzyldimethylamines by Hexamethylphosphoric Triamide

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Summary Benzyl alcohols react readily with hexamethylphosphoric triamide (HMPT) at reflux affording the corresponding benzyldimethylamines in modest yield.

THE exchange reaction between carboxylic acids and hexamethylphosphoric triamide (HMPT) has been reported to afford *NN*-dimethylamides.[1,2] We recently reported our results[3] on the reactions of primary and secondary alcohols in HMPT wherein dehydration to olefins was the main reaction. The observation[3] that small amounts of alkyldimethylamines were formed along with the olefins in certain cases prompted an investigation of the reactions of benzyl alcohols under the same conditions.

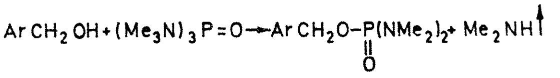
When benzyl alcohols (0·1 mol) are heated in HMPT (65 ml) at its b.p. (230—240°), a clouding of the solution and the copious generation of dimethylamine occurs immediately. After brief heating under reflux, the solution becomes dark. Work-up affords modest yields of the corresponding benzyldimethylamine. (M.p.s of picrates or hydrochlorides of all liquid products compared satisfactorily with literature values.) The yields of the products are given in the Table.

TABLE. *Benzyldimethylamines formed in HMPT*

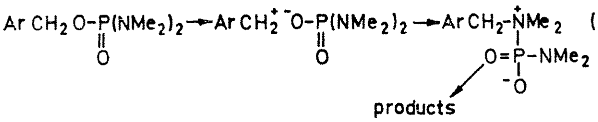
Alcohol	Reflux time in min	Yield of corresponding dimethylamines (%)	B.p.[a] or m.p.[b] of product
Benzyl alcohol ..	45	71	56—59°
Benzhydrol	30	46	(67—69°)
Triphenylmethanol ..	30	42	(93—95°)
p-Methoxylbenzyl alcohol	30	47	59°
m-Nitrobenzyl alcohol	30	31	89—90°
p-Chlorobenzyl alcohol	45	68	47—50°
1-Phenylethanol ..	60	*ca.* 1[c]	—

[a] At 0·75 mmHg. [b] From light petroleum. [c] Major product was styrene (47%).

The chemistry of HMPT,[4,5] as well as the report by White and Elliger[6] on the reactions of the analogous *NN*-dimethylsulphamates, suggest the reaction pathway (1) and (2).


(1)

$$\mathrm{ArCH_2OH + (Me_3N)_3P{=}O \longrightarrow ArCH_2O{-}P(O)(NMe_2)_2 + Me_2NH\uparrow} \quad (1)$$


(2)

$$\mathrm{ArCH_2O{-}P(O)(NMe_2)_2 \longrightarrow ArCH_2^{+}\ {}^{-}O{-}P(O)(NMe_2)_2 \longrightarrow ArCH_2{-}\overset{+}{N}Me_2{-}P(O)(O^{-})(NMe_2)} \quad (2)$$

The fate of the diamidophosphate fragment has in part been examined. In the course of the reflux, an insoluble oily layer was formed in every case. Upon cooling, the oil solidified to a gummy crystalline mass which was insoluble in aprotic solvents. The material was purified by dissolution in absolute alcohol followed by reprecipitation by isopropyl alcohol. Repetitions of this procedure gave a pure crystalline substance, m.p. 178—180° (decomp.) which gave analytical data consistent with the formulation as bisdimethylammonium dihydrogen pyrophosphate, $(Me_2NH_2)_2H_2P_2O_7$. An aqueous solution of the salt gave a precipitate with aqueous zinc acetate, a result said[7] to be characteristic of the pyrophosphate group. The formation of the pyrophosphate linkage has previously been reported[8] in connection with the thermal decomposition of alkyl tetraethylphosphorodiamidates, $R{-}O{-}P(O)(NEt_2)_2$. The generation of this linkage in the present case can readily be accounted for by subsequent reactions of the phosphate fragments generated in reaction (2).

The authors express their appreciation to the Research Foundation of California State College at Hayward for financial support.

(*Received, June* 11*th*, 1971; *Com.* 957.)

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