

SOLVENT CATALYZED DEHYDRATION OF ALCOHOLS

IN HEXAMETHYLPHOSPHORIC TRIAMIDE

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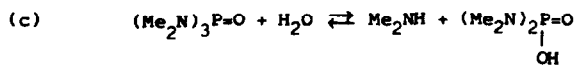
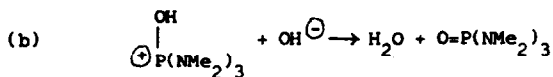
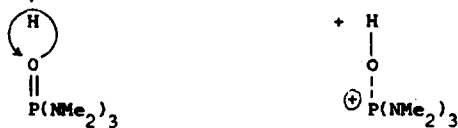
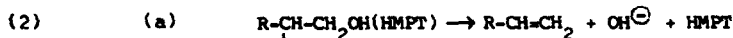
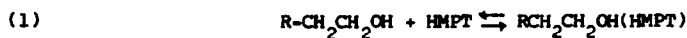
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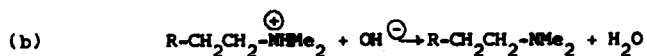
We have recently reported¹ our observations that primary alkyl halides undergo solvent catalyzed dehydrohalogenations in hexamethylphosphoric triamide (HMPT).² Continuing our studies on reactions in polar aprotic solvents, we wish now to report our findings that primary and secondary alcohols undergo direct dehydration in HMPT at temperatures of 220-240° with no added catalyst. The alcohol (0.10 mole) is heated with stirring in an excess of HMPT (65 ml). The solution, originally colorless, yellows just below 200°, and when the reaction temperature is reached, the products and dimethylamine distill from the reaction mixture. For purposes of analysis, the distillates so obtained were washed several times with saturated aqueous sodium chloride to remove dimethylamine. The dried (sodium sulfate) distillates were then subjected to glpc analysis (Aerograph Model 600 HyFi with flame ionization detector, column 15% SE-30 on acid washed Chromosorb, 1/8 in x 2 m). The reaction temperatures, percent recovery, and distillate compositions are given in Table I.

As can be seen, normal alcohols give modest yields of unrearranged 1-alkenes and 1-dimethylaminoalkanes. These products, plus the fact that primary alcohols are known³ to complex with HMPT, suggest the following elimination versus substitution pathway for the reaction:

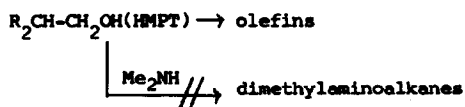
Table I. Products of HMPT Catalyzed Dehydration of Alcohols

Alcohol	Reaction Temp(°C)	Recovery	Composition of Distillate after Workup	
1-Octanol	230-243	26.9%	1-Octene	55%
			1-Dimethylaminoctane	45%
1-Decanol	228-234	30.0%	1-Decene	87.1%
			1-Dimethylaminodecane	12.9%
Cyclohexanol	222-229	73.9%	Cyclohexene	95.4%
			Cyclohexanol	4.6%
2-Octanol	228-236	94.0%	1-Octene	24.2%
			2-Octene	60.6%
			(cis:trans \approx 40:60)	
			2-Octanol	15.2%
2-Decanol	222-236	97.8%	Octalins	100%
(mixture of isomers)				
<u>trans</u> -4- <u>t</u> -Butylcyclohexanol	233-238	72.5%	4- <u>t</u> -Butylcyclohexene	100%





Secondary alcohols undergo the reaction rapidly (reaction complete in under two hours) to give good yields of unrearranged olefins. No dimethylaminoalkane formation is observed in these cases, suggesting that the secondary complexes are sufficiently hindered so that only elimination can proceed as shown.



The observation that unreacted straight chain 1-alkanols do not distill from the reaction mixture, even though pot temperatures exceed the boiling points of the alcohols, supports the idea that the equilibrium for step (1) lies far to the right for normal alcohols. On the other hand, the fact that unreacted secondary alcohols are obtained in the distillates in some cases suggests that the equilibrium (step (1)) is not completely shifted to the right for the secondary compounds. It follows that the extent of complex formation is sterically determined.

It has been verified that water-dimethylamine exchange occurs under the reaction conditions (step (2)(c)). HMPT with added water heated at 221-228° yields a distillate containing only water and dimethylamine. In the absence of added water, HMPT does not give the amine at this temperature.

The reaction applied to a commercial mixture of 2-decalols gives a mixture of three octalins. The absence of Δ^9 -octalin from the products was established by comparison with a sample of octalins prepared by the lithium-ethylenediamine reduction of tetralin known⁴ to give predominantly the Δ^9 -isomer. The failure of 2-decalol to form Δ^9 -octalin under the reaction conditions can be taken to mean that the corresponding carbonium ion is not formed, since acid catalyzed dehydration of 2-decalols yields Δ^9 -octalin as the major product through rearrangement.⁵ Carbonium ion intermediates are therefore probably not involved in the reaction.

Finally, the reaction applied to trans-4-t-butylcyclohexanol proceeds with no apparent reduction in rate or in yield. Since the hydroxyl group of this compound is prevented on steric ground⁶ from assuming an axial conformation, it is apparent that a trans-diaxial orientation of the hydroxyl and the β -hydrogen is not necessary for the reaction to occur readily.

The results reported here invite comparison with those obtained in the dehydration of alcohols in dimethyl sulfoxide,⁷ wherein secondary and tertiary benzyl alcohols and tertiary alkanols have been found to undergo dehydration in DMSO at temperatures of 150-185°. These workers concluded that carbonium ion intermediates are involved in the reaction in DMSO in contrast to our tentative conclusion that carbonium ion intermediates do not appear in HMPT catalyzed eliminations.

References

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