

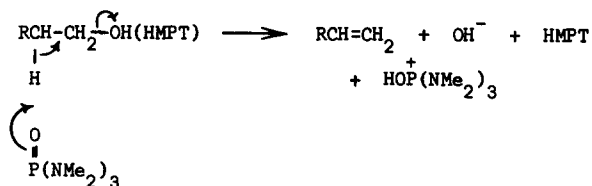
A CARBONIUM ION MECHANISM FOR THE DEHYDRATION OF ALCOHOLS IN
HEXAMETHYLPHOSPHORIC TRIAMIDE : COMPARISON WITH p-NITROBENZOATE PYROLYSIS.

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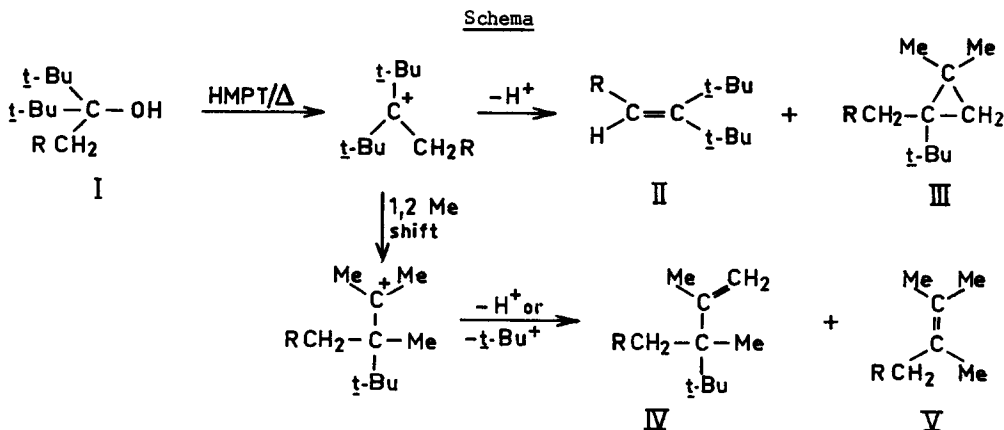
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Recently, Monson (1) reported that primary and secondary alcohols were dehydrated by treatment with hexamethylphosphoric triamide (HMPT) at 220-240°. The failure of 2-decalol to yield Δ^9 -octalin under these conditions was taken to show that carbonium ion intermediates were not involved, and that a mechanism with concerted (E2) elimination from an alcohol-HMPT complex was applicable :



Our interest in the synthesis of encumbered olefins (2) led us to attempt the dehydration of tertiary alcohols I (R = H, Me, Et, *i*-Pr, *t*-Bu) by this method. Although the major product is generally the normal olefin II, dehydration is accompanied by rearrangement and, in extreme cases, by fragmentation (Table 1).



Tables 1 and 2

Products from the dehydration of $\text{RCH}_2(\text{t-Bu})_2\text{COH}$ (I)
in HMPT and pyrolysis of the p-nitrobenzoates of I.

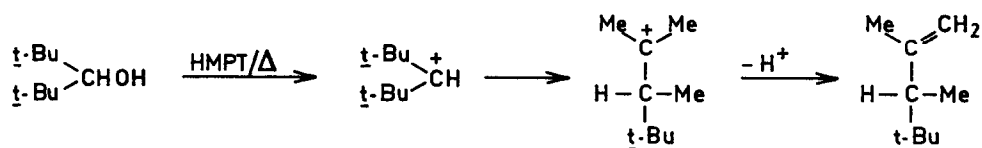
Table 1 : Dehydration (3)

Table 2 : Pyrolysis (4)

R	II (%)	III (%)	IV (%)	V (%)	II (%)	III (%)	IV (%)	V (%)
H	97	-	3	-	98	-	2	-
Me	47	13 ⁽⁵⁾	40	-	56	16 ⁽⁵⁾	28	-
Et	45	15 ⁽⁵⁾	40	-	54	19 ⁽⁵⁾	27	-
<i>i</i> -Pr	77	3 ⁽⁵⁾	20	trace	92	4 ⁽⁵⁾	4	trace
<i>t</i> -Bu	68	19 ⁽⁷⁾	11	2	57	26 ⁽⁷⁾	15	2

As has been observed (2) for thionyl chloride-pyridine dehydrations, little rearrangement occurs when $\text{R} = \text{H}$; the explanation in terms of the conflicting conformational requirements for deprotonation and carbonium ion stabilisation, previously advanced, would appear to be valid in the present case also. On the other hand, no simple explanation for the variations in product composition found for the other substituents can be offered at present.

The formation of rearranged and fragmented products in the dehydration of tertiary alcohols shows clearly that C-O fission and proton-loss are not entirely concerted. Furthermore, the secondary alcohol, di-*t*-butylcarbinol, was dehydrated cleanly to 2,3,4,4-tetramethylpentene-1 by refluxing for 3 hours with HMPT, despite the fact that Monson's concerted mechanism is blocked by the absence of β -hydrogens.



We were, however, unable to dehydrate the corresponding primary alcohol, neopentanol, to tri-methylethylene, obviously because the formation of a primary carbonium ion intermediate is energetically prohibited.

We find that dehydration in DMSO (8) of I ($\text{R} = \text{Me}, \text{Et}, \textit{i}\text{-Pr}, \textit{t}\text{-Bu}$) leads to more extensive rearrangement (ca. 80%) than dehydration in HMPT, and presumably goes through a longer-lived cation, DMSO being less basic than HMPT (9). Both solvents apparently promote ionisation of the alcohol to a carbonium ion intermediate, but the subsequent behaviour of this intermediate depends markedly on the identity of the solvent.

A striking parallel exists between dehydration in HMPT and ester pyrolysis. Thus, the pyrolysis of the p-nitrobenzoate (p-NB) of I (R = t-Bu) is reported (6) to yield a mixture of unsaturated compounds (54% yield ; 60% II, unspecified amounts of III and IV). Comparison of the products from the HMPT dehydration of I with those from the pyrolysis of the corresponding p-NB's (Table 2) confirms that these reactions are closely similar. It seems reasonable then to postulate that both reactions involve the formation of a short-lived carbocation ion or ion-pair, and that deprotonation is rapid compared to rearrangement. Nonetheless, formation of normal olefin via a concerted mechanism (E2 for HMPT, E₁ for p-NB pyrolysis) cannot at this stage be ruled out as a contributing process.

For synthetic purposes, HMPT dehydration of alcohols as a route to encumbered olefins is comparable to ester pyrolysis, and may be preferred when the preparation of esters is particularly delicate.

REFERENCES

- (1) R.S. Monson, Tetrahedron Letters, p. 567 (1971).
- (2) J.S. Lomas, D.S. Sagatya and J.E. Dubois, Tetrahedron Letters, p. 599 (1971).
- (3) The alcohol (10 mmole) was heated at $240 \pm 5^\circ$ in HMPT (20 ml) under reflux for a suitable time ; half-lives varied between 15 minutes (R = H) and about 5 hours (R = t-Bu). The cooled reaction mixture was extracted with pentane and thoroughly washed with water ; yields were in the range 62-89%, based on reacted alcohol. Products were estimated by glc on Apiezon L (10% on Chromosorb W). Product ratios were rigorously constant during or after the reaction, i.e. the products are stable under the reaction conditions.
- (4) The p-nitrobenzoates were pyrolysed in sealed tubes by melting (ca.100°) and raising the temperature to 160°. Data are based on glc analysis of the pentane extracts.
- (5) The products from the dehydration of I (R = Et) include, in addition to II and IV, a third component which is separated with difficulty from II on Apiezon L. Its nmr spectrum has well-defined singlets at δ 1.02 (9H), 1.15 (3H) and 1.30 (3H) ; the product is tentatively identified as III (R = Et) by comparison with III (R = t-Bu) which has corresponding singlets at δ 1.00, 1.12 and 1.38 (6). Similarly, from I (R = Me) is obtained a product of the same retention time as II but which can be detected by virtue of a signal at δ 1.05 which is absent from the spectrum of II ; the estimate of this component and of II are based on the assumption that the δ 1.05 signal is that of a t-butyl group in III (R = Me). Surprisingly, not more than 3% of III can be formed in the reaction of I (R = i-Pr).
- (6) G.J. Abruscato and T.T. Tidwell, J.Amer.Chem.Soc., 4125, 92 (1970).
- (7) The cyclopropyl derivative III and the olefin IV (R = t-Bu) cannot be conveniently separated by glc. It was possible, however, to convert IV to a mixture of V and 2,2,4,5,5,6,6-heptamethylheptene-3 in a 2% solution of sulphuric acid in acetic acid

at 25°. Compound III reacts about 50 times slower than IV under these conditions and can be easily separated (Apiezon L) from the other products. Mixtures of III and IV were analysed kinetically by a modification of the same procedure.

- (8) See V.J. Traynelis, W.L. Hergenrother, J.R. Livingston and J.A. Valicenti, J.Org.Chem., 2377, 27 (1962) ; V.J. Traynelis, W.L. Hergenrother, H.T. Hanson and J.A. Valicenti, ibid., 123, 29 (1964).
- (9) H. Normant, Angew.Chem., Int.Edn., 1046, 6 (1967).