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STERIC EFFECTS IN THE DEHYDRATION OF TERTIARY ALCOHOLS BY THIONYL CHLORIDE-PYRIDINE : AN EASY SYNTHESIS OF TRI-*t*-BUTYL-ETHYLENE

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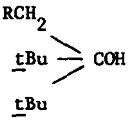
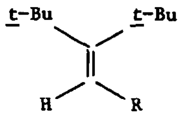
The first step in the reaction of the thionyl chloride-pyridine system with alcohols (1) would appear to be the formation of an alkyl chlorosulphite. For tertiary alcohols, by analogy with other elimination reactions of *t*-alkyl esters, this chlorosulphite would by expected to give a carbonium ion or an ion-pair in an essentially E1 process.

The observation (2) that the dehydration of the alcohol I (R = H) in thionyl chloride-pyridine at 0° gave very predominantly 1,1-di-*t*-butylethylene II (R = H) and little rearranged product prompted us to examine the utility of this reaction as a general route to the olefins II and, in particular, to tri-*t*-butylethylene II (R = *t*-Bu).

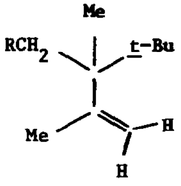
It was found, however, that the major product from I (R ≠ H) was always the rearranged olefin III. The minor products were, in order of importance, the normal Saytzeff elimination product II and the fragmented olefin IV in small amounts (Table). These findings confirm the carbonium ion character of the intermediate, although the possibility that an intramolecular Ei process plays some part cannot be entirely ruled out.



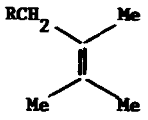
I



II



III

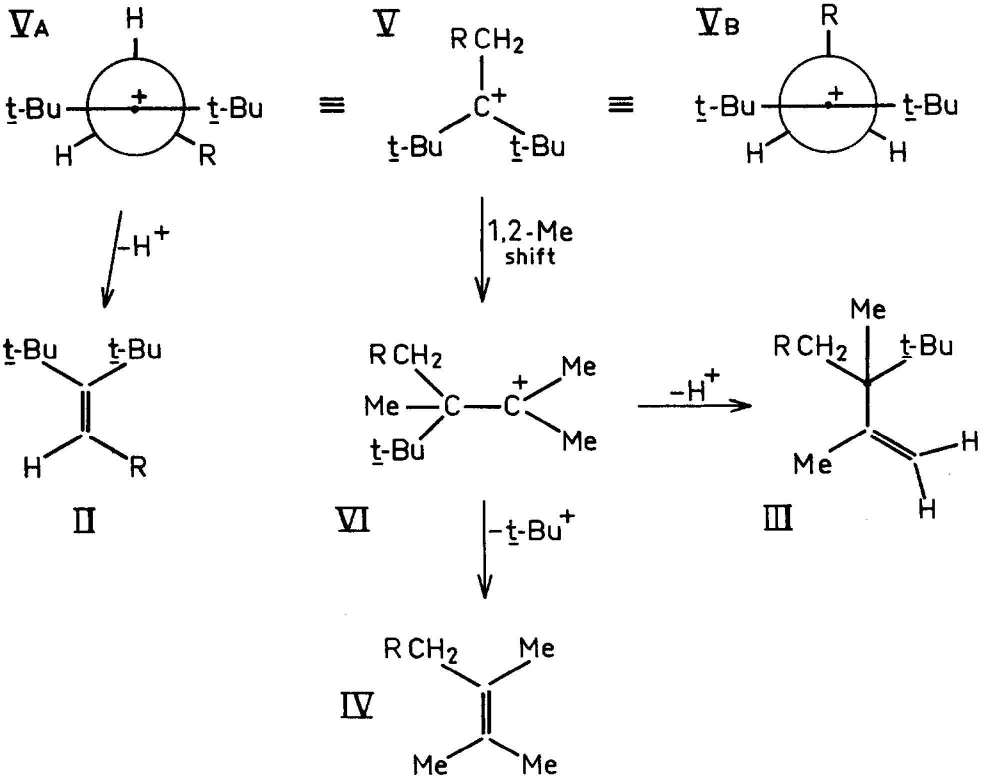


IV

TABLE

Products from the Reaction of $RCH_2(\underline{t}\text{-Bu})_2COH$ with Thionyl Chloride-Pyridine at 0° (3).

R	% II	% III	% IV (4)
H	94	5	1
Me	21	73	6
Et	18	74	8
i-Pr	25	73	2
t-Bu (5)	14	85	1



Although exceptional, the observation that the dehydration of I (R = H) leads essentially to unrearranged olefin in fully consistent with the proposed mechanism. Inspection of models of the presumed carbonium ion intermediates or their Newman projections reveals that the difference between this alcohol and the others is largely steric in origin.

The ionisation of the chlorosulphite results in the carbonium ion V. When R = H, the conformation V-A of this species strongly favours elimination of a proton which is coplanar with the unoccupied orbital of the electron-deficient carbon. However, when any other group is present (R ≠ H), putting a hydrogen in the orthogonal position results in significant steric strain between R and a t-butyl group which are on adjacent carbon atoms and in planes about 30° apart. The more stable conformer is that in which R is in a plane orthogonal to that of the t-butyl groups V-B, which is highly undesirable for proton abstraction. Under these circumstances, a 1,2-methyl shift occurs to give the rearranged ion VI, where no such steric resticitions on proton removal exist.

The steric requirements of methyl and i-propyl groups in a comparable situation (8) are known to be very similar. It is, therefore, not surprising that the product ratios for the dehydration of I (R = Me, Et, and i-Pr) should be approximately the same. On the other hand, when R = t-Bu, the interactions between the adjacent t-butyl groups are much higher and strongly favour conformer V-B or the rearranged ion VI. Very similar effects are evident in the solvolysis of dimethylalkylbromides $RCH_2(Me)_2CBr$, the difference between t-butyl and the other groups, as measured by the value of the endo/exo ratio, being even more dramatic in this case (9).

From a synthetic point of view, this method of dehydrating tertiary alcohols would appear to be useful when other methods lead to extensive fragmentation (c.f. 10). The Hibbert reaction (11) of I also leads to II and III but accompanied by fragmentation products, espcially when R = t-Bu . As a synthesis of tri-t-butylethylene, the thionyl chloride method (12) is much simpler than that recently published (7) in which pyrolysis of the p-nitrobenzoate of I (R = t-Bu) gave about 32% of the desired olefin. The synthesis of the p-nitrobenzoate is reported (6) to give a 51% yield but we have found great difficulty in reproducing this result.

REFERENCES

(1) For leading references see : J.K. Stille and F.M. Sonnenberg, J.Amer.Chem.Soc., 4915, 88 (1966).

(2) M.S. Newman, A. Arkell and T. Fukunaga, ibid., 2498, 82 (1960).

(3) To I (0.0025 moles) in analytical grade pyridine (1 ml.) at 0° was added dropwise an excess (0.25 ml. : 0.0035 moles) of distilled thionyl chloride. The reaction mixture was stirred at 0° for 3 hrs and was then allowed to warm slowly to room temperature overnight. The products were taken up in ether, washed thoroughly with water, and dried (K_2CO_3). Yields were 90-95%. Products were estimated by glc and were identified either by comparison with authentic samples or by elemental analysis, nmr, ir, and mass spectroscopy.

(4) We have as yet no adequate explanation for the variations in the small percentage of fragmentation observed.

(5) Solvolysis of the p-nitrobenzoate of I (R = t-Bu) gives a rather similar product ratio (6,7) : 6% from V and 94% from the rearranged ion VI.

(6) P.D. Bartlett and T.T. Tidwell, ibid., 4421, 90 (1968).

(7) G.J. Abruscato and T.T. Tidwell, ibid., 4125, 92 (1970).

(8) R.B. Turner, D.E. Nettleton and M. Perelman, ibid., 1430, 80 (1958).

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(11) J.S. Lomas, D.S. Sagatys and J.E. Dubois, unpublished results

(12) Conditions for the synthesis of III (R = t-Bu) have not been optimised : small modifications have given yields (glc estimate) of 19%.