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REACTIONS UNDER REDUCED PRESSURE. INCREASED REACTIVITY OF UNSOLVATED HYDROXIDE IONS, AND A SIMPLE PROCEDURE FOR OBTAINING REACTIVE OLEFINS SUCH AS CYCLOPROPENE.

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It has been recognised for many years that the most effective means for bringing about Hofmann degradation is to pyrolyze quaternary ammonium hydroxides under reduced pressure[1], but the reasons behind this have received scant attention in the literature. In the course of other work[2,3,4], we had observed many cases where an increase in the ratio of elimination to substitution was evident when the reactions were carried out under reduced pressure, and it was decided to investigate this behaviour critically. Accordingly the pyrolysis of N,N-dimethyl-1,2,3,4-tetrahydroquinoline (I) was carried out under several sets of conditions. Complete analysis of the products showed that the percentage of elimination varied from 5% (at 180°/760 mm.) to 75% (at 60°/0.005 mm.).

Several possibilities were considered to account for the results. It had already been established that the reaction was irreversible,[3] and it was therefore considered possible that slight increases in concentration, brought about by removal of a little water from the "dry" methohydroxide, could be responsible. In fact, the methohydroxide (I) concentrated at 40°/10 mm. and decomposed at 100°/10 mm. gave very similar results to a solution of (I) freeze-dried at 0.01 mm. and decomposed in the same way. As a result of this and other observations, we are led to believe that concentration of the solution beyond a certain point prior to degradation is not responsible for the large differences observed.

It is not possible at this stage to make a clear distinction between the remaining two possible explanations for this behaviour. On the one hand, the elimination reaction may proceed via a pressure dependant step; alternatively, (and much more likely) removal of water molecules solvating the ions may lower the energy of the transition state leading to elimination (increasing the reactivity of the base; this behaviour is similar to that first observed by Cram[5] for reactions in dimethylsulphoxide). A large number of similar comparative pyrolyses have been carried out, and without exception the elimination reaction is always favoured over the substitution reaction when the pyrolyses are carried out at low temperatures (ca. 60° in most cases) and under reduced pressure.

As a demonstration of the synthetic utility of the procedure, *cyclo*propene was obtained in good yield (based on recovery of trimethylamine as the only base, and a 70% yield of dibromo*cyclo*propane) by pyrolysis of *cyclo*propyltrimethylammonium hydroxide at 60°/0.005 mm. (At atmospheric pressure one way of obtaining *cyclo*propene is by pyrolysis of the corresponding methohydroxide at 325°, when some isomerisation[6] occurs. A more recent synthesis[7] of *cyclo*propene from allyl chloride gave only 10% yield). Using suitable apparatus other reactive olefins have been isolated or trapped. The increased basicity of hydroxide ion under these conditions has also been observed to have an important bearing on the rearrangement reactions of the other 'onium hydroxides[8].

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