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HOFMANN ELIMINATION OF N,N,N-TRIMETHYL-3,3-DIMETHYLCYCLOPENTYLAMMONIUM HYDROXIDE

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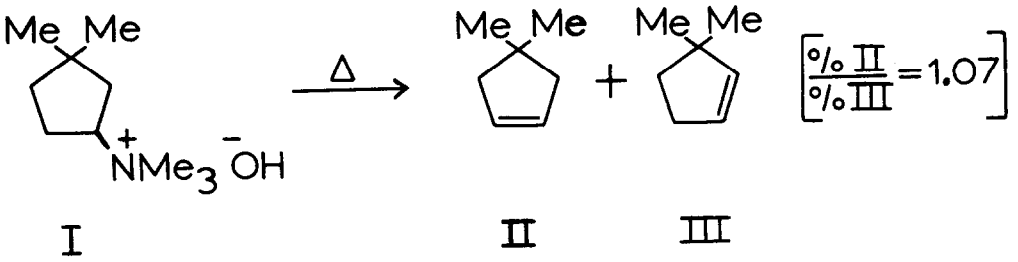
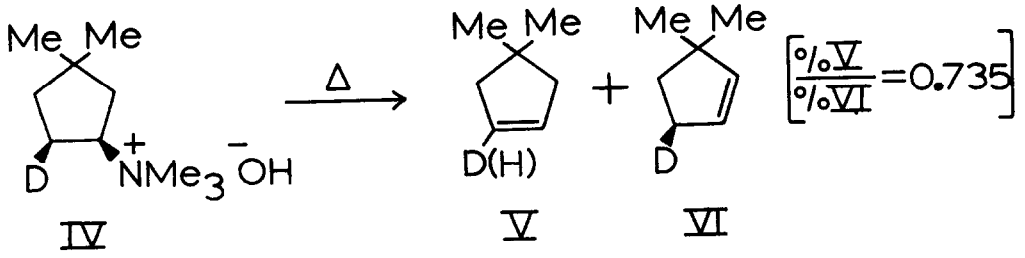
In the adjacent communication evidence is presented that many simple monocyclic trimethylammonium hydroxides undergo Hofmann elimination to give cis olefins by both a syn and anti mechanism. This requires modification of recent proposals (1,2,3,4) concerning the mechanism of Hofmann eliminations. Our work was carried out on monodeutero cyclic amines which had one cis position substituted with hydrogen and the other cis position substituted with deuterium. Analysis of the results and extrapolation back to the parent non-deuterated compound required the use of a model syn $\frac{k_H}{k_D}$ isotope effect for Hofmann elimination. In an effort to obtain this isotope effect and also to test rigorously the general conclusions reached we desired to study a system in which elimination to opposite sides of the trimethylammonium group would produce olefins which were position isomers. This approach has been used before in other systems (2,3).

The systems chosen were N,N,N-trimethyl-3,3-dimethylcyclopentylammonium hydroxide (I) and the corresponding cis-5-d_1-isomer (IV). Compounds I and IV were synthesized from 4,4-dimethylcyclopentene (II) (5) by reaction with diborane or diborane-d_6 followed by chloramine (6,7)

CHART I



I II III



IV V VI

(V = 35.5% d_1 and 64.5% d_0) ; (VI = 100% d_1 and 0.0% d_0)

$$\underline{\text{syn}}\ \frac{k_H}{k_D} = \left[\frac{\left(\frac{\%II}{\%III}\right) + \left(\frac{\%V\ d_1}{\%V\ d_0}\right)\left(\frac{\%II}{\%III}\right)}{\left(\frac{\%V}{\%VI}\right)}\right] - \left(\frac{\%V\ d_1}{\%V\ d_0}\right) = 1.71$$

and then methylation with methyl iodide and passage of the quaternary iodide over Dowex 1-X8 basic resin. Compounds I and IV were subjected to Hofmann elimination at 115° and the results are shown in Chart I.

Compound I gives a mixture of olefins II and III (%II/%III = 1.07) while compound IV gives a mixture of olefins V and VI (%V/%VI = 0.735). Olefins V and VI were separated by gas chromatography and were analyzed for deuterium by mass spectrometry at 75 ev. The fact that olefin VI was found to be 100% olefin-d_1 (this value is corrected for the 97% isotopic purity of the starting amine) indicates that the Hofmann elimination does not proceed to any extent by an Elcb mechanism. Analysis of olefin V indicated 64.5% olefin-d_0 and 35.5% olefin-d_1 (corrected for the 97% isotopic purity of the starting amine). From the equation shown in Chart I, which can be readily derived, and the experimental data one can calculate a syn $\frac{k_H}{k_D} = 1.71$ for the formation of olefins II and V. This value can in turn be used to calculate the amount of syn mechanism involved in formation of olefin II from compound I. This analysis leads to the conclusion that Hofmann elimination on I leads to olefin II by a 24% anti mechanism and a 76% syn mechanism.

It is felt that the isotope effect found in the present work is also valid for the parent unsubstituted cyclopentylammonium compound since the two ring methyl groups should not affect the transition state for syn elimination. Models indicate that they do affect the transition state for anti elimination. The present study clearly points out the danger in using alkyl substituted cyclic compounds as models for determining the amount of syn and anti elimination mechanism that would take place on the parent compound. Compound I shows a 76% syn and 24% anti mechanism for the formation of olefin II while N,N,N-trimethylcyclopentylammonium hydroxide shows a 46% syn and 54% anti mechanism for the formation of cyclopentene (see adjacent communication).

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