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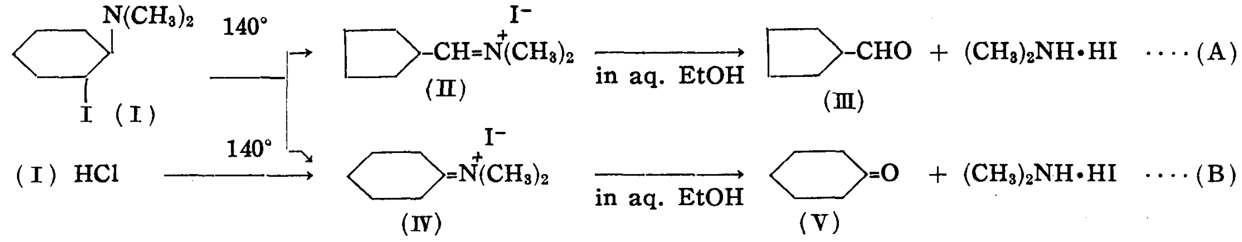
Thermal Behavior of *dl-trans*-2-Iodo-N,N-dimethylcyclohexylamine involving a New Rearrangement. The Formation of Cyclopentylmethanal and Cyclohexanone.

The reaction of N-methylcyclohexenimine with methyl iodide at room temperature did not afford its methiodide but gave *dl-trans*-2-iodo-N,N-dimethylcyclohexylamine (I), b.p$_5$ 91°, m.p. 24~25°, almost exclusively; forming a picrate of m.p. 154°(*Anal.* Calcd. for $C_8H_{16}NI \cdot C_6H_3O_7N_3$: C, 34.87; H, 3.94; N, 11.62. Found : C, 35.00; H, 3.84; N, 11.43); a hydrochloride, m.p. 123~124°(*Anal.* Calcd. for $C_8H_{16}NI \cdot HCl$: C, 33.16; H, 4.84; N, 5.87. Found : C, 33.27; H, 4.72; N, 5.89). The configurational assignment of the product (I) was given on the basis of stereochemical knowledge that the imine ring opens in the *trans* manner and the fact that treatment of N-methylcyclohexenimine with dimethyl sulfate gave *dl-trans*-2-dimethylaminocyclohexanol.

(I) was heated at 140°, avoiding moisture, to give a solid mass which was then washed with anhydrous ether and recrystallized from ethanol to give dimethylamine hydriodide almost quantitatively. From the ethanolic solution, cyclopentylmethanal (III) and cyclohexanone (V) were isolated as dinitrophenylhydrazones, m.p. 154~155° and 152~154°, which were characterized by mixed m.p. determinations : yields 24% and 27%, respectively (*Anal.* Calcd. for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07; N, 20.13. Found : C, 52.00; H, 5.03; N, 20.47. and *Anal.* Calcd. for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07; N, 20.13. Found: C, 51.88; H, 4.89; N, 20.23). In both reaction courses A and B, the formation of (II) or (IV) as an intermediate is supported by the fact that the carbonyl compound (III or V) was not found in the anhydrous ether washing, but in the ethanolic solution for recrystallization, thus indicating that the carbonyl compound (III or V) might be formed by hydrolysis with water contained in ethanol.

Analogous treatment of the hydrochloride of *dl-trans*-2-iodo-N,N-dimethylcyclohexylamine resulted only in the formation of cyclohexanone (V).



The discussion for reaction mechanisms and details of experimental data will be reported in the near future on further accumulation of experimental data.

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