

Reactions with pyridine. In the pyridine molecule there is only one nitrogen atom situated in the plane parallel to the CR'R''R''' plane and perpendicular to the ring (Fig. 2). Two "ortho"-hydrogens do not reach this plane (by $\sim 0.2\text{\AA}$), and two "ortho"-carbons - by 0.7\AA . A compression originates, in the reaction with methyl iodide, between nitrogen atom and three hydrogen atoms (1.85\AA), between one H in CH_3I and an H atom in $\text{C}_5\text{H}_5\text{N}$ (1.7\AA instead of 2.4\AA) and also between C atoms in $\text{C}_5\text{H}_5\text{N}$ and H atoms in CH_3I . The sum of these compressions is equal to 6.7\AA^3 , i.e. 4 cc/mol.;
 $\Delta v_{\text{mol.}}^{\neq} = -9 \text{ cc/mol.}$

In the reaction with ethyl iodide, one compression N...H is changed into N...CH₃ (2.15\AA instead of 3.6\AA) and there arise interactions with "ortho"-carbons; $\Delta v_{\text{mol.}}^{\neq} = -14 \text{ cc/mol.}$

The value $\Delta v_{\text{mol.}}^{\neq}$ does not change with further increase of the number of carbon atoms in the normal little chain of alkyl halide.

In the reaction with isopropyl iodide, there are two N...CH₃ compressions and the character of the interaction with "ortho"-carbons is somewhat changed,
 $\Delta v_{\text{mol.}}^{\neq} = -19 \text{ cc/mol.}$

Reactions with trimethylamine. Consider the reaction of trimethylamine with isopropyl iodide. The most preferable mutual disposition of the CR₃ plane and N(CH₃)₃ pyramide is represented by the scheme in Fig. 3a (along the C-I bond).

In the activated complex originate the following compressions: compression N...H (1.85\AA), two N...CH₃ compressions (2.6\AA) and four CH₃...CH₃ compressions (2.7\AA). The calculated value of $\Delta v_{\text{mol.}}^{\neq}$ is equal to -24 cc/mol. , i.e. larger than in the reaction of isopropyl iodide with pyridine. This value does not

** Including the compression in the formation of a C-N bond (see above).