

change upon substitution of trimethylamine by triethylamine.

Reactions with dimethylaniline. In a free dimethylaniline molecule,

the plane of benzene ring is drawn out from the



plane as a

consequence of steric interactions of two "ortho"-hydrogens with methyl groups.

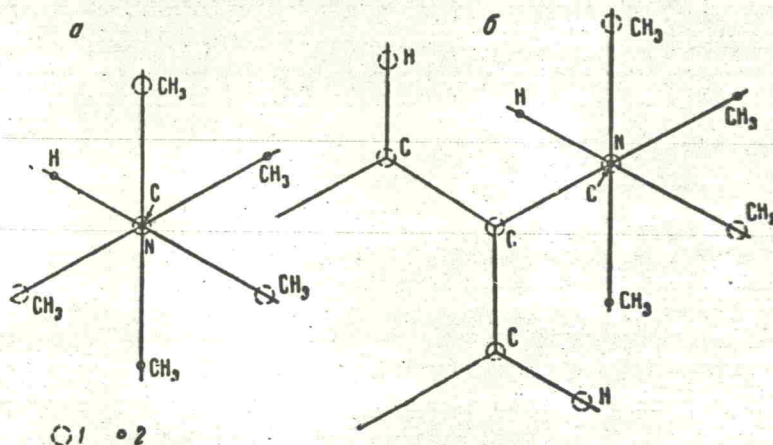


Fig. 3. Scheme of the structure of the activated complex (view along the C-I bond) in the following reactions: (a) -trimethylamine + isopropyl iodide; (b) dimethylaniline + isopropyl iodide; iodide; (1) -centers of the amine atoms; (2) -centers of the atoms of the alkyl halide.

The benzene ring is turned up, upon entering into an activated complex, in such a way that all carbon atoms are found in one plane. In this turning originate two contracted distances (inside the molecule) $\text{CH}_3 \dots \text{H}$, equal to 2.5\AA , which leads to a insignificant volume contraction.

The mutual disposition of the approaching planes in the reaction of dimethylaniline with isopropyl iodide is shown in Fig. 3b (from the side of the I atom). The following compressions originate in the activated complex:

one $\text{N} \dots \text{H}$ (1.85\AA), two $\text{N} \dots \text{CH}_3$ (2.15\AA), one $\text{H} \dots \text{H}$ (2.1\AA), two $\text{H} \dots \text{C}$ (1.9 and 2.1\AA), two $\text{CH}_3 \dots \text{H}$ (1.8 and 2.0\AA), two $\text{CH}_3 \dots \text{C}$ (2.0 and 2.1\AA), three $\text{CH}_3 \dots \text{CH}_3$ (2.1\AA). The value of $\Delta \ddot{V}_{\text{mol}}$ for this reaction is equal to

-44 cc/mol.