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THE REARRANGEMENT OF N-ACYL-AMINOSULFONIUMSALTS

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THE REARRANGE ENT OF N-ACYL-AMINOSULFONIUMSALTS

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The reaction of the azasulfonium salts $\frac{1}{2}$ with tertiary amines gives various amounts of the products $\frac{2}{2}$ and $\frac{3}{2}$, resulting from a 1.2- resp. a 2.3-shift.

The possibility of an ionpair $\frac{1}{2}$ as an intermediate in the rearrangement of $\frac{1}{2}$ is tested in the following ways:

- (i) the influence of the sulfide-moiety of the aminosulfonium salt $\underline{\underline{1}}$
- (ii) the influence of the solvent of the formation of $\frac{2}{3}$ and $\frac{3}{3}$
- (iii) the stereochemistry of the imidate 3 formed in the rearrangement
- (iv) the possibility to obtain the ionpair 4 on an independent way; this will be tried by an analogous rearrangement of an imidoxy-sulfonium salt 5, which is expected from the interaction of a sulfoxide with a nitrilium salt 6.

$$R^{1} - \stackrel{\bigoplus}{N} \equiv C - R^{2} + R^{3} \stackrel{\parallel}{-} S - CH_{2}R^{4}$$

$$\stackrel{\bigoplus}{SbC1_{6}} \bigcirc \qquad \qquad \stackrel{R^{1}}{\longrightarrow} \stackrel{\stackrel{R^{2}}{\longrightarrow}}{\longrightarrow} CH_{2} - R^{4}$$

$$\stackrel{\bigoplus}{\underline{\bullet}} \qquad \qquad \stackrel{\underline{\bullet}}{\longrightarrow} \qquad \qquad \stackrel{\underline{\bullet}}{\longrightarrow} CH_{2} - R^{4}$$

Addition of a tertiary amine to a mixture of $\underline{6}$ and dimethylsulfoxide at $-80^{\circ}\mathrm{C}$ gives products equal with those, formed from $\underline{1}$ and triethylamine. As shown by low temperature H-NMR-spectroscopy this is not the consequence of an ionpair $\underline{4}$ from $\underline{5}$ and the tertiary amine but of a very easy rearrangement of $\underline{5}$ to $\underline{1}$.