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N-ALKYLATION OF SULFILIMINES AND SULFOXIMINES (1, 2)

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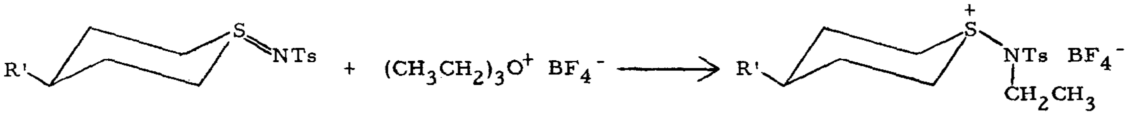
Although sulfilimines and sulfoximines have been long known and the basic character of the nitrogen atom in these substances is well established (4, 5) no study of the N-alkylation of these materials has appeared. A solitary example of a simple N-alkyl sulfilimine ($R_2S{=}NCH_2CH_2CN$) is mentioned in a paper by Appel and Büchner (5).

The most readily accessible sulfilimines are those prepared by the reaction of chloramine-T and sulfides. Although the nitrogen of N-p-toluenesulfonyl sulfilimines might be less nucleophilic than that of free sulfilimines (which appear to be quite unstable (6)) the former materials are smoothly alkylated on nitrogen by trimethyl or triethyloxonium fluoroborate.

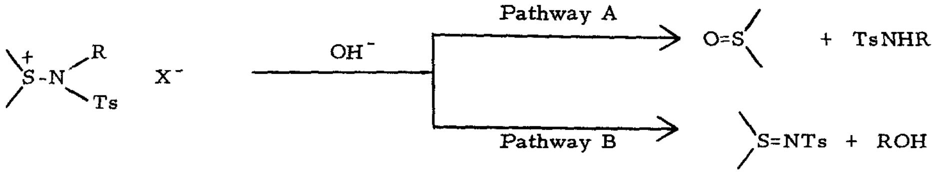
$$(CH_3)_2S{=}NTs \;+\; (CH_3)_3O^+\,BF_4^- \longrightarrow (CH_3)_2\overset{+}{S}{-}N{<}^{CH_3}_{Ts} \quad BF_4^-$$

95% mp 180.5-181°

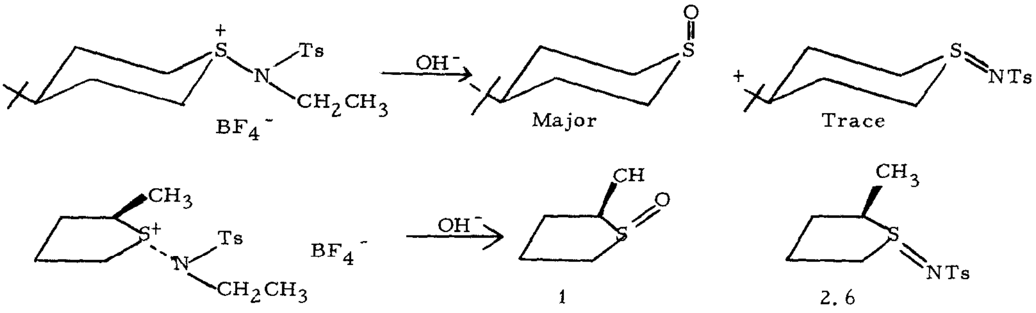


Ts = p-$CH_3C_6H_4$ R' = p-ClC_6H_4 83% mp 183-185°

These salts are readily attacked by aqueous base and, like alkoxysulfonium salts (7), their neutralization equivalents may be determined by titration to a phenolphthalein end point. Attack by hydroxide may provide sulfoxide and a secondary sulfonamide (pathway A) or may regenerate the starting sulfilimine (pathway B).

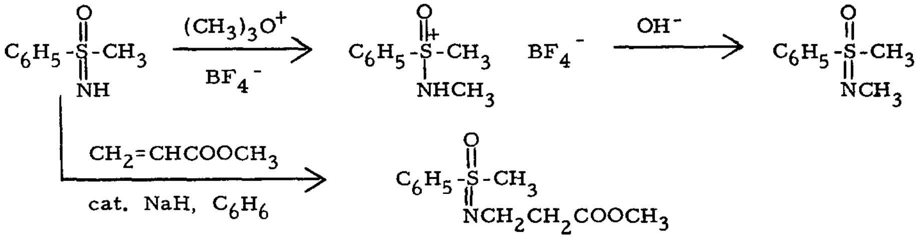


The actual distribution of products from pathways A and B appears to be highly dependent on the structure of the starting salt. In all cases examined to date both pathways appear to operate. Importantly, the sulfoxide obtained in such reactions is produced by backside nucleophilic displacement on the sulfonium sulfur and thus the reaction provides a clean chemical method for the correlation of the configuration of sulfilimines and sulfoxides (8). The hydrolysis of N-toluenesulfonyl sulfilimines per se by methanolic potassium hydroxide has been employed by Day and Cram (9) who made a similar correlation of the configurations of sulfoxides and sulfilimines.

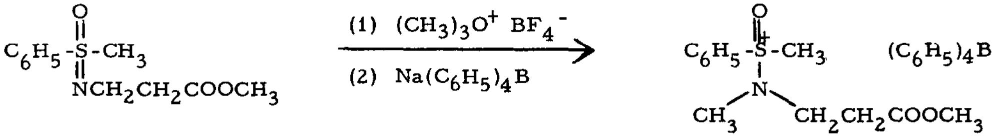


In almost all cases, in addition to the above mentioned products, the basic hydrolyses of the sulfilimine salts produced trace amounts of carbonyl compounds. A number of tenable possibilities for the origin of these materials exist, including the direct collapse of the salts to a carbonyl precursor or the intervention of an alkoxysulfonium salt (7). We have observed that a good yield of formaldehyde is obtained upon treatment of $C_6H_5\overset{+}{S}(CH_3)N(CH_3)Ts\ BF_4^-$ with methoxide. Exploration of these reactions is in progress.

Sulfoximines, prepared by the action of hydrazoic acid on sulfoxides, form N-alkyl derivatives with alkylating agents such as trimethyloxonium fluoroborate and electrophilic olefins.



Such N-alkyl sulfoximines may be further alkylated to form N, N-dialkyl salts, which may be considered to be new examples of oxosulfonium salts.



mp 139-140°

The chemistry of these materials, especially that concerned with the reactions of ylides derived from the dialkylamino-oxosulfonium salts will be discussed elsewhere (1b).

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4. For example see K. K. Andersen, W. H. Edmonds, J. B. Biasotti, and R. A. Strecker, J. Org. Chem., 31, 2859 (1966) and R. Appel, H. W. Falhaber, D. Hänssgen, and R. Schöllhorn, Chem. Ber., 99, 3108 (1966).
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