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SYNTHESES AND REACTIONS OF DIAMINOOXOSULFONIUM SALTS

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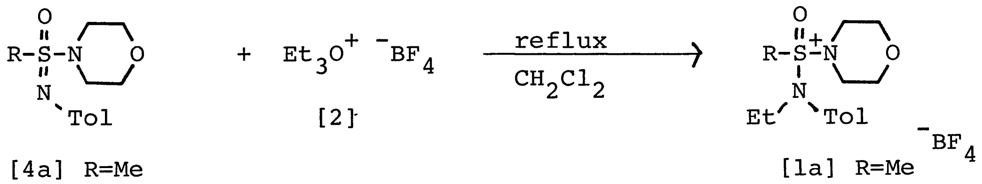
Diaminooxosulfonium salts were prepared by alkylation of aminosulfoximines. Their reactions with dimsyl sodium gave the corresponding ylides and sulfoximines. The intramolecular rearrangement of the ylide led to ortho substitution bia an intermediate cyclohexadienoneimine. Hydrogen transfer, accompanying rearomatization and the subsequent action of a base gave a dihydrobenzoisothiazole derivative.

Aminooxosulfonium ions, $\genfrac{}{}{0pt}{}{R}{R'}{>}\overset{O}{\overset{\|}{S}}{}^{+}{-}NR_2$, and diaminosulfonium ions, $R_2N{-}\underset{R'}{\overset{+}{S}}{-}NR''_2$, were well known and studied,[1)] but diaminooxosulfonium salts [1], $[R_2N{-}\underset{R'}{\overset{O}{\overset{\|}{S}}}{}^{+}{-}NR''_2]\ X^-$, have not yet been reported. In this paper, we wish to report the synthesis of [1] by alkylation of aminosulfoximines with two different alkylating agents, triethyloxonium tetrafluoroborate [2] and methyl trifluoromethanesulfonate [3], and reactions of [1] with dimsyl sodium.

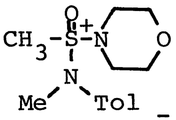
A dichloromethane soltion of S-methyl- or S-ethyl-S-morpholino-N-p-tolylsulfoximine [4a] or [4b][2)] and [2] was refluxed for 1 hr. The pale brown solution thus obtained was concentrated under reduced pressure. The resulting brown solid was recrystallized from methanol to give S-methyl- or S-ethyl-S-morpholino-N-ethyl-N-p-tolyloxosulfonium tetrafluoroborate [1a] or [1b] as crystals. In an analogous way, [1c] was synthesized by the reaction of [4a] with [3], followed by anion exchange with sodium tetraphenylborate. The data of [1] obtained by these reactions are shown in the Table.



[4a] R=Me
[4b] R=Et

[1a] R=Me
[1b] R=Et

Table. Preparation of Diaminooxosulfonium Salts*

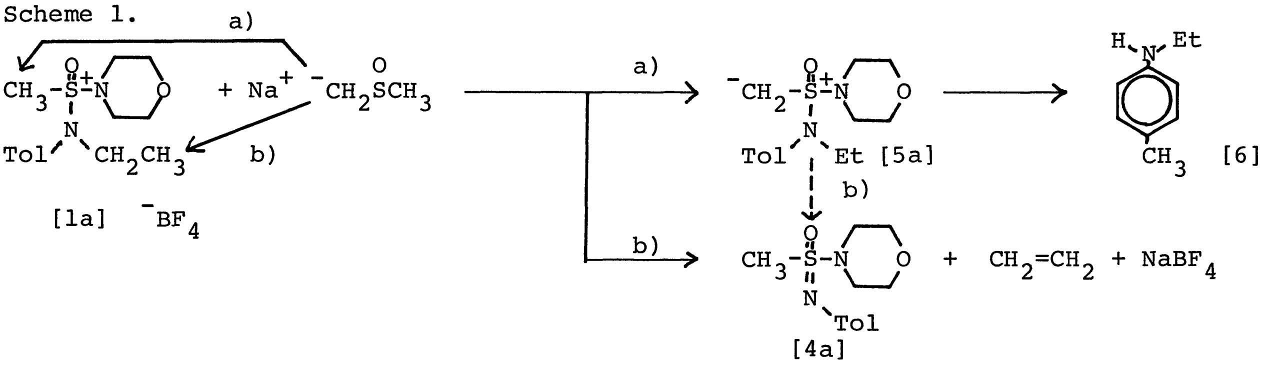
Product	Yield	m.p.	NMR
[1a]	64.0 %	153-154 °C	1.05 ppm (t), 2.29 (s), 3.25-3.35 (m), 3.64 (s), 7.07 (s).
[1b]	24.8	134-135	1.13 (t), 1.33 (t), 2.34 (s), 3.40-3.95 (m), 7.38 (s).
 [1c] $^-BPh_4$	56.0	141-142	2.30 (s), 3.20 (s), 3.25-3.55 (m), 3.79 (s), 6.40-7.15 (m), 7.11 (s).

*Satisfactory values of elemental analysis were obtained for all compounds.

Corey and Chaykovsky$^{3)}$ obtained many oxosulfonium ylides by the reaction of oxosulfonium salts with bases. If ylides are formed by the treatment of [1] with bases, two reaction courses may be considered, One is a methylene transfer reaction and the other is a Sommelet-Hauser type rearrangement.

When [1a] was allowed to react with dimsyl sodium in DMSO at 50 °C, N-ethyl-p-toluidine [6] and sulfoximine [4a] were obtained in 40 % and 16 % yields, respectively. Presumably, diaminooxosulfonium ylide [5a] was formed first and then was decomposed to give [6]. [4a] was probably formed by abstraction of β-proton from the N-ethyl group.

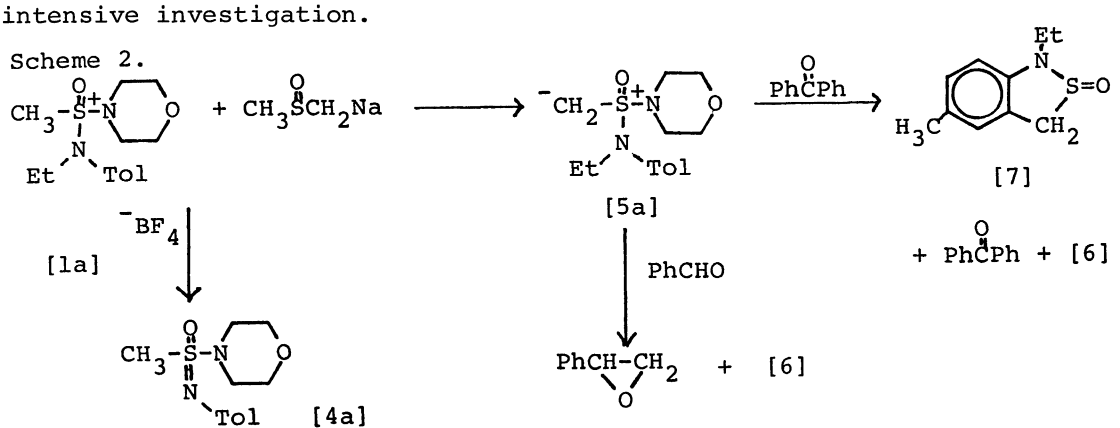
Scheme 1.



To confirm the above ylide formation, the reaction of a mixture of [1a] and dimsyl sodium with benzaldehyde was carried out. To a mixed solution of [1a] (13 mmol) and dimsyl sodium (13 mmol) was added a DMSO solution of benzaldehyde (10 mmol) in 30 min at rt. The resulting dark red solution was washed with water, extracted with ether, and dried over $MgSO_4$. Concentration of the orange-red solution, followed by vacuum distillation gave styrene oxide (30 %) and [6] (35 %). This fact suggests that [1a] may produce the corresponding ylide [5a] by the reaction with dimsyl sodium and the ylide[5a] may act as nucleophilic methylene transfer reagent.

However, when a mixture of [1a] and dimsyl sodium was allowed to react with benzophenone, 2-ethyl-2,7-dihydro-5-methylbenzoisothiazole-1-oxide [7][4)] was obtained in 26 % yield, [6] in 40 % yield, and the benzophenone was recovered almost quantitatively. At present the role of benzophenone is not clear, which is under intensive investigation.

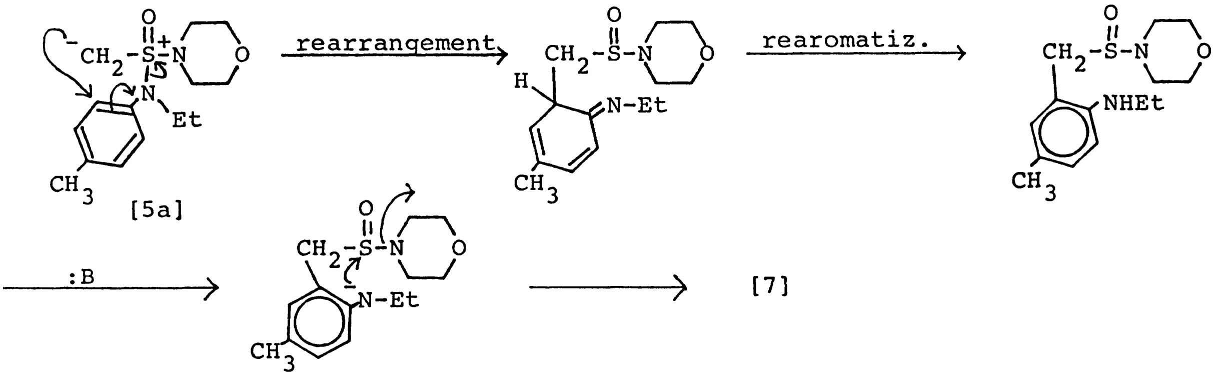
Scheme 2.



These results were quite different from those of Gassman et al.[5)] and those of Johnson et al.[6)] Johnson et al. reported that the reaction of aminooxosulfonium ylides with aldehydes yielded only the corresponding epoxides and they did not confirm the formation of products derived from attack on N-alkyl group. Gassman and Gruetzmacher reported that a [2,3]-sigmatropic rearrangement occurred as soon as aminosulfonium ylides derived from the treatment of an N-phenylaminosulfonium salts with bases were formed. But the above observation has led to the conclusion that the reactions of the ylide [5a] with carbonyl compounds give not only a rearranged product but also a methylene transferred product.

Benzoisothiazoles are easily prepared by the reaction of o-toluidines with thionyl chloride.[7)] But the preparation of dihydrobenzoisothiazoles has not yet been reported in the literature. The above reaction can, therefore, be a useful means for the preparation of dihydrobenzoisothiazole derivatives. [7] may be formed by the following mechanism.

Scheme 3.



In summary, Diaminooxosulfonium salts [1] were prepared by alkylation of amino sulfoximines [4], and reactions of [1a] with a base gave not only an ylide [5a] but also a sulfoximine [4a]. The intramolecular rearrangement of [5a] led to a new heterocyclic compound [7].

We are currently continuing synthetic studies of [1] and of dihydrobenzoisothiazole derivatives by the treatment of [1] with bases.

References and notes.

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2) E. U. Johnson, C. C. Bacon, and C. R. Johnson, J. Am. Chem. Soc., 93, 5307 (1971). R. E. Booms and D. J. Cram, J. Am. Chem. Soc., 94, 5438 (1972).

3) E. J. Corey and M. Chaycovsky, J. Am. Chem. Soc., 87, 1353 (1965).

4) M.P. 94.6-95.3 °C: NMR; δ 1.46 ppm (t) $N\text{-}CH_2C\underline{H}_3$, 2.29 (s) $-CH_3$, 3.70 (q) $N\text{-}C\underline{H}_2CH_3$, 3.94 (q) $Ar\text{-}CH_2$, 6.53-7.05 (m) Ar. Anal. Calcd for $C_{10}H_{13}NOS$; C, 61.54 %; H, 6.67 %; N, 7.18 %. Found C, 61.87 %; H, 6.94 %; N, 7.33 %.

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