Tetrahedron Letters No. 40, pp 4137 - 4140, 1972. Pergamon Press. Printed in Great Britain.

A NOVEL METHOD FOR SULFILIMINES AND SULFOXIMINES

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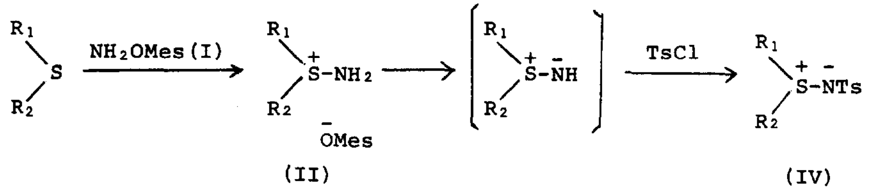
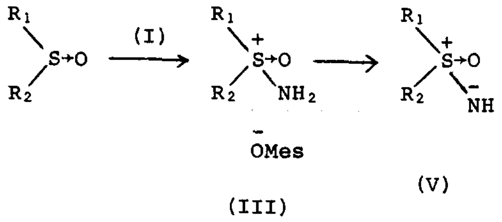
(Received in Japan 5 August 1972; received in UK for publication 5 September 1972)

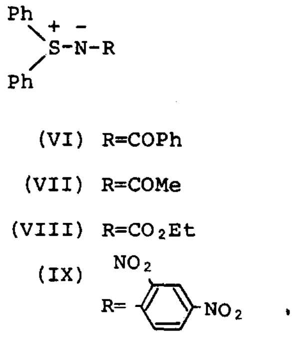
Although the chemistry of sulfilimines and sulfoximines has recently received wide attention,[1] only a few preparative methods[2] are available, most of which suffer from either limited scope or low yields. Only exception is the most recent report by Oae and his coworkers[3] which involves the acid hydrolysis of N-tosylsulfilimines. The successful preparation of N-amine salts of heteroaromatic[4] and tertiary amines[5] by reaction with O-mesitylenesulfonylhydroxylamine (MSH) (I) has prompted us to investigate the reaction of the reagent with sulfur compounds and it was found that a wide variety of sulfides and sulfoxides undergo facile amination under mild conditions to give the corresponding S-amine salts.

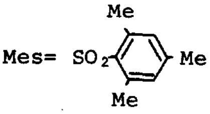
The present synthetic method offers certain advantages over the methods most used hitherto: it gives a crystalline product so that it is easy to separate the aminated product from the unreacted starting material, the scope is wide, the yields obtained are high, particularly in cases where the other methods give poor results, and the reaction conditions are extremely mild (for comparison, the preparation of sulfoximines by reaction with hydrazoic acid[2d,e] requires a catalyst by concentrated sulfuric acid.)

The procedure used is analogous to that described for N-amination,[4,5)] for example, equimolar admixture of diphenylsulfide or diphenylsulfoxide and MSH in methylene chloride was allowed to stand at room temperature for 30 min. After addition of ether (in the case of sulfoxides petroleum ether was used) the precipitated white crystals were collected and recrystallized to give S-









aminodiphenylsulfonium salt (IIg) and S-aminodiphenylsulfoxonium salt (IIIe) in 90 and 65 per cent yields, respectively. Some representative examples are shown in Table 1. The structures of the products were proved by microanalysis, and infrared and n.m.r. spectroscopy; in addition to the appearance of a broad signal due to an NH_2 group, the methylene or methyl protons adjacent to the $\overset{+}{S}\text{-}NH_2$ group showed a downfield shift (0.4-1.2 ppm) in the n.m.r. spectra of IIa-f and IIIa-d, while the other protons were almost unchanged. Furthermore, the S-aminosulfonium salts (II) except for trimethylenesulfonium salt (IIb) were transformed to the corresponding known tosylates (IV) in 60-70% yields by treatment with Amberlite IRA-410 ion-exchange resin in ethanol followed by addition of tosyl chloride and retreatment of the reaction mixture with the ion-exchange resin.[6] The S-aminosulfoxonium salts (III) were converted in high yields to the known stable sulfoximines by treatment with sodium methoxide in methanol for 10 min. at room temperature.

Table 1.

	R_1	R_2	M.p.	Yield(%)		R_1	R_2	M.p.	Yield(%)
IIa	Et	Et	137-138°	85	IIIa	Me	Me	176-178°	72
IIb	$-(CH_2)_3-$		92-93°	77[a)]	IIIb	$-(CH_2)_4-$		151-153°	100
IIc	$-(CH_2)_4-$		150-151°	79	IIIc	$-(CH_2)_5-$		167-169°	64
IId	$-(CH_2)_5-$		168-169°	86	IIId	Me	Ph	207-209°	93
IIe	$PhCH_2$	$PhCH_2$	172-174°	84	IIIe	Ph	Ph	179-182°	65
IIf	Me	Ph	110-111°	72					
IIg	Ph	Ph	119-120°	90					

a) Reaction was carried out at -20°.

An interesting application of MSH lies in its behavior toward allylsulfides. For example, the reaction of diallylsulfide with MSH in methylene chloride at room temperature gave allylamine mesitylenesulfonate, m.p. 176-178°, in 75% yield. The formation of allylamine is explained by a mechamism analogous to the rearrangement of N-tosyldiallylsulfilimine to N-tosylallylamine.[7]

These reactions, coupled with N-amination reactions,[4,5] indicate that MSH is a potentially useful aminating agent whose utility is currently under further scrutiny.

Footnotes and References

1. For example: J.B. Lambert, C.E. Mixan, and D.S. Bailey, J. Am. Chem. Soc., 94, 208 (1972), and references cited therein.

2. a) R. Appel, W. Buechner, and E. Guth, Ann., 618, 53 (1958); b) R. Appel and W. Buechner, Chem. Ber., 95, 849 (1962); c) R. Appel and W. Buechner, ibid., 95, 2220 (1962); d) J.K. Whitehead and H.R. Bentley, J. Chem. Soc., 1952, 1572; e) F. Misani, T.W. Fair, and L. Reiner, J. Am. Chem. Soc., 73, 459 (1951).

3. N. Furukawa, T. Omata, T. Yoshimura, T. Aida, S. Oae, Tetrahedron Letters, 1972, 1619.

4. Y. Tamura, J. Minamikawa, Y. Miki, S. Matsugashita, and M. Ikeda, Tetrahedron Letters, the preceding paper.
5. Y. Tamura, J. Minamikawa, Y. Kita, and M. Ikeda, in preparation.
6. The same procedure could be applied to the preparation of N-benzoyl-(VI) N-acetyl-(VII), N-carbethoxy-(VIII), and N-2,4-dinitrophenyl-(IX) diphenylsulfilimines by using benzoyl chloride, acetyl chloride, ethyl chloroformate and 2,4-dinitrofluorobenzene in place of tosylchloride;(VI, mp 124-125° in 60% yield, VII, characterized as its picrate, mp 177-179°, in 40% yield, VIII, mp 86.5-88° in 44% yield, and IX, mp 133.5-134° in 89% yield).
7. A.S.F. Ash, F. Challenger, and D. Greenwood, J. Chem. Soc., **1951**, 1877.