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OXIDATION OF SULFIDES WITH 1-CHLOROBENZOTRIAZOLE. PREPARATION OF AMINO- AND ALKOXYSULFONIUM SALTS[1]

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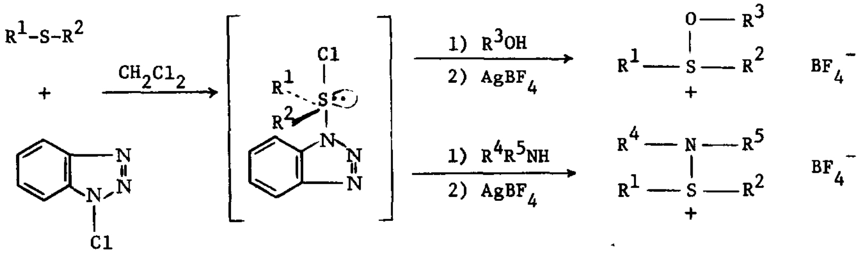
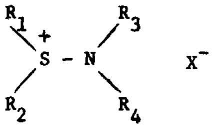
We have described the preparation of sulfoxides by the oxidation of sulfides with 1-chlorobenzotriazole.[2] We now wish to report a widely applicable and simple method for the preparation of alkoxy- and aminosulfonium salts utilizing the intermediate adduct between 1-chlorobenzotriazole and sulfides. Although we prefer to represent the intermediate adduct with covalent bonding,[2] at this time we do not have adequate evidence to rule out an ionic intermediate.



To a solution of sulfide dissolved in methylene chloride and cooled to -78° was added an equivalent of 1-chlorobenzotriazole. After 10 min, one equivalent of alcohol was added. The mixture was then allowed to stir at -78 to -40° for up to 3 hrs. Addition of silver fluoroborate, removal of precipitate silver chloride, and concentration of the methylene chloride solution produced the desired alkoxysulfonium fluoroborate. Thus thioanisole was combined with 2-propanol and cyclohexanol to yield methylphenylisopropoxysulfonium fluoroborate (42%, mp 56-58°) and methylphenylcyclohexoxysulfonium fluoroborate (30%, mp 104-105°), respectively. Reaction of benzyl p-tolyl sulfide with 1-chlorobenzotriazole followed by sequential addition of (-)-menthol and silver fluoroborate produced an optically active menthoxysulfonium salt, $[\alpha]_D$ +58.4° (c1, acetone). Recrystallization of this salt from benzene-ether (2:1) gave a salt $[\alpha]_D$ +137°. Hydrolysis of this salt with aqueous sodium hydroxide produced benzyl p-tolyl sulfoxide $[\alpha]_D$ -219° (acetone, 87% optically pure). This procedure for the preparation of optically active sulfoxides should have general applicability, but its utility will, of course, depend on the ease of separation of the diastereomeric alkoxysulfonium salts.

By utilizing a similar procedure, as outlined above for alkoxysulfonium salts, but substituting primary or secondary amines for the alcohol, aminosulfonium salts were produced. In those cases where oils were formed, crystalline tetraphenylborates were obtained by exchange with sodium tetraphenylborate in methanol.

TABLE I: Aminosulfonium Salts



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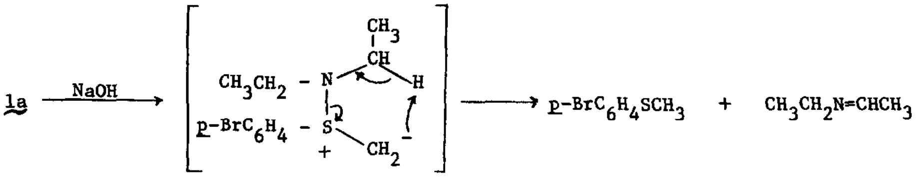
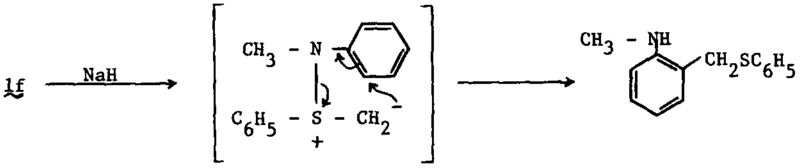
R_1	R_2	R_3	R_4	X^-	mp,°C	Yield,%
(a) p-BrC_6H_4	CH_3	Et	Et	BF_4	108-110	81
(b) -$(CH_2)_4$-		Et	Et	BPh_4	221-225	83
(c) p-$CH_3C_4H_4$	iso-C_3H_7	Et	Et	BPh_4	150-151	74
(d) p-BrC_6H_4	CH_3	C_6H_{11}	H	BPh_4	132-133	84
(e) p-BrC_6H_4	C_6H_{11}	Et	Et	BF_4	124-128	40
(f) C_6H_5	CH_3	C_6H_5	CH_3	BF_4	128-129	70

Aminosulfonium salts[4] are a relatively unknown class of compounds having chemical properties that display rational differences with and similarities to alkoxysulfonium salts. Whereas alkoxysulfonium salts are rapidly solvolyzed in aqueous solution principally by nucleophilic attack on sulfur,[5] salt 1a can be recovered unchanged from aqueous solution. Aqueous alkali immediately converts alkoxysulfonium salts to sulfoxides by nucleophilic attack at sulfur, whereas stirring 1a with 10% aqueous sodium hydroxide generates p-bromo-thioanisole.[6]



After acid workup, acetaldehyde was detected as the 2,4-dinitrophenylhydrazone. The differences in the reactivity of alkoxy- and these simple aminosulfonium salts is a reflection of differences in the "leaving group" ability of alkoxide (RO^-) and amide (R_2N^-).

Reaction of 1f with sodium hydride in THF resulted in the formation of an ortho substituted aniline, presumably formed by rearrangement of an unstable intermediate ylide.[7,8]



It is interesting to note that given the choice between abstraction of a proton from the methyl and collapse to produce $CH_2=N-C_6H_5$ and addition to the aromatic ring, the ylide reacts by the latter course.

The 1-chlorobenzotriazole used in this study was prepared by reaction of benzotriazole (15 g in 200 ml of 50% aqueous acetic acid) with 5.25% aqueous sodium hypochlorite (180 ml of household sodium hypochlorite bleach). The reaction mixture was shaken for 20 min, and the solid product was collected by filtration. The crude product was dissolved in dichloromethane, and the solution dryed over anhydrous magnesium sulfate. Concentration of the methylene chloride solution and addition of petroleum ether to the cloud point followed by cooling produced an 83% yield of 1-chlorobenzotriazole, mp 105-106°.

ACKNOWLEDGEMENT

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REFERENCES AND FOOTNOTES

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3. For pertinent examples of covalent sulfide adducts see: C. R. Johnson and J. J. Rigau, J. Amer. Chem. Soc., 91, 5398 (1969); D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, ibid., 91, 5239 (1969); N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, ibid., 91, 5749 (1969); J. C. Martin and R. J. Arhart, ibid., 93, 2339, 2341 (1971).
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5. C. R. Johnson and D. McCants, Jr., J. Amer. Chem. Soc., 87, 5404 (1965).
6. A similar reaction occurs with alkoxysulfonium salts in alkoxides and under a variety of other conditions. See: C. R. Johnson and W. G. Phillips, ibid., 91, 682 (1969) and references cited therein.
7. For a related reaction of phenoxysulfonium salts see: M. G. Burdon and J. G. Moffatt, ibid., 89, 4725 (1967) and K. E. Pfitzner, J. P. Marino, and R. A. Olofson, ibid., 87, 4658 (1965).
8. The reaction of anilines and dimethylsulfoxide in the presence of P_2O_5 and triethylamine gives similar ortho substituted products, P. Claus and W. Vyardilik, Tetrahedron Lett., 3607 (1968).
9. See accompanying paper by P. G. Gassman, G. Gruetzmacher, and R. H. Smith.