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Novel One-Step Synthesis of Sulfonyl Chlorides from Sulfides with Iodosobenzene and Hydrogen Chloride-Treated Silica Gel

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Alkyl and aryl benzyl sulfides were conveniently converted into the corresponding alkyl and aryl sulfonyl chlorides in high yields with a few minutes' pulverization of solid mixtures with iodosobenzene and hydrogen chloride-treated silica gel.

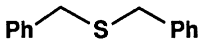
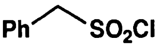
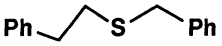
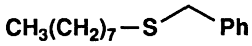
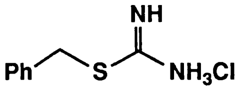
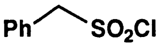
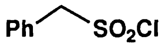
Much attention has been given to the convenient and efficient preparation of sulfonyl chlorides from various kinds of sulfur compounds by using a wide range of agents.1) Among them, one-step preparation of sulfonyl chlorides from sulfides has rarely been investigated. One successful work is that of Langler et al. who reported good yield preparation of sulfonyl chlorides from the chlorination of benzyl alkyl sulfides in aqueous acetic acid.1b) However, the previously reported methods suffer from difficulties in manipulation and the control of the reagent equivalence, as they employ Cl_2 gas as the chlorinating agent. Here we report a novel one-step synthesis of sulfonyl chlorides from sulfides using a convenient solid chlorinating agent without any solvent. Since the pulverization of iodosobenzene and hydrogen chloride-treated silica gel (HCl-silica gel) has been found to simultaneously bring about oxidation and chlorination,2) we applied these reaction procedures in order to cause one-step conversion of sulfides to sulfonyl chlorides. As a result, we succeeded in the efficient conversion of sulfides bearing benzylic C-S bond(s) into the corresponding sulfonyl chlorides (Eq.1) in high yields. Most advantageous is that the reaction is completed in a few minutes, and the manipulation and the control of the reagent equivalence is much easier due to the solid-state conditions.

$$\mathrm{R{-}S{-}R'} \xrightarrow[\text{5 min pulverization}]{\text{PhIO / HCl-Silica gel}} \mathrm{R{-}SO_2Cl}\ \text{ and/or }\ \mathrm{R'{-}SO_2Cl} \qquad (1)$$

The reaction and isolation procedures were the same as previously reported,2) except that the amount of iodosobenzene was changed to 4.4 equivalents to substrate.

As summarized in Table 1, sulfides bearing benzylic C-S bond(s) such as dibenzyl, alkyl benzyl, and benzyl phenyl sulfides were converted into the corresponding sulfonyl chlorides in high yields of 89-98% (entries 1-5) accompanied with the expulsion of the benzyl group.3) These yields are comparable or, in some cases (entries 1 and 4), superior to those of the previous work using Cl_2 gas.1b) In addition, several other sulfur compounds such as sulfoxides and disulfides could also be converted into sulfonyl chlorides in moderate to good yields (entries 10 and 11). Other kinds of sulfides such as benzyl amidinium, dialkyl, and alkyl phenyl sulfides gave the

Table 1. One-step Synthesis of Sulfonyl Chlorides from Sulfides

Entry	Substrate	Sulfonyl chloride	Yield/%[a]
1			98
2		$Ph-SO_2Cl$	96
3			89
4		CH_3-SO_2Cl	91[b]
5		$CH_3(CH_2)_7-SO_2Cl$	92
6			65
7	$CH_3(CH_2)_3-S-(CH_2)_3CH_3$	$CH_3(CH_2)_3-SO_2Cl$ / $CH_3(CH_2)_3-SO_2-(CH_2)_3CH_3$	56 / 38
8	CH_3-S-Ph	$Ph-SO_2Cl$ / CH_3-SO_2-Ph	4 / 47
9	$Ph-S-Ph$	$Ph-SO_2-Ph$	84
10			75
11	$Ph-S\,S-Ph$ [c]	$Ph-SO_2Cl$	56[d]

a) Isolated yields unless otherwise noted. b) Determined by GLC. c) 8.8 equiv of iodosobenzene was added. d) Yield based on the assumption of the production of 2 moles of sulfonyl chlorides from one mole of disulfides.

sulfonyl chlorides in less satisfactory yields (entries 6, 7, and 8); especially the latter two gave mixtures of sulfonyl chlorides and sulfones. Moreover, diphenyl sulfide gave no benzenesulfonyl chloride, but only its sulfone (entry 9). These results clearly indicate that the ease of the cleavage of the four types of C-S bonds in Table 1 is in the order of amidinium C-S > benzyl C-S > alkyl C-S >> phenyl C-S, which can be expected on the basis of the electron deficiency on the carbons α to the sulfur atoms.[4)] In conclusion, the present procedure proved to be the most convenient and advantageous for regioselective and efficient conversion of benzyl phenyl, alkyl benzyl, and dibenzyl sulfides to the corresponding sulfonyl chlorides.

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References

1) a) S. R. Sandler and W. Karo, "Organic Functional Group Preparations," Academic Press, New York (1983), Vol.I, p. 630; b) R. F. Langler, *Can. J. Chem.*, **54**, 498(1976).

2) H. Sohmiya, T. Kimura, P. Bauchat, M. Fujita, and T. Ando, *Chem. Lett.*, **1991**, 1391.

3) Considerable amounts of benzyl chloride were detected by GLC in several cases.

4) These facts strongly suggest the intermediacy of the nucleophilic substitution pathway by chloride ion, which was referred to in the previous work using Cl_2 gas. See: R. F. Langler, Z. A. Marini, and E. S. Spalding, *Can. J. Chem.*, **57**, 3193(1979).

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