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A SIMPLE AND EFFICIENT PREPARATION OF SULFINYL CHLORIDES FROM DISULFIDES AND SULFURYL CHLORIDE

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Abstract: Disulfides react with sulfuryl chloride in the presence of acetic acid to form the corresponding sulfinyl chlorides in nearly quantitative yield.

Chiral sulfoxides are of growing interest for the preparation of chiral compounds,particularly natural products[1,2].They are mostly obtained from the sulfinyl chlorides via the chiral menthyl sulfinates[3,4]. The methods for the preparation of sulfinyl chlorides involve the reaction of thionyl chloride with sulfinic acids (which are generally not commercially available,with only a few exceptions), or the chlorination of disulfides[5,6] or thiol esters[7] in the presence of acetic acid or acetic anhydride.As many disulfides are commercially available,this would be an attractive way if the use of chlorine gas could be avoided.We therefore investigated the more convenient sulfuryl chloride as chlorinating agent. Until now,only sulfenyl chlorides have been obtained from disulfides[8] and certain sulfides[9] with sulfuryl chloride. As we found, sulfinyl chlorides are formed in nearly quantitative yields according to the equation:

$$\text{R-S-S-R} + 3\ SO_2Cl_2 + 2\ CH_3CO_2H \longrightarrow 2\ \text{R-S(O)Cl} + 2\ CH_3COCl + 3\ SO_2 + 2\ HCl$$

The general procedure is as follows:

The disulfide (0.1 mol) and acetic acid (0.2 mol) are mixed and cooled to the temperature indicated in the table. Sulfuryl chloride (0.31 mol) is added dropwise with stirring over a period of 30 minutes.The mixture is then stirred for the time indicated in the table at -20°C and afterwords allowed to come to room temperature over a period of about two hours. Evolution of SO_2 and HCl is observed during this time.To complete the reaction,the mixture is warmed to 35°C for one hour. Acetyl chloride is stripped off in vacuum to leave the virtually pure sulfinyl chloride. Low-boiling sulfinyl chlorides may be distilled in vacuum. During the course of the reaction,the colour changes from colourless over red to orange and finally pale yellow.

Table. Preparation of sulfinyl chlorides from disulfides(RSSR ⟶ RS(O)Cl)

R	temp.(°C)	time (h)	crude yield(%) (dist. yield(%)	b.p. (°C/mm) lit.
Me	-20	3	100 (95)	55/40[6,7]
iPr	-20	3	100 (93)	49/12[7]
tBu	-30	20[a]	98 (86)	84/26[10]
$PhCH_2$	-40	4	98	- [6]
Ph	-40	3	100	- [7]
$4\text{-}CH_3\text{-}Ph$	-40	3	100	- [7]
$MeC(O)OCH_2CH_2$[b]	-40	4	98	- [c]

a) For short reaction times (3 h),t.-butyl sulfenyl chloride is the main product. b) prepared from the diol (acetic anhydride/pyridine, 87 %, b.p.$_{26}$ 170°C). c) NMR($CDCl_3$): 1.13(s,3H);3.75 (tr,2H);4.62(tr,2H);J=6.0 Hz.

As sulfinyl chlorides are known to be quite unstable,the new compound 2-acetoxy-ethanesulfinyl chloride was converted to the corresponding ethyl sulfinate (ethanol/pyridine) which gave the expected analytical and spectral data (e.g. IR (film), 1740 vs (C=O), 1120 vs (S=O)).

Note that t.-butylsulfinyl chloride could not be obtained from the disulfide nor from the thiol ester by chlorination[7]. The presence of an ester function does not influence the reaction,but no sulfinyl chloride was observed in the case of disulfides containing primary or secondary amide functions (e.g. $(Me\text{-}CH(Ph)\text{-}NH\text{-}C(O)\text{-}CH_2\text{-}S)_2$). Carbon-carbon double bonds are not preserved under the reaction conditions (e.g. diallyl disulfide gave a mixture of products with complete destruction of the allyl group).

Thus,the reaction of sulfuryl chloride with disulfides provides an easy access to sulfinyl chlorides if no acid-sensitive groups are included in the compounds.

References

(1) G.Solladié, Synthesis,1981, 185.
(2) S.Colonna,R.Annunziata and M.Cinquini, Phos.Sulf.,1981, 10, 197.
(3) K.K.Andersen, Tetrahedron Lett.,1962, 93.
(4) J.Drabowicz,B.Bujnicki and M.Mikolajczik, J.Org.Chem.,1982, 47, 3325.
(5) I.B.Douglass and B.S.Farah, J.Org.Chem.,1958, 23, 330.
(6) I.B.Douglass and R.V.Norton, J.Org.Chem., 1968, 33, 2104.
(7) M.L.Kee and I.B.Douglass, Org.Prep.Proc., 1970, 2, 235.
(8) H.Brintzinger,K.Pfannstiel,H.Koddebusch and K.E.Kling, Chem.Ber.,1950, 82, 87.
(9) N.Kharasch and R.B.Langford, J.Org.Chem., 1963, 28, 1903.
(10) D.Barnard,L.Bateman,M.E.Cain,T.Colclough and J.I.Cunneen, J.Chem.Soc., 1961, 5339.

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