Attempted Reaction of 9-Lithioxanthene with Thionyl Chloride. Thionyl chloride (7.65 g, 64.8 mmol) was added to a three-necked flask, cooled in a dry-ice acetone bath under nitrogen. Xanthene (0.91 g, 5.0 mmol) in dry diethyl ether (20 mL) was added to a dropping funnel attached to the above three-necked flask. *n*-Butyllithium (0.48 g, 7.5 mmol) was added to the ether solution and the reaction left for 15 min. The resulting deep red solution was then dropped into the thionyl chloride over a period of 20 min. The reaction was stirred for a further 20 min at −78 °C and for 2 h at 25 °C. Filtration yielded a solid which quickly decomposed in air and upon addition of water, fizzed, and gave the odor of xanthene. Evaporation of the slightly yellow ether solution yielded a deep purple solid. Extraction with water slowly eliminated the color, and a gas was evolved. TLC analysis indicated a complex mixture including xanthene.

Reaction of α-Chlorothiosulfenyl Chlorides with Triphenylphosphine. General Procedure. Sulfur dichloride (0.11 g, 1.1 mmol) in dry CS_2 (2 mL) was added to the corresponding thione (1.0 mmol) in dry CS_2 (5 mL) under N_2. After the mixture was stirred for 20 min, triphenylphosphine (0.27 g, 1.1 mmol) was added, and the reaction was stirred for a further 30 min. Addition of water, extraction, drying of the organic layer (Na_2SO_4), and evaporation yielded a mixture of four spots by TLC. Thick-layer chromatography (SiO_2, CH_2Cl_2) yielded thione (least polar), triphenylphosphine sulfide, ketone, and triphenylphosphine oxide (most polar). The results are summarized in Table III.

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Registry No. 1a, 1450-31-3; **1b**, 958-80-5; **1c**, 1226-46-6; **2a**, 79991-60-9; **3b**, 79991-61-0; **4**, 492-21-7; **5a**, 79991-62-1; **5b**, 79992-45-3; **6**, 90-47-1; **7**, 20735-05-1; **8**, 79992-47-5; **9**, 51933-61-0; **10**, 80010-06-6; **13**, 92-83-1; **15**, 79991-63-2; **16**, 54396-69-9; **17**, 23695-65-0; **18**, 875-06-9; **19**, 7519-74-6; **20**, 79991-64-3; **21**, 79991-65-4; **22a**, 79991-66-5; **22b**, 79991-67-6; **23a**, 79991-68-7; **23b**, 79991-69-8; **24a**, 79991-70-1; **24b**, 7419-57-0; **25**, 79991-71-2; 9-lithioxanthene, 40102-97-4; 1,1′-[(chloro)(chlorodithio)methylene]bisbenzene, 79991-72-3; 1,1′-[(chloro)(chlorodithio)methylene]bis[4-methoxybenzene], 79991-73-4; benzophenone, 119-61-9; bis(4-methoxyphenyl)methanone, 90-96-0; 2,2,4,4-tetramethyl-3-pentanone, 815-24-7; fenchone, 1195-79-5; adamantanone, 700-58-3; triphenylphosphine oxide, 791-28-6; triphenylphosphine sulfide, 3878-45-3.

Notes

Convenient Method for the Conversion of Thiols and Disulfides to the Corresponding Chlorides

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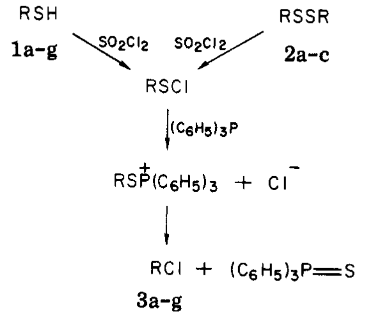
Many versatile procedures exist in the literature for the conversion of alcohols to alkyl chlorides. It is surprising, therefore, that few attempts have been made to develop reagents for the formally analogous conversion of thiols to alkyl chlorides. The reverse of this procedure, on the other hand, i.e., the conversion of alkyl halides to thiols, is, of course, a well-documented synthetic manipulation.[1]

Two of the early procedures which have been reported[2,3] for the conversion of thiols to alkyl chlorides are clearly limited to special cases, while another approach, using the reaction of sulfenyl chlorides with trialkyl phosphites,[4] although more general, leads to alkyl chlorides only as side products, resulting from Arbuzov reaction of chloride ion on the initially formed phosphonium salt. More recently, Weiss and Snyder[5] used the system triphenylphosphine–carbon tetrachloride for the conversion of alcohols and, in two instances only, thiols to chlorides at 50–55 °C. Clive and Denyer[6] also successfully converted a number of *primary* aliphatic thiols to the corresponding chlorides using a two-step procedure involving initial reaction of the thiol with (chlorocarbonyl)sulfenyl chloride, followed by triphenylphosphine. In the one case where a secondary thiol was used, these authors obtained an alkene as the major product under their reaction conditions.

Scheme I



As part of our recent study of the behavior of sulfenyl chlorides and thiosulfenyl chlorides[7] we have found a new procedure for the rapid conversion of aliphatic thiols (primary, secondary, tertiary, *and* benzylic) to the corresponding chlorides under very mild conditions (Table I). The method involves chlorination of the thiol at low temperatures with sulfuryl chloride (chlorine may also be used), followed by reaction of the intermediate sulfenyl chloride (not isolated) with triphenylphosphine[8] to give the chloride. The reaction gives somewhat higher yields with disulfides (Table I). In the latter case, we believe that our procedure again requires the intermediacy of the sulfenyl chloride, although the cleavage of disulfides to thiols directly, by using tri-*n*-butylphosphine[9] or triphenylphosphine and water,[10] has been reported and also

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[1] Patai, S., Ed. "The Chemistry of the Thiol Group"; Wiley: New York, 1974; Part 1, p 163 ff.

[2] Baganz, H.; Dransch, G. *Chem. Ber.* **1960**, *93*, 782.

[3] Brandt, G. A. R.; Emeléus, H. J.; Haszeldine, R. N. *J. Chem. Soc.* **1952**, 2198.

[4] Morrison, D. C. *J. Am. Chem. Soc.* **1955**, *77*, 181.

[5] Weiss, R. G.; Snyder, E. I. *J. Chem. Soc., Chem. Commun.* **1968**, 1358.

[6] Clive, D. L. J.; Denyer, C. V. *J. Chem. Soc., Chem. Commun.* **1972**, 773.

[7] Still, I. W. J.; Kutney, G. W.; McLean, D. *J. Org. Chem.*, companion paper in this issue.

[8] Triphenyl phosphite may be used with equal success. We thank one of the referees for this valuable suggestion.

[9] Nakagawa, I.; Hata, T. *Tetrahedron Lett.* **1975**, 1409.

0022-3263/82/1947-0560$01.25/0

Table I. Conversions of Thiols[a] and Disulfides[b] to Chlorides

product	substrate	% yield of RCl[c]	bp, °C obsd	bp, °C lit.[d]	n^{25}_D obsd	n^{20}_D lit.
3a	n-C_3H_7SH	62	*e*	47	1.3855	1.3879
3b	n-$C_6H_{13}SH$	66	134-137	135	1.4195	1.4199
3c	i-C_3H_7SH	42	33-34	36	1.3835	1.3777
3d	t-C_4H_9SH	37	*e*	52	1.3875	1.3857
3e	$C_6H_5CH_2SH$	67	176-184	179	1.5405	1.5391
3f	C_6H_5SH	29	131-133	132	1.5264	1.5241
3g	p-$CH_3C_6H_4SH$	12	150-155	162	1.5250	1.5150
3c	$(i\text{-}C_3H_7S)_2$	67	33-35	36		
3d	$(t\text{-}C_4H_9S)_2$	41	49-50	52		
3f	$(C_6H_5S)_2$	30	128-132	132		
4	$HOCH_2CH_2SH$	20[f]	*e*	83	1.4432	1.4448
5	CH_3COSH	71	45-48	51	1.3840	1.3898

[a] SO_2Cl_2 (1 mol) and $(C_6H_5)_3P$ (1 mol). [b] SO_2Cl_2 (1 mol) and $(C_6H_5)_3P$ (2 mol). [c] Isolated yields. ^1H NMR-indicated products were >98% pure. [d] "Handbook of Chemistry and Physics", 60th ed.; CRC Press: Boca Raton, FL, 1980. [e] Accurate boiling points could not be obtained in all cases. [f] 1,2-Dichloroethane.

studied mechanistically.[10] The overall reactions involved in our procedure are as shown in Scheme I.

Other features to emerge from this study include the observations that oxygen-containing substituents such as OH, COOH, NO_2 interfere seriously with the reaction. Thus, no trace of the corresponding chloride was obtained from the reaction of 3,3′-dithiobis[propanoic acid] under our conditions, while we also observed that 2-mercaptoethanol gives 1,2-dichloroethane (4), in rather low yield, as the sole isolated product. Only a trace of ethylene sulfide was observed spectroscopically in this reaction, in contrast to the results of Baldwin and Hesson.[11] In the two cases which these workers describe, however, it is perhaps significant that the β-hydroxy group involved is tertiary. 4-Nitrobenzenethiol led rapidly to intractible products, although whether this was primarily due to the nitro group or to the use of an aromatic thiol (q.v.) we are unable to say. In contrast to these findings, we have found (Table I) that thioacetic acid is efficiently converted to acetyl chloride (5) under our conditions.

In marked contrast to the successful procedure reported above for the aliphatic thiol → chloride conversions, we have met with very limited success in the aromatic series. In addition to the two examples quoted in Table I, which proceed in rather poor yield, we found no trace of the corresponding chloride in analogous reactions with 4-bromobenzenethiol and 3-methoxybenzenethiol, in addition to the 4-nitrobenzenethiol mentioned earlier. In the light of these disappointing results it seem inappropriate to speculate on a possible mechanism for those cases in the aromatic series where reaction did occur.

Since our study was completed, we have very recently noted the results of Oae and Togo[12] on the conversion of primary aliphatic thiols to the corresponding *iodides* by using a triphenylphosphine–iodine reagent system in refluxing benzene. The mechanism suggested by these authors does *not* invoke the intermediacy of a sulfenyl iodide, but rather displacement of iodide by the thiol (or thiolate ion) from the intermediate iodotriphenylphosphonium ion, formed by prior reaction of iodine with triphenylphosphine.

The method here described constitutes a reliable general procedure for the synthetic conversion RSH (or RSSR) → RCl under mild conditions, with the exceptions already noted.

Experimental Section

Preparation of 1-Chlorohexane. 1-Hexanethiol (5.9 g, 50 mmol) was cautiously added, with stirring, to sulfuryl chloride (6.75 g, 50 mmol) at −23 °C. The mixture was stirred for 30 min at this temperature, forming the corresponding sulfenyl chloride. Powdered triphenylphosphine (13.15 g, 50 mmol) was then added slowly to this orange-red liquid. The semisolid reaction mixture slowly lost color on manual stirring before becoming colorless upon completion of the addition of the triphenylphosphine. 1-Chlorohexane (4.0 g, 66%) was distilled directly from the mixture as a colorless liquid: bp 134–137 °C; n^{25}_D 1.4195.

When triphenyl phosphite (15.5 g, 50 mmol) was substituted for the triphenylphosphine above, a viscous liquid mixture resulted which avoided the need for manual stirring of the reaction mixture. The yield of 1-chlorohexane obtained on distillation in this case was 63%.

Preparation of Chlorobenzene. Benzenethiol (5.5 g, 50 mmol) was added dropwise, with stirring, to sulfuryl chloride (6.75 g, 50 mmol) at 0 °C, immediately forming the orange-red sulfenyl chloride. Powdered triphenylphosphine (13.15 g, 50 mmol) was added in portions over 1 h. In the final stages of the addition the reaction mixture became very stiff and had to be stirred manually with a spatula. The reaction flask was fitted with a stillhead and condenser, and chlorobenzene (1.6 g, 29%) was distilled from the mixture as a colorless liquid: bp 131–133 °C, n^{25}_D 1.5264.

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Registry No. 1a, 107-03-9; **1b**, 111-31-9; **1c**, 75-33-2; **1d**, 75-66-1; **1e**, 100-53-8; **1f**, 108-98-5; **1g**, 106-45-6; **2c**, 4253-89-8; **2d**, 110-06-5; **2f**, 882-33-7; **3a**, 540-54-5; **3b**, 544-10-5; **3c**, 75-29-6; **3d**, 507-20-0; **3e**, 100-44-7; **3f**, 108-90-7; **3g**, 106-43-4; **4**, 107-07-3; **5**, 75-36-5; $HOCH_2CH_2SH$, 60-24-2; CH_3COSH, 507-09-5.

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[10] Overman, L. E.; O'Connor, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 771.

[11] Baldwin, J. E.; Hesson, D. P. *J. Chem. Soc., Chem. Commun.* **1976**, 667.

[12] Oae, S.; Togo, H. *Synthesis* **1981**, 371.

Cyclobutylcarbinyl *p*-Bromobenzenesulfonate Solvolysis. A Study of Response to Solvent Ionizing Strength

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In our study of medium effects upon the rates of solvolysis of cyclopropylcarbinyl arenesulfonates, 3-OSO_2Ar, we found[1] that the log k_t values for the solvolysis of 3-

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[1] Roberts, D. D.; Snyder, R. C., Jr. *J Org Chem.* **1979**, *44* 2860.