Desulphurization of Alkyl Chlorocarbonyl Disulphides—a Method for Replacement of -SH by -Cl

By D. L. J. Clive* and C. V. Denyer
(*Chemistry Department, University of London, King's College, Strand, London* WC2R 2LS)

Summary Successive reaction with chlorocarbonylsulphenyl chloride and triphenylphosphine converts thiols efficiently to alkyl chlorides.

Replacement of alcoholic OH by halogen is an important synthetic operation for which procedures are available to deal with a wide range of circumstances[1,2]. However, comparable methods for analogous transformations of the thiol group have not hitherto been developed. We now report a new, general, and exceptionally mild† procedure for replacing a primary thiol group by chlorine.

In principle, the transformation (1) → (3) requires efficient

$$\underset{(1)}{\text{R-SH}} \longrightarrow \underset{(2)}{\text{R-S-Z}} \longrightarrow \underset{(3)}{\text{R-Cl}}$$

formation of a derivative (2) where Z is chosen so that the system can be made to collapse to place a halogen atom—either a component of Z or from an external source—at the site initially occupied by sulphur. We selected Z = S-COCl as fulfilling these requirements, guided in part by the report[3] that thiols react with chlorocarbonylsulphenyl chloride[4] by preferential displacement of sulphenyl halogen. The transformation (1) → (3) is shown to be carried out under very mild conditions by sequential treatment of a thiol with chlorocarbonylsulphenyl chloride and a phosphine. The reaction between thiols and chlorocarbonylsulphenyl chloride takes place readily in the required manner‡ even below 0 °C to give alkyl chlorocarbonyl disulphides (2; Z =

Table. *Yields from disulphides*

	(g.l.c.)[a]	(isolated)[b]
n-$C_7H_{15}Cl$	98%	75%
n-$C_6H_{13}Cl$	92%	69%
n-C_4H_9Cl	80%	48%[c]

[a] Based on an internal standard. [b] Isolated products were pure and identical with authentic specimens. [c] Losses due to co-distillation with solvent were appreciable; the material was isolated by preparative g.l.c.

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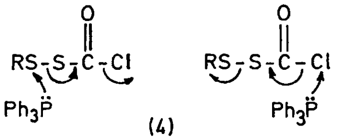
† For conversion of benzylthiol and 2-phenylethanethiol to the corresponding chlorides by heating with triphenylphosphine and carbon tetrachloride, see R. G. Weiss and E. I. Snyder, *Chem. Comm.*, 1968, 1358.

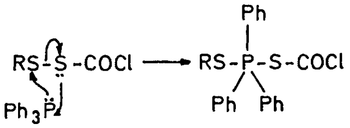
‡ An OH group displaces the other Cl usually at *ca.* 40 °C.[5]

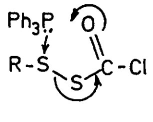
S–COCl) in better than 80% yield. These compounds§ have ν_{max} (film) 1782 cm^{-1} and δ (CCl_4) 2·90 p.p.m. (centre of triplet, *J* 7 Hz, $-CH_2SSCOCl$) or, for the cyclohexyl case δ 2·95 p.p.m. (centre of broad signal, $-\overset{|}{C}HSSCOCl$). Although triphenylphosphine is not an especially powerful thiophile[6] it is adequate in this respect to react rapidly with these disulphides at low temperature. An insoluble product forms almost instantly at −35° from ether solution and redissolves on warming to room temperature to give the alkyl chloride and triphenylphosphine sulphide. After an overnight reaction period¶ the halides are isolated (see Table) by chromatography and/or distillation.

In the case of cyclohexanethiol the present procedure gave cyclohexene, characterized by reaction with 2,4-dinitrobenzenesulphenyl chloride, as a major product.

Mechanistically, halide formation probably involves fission of the weak S–S bond by displacement [*e.g.*, (4)] or by insertion [*e.g.*, (5)–(6)] and in the latter case the process must be followed by rapid expulsion of COS because the initial adduct which was isolable as an unstable solid for R = Bu^n shows no i.r. carbonyl absorption. The thermally allowed six-electron process (7) is probably not an important pathway as formation of a P–O bond would be expected to lead eventually to triphenylphosphine oxide and this material is produced in small amount only (*ca.* 10% yield based on triphenylphosphine) except in the case of cyclohexyl chlorocarbonyl disulphide where the intervention of other reactions is evident.


(4)


(5) (6)


(7)

The desulphurization reported here makes the –SH and –Cl groups efficiently equivalent[6] in the sense thiol → halide which is opposite to that conventionally associated with these groups.

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§ New compounds had analytical values accurate to ±0·4%.

¶ The phosphine solution was added at −35° and the cooling bath left in place 1 h further. The minimum total reaction time was not measured.

[1] For recent work see L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, 1967, pp. 1247, 1249; M. Fieser and L. F Fieser, "Reagents for Organic Synthesis," Wiley-Interscience, 1969, Vol. 2, p. 136; *ibid.*, 1972, Vol. 3, pp. 151, 153.

[2] D. L. J. Clive and C. V. Denyer, *Chem. Comm.*, 1971, 1112 and references therein.

[3] G.P. 1219925/1965.

[4] G.P. 1224720/1964.

[5] G. P. Application 1568632/1966.

[6] See E. J. Corey, *Pure Appl. Chem.*, 1967, 54, 19.