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Reactions of chlorine dioxide with organic compounds

2.* Oxidation of thiols

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Oxidation of thiols with chlorine dioxide smoothly affords the corresponding disulfides.

Key words: chlorine dioxide, oxidation, thiol, disulfide.

Oxidation of thiols with various oxidants has been much investigated;[2—4] however, the use of chlorine dioxide (ClO_2) as an oxidant is only recent (see the relevant kinetic studies[5,6]).

We showed that oxidation of thiols **1a—c** with chlorine dioxide selectively affords disulfides **2a—c** in high yields.

$$\underset{\mathbf{1a-c}}{\mathrm{RSH}} \xrightarrow{\mathrm{ClO_2}} \underset{\mathbf{2a-c}}{\mathrm{RS-SR}}$$

R = Bn (**a**), C_6H_{13} (**b**), C_2H_4OH (**c**)

Oxidation was carried out in three ways: a solution of a thiol in an organic solvent was bubbled by passing an air—oxidant mixture (method *A*); a thiol was added dropwise to a solvent presaturated with the oxidant (method *B*); and ClO_2 dissolved in water was immediately mixed with a solution of the starting compound (method *C*).

In all cases, the molar thiol : ClO_2 ratio was 1 : 0.5; the yields of the corresponding disulfides were 96 to 98%.

Experimental

Commercial thiols **1a—c** (99% purity) were used as purchased. Aqueous ClO_2 was a commercial product; the concentration of ClO_2 in the initial solution was determined by titration according to a known procedure.[7]

TLC was carried out on Silufol plates; spots were visualized with aqueous 5% $KMnO_4$ acidified with several drops of conc. H_2SO_4. Eluents were light petroleum—Et_2O (7 : 3) for **1a**, Me_2CO—heptane (2 : 3) for **1b**, and Me_2CO—heptane (5 : 1) for **1c**.

GLC analysis was performed with a Chrom-5 chromatograph (flame ionization detector, column 3×3000 mm, SKTF-50 on Chromaton-N-AW-DMCS as the stationary phase, helium as a carrier gas). Organosulfur compounds were analyzed in a temperature range from 50 to 250 °C at a heating rate of 6 deg min^{-1}. Compounds were identified by comparing their retention times with those of authentic samples.

Mass spectra were recorded on a Shimadzu QP 5050A chromatomass-spectrometer (column SPB-5 (60 m × 0.32 mm), column temperature 50—250 °C, heating rate 5 deg min^{-1}).

Melting points were determined in an open capillary.

Typical procedures for oxidation of thiols. *A*. Bis(2-hydroxyethyl) disulfide (2c). A mixture of air and ClO_2 (0.22 g, 3.2 mmol) obtained from an aqueous solution was passed through a solution of ethanethiol **1c** (0.5 g, 6.4 mmol) in AcOEt (5 mL) for 2 h. Water vapors were collected in a trap with conc. H_2SO_4. The reaction mixture was magnetically stirred for 2 h. After the reaction was completed, the solvent was removed to give disulfide **2c** (0.47 g, 96%), m.p. 23—24 °C (*cf.* Ref. 8: 24—25 °C).

***B*. Dibenzyl disulfide (2a).** Benzylmercaptan **1a** (0.5 g, 4.0 mmol) was added dropwise at 20 °C to a solution of ClO_2 obtained by bubbling AcOEt (5 mL) with a mixture of air with ClO_2 (0.136 g, 2.0 mmol).[9] The reaction mixture was magnetically stirred for 120 min. After the reaction was completed, the solvent was removed to give dibenzyl disulfide **2a** (0.96 g, 98%), m.p. 70 °C (EtOH) (*cf.* Ref. 10: 70—71 °C).

***C*. Dihexyl disulfide (2b).** A solution of thiol **2** (0.5 g, 4.2 mmol) in hexane (5 mL) was mixed with aqueous ClO_2 (0.143 g, 2.1 mmol). The reaction mixture was magnetically stirred at 20 °C for 3 h. After the reaction was completed (decoloration of the solution), the organic phase was separated on a separating funnel, and the solvent was removed to give dihexyl disulfide **2b** (0.49 g, 98%), b.p. 71—73 °C (2 Torr). Found (%): C, 61.46; H, 11.26; S, 27.28. $C_{12}H_{26}S_2$. Calculated (%): C, 61.54; H, 11.11; S, 27.35. MS (EI, 70 eV), m/z (I_{rel} (%)): 234 $[M]^+$ (19); 150 $[C_6H_{13}SSH]^+$ (17); 117 $[C_6H_{13}S]^+$ (11); 85 $[C_6H_{13}]^+$ (24); 57 $[C_4H_9]^+$ (16); 55 $[C_4H_7]^+$ (16); 43 $[C_3H_7]^+$ (100).

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* For Part 1, see Ref. 1.

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