

Oxidation of 2-Chloro-1-phenylethane-1,1-dithiol

L. G. Shagun, L. P. Ermolyuk, G. I. Sarapulova, and M. G. Voronkov

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: tim@irioch.irk.ru

Received December 18, 2002

Abstract—Oxidation of 2-chloro-1-phenylethane-1,1-dithiol with bromine, iodine, and elemental sulfur, as well as under UV irradiation, leads to formation of 1,4-bis(chloromethyl)-1,4-diphenyl-2,3,5,6-tetrathiane in 50–95% yield. Oxidation of the same substrate with selenium dioxide gives 1,5-bis(chloromethyl)-1,5-diphenyl-2,4-dithia-3-selenapentane-1,5-dithiol. On heating to 60°C, the latter loses selenium to afford 1,4-bis(chloromethyl)-1,4-diphenyl-2,3-dithiabutane-1,4-dithiol.

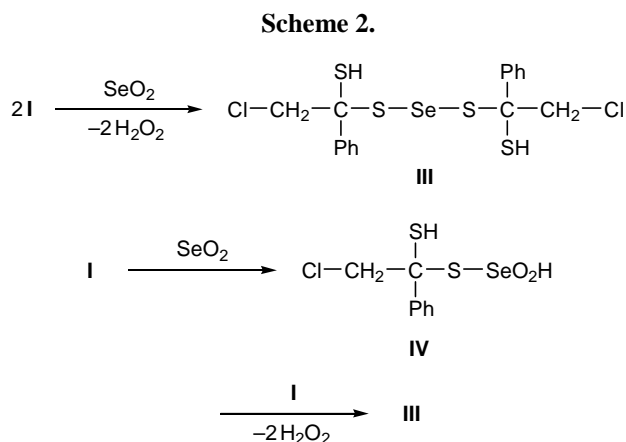
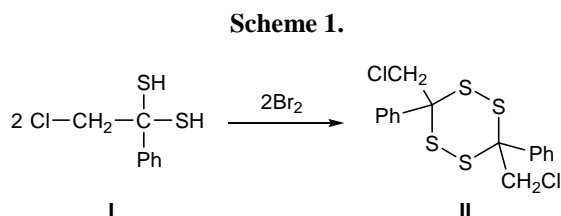
Oxidation of thiols has been well documented. It leads to formation of the corresponding disulfides or sulfonic and sulfinic acids [1, 2]. Various reagents are used as oxidants, e.g., oxygen, iodine, hydrogen peroxide, selenium dioxide, dimethyl sulfoxide, elemental sulfur, lead tetraacetate, etc. However, only a few publications are available on the oxidation of geminal dithiols possessing a C(SH)₂ moiety. As early as 1962, Mayer and co-workers [3] found that cycloalkane-1,1-dithiols are oxidized with iodine to the corresponding 1,2,4,5-tetrathiane derivatives in a very poor yield [3]. An attempt to oxidize 3,5,5-trimethylhexane-1,1-dithiol with nitric acid resulted in isolation of 3,5,5-trimethylhexanoic and 2,4,4-trimethylpentanoic acids [4].

We synthesized in quantitative yield previously unknown 2-haloethane-1,1-dithiols RC(SH)₂CH₂X (R = CH₃, C₆H₅, 4-CH₃C₆H₄, 1-C₁₀H₇; X = Cl, Br, I) by the action of hydrogen sulfide on the corresponding α-halo ketones in a solution of hydrogen chloride in ether [5]. Among the products thus obtained, the most stable and readily accessible was 2-chloro-1-phenylethane-1,1-dithiol (**I**). Just the latter was used in the present work as model compound for studying oxidation of geminal dithiols. As oxidants we used bromine,

iodine, hydrogen peroxide, selenium dioxide, and elemental sulfur.

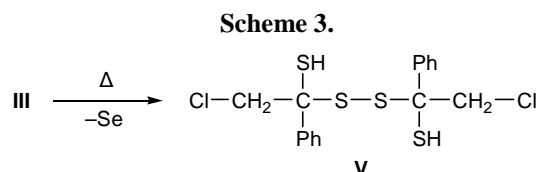
1-Chloro-1-phenylethane-1,1-dithiol (**I**) is readily oxidized with bromine, yielding 1,4-bis(chloromethyl)-1,4-diphenyl-2,3,5,6-tetrathiane (**II**) (Scheme 1). The same product, but in a considerably lower yield (15–20%) is formed by oxidation of **I** with iodine.

Selenium dioxide was used as oxidant in reactions with substituted benzenethiol [6] and indenethiol [7]. From arenethiols, the corresponding diaryl sulfides and diaryl thioselenides were obtained, whereas indenethiol was oxidized to diindenyl thioselenides. We have found that slow addition of a solution of selenium dioxide in methanol to a solution of dithiol **I** in the same solvent under argon leads to formation of 1,5-bis(chloromethyl)-1,5-diphenyl-2,4-dithia-3-selenapentane-1,5-dithiol (**III**) (Scheme 2). This reaction is likely to occur in two steps. In the first step,

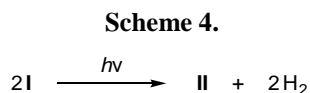


dithiol **I** reacts with selenium dioxide to give thio-selenate **IV** which then reacts with the second molecule of **I**, yielding dithioselenide **III**.

On prolonged storage (for 3 years) or on heating for 36 h at 60°C, compound **III** is quantitatively converted into 1,4-bis(chloromethyl)-1,4-diphenyl-2,3-dithiabutane-1,4-dithiol (**V**) with liberation of amorphous selenium (Scheme 3).



It is known that photolysis of alkanedithiols and dialkyl sulfides gives the corresponding disulfides [8, 9]. However, there are no published data on photochemical transformations of geminal dithiols. Under UV irradiation, 2-chloro-1-phenylethane-1,1-dithiol (**I**) was found to be quantitatively converted into tetra-thiane **II** (Scheme 4). The process is strongly accelerated in the presence of elemental sulfur.



The IR spectra of compounds **II**, **III**, and **V** contain characteristic absorption bands which confirm the assumed structures. The bands were assigned with account taken of the data in [10, 11]. The presence of a C–S–S–C fragment in molecule **II** follows from the appearance of a very strong $\nu_{\text{C-S}}$ band at 690 cm^{-1} and $\nu_{\text{S-S}}$ band at 520 cm^{-1} , while ν_{SH} absorption is lacking. A series of strong narrow peaks at 750, 1000, 1190, and 1448 cm^{-1} belongs to skeletal vibrations of the saturated ring; these bands are typical of such structures. Thus the above data suggest formation of a cyclic structure with endocyclic S–S bonds. The latter give rise to an absorption band in the UV spectrum at λ_{max} 526 nm due to electron transition between the sulfur *d* orbitals.

The IR spectrum of compound **III** contains an absorption band at 2550 cm^{-1} (ν_{SH}), indicating formation of an acyclic thiol. The S–Se–S fragment is characterized by UV absorption at λ_{max} 632 nm. In the IR spectrum of dithiol **V** we observed almost the same set of absorption bands as in the spectrum of **III**. However, the absorption band with its maximum at λ 526 nm in the UV spectrum of **V**, which is typical of

S–S moiety, is displaced by 100 nm toward shorter wavelengths relative to the absorption maximum of compound **III** containing a dithioselenide fragment. The UV absorption bands were assigned on the basis of the data given in [12, 13].

Treatment of all previously synthesized α -halo-substituted geminal dithiols, including compound **I**, with hydrogen peroxide resulted in formation of a multi-component mixture, and we failed to isolate and identify individual products.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples prepared as thin films (compounds **I**, **II**, and **V**) or KBr pellets (**II**, **III**), as well as from solutions in CDCl_3 or CHCl_3 (**II**, **III**; layer thickness 0.01 cm). The UV spectra were measured on a Specord UV-Vis spectrophotometer in CHCl_3 using 1-cm cells. The ^1H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 instrument using CDCl_3 as solvent and HMDS as internal reference. UV radiation was generated by an OKN-11 instrument (technical specification 64-1-1618-77). The progress of reactions was monitored by TLC on Silufol UV-254 plates with chloroform as eluent.

1,4-Bis(chloromethyl)-1,4-diphenyl-2,3,5,6-tetra-thiane (II). *a.* Bromine, 0.23 g (1.46 mmol), was slowly added to a solution of 0.2 g (0.98 mmol) of dithiol **I** in 10 ml of diethyl ether, cooled to -8°C , and the mixture was stirred under argon until the initial compound disappeared (24 h, TLC). Excess bromine was washed off with water. The organic phase was separated and dried over CaCl_2 , and the solvent was removed to obtain 0.2 g of a dark yellow oily liquid. It was dissolved in 5 ml of chloroform, and 20 ml of hexane was added to the solution. The precipitate was filtered off and dried under reduced pressure. Yield 0.1 g (50%), light yellow powder, mp 113–114°C. IR spectrum, ν , cm^{-1} : 520 w, 620 w, 690 w, 750, 820, 1000, 1070, 1190, 1270, 1400, 1448, 1490, 1570, 1600, 2860, 2920, 2940, 3000, 3020, 3050. UV spectrum: λ_{max} 526 nm. ^1H NMR spectrum, δ , ppm: 4.51 s (4H, CH_2Cl), 7.24–7.75 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_{C} , ppm: 45.31 (CH_2), 128.55 (C^p), 128.71 (C^o , C^m), 133.66 (C^i), 190.32 (S–C–S). Found, %: C 47.12; H 3.46; Cl 17.57; S 31.85. $\text{C}_{16}\text{H}_{14}\text{Cl}_2\text{S}_4$. Calculated, %: C 47.39; H 3.48; Cl 17.51; S 31.62.

b. A solution of 2 g (0.98 mmol) of dithiol **I** in 0.5 ml of carbon disulfide was cooled to -40°C and

was irradiated with UV light for 20 min. Yield of tetrathiane **II** 0.18 g (90%), mp 113–114°C. The IR and NMR spectra of the product were identical to those of a sample prepared as described in *a*.

c. A solution of 2 g (0.98 mmol) of dithiol **I** in 0.5 ml of carbon disulfide was cooled to –40°C, 0.8 g (3.12 mmol) of sulfur was added, and the mixture was irradiated with UV light for 5 min. The precipitate of tetrathiane **II** (which contained sulfur) was extracted into chloroform. Precipitation with hexane afforded 0.19 g (95%) of compound **II** with mp 113–114°C. The IR and NMR spectra of the product were identical to those given above.

1,5-Bis(chloromethyl)-1,5-diphenyl-2,4-dithia-3-selenapentane-1,5-dithiol (III). A solution of 0.09 g (0.78 mmol) of selenium dioxide in 5 ml of anhydrous methanol was slowly added in a dropwise fashion to a solution of 0.19 g (0.92 mmol) of dithiol **I** in 10 ml of anhydrous methanol on cooling to –10°C. The mixture was stirred at room temperature until dithiol **I** disappeared (1 h, TLC). The yellow precipitate was filtered off, dried, dissolved in 2 ml of chloroform, and reprecipitated with 10 ml of hexane. Yield 0.12 g (52%), mp 91–92°C. IR spectrum, ν , cm^{-1} : 690 w, 770, 970, 1280, 1450, 1500, 1580, 1600, 2550, 2850, 2960, 3000, 3060. UV spectrum: λ_{max} 632 nm. ^1H NMR spectrum, δ , ppm: 3.25 (2H, SH), 4.45 s (4H, CH_2Cl), 7.12–7.60 m (10H, H_{arom}). Found, %: C 39.50; H 3.38; Cl 14.93; S 26.31; Se 15.88. $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{S}_4\text{Se}$. Calculated, %: C 39.50; H 3.31; Cl 14.60; S 26.36; Se 16.22.

1,4-Bis(chloromethyl)-1,4-diphenyl-2,3-dithia-butane-1,4-dithiol (V). A solution of 0.1 g (0.21 mmol) of dithioselenide **III** in 5 ml of chloroform was heated for 36 h at 60°C. During the reaction, red amorphous selenium separated from the solution. The mixture was filtered, and disulfide **V** was precipitated from the filtrate with hexane. Yield 0.08 g (95%), mp 50–54°C. IR spectrum, ν , cm^{-1} : 520, 600, 690 w, 750, 1020, 1120, 1210, 1270, 1330, 1370, 1490, 1580, 1600, 2550, 2850, 2920, 2940, 3000, 3020, 3050. UV spectrum: λ_{max} 526 nm. ^1H NMR spectrum, δ , ppm: 3.31 (2H, SH), 4.69 s (4H, CH_2Cl), 7.37–

7.65 m (10H, H_{arom}). Found, %: C 46.97; H 4.02; Cl 17.29; S 31.72. $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{S}_4$. Calculated, %: C 47.15; H 3.96; Cl 17.42; S 31.47.

REFERENCES

1. Koval', I.V., *Usp. Khim.*, 1993, vol. 62, p. 813.
2. Capozzi, G. and Modena, G., *The Chemistry of the Thiol Group*, Patai, S., Ed., London: Wiley, 1974, part 2, p. 806.
3. Jentzsch, J., Fabian, J., and Mayer, R., *Chem. Ber.*, 1962, vol. 95, p. 1764.
4. Cairns, T.L., Evans, G.L., Larchar, A.W., and McKusic, V.S., *J. Am. Chem. Soc.*, 1952, vol. 74, p. 3982.
5. Shagun, L.G., Dorofeev, I.A., Ermolyuk, L.P., Sarapulova, G.I., and Voronkov, M.G., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 1207.
6. *Comprehensive Organic Chemistry*, Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 3. Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1983, vol. 6, p. 40.
7. Petriashvili, K.A., Usov, V.A., Larin, M.F., and Voronkov, M.G., *Zh. Org. Khim.*, 1986, vol. 22, p. 454.
8. Pachvidze, M.V. and Dalokishvili N.Z., Abstracts of Papers, *XIII Nauchnaya sessiya po khimii i tekhnologii organicheskikh soedinenii sery i sernistykh neftei* (XIIIth Scientific Session on the Chemistry and Technology of Organic Sulfur Compounds and Sulfur-Containing Petroleum), Riga, 1974, p. 283.
9. Chirakadze, G.G., Nanobishvili, E.M., and Katsadze, D.V., Abstracts of Papers, *IX Mezhdunarodnyi simposium po khimii organicheskikh soedinenii sery* (IXth Int. Symp. on the Chemistry of Organic Sulfur Compounds), Riga, 1980, p. 253.
10. Smith, A.L., *Applied Infra-Red Spectroscopy*, New York: Wiley, 1979. Translated under the title *Prikladnaya IR spektroskopiya*, Moscow: Mir, 1982, p. 328.
11. Karimova, N.M., Lin'kova, M.G., and Knunyants, I.L., *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1985, p. 382.
12. Oae, S., *Khimiya organicheskikh soedinenii sery* (Chemistry of Organic Sulfur Compounds), Moscow: Khimiya, 1975.
13. Sverdlova, O.V., *Elektronnye spektry v organicheskoi khimii* (Electronic Spectra in Organic Chemistry), Leningrad: Khimiya, 1973.