Table I

1,10-Phenanthroline	1st component, quinoline	2nd component	M. p., °C.	Yield, %	Analyses,[d] % Calcd. C	H	Found C	H
3,5-Dimethyl	6-Methyl-8-amino-	MAD	169–170	4.2	80.74	5.81	80.90	5.44
4,5-Dimethyl[a,c]	4,5-Dimethyl-8-amino-	G	151–152	24.0	80.74	5.81	80.42	5.73
3,6-Dimethyl[b,c]	3,6-Dimethyl-8-amino-	G	117–118	2.6	80.74	5.81	80.49	5.93
4,6-Dimethyl	4,6-Dimethyl-8-amino-	G	161–162	11.4	80.74	5.81	80.67	5.73
3,5,7-Trimethyl	4,6-Dimethyl-8-amino-	MAD	201–202	14.5	81.05	6.35	81.21	6.10
3,5,8-Trimethyl[c]	3,5-Dimethyl-8-amino-	MAD	185–186	8.7	81.05	6.35	80.78	6.12
3,6,7-Trimethyl[a,c]	4,5-Dimethyl-8-amino-	MAD	177–178	2.1	81.05	6.35	81.07	6.24
4,5,7-Trimethyl	4,6-Dimethyl-8-amino-	MVK	184–185	1.3	81.05	6.35	80.84	6.37

[a] These samples are hygroscopic. [b] Crystallized from benzene–petroleum ether. [c] Alternate method tried, but yield of phenanthroline negligible. [d] Analyses were done by the Clark Microanalytical Laboratory, Urbana, Illinois.

3,5-Dimethyl-8-nitroquinoline.[3]—The preparation of this compound was similar to that of 3,6-dimethyl-8-nitroquinoline except that 2-nitro-5-methylaniline was used as the first component; yield, 9.5 g. or 28.0%, m.p. 189–190° (from 25.5 g. of 2-nitro-5-methylaniline).

4,5-Dimethyl-8-nitroquinoline.[3]—This compound was prepared exactly as in the case of 4,6-dimethyl-8-nitroquinoline except that 2-nitro-5-methylaniline was used as the first component; yield, 3 g. or 8.9%, m.p. 139–140° (from 25.3 g. of 2-nitro-5-methylaniline).

General Procedure for the Synthesis of Di- and Trimethyl-1,10-Phenanthrolines.—A mixture of one molar proportion of the appropriate methyl- or dimethyl-8-aminoquinoline, 0.65 mole of arsenic oxide, 4 moles of sulfuric acid in 96.8% solution and a volume of water equal to one third of the volume of sulfuric acid used was heated to 100° and treated with glycerol (3.6 moles), α-methylacrolein diacetate (1.8 moles), or methyl vinyl ketone (1.8 moles) at such a rate that the temperature did not exceed 140°. It was then heated with stirring for two more hours at this temperature. The mixture was then poured into water, made alkaline, and the tarry precipitate removed by filtration. The filtrate was extracted three times with hot benzene, which was then used to extract the phenanthroline from the solid material. After removal of the benzene the phenanthroline was crystallized from benzene. The results are shown in Table I.

Summary

The following phenanthrolines have been synthesized: 3,5-, 4,5-, 3,6-, 4,6-dimethyl- and 3,5,7-, 3,5,8-, 3,6,7- and 4,5,7-trimethyl-1,10-phenanthrolines.

3,6- and 4,6-dimethyl-8-nitroquinolines and the corresponding amino derivatives have been prepared.

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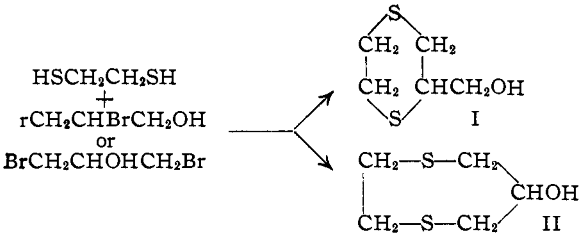
[Contribution from the Noyes Chemical Laboratory, University of Illinois]

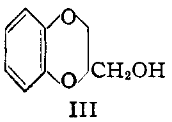
Formation of a Seven-membered Cyclic Disulfide from 1,2-Dibromohydrin and a 1,2-Dithiol

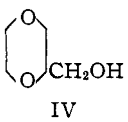
By Reynold C. Fuson and A. John Speziale[1]

In connection with other studies, an attempt was made to prepare 2-hydroxymethyl-1,4-dithiane (I) and 6-hydroxy-1,4-dithiacycloheptane (II) by condensing ethanedithiol with 2,3-dibromo-1-propanol and 1,3-dibromo-2-propanol, respectively. It was found that the two reactions yielded the same product—the carbinol with the seven-membered ring (II).



It had been observed that, in the preparation of acyclic diethers from 1,2- or 1,3-dihalohydrins or from epihalohydrins, the 1,3-diethers are produced in preference to the 1,2-diethers.[2] In the formation of cyclic ethers, however, it was to be expected that a six-membered ring would be produced to the exclusion of a seven-membered ring as observed in the synthesis of 2-hydroxymethyl-1,4-benzodioxane (III) from pyrocatechol and the dihalohydrins,[3] and of 2-hydroxymethyl-1,4-dioxane (IV) from ethylene glycol and epichlorohy-


III


IV

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[1] American Chemical Society Predoctoral Fellow, 1946–1947; present address: Monsanto Chemical Company, St. Louis, Mo.

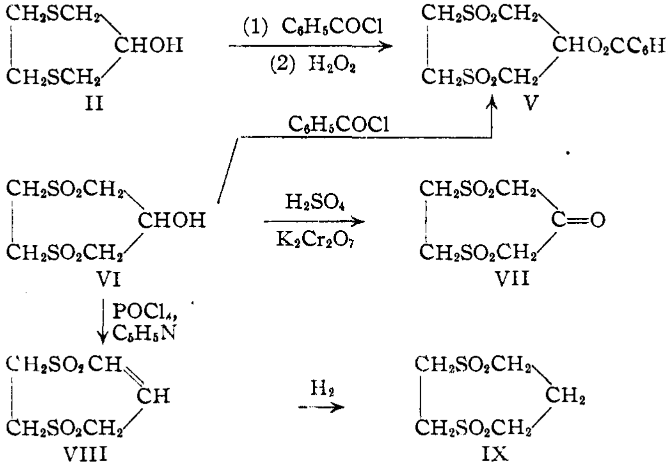
[2] (a) Gilchrist and Purvis, *J. Chem. Soc.*, **127**, 2735 (1925); (b) Zunino, *Atti. accad. Lincei*, **6**, 348 (1897); *J. Chem. Soc.*, **76**, 410 (1899); (c) Rossing, *Ber.*, **19**, 63 (1886); (d) Lindemann, *ibid.*, **24**, 2145 (1891); (e) Fairbourne, *J. Chem. Soc.*, 1151 (1929); (f) Fairbourne, Gibson and Stephens, *ibid.*, 1965 (1932); (g) Fairbourne, Gibson and Stephens, *ibid.*, 445 (1931); (h) Boyd, *ibid.*, **79**, 1221 (1901); (i) Boyd and Marle, *ibid.*, **93**, 838 (1908); (j) Delaby and Dubois, *Bull. soc. chim.*, **47**, 565 (1930).

[3] (a) Moureu, *Ann. chim. phys.*, **18**, 76 (1899); (b) Fourneau, *J. pharm. chim.*, **1**, 55 (1910); (c) French Patent 770,485, September 14, 1934; (d) U. S. Patent 2,366,661, January 2, 1945.

drin.[4] Our observation that a seven-membered ring (II) is produced with either 2,3-dibromo-1-propanol or 1,3-dibromo-2-propanol appears, accordingly, to be anomalous.

The low yield (average 30%) of the 6-hydroxy-1,4-dithiacycloheptane (II) may be attributed to the predominance of intermolecular condensation; large amounts of polymer were formed.

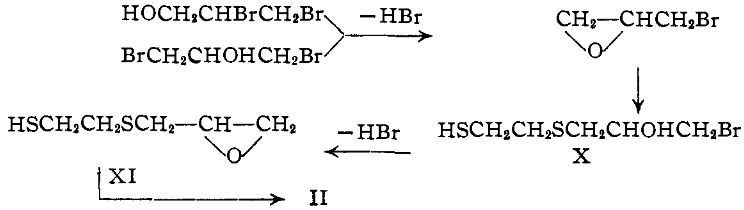
Proof of the structure of this carbinol is afforded by the following transformations.



Careful oxidation of 6-hydroxy-1,4-dithiacycloheptane tetroxide (VI) with potassium dichromate and sulfuric acid led to the keto sulfone (VII) from which a phenylhydrazone was prepared. Dehydration of the tetroxide (VI) with phosphorus oxychloride in pyridine produced the cycloheptene tetroxide (VIII) which gave the known[5,6,7] 1,4-dithiacycloheptane tetroxide (IX, m. p. 279–280° (dec.)) when hydrogenated catalytically with 10% palladium chloride on carbon.

If the initial condensation product had been 2-hydroxymethyl-1,4-dithiane (I), oxidation of its sulfone would have given the corresponding acid, and dehydration and hydrogenation of the sulfone would have produced 2-methyl-1,4-dithiane tetroxide. 2-Methyl-1,4-dithiane, prepared from ethanedithiol and propylene bromide, had a melting point which was in agreement with that reported.[5] The disulfone, not previously described, was obtained by treating 2-methyl-1,4-dithiane with 30% hydrogen peroxide in glacial acetic acid. It had a melting point of 304–306°.

The cyclization can be accounted for by assuming the following changes, involving two epoxide intermediates.



Kharasch and Nudenberg[4] reported the formation of the oxygen analogs of X and XI by the reaction between ethylene glycol and epichlorohydrin.

Experimental

6-Hydroxy-1,4-dithiacycloheptane (II).—A modification of the method of Tucker and Reid[5] was adopted. To 500 ml. of absolute ethanol, 24 g. of clean sodium was added. After the reaction was completed, 48.9 g. of freshly distilled ethanedithiol[8] was added dropwise over a period of one-half hour at 20°. The sodium mercaptide solution and a solution of 113.3 g. of freshly distilled 2,3-dibromo-1-propanol in 500 ml. of absolute ethanol were added dropwise and at approximately the same rate to 500 ml. of absolute ethanol in a 2-l. flask equipped with a stirrer. The temperature was maintained at 20–25° during the addition, which required seven hours. The mixture was stirred overnight at room temperature. The white solid consisting of sodium bromide and polymeric material was discarded. The volume of the alcohol solution was reduced to about 150 ml. by evaporation under slightly diminished pressure. One liter of benzene was added, the insoluble material separated by filtration and the benzene filtrate dried over anhydrous magnesium sulfate. Evaporation of the solvent left an oil which crystallized when allowed to stand in the cold. After recrystallization from a cyclohexane–ethanol mixture (9:1), the hydroxy sulfide melted at 64.5–65.5°; yield 25 g. (32%).

Anal. Calcd. for $C_5H_{10}OS_2$: C, 39.96; H, 6.71; S, 42.67. Found: C, 40.13; H, 6.64; S, 42.33.

The same compound was formed when 1,3-dibromo-2-propanol was used in place of the 1,2-dibromohydrin.[9]

The benzoate, made in the usual manner and recrystallized from ethanol, melted at 75–76°; yield 76%.

Anal. Calcd. for $C_{12}H_{14}O_2S_2$: C, 56.66; H, 5.55. Found: C, 56.63; H, 5.54.

The disulfone (V) was produced by dissolving 0.4 g. of the benzoate in 10 ml. of glacial acetic acid and adding to the mixture slowly and with stirring, 0.11 g. of hydrogen peroxide (30%). After the exothermic reaction had subsided, 0.22 g. of hydrogen peroxide was added rapidly. The reaction mixture was stirred at 60° for 24 hours and the white, matted crystals of the sulfone benzoate were collected on a filter; m. p. 229–230°; yield 0.43 g. (86.5%). Repeated recrystallization of the sulfone from acetone did not change its melting point.

Anal. Calcd. for $C_{12}H_{14}O_6S_2$: C, 45.27; H, 4.43. Found: C, 45.32; H, 4.46.

6-Hydroxy-1,4-dithiacycloheptane Tetroxide (VI).—This compound was prepared in the usual manner from 1.35 g. of 6-hydroxy-1,4-dithiacycloheptane in 25 ml. of glacial acetic acid and 1.8 g. of hydrogen peroxide (30%). After the mixture had been stirred at 70° for twenty-four hours, the white, needle-like crystals (VI) were collected

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[4] Kharasch and Nudenberg, *J. Org. Chem.*, **8**, 189 (1943).

[5] Tucker and Reid, THIS JOURNAL, **55**, 775 (1933).

[6] Meadow and Reid, *ibid.*, **56**, 2177 (1934).

[7] Autenrieth and Wolff, *Ber.*, **32**, 1375 (1899).

[8] Mathias, *Bol. faculdade filosofia, cienc. letras, Univer. Sao Paulo*, 14, Quimica No. **1**, 75 (1942).

[9] The melting points of the *p*-nitrobenzoates of these dibromohydrins, prepared according to the procedures of Fairbourne and Foster (*J. Chem. Soc.*, 3146, 3148 (1926)) and Conant and Quayle, (THIS JOURNAL, **45**, 2771 (1923)) were in agreement with the reported values.

on a filter, washed with cold water and dried over potassium hydroxide in a vacuum desiccator; m. p. 230–231°; yield 1.40 g. (72.5%). Removal of the solvent left a solid which weighed 0.3 g. and melted at 209–210°. Recrystallization of these solids from water raised their melting points to 233–234° and 210–211°, respectively.

The benzoate of the higher melting material, prepared in the usual manner, melted at 228–230° after recrystallization from acetone. A mixture melting point with the benzoate of 6-hydroxy-1,4-dithiacycloheptane tetroxide (V) showed no depression. Attempts to prepare the benzoate of the lower melting material failed.

1,4-Dithia-6-cycloheptanone Tetroxide (VII).—One gram of the hydroxy sulfone (VI) was suspended in 10 ml. of water to which had been added 0.92 g. of potassium dichromate. Concentrated sulfuric acid (10 ml.) was added dropwise over a period of one-half hour at 20–25°. Stirring was continued for one hour after which 50 ml. of water was added to the green reaction mixture. The ketone was collected on a filter and recrystallized from dioxane or water; yield 0.72 g. (72.7%); m. p. 252–253° (dec.).

Anal. Calcd. for $C_5H_6O_5S_2$: C, 28.29; H, 3.79; S, 30.21. Found: C, 28.68, 28.71; H, 3.66, 3.42; S, 30.07.

The phenylhydrazone was prepared by dissolving 0.2 g. of the ketone in 10 ml. of hot dioxane, cooling the solution and adding 1 ml. of phenylhydrazine and two drops of glacial acetic acid. The mixture was then heated on the steam-bath for ten minutes and cooled in ice. The addition of 20 ml. of water caused the immediate precipitation of the phenylhydrazone; m. p. 235–236° (dec.); yield 0.2 g. (70%). Recrystallization of the derivative from a dioxane–water mixture did not change its melting point.

Anal. Calcd. for $C_{11}H_{14}N_2O_4S_2$: C, 43.69; H, 4.66; N, 9.26; S, 21.21. Found: C, 43.95; H, 4.93; N, 9.24; S, 21.09.

1,4-Dithia-5-cycloheptene Tetroxide (VIII).—Five grams of 6-hydroxy-1,4-dithiacycloheptane tetroxide was dissolved in 75 ml. of hot anhydrous pyridine. The mixture was cooled in an ice-bath, and 4.6 ml. of phosphorus oxychloride was added dropwise with stirring. The reaction mixture was allowed to come to room temperature and then stirred at 60–70° for three hours. The slightly colored cycloheptene tetroxide was collected on a filter and washed well with ice-water; m. p. 279–280° (dec.); yield 3.4 g. (74%). Repeated recrystallization of the unsaturated sulfone from water raised its melting point to 280–280.5° (dec.). An aqueous solution of potassium permanganate was instantly decolorized when added to a dioxane solution of this compound.

Anal. Calcd. for $C_5H_8O_4S_2$: C, 30.60; H, 4.11. Found: C, 30.80, 30.75; H, 3.78, 3.71.

1,4-Dithiacycloheptane Tetroxide (IX).—Five grams of 10% palladium chloride on carbon[10] was reduced in 25 ml. of anhydrous dioxane at three atmospheres pressure. To the reduced catalyst a solution of 0.6 g. of the cycloheptene tetroxide (VIII) in 75 ml. of dioxane was added. The hydrogenation was completed after seven hours at three atmospheres pressure. The contents were transferred to a flask, boiled and filtered. Two additional extractions of the catalyst were carried out with 100-ml. portions of dioxane. The 1,4-dithiacycloheptane tetroxide, which separated when the combined extracts were allowed to stand in the cold, was recrystallized from water; m. p. 279–280° (dec.); yield 0.4 g. (66%).

Anal. Calcd. for $C_5H_{10}O_4S_2$: C, 30.29; H, 5.08. Found: C, 30.41; H, 5.38.

1,4-Dithiacycloheptane was synthesized in 7.9% yield (m. p. 47°) according to the procedure of Reid,[5,6] who reported the same melting point and a yield of 8.2%. The sulfone was prepared with 30% hydrogen peroxide in glacial acetic acid in a yield of 59%; m. p. 277.5–278.5° (dec.). A mixture of this sulfone with that prepared in the preceding experiment decomposed at 278–279°. The melting point of the sulfone has been given as 282°[7] and 287–288°[5,8].

Anal. Calcd. for $C_5H_{10}O_4S_2$: C, 30.29; H, 5.08. Found: C, 30.41; H, 5.00.

2-Methyl-1,4-dithiane Tetroxide.—2-Methyl-1,4-dithiane, prepared according to the method of Tucker and Reid,[5] melted at 20–22°. The reported melting point is 20°. After two sublimations at low pressure, the clear, colorless sulfide was converted to the sulfone by the usual method. It was recrystallized from water; m. p. 304–306° (dec.).

Anal. Calcd. for $C_5H_{10}O_4S_2$: C, 30.09; H, 5.11.

Summary

Ethanedithiol has been found to react with 2,3-dibromo-1-propanol or 1,3-dibromo-2-propanol to give 6-hydroxy-1,4-dithiacycloheptane. The structure of the product has been established by unequivocal methods.

(10) Mozingo, "Org. Syntheses," **26**, 77 (1946).

URBANA, ILLINOIS RECEIVED OCTOBER 14, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

A Polymer-homologous Series of Sugar Acetates from the Acetolysis of Cellulose[1]

BY E. E. DICKEY[2] AND M. L. WOLFROM

The chain scission of cellulose by hydrolysis in mineral acids and by acetolysis has yielded, in addition to D-glucose and cellobiose, specific sugars composed of three, four and six D-glucopyranose units as fragments of the original cellulose chains.[3] We wish to report herein the isolation of such a polymer-homologous series of sugars (as the α-D form of the acetates) complete from α-D-glucopyranose pentaacetate through a α-cellohexaose eicosaacetate (Table I). This has been accomplished through the application of the general method for the chromatography of sugar acetates as developed in this Laboratory.[4,5]

α-D-Glucopyranose pentaacetate, *aldehydo*-D-glucose heptaacetate[6] and α-cellobiose octaacetate

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[1] Presented before the combined meeting of the Division of Cellulose Chemistry and the Division of Sugar Chemistry and Technology at the 114th Meeting of the American Chemical Society, Portland, Oregon, September 13-17, 1948.

[2] Research Foundation Associate, The Ohio State University, Project 212.

[3] A survey of the products obtained from the acid degradation of cellulose may be found in E. Heuser, "The Chemistry of Cellulose," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 512-515.

[4] W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945).

[5] L. W. Georges, R. S. Bower and M. L. Wolfrom, *ibid.*, **68**, 2169 (1946).

[6] K. Freudenberg and K. Soff, *Ber.*, **70**, 264 (1937).