for 4 hr. Dilution of the yellow solution with aqueous methanol gave a pale yellow crystalline precipitate (80 mg) with blue fluorescence. Its ir spectrum was superimposable with that of **3e** prepared by cyanide ion catalyzed dimerization of **1e** in DMF.

Benzildianil (4a).—A solution of α,α'-dianilinostilbene (1 g) in a mixture of chloroform (120 ml) and methanol (25 ml) was kept standing in an open beaker at room temperature under the hood. After 12 hr, when all solvent had evaporated the brownish crystalline residue was washed with little methanol and recrystallized from boiling methanol, yield 800 mg (80%), mp 146–148° (lit. 145–147°).

Anal. Calcd for $C_{26}H_{20}N_2$ (360.44): C, 86.63; H, 5.59; N, 7.77. Found: C, 86.49; H, 5.60; N, 7.70.

The oxidation of α,α'-dianilinostilbenes **3b–3e** was carried out in the same manner as described for **3a**.

4,4'-Dimethylbenzildianil (4b).—Yellow crystals, mp 149–150°, yield 90%.

Anal. Calcd for $C_{28}H_{24}N_2$ (388.49): C, 86.56; H, 6.23; N, 7.21. Found: C, 86.61; H, 6.32; N, 7.20.

4,4'-Dimethoxybenzil Dianil (4c).—Yellow crystals, mp 153–154°, yield 75%.

Anal. Calcd for $C_{28}H_{24}N_2O_2$ (420.49): C, 79.97; H, 5.75; N, 6.66. Found: C, 79.90; H, 5.82; N, 6.66.

3,4-Methylenedioxy-3',4'-methylenedioxybenzil Dianil (4d).—Yellow crystals, mp 127–128°, yield 95%.

Anal. Calcd for $C_{28}H_{20}N_2O_4$ (448.46): C, 74.99; H, 4.50; N, 6.25. Found: C, 74.74; H, 4.65; N, 6.21.

Benzil-4,4'-dimethyl Dianil (4e).—Yellow crystals, mp 163–164°, yield 96%.

Anal. Calcd for $C_{28}H_{24}N_2$ (388.49): C, 86.56; H, 6.23; N, 7.21. Found: C, 86.46; H, 6.15; N, 7.26.

1,3,4,5-Tetraphenylimidazolone-2 (5).—Phosgene was introduced into a solution of α,α'-dianilinostilbene (3.62 g, 10 mmol) in methylene chloride (250 ml) and pyridine (2 ml) which was agitated with a stream of nitrogen. By varying the rate of nitrogen introduction, the reaction temperature was kept between 20 and 26°. The solution first turned dark brown and then light yellow. After 1 hr the reaction mixture was diluted with 20 ml of methanol and 0.5 ml of concentrated hydrochloric acid. Vacuum evaporation of the methylene chloride and dilution of the residual methanol solution with 10 ml of water gave 3 g (77%) of colorless crystalline precipitate, mp 208–209° (lit.[10] 207°).

Anal. Calcd for $C_{27}H_{20}N_2O$ (388.45): C, 83.48; H, 5.19; N, 7.21. Found: C, 83.7; H, 5.26; N, 7.24.

Registry No.—**2e**, 24099-47-6; **3a**, 24099-48-7; **3b**, 24099-49-8; **3c**, 24099-50-1; **3d**, 24099-51-2; **3e**, 24099-52-3; **4b**, 21854-88-6; **4c**, 21854-89-7; **4d**, 24099-55-6; **4e**, 24099-56-7.

Acknowledgments.—The author is indebted to Mrs. D. V. Temple for recording ir and uv spectra, to Mr. J. D. Cargioli for recording 100-Mc nmr spectra, and to Miss W. Racela for elemental analyses.

(10) H. Biltz, *Justus Liebigs Ann. Chem.*, **368**, 156 (1909).

Reactions of *gem*-Dithio Compounds

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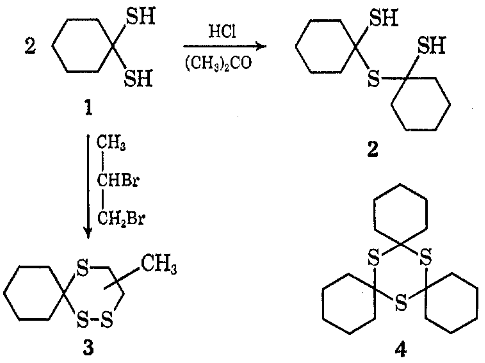
Received September 28, 1969

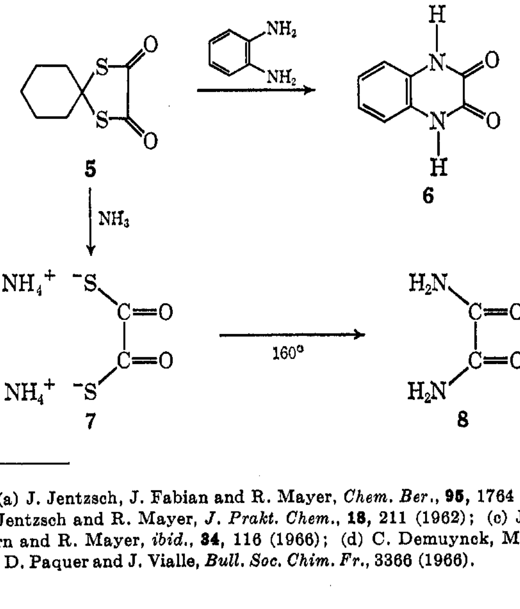
The relatively stable *gem*-dithiol function is intriguing when compared with the analogous *gem*-diols, which undergo spontaneous dehydration to yield carbonyl groups. It was our desire to further extend the interesting chemistry already reported on this system, and which often resulted from cleavage of the dithio group.[1]

Cyclohexane-1,1-dithiol (**1**) reacted in acidified acetone to yield bis(1-mercaptocyclohexyl) sulfide (**2**) in preference to a 1,3-dithietane which could arise through dithioketal formation with acetone. Compound **2** represents the dimer intermediate in the synthesis of 2,4,6-tris(pentamethylene)-1,3,5-trithiane (**4**), a known product of reaction of cyclohexane-1,1-dithiol with hydrogen chloride.[1a]

A displacement reaction between cyclohexane-1,1-dithiol and 1,2-dibromopropane in alkaline medium did not yield a dithioketal but afforded instead the trithiane **3**. This product must arise by capture of a sulfur from a second molecule of cyclohexane-1,1-dithiol.



The facile cleavage of *gem*-dithio compounds was observed in the following two reactions. 2,3-Dioxyquinoxaline (**6**) formed rapidly upon admixture of equimolar amounts of 2,2-pentamethylene-1,3-dithiolane-4,5-dione (**5**) and *o*-phenylenediamine in benzene. The substitution of excess ammonia for *o*-phenylenediamine in this reaction gave as an isolable intermediate, ammonium 1,2-dithiooxalate (**7**). Ammonium 1,2-dithiooxalate gave a quantitative yield of oxamide upon being heated to 160°. Although the products isolated from the reactions of 2,2-pentamethylene-1,3-dithiolane-4,5-dione (**5**) with *o*-phenylenediamine and with ammonia suggest different reaction mechanisms, this



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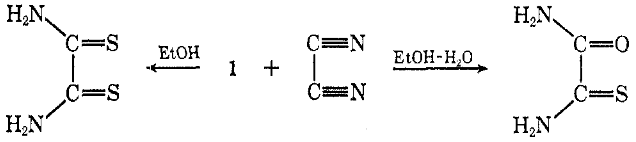
[1] (a) J. Jentzsch, J. Fabian and R. Mayer, *Chem. Ber.*, **95**, 1764 (1962); (b) J. Jentzsch and R. Mayer, *J. Prakt. Chem.*, **18**, 211 (1962); (c) J. Morgenstern and R. Mayer, *ibid.*, **34**, 116 (1966); (d) C. Demuynck, M. Demuynck, D. Paquer and J. Vialle, *Bull. Soc. Chim. Fr.*, 3366 (1966).

need not be the case. We assume that dithiooxalate is displaced in both instances by attack of nitrogen at the dithioketal carbon. Ammonium dithiooxalate is stable at room temperature, whereas the salt with *o*-phenylenediamine may lose hydrogen sulfide spontaneously to give 2,3-dioxyquinoxaline (**6**). When potassium dithiooxalate[2] is mixed with *o*-phenylenediamine hydrochloride in dilute hydrochloric acid, compound **6** is formed readily. Dithiooxalic acid is unstable and even its metal salts vary greatly in stability.[2]

The loss of hydrogen sulfide from cyclohexane-1,1-dithiol was observed in a capricious reaction with cyanogen. Depending on reaction conditions, rubeanic acid (dithiooxamide) (**9**) or thiooxamide (**10**) is formed.



9 **10**

Oxidation of cyclohexane-1,1-dithiol with hydrogen peroxide yielded cyclohexanone.

Experimental Section[3]

Bis(1-mercaptocyclohexyl) Sulfide (2).—A solution of 14.8 g of cyclohexane-1,1-dithiol[1a] in 50 ml of acetone was added to 100 ml of acetone saturated with hydrogen chloride. After 15 min. of stirring, the solvent was removed under vacuum. The residue, dissolved in ether, was washed with water until neutral. Magnesium sulfate was used to dry the solution. Evaporation of the solvent and distillation of the residue afforded 4.2 g of bis(1-mercaptocyclohexyl) sulfide (32% yield), bp 115–118° (0.9 mm). The product possessed the correct molecular weight, 262, as confirmed by mass spectroscopy. The ir spectrum was consistent with the proposed structure: ir (film) 2924, 2849, 1453, 1439, 1368, 1350, 1145, and 1120 cm^{-1}. Inspection of molecular models and comparison with the nmr data of the trithiane **4** suggested the following assignments: nmr ($CDCl_3$) δ 2.1 (m, ~4, equatorial -CHCS), 1.73 (s, ~12, 3,4,5,3′,4′,5′-CH_2) and 1.53 ppm (m, ~4, axial -CHCS). No other resonance was evident; thus the sulfhydryl protons must lie beneath the other signals and are responsible for the deviations from the calculated signal integrations.

Anal. Calcd for $C_{12}H_{22}S_3$: C, 54.90; H, 8.45; S, 36.65. Found: C, 54.76; H, 8.51; S, 36.81.

5- (or 6-) Methyl-3,3-pentamethylene-1,2,4-trithiane (3).—A mixture of 6.0 g of cyclohexane-1,1-dithiol,[1a] 3.4 g of sodium hydroxide and 8.5 g of 1,2-dibromopropane in 500 ml of ethanol was refluxed for 6 hr. The solvent was removed and the partially solid residue (NaBr) was extracted with ether. Evaporation of the ether yielded an oil which was distilled to give 4.0 g of product: bp 108–111° (0.4 mm) (bath temperature); ir (film) 2907, 2841, 1437, 1399, 1362, 1305, 1263, 1248, 1189, 1126, 1008, 867, and 754 cm^{-1}. The mass spectrum of this compound was consistent with the proposed structure. Peaks in evidence included the parent ion, *m/e* 220; propylcyclohexenyl sulfide carbonium ion, 155; cyclohexenethiol ion, 114; and cyclohexenyl carbonium ion, 81. The nmr spectrum of this product was too complex to allow unambiguous structural assignments. The signals occur between δ 1.1 and 3.6 ppm ($CDCl_3$). Four protons deshielded by proximity to sulfur gave a separated pattern centered at δ 3.1 ppm.

Anal. Calcd for $C_9H_{16}S_3$: C, 49.04; H, 7.32; S, 43.64. Found: C, 48.78; H, 7.57; S, 43.83.

2,3-Dioxyquinoxaline (6).—Admixture of two solutions of 200 mg of 2,2-pentamethylene-1,3-dithiolane-4,5-dione[1a] and of 107 mg of *o*-phenylenediamine, each in a minimum amount of benzene, yielded a precipitate immediately. The mixture was stirred for an additional 4 hr, after which 80 mg of product (50% yield) was removed by filtration, mp >300°. The ir spectrum of the product was identical with that of an authentic sample of 2,3-dioxyquinoxaline prepared by pyrolysis of a mixture of oxalic acid and *o*-phenylenediamine.[4]

Anal. Calcd for $C_8H_6N_2O_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.12; H, 3.77; N, 17.12.

Ammonium Dithiooxalate (7) and Oxamide (8).—Gaseous ammonia was passed into a solution of 1 g of 2,2-pentamethylene-1,3-dithiolane-4,5-dione[1a] in 50 ml of benzene for 25 min. An orange precipitate developed and this was removed by filtration, 640 mg (83%) yield). An analytical sample was obtained by water–acetone recrystallization. The sample did not melt, but at 160° it was quantitatively transformed into oxamide as identified by its ir spectrum which was superimposable on that of an authentic sample.

Anal. Calcd for $C_2H_8N_2O_2S_2$: C, 15.38; H, 5.16; N, 17.93; S, 41.05. Found: C, 15.23; H, 5.22; N, 17.33; S, 41.45.

Rubeanic Acid (Dithiooxamide) (9).—A solution of 6.0 g of cyclohexane-1,1-dithiol in 50 ml of 95% ethanol was slowly added to a solution of 2.0 g of cyanogen in 500 ml of 95% ethanol with cooling in ice. The yellow mixture was allowed to stand at room temperature for 2 days. The solvent was removed and the residue was triturated first with cyclohexane and then with methanol. An orange powder weighing 900 mg was obtained (40% yield).[5] The material darkened from orange to black between 180 and 210° (reported decomposition at about 200° [6]). The ir spectrum of the product was identical with that of an authentic sample of rubeanic acid. The mass spectrum showed the correct molecular ion at *m/e* 120.

Anal. Calcd for $C_2H_4N_2S$: C, 19.98; H, 3.35. Found: C, 20.26; H, 3.54.

Thiooxamide (10).—A solution of 8.0 of cyclohexane-1,1-dithiol dissolved in alcohol–water (3:1) was slowly added to a solution of 3.0 g of cyanogen in 400 ml of 95% ethanol cooled in ice. The mixture was allowed to stand at room temperature overnight. The solvent was removed and the residue was recrystallized from acetone–chloroform. This material (3.2 g) was approximately 95% pure by tlc [silica gel G, ethyl acetate–benzene (3:2)]. The ir spectrum of this sample was satisfactory but several more recrystallizations were necessary to produce an analytically pure sample, mp 180° dec (reported[7] 179–181°). The molecular weight of the product, 104, was confirmed by mass spectrometry.

Anal. Calcd for $C_2H_4N_2OS$: C, 23.07; H, 3.87; N, 26.90. Found: C, 22.98; H, 4.05; N, 26.97.

Cyclohexanone.—A solution of 14.8 g of cyclohexane-1,1-dithiol in 160 ml of 5% aqueous sodium hydroxide was cooled in ice while 200 ml of 6% aqueous hydrogen peroxide was slowly added. The excess hydrogen peroxide was decomposed with sodium thiosulfate. The solution was extracted with chloroform and the extract was dried over magnesium sulfate. Evaporation of the solvent left 4.3 g of cyclohexanone (44% yield) as confirmed by its ir absorption spectrum and its retention time on glc (5 ft × 10% Carbowax column) on comparison with authentic samples.

Registry No.—**2**, 24265-66-5; **6**, 15804-19-0; **7**, 24265-68-7; **8**, 471-46-5; **9**, 79-40-3.

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[2] H. O. Jones and H. S. Tasker, *J. Chem. Soc.*, **95**, 1904 (1909).

[3] All melting points were determined with a Mettler FPI melting point apparatus equipped with a Bausch and Lomb VOM 5 recorder. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. A Varian A-60 spectrometer was used to obtain the nmr spectra with tetramethylsilane as the internal standard. The mass spectra were determined on a Consolidated Electrodynamics Corp. Model 21-103C spectrometer at 70 eV.

[4] O. Hinsberg, *Chem. Ber.*, **41**, 2031 (1908).

[5] The theoretical yield of this reaction is calculated on the assumption that only 1 mol of hydrogen sulfide is lost from cyclohexane-1,1-dithiol. The reaction might be better performed by changing the reactant ratio so that the reaction would occur between 2 mol of cyclohexane-1,1-dithiol and 1 mol of cyanogen. The ratio used was chosen in an attempt to produce a 1:1 adduct between the reactants.

[6] P. G. Stecher, Ed., "The Merck Index," 8th ed, Merck and Co., Inc., Rahway, N. J., 1968, p 924.

[7] R. P. Welcher, M. E. Castellion and V. P. Wystrach, *J. Amer. Chem. Soc.*, **81**, 2541 (1959).