# The Reactions of 1,3-Diphenylpropane-2,2-dithiol[1]

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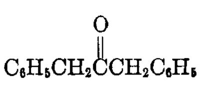
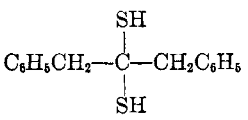
1,3-Diphenylpropane-2,2-dithiol lost the elements of hydrogen sulfide under ordinary acetylating or alkylating conditions, to form enethiol derivatives. The diacetate was obtained under special conditions. Oxidation of the dithiol led to a mixture of the disulfide derived from the enethiol and a tetrabenzyltrithiole. The dithiol reacts with chalcone, but not with more hindered $\alpha,\beta$-unsaturated ketones, forming a 1,3-dithiene derivative. It also forms unsymmetrically substituted trithianes with benzaldehyde. These various derivatives are characterized by molecular weight and n.m.r. spectra.

On treatment with hydrogen sulfide and hydrogen chloride in methanol, 1,3-diphenyl-2-propanone (I) yields 1,3-diphenyl-2,2-dithiol (II) a stable



$C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_2C_6H_5$

I

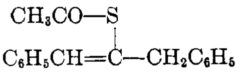


$C_6H_5CH_2{-}\underset{SH}{\overset{SH}{C}}{-}CH_2C_6H_5$

II

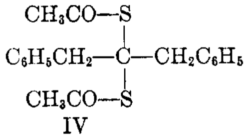
crystalline *gem*-dithiol.[2] So far, in a continuing study of the scope of this reaction,[3] I and two *p,p'*-disubstituted derivatives of I are unique in forming crystalline *gem*-dithiols under these conditions. Recently Djerassi[4] reported a method of preparing *gem*-dithiols from eneamines, which may provide further examples of this interesting class of compounds. The properties of the *gem*-dithiols, such as II, seem to differ somewhat from those of the *gem*-dithiols prepared by Cairns and co-workers[5] by treatment of carbonyl compounds with hydrogen sulfide at high pressures, or from those of the compound prepared by Barrera and Lyle[6] by addition of hydrogen sulfide to 1-methyl-4-piperidone in isopropyl alcohol.

Attempted acetylation with acetic anhydride in pyridine led to the enethiol acetate (III) rather than the expected diacetate (IV). The impure diacetate (IV) was obtained by perchloric acid catalyzed acetylation[7] of II.



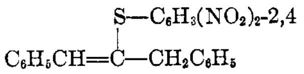
$C_6H_5CH{=}\overset{CH_3CO{-}S}{C}{-}CH_2C_6H_5$

III



$C_6H_5CH_2{-}\underset{CH_3CO{-}S}{\overset{CH_3CO{-}S}{C}}{-}CH_2C_6H_5$

IV

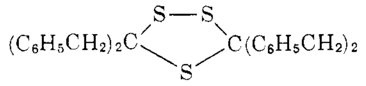


$C_6H_5CH{=}\overset{S{-}C_6H_3(NO_2)_2\text{-}2,4}{C}{-}CH_2C_6H_5$

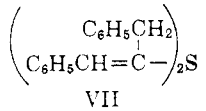
V

The loss of the elements of hydrogen sulfide was also observed on addition of 2,4-dinitrochlorobenzene to II. No product was obtained from reactions using alcoholic sodium or potassium hydroxide as catalyst, but with potassium fluoride[8] in dimethyl sulfoxide, 2,4-dinitrophenyl-1,3-diphenyl-2-propenyl sulfide (V) was obtained, along with some bis-2,4-dinitrophenyl sulfide. (Cairns and co-workers[5] report bis-2,4-dinitrophenyl sulfide as the only product of the reaction of 1,1-propanedithiol was 2,4-dinitrochlorobenzene and potassium hydroxide or pyridine.)

II was oxidized with iodine in hopes of preparing the 1,2,4,5-tetrathiane, or perhaps bis-1,3-diphenyl-2-propenyl disulfide. First attempts with iodine and a number of other oxidizing agents gave only viscous oils, probably similar to the polydisulfides encountered by Cairns and co-workers.[5] However, when one mole of iodine was added to one mole of II, in benzene at ice-bath temperature, and the mixture let stand at room temperature for two days, two crystalline products were obtained from the reaction mixture. One is 3,3,5,5-tetrabenzyl-1,2,4-trithiole (VI) and the other, bis-1,3-diphenyl-2-propenyl sulfide (VII).



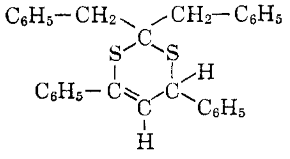
VI



$(C_6H_5CH{=}\overset{C_6H_5CH_2}{C}{-})_2S$

VII

The addition of II to chalcone in ethanolic hydrogen chloride gave 2,2-dibenzyl-4,6-diphenyl-1,3-dithiene (VIII). The n.m.r. spectrum of VIII is shown in Fig. 1. The signals for the aromatic hydrogens appear as the complex pattern at the extreme left of the figure. The vinyl hydrogen signal consists of a doublet centered at $\tau$ 3.91, spin–spin split by the adjacent tertiary hydrogen. The next doublet, centered at $\tau$ 5.43, arises from the



VIII

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[2] G. A. Berchtold, B. E. Edwards, E. Campaigne, and M. Carmack, *J. Am. Chem. Soc.*, **81**, 3148 (1959).

[3] E. Campaigne and B. E. Edwards, *J. Org. Chem.*, **27**, 3760 (1962).

[4] C. Djerassi and B. Tursch, *ibid.*, **27**, 1041 (1962).

[5] T. L. Cairns, G. L. Evans, A. W. Larchar, and B. C. McCusick, *J. Am. Chem. Soc.*, **74**, 3982 (1952).

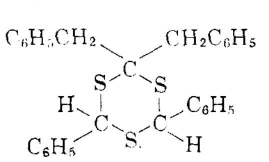
[6] H. Barrera and R. E. Lyle, *J. Org. Chem.*, **27**, 641 (1962).

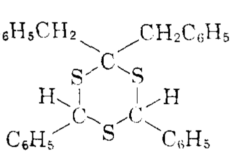
[7] G. H. Schenk and J. S. Fritz, *Anal. Chem.*, **32**, 987 (1960).

[8] N. N. Vorozhtsov, Jr., and G. G. Iakobson, *J. Gen. Chem. USSR* (Eng. Transl.), **28**, 40 (1958).

tetiary hydrogen, split by the vinyl hydrogen. The apparent doublet centered at τ 6.60 and the singlet at τ 6.92 are due to the two pairs of benzylic hydrogens. One pair, probably those of the axial benzyl group, are magnetically non-equivalent, and therefore spin–spin split each other (the AB case[9]). The outer bands of the AB quartet are revealed when this region of the spectrum is scanned at high gain level (Fig. 1, inset). $J_{AB}$ is found to be 14 c.p.s. and $\delta_{AB}$, 5 c.p.s. Attempted addition of II to dypnone, mesityl oxide, and crotonaldehyde under similar conditions gave only unchanged starting materials.

The reaction of II with benzaldehyde in ethanolic hydrogen chloride gave two isomeric products, IXa and IXb, separated by chromatography


IXa


IXb

on a column of silicic acid. IXa, m.p. 168–169°, is assigned the *trans* configuration, and IXb, m.p. 166–167°, the *cis* on the basis of their n.m.r. spectra (Fig. 2). The spectrum of IXa shows only one peak (τ 5.32) for the ring hydrogens and one peak (τ 6.88) for the methylene hydrogens (ratio 2:1), indicating a boat (twist) or rapidly flipping chair configuration[10] in which the two ring hydrogens and the two pairs of methylene hydrogens cannot be differentiated. IXb clearly shows the characteristic peak (τ 4.85 in carbon disulfide) for axial (*cis*) ring hydrogens in a rigid chair trithiane.[10] The two peaks (τ 6.58, 6.98) are characteristic of one axial and one equatorial methylene group on the trithiane. The three peaks are in the expected ratio, 1:1:1.

The reaction of II with cinnamaldehyde in ethanolic hydrogen chloride gave, in low yield, a white solid, m.p. 215–216°, after recrystallization from dimethoxyethane. The remainder of the reaction mixture was a red-brown ether-soluble oil, which on the basis of thin-layer chromatographic analysis consisted of at least ten components. Elemental analysis of the product melting at 215–216° suggests that it is analogous in structure to IX. However, the product is too insoluble in available solvents to allow the determination of its molecular weight or n.m.r. spectrum.

## Experimental

Hydrogen sulfide and hydrogen chloride gases were obtained in cylinders from the Matheson Co., Inc. Melting points are capillary and corrected. Infrared spectra were

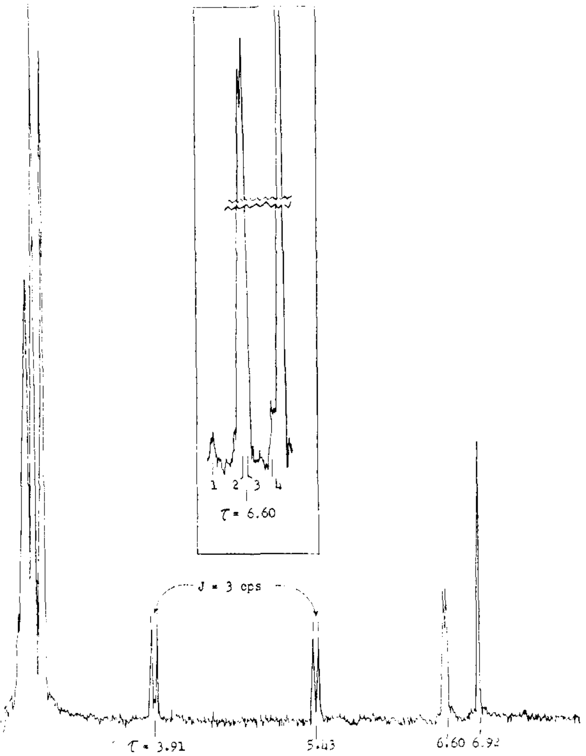


Fig. 1.—N.m.r. spectrum of VIII in carbon disulfide.

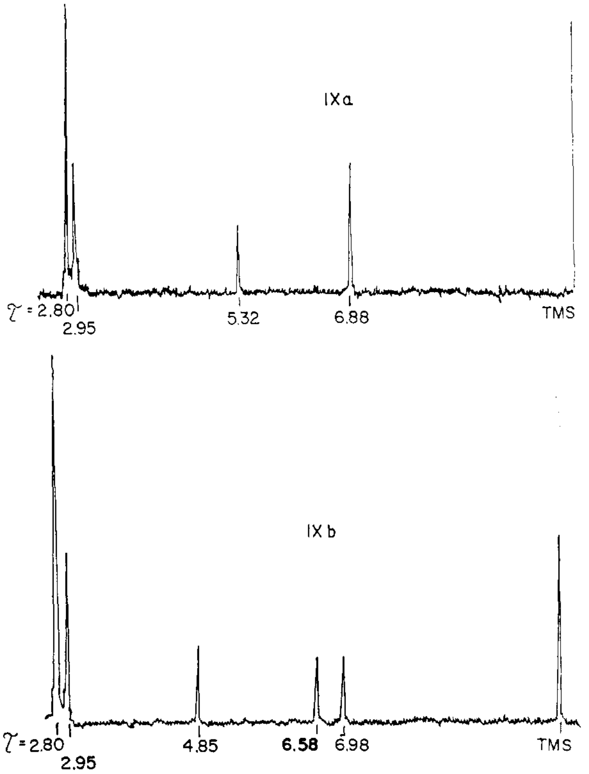


Fig. 2.—N.m.r. spectra of IXa and IXb in carbon disulfide.

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[9] P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957).

[10] E. Campaigne, N. F. Chamberlain, and B. E. Edwards, *J. Org. Chem.*, **27**, 135 (1962). E. Campaigne, *et al.*, *ibid.*, **27**, 4428 (1962).

determined in potassium bromide mulls, and ultraviolet spectra in cyclohexane solutions. N.m.r. spectra were obtained in solvents noted on a Varian Associates Model Hr 60 high resolution spectrometer with the assistance of Mr. Art Clause. Peak positions were determined relative to internal tetramethylsilane by the usual side band technique. Microanalyses were carried out by Midwest Microlabs, Inc. Molecular weights were determined using a Mechrolabs vapor pressure osmometer, Model 301A, in solvents noted.

**1,3-Diphenylpropane-2,2-dithiol (II).**[2]—The following is an improved preparation of II. A solution of 14 g. (0.066 mole) of 1,3-diphenyl-2-propanone (I) (Eastman practical grade, recrystallized to m.p. 34°) in 50 ml. of absolute methanol was saturated with hydrogen sulfide and hydrogen chloride at 0–5° with stirring. The solution turned pink almost immediately. After 4.5 hr., a white solid appeared. After 6 hr. the flask was stoppered and stored in a refrigerator overnight. The white solid was collected on a fritted glass funnel, washed with cold methanol, and dried in a vacuum desiccator over sodium hydroxide, yielding 13.5 g. of faintly pink crystals, m.p. 73–76°. The mother liquor yielded an additional 1.25 g., m.p. 70–75°, on evaporation and recrystallization of the residue. Total crude yield was 85%. The material was further recrystallized from *n*-pentane to m.p. 80–81°, $\nu_{max}$ 2564 cm.$^{-1}$, $\lambda_{max}$, m$\mu$ (log $\epsilon$); 248.5 (2.69), 253 (2.73), 259 (2.76), 266 (2.65); n.m.r. $\tau$ 2.78, 6.84, 7.78.

**1,3-Diphenyl-2-thioacetylpropene (III).**—To 0.46 g. (0.178 mole) of II was added 0.44 ml. (0.45 mole) of acetic anhydride in 5 ml. of anhydrous pyridine. The solution was stoppered and let stand at room temperature for 18 hr. The resulting dark orange solution was partially evaporated in a stream of air, 5 ml. of 2 *N* hydrochloric acid were added, the mixture shaken and extracted with ether. The extract was washed with 5% sodium bicarbonate, dried over magnesium sulfate and treated with Norit. The ether was evaporated and the yellowish brown residual oil was dissolved in *n*-pentane and refrigerated. After a number of recrystallizations in which both a white solid and a yellow oil were present, 0.08 g. (19%) of a pure white crystalline solid, m.p. 45–46°, was obtained, $\nu_{max}$ 1681 cm.$^{-1}$, $\lambda_{max}^{cyclohexane}$ 259 m$\mu$ (log $\epsilon$ 4.08).

*Anal.* Calcd. for $C_{17}H_{16}OS$: C, 76.08; H, 6.01; S, 11.95. Found: C, 76.72; H, 6.16; S, 11.70.

**1,3-Diphenylpropane-2,2-dithiol Diacetate (IV).**—To 0.2 g. of II in 1 ml. of acetic anhydride was added 8 ml. of absolute ethyl acetate containing 2 drops of 66% perchloric acid. The solution was let stand at room temperature for 4 hr., then evaporated to half its original volume in a stream of nitrogen, poured into water, and the mixture extracted with ether. The ether extract was washed with sodium bicarbonate, saturated sodium chloride solution and dried over magnesium sulfate. Evaporation of the ether and recrystallization of the residue from *n*-hexane gave 0.16 g. (60%) of IV as white needles, m.p. 83–87°, $\nu_{max}$ 1695, 1669 cm.$^{-1}$, $\lambda_{max}$, m$\mu$ (log $\epsilon$); 266 (2.74), 235.5 (3.83), n.m.r. $\tau$ 6.33, 7.81. Repeated recrystallization from hexane, cyclohexane, and benzene did not alter the melting point.

*Anal.* Calcd. for $C_{19}H_{20}O_2S_2$: C, 66.24; H, 5.85; S, 18.62; mol. wt., 348.5. Found: C, 66.66, 66.99; H, 6.35, 6.19; S, 17.63, 17.72; mol. wt. ($CCl_4$), 350.

**1,3-Diphenyl-2-(2′,4′-dinitrophenylthio)propene (V).**—To 0.51 g. (2.5 mmoles) of 2,4-dinitrochlorobenzene and 0.29 g. (5 mmoles) of potassium fluoride[8] in 5 ml. of dimethyl sulfoxide was added 0.35 g. (1.25 mmoles) of II. The mixture was stirred vigorously at room temperature. A red color appeared at the surface of the undissolved potassium fluoride, but was dissipated by stirring. After 1 hr. the red color no longer appeared. The resulting yellow solution was poured into 50 ml. of ice water. The mixture was extracted with ether, the extract washed with water, then saturated sodium chloride solution, and dried over magnesium sulfate. A yellow solid, insoluble in ether or water, which appeared at the interface during the extraction was collected by filtration. The material was recrystallized from benzene–acetone, yielding 145 mg. (0.4 mmole) of bis-2,4-dinitrophenylsulfide, m.p. 196–197°.[11] The ether extract was evaporated to dryness and the residue recrystallized repeatedly from ethanol to give 80 mg. of yellow needles, m.p. 135–136°.

*Anal.* Calcd. for $C_{21}H_{16}O_4N_2S$: C, 64.10; H, 4.36; N, 7.12; S, 8.15. Found: C, 63.64; H, 4.23; N, 6.96; S, 8.01.

**Oxidation of 1,3-Diphenylpropane-2,2-dithiol.**—A solution of 2.5 g. (0.01 mole) of iodine in 50 ml. of benzene was added, with stirring, to 2.6 g. (0.01 mole) of II in 100 ml. of benzene in an ice bath. The first portion of the iodine was rapidly decolorized, but the color soon persisted. The flask was allowed to warm to room temperature and stirring was continued for 2 days. The unchanged iodine was then destroyed by washing the benzene solution with aqueous sodium bisulfite. The pale yellow benzene layer was washed with saturated sodium chloride solution and dried over Drierite. Evaporation of the benzene at reduced pressure gave a reddish semisolid which was extracted with hot *n*-hexane. The *n*-hexane soluble material was treated with Norit and recrystallized from *n*-hexane–chloroform to give 0.30 g. of 3,3,5,5-tetrabenzyl-1,2,4-trithiole (VI), m.p. 144–145°.

*Anal.* Calcd. for $C_{30}H_{28}S_3$: C, 74.31; H, 5.15; S, 19.84; mol. wt., 484. Found: C, 74.47; H, 5.85; S, 19.84; mol. wt. ($CHCl_3$), 485.

The *n*-hexane-insoluble residue was a pale beige powder which on treatment with Norit and recrystallization from chloroform gave 0.31 g. of bis-1,3-diphenyl-2-propenyl sulfide (VII), m.p. 212–213°.

*Anal.* Calcd. for $C_{30}H_{26}S$: C, 86.07; H, 6.28; S, 7.65; mol. wt., 420. Found: C, 86.19; H, 6.48; S, 7.55; mol. wt. ($CHCl_3$), 415.

**4,6-Diphenyl-2,2-dibenzyl-1,3-dithiene (VIII).**—To 2 g. of II in 100 ml. of ethanol saturated with hydrogen chloride was added 1.54 g. of chalcone in 20 ml. of hydrogen chloride saturated ethanol. The solution was allowed to stand overnight at room temperature, then placed in a refrigerator for 2 days. A peach-colored, flaky solid was collected, washed, and air-dried. On warming in cyclohexane, a portion of the material dissolved, leaving an orange oil, immiscible in cyclohexane. The cyclohexane solution was decanted from the oil, and on cooling, 1.93 g. (57%) of white crystalline material was deposited from the solution. Further recrystallization of this material from cyclohexane gave VIII, m.p. 120–121°, $\lambda_{shoulder}$ m$\mu$ (log $\epsilon$), 258 (3.84), 285 (3.59), n.m.r., see Fig. 1.

*Anal.* Calcd. for $C_{30}H_{26}S_2$: S, 14.26; mol. wt., 451. Found: S, 14.11; mol. wt. ($CCl_4$), 462.

**Addition of II to Benzaldehyde (IX).**—To 0.26 g. (1 mmole) of II in 5 ml. of ethanol saturated with hydrogen chloride was added 0.10 g. (1 mmole) of benzaldehyde in 1 ml. of ethanol saturated with hydrogen chloride. The mixture was warmed to complete the solution of II, then let stand at room temperature for 36 hr. The pale yellow solution was evaporated to one half its original volume in a stream of dry air, and the resulting solid collected, (0.22 g.). This solid was chromatographed on a column of 12 g. of 100 mesh silicic acid in *n*-hexane–10% chloroform. Assay of the chromatographic fractions by thin-layer chromatography showed two major fractions: IXa, m.p. 168–169°, 28 mg., and IXb, m.p., 166–167°, 103 mg.

*Anal.* Calcd. for $C_{29}H_{26}S_3$: C, 74.00; H, 5.58; S, 20.49; mol. wt., 470. Found: (IXa) C, 73.88; H, 5.51; S, 19.94; mol. wt. ($CHCl_3$), 465. Compound (IXb) C, 74.31; H, 5.65; S, 20.43; mol. wt. ($CHCl_3$), 475. For n.m.r. of both structures, see Fig. 2.

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[11] V. O. Lukashevich and M. M. Sergoeva, *J. Gen. Chem. USSR*, **19**, 1487 (1949).