

1,3-Dithioles and 1,3-Dithiole-S-oxides (1)

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1,3-Dithioles have been prepared by a new route from α -haloketones and a *gem*-dithiol. The reaction was carried out with aliphatic and aromatic α -haloketones, which were condensed with 1,3-diphenylpropane-2,2-dithiol to give 2,2-dibenzyl-4-hydroxy-1,3-dithiolanes. These intermediates were dehydrated in the presence of acids to 2,2-dibenzyl-1,3-dithioles. Two of the 2,2-dibenzyl-1,3-dithioles were oxidized with hydrogen peroxide to the corresponding S-dioxides, S-trioxides, and S-tetroxides, which were separated by preparative thin layer chromatography. The condensation of 1,3-diphenylpropane-2,2-dithiol with oxalyl chloride gave 2,2-dibenzyl-1,3-dithiolane-4,5-dione. Infrared and n.m.r. data of these compounds confirm the structural assignments.

The 1,3-dithiole system has been reported previously in the form of its 2-thione or its 2-ylidene derivatives (2-8). Furthermore, 1,3-dithioles have been prepared which carry nitrile groups in positions 4 and 5, or are fused with aromatic ring systems (9-13).

The synthesis of the 2,2-disubstituted 1,3-dithiole system with various substituents in the 4 and 5 positions has now been accomplished by the reaction of α -haloketones with the stable *gem*-dithiol, 1,3-diphenylpropane-2,2-dithiol (1), which can be obtained in excellent yield from 1,3-diphenyl-2-propanone and hydrogen sulfide in the presence of hydrogen chloride (14). The reaction of 1 with α -haloketones produced the 2,2-dibenzyl-4-hydroxy-1,3-dithiolanes 3a and 3b, which could be isolated because of their insolubility. Dehydration of 3a and 3b to the corresponding 1,3-dithioles was carried out under mild conditions by saturating an ether solution of 3 with dry hydrogen chloride. In the cases where no crystalline 4-hydroxy-1,3-dithiolane was isolated, the dehydration was achieved by the addition of sulfuric acid to the solution of the crude product in ethanol.

The first step in 1,3-dithiole formation probably consists of the alkylation of one of the *gem*-dithiol groups with α -haloketone. The alkylated product (2) undergoes cyclization by the addition of the free thiol group to the carbonyl group to form 3, which can be dehydrated in the presence of acids to the 1,3-dithiole system (4).

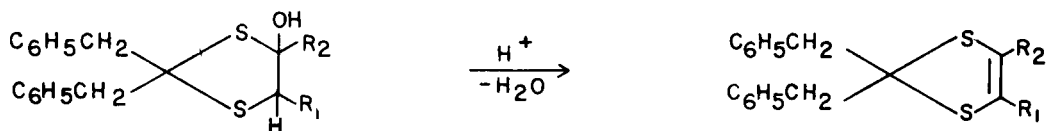
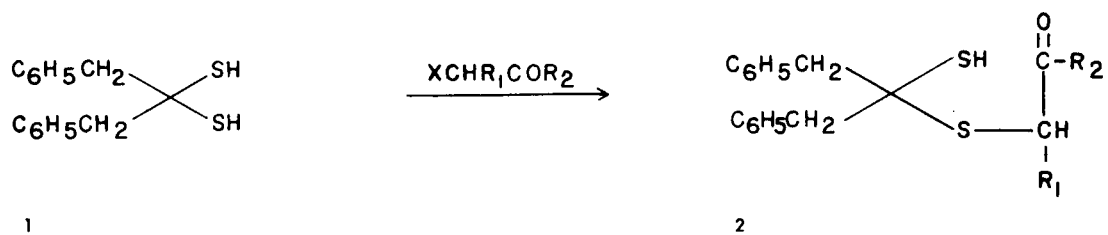
Previous alkylation and acetylation studies of 1 (15) showed that the vinyl sulfide (5a) or the vinyl thiolacetate (5b) were produced by the elimination of hydrogen sulfide from the mono-substituted dithiol. Elimination of hydrogen sulfide did not occur under the mild conditions used in this work when an α -haloketone was the alkylating agent. Rather, the stable five-membered 1,3-dithiole ring was obtained. However, when the reaction product of 1 with phenacyl bromide was warmed, hydrogen sulfide was eliminated and phenacyl 1,3-diphenyl-2-propenyl sulfide

(5c) was isolated and identified. The same product was obtained earlier (16) in the reaction of 1 with phenacyl bromide in pyridine, but was not fully characterized at that time.

Acetylation of both thiol groups in 1 was achieved only under specific conditions which avoided the elimination of hydrogen sulfide (15). However, with oxalyl chloride, acylation of 1 occurred very easily, and 2,2-dibenzyl-1,3-dithiolane-4,5-dione (6) was obtained. The analogous formation of 1,3-dithiolane-4,5-diones by the reaction of *gem*-dithiols with oxalyl chloride has been investigated previously (17).

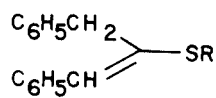
In connection with studies on the 1,3-dithiolium system, it seemed interesting to attempt the conversion of the 1,3-dithioles into the pseudo-aromatic 1,3-dithiolium salts. Reaction of 2-benzylidene-4-phenyl-1,3-dithiole with perchloric acid to afford 2-benzyl-4-phenyl-1,3-dithiolium perchlorate has been reported (5). In the reaction of 2,2-dibenzyl-4-phenyl-1,3-dithiole (4a) with perchloric acid, elimination of one of the benzyl groups as toluene to form 2-benzyl-4-phenyl-1,3-dithiolium perchlorate might occur. Although transformation of a non-aromatic heterocyclic ring system into an aromatic system by the elimination of toluene has been observed earlier (18), all attempts to achieve this with the 1,3-dithioles were unsuccessful.

In further studies of the chemistry of the 1,3-dithioles, their reactivity towards oxidizing agents was investigated. Oxidation of 1,3-dithioles with peracetic acid has been reported previously in the case of the 2-ylidene compounds, from which the corresponding disulfones were obtained (5). Several investigations have been made on the oxidation of the saturated 1,3-dithiolane system (19,20). When the 1,3-dithioles 4a and 4b were oxidized with hydrogen peroxide in glacial acetic acid, the oxidation products 7-9 were obtained. In all oxidation reactions, mixtures of the oxidation products were found. The mixtures were separated by preparative t.l.c., since purification by recrystallization was unsuccessful.

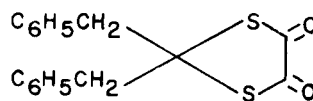


3a, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$
 b, $\text{R}_1 = \text{H}; \text{R}_2 = \text{CH}_3$

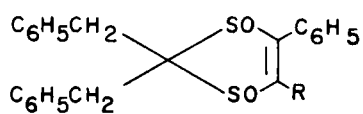
4a, $\text{R}_1 = \text{H}; \text{R}_2 = \text{C}_6\text{H}_5$
 b, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$
 c, $\text{R}_1 = \text{H}; \text{R}_2 = \text{CH}_3$
 d, $\text{R}_1 = \text{H}; \text{R}_2 = \text{p-NO}_2\text{C}_6\text{H}_4$
 e, $\text{R}_1 = \text{H}; \text{R}_2 = \text{p-CH}_3\text{OC}_6\text{H}_4$



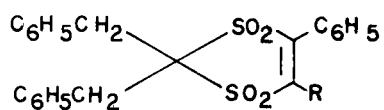
5a, $\text{R} = 2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3$
 b, $\text{R} = \text{COCH}_3$
 c, $\text{R} = \text{CH}_2\text{COC}_6\text{H}_5$



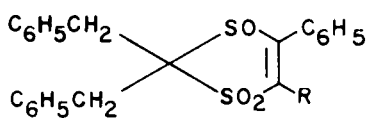
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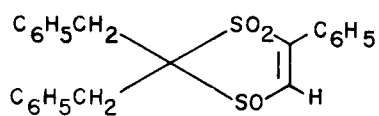
7a, $\text{R} = \text{H}$
 b, $\text{R} = \text{C}_6\text{H}_5$



8a, $\text{R} = \text{H}$
 b, $\text{R} = \text{C}_6\text{H}_5$



9a, $\text{R} = \text{H}$
 b, $\text{R} = \text{C}_6\text{H}_5$



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Table I

Infrared Data of 1,3-Dithiole-1,3-oxides (a)

1,3-Dithiole-1,3-oxide	ν (SO ₂) (cm ⁻¹)	ν (SO) (cm ⁻¹)
7a		1035
		1058 (b) (B)
7b		1045 (b)
		1060 (B)
8a	1328 (B)	1122
8b	1310 (b)	1138 (b)
	1325	1150
9a	1298	1130 1060 (B)
9b	1300	1135 1060
		1072 (b) (B)

(a) Infrared spectra were determined in potassium bromide discs. (b) Band of higher intensity. B = broad.

Table II

Oxidation of 1,3-Dithioles with Hydrogen Peroxide in Glacial Acetic Acid

1,3-Dithiole	Conditions		% Yields (a) of Products
	Time (hrs.)	Temp. (°C)	
4a	48	25	30% 7a, 14% 9a
	10	75	58% 9a, 8a (b)
	40	75	43% 8a, 9a (b)
4b	60	25	58% 7b, 14% 9b
	40	75	47% 9b, 28% 8b

(a) Isolated from preparative t.l.c. plates; (b) Compound was identified by its R_f value, but not recovered from the t.l.c. plates.

Table III (a)

N.m.r. Data of 1,3-Dithiolanes and 1,3-Dithioles

Compound	τ values	Multiplicity (J = c.p.s.)	No. of Protons	Proton Assignments
3a	2.25-3.50	m	20	Aromatic
	6.71	s	4	Benzylic
	7.05	s	1	C ₄ -OH
	6.00	s	1	C ₅ -H
3b	2.45-2.83	m	10	Aromatic
	6.82	s	2	Benzylic
	6.85	s	2	Benzylic
	7.32	s	1	C ₄ -OH
	8.52	s	3	C ₄ -CH ₃
	6.82	d (12)	1	C ₅ -H
	6.85	d (12)	1	C ₅ -H
4a	2.50-2.91	m	15	Aromatic
	6.68	s	4	Benzylic
	4.12	s	1	C ₅ -H
4b	2.33-3.42	m	20	Aromatic
	6.65	s	4	Benzylic
4c	2.58-2.92	m	10	Aromatic
	6.67	s	4	Benzylic
	8.38	d (1.5)	3	C ₄ -CH ₃
	4.87	q (1.5)	1	C ₅ -H
4d	1.88-2.88	m	14	Aromatic
	6.67	s	4	Benzylic
	3.90	s	1	C ₅ -H
4e	2.50-3.67	m	14	Aromatic
	6.68	s	4	Benzylic
	6.30	s	3	CH ₃ -O
	4.27	s	1	C ₅ -H
5c	2.12-2.93	m	15	Aromatic
	3.40	broad s	1	Vinyllic
	6.12	s	2	α -H to CO
	6.20	broad s	2	Benzylic
6	2.67-2.83	m	10	Aromatic
	6.57	s	4	Benzylic
7a	2.33-3.08	m	16	Aromatic and C ₅ -H
	6.30	s	2	Benzylic
	6.72	s	2	Benzylic
7b	2.25-3.12	m	20	Aromatic
	6.25	s	2	Benzylic
	6.63	s	2	Benzylic
8a	2.33-2.95	m	15	Aromatic
	6.43	s	4	Benzylic
	3.30	s	1	C ₅ -H
8b	2.25-3.17	m	20	Aromatic
	6.37	s	4	Benzylic
9a	2.33-3.08	m	16	Aromatic and C ₅ -H
	6.15	d (15)	1	Benzylic
	6.45	d (15)	1	Benzylic
	6.47	d (15)	1	Benzylic
9b	2.25-3.25	m	20	Aromatic
	6.12	d (15)	1	Benzylic
	6.38	d (15)	1	Benzylic
	6.37	d (15)	1	Benzylic
	6.63	d (15)	1	Benzylic

(a) Spectra were obtained with a Varian A-60 spectrometer, using chloroform-d as solvent and tetramethylsilane as an internal standard; s = singlet, d = doublet, q = quartet, m = multiplet.

Although attempts to form only one of the isomeric oxides failed, it was possible to change the product ratios by variation of the reaction conditions (Table II).

The infrared spectra of 7-9 indicated that the oxidation products of 4a and 4b were cyclic disulfides (7), disulfones (8) or sulfoxide-sulfones (9). Absorption bands of the sulfoxide and sulfone groups are summarized in Table I. Absorption frequencies of the sulfoxide and sulfone bands slightly exceeded the ranges reported by Bellamy (21), but were in agreement with the values found for 1,3-dithiolane-1,3-oxides (20) in the range 1037-1085 cm^{-1} for the sulfoxide band, and 1129-1149 cm^{-1} and 1285-1339 cm^{-1} for the sulfone frequencies.

The structures of the oxidation products 7-9 were furthermore supported by their n.m.r. spectra (Table III). The n.m.r. data were especially helpful in those instances where the formation of geometrical isomers was possible. In the disulfides 7, the oxygen atoms can be either *cis* or *trans*. Formation of *cis* and *trans* isomers has been reported for 2,2-diphenyl-1,3-dithiolane-1,3-dioxide (19). In the case of 7a and 7b only one isomer was detected by t.l.c., and it was assigned the *cis* configuration on the basis of its n.m.r. spectrum, which showed two singlets for the benzylic protons, thus indicating different environments for the two methylene groups. Formation of the *cis* isomer would be favored since both oxides could be in the energetically more stable equatorial positions.

A comparison of the chemical shift values of the C_5 proton in the oxidation products 7a, 8a, and 9a showed a rather unexpected deshielding effect; in the dioxide and trioxide the signal occurred further downfield than in the tetroxide, thus giving evidence that the sulfoxide group has a stronger deshielding effect than the sulfone group. It is not possible to decide whether the trioxide from 4a has structure 9a or 10 on the basis of the available data. The n.m.r. spectra of all other compounds could be easily interpreted, and were used in support of the assigned structures. The positions of the hydroxylic protons in the 4-hydroxy-1,3-dithioles (3) were determined by exchange with deuterium oxide.

EXPERIMENTAL (22)

2,2-Dibenzyl-4-hydroxy-4,5-diphenyl-1,3-dithiolane (3a).

To a solution of 2.6 g. (0.01 mole) of 1 in 50 ml. of ethanol, 2.0 g. of sodium bicarbonate and 2.3 g. (0.01 mole) of desyl chloride were added. The mixture was stirred for 48 hours at room temperature. The precipitate was collected by filtration, washed with water, dried and recrystallized from *n*-hexane to give 2.3 g. (51%) of 3a as white cubic crystals which melted at 150-153° to a pink liquid.

Anal. Calcd. for $\text{C}_{28}\text{H}_{26}\text{O}_2\text{S}_2$: C, 76.61; H, 5.76; S, 14.10. Found: C, 76.84; H, 6.05; S, 13.97.

2,2-Dibenzyl-4-hydroxy-4-methyl-1,3-dithiolane (3b).

A solution of 5.2 g. (0.02 mole) of 1 in 50 ml. ethanol was treated with 4.0 g. of sodium bicarbonate and 1.86 g. (0.02 mole) of α -chloroacetone as above. Water was added and the precipitate was collected by filtration, dried and recrystallized from *n*-hexane to give 3.6 g. (57%) of 3b as colorless crystals, m.p. 79-80°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}_2$: C, 68.31; H, 6.37; S, 20.26. Found: C, 68.17; H, 6.34; S, 20.16.

2,2-Dibenzyl-4-phenyl-1,3-dithiole (4a).

A suspension of 5.2 g. (0.02 mole) of 1, 4.0 g. sodium bicarbonate and 4.0 g. (0.02 mole) phenacyl bromide in 100 ml. ethanol was stirred for 48 hours at room temperature, and 35 ml. of 96% sulfuric acid was added to the chilled reaction mixture (-10°). The mixture was kept over-night at room temperature, water was added, and the precipitate was collected by filtration and recrystallized from glacial acetic acid to give 4.4 g. (61%) of 4a as yellow crystals, m.p. 126.5-127.5°.

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{S}_2$: C, 76.63; H, 5.59; S, 17.78. Found: C, 76.23; H, 5.51; S, 17.87.

2,2-Dibenzyl-4,5-diphenyl-1,3-dithiole (4b).

A solution of 0.50 g. (0.0011 mole) of 3a in 50 ml. anhydrous ether was treated with hydrogen chloride at 0° for 30 minutes, and allowed to stand for 30 minutes at room temperature. Evaporation of the ether yielded a white solid which was recrystallized from *n*-hexane to give 0.38 g. (79%) 4b as colorless crystals, m.p. 124.5-125.0°.

Anal. Calcd. for $\text{C}_{23}\text{H}_{24}\text{S}_2$: C, 79.78; H, 5.54; S, 14.68. Found: C, 79.73; H, 5.62; S, 14.88.

2,2-Dibenzyl-4-methyl-1,3-dithiole (4c).

A solution of 0.63 g. (0.002 mole) of 3b in 50 ml. anhydrous ether was treated with hydrogen chloride at 0° for 1 hour, and stored for two hours at room temperature. Evaporation of the ether gave an oil, which was purified by column chromatography on 100 g. aluminum oxide, standardized according to Brockmann (E. Merck). Elution with *n*-hexane gave, after removal of solvent, 0.36 g. (60%) of 4c as colorless crystals, m.p. 68-70°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{S}_2$: C, 72.43; H, 6.08; S, 21.48. Found: C, 72.47; H, 6.35; S, 21.20.

2,2-Dibenzyl-4-(*p*-nitrophenyl)-1,3-dithiole (4d).

A suspension of 2.6 g. (0.01 mole) of 1, 2.0 g. sodium bicarbonate and 2.4 g. (0.01 mole) *p*-nitrophenacyl bromide in 50 ml. methanol was stirred for 24 hours at room temperature. The solvent was evaporated at room temperature, and the residue was suspended in 150 ml. anhydrous ether. The ether solution was saturated with hydrogen chloride at 0° for 1 hour and allowed to stand for 1 hour at room temperature. After evaporation of the ether, the residue was chromatographed on a column of 200 g. aluminum oxide, standardized according to Brockmann (E. Merck), and eluted with ethyl acetate. Evaporation of the solvent yielded a yellow solid, which was recrystallized from 1-propanol to give 2.2 g. (54%) of 4d as yellow crystals, m.p. 138-142°. Two recrystallizations from 1-propanol raised the melting point to 147-148°.

Anal. Calcd. for $\text{C}_{23}\text{H}_{19}\text{NO}_2\text{S}_2$: C, 68.11; H, 4.72; N, 3.45; S, 15.81. Found: C, 68.03; H, 4.79; N, 3.42; S, 15.63.

2,2-Dibenzyl-4-(*p*-methoxyphenyl)-1,3-dithiole (4e).

A suspension of 2.6 g. (0.01 mole) 1, 2.0 g. sodium bicarbonate and 1.85 g. (0.01 mole) *p*-methoxyphenacyl chloride (23) in 50 ml. methanol was stirred for 6 hours at room temperature. The solvent was evaporated at room temperature, and the residue was suspended in 100 ml. anhydrous ether and saturated with hydrogen chloride at 0° for 30 minutes. The ether solution was poured on ice, washed with aqueous sodium bicarbonate and dried over magnesium sulfate. Evaporation of the ether afforded 3.95 g. of a colorless solid, which was recrystallized from 1-propanol to give 2.10 g. (54%) of 4e, m.p. 121-122°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{22}\text{O}_2\text{S}_2$: C, 73.80; H, 5.68; S, 16.42. Found: C, 73.73; H, 5.72; S, 16.29.

Phenacyl 1,3-diphenyl-2-propenyl sulfide (5c).

A suspension of 2.6 g. (0.01 mole) of 1, 2.0 g. sodium bicarbonate and 2.0 g. (0.01 mole) phenacyl bromide in 75 ml. ethanol was stirred for 48 hours at room temperature. The solvent was evaporated at 100°, and ethyl acetate added to the residue giving a white precipitate of salts which was removed by filtration. When the solvent was evaporated from the filtrate, a yellow oil, which crystallized partially after several days, was obtained. The solid was recrystallized three times from 1-propanol to give 0.55 g. (16%) of 5c as colorless crystals, m.p. 91-92°, ν (CO) 1670 cm^{-1} .

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{OS}$: C, 80.19; H, 5.85; S, 9.31. Found: C, 80.10; H, 5.98; S, 9.59.

2,2-Dibenzyl-1,3-dithiolane-4,5-dione (6).

A mixture of 5.2 g. (0.02 mole) of 1, 3.4 g. of sodium carbonate and 3.9 g. (0.03 mole) of oxalyl chloride in 100 ml. anhydrous ether was stirred for 48 hours at room temperature. Evaporation of the ether and extraction of the residue with water left 6.33 g. of a solid material, which was recrystallized from 1-propanol to give 5.0 g. (80%) of 6 as colorless needles, m.p. 136-137°.

Anal. Calcd. for $C_{17}H_{14}O_2S_2$: C, 64.95; H, 4.49; S, 20.39. Found: C, 65.08; H, 4.51; S, 20.55.

2,2-Dibenzyl-4-phenyl-1,3-dithiole-1,3-dioxide (7a).

A mixture of 0.90 g. (0.0025 mole) of 4a and 1.71 g. (0.015 mole) of 30% hydrogen peroxide in 100 ml. of glacial acetic acid was kept for 58 hours at room temperature, water was added and the precipitate was collected by filtration to give 0.73 g. of a pale yellow solid, which melted at 136-138°. Development of the crude product on t.l.c. plates (silica gel G, E. Merck) with chloroform gave two spots, $R_f = 0.18$ and 0.36. A sample of the crude product (200 mg.) was placed on a preparative t.l.c. plate (silica gel H, 1.5 mm. thick, E. Merck), which was developed with chloroform. The bands containing the separated materials were developed by iodine vapors, scraped off and extracted with acetone. From the top band 40 mg. (20%) of light yellow crystals, m.p. 150-153° (from 1-propanol), were obtained. These crystals proved to be identical to 9a by their infrared spectrum and R_f value. Extraction of the lower band gave 80 mg. (40%) of 7a as light yellow crystals, m.p. 145-146° (from 1-propanol).

Anal. Calcd. for $C_{23}H_{20}O_2S_2$: C, 70.38; H, 5.14; S, 16.34. Found: C, 70.56; H, 5.29; S, 16.32.

2,2-Dibenzyl-4,5-diphenyl-1,3-dithiole-1,3-dioxide (7b).

A solution of 0.44 g. (0.001 mole) of 4b in 40 ml. of glacial acetic acid, to which 0.68 g. (0.006 mole) of 30% hydrogen peroxide were added, was allowed to stand at room temperature for 60 hours. The product was precipitated by the addition of water and collected by filtration to give 0.45 g. of colorless crystals, m.p. 181-189°. Development of this material on t.l.c. plates (silica gel G) with chloroform gave two spots, $R_f = 0.23$ and 0.39. The two compounds were separated by preparative t.l.c. (silica gel H, 1.5 mm. thick); a 200 mg. sample was placed on the plate and developed with chloroform. Extraction of the upper band with acetone gave 30 mg. (15%) of 9b, m.p. 190-191°, $R_f = 0.39$. Extraction of the lower band gave 120 mg. (60%) of 7b as colorless crystals, m.p. 184-185°, $R_f = 0.23$.

Anal. Calcd. for $C_{29}H_{24}O_2S_2$: C, 74.33; H, 5.16; S, 13.68. Found: C, 74.09; H, 5.24; S, 13.69.

2,2-Dibenzyl-4-phenyl-1,3-dithiole-1,1,3,3-tetroxide (8a).

A solution of 0.90 g. (0.0025 mole) of 4a in 25 ml. of glacial acetic acid containing 1.71 g. (0.015 mole) of 30% hydrogen peroxide was kept for 40 hours at 75°, then 1.14 g. (0.01 mole) of 30% hydrogen peroxide was added and the temperature of the mixture was maintained at 75° for an additional 10 hours. The product, which was precipitated by addition of water to the cooled reaction mixture, was collected by filtration and recrystallized from 1-propanol to give 0.54 g. of colorless crystals, m.p. 167-168°. Development of these crystals on t.l.c. plates (silica gel G) with chloroform gave two spots, $R_f = 0.36$ and 0.64. Purification of a 250 mg. sample was achieved using a preparative t.l.c. plate (silica gel H, 1.5 mm. thick, chloroform). Extraction of the top band with acetone gave 210 mg. (84%) of 8a as colorless crystals, m.p. 169-170° (from 1-propanol).

Anal. Calcd. for $C_{23}H_{20}O_4S_2$: C, 65.08; H, 4.74; S, 15.10. Found: C, 65.05; H, 4.94; S, 15.11.

2,2-Dibenzyl-4,5-diphenyl-1,3-dithiole-1,1,3,3-trioxide (9b) and 2,2-Dibenzyl-4,5-diphenyl-1,3-dithiole-1,1,3,3-tetroxide (8b).

A colorless solid, which precipitated after oxidation of 1.10 g. (0.0025 mole) of 4b exactly as described for 4a above, was collected by filtration to give 1.10 g. of crystals, m.p. 205-210°. A sample, developed on a t.l.c. plate (silica gel G) with chloroform, showed two spots, $R_f = 0.39$ and 0.66. A 250 mg. sample was chromatographed on a preparative t.l.c. plate (silica gel H, 1.5 mm. thick, chloroform). Extraction of the top band with acetone gave 80 mg. (32%) of 8b as colorless crystals, m.p. 267-268° (from 1-propanol).

Anal. Calcd. for $C_{29}H_{24}O_3S_2$: C, 69.58; H, 4.83; S, 12.81. Found: C, 69.66; H, 4.88; S, 13.12.

Extraction of the lower band gave 130 mg. (52%) of 9b as colorless crystals, m.p. 191-192° (from 1-propanol).

Anal. Calcd. for $C_{29}H_{24}O_4S_2$: C, 71.88; H, 4.99; S, 13.22. Found: C, 71.84; H, 4.90; S, 13.41.

2,2-Dibenzyl-4-phenyl-1,3-dithiole-1,1,3-trioxide (9a).

A solution of 0.36 g. (0.001 mole) of 4a in 10 ml. of glacial acetic acid, to which 0.46 g. (0.004 mole) of 30% hydrogen peroxide was added, was kept for 4 hours at 75°, 0.46 g. of 30% hydrogen peroxide was again added, and the temperature was maintained at 75° for an additional six hours. After the reaction mixture was allowed to cool, the product was precipitated by the addition of water, and collected by filtration to give 0.37 g. of a white solid, m.p. 152-154°. Development of the solid on t.l.c. plates (silica gel G) with chloroform showed that the product was mainly the trioxide 9a, $R_f = 0.36$, contaminated

with the tetroxide 8a, $R_f = 0.64$. Development of 250 mg. of the colorless solid on a preparative t.l.c. (silica gel H, 1.5 mm. thick), gave 160 mg. (64%) of 9a as colorless crystals, m.p. 159-160°.

Anal. Calcd. for $C_{23}H_{20}O_3S_2$: C, 67.62; H, 4.93; S, 15.70. Found: C, 67.52; H, 5.17; S, 15.60.

Attempts to Convert 4a into 2-Benzyl-4-phenyl-1,3-dithiolium Perchlorate.

A suspension of 0.5 g. of 4a in five ml. of 70% perchloric acid was warmed on a steam bath for 15 minutes. Ethyl acetate was added to the cooled solution, and the residue was collected by filtration to give 0.10 g. of colorless crystals, m.p. 123-125°, which were identical to 4a by infrared spectrum.

A suspension of 0.5 g. of 4a in five ml. of 70% perchloric acid was warmed for five hours on a steam bath. Cooling of the reaction mixture gave a tarry product, which was soluble in ethyl acetate. When 4a (0.5 g. in 5 ml.) was slowly heated in perchloric acid to 120°, an explosion occurred.

Attempts to Convert 4a into 2-Benzylidene-4-phenyl-1,3-dithiole.

Heating of 0.5 g. of 4a to 200° for 30 minutes gave a red, viscous oil. By trituration with glacial acetic acid, yellow crystals were obtained which melted at 126-127°, and gave a mixture melting point with 4a of 126-127°. Heating of 4a to 200° for 15 hours afforded a red oil, which did not crystallize on cooling.

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