vinyl proton, J = 3.5 cps), 5.58 (2 H singlet, methylene proton), 6.76 (3 H singlet, methoxy proton), and 7.55 (3 H singlet, methyl proton).

Anal. Calcd for $C_7H_{10}OS$: C, 59.12; H, 7.09; S, 22.54. Found: C, 59.23; H, 7.22; S, 22.10.

The ir and nmr spectra of this material were identical with an authentic sample of 2-methoxymethyl-5-methylthiophene (II).

The vpc analysis of fraction 3 showed three peaks with a small amount of 2-methoxymethyl-5-methylthiophene. Each component was then separated in pure form by preparative vpc, the column packing being PEG 6000.

The first substance was liquid: ir spectrum 2240 cm^{-1} (CN); nmr spectrum τ 3.30 (1 H singlet), 7.43 (3 H singlet, methyl proton), and 7.58 (3 H singlet, methyl proton).

Anal. Calcd for C_7H_7NS: C, 61.31; H, 5.15; N, 10.21. Found: C, 61.28; H, 5.15; N, 10.01.

These results suggest that this product material is 3-cyano-2,5-dimethylthiophene (IV).[22]

The second substance was also liquid: ir spectrum 3000 (=CH) 2830 (OCH_3), 2240 (CN), 1645 (C=C), 1125, 1110, 1080, 1050, and 1045 cm^{-1} (COC); nmr spectrum τ 4.16 (1 H doublet, vinyl proton, J = 6.0 cps), 4.38 (1 H doublet, vinyl proton, J = 6.0 cps), 6.76 (3 H singlet, methoxy proton), 8.24 (3 H singlet, methyl proton), and 8.26 (3 H singlet, methyl proton).

Anal. Calcd for $C_8H_{11}NOS$: C, 56.78; H, 6.55; N, 8.28; S, 18.94. Found: C, 56.86; H, 6.53; N, 8.25; S, 18.88.

The third substance had mp 48–48.5°; ir spectrum 3000 (=CH), 2830 (OCH_3), 2240 (CN), 1645 (C=C), 1130, 1105, 1080, and 1045 cm^{-1} (COC); nmr spectrum τ 4.18 (1 H doublet, J = 6.0 cps), 4.30 (1 H doublet, J = 6.0 cps), 6.83 (3 H singlet), and 8.15 (6 H singlet).

Anal. Calcd for $C_8H_{11}NOS$: C, 56.78; H, 6.55; N, 8.28; S, 18.94. Found: C, 56.43; H, 6.49; N, 7.93; S, 18.81.

These data suggest that the latter two substances are geometrical isomers of 2-cyano-5-methoxy-2,5-dimethyldihydrothiophene (III_c and III_t). The structural assignments for the two isomers, III_c and III_t, were based on their nmr spectra. The methoxy protons of III_c (τ 6.76) resonated at a magnetic field a little lower than did those of III_t (τ 6.83). It is apparent from molecular models that the methoxy protons in the cis isomer are located closer to the cyano group than those in the trans isomer, indicative of the lower-field shift of the methoxy protons in the former compound.[1] This implies that the product III_c is assignable cis configuration. The individual isomers were unchanged both at room temperature and on vpc, but on warming in carbon tetrachloride there was a significant interconversion accompanied by some decomposition. A trace of sulfuric acid also exerted the same agency.

Fraction 2 was a mixture of 2-methoxymethyl-5-methylthiophene (II), 3-cyano-2,5-dimethylthiophene (IV), and 2-cyano-5-methoxy-2,5-dimethyldihydrothiophene (III_c and III_t).

The current efficiencies of the products were as follows: 2-methoxymethyl-5-methylthiophene (II), 0.54 g (14%, based on 2e process); 3-cyano-2,5-dimethylthiophene (IV), 0.28 g (7%); *cis*-2-cyano-5-methoxy-2,5-dimethyldihydrothiophene (III_c), 0.72 g (20%); *trans*-2-cyano-5-methoxy-2,5-dimethyldihydrothiophene (III_t), 0.32 g (9%).

Electrochemical Cyanation of 2,5-Dimethylthiophene in Acetonitrile.—An acetonitrile solution (50 ml) of 2,5-dimethylthiophene (4.49 g, 0.04 mol) and tetraethylammonium cyanide (6.25 g, 0.04 mol) was electrolyzed at 3–6°, with a current of 0.1 A at 33 V for 7 hr, until 0.027 F of charge was passed through the solution. The catholyte was a acetonitrile solution of tetraethylammonium cyanide (0.8 M). The electrolyzed mixture was treated with a large volume of water and the organic material was extracted with ether. The combined ether extract was washed thoroughly with water, dried over anhydrous magnesium sulfate, and filtered. Vpc analysis (internal standard, anisole) showed that 1.18 g of 2,5-dimethylthiophene had been consumed, corresponding to 2.5 electrons lost per 2,5-dimethylthiophene molecule. The thiophene remaining unchanged as well as ether was then evaporated off under reduced pressure. Vacuum distillation of the residual liquid yielded 0.1 g of liquid boiling at 70–75° (1 mm) and a tarry residue. The vpc analysis showed that this fraction contained a small amount of 3-cyano-2,5-dimethylthiophene. No attempt was made to identify other components.

Electrochemical Methoxylation of 2,5-Dimethylthiophene.—In a typical experiment a methanolic solution (50 ml) of sodium methoxide (sodium, 0.92 g, 0.04 g-atom) and 2,5-dimethylthiophene (4.49 g, 0.04 mol) was electrolyzed at 4–6°, with a current of 0.08 A at 33 V for 12 hr, until 0.038 F of charge had passed through the solution. The catholyte was a methanolic solution of sodium methoxide (0.8 M). The electrolysate was treated as usual. Vacuum distillation yielded 1.1 g of liquid boiling at 52–52.5° (4 mm). The vpc analysis and ir and nmr data showed that this material was 2-methoxymethyl-5-methylthiophene. The current efficiency is 41%.

In experiments with sodium perchlorate as the electrolyte, a methanolic solution (50 ml) of 2,5-dimethylthiophene (4.49 g, 0.04 mol) and sodium perchlorate (4.90 g, 0.04 mol) was electrolyzed at 25° for 3.5 hr, using an anode potential of 1.20 V. The catholyte was a methanolic solution of sodium perchlorate (0.8 M). The electricity was 0.030 F. The electrolyzed mixture was treated as usual and the ethereal solution was concentrated to 50 ml at 0°. Vpc analysis showed that 2.17 g of 2,5-dimethylthiophene had been consumed (corresponding to 1.6 F per mole of substrate) and 0.26 g of 2-methoxymethyl-5-methylthiophene had been produced.

Registry No.—I, 31819-37-1; II, 31819-38-2; III_c, 31819-39-3; III_t, 31819-40-6; IV, 31883-38-2; 2,5-dimethylthiophene, 638-02-8.

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[22] R. Justoni, *Gazz. Chim. Ital.*, **71**, 375 (1941).

Aryl Hydrodisulfides

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Received March 1, 1971

Phenyl hydrodisulfide and its para-substituted derivatives, as well as β-naphthyl hydrodisulfide, were synthesized, and their ir and nmr spectra were measured. Sulfhydryl proton chemical shifts of para-substituted phenyl hydrodisulfides were best correlated with Taft's σ_R, $\Delta\nu_{SSH} = 15.8\sigma_R - 200.8$ ($r = 0.993$).

An attempt to synthesize phenyl hydrodisulfide (**2e**) has been reported by Böhme and Zinner[1] in connection with alkyl hydrodisulfides and related derivatives. However, they obtained an oily substance which unfortunately was not identified as phenyl hydrodisulfide. Special interest was generated in this oily substance during our studies on aralkyl hydrodisulfide.[2] If aryl hydrodisulfides were successfully synthesized, we would be able to compare and correlate their nmr spectra with those of the corresponding arenethiols. Several years ago, Marcus and Miller[3] found that nmr frequencies of sulfhydryl groups in meta- and para-substituted benzenethiols correlate with Hammett's σ ($\rho = -21.8$). Later, Marcus, *et al.*,[4] pointed out that insertion of such

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[1] H. Böhme and G. Zinner, *Justus Liebigs Ann. Chem.*, **585**, 142 (1954).

[2] J. Tsurugi, Y. Abe, T. Nakabayashi, S. Kawamura, T. Kitao, and M. Niwa, *J. Org. Chem.*, **35**, 3263 (1970).

[3] S. H. Marcus and S. I. Miller, *J. Phys. Chem.*, **68**, 331 (1964).

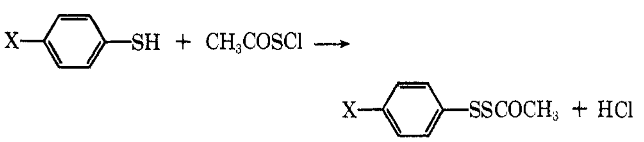
[4] S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966).

an atom as tetrahedral carbon or divalent sulfur diminishes the substituent effects between one-half to one-third of the original value. These papers predict that insertion of an additional sulfur atom into the sulfur–hydrogen bond of an arenethiol may give ρ values of *ca.* −5.7 to −8.5. The present paper reports the synthesis and ir and nmr spectra of para-substituted phenyl and β-naphthyl hydrodisulfides.

Results and Discussion

Preparation and Identification of Aryl Hydrodisulfides.—Acetyl aryl disulfides (**1a–h**), the precursors of the respective hydrodisulfides (**2a–h**), and acetyl β-naphthyl disulfide (**1i**)[5] were synthesized as shown in Scheme I (for yields, see Table IV). An attempt to prepare acetyl *p*-nitrophenyl disulfide was unsuccessful.

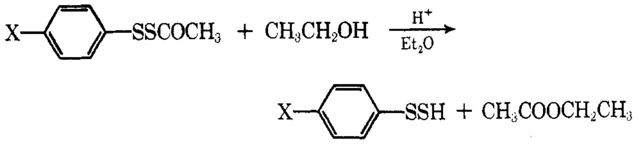
SCHEME I



1a, $X = C_2H_5O$
b, $X = CH_3O$
c, $X = tert\text{-}C_4H_9$
d, $X = CH_3$
e, $X = H^5$
f, $X = F$
g, $X = Br$
h, $X = Cl$

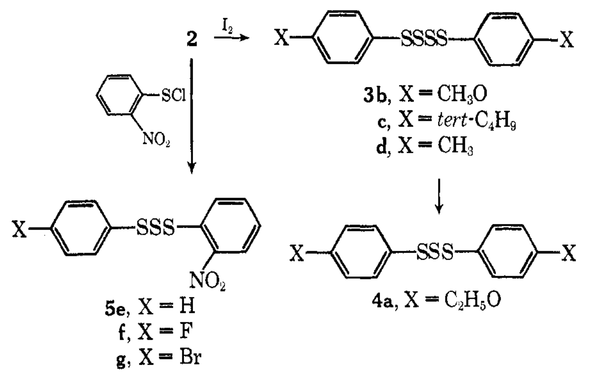
In our previous paper[6] it was shown that acetyl aralkyl disulfides are solvolyzed in ethanol containing hydrogen chloride for 4 hr to produce the hydrodisulfides in over 99% purity. In the present work nmr analyses indicate that ethanolyses of the acetyl disulfides, **1d**, **1e**, and **1i**, gave only 70, 60, and 15% of **2d**, **2e**, and **2i**, respectively, and that the remaining starting material gave the corresponding thiols. When the reaction mixture in ethanolic hydrogen chloride was diluted with ether and the reaction time was prolonged to 16–20 hr, the yields of the aryl hydrodisulfides **2** were improved (Scheme II, **2d**, **2e**, and **2i** in 95, 95, and 70% yield, respectively). In the case of **1a–c** the yields of **2a–c** were 100% on the basis of the nmr spectra. Of these hydrodisulfides **2c** was most stable and elemental analysis could be carried out before decomposition occurred. Compounds **2f** and **2g** could not be produced efficiently. In general, aryl hydrodisulfides presented here were slightly yellow viscous oils that gradually decomposed at room temperature to give hydrogen sulfide, thiol, and so on. They were comparably stable, however, in carbon tetrachloride, chloroform, cyclohexane, and carbon disulfide solutions, and could be stored as such for several days at room temperature. Distillation of the hydrodisulfides did not always improve their purity. An additional proof for the formation of **2a–g** was their conversion to polysulfidic compounds *via* the route shown in Scheme III. The oxidation product of **2a** was the corresponding trisulfide (**4a**), which seemed to form by the desulfurization of the tetrasulfide. β-Naphthyl hydrodisulfide (**2i**) was also oxidized to its tetrasulfide (**3i**). Ethanolysis of **1h** gave only decomposition products, thiol, di- and trisulfide, sulfur, hydrogen sulfide, and *ethyl acetate*. This suggests that *p*-chlorophenyl hydrodisulfide is highly unstable and that it decomposes soon after formation. All the above results seem to elucidate the reason why Böhme, *et al.*,[1] could not obtain phenyl hydrodisulfide.

SCHEME II



2a, $X = C_2H_5O$
b, $X = CH_3O$
c, $X = tert\text{-}C_4H_9$
d, $X = CH_3$
e, $X = H$
f, $X = F$
g, $X = Br$

SCHEME III



3b, $X = CH_3O$
c, $X = tert\text{-}C_4H_9$
d, $X = CH_3$

4a, $X = C_2H_5O$

5e, $X = H$
f, $X = F$
g, $X = Br$

Infrared Spectra.—The infrared spectra of para-substituted phenyl and β-naphthyl hydrodisulfides indicate weak absorptions at 2515–2540 cm^{-1} (Table I) that are assigned to the S–H stretching. The S–H stretching absorption bands of the corresponding arenethiols[7] appear at 2575–2600 cm^{-1}, that is, about 50–70 cm^{-1} higher than in the former. This tendency is similar to that observed in alkyl hydrodisulfides and alkanethiols.[8]

TABLE I
IR S–H STRETCHING ABSORPTION OF ARYL HYDRODISULFIDES AND ARENETHIOLS

	cm^{-1}			cm^{-1}	
Ar	SSH	SH	Ar	SSH	SH
$p\text{-}C_2H_5OC_6H_4$	2520	2575	C_6H_5	2515	2580
$p\text{-}CH_3OC_6H_4$	2525	2575	$p\text{-}FC_6H_4$	2525	2580
$p\text{-}tert\text{-}C_4H_9C_6H_4$	2520	2575	$p\text{-}BrC_6H_4$	2540	2600
$p\text{-}CH_3C_6H_4$	2520	2575	$\beta\text{-}C_{10}H_7$	2530	2600

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[5] H. Böhme and M. Clement, *Justus Liebigs Ann. Chem.*, **576**, 61 (1952).

[6] T. Nakabayashi and J. Tsurugi, *J. Org. Chem.*, **28**, 813 (1963).

[7] According to L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Methuen, London, 1958, the S–H bond in thiols absorbs at 2550–2600 cm^{-1}.

[8] (a) J. Tsurugi, Y. Abe, and S. Kawamura, *Bull. Chem. Soc. Jap.*, **43**, 1890 (1970). (b) Sulfur–hydrogen stretching absorptions of benzyl and benzhydryl hydrodisulfide were at 2515 and 2510 cm^{-1}, respectively, while the corresponding thiols absorb at 2570 cm^{-1}.

Nmr Spectra.—It is known that the sulfhydryl proton magnetic resonance of monosubstituted benzenethiols is correlated with Hammett's σ value ($\Delta\nu_{SH} = -21.8\sigma - 195.1$, $r = 0.952$),[3] while the absence of such a correlation can be noted for para-substituted phenyl hydrodisulfides (Tables II and III). However, when the nmr data are related to values which incorporate resonance effects, excellent correlations are obtained. For example, a relationship between $\Delta\nu_{SSH}$ and $\sigma_R{}^\circ$ values[9] is given by $\Delta\nu_{SSH} = 18.2\ \sigma_R{}^\circ - 200.7$ ($r = 0.972$). A correlation of $\Delta\nu_{SSH}$ to σ_R values is more satisfactory, $\Delta\nu_{SSH} = 15.8\sigma_R - 200.8$ ($r = 0.993$) (Figure 1). When a set of $\sigma_I - \sigma_R$ is used, $\Delta\nu_{SSH} = -0.381\ \sigma_I + 15.5\sigma_R - 200.8$ ($r = 0.993$) is obtained. A fit of the resonance values into the Yukawa–Tsuno equation[10] gives a correlation, $\Delta\nu_{SSH} = -7.81\ \sigma_i + 22.2\sigma_\pi - 201.3$ ($r = 0.963$). It is noteworthy that in these correlations the proton magnetic resonance of sulfhydryl protons in para-substituted phenyl hydrodisulfides appears to be governed largely by the resonance term, and that ρ values have opposite signs as compared with those of the Hammett relation with thiols. If the present observation were to result from an electronic effect, then a chemical shift to higher fields would result from introduction of an electron-donating group in the benzene nucleus and this would lead to a negative ρ value. The above observation, therefore, indicates that large electron-releasing resonance in the benzene nucleus gives a minus anisotropic effect to the terminal sulfhydryl proton which, in turn, causes a shift to the lower field.[11]

TABLE II

CHEMICAL SHIFTS OF SULFHYDRYL PROTONS IN PARA-SUBSTITUTED PHENYL HYDRODISULFIDES AND THIOLS (HERTZ)

X	In p-XC_6H_4SSH	In p-XC_6H_4SH
C_2H_5O	−208.3	−187.9
CH_3O	−208.6	−188.3
tert-C_4H_9	−202.3	−190.8[a]
CH_3	−202.6	−191.0[a]
H	−201.3	−195.4[a]
F	−208.1	−195.4[a]
Br	−203.9	−197.2[a]

[a] Reference 3.

TABLE III

CHEMICAL SHIFTS OF SULFHYDRYL PROTONS IN PARA-SUBSTITUTED PHENYL HYDROSULFIDES p-XC_6H_4SSH DISSOLVED IN A FEW SOLVENTS (7%)

	Hz			
X	Cyclohexane	CCl_4	CS_2	$CDCl_3$
C_2H_5O	−205.0	−209.5	−211.2	−219.5
CH_3O	−205.5	−210.3	−211.3	−219.6
H	−193.9	−199.7	−203.6	−209.0
F		−208.2	−211.8	−217.4

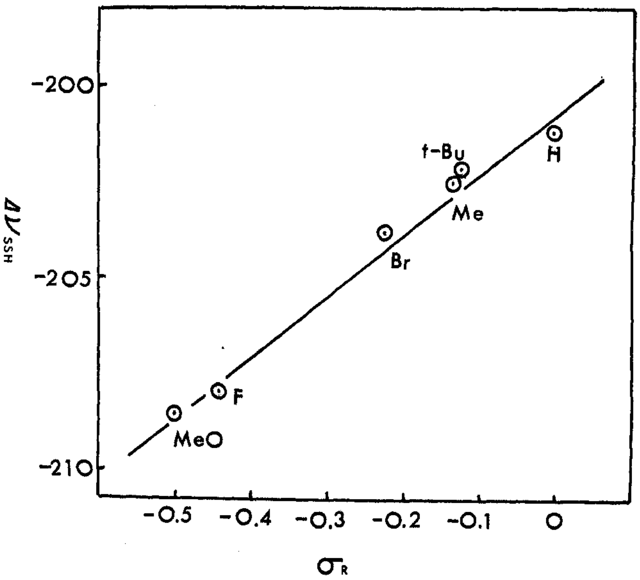
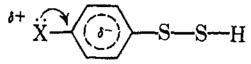


Figure 1.—A plot of Taft's σ_R *vs.* values of $\Delta\nu_{SSH}$ from Table II, for para substituents in CCl_4.

It is apparent that the sulfur–sulfur bond in the hydrodisulfide molecule does not transmit conjugation and permits only very little *I* effect, at least in its ground state.



Experimental Section

All melting points were determined on a Shimazu micro melting point apparatus and are uncorrected. Infrared spectra were taken with a JASCO IR-S spectrometer on neat samples. Proton magnetic resonance spectra were produced by means of a JNM 3H-60 spectrometer with tetramethylsilane as an internal standard. All chemical shifts were determined by the side-band technique. Chemical shifts reported in Table II were obtained by taking the average of three values at each of three concentrations in the dilute range,[3] below *ca.* 1 *M*, and extrapolating to zero concentration. The three-parameter equations ($\Delta\nu_{SSH}$, σ_I, σ_R: $\Delta\nu_{SSH}$, σ_i, σ_π) are results of computer-programmed computations.

p-Methoxy-[12], p-ethoxy-[12], and p-fluorobenzenethiols[13] acetyl sulfenyl chloride,[14] and o-nitrobenzenesulfenyl chloride[15] were prepared by the known procedures. Other thiols were commercial samples of pure grade and were used without purification. Acetyl phenyl disulfide (**1e**), bp 93–95° (0.05 mm) [lit. bp 146–148° (11 mm)], and acetyl β-naphthyl disulfide (**1i**), mp 56–57° (lit. mp 58–59°), were prepared by the method of Böhme and Clement.[5]

Acetyl Para-Substituted Phenyl Disulfides (1a–d, 1f–h).—Acetyl p-ethoxyphenyl disulfide (**1a**) was prepared as follows. To a stirred solution of p-ethoxybenzenethiol (1.95 mmol) in 20 ml of anhydrous ether was added acetyl sulfenyl chloride (2.15 mmol) in 10 ml anhydrous ether under nitrogen atmosphere with stirring for 15 min at −10°. Stirring was stopped after additional 30 min, the solution was kept overnight, and volatiles were removed at 7 mm. The highly viscous yellow oil was purified by distillation under vacuum.

Other disulfides (**1b–d, 1f–h**) were prepared similarly, and are characterized in Table IV.

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(9) R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topson, *J. Amer. Chem. Soc.*, **90**, 1757 (1968).

(10) Y. Tsuno, Symposium on the Hammett Relationship Abstr., Kyoto, Japan, Oct 12, 1967, p 1.

(11) p-Trimethylsilylphenyl hydrodisulfide is an interesting compound, because, in contrast to the compounds in Table II which have minus σ_R substituents, it has an opposite σ_R sign. In spite of all our efforts, acetyl p-trimethylsilylphenyl disulfide was not obtained in a relatively pure state. However, a product of ethanolysis of this slightly impure disulfide was satisfactory (*ca.* 98%) for nmr measurements. The chemical shift, −199.5 Hz (the corresponding thiol, −194.9 Hz), was fitted to the above correlations, *e.g.*, $\Delta\nu_{SSH} = -0.395\sigma_I + 15.0\sigma_R - 200.9$ ($r = 0.994$).

(12) M. Protiva, M. Rajsner, E. Adlerova, V. Seidlova, and Z. J. Vejdelek, *Collect. Czech. Chem. Commun.*, **29**, 2161 (1964); *Chem. Abstr.*, **62**, 524 (1965).

(13) M. Rajsner, V. Seidlova, and M. Protiva, *Cesk. Farm.*, **11**, 451 (1962); *Chem. Abstr.*, **49**, 2773 (1963).

(14) J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **24**, 807 (1959).

(15) M. H. Hubacher in "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 455.

TABLE IV

Compd	Bp, °C (mm)	Yield, %	Formula	Calcd, % C	Calcd, % H	Calcd, % S or others	Found, % C	Found, % H	Found, % S or others
1a	113–115 (0.1)	72	$C_{10}H_{12}O_2S_2$	52.61	5.30	28.08	52.57	5.40	28.18
1b	112–115 (0.1)	71	$C_9H_{10}O_2S_2$	50.44	4.70	29.92	50.21	4.64	30.08
1c	123–127 (0.05)	>80	$C_{12}H_{16}OS_2$	59.96	6.71	26.67	59.91	6.87	26.79
1d	95–103 (0.05)	>80	$C_9H_{10}OS_2$	54.51	5.08	32.33	54.41	5.13	32.37
1f	74–75 (0.15), mp 26°	84	$C_8H_7OFS_2$	47.51	3.49	F, 9.39	47.69	3.74	F, 9.24
1g	113–118 (0.01)	84	$C_8H_7OBrS_2$	36.51	2.68		36.59	2.97	
1h	84 (0.05)	>80	$C_8H_7OClS_2$	43.98	3.23		43.93	3.45	

Ethanolyses of Acetyl Para-Substituted Phenyl Disulfides (1a–g) and Acetyl β-Naphthyl Disulfide (1i).—To a solution of acetyl para-substituted phenyl disulfide (2 g, 7.6–10.8 mmol) or acetyl β-naphthyl disulfide (2 g, 8.5 mmol) in anhydrous ether (20 ml) was added 5 *N* alcoholic hydrogen chloride (8 ml) at room temperature. After 16–20 hr, volatiles were removed and the residual high viscous yellow oil was subjected to nmr analysis. Nmr spectra showed that some para-substituted phenyl hydrodisulfides were pure. Distillation did not always improve the purities of the hydrodisulfides (Table V).

TABLE V

Compd	Bp, °C (mm)	Purity in nmr, % Before distn	Purity in nmr, % After distn
2a	71–72.5 (0.05)	100	99
2b	53–56.5 (0.05)	100	99
2c		100	
2d	95–100 (0.06)	95	
2e	60 (0.05)	95	
2f	29–32 (0.05)	92	91
2g		70	
2i		80	

***p-tert*-Butylphenyl Hydrodisulfide (2c).**—The highly viscous oil described above was subjected to elemental analysis without further purification.

Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.56; H, 7.12; S, 32.33. Found: C, 60.50; H, 7.07; S, 32.12.

Bis(*p*-methoxyphenyl) Tetrasulfide (3b).—To *p*-methoxyphenyl hydrodisulfide (**2b**, 0.27 mmol) was added an excess of 1 *N* alcoholic iodine solution. To this was added benzene (*ca.* 20 ml). The solution obtained was washed with 1 *N* aqueous sodium thiosulfate solution followed by water, and dried over magnesium sulfate. Benzene was replaced by a small amount of alcohol and the mixture was chilled with liquid nitrogen. The yellow crystals obtained were recrystallized once from alcohol–benzene, then twice from ether–hexane, mp 56.5–58.5° (0.035 mmol, 24%). For elemental analysis, additional recrystallization was performed from ether–hexane, mp 58–58.5° (0.0096 mmol, 7%).

Anal. Calcd for $C_{14}H_{14}O_2S_4$: C, 49.10; H, 4.12; S, 37.44. Found: C, 49.07; H, 4.03; S, 37.50.

Bis(*p-tert*-butylphenyl) Tetrasulfide (3c).—Under conditions similar to those mentioned above a yellow oil was obtained from *p-tert*-butylphenyl hydrodisulfide (**2c**). The oil was crystallized from petroleum ether (bp 30–40°) at −20°. The crystals, after removal of the insoluble portion in petroleum ether (bp 30–40°), were recrystallized from ethanol–petroleum ether, mp 66–68°.

Anal. Calcd for $C_{20}H_{26}S_4$: C, 60.87; H, 6.64; S, 32.49. Found: C, 60.58; H, 6.43; S, 32.64.

***p*-Tolyl Tetrasulfide (3d).**—Under conditions similar to those mentioned above, a white solid was obtained from *p*-tolyl hydrodisulfide (**2d**). The solid was recrystallized from ethanol, mp 67–68°. The crystals were recrystallized from ether–petroleum ether, mp 71–72° (lit. mp 75°).[16]

Anal. Calcd for $C_{14}H_{14}S_4$: C, 54.15; H, 4.54; S, 41.30. Found: C, 54.20; H, 4.26; S, 41.39.

β-Naphthyl Tetrasulfide (3i).—Under conditions similar to those mentioned above, a white solid was obtained from β-naphthyl hydrodisulfide (**2i**). The solid was recrystallized from ethanol–benzene three times, mp 102–103° (lit. 101°).[16]

Anal. Calcd for $C_{20}H_{14}S_4$: C, 62.79; H, 3.69; S, 33.52. Found: C, 63.02; H, 3.57; S, 33.35.

Bis(*p*-ethoxyphenyl) Trisulfide (4a).—By means of a procedure similar to that described for the *p*-methoxy derivative, a low-melting solid was obtained from *p*-ethoxyphenyl hydrodisulfide (**2a**, 0.27 mmol). The solid was crystallized from ether–hexane to give pale yellow crystals, which were recrystallized from the same solvent, mp 61–64.5° (0.024 mmol, 22%). For elemental analysis, the crystals were carefully recrystallized again from the same solvent, mp 64.5–65.5° (0.0053 mmol, 5%).

Anal. Calcd for $C_{16}H_{18}O_2S_3$: C, 56.77; H, 5.46; S, 28.41. Found: C, 56.72; H, 5.51; S, 28.55.

***p*-Bromophenyl *o*-Nitrophenyl Trisulfide (5g).**—To a stirred solution of *p*-bromophenyl hydrodisulfide (**2g**, 2.26 mmol) in 20 ml of anhydrous ether was added *o*-nitrobenzenesulfenyl chloride (2.3 mmol) in 40 ml of anhydrous ether under a nitrogen stream at 0°. The oil obtained after evaporation of the solvent was crystallized in ether–hexane, mp 102–104° (1.1 mmol, 48%). The crude product was recrystallized twice from ether–ethyl acetate, mp 110.5–111.5°.

Anal. Calcd for $C_{12}H_8O_2BrNS_3$: C, 38.51; H, 2.15; N, 3.74. Found: C, 38.52; H, 2.03; N, 3.46.

***p*-Fluorophenyl *o*-Nitrophenyl Trisulfide (5f).**—Under conditions similar to those mentioned above, a yellow oil was obtained from *p*-fluorophenyl hydrodisulfide (**2f**). A solution of the oil in hot hexane (40°), after removal of the insoluble portion by filtration, was chilled to give crystals. The crystals were recrystallized twice from the same solvent, mp 46–47°.

Anal. Calcd for $C_{12}H_8O_2FNS_3$: C, 45.99; H, 2.57; N, 4.47; S, 30.69. Found: C, 46.03; H, 2.48; N, 4.44; S, 30.31.

***o*-Nitrophenyl Phenyl Trisulfide (5e).**—Under conditions similar to those mentioned above, a yellow oil was obtained from phenyl hydrodisulfide (**2e**). The oil was crystallized in ether–hexane at −20°. The crude product (mp 86.5–88.5°) was recrystallized from hexane–benzene three times, mp 93.5–94.5°.

Anal. Calcd for $C_{12}H_9O_2NS_3$: C, 48.79; H, 3.07; N, 4.74; S, 32.57. Found: C, 48.98; H, 3.05; N, 4.64; S, 32.75.

Registry No.—**1a**, 31818-97-0; **1b**, 31570-54-4; **1c**, 31818-99-2; **1d**, 14227-19-1; **1f**, 31819-01-9; **1g**, 31819-02-0; **1h**, 14193-03-4; **2a**, 31883-35-9; **2b**, 31819-04-2; **2c**, 31819-05-3; **2d**, 31819-06-4; **2e**, 31819-07-5; **2f**, 31819-08-6; **2g**, 31819-09-7; **3b**, 31819-10-0; **3c**, 31819-11-1; **3d**, 25769-92-0; **3i**, 31819-17-7; **4a**, 31121-14-9; **5e**, 31819-14-4; **5f**, 31819-15-5; **5g**, 31819-16-6.

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[16] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., Inc., New York, N. Y., 1960, p 413.