[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY, COLLEGE OF ENGINEERING, UNIVERSITY OF OSAKA PREFECTURE]

Organic Polysulfides. III. Synthesis and Some Properties of Several Unsymmetrical Polysulfides[1]

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Several unsymmetrical trisulfides, RSSSR′, were prepared by condensation of alkyl hydrodisulfide RSSH with an arenesulfenyl chloride R′SCl or thiocyanate R′SSCN. Here R represents benzhydryl or benzyl groups, and R′ 2-nitrophenyl, 2-nitro-4-chlorophenyl, 2,4-dinitrophenyl, or 2-naphthyl groups. Ultraviolet absorption spectra of these unsymmetrical trisulfides were determined and compared with those of the corresponding unsymmetrical mono- and disulfides as well as with symmetrical ones.

Recently some unsymmetrical disulfides have been prepared by various investigators,[2] but only a few literature references have been found on the synthesis of unsymmetrical trisulfides. A synthetic method for unsymmetrical trisulfides is the condensation reaction of a disulfide chloride with a mercaptan

$$\mathrm{RSSCl + R'SH \longrightarrow RSSSR'}$$

by which ethyl methyl[3] and ethyl benzyl trisulfides[4] were obtained as oily substances and 2-nitrophenyl hydroxyphenyl trisulfide[4] as a crystalline substance. More recently some liquid unsymmetrical (alkyl aryl) trisulfides were prepared by a rather complicated reaction[5] indicated below.

$$\mathrm{RNH{-}SO{-}SR' + 3\,R''SH \longrightarrow R''{-}SSS{-}R' + RNH_2 + R''{-}SS{-}R'' + H_2O}$$

where R″ represents alkyl and R′ aryl groups. Formation of a symmetrical disulfide as well as a desired trisulfide makes it necessary to isolate the desired product by distillation.

Another probable synthetic method for unsymmetrical trisulfides may be a condensation reaction of arenesulfenyl chloride[6] (R′SCl) or thiocyanate[6] (R′SSCN) with alkyl hydrodisulfides (RSSH), which were prepared by Böhme[7] and were utilized by the present authors[8] to synthesize dialkyl pentaane hexasulfides. In the present paper some crystalline unsymmetrical trisulfides were prepared by this method.

$$\mathrm{RSSH + XSAr \longrightarrow RSSSAr} \qquad (1)$$

where RSSH represents benzhydryl or benzyl hydrodisulfide and ArSX represents nitrobenzenesulfenyl chloride or 2-naphthalenesulfenyl thiocyanate. In order to determine some physical properties and ultraviolet spectra, it is easier to use crystalline substances.

The corresponding unsymmetrical mono- and disulfides, few of which have been reported in the literature, were prepared in the present paper to compare some of their properties and ultraviolet spectra with those of the trisulfides.

$$\mathrm{RSH + XSAr \longrightarrow RSSAr} \qquad (2)$$

$$\mathrm{RX + HSAr \longrightarrow RSAr} \qquad (3)$$

or

$$\mathrm{RSH + XAr \longrightarrow RSAr} \qquad (4)$$

where X represents halogen or thiocyanate group. Table I indicates melting points and analytical data of these series of unsymmetrical mono-, di- and trisulfides, one group of which is benzhydryl or benzyl and another is one of three types of nitrophenyl groups or a 2-naphthyl group. For synthesis of the 2-naphthyl benzhydryl or benzyl di- and trisulfides, the naphthalenesulfenyl thiocyanate rather than the chloride was used, because the former is more easily prepared and more stable than the latter. Besides the series of unsymmetrical polysulfides cited in Table I the symmetrical polysulfides, 2,2′-dinaphthyl mono-, di- and trisulfides were also prepared, in order to compare some properties of the unsymmetrical polysulfides with those of the symmetrical ones. The other symmetrical polysulfides, dibenzhydryl or dibenzyl polysulfides (mono-, di- and trisulfides) were reported in Part I[8] of this series.

Ultraviolet absorption spectra of benzhydryl 2-nitrophenyl mono-, di-, and trisulfides were measured in alcoholic solution between 220 and 400 mμ and are indicated in Fig. 1. The ultraviolet absorption spectra of various unsymmetrical sul-

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(1) Part II, J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **25**, 1744 (1960).

(2) (a) G. Jacini and F. Lauria, *Gazz. chim. ital.*, **80**, 762 (1950); *Chem. Abstr.*, **46**, 4499 (1952). G. Jacini *et al.*, *Gazz. chim. ital.*, **82**, 297 (1952); *Chem. Abstr.*, **47**, 8680 (1953); (b) S. Mugnusson, J. E. Christian, and G. L. Jenkins, *J. Am. Pharm. Assoc., Sci. Ed.*, **36**, 257, 261 (1947); (c) H. Brintzinger and M. Langheck, *Chem. Ber.*, **86**, 557 (1953); **87**, 325 (1954); (d) A. Schöberl, H. Tausent, and H. Gräfji, *Angew. Chem.*, **68**, 213 (1956).

(3) H. Böhme and G. V. Ham, *Ann.*, **617**, 62 (1958).

(4) J. F. Harris, Jr., Univ. Microfilms Pub. No. 4927, 111 p.; *Chem. Abstr.*, **48**, 2636 (1954).

(5) G. Kresze and H. P. Patzschke, *Chem. Ber.*, **93**, 380 (1960).

(6) N. Kharasch, *et al.*, *Chem. Rev.*, **39**, 269 (1946).

(7) H. Böhme and G. Zinner, *Ann.*, **585**, 142 (1954).

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

TABLE I

MELTING POINTS, YIELDS, AND ANALYTICAL DATA OF UNSYMMETRICAL POLYSULFIDES

No.	Compound	Yield, %	Formula	M.P.	Calcd.			Found		
					C	H	S	C	H	S
2-NITROPHENYL BENZHYDRYL SERIES										
1	Monosulfide	65.4	$C_{19}H_{15}NO_2S$	111–112	71.00	4.70	9.98	70.88	4.91	9.71
2	Disulfide	95	$C_{19}H_{15}NO_2S_2$	81–82	64.56	4.28	18.15	64.36	4.61	17.99
3	Trisulfide	70	$C_{19}H_{15}NO_2S_3$	94–96	59.19	3.92	24.95	59.35	4.29	24.73
2-NITRO-4-CHLOROPHENYL BENZHYDRYL SERIES										
4	Monosulfide	53.6	$C_{19}H_{14}ClNO_2S$	133.5–134.5	64.13	3.97		63.81	3.97	
5	Disulfide	87.6	$C_{19}H_{14}ClNO_2S_2$	109–110	58.83	3.64		58.62	3.63	
6	Trisulfide	88	$C_{19}H_{14}ClNO_2S_3$	80–81	54.34	3.36		54.04	3.19	
2,4-DINITROPHENYL BENZHYDRYL SERIES										
7	Monosulfide	95.6	$C_{19}H_{14}N_2O_4S$	122–123 (122–123)[a]	62.28	3.85	8.75	62.51	4.25	8.48
8	Disulfide	92.5	$C_{19}H_{14}N_2O_4S_2$	120.5–121	57.27	3.54	16.10	57.23	3.81	15.83
9	Trisulfide	98	$C_{19}H_{14}N_2O_4S_3$	129–130	53.00	3.28	22.35	53.26	3.52	22.39
2-NITROPHENYL BENZYL SERIES										
10	Monosulfide	77.5	$C_{13}H_{11}NO_2S$	82–83 (82–83)[b]	63.65	4.52	13.36	64.12	4.77	13.27
11	Disulfide	95	$C_{13}H_{11}NO_2S_2$	53–54 (54)[c]	56.29	4.00	23.10	56.34	4.32	23.49
12	Trisulfide	53	$C_{13}H_{11}NO_2S_3$	80.5–81	50.46	3.58	31.09	50.28	3.85	31.32
2-NITRO-4-CHLOROPHENYL BENZYL SERIES										
13	Monosulfide	56	$C_{13}H_{10}ClNO_2S$	129–130.5	55.81	3.60		55.75	4.26	
14	Disulfide	77	$C_{13}H_{10}ClNO_2S_2$	81–82	50.07	3.23		50.30	3.23	
15	Trisulfide	56	$C_{13}H_{10}ClNO_2S_3$	82.5–83.5	45.39	2.86		45.73	3.10	
2,4-DINITROPHENYL BENZYL SERIES										
16	Monosulfide	90	$C_{13}H_{10}N_2O_4S$	128–129 (130)[d]	53.78	3.47	11.05	53.88	3.65	11.28
17	Disulfide	94	$C_{13}H_{10}N_2O_4S_2$	112–112.5	48.43	3.13	19.87	48.36	3.31	19.78
18	Trisulfide	76.5	$C_{13}H_{10}N_2O_4S_3$	112.5–113	44.05	2.84	27.14	43.85	3.00	27.07
2-NAPHTHYL BENZHYDRYL SERIES										
19	Monosulfide	69	$C_{23}H_{18}S$	120–121	84.62	5.56	9.82	84.49	5.42	10.0
20	Disulfide	71	$C_{23}H_{18}S_2$	94–95	77.05	5.06	17.90	76.58	5.01	18.1
21	Trisulfide	90.4	$C_{23}H_{18}S_3$	69–71	70.72	4.65	24.63	71.24	4.75	24.0
2-NAPHTHYL BENZYL SERIES										
22	Monosulfide	96.4	$C_{17}H_{14}S$	89–90 (89.8–90.5)[e]	81.55	5.64	12.81	81.35	5.33	12.5
23	Disulfide	61	$C_{17}H_{14}S_2$	60–61.5	72.29	5.00	22.71	71.60	4.86	22.6
24	Trisulfide	73	$C_{17}H_{14}S_3$	69–71	64.92	4.49	30.59	64.99	4.55	30.6

[a] J. Tsurugi and T. Nakabayashi, *Nippon Kagaku Zasshi*, 77, 581 (1956). [b] A. Sieglitz and H. Koch, *Chem. Ber.*, 58, 82 (1925). [c] H. B. Footner and S. Smiles, *J. Chem. Soc.*, 127, 2887 (1925); *Chem. Abstr.*, 20, 747 (1926). [d] R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, 54, 1986 (1932). [e] A. H. Weinstein and R. M. Pierson, *J. Org. Chem.*, 23, 557 (1958).

fides as well as symmetrical ones have already been interpreted by Koch.[9] However, the interpretation of the ultraviolet absorption spectra of unsymmetrical disulfides and trisulfides have never been presented. Koch[9] suggested that the weak absorption band near 350 mμ of phenyl 2-nitrophenyl sulfide may be attributed to its canonical resonance structure (I), which seems both sterically and energetically reasonable. A postulated polar excited structure of the *o*-quinoid type (II) was considered by Koch to be improbable because of the resulting interference between the van der Waals radii of oxygen and sulfur. Weak absorption bands near 350 mμ of benzhydryl 2-nitrophenyl mono-, di-, and trisulfides in Fig. 1 may be associated with the similar band of phenyl 2-nitrophenyl sulfide or with that of di-2-nitrophenyl sulfide, although intensities of the band of the unsymmetrical disulfides are a little less than those of the latter two. Absorption maxima shift to shorter wave length as the number of sulfur atoms increases from one to three. The 245 mμ absorption of the unsymmetrical monosulfide in Fig. 1 cannot be interpreted at the present time, but the similar absorption is found in (symmetrical) di-2-nitrophenyl sulfide and the similar absorption with the higher intensity is displayed by (symmetrical) di-2-nitrophenyl disulfide. However, both benzhydryl 2-nitrophenyl di-and trisulfides do not have similar absorption maxima in the same range. Generally it can be said that as compared with the spectra of (symmetrical) dibenzhydryl

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(9) H. P. Koch, *J. Chem. Soc.*, 387 (*1949*).

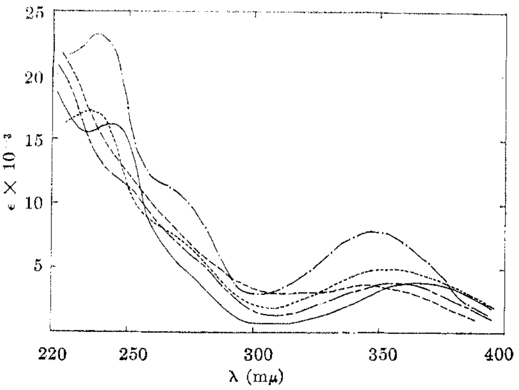
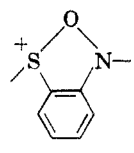


Fig. 1. Ultraviolet absorption spectra of a series of 2-nitrophenyl benzhydryl sulfides (———, mono-; — — —, di-; - - - -, trisulfides) and of di-2-nitrophenyl sulfides (------, mono-; — · —, disulfides)

mono-, di-, and trisulfides and with that of (symmetrical) di-2-nitrophenyl sulfide, those of unsymmetrical ones seem to be the corresponding resultants of di-2-nitrophenyl sulfide and the dibenzhydryl series, except for the deficiency of the maxima in the range of shorter wave length of the unsymmetrical di- and trisulfides. Canonical structures of type III and of polar (*o*- or *p*-) quinoid type IV in addition to I make contribution to the optical excited states of benzhydryl 2-nitrophenyl monosulfide. However, the following canonical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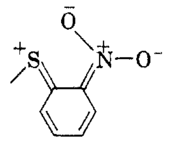
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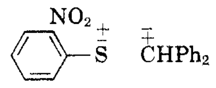
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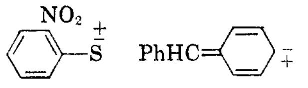
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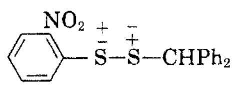
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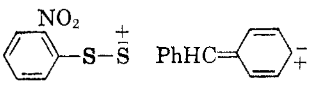
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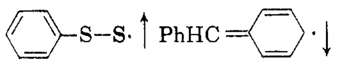
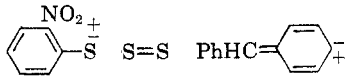

VII


VIII

structures V, VI, and VII besides I may contribute to the optical excited states of benzhydryl 2-nitrophenyl disulfide. The additional canonical structure VIII may be plausible for benzyhydryl 2-nitrophenyl trisulfide in addition to the ones similar to V, VI, and VII and in addition to I mentioned above. Therefore, the absorption of the unsymmetrical trisulfide in the range between 220–300 mμ becomes more intensive and shifts to longer wave lengths. Flatter curves of the unsymmetrical disulfide and trisulfide as compared to the monosulfide may result for the same reason.

Similar observations are found in a series of benzyl 2-nitrophenyl mono-, di-, and trisulfides and of benzyl 2-nitro-4-chlorophenyl mono-, di-, and trisulfides as well as in a series of benzhydryl 2-nitro-4-chlorophenyl mono-, di-, and trisulfides. The absorption maxima and their intensities are tabulated in Table II.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF UNSYMMETRICAL MONO-, DI-, AND TRISULFIDES

	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
BENZYL 2-NITROPHENYL SERIES				
Monosulfide	245	20,700	365	4,500
Disulfide	250 (shoulder)	13,500	355	4,300
Trisulfide	—	—	345	3,700
BENZYL 2-NITRO-4-CHLOROPHENYL SERIES				
Monosulfide	250 270 (shoulder)	24,700 11,500	380	4,700
Disulfide	240 (shoulder)	14,100	365	3,800
Trisulfide	—	—	355	3,400
BENZYL 2,4-DINITROPHENYL SERIES				
Monosulfide	—	—	330	12,900
Disulfide	—	—	320	9,200
Trisulfide	—	—	315	8,900
BENZHYDRYL 2-NITRO-4-CHLOROPHENYL SERIES				
Monosulfide	250	19,700	380	4,100
Disulfide	—	—	365	3,900
Trisulfide	—	—	360	3,800

The absorption spectra of benzhydryl 2,4-dinitrophenyl mono-, di-, and trisulfides are indicated in Fig. 2. The 330 mμ absorption maximum of the monosulfide and those of the disulfide and trisulfide near there may be ascribed to a group —S—$C_6H_4(NO_2)_2$-(2,4), because an intense absorption band of phenyl 4-nitrophenyl sulfide was found at 337,5 mμ,[9] and the corresponding *ortho* compound has the maximum near 365 mμ. Flattening of the spectra also occurs as the number of sulfur atoms increase from one to three. No further interpretation of the spectra will be attempted in view of the paucity of the reference data.

With regard to the spectra of naphthyl benzyl polysulfides shown in Fig. 3, that of the monosulfide, if it is indicated in logarithmic scale, is in complete agreement with that recorded by Weinstein and Pierson.[10] They observed a maximum similar to the 285 mμ peak of 2-naphthyl benzyl sulfide in 2-thionaphthol at 283 mμ, and ascribed it to a

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[10] A. H. Weinstein and R. M. Pierson, *J. Org. Chem.*, **23**, 554 (1958).

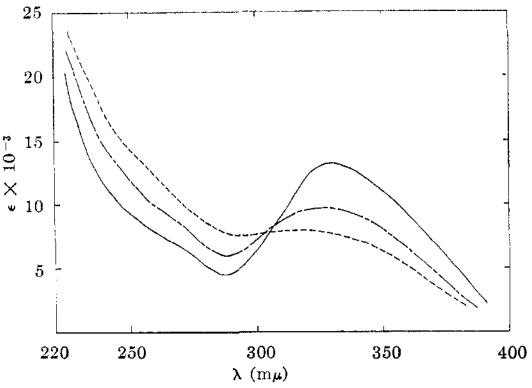

Fig. 2. Ultraviolet absorption spectra of a series of 2,4-dinitrophenyl benzhydryl sulfides (———, mono-; — — —, di-; - - - -, trisulfides)

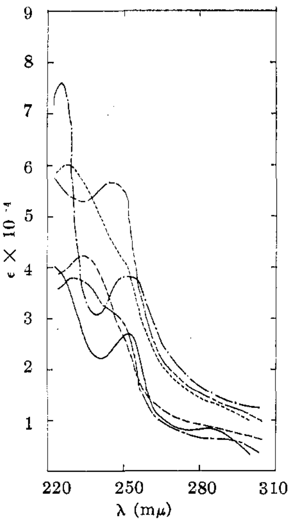

Fig. 3. Ultraviolet absorption spectra of a series of 2-naphthyl benzyl sulfides (———, mono-; — — —, di-; - - - -, trisulfides) and of di-2-naphthyl sulfides (— · —, mono-; — — —, di-; - - - - - -, trisulfides)

naphthalene chromophore bathochromically shifted by a thiol auxochrome. The 253 mμ absorption peak of 2-naphthyl benzyl sulfide resembles the absorption of 2,2′-dinaphthyl sulfide, although intensity of the former is considerably weaker than that of the latter, and may be ascribed to a modified naphthalene chromophore. As for the series of alkyl nitrophenyl polysulfides mentioned above, in this series also flattening of the curves is observed as the number of sulfur atoms increases from one to three. The same relationship was observed in ultraviolet spectra of a series of 2-naphthyl benzhydryl mono-, di- and trisulfides.

Molecular refraction of a series of unsymmetrical 2-naphthyl benzhydryl or benzyl polysulfides were determined. The results are indicated in Table III.

Calculated values of the sulfur atoms in the mono-, di-, and trisulfides in each series are in good agreement within experimental error. This confirms the existence of linear sulfur chains in each trisulfide as in the disulfide.

TABLE III

MOLAR REFRACTIONS OF 2-NAPHTHYL BENZHYDRYL OR BENZYL POLYSULFIDES AND ATOMIC REFRACTION OF SULFUR IN THESE COMPOUNDS

Unsymmetrical Sulfides R—Sn—R′	Molar Refraction MRD-(RSnR′)	Refraction of Group Sn RD(Sn)	Atomic Refraction of Sulfur RD(Sn)/*n*
2-$C_{10}H_7$—S—$CH(C_6H_5)_2$	106.7	10.2	10.2
2-$C_{10}H_7$—S_2—$CH(C_6H_5)_2$	116.8	20.3	10.1
2-$C_{10}H_7$—S_3—$CH(C_6H_5)_2$	126.0	29.5	9.8
			10.0 ± 0.2
2-$C_{10}H_7$—S—$CH_2C_6H_5$	81.1	9.8	9.8
2-$C_{10}H_7$—S_2—$CH_2C_6H_5$	92.6	21.3	10.7
2-$C_{10}H_7$—S_3—$CH_2C_6H_5$	101.3	30.0	10.0
			10.2 ± 0.5

EXPERIMENTAL

Unsymmetrical monosulfides. According to Equation 3, 0.02 mole of arenethiol (2-nitrobenzenethiol or 2-naphthalenethiol) in 50 ml. of ethanol was converted to potassiumthiolate by potassium hydroxide, and then was allowed to react with an equivalent amount of benzyl bromide in 50 ml. of dry benzene in an atmosphere of inert gas at refluxing temperature for 2 hr. under stirring. When benzhydryl bromide was used in place of benzyl bromide, not potassium arenethiolate but arenethiol itself was refluxed with benzhydryl bromide to avoid the probable hydrolysis of the bromide, and the reaction was carried out in benzene solution. The solution was washed with water and dried with anhydrous sodium sulfate. After the solvent was evaporated, compounds No. 1 and No. 19 were recrystallized from a benzene-ethanol mixture. No. 10 was recrystallized from ether, and No. 22 from ethanol.

The other unsymmetrical monosulfides were prepared by Equation 4. To an absolute alcoholic solution of potassium α-diphenylmethane- or α-toluenethiolate was added an equivalent amount of chloronitrobenzene (1,4-dichloro-2 nitrobenzene or 2,4-dinitrochlorobenzene) in ethanol in a stream of inert gas under stirring. The mixture was heated for 3 hr. at 50–70°, and diluted with 10 volumes of water. Compounds No. 4 and No. 13 were recrystallized from benzene, No. 7 and No. 16 recrystallized from a mixture of benzene and ethanol.

Unsymmetrical disulfides. To a solution of 0.01 mole of alkanethiol (α-diphenylmethane- or α-toluenethiol) in 50 ml. of dry benzene was added a soution of arenesulfenyl chloride (2-nitrobenzenesulfenyl,[11] 2-nitro-4-chlorobenzenesulfenyl,[12] or 2,4-dinitrobenzenesulfenyl chloride[13]) at room temperature. The flask was protected by a calcium chloride tube and kept standing overnight. The solution was washed with water and dried. After the solvent was evaporated under diminished pressure, the solid obtained was recrystallized from a mixture of benzene and ethanol. Compounds No. 2, 5, 8, 11, 14, and 17 were thus prepared.

2-Naphthalenesulfenyl thiocyanate[14] was used to prepare unsymmetrical naphthyl alkyl disulfides. The sulfenyl thiocyanate (0.01 mole) in 50 ml. of dry ether was added to a solution of alkanethiol (α-diphenylmethane- or α-toluenethiol) in 50 ml. of dry ether at room temperature in a stream of inert gas with stirring. The mixture was stirred for an

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(11) Max H. Hubacher, *Org. Syntheses*, **Coll. Vol. II**, 455 (1948).

(12) Th. Zincke and J. Baeumer, *Ann.*, **416**, 86 (1918).

(13) N. Kharasch, G. I. Gleason, and C. M. Buess, *J. Am. Chem. Soc.*, **72**, 1796 (1950).

(14) H. Lecher and M. Wittwer, *Chem. Ber.*, **55**, 1474 (1922).

hour. After being washed and dried, the solvent was evaporated. The solid obtained was recrystallized from ethanol. Compounds No. 20 and 23 were prepared by the method described above.

Unsymmetrical trisulfides. To a solution of 0.02 mole of alkyl hydrodisulfide (benzhydryl or benzyl hydrodisulfide) in 50 ml. of dry ether was added a solution of arenesulfenyl chloride (2-nitrobenzenesulfenyl, 2-nitro-4-chlorobenzenesulfenyl, or 2,4-dinitrobenzenesulfenyl chloride) in 50 ml. of dry ether at room temperature in a stream of inert gas under stirring. A very slight excess of the hydrosulfide was used, otherwise diaryl disulfide was formed from the arenesulfenyl chloride. This made it difficult to isolate the unsymmetrical from the symmetrical disulfide. The reaction system was protected against moisture by a calcium chloride tube. Stirring was continued for 2 hr., and the solution was washed, dried, and concentrated by evaporation. The solid obtained was recrystallized from ether.

For the synthesis of 2-naphthyl benzhydryl or benzyl trisulfide, 2-naphthalenesulfenyl thiocyanate was used in place of the sulfenyl chloride. The procedure was the same as for the above nitrophenyl alkyl trisulfides.

2,2'-Dinaphthyl mono-, di-, and trisulfides. These were also prepared as specimens for determining the spectra. The monosulfide was obtained by pyrolysis of lead 2-naphthalenethiolate[15] at 300–320° under 100 mm., and after several recrystallizations from a benzene-ethanol mixture, m.p. 148–149° (lit.,[15] m.p. 151°), the yield was 45%.

Anal. Calcd. for $C_{20}H_{14}S$: C, 83.88; H, 4.93; S, 11.20. Found: C, 84.04; H, 5.33; S, 11.0.

The disulfide was the oxidation product of 2-naphthalenethiol by iodine,[10] recrystallized from benzene, m.p. 139° (lit.,[10] m.p. 141.8–142.6°), yield 98%.

Anal. Calcd. for $C_{20}H_{14}S_2$: C, 75.43; H, 4.43; S, 20.1. Found: C, 75.19; H, 4.33; S, 20.0.

The trisulfide was prepared by the ordinary method from the thiol and sulfur dichloride, recrystallized from benzene-ethanol mixture, m.p. 115–116° (Lit.,[16] m.p. 108–109°), yield 79%.

Anal. Calcd. for $C_{20}H_{14}S_3$: C, 68.53; H, 4.03; S, 27.45. Found: C, 68.75; H, 3.93; S, 26.8.

Determination of ultraviolet absorption spectra and molecular refraction. These were the same as those reported in Part I[8] of this series.

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SAKI CITY, OSAKA, JAPAN

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[CONTRIBUTION 984 FROM THE CHEMISTRY LABORATORIES OF INDIANA UNIVERSITY]

The Ultraviolet Absorption Spectra of Some Unsymmetrical Disulfides[1]

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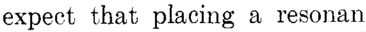
The ultraviolet absorption curves of certain unsymmetrical diaryl disulfides, Ar—S—S—Ar', were calculated as one-half the sum of the absorption curves of the two symmetrical disulfides, ArSSAr and Ar'SSAr'. Slight deviations from the calculated values in the observed curves were consistent with inductive effects of groups attached to sulfur in the two halves of the molecule, ArS— and Ar'S—. No transmission of electronic effects through the sulfur-sulfur bond could be detected in the ultraviolet spectra of the diaryl disulfides.

It is certain that disulfides undergo heterolytic cleavage in polar reactions. Nucleophilic cleavage of disulfide is evidenced by the reaction with organometallic reagents[3] and by Lewis-acid catalyzed electrophilic attack of disulfide on aromatic systems[4] and olefins.[5] Electrophilic cleavage may be illustrated by the reaction of disulfides with halides such as methyl iodide[6] or 2,4-dinitrochlorobenzene.[7] The whole question of heterolytic scission of the sulfur-sulfur bond in disulfides has recently been reviewed[8] with numerous examples of both types of cleavage. Such cleavage must be initiated by polarization of the disulfide bond.

Polarization of the disulfide bond may be considered to be stabilized by resonance involving a 10-electron sulfur shell, as in A ⟷ B. One might



A B

logically expect that placing a resonance system such as the two sulfur atoms of A ⟷ B between two chromophoric groups would be reflected in a bathochromic shift of the ultraviolet absorption of the simple chromophore. However, the opposite

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