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Synthesis of Dibenzhydryl and Dibenzyl Penta- and Hexasulfides

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New methods are here reported for the preparation of dibenzhydryl and dibenzyl penta- and hexasulfides by condensation of the corresponding alkyl hydrodisulfide with sulfur di- or monochloride. The ultraviolet absorption spectra and molar refractions of these compounds were determined and compared with those of the corresponding mono-, di-, tri- and tetrasulfides. No anomaly was observed among them as the number of sulfur atoms increased from one to six.

Some organic polysulfides have been prepared by condensation of two moles of a mercaptan and one mole of sulfur mono- or dichloride. It has been proved by various methods, for instance, by determining ultraviolet absorption spectra,[1-3] dipole moments,[4] x-ray,[5] and electron diffraction[6] diagrams, that the tri- and tetrasulfides thus obtained have linear S—S linkages. Polysulfides which contain a definite number of sulfur atoms, more than four, and linear sulfur linkages, are rare. Thomas and Riding[7] prepared dibenzyl pentasulfide as an oily substance from benzyl chloride and sodium pentasulfide. Recently Fehér *et al.*[8] prepared diethyl pentasulfide by condensation of ethylmercaptan with trisulfur dichloride (ClS_3Cl). Organic polysulfides containing more than four sulfur atoms were often isolated from the reaction products of hydrocarbons[9,10] with sulfur, but these compounds were found to be a mixture of polysulfides, each of which contains a different number of sulfur atoms. Higher polysulfides have also been obtained by sulfur disproportionation reactions such[10] as

$$RS_nR \longrightarrow RS_mR + RS_{m-n}R \qquad (m > n)$$

or by exchange reaction[11] of polysulfides with sulfur such as

$$RS_nR + S_8 \longrightarrow RS_mR \qquad (m > n)$$

but the products are considered to be merely a mixture of polysulfides, each of which contains a different number of sulfur atoms, unless the products are separable from each other by vacuum distillation or by other methods.

Recently Böhme and Zinner[12] have prepared so called alkyl hydropolysulfides (RS_nH) in which the sulfur linkage has been shown to be linear. They oxidized the alkyl hydrotrisulfide with iodine and isolated the organic hexasulfides (dibenzyl and dimethyl and diethyl hexasulfides) containing linear sulfur linkages. The organic pentasulfides (dibenzyl and diethyl) were also obtained as an oily substance in their laboratory by distilling the corresponding alkyl hydrotrisulfide under high vacuum.

However, the higher polysulfides may be prepared by condensation of the alkyl hydropolysulfide with sulfur mono- or dichloride. Polysulfides containing an odd number of sulfur atoms, for instance, pentasulfide can be prepared by condensation of alkyl hydrodisulfide with sulfur dichloride more easily than by other methods. In this paper dibenzhydryl and dibenzyl penta- and hexasulfides were prepared by condensation of the corresponding alkyl hydrodisulfide with sulfur di- or monochloride, respectively, some of which were obtained in crystalline state (the pentasulfides) and some of which were new compounds (dibenzhydryl penta- and hexasulfides). Apparently this synthetic method is preferable to other methods, by which dibenzyl pentasulfide was obtained as an oily substance. The synthetic method is indicated in Equations 1 to 7, where R represents benzhydryl or benzyl groups.

$$(CH_3CO)_2O + H_2S \longrightarrow CH_3COSH + CH_3COOH \qquad (1)^{13}$$

$$CH_3COSH + CH_3COCl \longrightarrow CH_3COSCOCH_3 + HCl \qquad (2)^{14}$$

$$CH_3COSCOCH_3 + Cl_2 \longrightarrow CH_3COSCl + CH_3COCl \qquad (3)^{15}$$

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[1] H. P. Koch, *J. Chem. Soc.*, 394 (1949).

[2] Y. Minoura, *Nippon Kagaku Zasshi*, **73**, 131 (1952).

[3] J. E. Baer and M. Carmack, *J. Am. Chem. Soc.*, **71**, 1251 (1949).

[4] L. M. Kushner, G. Gorin, and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 477 (1950); H. E. Westlake, Jr., H. L. Lacquer, and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 436 (1950).

[5] I. M. Dawson, A. M. Mathieson, and J. M. Robertson, *J. Chem. Soc.*, 322, 1256 (1948).

[6] J. Donohue and V. Shomaker, *J. Chem. Phys.*, **16**, 92 (1948).

[7] J. S. Thomas and R. W. Riding, *J. Chem. Soc.*, **125**, 2214 (1924).

[8] F. Fehér, G. Krause, and K. Vogelbruch, *Chem. Ber.*, **90**, 1570 (1957).

[9] R. T. Armstrong, J. R. Little, and K. W. Doak, *Ind. Eng. Chem.*, **36**, 628 (1944); M. L. Selker and A. R. Kemp, *Ind. Eng. Chem.*, **39**, 895 (1947); A. S. Broun, M. G. Moronkov, and K. P. Katkova, *Zhur. Obshchĭ Khim.*, **20**, (82) 726 (1950); *Chem. Zentr.*, **123**, 34 (1952); E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, 1519 (1947); J. Tsurugi, H. Fukuda, and T. Nakabayashi, *Nippon Kagaku Zasshi*, **76**, 111, 113 (1955).

[10] G. F. Bloomfield, *J. Chem. Soc.*, 1546 (1947).

[11] E. N. Guryanova, V. N. Vasilyeva, and L. S. Kuzina, *Rubber Chem. Tech.*, **29**, 534 (1956).

[12] H. Böhme and G. Zinner, *Ann.*, **585**, 142 (1954).

[13] E. K. Ellingboe, *Org. Syntheses*, **31**, 105.

[14] W. A. Bonner, *J. Am. Chem. Soc.*, **72**, 4270 (1950).

[15] H. Böhme and M. Clement, *Ann.*, **576**, 65 (1952).

$$CH_3COSCl + RSH \longrightarrow RSSCOCH_3 + HCl \quad (4)$$[12]

$$RSSCOCH_3 + C_2H_5OH \longrightarrow RSSH + CH_3COOC_2H_5 \quad (5)$$

$$2RSSH + ClSCl \longrightarrow RSSSSSR + 2HCl \quad (6)$$

$$2RSSH + ClSSCl \longrightarrow RSSSSSSR + 2HCl \quad (7)$$

Some of the physical constants and ultraviolet absorption spectra of these polysulfides were determined together with the corresponding mono-, di-, tri-, and tetrasulfides. Table I indicates melting points and color of these compounds.

TABLE I

MELTING POINTS AND COLOR OF DIBENZHYDRYL AND DIBENZYL SULFIDES AND POLYSULFIDES

	Dibenzhydryl		Dibenzyl	
	(Color)	(M.P.)	(Color)	(M.P.)
Mono-	White	(66.5°)[16]	White	(48.5°)[2]
Di-	White	(152°)[16]	White	(71°)[2]
Tri-	White	(72.8°)	White	(49°)[2]
Tetra-	Faintly yellow	(82–83°)[17]	Faintly yellow	(54°)[2]
Penta-	Faintly yellow	(80–81.5°)	Faintly yellow	(57.5–58.5°)
Hexa-	Yellow oil		Yellow oil	

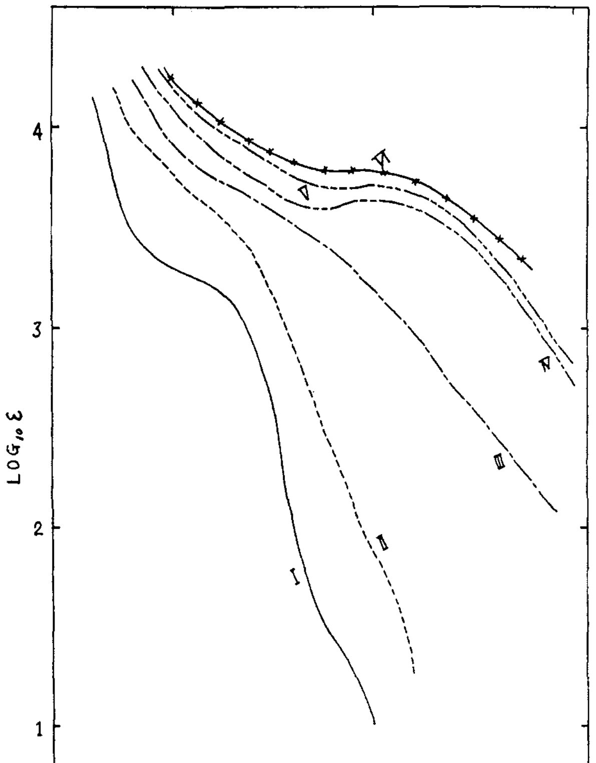

Fig. 1. Ultraviolet absorption spectra of dibenzhydryl polysulfides in alcoholic solution. I, mono-[17]; II, di-[17]; III, tri-; IV, tetra-[17]; V, penta-; VI, hexa-[18]

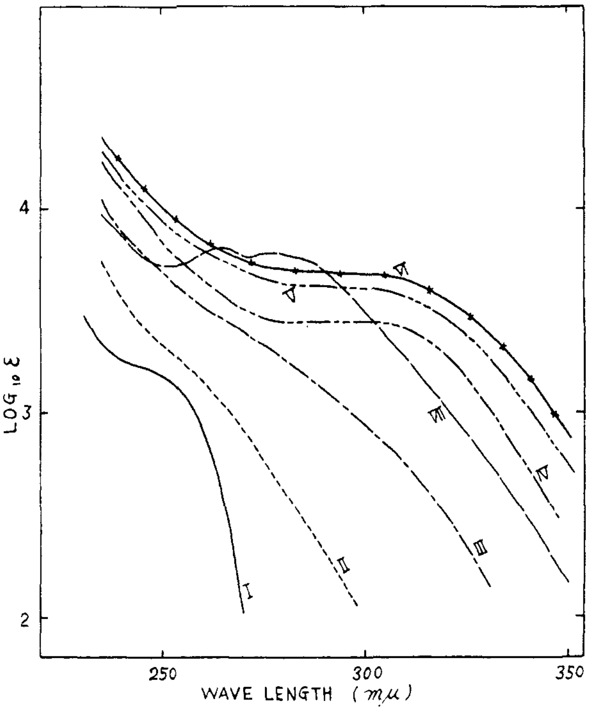

Fig. 2. Ultraviolet absorption spectra of dibenzyl polysulfides in alcoholic solution. I, mono-; II, di-; III, tri-; tetra-; V, penta-; VI, hexa-[18]; VII, sulfur molecule.[3] The spectra of dibenzyl mono- to tetra-sulfide have been already determined in n-hexane solution.[2] These coincide with those indicated in Fig. 1, completely in the range of the wave length determined.

The ultraviolet absorption spectra (Figs. 1 and 2) were measured in alcoholic solution between 230 and 360 mμ.

It is noteworthy that as the number of sulfur atoms in these compounds increases, the absorbance becomes more intense, and the displacement toward the longer wave lengths occurs as in the polyene series.[19] However, passing through from tetrasulfide to hexasulfide, the increase of intensity of the absorbance and the wave-length displacement become smaller for each additional sulfur atom. The shape of curves of tetra-, penta- and hexasulfides resembles each other. Especially that of the pentasulfide can coincide almost completely with that of the hexasulfide by shifting the former toward the longer wave lengths. This means that as the sulfur chain becomes longer, the excitation energy decreases, but the excited state is almost the same regardless of the chain length. Comparing the curves of the corresponding higher polysulfides in Figs. 1 and 2 with each other, one can conclude

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(16) J. Tsurugi and T. Nakabayashi, *Nippon Kagaku Zasshi*, **77**, 578 (1956).

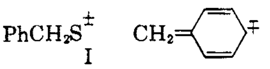
(17) J. Tsurugi and T. Nakabayashi, *Nippon Kagaku Zasshi*, **77**, 583 (1956).

(18) After long standing, the hexasulfide in the solution, especially in a polar solvent, decomposes slowly to a mixture of sulfur and lower polysulfides, but within the time period necessary for the determination no alteration in the shape of the spectra was observed.

(19) A. E. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy*, E. Arnold Ltd., London, 1954, p. 67.

that even if the organic group attached to the sulfur chain differs, the absorption spectra do not differ very much. The yellow color of the higher polysulfides indicated in Table I can be accounted for by the fact that the spectra of higher polysulfides are in the same range of that of the sulfur molecule.

Koch suggested that canonical structures of the polar (*o*- or *p*-) quinoid type I make a significant contribution to the optically excited state of benzyl monosulfide,[20] and canonical structures II in addition to III to that of benzyl disulfide.[1] He also suggested that the enhanced absorption of dialkyl tetrasulfide over the disulfide may be correlated with the fact that further possible conjugated polar structures IV would be expected to stabilize the excited level of the tetrasulfide, and that the still greater absorption of a dialkyl hexasulfide may follow from the more highly conjugated polar structure V participating in the excited state. By analogy with Koch's consideration it is deduced that canonical structures VI and VII may participate in the excited state of dibenzyl tri- and pentasulfide, respectively. Additional canonical structures may be plausible in correspondence with the related formulations above, for instance, in hexasulfide the VIII structures and the similar ones may be plausible in correspondence with V structures.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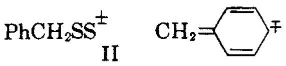

II

$RS^{\pm}\ {}^{\mp}SR$

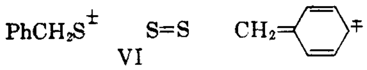
III

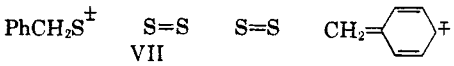
$RS^{\pm}\quad S{=}S\quad {}^{\mp}SR$

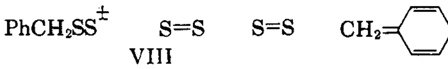
IV

$RS^{\pm}\quad S{=}S\quad S{=}S\quad {}^{\mp}SR$

V


VI


VII


VIII

Various canonical forms cited above were written with regard to dibenzyl polysulfides. However, if an α-hydrogen atom of the benzyl group is replaced by a phenyl group, the same structures may be applicable to benzhydryl polysulfides. The results on the ultraviolet absorption spectra of these polysulfides indicated in Figs. 1 and 2 can be interpreted qualitatively by the above discussion.

It is more important that no anomaly was observed among the curves of a series of polysulfides as the number of sulfur atoms increases from one to six. If the higher polysulfides would have any coordinate sulfur atoms in branches, its spectrum would differ from that of the linear one. As stated above the tetra- and trisulfides have been proved to have linear sulfur chains. It is concluded that polysulfides thus prepared have suffered no rearrangement of sulfur atoms. Here also no evidence has come to light in support of the possible existence of structural isomers of the branched chain type.

TABLE II

MOLAR REFRACTIONS OF DIBENZHYDRYL AND DIBENZYL POLYSULFIDES AND ATOMIC REFRACTION OF SULFUR IN THESE COMPOUNDS

Polysulfides, RS_nR	Molar Refraction, $MR_D(RS_nR)$	Refraction of Group S_n, $R_D(S_n)$	Atomic Refraction of Sulfur $R_D(S_n)/n^a$	$R_D(S_n) - R_D(S_{n-1})$
$(Ph_2CH)_2S$	120.8	9.8	9.8	9.8
$(Ph_2CH)_2S_2$	131.0	20.0	10.0	10.2
$(Ph_2CH)_2S_3$	141.2	30.2	10.1	10.2
$(Ph_2CH)_2S_4$	151.0	40.0	10.0	9.8
$(Ph_2CH)_2S_5$	160.3	49.3	9.8	9.3
$(Ph_2CH)_2S_6$	170.1	59.1	9.8	9.8
			9.9 ± 0.2	9.9 ± 0.5
$(PhCH_2)_2S$	70.5	10.0	10.0	10.0
$(PhCH_2)_2S_2$	81.3	20.8	10.4	10.8
$(PhCH_2)_2S_3$	91.7	31.2	10.4	10.4
$(PhCH_2)_2S_4$	100.2	39.7	9.9	8.5
$(PhCH_2)_2S_5$	109.3	48.8	9.7	9.1
$(PhCH_2)_2S_6$	118.2	57.7	9.6	8.9
			10.0 ± 0.4	9.6 ± 1.2

[a] The much better agreement was obtained by this method. In Table III cited below the values of atomic refraction of sulfur calculated by this method are indicated.

The above conclusion is supported by the determination of molar refraction of the polysulfides. The results are indicated in Table II.

Table II indicates that even if the length of the sulfur chain increases or the organic group attached to sulfur chain differs, the atomic refraction of sulfur remains nearly constant. The same constant value of atomic refraction of sulfur has been observed by others in various polysulfides containing sulfur atoms less than four or five. These values are shown in Table III.

EXPERIMENTAL

The preparation of dibenzhydryl mono-, di-, and tetrasulfides has been already reported in other papers.[16,17] Dibenzyl mono-, di-, tri-, and tetrasulfides were prepared by method in the literature.[2]

Dibenzhydryl trisulfide was prepared by the ordinary method from benzhydrylmercaptan[16] and sulfur dichloride.

Anal. Calcd. for $C_{26}H_{22}S_3$: C, 72.51; H, 5.15; S, 22.34. Found: C, 72.37; H, 5.44; S, 21.74.

In order to prepare acetyl sulfenyl chloride the most convenient method appeared in the literatures was found to be the course indicated in Equations 1 to 3.

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[20] H. P. Koch, *J. Chem. Soc.*, 387 (1949).

TABLE III

ATOMIC REFRACTION OF SULFUR $R_D(S_n)/n$ IN VARIOUS POLYSULFIDES RS_nR

R — n	Tolyl[21]	Ethyl[8]	Methyl[9]	n-Hexadecyl[22]
1	9.2	7.85	—	8.4
2	9.5	8.0	7.9	9.0
3	10.4	8.3	8.3	8.7
4	10.2	8.4	11.1	9.2
5	—	8.5	—	—

Acetyl benzhydryl disulfide (Eq. 4). A solution of 9.2 g. of benzhydrylmercaptan in absolute ether was added dropwise under stirring in the stream of carbon dioxide to a solution of 6 g. of acetyl sulfenyl chloride in 30 ml. of absolute ether. During the reaction the temperature should be kept under 5° by cooling. After standing for 1 hr. the mixture was washed with water, aqueous sodium bicarbonate solution, and dried with anhydrous sodium sulfate. After evaporating the solvent, 8.6 g. of white crystals remained, recrystallized from petroleum ether, m.p. 43.5–45°.

Anal. Calcd. for $C_{15}H_{14}OS_2$: S, 23.37. Found: S, 23.57.

Benzhydryl hydrodisulfide. (Eq. 5.) Ten g. of acetyl benzhydryl disulfide and 100 ml. of absolute alcohol were placed in a four necked flask equipped with reflux condenser, the top of which was protected with a calcium chloride tube, dropping funnel, thermometer, and carbon dioxide inlet tube. In the stream of carbon dioxide 20 ml. of dry 5*N* alcoholic hydrogen chloride was added to the content of the flask, which was kept at 25°. The crystals of acetyl benzhydryl disulfide disappeared completely after 4 hr. By evaporating alcohol and ethyl acetate (which was formed during the reaction) at room temperature under reduced pressure, separating the solid by cooling, adding a small amount of petroleum ether–ether mixture, and again cooling, 8.3 g. of raw crystals were obtained, from petroleum ether, m.p. 32.5–34°. This compound in absolute alcohol was oxidized by alcoholic iodine solution and gave quantitatively dibenzhydrul tetrasulfide, m.p. 82–83°, mixed m.p. with authentic sample,[16] 82–83°. Under room temperature the slow evolution of hydrogen sulfide was observed from benzhydryl hydrodisulfide. This compound should be stored in a solid carbon dioxide bath in an inert atmosphere.

Dibenzhydryl pentasulfide. (Eq. 6.) Under cooling 0.45 g. of freshly distilled sulfur dichloride in absolute ether was added dropwise under stirring in the stream of carbon dioxide gas to 2 g. of benzhydryl hydrodisulfide in absolute ether. After the evolution of hydrogen chloride gas the solvent was evaporated at room temperature. The residue gave 2 g. of raw crystals from petroleum ether–ether mixture, recrystallized once more from the same solvent mixture, m.p. 80–81.5°.

Anal. Calcd. for $C_{26}H_{22}S_5$: C, 63.11; H, 4.48; S, 32.40. Found: C, 62.78; H, 4.75; S, 31.28.

Dibenzhydryl hexasulfide. (Eq. 7.) Freshly distilled sulfur monochloride (0.55 g.) was added to benzhydryl hydrodisulfide (2 g.) as above. After evaporating the solvent, the residue could not be crystallized by any method. Distillation under high vacuum resulted in its decomposition. After washing with petroleum ether, cooling separates the oily substance. A slight excess of benzhydryl hydrodisulfide was dissolved in petroleum ether and detected by iodine. The washing was repeated as long as the formation of tetrasulfide was observed. The oily residue, dried in vacuum, weighed 1.5 g.

Anal. Calcd. for $C_{26}H_{22}S_6$: C, 59.27; H, 4.21; S, 36.52. Found: C, 59.04; H, 4.42; S, 35.30.

Acetyl benzyl disulfide. (Eq. 4.) As in the preparation of acetyl benzhydryl disulfide, 8.15 g. of benzylmercaptan was added to 14.5 g. of acetyl sulfenyl chloride. The crude product was recrystallized from petroleum ether, m.p. 54–55° (lit.[11] 58–59°).

Benzyl hydrodisulfide. (Eq. 5.) As for the benzhydryl compound, 10 g. of acetyl benzyl disulfide was treated with 25 ml. of dry 5*N* alcoholic hydrogen chloride. After evaporating the solvent and ethyl acetate, the residue was distilled under vacuum, b.p. 65–70°/0.01 mm. (lit.[11] 67–70°/0.01 mm.) to yield, 5.6 g. This oil was oxidized by iodine, and gave dibenzyl tetrasulfide, m.p. 53.5–54°, mixed m.p. with an authentic sample, 53.5–54°.

Dibenzyl pentasulfide. (Eq. 6.) From 1.5 g. of benzyl hydrodisulfide and 0.5 g. of sulfur dichloride, 1.5 g. of crude product was obtained. After recrystallization from ether, it melted at 57.5–58.5° (lit.[7,12] oily substance).

Anal. Calcd. for $C_{14}H_{14}S_5$: C, 49.1; H, 4.12; S, 46.78. Found: C, 49.08; H, 3.93; S, 45.40.

Dibenzyl hexasulfide. (Eq. 7.) From 3 g. of benzyl hydrodisulfide and 1.1 g. of sulfur monochloride 2 g. of an oily substance was obtained. The preparing and refining procedures were the same as for the benzhydryl compound.

Anal. Calcd. for $C_{14}H_{14}S_6$: S, 51.53. Found: S, 50.70.

Determination of the spectra. The ultraviolet absorption spectra were determined with a Hitachi EPU-2 spectrophotometer, using alcohol as the solvent.

Determination of the molar refractions. The refractive indices n_D^{20} of dilute carbon tetrachloride solutions of a polysulfide in various concentrations were determined by Abbe Refractometer, and densities D_4^{20} of the same solutions were determined by Ostwald-Sprengel pycnometer. Molar refraction values were calculated by Lorenz-Lorentz equation from n_D^{20} and D_4^{20} of the dilute solutions, and the value of a polysulfide was obtained by extrapolating these values to infinite dilution.[23]

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