[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BUFFALO]

Preparation and Ultraviolet Absorption Spectra of Certain Alkyl Polysulfides

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Improved procedures are here reported for the preparation of di-*n*-butyl, di-*n*-amyl, and di-isoamyl disulfides by the Bunte salt method. In addition, di-*n*-propyl, di-isopropyl, and di-*n*-butyl trisulfides have been synthesized by the interaction of the respective mercaptans and sulfur dichloride. The ultraviolet absorption spectra of these compounds have also been determined.

Di-*n*-butyl disulfide[1,2] and di-*n*-amyl disulfide[1] have already been prepared through the medium of the Bunte salts. Di-*n*-propyl trisulfide and di-isopropyl trisulfide have been prepared by Cairns, *et al.* as[3] some of the products resulting from the action of hydrogen sulfide on certain carbonyl compounds. Di-*n*-butyl trisulfide has been prepared by the reaction of thionyl chloride with *n*-butyl mercaptan.[4]

Di-*n*-butyl, di-*n*-amyl and di-isoamyl disulfides have been prepared here in percentage yields of 56.2, 53.3, and 47.3 respectively, through the medium of the corresponding Bunte salts:

$$2SO_2(ONa)SC_4H_9\text{-}n + 2KOH \longrightarrow (n\text{-}C_4H_9S)_2 + HOH + K_2SO_3 + Na_2SO_4 \quad (I)$$

Di-*n*-propyl, di-isopropyl, and di-*n*-butyl trisulfides have resulted from the action of sulfur dichloride of the respective mercaptans in percentage yields of 64.7, 46.0, and 45.0, respectively:

$$2n\text{-}C_3H_7SH + (SCl)_2 \longrightarrow 2HCl + (n\text{-}C_3H_7S)_2 \quad (II)$$

Di-*n*-butyl sulfide has been satisfactorily prepared by an adaptation of the Williamson synthesis on the interaction of sodium *n*-butyl mercaptide and *n*-butyl bromide, yield 40.7%.

The ultraviolet absorption spectra of these polysulfides were measured between 220 and 340 mm. Almost identical spectra were obtained for the three disulfides. The spectra for *n*-propyl, isopropyl, and *n*-butyl trisulfides were also nearly identical with each other. A comparison of the inflection points of the disulfide spectra with those reported by Gorin and Dougherty[5] and Koch[6] show close agreement. An interesting comparison spectrum was run using di-*n*-butyl sulfide, disulfide, and trisulfide. It is noteworthy that as the rank of these compounds increases, the absorbance becomes more intense at a much greater rate. An increase in absorbance is to be expected due to the electronic excitation on the additional sulfur atom or atoms. The first maximum in trisulfide spectra, around 251 mm. as already reported by Baer and Carmack[7] agrees quite well with the measured values herein recorded.

TABLE I

PHYSICAL PROPERTIES

	B.P., °C.	Mm.	n_D^{25}	Yield, %
$(n\text{-}C_4H_9)_2S$	121–124	26	1.4907	56.2
$(n\text{-}C_4H_9S)_2$	105–108	2	1.4872	53.5
$(n\text{-}C_5H_{11}S)_2$	124.0–126.5	10	1.4810	47.3
$(\text{iso-}C_5H_{11}S)_2$	86–89	1.5	1.5440	64.7
$(n\text{-}C_3H_7S)_2S$	86–90	8	1.5382	46.0
$(\text{iso-}C_3H_7S)_2S$	87–90	0.7	1.5287	45.0
$(n\text{-}C_4H_9S)_2S$	180–183	740	1.4493	40.7

TABLE II

WAVE LENGTHS, mμ

	Minima	Maxima
$(n\text{-}C_4H_9S)_2$	227	252
$(n\text{-}C_5H_{11}S)_2$	227	254
$(\text{iso-}C_5H_{11}S)_2$	227	252
$(n\text{-}C_3H_7S)_2S$	—	251
$(\text{iso-}C_3H_7S)_2S$	—	254
$(n\text{-}C_4H_9S)_2S$	—	251

EXPERIMENTAL

Di-n-butyl sulfide. Sodium (5.1 g., 0.22 g.-atom) was dissolved in 125 cc. of absolute ethyl alcohol in a three necked flask protected by a calcium chloride tube and an atmosphere of dry nitrogen. With stirring and cooling in an ice bath, 20.0 g. (0.22 mole) of *n*-butyl mercaptan was added, followed by 31.0 g. (0.23 mole) of *n*-butyl bromide, over a 15 min. period. After the addition had been completed, the reaction mixture was refluxed for 2 hr., cooled, the organic layer separated from the solid which had formed during reaction, and dried over calcium sulfate. Distillation of the product yielded 13.0 g. (0.09 mole) of di-*n*-butyl sulfide, yield 40.7%, b.p. 180–183°/740 mm. (lit.[8] 182°); n_D^{25} 1.4493 (lit.[9] 1.4530).

Di-n-butyl disulfide. Di-*n*-butyl disulfide was prepared by a procedure similar to that reported by Stutz and Shriner.[2] Sodium thiosulfate pentahydrate (300 g., 1.21 mole) in 500 cc. of ethyl alcohol and 400 cc. of water was stirred

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(1) Springer and LeGros, *Ber.*, **15**, 1938 (1882).

(2) Stutz and Shriner, *J. Am. Chem. Soc.*, **55**, 1242 (1933).

(3) Cairns, Evans, Larchar, and McKysick, *J. Am. Chem. Soc.*, **74**, 3982 (1952).

(4) Birch, Cullum, and Dean, *J. Inst. Petroleum*, **39**, 206 (1953).

(5) Gorin and Dougherty, *J. Org. Chem.*, **21**, 241 (1956).

(6) Koch, *J. Chem. Soc.*, 394 (1949).

(7) Baer and Carmack, *J. Am. Chem. Soc.*, **71**, 1215 (1949).

(8) Chemical Rubber Co., *Handbook of Chemistry and Physics*, page 821.

(9) Vaughan and Rust, *J. Org. Chem.*, **7**, 472–6 (1942).

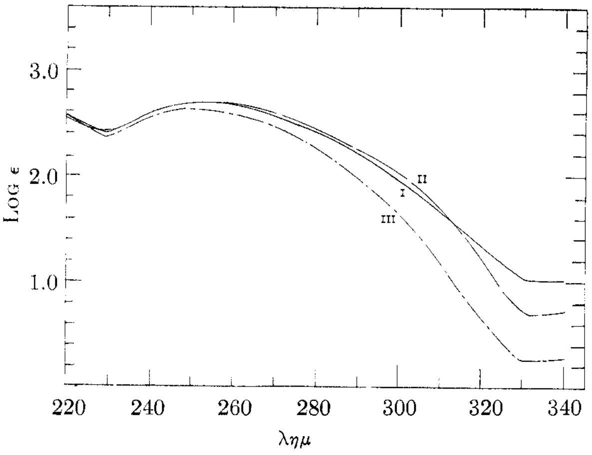

FIG. 1.—ULTRAVIOLET ABSORPTION SPECTRA OF ALKYL DISULFIDES, I, *n*-BUTYL DISULFIDE; II, *n*-AMYL DISULFIDE; III, ISOAMYL DISULFIDE.

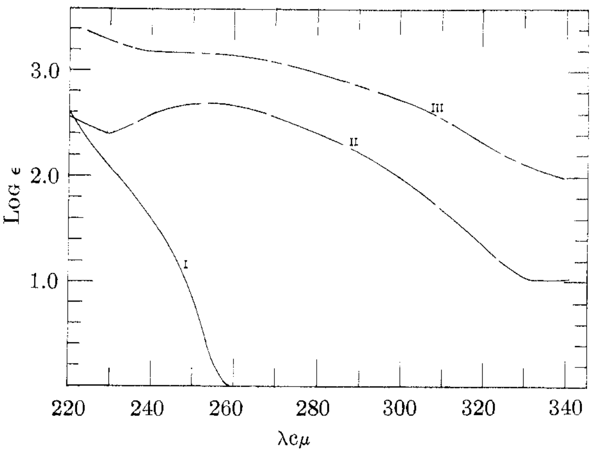

FIG. 3.—ULTRAVIOLET ABSORPTION COMPARISON SPECTRA OF *n*-BUTYL SULFIDE AND POLYSULFIDES, I, *n*-BUTYL SULFIDE; II, *n*-BUTYL DISULFIDE; III, *n*-BUTYL TRISULFIDE.

until solution had been completed, after which 137.0 g. (1.00 mole) of *n*-butyl bromide was added over a 1-hr. period. Stirring and refluxing were continued for 2 hr. On partial cooling, 140 g. (2.5 moles) of potassium hydroxide in 300 cc. of water was added with 45 min. stirring and refluxing. The organic layer was separated, washed with 200 cc. of distilled water and dried over calcium chloride. Distillation yielded di-*n*-butyl disulfide (49.9 g., 56.2%), b.p. 121–124°/26 mm. (lit.[2] 120–123°/26–30 mm.); n_D^{25} 1.4907 (lit.[2] n_D^{20} 1.4926).

Di-n-amyl disulfide. Di-*n*-amyl disulfide was also prepared by the method outlined above using the same molar proportions of reactants, including 151.0 g. (1.00 mole) of *n*-amyl bromide. Di-*n*-amyl disulfide (55.0 g., 0.27 mole) was isolated by distillation; yield 53.5%, b.p. 105–108°/2 mm. (lit.[10] 90–92°/1 mm.); n_D^{25} 1.4872 (lit.[10] 1.4875).

Di-isoamyl disulfide. Di-isoamyl disulfide was prepared as was the *n*-isomer. 1-Bromo-3-methylbutane (151.0 g., 1.00 mole) was used, yielding 48.6 g. (0.24 mole) of di-isoamyl disulfide, yield 47.3%, b.p. 124.0–126.5°/10 mm. (lit.[11] 123.5–124.0°/12 mm.); n_D^{25} 1.4810 (lit.[12] 1.4832).

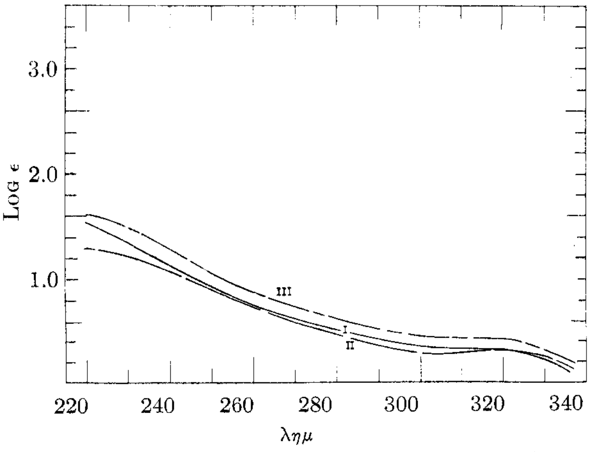

FIG. 2.—ULTRAVIOLET ABSORPTION SPECTRA OF ALKYL TRISULFIDES, I, *n*-PROPYL TRISULFIDE; II, ISOPROPYL TRISULFIDES; III, *n*-BUTYL TRISULFIDE.

Di-n-propyl trisulfide. Di-*n*-propyl trisulfide was prepared by a similar procedure, as reported by Clayton and Etzler.[13] *n*-Propyl mercaptan (30.5 g., 0.40 mole) dissolved in 300 cc. of carbon disulfide was placed in a 1 l. three-necked flask, equipped with a condenser, mechanical stirrer, and calcium chloride tube. With stirring, 20.6 g. (0.2 mole) of sulfur dichloride in 200 cc. of carbon disulfide was added over a period of 3 hr. After all the sulfur dichloride had been added, the mixture was refluxed for 1 hr. After cooling, the solvent was distilled off under reduced pressure and the residue fractionated, giving di-*n*-propyl trisulfide, 23.5 g. (64.7%), b.p. 86–89°/1.5 mm. (lit.[3] 68–69°/0.9 mm.); n_D^{25} 1.5440 (lit.[3] 1.5424)

Di-isopropyl trisulfide. By the same procedure, using 16 g. (0.21 mole) of isopropyl mercaptan and the other reactants in relative amounts, di-isopropyl trisulfide was isolated (8.5 g., 46%), b.p. 86–90°/8 mm. (lit.[3] 75–76°/5 mm.); n_D^{25} 1.5352 (lit.[3] 1.5351).

Di-n-butyl trisulfide. Similarly, using 36 g. (0.40 mole) of *n*-butyl mercaptan and other reactants in proportion, di-*n*-butyl trisulfide was isolated (19.0 g., 45%) b.p. 87–90°/0.7 mm. (lit.[11] 119–21°/6 mm.); n_D^{25} 1.5287 (lit.[4] n_D^{20} 1.5320).

Determination of the spectra. The ultraviolet spectra were measured with a Beckman Model DK-2 spectrophotometer. After the instrument was balanced, the spectra were determined using isooctane as the solvent. The solvent, spectro grade isooctane, was purchased from the Phillips Petroleum Co. The concentration of the solutions of mono- and disulfides were about 0.001*M* and of trisulfides 0.0005*M*. The solutions of the polysulfides were prepared in a more concentrated form, then diluted to the above mentioned lower grade.

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(11) Hunter and Sorenson, *J. Am. Chem. Soc.*, **54**, 3364 (1932).

(12) Vogel and Cowan, *J. Chem. Soc.*, 16 (1943).

(13) Clayton and Etzler, *J. Am. Chem. Soc.*, **69**, 974 (1947).