Anal. Calcd. for $C_{10}H_{12}ClNO$: N, 7.1; Cl, 17.9. Found: N, 7.0; Cl, 17.6.

γ-Hydroxybutyranilide.—γ-Chlorobutyranilide (3.9 g., 0.02 mole) was heated in a solution of sodium carbonate (10.6 g., 0.01 mole) in 150 ml. of 33% ethanol until it dissolved. The solution was refluxed for 2 hr. with stirring and, after storage overnight in the cold (0°), sodium carbonate was filtered off and the filtrate was evaporated to dryness under reduced pressure. The solid residue was taken into hot benzene, and the benzene solution was concentrated to a semisolid. Petroleum ether was added, and the precipitate, obtained after storage in the cold (0°) overnight, was recrystallized from benzene–petroleum ether. The γ-hydroxybutyranilide thus obtained, 0.6 g. (17%), melted at 74–75°; $\lambda_{\max}^{\text{Nujol}}$ 3.0, 3.1, 3.15 (OH, NH-secondary amide); 6.0, 6.5 (CO–NH); 13.0–13.7, 14.4 μ (monosubstituted aromatic).

Anal. Calcd. for $C_{10}H_{13}NO_2$: N, 7.8. Found: N, 7.6.

Evaporation of the petroleum ether precipitation solvent left 1.1 g. (34%) of 1-phenylpyrrolidin-2-one, identified by mixture melting point and infrared spectrum.

α-Benzamido-γ-chlorobutyr-N-benzylamide (V).—α-Benzamido-γ-hydroxybutyr-N-benzylamide (3.2 g., 0.01 mole) was dissolved with cooling (ice–salt bath) in 10 ml. of thionyl chloride. The reaction mixture was stirred, brought to room temperature, and then heated to boiling. After cooling, ether and petroleum ether were added. The separated oil was washed with water and dissolved in ethanol. The product was precipitated by addition of water and crystallized from ethanol, yielding 2.8 g. (85%), m.p. 168°.

Anal. Calcd. for $C_{18}H_{19}ClN_2O_2$: C, 65.3; H, 5.8; N, 8.5; Cl, 10.7. Found: C, 65.5; H, 5.4; N, 8.5; Cl, 11.0.

α-Benzamido-γ-chlorobutyr-N-cyclohexylamide was prepared as above (52%), m.p. 195°.

Anal. Calcd. for $C_{17}H_{23}ClN_2O_2$: C, 63.3; H, 7.2; N, 8.7; Cl, 11.0. Found: C, 64.0; H, 6.8; N, 8.5; Cl, 10.6.

1-Benzyl-3-benzamidopyrrolidin-2-one (VI).—α-Benzamido-γ-chlorobutyr-N-benzylamide (1.6 g., 0.005 mole) was dissolved in 50 ml. of 1 *N* methanolic sodium methoxide and heated for 4 hr. at reflux. The solvent was evaporated, and the residue was washed with water and crystallized from ether–petroleum ether. The product, 1.2 g. (80%), m.p. 160°, was identified by mixture melting point and infrared spectrum.[3]

α-Amino-γ-N-benzylaminobutyric Acid Dihydrochloride (VII).—1-Benzyl-3-benzamidopyrrolidin-2-one (1 g., 0.0034 mole) was heated in 25 ml. of 20% aqueous hydrochloric acid. After cooling, benzoic acid was filtered, and the solution was washed with ether and evaporated. The semisolid residue was crystallized twice from ethanol–ether yielding the product, 0.5 g. (52%), m.p. 185–188°.

Anal. Calcd. for $C_{11}H_{18}Cl_2N_2O_2$: C, 47.0; H, 6.5; N (Kj.), 10.0; N (V. Sl.), 5.0. Found: C, 47.4; H, 6.5; N (Kj.), 10.1; N (V. Sl.), 5.3.

Acknowledgment.—We wish to thank Professor Max Frankel for his interest in this work.

Organic Polysulfides.[1] IV. Synthesis of Bis(triphenylmethyl) Polysulfides

TAKESHIGE NAKABAYASHI, JITSUO TSURUGI, AND TAKUZO YABUTA

The Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai City, Osaka, Japan

Received July 26, 1963

Bis(triphenylmethyl) penta-, hexa-, hepta-, and octasulfides were obtained in crystalline state by condensation of the triphenylmethyl hydrodi- or hydrotrisulfide with sulfur di- or monochloride, respectively. For comparison, the bis(triphenylmethyl) mono-, di-, tri-, and tetrasulfides were prepared also by the ordinary methods. The ultraviolet absorption spectra of a series of these polysulfides were measured. No anomaly was observed among the spectra as the number of sulfur atoms increased from one to eight.

In a previous paper,[2] dibenzyl and dibenzhydryl penta- and hexasulfides were prepared by condensation of the corresponding aralkyl hydrodisulfides with sulfur di- and monochloride, respectively.

$$2RSSH + SCl_2 \longrightarrow RSSSSSR \quad (1)$$

$$2RSSH + S_2Cl_2 \longrightarrow RSSSSSSR \quad (2)$$

The corresponding mono-, di-, tri-, and tetrasulfides were prepared also to compare some properties of each series of polysulfides from mono- to hexasulfide. All the results obtained there supported linear sulfur linkages of the polysulfides.

Alkyl hydrotrisulfides, RSSSH, were prepared by Böhme and Zinner[3] as indicated in eq. 3–5, where R represents methyl, ethyl, or benzyl group. In the present paper, this method was applied to prepare triphenylmethyl hydrotrisulfide. Bis(triphenylmethyl) hepta- and octasulfides were prepared by condensation of 2 moles of triphenylmethyl hydrotrisulfide and 1 mole of sulfur di- and monochlorides, respectively. The synthetic method is indicated in eq. 3–7, where R represents the triphenylmethyl group.

$$2CH_3COSH + 2Cl_2 \longrightarrow CH_3COSSCl + CH_3COCl + 2HCl \quad (3)^4$$

$$CH_3COSSCl + RSH \longrightarrow CH_3COSSSR + HCl \quad (4)^4$$

$$CH_3COSSSR + C_2H_5OH \longrightarrow RSSSH + CH_3COOC_2H_5 \quad (5)^3$$

$$2RSSSH + SCl_2 \longrightarrow RSSSSSSSR + 2HCl \quad (6)$$

$$2RSSSH + S_2Cl_2 \longrightarrow RSSSSSSSSR + 2HCl \quad (7)$$

As reported in part I for dibenzyl and dibenzhydryl compounds, bis(triphenylmethyl) penta- and hexasulfides were prepared according to eq. 1 and 2, respectively. The bis(triphenylmethyl) mono-, di-, tri-, and tetrasulfides also were prepared to obtain a series of polysulfides from mono- to octasulfide. All of the polysulfides were obtained in the crystalline state, although dibenzyl and dibenzhydryl hexasulfides could not be obtained in the crystalline state but only in the oily state as reported in a previous paper.

Table I indicates melting points, color, yields, and analytical data of these compounds.

The ultraviolet absorption spectra (Fig. 1) were measured in chloroform solution between 240 and 380 mμ. The strong absorption band with a maximum between 240 and 250 mμ may be ascribed to triphenylmethyl group. The broad absorption band in the range of 290–330 mμ is probably due to linear S–S linkages in the polysulfides, because ultraviolet absorption spectra[2] of dibenzyl and dibenzhydryl polysulfides indicate the similar broad band in the same region. Figure 1 shows that, as the number of sulfur atoms in these polysulfides increases, the absorbance becomes

---

[1] Part III: T. Nakabayashi and J. Tsurugi, *J. Org. Chem.*, **26**, 2482 (1961).

[2] J. Tsurugi and T. Nakabayashi, *ibid.*, **24**, 807 (1959).

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

[4] H. Böhme and M. Clement, *ibid.*, **576**, 61 (1952).

TABLE I

MELTING POINTS, COLOR, YIELDS, AND ANALYTICAL DATA OF BIS(TRIPHENYLMETHYL) POLYSULFIDES

Compound	Yield, %[a]	Color	M.p., °C.	Calcd., % C	Calcd., % H	Calcd., % S	Found, % C	Found, % H	Found, % S
Monosulfide	29	White	165 (182 dec.)[b]	87.99	5.83	6.18	87.32	5.75	6.1
Disulfide	70	White	155 dec. (155 dec.)[b]	82.87	5.49	11.64	83.79	5.74	11.3
Trisulfide	74	Faintly yellow	147–148.5	78.31	5.19	16.51	78.05	5.00	16.6
Tetrasulfide	81	Faintly yellow	146–148	74.22	4.92	20.86	74.17	5.13	20.5
Pentasulfide	56	Faintly yellow	146–147	70.54	4.68	24.78	70.38	4.59	24.5
Hexasulfide	82	Faintly yellow	146–147	67.21	4.45	28.33	67.05	4.58	28.9
Heptasulfide	54	Faintly yellow	136–137	64.18	4.25	31.57	64.63	4.37	30.9
Octasulfide	52	Yellow	43–47 dec.	61.41	4.07	34.52	60.62	4.00	34.7

[a] Yields calculated on the basis of the thiol, hydrodisulfide, or hydrotrisulfide. [b] D. Vorländer and E. Mittag, *Chem. Ber.*, **52**, 413 (1919).

more intense, and the displacement toward the longer wave length occurs as in the dibenzyl and dibenzhydryl polysulfides.[2] No anomaly was observed among the curves of a series of polysulfides as the number of sulfur atoms increases from one to eight. If the higher polysulfides have any coordinate sulfur atoms in branches, their spectrum would differ from that of the linear one. It is concluded that the polysulfides thus prepared have suffered no rearrangement of sulfur atoms and, therefore, have linear sulfur chains.

It is well-known that primary and secondary thiols are readily oxidized by iodine to the corresponding disulfides. On the other hand, tertiary thiols[5,6] were reported to react with iodine to form sulfenyl iodide.

$$t\text{-RSH} + I_2 \longrightarrow \text{RSI} + \text{HI}$$

However, preliminary work in the present study showed that triphenylmethanethiol did not consume iodine in ethanol. This fact is ascribed to a steric effect, the bulky triphenylmethyl group of triphenylmethanethiol hindering the attack of the iodine molecule. In contrast to triphenylmethanethiol, triphenylmethyl hydrodi- and trisulfides were oxidized readily by the same method to the tetra- and hexasulfides.

Figure 2 shows the relation between the melting point and the number of sulfur atoms in three series of aralkyl polysulfides. The melting points of the dibenzyl- and dibenzhydryl polysulfides were reported in a previous paper[2] and are cited here.

A similar relation is observed between melting point and number of sulfur atoms of benzyl and benzhydryl series, although the increase of melting temperature of dibenzhydryl disulfide is more prominent than that of dibenzyl disulfide. As the sulfur chain of the bis(triphenylmethyl) series increases from one to seven, only a gradual decrease of melting temperature is observed in contrast to the benzyl and benzhydryl series. Figure 2 also shows that the melting temperatures of dibenzyl and dibenzhydryl hexasulfides and of bis(triphenylmethyl) octasulfide decrease suddenly. This sudden decrease as well as the anomalously high melting temperatures of dibenzyl and dibenzhydryl disulfides cannot be interpreted at the present time. Paucity of knowledge on conformations both in the solid and in the liquid state and on possible rotation about S–S bonds of the polysulfides prevents detailed discussion of the results indicated in Fig. 2.

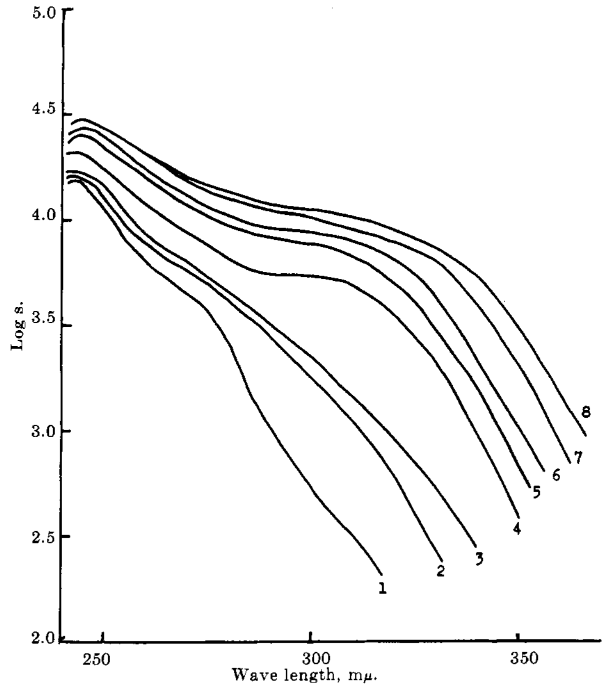

Fig. 1.—Ultraviolet absorption spectra of bis(triphenylmethyl) polysulfides in chloroform solution: 1, mono-; 2, di-; 3, tri-; 4, tetra-; 5, penta-; 6, hexa-; 7, hepta-; and 8, octasulfide.

Experimental

Acetyl sulfenyl chloride,[4] acetyl disulfide,[4] and triphenylmethanethiol[7] were prepared by methods in the literature. All the solvents used here were purified and dried by conventional methods. Sulfur di- and monochlorides were distilled directly before use.

Acetyl Triphenylmethyl Disulfide.—A solution of 82 g. (0.297 mole) of triphenylmethanethiol in a mixture of ether and benzene was added dropwise with stirring in a stream of nitrogen to a solution of 41 g. (0.371 mole) of acetyl sulfenyl chloride in ether. The temperature was kept below 5° by cooling during the reaction. After standing for 2 hr., the mixture was washed with water and aqueous sodium bicarbonate solution, and dried with anhydrous sodium sulfate. After evaporating the solvent, 89 g. (0.254 mole) of white crystals remained which were recrystallized from a mixture of ether and petroleum ether, m.p. 82–82.5° (85%).

Anal. Calcd. for $C_{21}H_{18}OS_2$: S, 18.30. Found: S, 18.10.

Acetyl Triphenylmethyl Trisulfide.—Triphenylmethanethiol was coupled with acetyl disulfide chloride ($CH_3COSSCl$) by the same procedure as for acetyl triphenylmethyl disulfide. A solution of 28 g. (0.101 mole) of triphenylmethanethiol in a mixture of ether (200 ml.) and benzene (70 ml.) was added to 17 g. (0.119 mole) of acetyl disulfide chloride in ether (50 ml.). The yield of white crystals which melted at 127–128° was 33 g. (0.863 mole,

---

(5) H. Rheinboldt and E. Motzkus, *Chem. Ber.*, **72**, 657 (1939).

(6) I. M. Kolthoff and W. E. Harris, *Anal. Chem.*, **21**, 963 (1949).

(7) N. Kharasch and H. R. Williams, *J. Am. Chem. Soc.*, **72**, 1843 (1950).

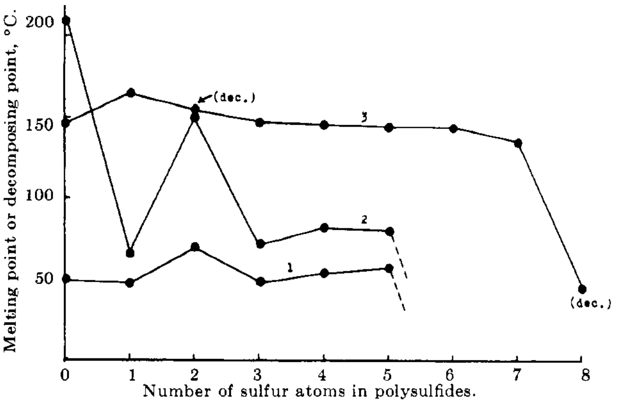

Fig. 2.—Relation between melting point and number of sulfur atoms of polysulfides: 1, dibenzyl; 2, dibenzhydryl; and 3, bis-(triphenylmethyl) series. Melting points of dibenzyl, *sym*-tetraphenylethane, and hexaphenylethane cited from the literature (I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953).

85%). Recrystallization from a mixture of benzene and ether gave white crystals, m.p. 127.5–128.5°.

Anal. Calcd. for $C_{21}H_{18}OS_3$: S, 25.15. Found: S, 24.7.

Triphenylmethyl Hydrodisulfide.—Ten grams (28.5 mmole) of acetyl triphenylmethyl disulfide and 70 ml. of a mixture of benzene–ethanol (3:4 by vol.) were placed in a four-necked flask equipped with a dropping funnel, thermometer, nitrogen inlet tube, and reflux condenser, the top of which was protected with a calcium chloride tube. In a stream of nitrogen, 25 ml. of dry 5 *N* ethanolic hydrogen chloride was added to the contents of the flask, which was kept at 25–30°. The crystals of acetyl triphenylmethyl disulfide disappeared completely after 4–5 hr. After standing at room temperature, white crystals of triphenylmethyl hydrodisulfide separated from the solution. By evaporating under reduced pressure the solvent and the ethyl acetate which were formed during the reaction, 8 g. (25.9 mmoles, 91%) of a crude product (m.p. 110–114°) was obtained which was recrystallized from a mixture of benzene and ether. This compound had m.p. 114–116° and was easily oxidized by ethanolic iodine to the corresponding tetrasulfide (m.p. 146–148°), which was identified by mixture melting point with a sample prepared from the thiol and sulfur monochloride.

Triphenylmethyl Hydrotrisulfide.—Six grams (15.7 mmoles) of acetyl triphenylmethyl trisulfide in a mixture of benzene (50 ml.) and absolute ethanol (60 ml.) was treated with 15 ml. of dry 5 *N* ethanolic hydrogen chloride. After evaporating the solvent and ethyl acetate, 3 g. (8.8 mmoles, 56%) of the white solid was obtained and recrystallized from a mixture of ether and petroleum ether. This compound, m.p. 65–69°, should be stored in a refrigerator under an inert gas atmosphere. The compound was oxidized by ethanolic iodine to the hexasulfide, which was identified by mixture melting point with an authentic sample described later.

Bis(triphenylmethyl) Monosulfide.[8]—This compound was prepared by condensation of triphenylmethanethiol with triphenylmethyl chloride, was recrystallized from chloroform–ethanol, and had m.p. 165°, lit.[8] m.p. 182° dec.

Bis(triphenylmethyl) Disulfide.[8]—By the same method described in the literature, the disulfide was prepared by condensation of triphenylmethyl sulfenyl chloride with triphenylmethanethiol and was recrystallized from a mixture of benzene–petroleum ether. This compound should be recrystallized with the utmost care, because of its instability to heat or moisture.

Bis(triphenylmethyl) Trisulfide.—To a solution of 5.5 g. (19.9 mmoles) of the triphenylmethanethiol in ether (100 ml.) with cooling and stirring was added dropwise in a stream of nitrogen 1.1 g. (10.1 mmoles) of sulfur dichloride (b.p. 58.5–60°) in 30 ml. of ether at room temperature. After the evolution of hydrogen chloride gas, the solvent was evaporated under reduced pressure. The residue gave 4.3 g. (7.4 mmoles) of crude crystals (m.p. 143–145°) which were recrystallized from a mixture of benzene–petroleum ether.

Bis(triphenylmethyl) Tetrasulfide.—Sulfur monochloride (b.p. 136–137°) was used in place of sulfur dichloride in the above preparation. The crude crystals were recrystallized from a mixture of chloroform–ethanol.

Bis(triphenylmethyl) Pentasulfide.—To a solution of 2.2 g. (7.1 mmoles) of triphenylmethyl hydrodisulfide in a mixture of ether (50 ml.) and benzene (10 ml.) with stirring at room temperature was added dropwise an equivalent amount (0.4 g., 3.9 mmoles) of sulfur dichloride in a stream of nitrogen. After the solvent was evaporated under reduced pressure, 1.3 g. (2.0 mmoles) of the crude product was recrystallized from a mixture of chloroform–ethanol.

Bis(triphenylmethyl) Hexasulfide.—Sulfur monochloride (0.7 g., 5.2 mmoles) was added dropwise to triphenylmethyl hydrodisulfide (3.1 g., 10.1 mmoles) as for the pentasulfide. After evaporating the solvent, the crude compound was obtained in crystalline state and recrystallized from the same solvent mixture.

Bis(triphenylmethyl) Heptasulfide.—To a solution of triphenylmethyl hydrotrisulfide (1.6 g., 4.7 mmoles) in 60 ml. of ether was added slowly 0.23 g. (2.2 mmoles) of sulfur dichloride in 20 ml. of the same solvent. After evaporating the solvent under reduced pressure and adding a small amount of petroleum ether to the solution, cooling gave 0.9 g. (1.3 mmoles) of crude crystals. Recrystallization from a mixture of benzene and petroleum ether gave pure compound.

Bis(triphenylmethyl) Octasulfide.—The synthetic procedure was the same as for the heptasulfide. From 1.4 g. (4.1 mmoles) of triphenylmethyl hydrotrisulfide and 0.3 g. (2.2 mmoles) of sulfur monochloride, 0.8 g. (1.1 mmoles) of crude product was obtained as a yellow solid which was recrystallized from a mixture of ether and petroleum ether in a Dry Ice bath; it decomposed at 43–47° with evolution of gas.

Ultraviolet Absorption Measurements.—The ultraviolet absorption spectra were determined with a Hitachi EPU-2 spectrophotometer, using chloroform as the solvent.

---

(8) D. Vorländer and E. Mittag, *Chem. Ber.*, **52**, 413 (1919).