Reactions of 2,2′-Dithiobis(2-methylpropionaldehyde)

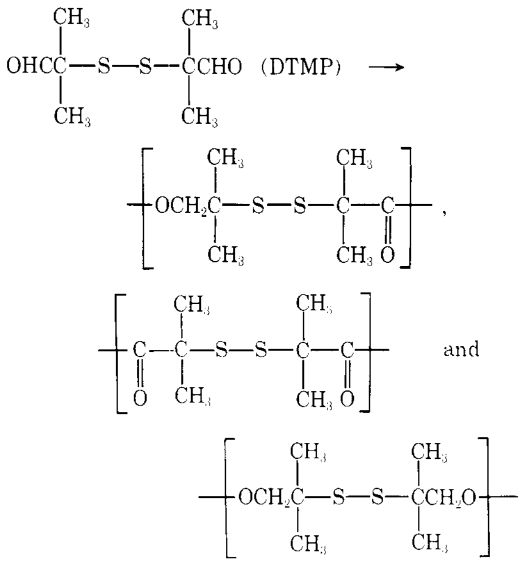
Katsumi Hayashi

The Lubrizol Corporation, Cleveland, Ohio 44117. *Received November 10, 1969*

ABSTRACT: 2,2′-Dithiobis(2-methylpropionaldehyde) (DTMP) polymerized with butyllithium, alkylaluminum, alkoxide, and metal hydride catalysis to form a linear polyester. In the presence of 1,4-butanediol or 1,10-decanediol, the reaction produced a polyester glycol. The molecular weight of the polyester glycol could be controlled by varying the ratio of DTMP to 1,4-butanediol. The polyester glycol formed elastomeric polyurethans. DTMP oligomerized with a catalytic amount of sodium hydride in pyridine to a 28-membered cyclic ester tetramer. The yield was about 95%. In methanol or ethanol containing a small amount of the corresponding alkoxide, DTMP was converted to methyl or ethyl 6-hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanoate in 70% yield. A Cannizzaro reaction of DTMP in dilute aqueous sodium hydroxide solution produced exclusively 6-hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanoic acid (I). The hydroxy acid (I) has failed to polymerize under the normal conditions for polycondensation. However, the corresponding lactone which is made readily by dehydrating I with acetic anhydride polymerized with butyllithium catalysis to afford a high molecular weight polyester.

Polyester from 2,2′-Dithiobis(2-methylpropionaldehyde) (DTMP). It has been reported that terephthalaldehyde and other aromatic dialdehydes polymerize with trialkylaluminum and dialkylaluminum halide catalysis to form polyesters by the Tishchenko reaction.[1,2] Thus far, glutaraldehyde is the only aliphatic dialdehyde which has been reported to undergo this polymerization.[3]

We have found that DTMP polymerizes easily at room temperature or above with a catalytic amount of butyllithium in bulk or in solution to form a polyester. The polyester was obtained as a white crystalline precipitate in *n*-hexane and as a viscous solution in benzene. Evaporation of the benzene solvent left a viscous amorphous material which crystallized slowly to give the same crystalline polymer as obtained from *n*-hexane.



$$\mathrm{OHC{-}C(CH_3)_2{-}S{-}S{-}C(CH_3)_2{-}CHO}\ \text{(DTMP)} \longrightarrow$$

$$\left[\mathrm{{-}OCH_2C(CH_3)_2{-}S{-}S{-}C(CH_3)_2{-}C({=}O){-}}\right],$$

$$\left[\mathrm{{-}C({=}O){-}C(CH_3)_2{-}S{-}S{-}C(CH_3)_2{-}C({=}O){-}}\right] \text{ and}$$

$$\left[\mathrm{{-}OCH_2C(CH_3)_2{-}S{-}S{-}C(CH_3)_2CH_2O{-}}\right] \quad (1)$$

The polymerization is highly exothermic. At a temperature between 30 and 50°, the reaction proceeds at a moderate rate and can be controlled easily by external cooling. No appreciable reaction takes place at 0° and too vigorous a reaction occurs at 70° or above.

The melting point of poly-DTMP is around 65°. It is soluble in aromatic and chlorinated hydrocarbons.

The polymer was hydrolyzed by heating with a 20% aqueous sodium hydroxide solution. The reaction gave three compounds: 6-hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanoic acid (I), 2,2,5,5-tetramethyl-3,4-dithiaadipic acid (II), and 2,2,5,5-tetramethyl-3,4-dithia-1,6-hexanediol (III). The mole ratio of I to (II + III) was nearly 1.

The nmr spectrum of poly-DTMP shows three sharp singlets at δ 1.32 (6 H, the *gem*-dimethyl protons adjacent to the methylene), 1.56 (6 H, the *gem*-dimethyl protons adjacent to the carbonyl), and 4.01 (2 H, the methylene protons).

The ir shows peaks at 1730 and 1250 cm^{-1} for the ester group and peaks at 1370 and 1680 cm^{-1} for the *gem*-dimethyl group. The polymer was absolutely free of aldehyde function on the basis of both the nmr and ir.

An increase in the amount of butyllithium catalyst resulted in a decrease of solution viscosity of the product. The highest reduced viscosity value, 0.29, was obtained when 0.5 mol of DTMP was polymerized with 0.001 mol of butyllithium in 200 ml of benzene. A catalyst concentration below this level did not initiate the polymerization.

When a high mole ratio of the catalyst to DTMP such as 1:2 of run no. 4 in Table I was employed in the polymerization, the product had an extremely low viscosity (0.036) and showed a strong ir absorption at 3450 cm^{-1} due to the hydroxyl group. The hydroxy-containing low molecular weight polymer was treated with a stoichiometric amount of 4,4′-methylenebis-(phenyl isocyanate) based on the hydroxy content. The treatment approximately doubled the molecular weight. This indicates that the initial polymer contained one hydroxyl group in each molecule on the average.

The polymerization of DTMP was also initiated by triisobutylaluminum, *sec*-butyllithium, lithium aluminum hydride, aluminum isopropoxide, and sodium ethoxide. Some results are listed in Table I.

---

(1) Ya. V. Mitin, N. Sazahov, and G. P. Vlasov, *Vysokomol. Soedin.*, **2**, 716 (1960).

(2) S. Sweeny, *J. Appl. Polym. Sci.*, **7**, 1983 (1963).

(3) K. Yokota, T. Ito, and Y. Ishii, *Kogyo Kagaku Zasshi*, **66**, 1112 (1962); *Chem. Abstr.*, **60**, 9362 (1964).

TABLE I
POLYMERIZATION OF DTMP

Run no.	DTMP, mol	Catalyst,[a] mol	Solvent,[b] ml		Yield, %	$\eta_{sp/c}$,[c] g^{-1} dl
1	0.486	BuLi	0.001	B 200	91	0.29
2	0.486	BuLi	0.010	B 200	89	0.21
3	0.486	BuLi	0.055	B 200	88	0.074
4	0.486	BuLi	0.22	B 200	96	0.036
5	0.134	BuLi	0.002	H 100	84	0.17
6	0.486	BuLi	0.008	None	89	0.14
7	0.097	*sec*-BuLi	0.003	B 80	79	0.12
8	0.486	Al(*i*-Bu)$_3$	0.008	B 200	91	0.10

[a] BuLi: a solution of 1.6 mol/l. in *n*-hexane; *sec*-BuLi and Al(*i*-Bu)$_3$: 20 wt % solutions in *n*-hexane. [b] B, benzene; H, *n*-hexane. [c] Measured at a concentration of 0.50 g/100 ml of chloroform at 30°.

TABLE II
MACROGLYCOLS FROM DTMP

DTMP, mol	Diol (mol)	BuLi,[a] mol	Benzene, ml	$\eta_{sp/c}$,[b] g^{-1} dl	Hydroxy equiv Calcd[c]	Hydroxy equiv Found[d]
2.00	1,4-Butane (0.10)	0.056	800	0.056	2830	2850
2.00	1,4-Butane (0.20)	0.042	800	0.042	1075	1080
1.05	1,4-Butane (0.21)	0.04	400	0.034	560	600
1.00	1,10-Butane (0.10)	0.02	400		1117	1100

[a] A solution of BuLi in *n*-hexane was added to a mixture of diol and benzene to form lithium alkoxide of the diol. [b] Measured at a concentration of 0.500 g/100 ml of chloroform at 30°. [c] Based on the structure shown in reaction 2. [d] Determined by the acetic anhydride–pyridine method.

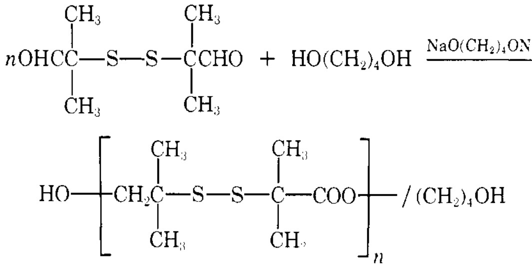
TABLE III
POLYURETHAN ELASTOMER FROM DTMP–MACROGLYCOL

Macroglycol OH equiv (g)	Diisocyanate (g)	Mole ratio at macroglycol to diisocyanate	Chain extender	Yield, %	$\eta_{sp/c}$,[c] g^{-1} dl
1060[a] (21.4)	TDI (1.76)	1:1	None	94	0.22
1070[a] (47.2)	MDI (11.1)	1:2	Water	94	0.34
1030[a] (48.6)	MDI (9.35)	1:2	Hydrazine	91	0.38
1180[b] (46.7)	MDI (9.90)	1:2	Hydrazine	95	0.45

[a] Macroglycols from DTMP and 1,4-butanediol. [b] Macroglycol from DTMP and 1,10-decanediol. [c] Measured at a concentration of 0.500 g/100 ml of DMF at 30°.

It seems reasonable that the actual catalytic species is not butyllithium but an alkoxide ion which is formed by the reaction of butyllithium and the aldehyde group of DTMP.

Macroglycol from DTMP and Polyurethan Elastomer Therefrom. Subjection of DTMP to the Tishchenko reaction in the presence of 1,4-butanediol or 1,10-decanediol and a catalytic quantity of the corresponding glycolate gave macroglycols having a molecular weight of 500–4000. The macroglycols were obtained as highly viscous liquids. The molecular weights determined by hydroxyl end group analysis agree well with the values calculated from the mole ratio of the two reagents.



$$n\mathrm{OHC}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-S-S-}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CHO} + \mathrm{HO(CH_2)_4OH} \xrightarrow{\mathrm{NaO(CH_2)_4ONa}} \mathrm{HO}\left[\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-S-S-}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-COO}\right]_n\mathrm{/(CH_2)_4OH} \qquad (2)$$

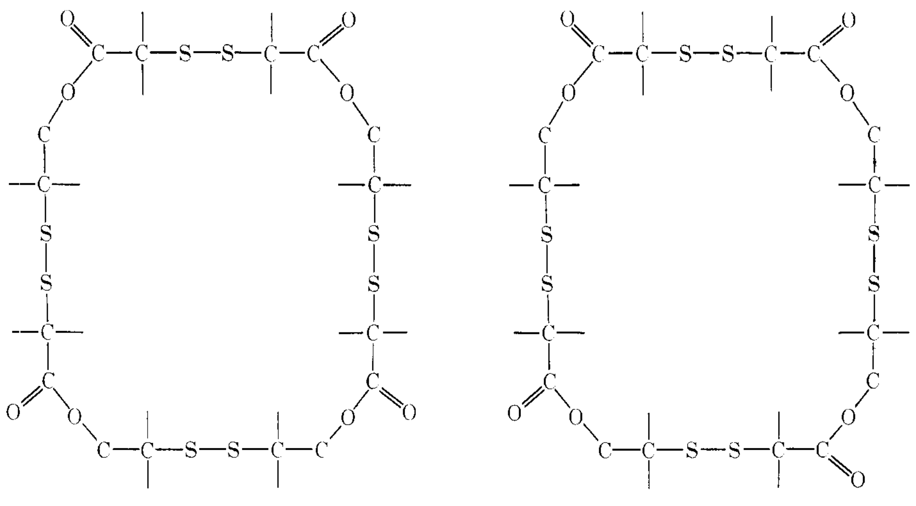
The structure of the macroglycol shown in reaction 2 is one of the possible structures. The unit from 1,4-butanediol may be located inside the macroglycol chain. The repeating units from DTMP consist of three different structures: hydroxy acid, diacid, and glycol which are shown in reaction 1. This was again confirmed by alkaline hydrolysis of a macroglycol which afforded the three compounds, I, II, and III. The molecular weight of the product can be varied by changing the ratio of DTMP to 1,4-butanediol.

A similar macroglycol was obtained using 1,10-decanediol instead of 1,4-butanediol. Typical examples are given in Table II. The ir and nmr spectra of the macroglycols are the same as that of poly-DTMP except for peaks due to methylene and hydroxy groups derived from the 1,4-butanediol unit.

Polyurethan elastomers were synthesized from these macroglycols and tolylene diisocyanate (TDI) or 4,4′-methylenedi(phenyl isocyanate) (MDI) by the well-established "prepolymer process."[4] Table III lists four examples of the polyurethan preparation. The

---

(4) J. H. Saunders and K. C. Frisch, "Polyurethanes, Chemistry and Technology," Part II, Interscience Publishers, New York, N. Y., 1964, p 299.

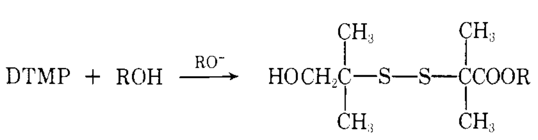


IVa IVb

Figure 1. Two possible structures for the ester tetramer of DTMP.

polyurethans thus obtained were colorless elastic materials and were soluble in N,N-dimethylacetamide. A transparent elastic film was cast from solution. Mechanical properties such as ultimate tensile strength, modulus, and elongation of the film were comparable to those of commercial polyurethan materials. The hydrolytic stability of the macroglycol was extremely good. The treatment of a macroglycol with 10% sodium hydroxide or 10% hydrochloric acid solution at 80° for 24 hr did not cause hydrolysis. However, the polyurethan film degraded rapidly when exposed to uv light (3600 Å) in air or to heat (100° or above) in the dark. The degradation was accompanied with a dramatic deterioration in mechanical properties, reduction of solution viscosity, and evolution of an unpleasant odor. The degradation apparently involved cleavage of carbon sulfur–sulfur linkages in the polyester chains.

Reaction of DTMP with Alcohols. DTMP reacted exothermically with methanol or ethanol in the presence of a catalytic amount of sodium alkoxide to form methyl or ethyl 6-hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanoate.



$$\mathrm{DTMP} + \mathrm{ROH} \xrightarrow{\mathrm{RO^-}} \mathrm{HOCH_2}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-S-S-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{COOR}$$

The yield was 60–70%; the remaining 30–40% was an undistillable brown residue. The structure of the residue was not fully characterized, but it appears to be a low molecular weight polyester on the basis of ir.

A Cyclic Ester Tetramer of DTMP. When DTMP was treated with *t*-butyl alcohol instead of methanol or ethanol, the major product was not the *t*-butyl ester of I, but a crystalline compound (IV) which had a high melting point, 182°, and was highly insoluble in many solvents. The yield of *t*-butyl ester was less than 10% even if a large excess of *t*-butyl alcohol was employed. The yield of IV was around 65%. Surprisingly, compound IV was obtained quantitatively when DTMP was treated with a mixture of catalytic amount of sodium hydride and pyridine.

IV was shown to be a cyclic ester tetramer of DTMP. The nmr spectrum of the compound was identical with that of poly-DTMP formed by the Tishchenko polymerization of DTMP. There were three sharp singlet proton signals at δ 1.32 (6 H), 1.56 (6 H), and 4.01 (2 H) and no signal due to an end group. The molecular weight determined by vapor phase osmometry was 812 which agrees with the value, 824, for a DTMP tetramer. The elementary analysis and ir were also consistent with the ester tetramer structure.

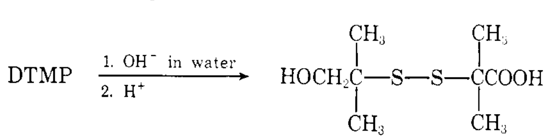
The compound resisted alkaline hydrolysis. Nevertheless, it hydrolyzed when heated in 40% aqueous sodium hydroxide for 3 days.

Three compounds, I, II, and III, were obtained from the hydrolysate. On the basis of these data, two structures, IVa and IVb shown in Figure 1, can be postulated for the tetramer. Both IVa and IVb are 28-membered cyclic esters and consist of four structural units from two of I, one of II, and one of III. Information obtained to date does not permit us to distinguish between the two structures for IV.

The cyclic ester tetramer formation was highly dependent upon the nature of the reaction solvent. In pyridine, DTMP was converted to IV in more than 95% yield. In dimethyl sulfoxide and *t*-butyl alcohol the yields were 50–60%. DTMP polymerized in dimethylformamide and hydrocarbons[5] to form a high molecular weight polyester.

Cannizzaro Reaction of DTMP. DTMP reacts exothermically with an aqueous solution of sodium hydroxide to form the hydroxy acid I in a yield above 95%.

This Cannizzaro reaction is unique in two respects. First, the sole product is I. This indicates that the



$$\mathrm{DTMP} \xrightarrow[\mathrm{2.\ H^+}]{\mathrm{1.\ OH^-\ in\ water}} \mathrm{HOCH_2}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-S-S-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{COOH}$$

I

---

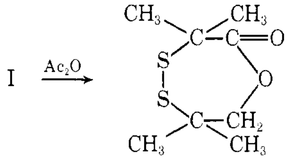
(5) BuLi was used as a catalyst. In all other solvents, the reaction was initiated with sodium hydride. Since sodium hydride is insoluble in hydrocarbons, the Tishchenko reaction of DTMP was not initiated with this catalyst.

reaction proceeds intramolecularly. Second, the reaction goes under mild conditions compared with normal Cannizzaro reactions. The reaction starts at room temperature in a dilute aqueous solution of 5, 10, or 20 wt % of sodium hydroxide. In general, a Cannizzaro reaction requires an aqueous solution of 40–50 wt % of sodium hydroxide.[6] Lithium hydroxide, potassium hydroxide, barium hydroxide, and calcium hydroxide were also effective as reagents.

Hydroxy Acid, I, and Its Derivatives. I is a new hydroxy acid. It was characterized by elementary analysis, ir, nmr, and neutralization equivalent determination. The hydroxy group of I was acetylated, and the carboxy group was esterified by methanol and ethanol under conventional conditions. However, all attempts have failed to derive a polyester by polycondensations of I, the methyl ester and I and the O-acetate of I.

It seems that the steric hindrance of *gem*-dimethyl groups reduces the reactivity of both the hydroxy and carbonyl groups of I.

I was converted to the corresponding lactone, 6-hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanoic acid ϵ-lactone (V), by dehydration with acetic anhydride. When I was heated with a slight excess of acetic anhydride at reflux for 2 hr followed by distillation, V was obtained in 90% yield.



V

V reacted easily with ammonia and amines to give the corresponding amides of I which could not be obtained by direct amidation of I. V also reacted with alcohols in the presence of an acid or alkoxide catalyst to form esters of I. V polymerized with butyllithium catalysis to afford a high molecular weight polyester. An inherent viscosity higher than 0.6 was attained.

The polymer derived from V was similar to the one obtained by a Tishchenko reaction of DTMP by its appearance, melting point (about 65°), solubility, and ir and nmr spectra. The polymer also degraded quickly upon subjection to uv light radiation and heat.

Experimental Section

2,2′-Dithiobis(2-methylpropionaldehyde) (DTMP).[7] To 1350 g (10 mol) of sulfur monochloride maintained at 50°, 1440 g (20 mol) of isobutyraldehyde was added dropwise. Evolution of hydrogen chloride began immediately. The isobutyraldehyde was added over a period of 4 hr. The temperature was maintained at 50–55°. Since the reaction was exothermic, no external heating was necessary to maintain the temperature. Stirring was continued for 1 hr after the addition was completed. A rapid flow of nitrogen was introduced into the mixture for approximately 1 hr. Upon distillation the fraction boiling at 80–120° (0.1 mm) was collected; it weighed 1660 g. This was redistilled. The fraction boiling at 90–93° (0.1 mm) was collected. It was a yellow oil and weighed 1520 g (74%). The material was dissolved in 3 l. of ligroin. The solution was cooled to −20° with efficient stirring. The white crystalline precipitate was collected by filtration and washed with cold ligroin. Distillation of the precipitate gave 1375 g (67%) of colorless DTMP: bp 81–83° (0.02 mm); n^{25}D 1.524; mp 24.3°.

Anal. Calcd for $C_8H_{14}O_2S_2$: S, 31.1. Found: S, 31.3.

The compound shows the infrared absorptions of the aldehyde groups at 2810, 2710, 1735, and 1715 cm^{-1} and the absorptions of the *gem*-dimethyl groups at 1370 and 1390 cm^{-1}.

Polymerization of DTMP. A solution of 206 g (1.0 mol) of DTMP in 500 ml of benzene was submitted to distillation and 200 ml of the solvent was removed. The remaining solution was cooled to 50°. To this stirred solution was added 1.0 ml of a 1.6-mol/l. *n*-butyllithium solution in *n*-hexane by means of a hypodermic syringe through a rubber serum cap. An exothermic reaction soon began and the reaction temperature was maintained at 55–60° by external ice–water cooling. The exotherm continued approximately 20 min. The mixture became viscous. Stirring was continued for 3 hr at ambient temperature. The solution was poured into methanol and the highly viscous precipitate was washed twice with methanol by decantation. The precipitate crystallized gradually to form a hard solid mass. The solid was further washed with methanol by means of a Waring Blendor and the product was dried under vacuum at 65° for 48 hr. The yield was 195 g (95%).

Anal. Calcd for $(C_8H_{14}O_2S_2)_n$: C, 46.6; H, 6.85; S, 31.1. Found: C, 46.6; H, 6.89; S, 31.2.

The ir shows peaks at 1730, 1260 cm^{-1} for the esters and peaks at 1365, 1380 cm^{-1} for the *gem*-dimethyl groups; $\eta_{sp/c}$ = 0.29 (measured at a concentration of 0.500 g/100 ml of chloroform and at 30°).

Hydrolysis of a Poly-DTMP. A mixture of 70 g of a poly-DTMP ($\eta_{sp/c}$ = 0.21), 30 g of sodium hydroxide, and 120 ml of water was heated at gentle reflux with efficient stirring for 20 hr. A light brown homogeneous solution was obtained. The solution was diluted with about 100 ml of water and extracted with methylene chloride. The methylene chloride solution was dried over magnesium sulfate and evaporated. The dried residue was recrystallized from cyclohexane to obtain 8.9 g of pale yellow crystals melting at 51–53°. It was shown by ir, nmr, and melting point studies that the compound was identical with an authentic sample of 2,2,5,5-tetramethyl-3,4-dithia-1,6-hexanediol which was synthesized by the reduction of DTMP with sodium borohydride. The aqueous layer obtained after the methylene chloride extraction was acidified with hydrochloric acid with ice–water cooling. The precipitate was collected by filtration, washed repeatedly with cold water, and dried. It melted at 140–175° and weighed 49.9 g. The neutralization equivalent was 172. This material was treated with 300 ml of boiling cyclohexane to leave 18.4 g of an insoluble portion. It was recrystallized from 1 l. of water to give 10.8 g of colorless needles melting at 196–197°. The melting point reported for 2,2′-dithiobis(2-methylpropionic acid) is 197°.[8] The neutralization equivalent was 121 (theory 119). The ir and nmr were consistent with this diacid. The hot cyclohexane solution was cooled to room temperature and the precipitate (15.9 g) was crystallized from warm cyclohexane to give colorless needles. The melting point was 84–86°. The compound was identical with an authentic sample of 6-hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanoic acid, the preparation of which is given below.

A Macroglycol from DTMP and 1,4-Butanediol at a 10/1

---

(6) T. A. Gaissman, *Org. Reactions*, II, 94 (1944).

(7) DTMP as described in U. S. Patent 2,580,695 (1952) [*Chem. Abstr.*, **46**, 7116 (1952)] by W. D. Niederhauser affords a yellow oil on distillation. A modified procedure given here gives a colorless product.

(8) E. Bilmann, *Ann.*, **348**, 127 (1906).

Mole Ratio. A mixture of 22.5 g (0.25 mol) of 1,4-butanediol and 0.3 g (0.013 g-atom) of sodium cut in small pieces was heated under nitrogen until all the metal disappeared. To this, 1000 ml of dry benzene was added. To the stirred mixture heated at 55°, was added dropwise 515 g of DTMP over a period of 20 min. The temperature was kept between 50 and 55° by external ice–water cooling. Stirring was continued overnight at ambient temperature. The mixture was diluted with 1000 ml of benzene and the solution was washed twice with dilute hydrochloric acid, five times with water, and dried over magnesium sulfate. The solvent was evaporated and the residue was dried in a rotary evaporator at 60–70° and at <0.1 mm for 24 hr. The product was a slightly yellow viscous liquid and weighed 510 g (95%). The hydroxy equivalent was 1090 which was determined by the acetic anhydride/pyridine method.

Polyurethan from the Macroglycol Prepared Above. A mixture of 47.2 g (0.0442 mol) of the macroglycol and 11.1 g (0.0884 mol) of 4,4′-methylenebis(phenyl isocyanate) was stirred at 70° for 3 hr under nitrogen. To this, 50 ml of N,N-dimethylacetamide was added to give a clear solution. To this solution was added 10 ml of N,N-dimethylacetamide containing 0.39 g (0.0221 mol) of water. Stirring was continued at 40° for 3 hr. The resulting viscous solution was poured into methanol and the precipitate which formed was washed repeatedly with methanol. The product was a virtually colorless, rubbery material and weighed 55 g (94%). The inherent viscosity was 0.34 measured at a concentration of 0.500 g/100 ml of N,N-dimethylformamide (DMF) at 30°. A transparent, tough elastic film was cast from DMF.

Reaction of DTMP with Methanol, Methyl 6-Hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanoate. Metallic sodium (2.0 g) was added to 1000 ml of methanol. To the stirred mixture was added dropwise 206 g (1.0 ml) of DTMP at 50–52°, over a period of 1 hr. The mixture was allowed to stand overnight at room temperature. The solvent was evaporated and the residue was dissolved in ether. The ether solution was washed with dilute hydrochloric, water, and dried. After removal of the solvent the residue was distilled. The fraction boiling at 82–83° (0.05 mm) was collected. The product was a colorless liquid and weighed 172 g (72%), $n^{25}\text{D}$ 1.5177.

Cyclic Ester Tetramer of DTMP. A mixture of 1.15 g of sodium hydride and 400 ml of pyridine was stirred at room temperature for 30 min. To this, 206 g (1.0 mol) of DTMP was added at one time. An exothermic reaction took place and the temperature reached approximately 95°. After the distinct exotherm ceased, precipitation started and soon the whole mixture solidified. The mixture was allowed to stand at room temperature overnight. Acetone was added to the mixture and the slurry was filtered. The precipitate was washed repeatedly with acetone and dried. The product was obtained as a faintly brown, powdery material and weighed 189 g (92%), mp 179–180°. It was recrystallized from 1000 ml of toluene to give 181 g of colorless needles, mp 179–180°.

Anal. Calcd for $C_8H_{14}O_2S_2)_4$: C, 46.57; H, 6.84; S, 31.08; mol wt, 824. Found: C, 46.57; H, 6.88; S, 31.24; mol wt. 812 (by vapor phase osmometry in chloroform).

Cannizzaro Reaction of DTMP 6-Hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanoic Acid (I). To 1200 g (3.0 mol) of 10% aqueous sodium hydroxide solution was added 412 g (2.0 mol) of DTMP at one time at room temperature. An exothermic reaction occurred. The temperature reached about 65° within 10 min and then gradually fell. Stirring was continued for 2 hr. The reaction mixture was a light brown homogeneous solution. The mixture was extracted once with ether. The aqueous layer was acidified with hydrochloric acid with ice–water cooling. The mixture was allowed to stand at ice–water temperature for 1 hr. The precipitate was collected by filtration, washed repeatedly with cold water, and dried. The product was almost colorless crystals melting at 86–88° and weighed 426 g (95%). It was recrystallized from 900 ml of toluene to give 380 g (85%) of colorless plates, mp 89–89.5°.

Anal. Calcd for $C_8H_{14}O_2S_2$: C, 42.8; H, 7.15; S, 28.5; neut equiv, 224. Found: C, 42.9; H, 7.32; S, 28.7; neut equiv, 223.

6-Hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanoic Acid Lactone (V). A mixture of 224 g (1.0 mol) of I and 153 g (1.5 mol) of acetic anhydride was heated under reflux for 4 hr. Acetic acid and the excess anhydride were evaporated. The residue was distilled. The fraction boiling at 75–90° (0.1–0.05 mm) was collected. It weighed 180 g (87%). Redistillation gave a colorless material which boiled at 79° (0.025 mm) and weighed 171 g (83%), mp 55–56°.

Anal. Calcd for $C_8H_{14}O_2S_2$: C, 46.6; H, 6.79; S, 31.1. Found: C, 46.2; H, 6.51; S, 31.1.

V reacted with aqueous ammonia to give 6-hydroxy-2,2,5,5-tetramethyl-3,4-dithiahexanamide as colorless needles, mp 85–86° (recrystallized from water).

Anal. Calcd for $C_8H_{14}O_2S_2$: C, 43.1; H, 7.63; N, 6.28; S, 28.7. Found: C, 43.1; H, 7.75; N, 6.16; S, 29.4.

An alkaline hydrolysis of V afforded a hydroxy acid which was identical with an authentic sample of I.