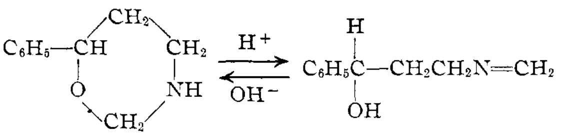
amino-1-phenylpropanol to form the oxazine derivatives probably involves a formaldimine intermediate. It is possible that a tautomeric equilibrium exists between oxazine and formaldimine.



Some evidence for this is derived from the reaction of oxazine derivatives with methanol and acid to form 3-amino-1-phenylpropanol. This reaction is actually a reversal of the last steps in the aminomethylation reaction. Based on work in the thiophene series,[8] it seems likely that this reaction of the oxazines goes through a formaldimine intermediate. Treatment of the oxazines with sulfuric acid or urea and hydrochloric acid also produces the primary amine. Similar reactions were observed with the formaldimines of the thiophene series. However, in both the oxazine and thiophene series, the primary amines are synthesized best by the methanol procedure.

Styrene can also be condensed with methylamine hydrochloride. However, this reaction goes less readily than the one with ammonium chloride. Improved yields can be obtained with paraformaldehyde and acetic acid as the solvent. The identity of the nitrogen compounds was not investigated.

A series of olefins, other than styrene, which can be condensed with formaldehyde and ammonium chloride include α-methylstyrene, isobutylene, 2-ethyl-1-butene, 2-methyl-1-pentene, α-pinene and β-pinene and butadiene.[3] Olefins such as 1-octene and 1-hexene did not react. Reaction conditions were generally similar to those used for styrene. Exceptions were with isobutylene, where a pressure vessel was used, and with the very reactive olefins, α-methylstyrene and β-pinene, where lower reaction temperatures were used.

The structures of these amines were not determined. On the basis of our work and that of Schmidle and Mansfield,[9] it seems likely that they are mixtures which contain the 6-substituted tetrahydro-1,3-oxazine and 4-substituted-4-piperidinol systems. The latter systems cannot form with olefins of the $RCH{=}CH_2$ type, such as styrene.

(8) H. D. Hartough and S. L. Meisel, THIS JOURNAL, **70**, 4018 (1948).

(9) C. J. Schmidle and R. C. Mansfield, *ibid.*, **77**, 5698 (1955); **78**, 1702 (1956).

PAULSBORO, NEW JERSEY

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

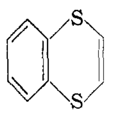
Heterocyclic Vinyl Ethers. XII. The Synthesis of Arylmercaptoacetylenes and a New Cleavage Reaction of Benzo-1,4-dithiadiene[1,2]

BY WILLIAM E. PARHAM AND PAUL L. STRIGHT[3]

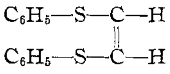
RECEIVED APRIL 5, 1956

This paper describes comparative studies of the reaction of *cis* and *trans*-bis-(phenylmercapto)-ethylene (II) and benzo-1,4-dithiadiene (I), with butyllithium. Both *cis* and *trans* II react with butyllithium in ethyl ether at 0° to give phenylmercaptoacetylene (III). The ease of preparation of ethylenes of type II and the high yield of products suggest that this reaction will serve as a convenient source for terminal mercaptoacetylenes. Benzo-1,4-dithiadiene, the cyclic analog of *cis*-II, does not undergo appreciable metalation by reaction with butyllithium in ethyl ether at 0°; however, when such reaction mixtures are treated with dimethyl sulfate, a substitution–elimination (SN-ε) reaction occurs, leading to the formation of 1-(*n*-butylthio)-2-methylthiobenzene (XIII) and acetylene. Possible mechanisms for these reactions are discussed.

In paper IX[4] of this series, attention was called to the fact that open chain analogs of benzo-1,4-dithiadiene (I), such as II, also undergo certain electrophilic substitution reactions at the ethylenic double bond.



I



II

This report describes comparative studies of the reaction of I, and *cis* and *trans* II, with butyllithium.

cis-Bis-(phenylmercapto)-ethylene (II) was treated with *n*-butyllithium in ethyl ether at 0°, and the product was separated into a water-soluble and an ether-soluble fraction. The water-soluble fraction contained the lithium salt of thiophenol, which was characterized by its oxidation to the known diphenyl disulfide. Distillation of the ether solution afforded an orange-yellow oil (60%),[5] which rapidly changed in color to red-brown. The composition of this product (C_8H_6S) suggested that it was phenylmercaptoacetylene,[6] and the infrared spectrum showed absorption typical of terminal acetylene (3290 and 2040 cm.$^{-1}$). The terminal acetylenic group was confirmed by the conversion of the product into the corresponding mercury derivative IV (m.p. 137°). The reaction sequence can thus be formulated as shown in the equation

$$\mathrm{II} + C_4H_9Li \xrightarrow[H_2O]{\text{then}} \underset{>50\%}{C_6H_5SLi} + \underset{\mathrm{III}\ (60\%)}{C_6H_5S{-}C{\equiv}CH} \xrightarrow{Hg^{++}} \underset{\mathrm{IV}\ (82\%)}{(C_6H_5S{-}C{\equiv}C)_2Hg}$$

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[1] This work was supported by the Office of Ordnance Research, U. S. Army, Contract No. DA-11-022-ORD-1716.

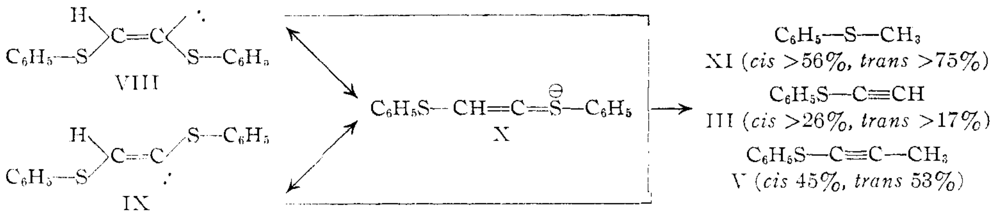
[2] Presented before the 129th Meeting of the American Chemical Society in Dallas, 1956.

[3] From the Ph.D. thesis of P. L. Stright, University of Minnesota, 1955.

[4] W. E. Parham and J. Heberling, THIS JOURNAL, **77**, 1175 (1955).

[5] The yield of undistilled product was estimated to be 80%.

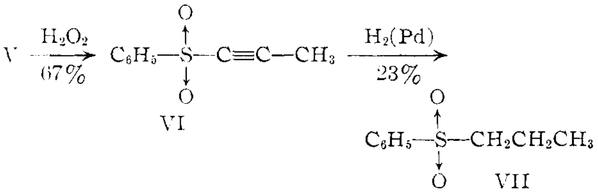
[6] W. E. Truce, J. A. Simms and M. Boudakian, THIS JOURNAL, **78**, 695 (1956), report the first instance of substituted acetylenes of this type.



The structure of phenylmercaptoacetylene (a member of a new class of acetylenes)[7] was established by its conversion into phenyl *n*-propyl sulfone (VII), as shown in the equations

$$\mathrm{III} \xrightarrow[(CH_3)_2SO_4]{n\text{-}C_4H_9Li} C_6H_5S{-}C{\equiv}C{-}CH_3 + \mathrm{I}$$

V (>25%) (45%)

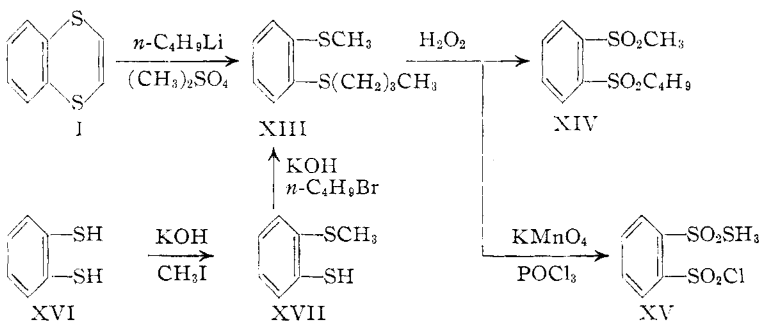


$$\mathrm{V} \xrightarrow[67\%]{H_2O_2} C_6H_5{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}C{\equiv}C{-}CH_3 \xrightarrow[23\%]{H_2(Pd)} C_6H_5{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}CH_2CH_2CH_3$$

VI VII

The product VII was identical in all respects with an authentic sample of phenyl *n*-propyl sulfone. The intermediates V and VI are new; details are found in the Experimental section of this report.

Comparison of the reactivity of *cis* and *trans* II with butyllithium was made in similar reactions in which the product was treated with dimethyl sulfate. Almost identical results were obtained. The product was divided, in each case, into a lower boiling mixture of XI and III and the higher boiling alkylated acetylene V.

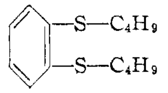


Methy phenyl sulfide apparently acts as a stabilizer for phenylmercaptoacetylene, for these mixtures showed no tendency to darken. The composition of the lower boiling fractions was estimated by conversion of XI to its sulfone and III into the corresponding mercury derivative IV. The estimated yields of products are shown in the equations.

A number of mechanisms (*i.e.*, α-elimination,[8] cyclic transition state[9] and β-elimination[10]) can be postulated for these reactions, and no decision as to the correct one can be made at this time. However, if the β-elimination mechanism should prove correct, then these data suggest that the anions VIII and IX are rapidly equilibrated, possibly through hybrid X which involves expansion of the valence shell of sulfur.[11]

Very little reaction was observed when benzo-1,4-dithiadiene (I) was treated with *n*-butyllithium in ethyl ether at 0°. These results were in sharp contrast to those expected by analogy with the reactions described above.

$$\mathrm{I} + n\text{-}C_4H_9Li \xrightarrow[H_2O]{\text{then}} \mathrm{I}\ (65\%) + \underset{84\%}{CH_3CH_2CH_2CH_3} +$$


XII

When the reaction mixture was treated with water, 84% of butane was liberated from unreacted butyllithium, and a 65% recovery of benzo-1,4-dithiadiene was realized. In addition, a small quantity (<9%) of higher boiling material was obtained, the composition and spectra of which suggested it to be 1,2-bis-(*n*-butylthio)-benzene (XII).[12] There was no analogy or precedent for the formation of XII in this reaction, and we assumed XII to be the result of a new reaction involving butyllithium, an alkylating agent (residual butyl bromide) and I. To test this possibility we repeated the reaction using excess *n*-butyllithium and one equivalent of dimethyl sulfate. A vigorous reaction occurred, and the neutral product (46% yield), thus obtained, was subsequently identified as the hitherto unknown 1-(*n*-butylthio)-2-methylthiobenzene (XIII). This product was characterized by conversion to sulfone XIV and the sulfonyl chloride XV.[13] The structures of XIII, XIV and XV were established by their independent synthesis as shown in the equations above. Authentic samples

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[7] Phenylmercaptoacetylene, and its analogs, may serve as synthetic intermediates in much the same way as do the analogous acetylenic ethers (*cf.* J. F. Arens, *Rec. trav. chim.*, **74**, 769 (1955)). Furthermore, the synthesis described for phenylmercaptoacetylene should be capable of extension to the oxygen analogs. We are currently investigating these possibilities.

[8] *Cf.* S. J. Cristol and R. F. Helmreich, THIS JOURNAL, **77**, 5034 (1955); A. Bothner-By, *ibid.*, **77**, 3293 (1955); D. Y. Curtin, E. W. Flynn, R. F. Nystrom, private communication to S. J. Cristol (see reference 8a).

[9] *Cf.* R. L. Letsinger and E. Bobko, THIS JOURNAL, **75**, 2649 (1953).

[10] *Cf.* D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716, 4519 (1951). See also reference 6.

[11] The stereospecific nucleophilic addition of thiophenolate ion to phenylmercaptoacetylene, reported by Truce, Simms and Boudakian (see reference 6), demands that VIII (and consequently IX) maintain its stereochemical identity if the reaction is stepwise and involves VIII as an intermediate. However, their reaction was carried out in polar solvent, and the addition may very well be concerted and thus not involve the free carbanion VIII.

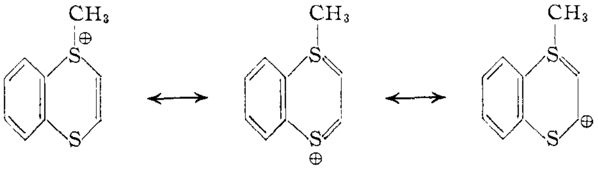
[12] The identity of this product was not further established; however, experiments described later in this report establish XII as an expected product from the reaction of I, butyllithium and butyl bromide.

[13] The apparent preferential oxidation of the *n*-butyl group in XIII was unexpected.

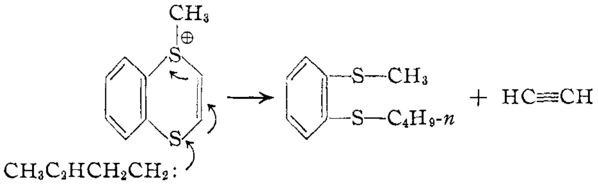
of XIV and XV, prepared from XVII, were shown to be identical to those prepared from I by comparison of melting points, mixed melting points, infrared and ultraviolet spectra and X-ray diffraction patterns.

The sequence by which XIII is formed from I, dimethyl sulfate and *n*-butyllithium is now known with a fair degree of certainty.

I + $(CH_3)_2SO_4 \longrightarrow$



XVIII XX XIX



XXI XIII

The sulfonium salt formed when benzo-1,4-dithiadiene reacts with dimethyl sulfate would be expected to be a resonance hybrid (XVIII ←→ XX); the sulfur atom not attached to methyl would have a partial positive charge and would thus be susceptible to nucleophilic attack. The butyl carbanion, formed when butyllithium reacts with the sulfonium salt, could then attack this sulfur atom with a concerted elimination of acetylene (an SN-e-reaction) as shown in formula XXI. In support of this mechanism, acetylene was found to be a major product of the reaction.

We are currently examining the scope of this elimination reaction in related heterocyclic and open chain systems containing sulfur, oxygen and nitrogen.

Experimental

Phenylmercaptoacetylene (III).—A solution of *n*-butyllithium in ether (55 ml.) was prepared from lithium wire (1.65 g., 0.238 g. atom), and *n*-butyl bromide (14.10 g., 0.103 mole) by the procedure of Gilman.[14] *cis*-1,2-Bis-(phenylmercapto)-ethylene[4,15] (II, *ca.* 2 g. in 5 ml. of ether) was added dropwise, with stirring, to the cold (0 to 20°) solution of butyllithium. The reaction mixture was then cooled (−10° to −15°), and the major portion of II (a total of 14.03 g., 0.0574 mole) was added dropwise. The resulting mixture was stirred for 2 hr. (−10°), then warmed to 0° and treated with water (40 ml. added dropwise). The resulting mixture was stirred for 2 hr. at room temperature and then for 0.5 hr. at reflux temperature. The aqueous layer and the ether layer were processed separately.

The aqueous layer was treated with iodine (7.34 g., 0.0289 mole) and the resulting mixture was heated on a steam cone for 0.5 hr. (with stirring). The solid (3.21 g., 51% yield, m.p. 60–61°) that separated from the cool mixture was identified as diphenyl disulfide (m.p., from ethanol, and mixed m.p.[16] 60.5–61°).

The ether layer was dried ($MgSO_4$) and concentrated, and the orange-yellow residue (9.37 g.) was distilled. The product (III, 4.63 g., 60% yield, b.p. 78–79° (7 mm.), $n^{25}D$ 1.5938) was yellow in color and turned red-brown almost immediately. About 25% of phenylmercaptoacetylene was lost on each successive distillation; consequently, the yield of undistilled product was estimated to be 80%.

Anal. Calcd. for C_8H_6S: C, 71.60; H, 4.51. Found: C, 70.15, 70.61; H, 4.52; H, 4.94.

The infrared spectrum of III showed bands at 3275 cm.$^{-1}$ and 2035 cm.$^{-1}$, indicative of the terminal acetylenic group.[17a]

The Mercury Derivative IV.—A solution of III (0.152 g., 1.13 mmoles) in alcohol (equal volume) was added dropwise, with stirring, to a solution prepared from potassium hydroxide (85%, 0.21 g., 3.2 mmoles), mercuric cyanide (0.24 g., 0.95 mmole) and water (1 ml.). The solid that formed was recrystallized from ethanol (38 ml.). The pure product (0.217 g., 82% yield) was obtained as beautiful hair-like needles melting at 137–138.5°.

Anal. Calcd. for $C_{16}H_{10}S_2Hg$: C, 41.15; H, 2.16; Hg, 42.96. Found: C, 41.53; H, 2.31; Hg (sample had darkened), 43.91.

Proof of Structure of Phenylmercaptoacetylene. 1. 1-Phenylmercaptopropyne-1 (V).—A solution of phenylmercaptoacetylene (3.19 g., 0.0237 mole) in absolute ether (10 ml.) was added (15 minutes) to a cold (0°) ethereal solution (25 ml.) of *n*-butyllithium (prepared[14] from lithium wire (0.68 g., 0.098 atom) and *n*-butyl bromide (5.48 g., 0.0427 mole)). The cold (−15°) mixture was stirred for 2 hr. while the temperature was allowed to warm to 0°. Dimethyl sulfate (6.00 g., 0.0475 mole) in ether (10 ml.) was then added over a 20 minute period (temperature maintained at 0°), and the resulting mixture was stirred at room temperature for 0.5 hr., at the reflux temperature for 1 hr. and finally at room temperature for 1 hr. Water (5 ml.) and 10% sodium hydroxide (10 ml.) were added, and the mixture was stirred for 1.5 hr. The ether solution was then removed, dried ($MgSO_4$) and distilled, and three fractions were collected. The first fraction (1.442 g., b.p. 73–77° (6 mm.), n^{25} 1.5928) was shown to be essentially pure unchanged phenylmercaptoacetylene (45% recovery) by its infrared spectrum and by its conversion into IV (67% yield, m.p. and mixed m.p. 137–138°). The middle fraction (0.339 g., n^{25} 1.5938–1.5942) was shown to be a mixture of III and V but was not processed further. The third fraction (0.883 g., $n^{25}D$ 1.5953, b.p. 78–81° (0.75 mm.) was almost pure 1-phenylmercaptopropyne-1 (V).

Anal. Calcd. for C_9H_8S: C, 72.93; H, 5.44; S, 21.63. Found: C, 73.36, 73.30; H, 5.68, 5.73; S, 21.99, 22.34.

The infrared spectrum of V showed weak absorption at 2190 cm.$^{-1}$ which indicated the presence of disubstituted acetylene.[17a] Weak absorption at 3290 and 2030 cm.$^{-1}$ indicated the presence of small amounts of III.

The ultraviolet spectrum showed λ_{max} 251 mμ (ϵ 12200).

Phenyl 1-Propynyl Sulfone (VI).—1-Phenylmercaptopropyne-1 (V, 0.189 g., 1.28 mmoles) was oxidized in hot acetic acid (4 ml.) by the usual procedure with hydrogen peroxide (30%, 0.55 g., 4.85 mmoles). Crude VI (0.155 g., 67%, m.p. 65–69°) was recrystallized from petroleum ether to give white needles melting at 68.5–69.5°.

Anal. Calcd. for $C_9H_8O_2S$: C, 59.98; H, 4.47. Found: C, 59.91; H, 4.20.

Infrared spectrum: bands at 1340 and 1165 cm.$^{-1}$, typical of the sulfone group,[17b] strong absorption at 2210 cm.$^{-1}$ typical of disubstituted acetylenes.[17a]

Ultraviolet spectrum: λ_{max} 266 mμ (ϵ 13400), λ_{max} 261 mμ (ϵ 1130), λ_{max} 267 mμ (ϵ 1400), λ_{max} 274 mμ (ϵ 1220).

Phenyl *n*-Propyl Sulfone (VII).—A solution of VI (78 mg., 0.43 mm.) in ethanol (100 ml.) was reduced (5 hr.) at room temperature with hydrogen (36 p.s.i. in the presence of 10% palladium-on-charcoal (78 mg.)), and the mixture was processed in the usual way. The oily product (64 mg.) was triturated with petroleum ether (Dry Ice temperature), and the white solid (18 mg., 23% m.p. 43–45°), thus obtained, was recrystallized from water. The product melted at 43–44° (reported m.p.[18] 46°). This product had an identical infrared spectrum, and did not depress the melting point of a sample of phenyl *n*-propyl sulfone prepared in

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[14] H. Gilman and J. W. Morton, Jr., "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 285 ff.

[15] W. E. Truce and R. J. McManimie, THIS JOURNAL, **76**, 695 (1954).

[16] H. Hubner and J. Alsberg, *Ann.*, **156**, 330 (1870).

[17] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, (a) p. 48 ff., (b) p. 288, (c) p. 24, (d) p. 297.

[18] W. A. Baldwin and R. Robinson, *J. Chem. Soc.*, 1447 (1932).

90% yield by the oxidation of phenyl *n*-propyl sulfide (79% yield from thiophenol[19]) with hydrogen peroxide.

The Reaction of *cis* and *trans*-II with Butyllithium with Subsequent Alkylation of the Product with Dimethyl Sulfate.—The reactions of *cis*-II (4.45 g., 0.0182 mole) and *trans*-II (4.45 g., 0.0182 mole) with *n*-butyllithium (from 8.02 g., 0.0586 mole of butyl bromide) were carried out in a nitrogen atmosphere employing identical reaction conditions. The initial details of this phase of the reaction were essentially identical to those described previously for the preparation of III.

A small quantity of dimethyl sulfate (*ca.* one-half gram) in ether was added to the reaction mixture, and the resulting mixture was heated to reflux, then cooled to 0 to −5°. The major portion of dimethyl sulfate (total 9.22 g., 0.073 mole) in ether (total 10 ml.) was added dropwise. The resulting mixture was stirred for 0.5 hr., during which time the temperature was allowed to rise to room temperature. The stirred mixture was then heated to the reflux temperature for 1 hr. and then maintained at room temperature for an additional 1.5 hr. Water (5 ml.) and 5% sodium hydroxide (10 ml.) were then added, and the mixture was stirred for 1.5 hr. at room temperature. The ether layer was removed, dried and concentrated. The reddish-yellow residue, 4.8 g. from both *cis*- and *trans*-II, was separated by distillation through a 12-inch spiral wire column into two fractions: a lower boiling fraction (2.5–3.04 g., b.p. 67–76° (9 mm.), n^{25}_{D} 1.5840–1.5880) and a higher boiling fraction (1.16–1.38 g., b.p. 40–52° (0.26 mm.), n^{25}_{D} 1.5919–1.5947). The higher boiling fraction was shown to be essentially pure 1-phenylthiopropyne-1 (V, b.p. 78–81° (0.75 mm.), n^{25}_{D} 1.5953). The lower boiling fraction was a mixture of methyl phenyl sulfide (XI) and phenylmercaptoacetylene (III). Oxidation of this mixture with hydrogen peroxide gave the sulfone of XI (m.p. and mixed m.p. 88°[18]). Reaction of the mixture with mercuric cyanide reagent[20] gave IV. Distillation data, together with the amounts of IV and the sulfone of XI that were obtained, indicated the following approximate yield of products

from	XI	III	V
cis-II	>56%	>26%	45%
trans-II	>75%	>17%	53%

This analysis, though highly qualitative, does establish that *cis*- and *trans*-II give the same products in comparable yields.

The Reaction of I with Butyllithium and Dimethyl Sulfate.—A small quantity (*ca.* 0.25 g.) of I in ether was added to a cold (0°) solution of butyllithium (prepared[14] as previously described from *n*-butyl bromide, 13.2 g., 0.096 mole) in ether (25 ml.). The mixture was cooled to −10°, and I (total of 5.00 g., 0.030 mole) in ether (10 ml.), was added over a period of 45 minutes. The mixture was stirred at −10° for 2 hr., then warmed to 0° and a small quantity of dimethyl sulfate in ether was added. The mixture was warmed briefly (35°), cooled to 0°, and dimethyl sulfate (total of 15.1 g., 0.119 mole) in ether (10 ml.) was added dropwise. The mixture was stirred for 0.5 hr., refluxed for 1 hr. and stirred for 1 hr. at room temperature. Water (5 ml.) and 10% sodium hydroxide (5 ml.) were added, and the mixture was stirred vigorously. More water (50 ml.) was added to dissolve the salts that separated. During the addition of water, copious quantities of acetylene were liberated (characterized by conversion to silver and copper acetylide). The ether layer was separated, dried ($MgSO_4$) and concentrated. The residue (5.70 g. of orange-yellow oil) was distilled through a 12-inch spiral wire column. The main fraction (pale-yellow, 2.917 g., 46% yield, b.p. 100–101° (0.3 mm.), $n^{24.5}_{D}$ 1.6177) was redistilled (b.p. 106° (0.3 mm.)) with essentially no loss; however, the refractive index varied from n^{25}_{D} 1.6168–1.6193.

Anal. Calcd. for $C_{11}H_{16}S_2$: C. 62.21; H, 7.60. Found: C, 62.67; H, 7.38.

Ultraviolet spectrum: λ_{max} 232 mμ (ϵ 10,600), λ_{max} 251 mμ (ϵ 11800), λ_{max} 296 mμ (ϵ 1880).

This material was subsequently shown to be slightly impure (1-*n*-butylthio)-2-methylthiobenzene (XIII).

1-(*n*-Butylsulfonyl)-2-methylsulfonylbenzene (XIV).—A sample of XIII (0.034 g., 1.62 mmoles) prepared from I, was treated with hydrogen peroxide (30%, 4.55 g., 40.2 mm.) in acetic acid (8 ml.), and the resulting solution was heated at the reflux temperature for 45 minutes. The mixture was poured onto ice; however, only a trace of gum separated. The mixture was made alkaline by the addition of concentrated sodium hydroxide and was then extracted with ether. The light yellow oil, obtained from the ether extract, solidified (56% yield) and was recrystallized from petroleum ether. The pure sulfone melted at 72.5–75° and was identical (m.p., mixed m.p., infrared spectrum, ultraviolet spectrum, X-ray diffraction pattern) to authentic XIV (prepared in 78% yield from XIII, which in turn was prepared from XVII).

Anal. Calcd. for $C_{11}H_{16}O_4S_2$: C, 47.80; H, 5.84. Found: C, 47.94; H, 5.99.

2-Methylsulfonylbenzenesulfonyl Chloride (XV).—A mixture of the XIII (284 mg., 1.34 mmoles), prepared from I, 5% sodium hydroxide (1 ml.) and 5% aqueous potassium permanganate (50 ml.) was heated at the reflux temperature for 5.5 hr. The excess permanganate was destroyed with ethanol, and the mixture was filtered through Hi-Flo. The solids were washed with hot water, and water was removed from the combined aqueous solution by distillation (reduced pressure). The tan solid residue (0.96 g.) was ground with phosphorus pentachloride (4.00 g.), mixed with phosphorous oxychloride (5 ml.) and the entire mixture heated at the reflux temperature for 4 hr. The mixture was poured onto ice, stirred for 20 minutes, and the light tan solid that separated (125 mg., m.p. 121–131°, 37% yield) was extracted with three 3-ml. portions of benzene. The benzene extract was concentrated to 4 ml. and a solid was precipitated by the addition of petroleum ether. The crystals (69 mg., 20% yield, m.p. 128–134°), thus obtained, were recrystallized several times from petroleum ether. The product melted at 136–137° and was identical (m.p., mixed m.p., ultraviolet spectrum, infrared spectrum, X-ray diffraction pattern) to a sample prepared[21] from XIII which, in turn, was prepared from XVII.

Anal. Calcd. for $C_7H_7O_4S_2Cl$: C, 33.01; H, 2.77; Cl, 13.92. Found: C, 33.46, 33.46; H, 2.33, 2.79; Cl, 14.34, 13.83.

The Reaction of I with Butyllithium with Subsequent Hydrolysis of the Product with Water.—The reaction of I (3.00 g., 0.018 mole) with butyllithium was carried out as described above. There was little evidence for reaction, and only a small amount of butane was liberated (the butane was separated from the nitrogen employed by condensation in a Dry Ice trap). Water was added and butane (84% of that calculated from the available butyllithium), and unreacted I (65%, b.p. 85–88° (0.7 mm.), n^{25}_{D} 1.6747) were recovered. A higher boiling fraction (b.p. 122° (0.3 mm.), n^{25}_{D} 1.5785, 229 mg., about 9%) was obtained which has been tentatively assigned structure XII.

Anal. Calcd. for $C_{14}H_{22}S_2$: C, 66.08; H, 8.72. Found: C, 66.61; H, 8.79.

Proof of Structure of 1-(*n*-Butylthio)-2-methylthiobenzene (XIII). 1. 2-Methylthiobenzenethiol (XVII).—A solution of XVI[22] (24.8 g., 0.175 mole) in ethanol (120 ml.) was added dropwise (20 min.) to a solution (nitrogen atmosphere) of potassium hydroxide (85%, 11.5 g., 0.175 mole) in ethanol (95%, 100 ml.). The solution was stirred (45 min.), methyl iodide (24.9 g., 0.175 mole) in ethanol (40 ml.) was added, and the resulting mixture was stirred at 25° for 2 hr. The mixture was filtered, the salts washed with ethanol and the combined alcoholic solution was concentrated (ethanol removed) by distillation at reduced pressure from zinc dust (1 g.). Water (100 ml.) and dilute sulfuric acid (10%, 10 ml.) were added to the residue, and the mixture was distilled with steam. The ether-soluble distillate was washed with dilute potassium iodide (100 ml.), dilute sodium bisulfite (100 ml.) and finally with water (200 ml.). The dried ($MgSO_4$) ether concentrate (10.98 g., yellow oil) was distilled (12-inch spiral wire column), and the product

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[19] V. N. Ipatieff, H. Pines and B. S. Friedman, This Journal, **60**, 12732 (1938).

[20] K. A. Hoffmann and H. Kirmreuter, *Ber.*, **41**, 314 (1908).

[21] The crude sulfonyl chloride prepared from XIII (which was prepared from XVII) was obtained in 40% yield. This product, m.p. 133–135°, was a mixture (separated by chromatography on alumina, with ether eluent) of XV and *o*-benzenedisulfonyl chloride, m.p. and mixed m.p. 145°).[4]

[22] W. E. Parham, T. M. Roder and W. R. Hasek, This Journal, **75**, 1647 (1953).

(20.64 g.) was collected in several fractions (b.p. 80–103° (1.5 mm.), $n^{25}\mathrm{D}$ 1.6418–1.6462). This corresponds to a 75% yield of crude XVII; however, the product was shown to contain the dimethyl sulfide of dithiocatechol. The principal product (13.6 g., b.p. 80–88° (1.5 mm.), $n^{25}\mathrm{D}$ 1.6462) was used without further purification. A purer sample of XVII was obtained in the following way.

An ethereal solution (30 ml.) of the crude product (4.55 g.) was extracted with four 10-ml. portions of 10% sodium hydroxide and three 10-ml. portions of water. The dried ether layer was evaporated, affording a pale yellow oil (1.74 g.) which crystallized to a white solid (m.p. 24–27°). The reported[23] melting point of the dimethyldithiocatechol is *ca.* 25°. The basic extract was acidified (sulfuric acid), and the oil that separated was extracted (ether), dried ($MgSO_4$) and distilled. The distillate (b.p. 85–87° (1.6 mm.), 2.2 g., $n^{25}\mathrm{D}$ 1.6470) showed absorption in the infrared at 2510 and 1317 cm.$^{-1}$ (characteristic of SH[17b] and S–CH_3,[17c] respectively).

Anal. Calcd. for $C_7H_8S_2$: C, 53.80; H, 5.16. Found: C, 53.22; H, 5.26.

Bis-(2-methylthiophenyl)-disulfide.—A mixture of XVII (0.774 g.), sodium hydroxide (97%, 0.35 g., 8.5 mmoles) and water (10 ml.) was heated on a steam-bath. The basic aqueous layer was decanted from the colorless, insoluble oil (m.p. 28–29°, presumably dimethyldithiocatechol), and iodine (0.23 g., 0.91 mmole) was added in small portions. The mixture was heated on a steam-bath for 1.5 hr. and was then cooled. The yellow solid (197 mg., m.p. 77–85°) that separated was recrystallized from petroleum ether, and the solid (108 mg., m.p. 82–85°), thus obtained, was chromatographed on Merck alumina (13 g., petroleum ether (3)–ether (1) as eluent). The product (53 mg.) melted at 85.5–86°.

Anal. Calcd. for $C_{14}H_{14}S_4$: C, 54.15; H, 4.55. Found: C, 54.14; H, 4.52.

2. **1-(*n*-Butylthio)-2-methylthiobenzene (XIII).**—A solution of impure XVII (5.0 g.) in ethanol (15 ml.) was added (20 min.) to a solution of potassium hydroxide (2.12 g., 0.032 mole) in ethanol (95%, 25 ml.), and the resulting mixture (nitrogen atmosphere) was stirred for 45 minutes. Butyl bromide (4.38 g., 0.032 mole) in ethanol (10 ml.) was added dropwise (10 min.), and the resulting mixture was stirred for 1.5 hr. at 25° and then for 1 hr. at the reflux temperature. The resulting mixture was filtered, concentrated, diluted with water and extracted with ether, and the resulting ether extract was extracted with 5% sodium hydroxide and washed with water. The resulting ether solution was dried and the concentrate (5.90 g.) was distilled (Piros–Glover column). The principal fraction (b.p. 147–149° (3.8 mm.), $n^{25}\mathrm{D}$ 1.5949–1.5967) weighed 4.09 g. (60%).

Anal. Calcd. for $C_{11}H_{16}S_2$: C, 62.21; H, 7.60; S, 30.19. Found: C, 62.30; H, 7.61; S, 30.62.

The infrared spectrum was almost identical to a sample of XIII prepared from I. The preparation of derivatives of XIII has been described above.

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[23] J. Pollak, *Monatsh. Chem.*, **34**, 1681 (1913).

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

The Polymerization of *l*-Propylene Oxide[1]

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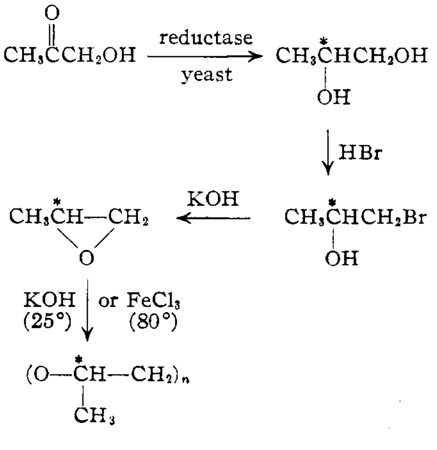
The polymerization of *l*-propylene oxide by potassium hydroxide gives low molecular weight, optically-active polymer, m.p. 55.5–56.5°, in sharp contrast to the liquid polymer formed from *dl*-propylene oxide under the same conditions. With ferric chloride catalysis, both *l*- and *dl*-propylene oxide give polymeric material which can be separated into amorphous intermediate molecular weight and crystalline (m.p. 70°) high molecular weight fractions. In this case there is no detectable difference, except for optical activity, between the products from optically-active and racemic monomer. This supports the view that catalysts can be highly selective in orienting the configuration of asymmetric centers along the polymer chain, and that such "isotactic" polymers have identical configurations of the asymmetric centers along the chain.

The list of polymers which have asymmetric centers along the chain and which have been prepared in amorphous and crystalline modifications includes polyvinyl ethers,[2] polypropylene and polystyrene[3] and polypropylene oxide.[4] The suggestion has been made that these differ due to the configuration of the asymmetric centers.[2,3] The term "isotactic" has been proposed for such polymers in which each successive asymmetric center has the same configuration.[3]

The purpose of the present investigation was to study the polymerization of *l*-propylene oxide,[5] since, of those monomers listed above, this is unique in having the asymmetric atom prior to polymerization. Should the polymerization proceed with either complete retention or complete inversion at the asymmetric center, the polymer would have not only all of the asymmetric centers of any one polymer molecule of the same configuration, but all the centers of all the polymer molecules would have the same configuration. It should, in short, be an optically active polymer.



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[1] Presented at the Delaware Valley A.C.S. Meeting, 16 February 1956 and the 129th National Meeting, Am. Chem. Soc., Dallas, Texas, April 1956; see also C. C. Price, M. Osgan, R. E. Hughes and C. Shambelan, THIS JOURNAL, **78**, 690 (1956).

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[4] (a) H. Staudinger, "Hochmolekulare Organische Verbindungen," Springer, Berlin, 1932, p. 295; (b) U. S. Pat. 2,706,181 (April 12, 1955), M. E. Pruitt and J. M. Baggett (to the Dow Chemical Co.); U. S. Pat. 2,706,182 (April 12, 1955), M. E. Pruitt, J. M. Baggett, R. J. Bloomfield and J. H. Templeton (to the Dow Chemical Co.), *cf. C. A.*, **49**, 2395 (1955).

[5] P. A. Levene and A. Walti, *J. Biol. Chem.*, **68**, 415 (1926).