salt prepared (*m*-methylbenzyl derivative) required several days, although seeds of this salt induced crystallization of other salts in a much shorter time. In every case crystallization stopped after approximately 70% of the less soluble isomer had been removed. The first fractions were nearly optically pure, and recrystallization from ethanol did not change the specific rotation by an amount greater than the experimental error. The characteristics of the salts are described in Table V.

Isolation and Racemization of Optically Active Acids.—The technique employed was essentially the same as that previously described.[2] The characteristics of the acids and a sample rate determination are described in Table VI. The errors in the rate constants and rotations are commensurate with the error in setting and reading the polarimeter (±0.01°).

URBANA, ILLINOIS

[Contribution from the Department of Chemistry, Institute of Polymer Research, Polytechnic Institute of Brooklyn]

Preparation of *o*-Vinylbenzyl *d*-*sec*-Butyl Sulfide.[1] An Attempted Asymmetric Polymer Synthesis

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The preparation of *o*-vinylbenzyl *d*-*sec*-butyl sulfide is described. This optically active monomer was polymerized and copolymerized with a free radical catalyst in an attempt to effect an asymmetric polymer synthesis. After quantitatively removing the sulfur and the optically active group by hydrogenolysis with Raney nickel, the resulting polymer and copolymer were found to be optically inactive and an X-ray diagram of a stretched polymer film showed it to be non-oriented.

A number of amorphous polymers such as polystyrene and polymethyl methacrylates contain asymmetric carbon atoms in the backbone of the chain. It has been suggested that the presence of asymmetric carbon atoms randomly distributed in the polymer chain of both the *d*- and *l*-configurations makes each chain a racemic mixture or *meso* form which prevents proper orientation of chain segments for crystal formation. A polymer containing an excess of either the *d* or *l*-configuration would be of interest to test the validity of this postulate.

When a new asymmetric center is created in a molecule which already contains an optically active center adjacent to it, the resulting product may contain an excess of one diastereoisomer.[3] This well known concept of asymmetric synthesis has been employed previously in an attempt to prepare an asymmetric polymer; thus, Marvel, Frank and Prill[4] reported the polymerization of styrene and methyl methacrylate with two optically active peroxide initiators. A comparison of the physical properties of the above polymers with polymers prepared using the corresponding *dl*-initiators showed no essential differences. This result might be expected in view of a recent mathematical analysis of this type of situation by Frisch, Schuerch and Szwarc[5] who concluded that it was unlikely that an asymmetric polymer could be prepared by this method. Marvel and Overberger[6] polymerized an optically active monomer, *d*-*sec*-butyl *p*-vinylbenzoate, with a free radical initiator followed by hydrolysis of the active *sec*-butyl alcohol groups. The resulting polymer was optically inactive, again indicating no asymmetric induction in the growing polymer chain.

There is some reason to doubt that a polymer chain containing an excess of one configuration will exhibit optical activity since each carbon atom is asymmetric only by virtue of the fact that the chain is of different lengths on either side. The optical rotation of an asymmetric carbon atom appears to be strongly dependent on differences in the groups immediately attached to it but as the differences in two of the groups are removed further and further from the asymmetric center, the optical rotation decreases toward zero.[5,7] This particular difficulty may be avoided if the chain length is kept short or if the monomer is copolymerized.[5] Thus, in a copolymer, the groups immediately adjacent to some of the asymmetric centers would be different and these centers would be capable of rotating plane polarized light. The question of whether a completely alternating copolymer would be expected to be asymmetric does not concern us here.

The work reported here was concerned with the preparation of a monomer containing an optically active center sterically close to the double bond. It was desired to prepare a monomer which would polymerize by an ionic mechanism, as well as by a free radical mechanism for the ease of inducing asymmetry in an ionic transition state may be different from that for a free radical transition state. For a discussion of the generally accepted

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[1] This is the eleventh in a series of articles concerned with the synthesis of monomers and their polymerization; for the tenth paper in this series, see C. G. Overberger and I. C. Kogon, This Journal, **76**, 1879 (1954).

[2] This paper comprises a portion of a thesis presented by Mr. Louis C. Palmer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd ed., p. 231.

(4) C. S. Marvel, R. L. Frank and E. Prill, This Journal, **65**, 1647 (1943).

(5) H. L. Frisch, C. Schuerch and M. Szwarc, *J. Polymer Sci.*, **11**, 559 (1953).

(6) C. S. Marvel and C. G. Overberger, This Journal, **68**, 2106 (1946).

(7) R. E. Marker, *ibid.*, **58**, 976 (1936). Since this work has been completed, crystalline polystyrene and polypropene have been reported (G. Natta, *et al.*, *ibid.*, **77**, 1708 (1955); G. Natta, *J. Polymer Sci.*, **16**, 143 (1955); C. W. Bunn and E. R. Howells, *ibid.*, **18**, 307 (1955)). These polymers, called isotactic, have been reported to contain crystalline areas having at least three monomer units with the same configuration. They are not optically active since they are long chains and contain planes of symmetry.

theory of cationic polymerization and the propagation step see reference 8.

It was believed that an ideal optically active monomer to demonstrate an asymmetric synthesis should fulfill the following requirements. It must polymerize to give a polymer with an asymmetric carbon atom in the backbone of the chain. The optically active center should be sterically as close as possible to the double bond and still allow polymerization. The optically active group must be removable quantitatively without disturbing the stereochemistry of the asymmetric center of the polymer chain. A quantitative method for measuring the loss of the optically active group must be available.

A monomer believed to fulfill the above requirements was *o*-vinylbenzyl *d-sec*-butyl sulfide and accordingly this monomer was prepared by the following scheme using *dl*-compounds initially to determine the yield and best method for each of the steps.

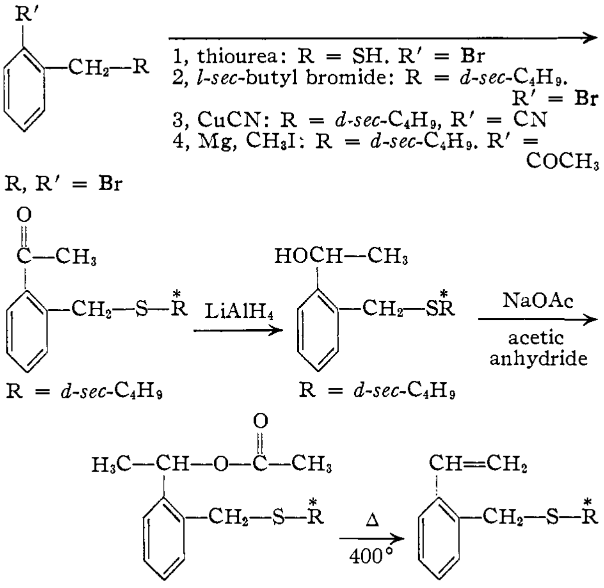
o-Bromobenzyl mercaptan was prepared in a 75% yield from *o*,α-dibromotoluene and thiourea according to the general procedure for mercaptans in "Organic Syntheses."[9] The sodium salt of the mercaptan was heated with *l-sec*-butyl bromide to give a 78% yield of *o*-bromobenzyl *d-sec*-butyl sulfide.

l-sec-Butyl bromide was obtained in a 79% yield by treating *d-sec*-butyl alcohol with dry hydrogen bromide according to the procedure of Levene and Marker.[10] The method of "Organic Reactions" as modified by Stevens, Morrow and Lawson[11] was used to prepare the optically active *sec*-butyl alcohol except that fractional recrystallization was not repeated enough times to obtain the highest optical rotation.

Several attempts were made to prepare the Grignard derivative of *o*-bromobenzyl *sec*-butyl sulfide in ethyl ether and in butyl ether, but no reaction with magnesium was observed. As an alternative, the bromine was replaced by a nitrile group in a Rosenmund–Von Braun reaction. When the above sulfide was treated with cuprous cyanide in pyridine at 210° according to the general procedure of Marvel and Overberger,[12] *o*-cyanobenzyl *d-sec*-butyl sulfide was obtained in yields between 80–94%.

Very little reaction occurred when the nitrile was treated with methylmagnesium iodide in ethyl ether. At 85° in butyl ether, however, *o*-acetobenzyl *d-sec*-butyl sulfide was obtained in 80% yield.

Initially, the ketone was reduced to the alcohol, *o*-(α-hydroxyethyl)-benzyl *d-sec*-butyl sulfide, with aluminum isopropoxide in isopropyl alcohol. While this method was successful, the yields were between 50–65% and it was difficult to obtain the alcohol free from unreacted ketone. Lithium aluminum hydride in ethyl ether reduced the ketone smoothly to the alcohol in a 90% yield.



Several attempts were made to obtain the monomer by dehydration of the alcohol using potassium acid sulfate as the dehydrating agent. The only product isolated, other than unreacted alcohol, was a liquid which analyzed correctly for a compound in which both water and the *sec*-butyl group had been lost. The infrared spectrum indicated that no hydroxyl group, thiol or vinyl type double bond was present. *o*-(α-Acetoxyethyl)-benzyl *d-sec*-butyl sulfide was then prepared in an 88% yield by refluxing the alcohol with acetic anhydride and sodium acetate.

The acetate was pyrolyzed by dropping it through a column packed with cut glass tubing at 394°. The cracking reaction was complicated by the cleavage of the carbon-to-sulfur bond yielding side products which included *o*-methylstyrene, the unknown compound previously mentioned and a product which was probably *o*-vinylbenzyl mercaptan. This last product polymerized on standing and during distillation but could be removed by washing the crude reaction product initially with sodium hydroxide solution. Because of the difficulties outlined above, *o*-vinylbenzyl *d-sec*-butyl sulfide was obtained in yields of only 25–36%.

The monomer was polymerized using azo-bis-isobutyronitrile as the initiator. The polymer obtained had a specific rotation of $[\alpha]^{24.7}\text{D}$ +9.59° (*c*, 6.67 g. in benzene).

The original optically active groups were removed by treating the polymer with excess Raney nickel in *sec*-butyl alcohol at 150° and 1800 lb. hydrogen pressure for 13 hours. An analysis showed that the sulfur had been quantitatively removed and the resulting polymer had an optical rotation of $[\text{obs.}]^{24.7}\text{D}$ 0.00° (*c* 13.3 g. in benzene). An X-ray diagram of a stretched film prepared from this polymer showed it to be non-oriented.

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[8] D. C. Pepper, *Quart. Revs.*, **8**, 88 (1954); P. H. Plesch, "Cationic Polymerization and Related Complexes," W. Heffer and Sons, Ltd., Cambridge, England, 1953; C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor and T. Alfrey, Jr., This Journal, **74**, 4848 (1952).

[9] G. G. Urquhart, J. W. Gates, Jr., and R. Connor, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 363.

[10] P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **91**, 405 (1931).

[11] A. W. Ingersoll, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 376; C. L. Stevens, D. Morrow and J. Lawson, This Journal, **77**, 2341 (1955).

[12] C. S. Marvel and C. G. Overberger, *ibid.*, **66**, 475 (1944).

Mozingo and co-workers[13] reported the removal of sulfur from many organic molecules by simply refluxing the compound with excess Raney nickel. All attempts to remove sulfur from the polymer by this method failed. The severe conditions that were found necessary to remove the sulfur from the polymer introduced the additional complication that probably some of the phenyl rings were also reduced as indicated by the analysis. The reduction of a phenyl ring introduces two new asymmetric centers and changes the properties of the final polymer.

Compound I was copolymerized with methyl methacrylate in a 50–50 mole per cent. mixture using azo-bis-isobutyronitrile as the initiator. The mole fraction of monomer I found in the copolymer was 0.43 based on the sulfur analysis. The copolymer had an optical rotation of $[\alpha]^{24.7}_{\mathrm{D}}$ +6.89° (*c* 6.67 g. in benzene).

The sulfur was removed from the copolymer as described previously yielding a copolymer with an optical rotation of $[\mathrm{obs.}]^{24.7}_{\mathrm{D}}$ 0.00° (*c* 12 g. in benzene).

Both polymer and copolymer were prepared from the *dl*-mixture of I under the identical conditions that were employed for the optically active form. A comparison with the polymers described previously showed no essential differences.

The above results would indicate that little or no asymmetric induction took place during polymerization. This conclusion is based on the premise that the polymer should possess increased orientation and that the copolymer would show optical activity if an excess of one configuration were present.

Many attempts were made to polymerize I with cationic catalysts but all proved to be unsuccessful. The catalysts employed were stannic chloride, boron trifluoride, titanium tetrachloride, ferric chloride, zinc chloride and iodine at various temperatures from −78 to 115° depending on the catalyst. Not only did compound I fail to polymerize in the above systems, but actually inhibited the polymerization of styrene in nitrobenzene at 0° with stannic chloride as the catalyst.

Experimental

o-**Bromobenzyl Mercaptan.**—The general procedure of reference 9 for mercaptans was employed with some modifications. *o*,α-Dibromotoluene,[14,15] 75 g. (0.25 mole), and 19 g. (0.25 mole) of thiourea in 225 ml. of 95% ethanol were heated on the steam-bath for 2 hours. A solution of 14.8 g. (0.37 mole) of sodium hydroxide in 200 ml. of water was added and heating was continued for 3 hours. The product was isolated as reported in reference 9. Distillation gave 38.3 g. (75.5%) of a colorless oil, b.p. 82° (1 mm.), n^{25}_{D} 1.6089, d^{25}_{4} 1.5118.

Anal.[16] Calcd. for C_7H_7BrS: C, 41.39; H, 3.47. Found: C, 41.80; H, 3.54.

o-**Bromobenzyl** *d-sec*-**Butyl Sulfide.**—Sodium, 4.5 g. (0.195 g. atom), in 100 ml. of ethanol, was cooled to 5° and 38.2 g. (0.187 mole) of *o*-bromobenzyl mercaptan was added rapidly. After 10 minutes, 27 g. (0.195 mole) of *l-sec*-butyl bromide,[10,17-20] $[\alpha]^{24.7}_{\mathrm{D}}$ −14.98°, was added and the reaction heated to reflux. After one hour of reflux, the reaction was poured into 300 ml. of cold water. The oil layer was separated and the aqueous layer extracted twice with benzene. The combined oil–benzene layers were dried over magnesium sulfate and after distillation gave 37 g. (78%) of a colorless oil, b.p. 142° (5.5 mm.), n^{25}_{D} 1.5646, d^{25}_{4} 1.2920, $[\alpha]^{24.7}_{\mathrm{D}}$ +10.62°.

Anal. Calcd. for $C_{11}H_{15}BrS$: C, 50.97; H, 5.83. Found: C, 51.21; H, 6.09.

o-**Cyanobenzyl** *d-sec*-**Butyl Sulfide.**—The general procedure of Marvel and Overberger[12] was followed with a few modifications. About 0.1 g. of dry copper sulfate, 0.1 g. of *p*-cyanobenzoic acid, 20 g. (0.077 mole) of *o*-bromobenzyl *d-sec*-butyl sulfide, 6.8 g. (0.079 mole) of anhydrous cuprous cyanide and 15 ml. of dry pyridine were heated for 17 hours at 210°. The reaction was cooled to about 100° and poured into a mixture of 125 ml. of water and 125 ml. of concentrated ammonia. The reaction was permitted to stand for 30 minutes, after which most of the blue water layer was discarded and the remaining oil–water layer was then extracted with benzene and worked up according to the procedure of Marvel and Overberger.[12] Distillation gave 14.3 g. (94%) of a colorless oil, b.p. 106° (0.5 mm.), n^{25}_{D} 1.5474. d^{25}_{4} 1.0310, $[\alpha]^{24.7}_{\mathrm{D}}$ +12.77°. The yields varied from 80–94%.

Anal. Calcd. for $C_{12}H_{15}NS$: C, 70.20; H, 7.36; N, 6.83. Found: C, 70.44; H, 7.44; N, 6.77.

o-**Acetobenzyl** *d-sec*-**Butyl Sulfide.**—To 30 g. (1.24 g. atoms) of magnesium covered with ethyl ether was added 174 g. (1.23 moles) of methyl iodide in 200 ml. of di-*n*-butyl ether under nitrogen. Cooling was required toward the middle of the addition to maintain the temperature at approximately 55°. Stirring was continued for 20 minutes after the addition was completed and the reaction was heated to 75°. The nitrile prepared above, 62.5 g. (0.30 mole), was then added rapidly after which the temperature rose to 85°. The reaction temperature was maintained at 85–90° for 1 hour and after cooling the reaction was poured cautiously into 175 ml. of concentrated hydrochloric acid and 500 g. of ice. Three layers were present including a heavy dark red oil. The oil was separated, the water layer extracted 4 times with benzene, and the combined red oil, organic layer, and benzene extracts were refluxed with 8 ml. of concentrated hydrochloric acid and 80 ml. of water for 1.25 hours. After cooling, the water layer was separated, and the organic layer dried over magnesium sulfate. Distillation gave 54 g. (79.5%) of a colorless oil, b.p. 123° (1 mm.), n^{25}_{D} 1.5440, d^{25}_{4} 1.0314, $[\alpha]^{25}_{\mathrm{D}}$ +16.21°.

Anal. Calcd. for $C_{13}H_{18}OS$: C, 70.22; H, 8.16. Found: C, 70.17; H, 8.28.

o-(α-**Hydroxyethyl**)-**benzyl** *d-sec*-**Butyl Sulfide.**—Lithium aluminum hydride, 2.4 g. (0.063 mole), was carefully ground in a mortar under nitrogen and then refluxed for two hours in 200 ml. of anhydrous ether. The heat was removed and 43 g. (0.194 mole) of the above ketone in 120 ml. of ether was added dropwise over a period of 30 minutes. Stirring was continued for an additional 10 minutes and then water was cautiously added dropwise to hydrolyze the complex. After removal of solids by filtration and evaporation of the ether, distillation gave 39.5 g. (91%) of a colorless oil, b.p. 122° (1 mm.), n^{25}_{D} 1.5459, d^{25}_{4} 1.0331, $[\alpha]^{24.7}_{\mathrm{D}}$ +11.20°.

Anal. Calcd. for $C_{13}H_{20}OS$: C, 69.59; H, 8.99. Found: C, 69.92; H, 8.98.

o-(α-**Acetoxyethyl**)-**benzyl** *d-sec*-**Butyl Sulfide.**—The alcohol prepared above, 130 g. (0.58 mole), was refluxed with 200 ml. of acetic anhydride and 20 g. of fused sodium acetate for 2 hours. While still hot, 35 ml. of water was cautiously added dropwise; refluxing was maintained by the heat of reaction. The reaction was cooled and poured into 600 ml. of water, the product was extracted with 3 portions of benzene and the benzene layer washed with sodium carbonate solution and then with water until neutral. Distillation gave 136 g. (88%) of a colorless oil, b.p. 116° (0.6 mm.), n^{25}_{D} 1.5220, d^{25}_{4} 1.0346, $[\alpha]^{24.7}_{\mathrm{D}}$ +9.98°.

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(18) R. L. Letsinger, *ibid.*, **70**, 406 (1948).

(19) J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.*, 1072 (1935).

(20) A. Franke and R. Dworzak, *Monatsh. Chem.*, 661 (1922).

Anal. Calcd. for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.33. Found: C, 67.78; H, 8.50.

***o*-Vinylbenzyl *d-sec*-Butyl Sulfide.**—An apparatus and procedure similar to that used by Overberger and Tanner[21] was employed. An iron–constantan thermocouple was placed outside the cracking tube halfway into the furnace. The column was flushed with nitrogen and 41 g. (0.154 mole) of the acetate was added dropwise (60 drops per minute) at 394°. The crude product was distilled, collecting the material distilling below 100° (0.5 mm.). The material distilling above this temperature was recycled through the cracking tube. The combined product was washed with sodium hydroxide solution, and then with water until neutral. After drying, fractional distillation gave 11.4 g. (36%) of a slightly colored liquid, b.p. 90° (0.8 mm.), $n^{25}\text{D}$ 1.5565, $d^{25}{}_4$ 0.9836, $[\alpha]^{24.7}\text{D}$ +13.92°.

Anal. Calcd. for $C_{13}H_{18}S$: C, 75.67; H, 8.79; S, 15.54. Found: C, 75.86; H, 8.82; S, 15.37.

Polymerization of *o*-Vinylbenzyl *d-sec*-Butyl Sulfide.—An evacuated sealed tube containing 4 g. (0.019 mole) of the monomer and 58 mg. of azo-bis-isobutyronitrile was heated at 76° for 13 hours. The contents of the tube were dissolved in 20 ml. of benzene and precipitated by adding the benzene solution dropwise to 200 ml. of methanol. The polymer was reprecipitated twice more using the same procedure. The polymer weighed 3.4 g., softening range 110–125° (capillary), $[\alpha]^{24.7}\text{D}$ +9.57° (*c* 6.67 g. in benzene), $[\eta]$ 0.12.

Anal. Calcd. for $C_{13}H_{18}S$: C, 75.67; H, 8.79; S, 15.54. Found: C, 75.57; H, 8.75; S, 14.32.

Desulfurization of Poly *o*-Vinylbenzyl *d-sec*-Butyl Sulfide.—Attempts to desulfurize the polymer according to the procedure of Mozingo and co-workers[13] failed. The polymer was refluxed in various solvents including ethanol, benzene, benzene–ethanol and *sec*-butyl alcohol with excess Raney nickel. In each instance, a positive sulfur test was obtained after a sodium fusion. The sulfur was removed quantitatively by heating 1.5 g. of the polymer at 150° for 13 hours in a bomb with 6 heaping teaspoons of Raney nickel W-2[22] catalyst at 1800 lb. hydrogen pressure. The initial hydrogen pressure was 1200 lb. The *sec*-butyl alcohol was decanted from the Raney nickel and discarded. The Raney nickel was then treated several times with 300-ml. portions of hot benzene, the benzene solution filtered through infusorial earth to remove the Raney nickel and the solvent removed on the steam-bath to a volume of about 10 ml. The polymer was then precipitated by adding the benzene solution dropwise to 150 ml. of methanol. The polymer was dissolved and reprecipitated twice more from benzene and methanol to give 0.43 g., softening range 165–180° (capillary), $[\eta]$ 0.097, $[\alpha]^{24.7}\text{D}$ 0.00° (*c* 13.33 g. in benzene). An X-ray diagram of a stretched film showed no crystallinity.

Anal. Calcd. for C_9H_{10}: C, 91.47; H, 8.53. Calcd. for C_9H_{16}: C, 87.01; H, 13.99. Found: C, 88.98; H, 11.06.

Copolymerization of *o*-Vinylbenzyl *d-sec*-Butyl Sulfide and Methyl Methacrylate.—A mixture of 3.07 g. (0.0149 mole) of the *d*-monomer, 1.45 g. (0.0145 mole) of methyl methacrylate and 90 mg. of azo-bis-isobutyronitrile was heated in a sealed degassed tube at 75° for 12 hours. The copolymer formed was dissolved in 15 ml. of benzene and precipitated by adding the benzene solution dropwise to 100 ml. of methanol cooled in Dry Ice. The copolymer has a tendency to come out as an oil and some of the copolymer is lost during each precipitation step. After a second reprecipitation, there was obtained 2.8 g., softening point 108–125° (capillary), $[\eta]$ 0.12, $[\alpha]^{24.7}\text{D}$ +6.89° (*c* 6.67 g. in benzene). The mole fraction of *o*-vinylbenzyl *d-sec*-butyl sulfide in the copolymer was 0.43.

Anal. Found: C, 70.69; H, 8.64; S, 9.49.

Desulfurization of Copolymer.—The same procedure described for the polymer was followed. From 1.5 g. of copolymer, 6 heaping teaspoons of Raney nickel and 60 ml. of *sec*-butyl alcohol in a bomb at 1800 lb. hydrogen pressure and at 150° for 13 hours, there was obtained 0.2 g. of product, softening range 125–145° (capillary), $[\alpha]^{24.7}\text{D}$ 0.00° (*c* 12 g. in benzene).

Anal. Found: C, 75.55; H, 9.39; S, 0.00.

Attempted Cationic Polymerization of *o*-Vinylbenzyl *sec*-Butyl Sulfide.—The monomer was treated in bulk, nitrobenzene and in ethylene chloride at −78°, 0°, 25° and 115°, with various cationic catalysts including stannic chloride, boron trifluoride, titanium tetrachloride, ferric chloride, zinc chloride and iodine. No solid polymers were obtained. When 2 g. of styrene and 0.1 g. of the sulfur monomer in nitrobenzene at 0° were treated with stannic chloride, the styrene failed to polymerize after one hour. A control without the sulfur monomer polymerized within one minute.

Attempted Dehydration of *o*-(α-Hydroxyethyl)-benzyl *sec*-Butyl Sulfide.—The general procedure of Marvel and Overberger[12] was followed except that the alcohol was added intermittently in 4-ml. portions and the pressure reduced to 2 mm., 1.5 minutes after addition of each portion. From 4 g. of the alcohol, there was obtained 2.5 g. of a colorless oil, b.p. 55° (0.5 mm.), $n^{25}\text{D}$ 1.5788, which analyzed correctly for loss of water and the secondary butyl group. The infrared spectrum indicated no vinyl double bond, hydroxyl or thiol group.

Anal. Calcd. for $C_9H_{10}S$: C, 71.95; H, 6.71; S, 21.34. Found: C, 71.99; H, 6.76; S, 20.35.

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[21] C. G. Overberger and D. Tanner, THIS JOURNAL, **77**, 369 (1955).

[22] R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 181.