ration of the ether gave 236 g of 6-(2-furyl)-2-isopropyl-5,5-dimethyl-*m*-dioxan-4-ol: nmr spectrum[3] (CCl_4), multiplets at 0.9 (methyl groups), 1.8 (CH), 4.0–5.0 [OH, OCH, and –OCHO–], and 6.2 (=CH in ring) and a doublet at 7.2 ppm (OCH in ring). Areas were in the proportions of 12:1:4:2:1. The viscous oil was dissolved in methanol (250 ml) and hydrogenated at 100° and 3000 psi in the presence of alcohol-washed Raney nickel (12 g) until no further hydrogen was absorbed. The catalyst was removed by filtration and the product was distilled to give, after removal of methanol and isobutyl alcohol, 129.5 g (74.4%) of **1**: bp 94–97° (0.3–0.4 mm); $n^{20}D$ 1.4772; infrared absorptions[4] (smear), 3.0 (s) μ and 9.6 (s) μ; nmr spectrum (CCl_4), singlet at 0.90 (methyl groups), and multiplets at 1.89 (CH_2CH_2 in ring) and 3.10–4.35 ppm (OH, OCH, and OCH_2 groups). Areas were in the proportions of 6:4:8.

Hexahydro-3,3-dimethylfuro[3.2-*b*]pyran (3).—A mixture of xylene (150 ml), **1** (174 g, 1 mole), and *p*-toluenesulfonic acid (5 g) was heated at 150–192° for 6 hr, and during this time, water (18 ml) was removed by azeotropic distillation. The crude product was washed with a dilute sodium hydroxide solution and then with water. After the xylene was removed, the product was distilled to give 29.5 g (18.9%) of **3**: bp 101–102° (46 mm); $n^{20}D$ 1.4440; infrared absorptions (smear), 8.87 (m), 9.08 (s), 9.40 (m), and 9.65 (s) μ; nmr spectrum (neat), singlet at 1.0 (methyl groups) and multiplets at 1.1–2.1 (CH_2CH_2 in ring) and 2.9–4.0 ppm (OCH and OCH_2 groups). Areas were in the proportions of 6:4:6.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.3; H, 10.3. Found: C, 69.1; H, 10.5.

3-Chlorotetrahydro-β,β-dimethylpyran-2-ethanol (4).—A mixture of **1** (522 g, 3 moles) and concentrated hydrochloric acid (200 g) was refluxed for 16 hr. The organic layer which separated on cooling was washed with saturated sodium bicarbonate solution and then with water until the washings were neutral. The products obtained on distillation were 170 g (36.4%) of **3**, bp 101° (46 mm), and 209 g (36.2%) of **4**: bp 104–106° (1 mm); $n^{20}D$ 1.4751; infrared absorptions (smear), 3.0 (s), 9.65 (s), and 15.45 (m) μ; nmr spectrum (CCl_4), triplet at 1.03 (methyl groups), broad peak at 1.85 (CH_2CH_2 in ring), singlet at 3.36 (OH group), and a multiplet at 3.48–3.78 ppm (OCH, OCH_2, and CHCl groups). Areas were in the proportions of 6:4:1:6.

Anal. Calcd for $C_9H_{17}ClO_2$: C, 56.2; H, 8.9; Cl, 18.4. Found: C, 56.5; H, 8.8; Cl, 18.3.

Tetrahydro-3-hydroxy-β,β-dimethylpyran-2-ethanol (2).—Aqueous 5.8 *N* hydrochloric acid (217.5 g) and **1** (572 g, 3.29 moles) were refluxed for 55 min, and 37 g of the crude reaction mixture was removed for further study. The remainder was separated into two layers after being neutralized with sodium bicarbonate. Benzene (100 ml) was added and the water layer was saturated with sodium chloride. The aqueous phase was withdrawn and concentrated. Additional organic material separated and was added to the main organic layer. After the water was removed from this layer by azeotropic distillation and a forecut was taken, the crude dry product was distilled to give 367.5 g (67.1%) of **2**, bp 112–119° (1 mm). A 252-g portion of this material was recrystallized from an equal weight of ethyl acetate. The crystals were washed with cold ethyl acetate (250 ml) and dried at 50° (10 mm) in a vacuum oven. The yield was 139 g of an odorless, white solid (pure **2**): mp 64–65°; infrared absorptions (KBr), 3.0 (s) μ and 9.6 (s) μ; nmr spectrum (CCl_4), singlet at 1.06 (methyl groups), broad peak at 1.66 (CH_2CH_2 in ring), multiplet at 3.3–4.1 (OCH_2 and OCH groups), and a singlet at 4.4 ppm (OH groups). Areas were in the proportions of 6:4:6:2.

Anal. Calcd for $C_9H_{18}O_3$: C, 62.5; H, 10.4. Found: C, 61.8; H, 10.8.

Acknowledgment.—The authors express their appreciation to V. W. Goodlett of these laboratories for his interpretation of the nmr spectra.

(3) Nmr spectra were recorded on a Varian A-60 instrument at 60 Mc and are reported in parts per million, relative to tetramethylsilane as an internal standard.

(4) Infrared spectra were recorded on a Baird AB-2 instrument.

A Correction on the Optical Rotations of Propylene Bromohydrin and Propylene Oxide

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In the course of some of our studies we had need for propylene oxide of known optical activity; consequently, we embarked on the synthesis of this compound *via* the published procedures shown in eq 1 and 2.[1–3]

$$CH_3\overset{OH}{\overset{|}{C}}HCH_2OH + HBr \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HCH_2Br \qquad (1)$$

$$CH_3\overset{OH}{\overset{|}{C}}HCH_2Br + OH^- \longrightarrow CH_3\overset{O}{\overset{/\backslash}{C}}H—CH_2 + Br^- + H_2O \qquad (2)$$

It seemed unusual to us that the reaction of hydrogen bromide with *dl*-1,2-propanediol should occur only at the primary carbon without concomitant attack at the secondary carbon. Since we wanted to obtain propylene oxide of the highest optical purity, we had to determine the extent of secondary carbon attack which, when starting with optically active glycol, could lead to formation of racemic 2-bromo-1-propanol, for, indeed, the amount of racemic 2-bromo-1-propanol would in turn be reflected in reduced optical activity of propylene oxide. Consequently, we examined the products from the reaction of *dl*-1,2-propanediol and HBr at several temperatures by glpc and nmr spectroscopy and found that the reaction *does not proceed with exclusive formation of 1-bromo-2-propanol* (**1**), *but rather produces substantial amounts of 2-bromo-1-propanol* (**2**). The results of this examination are shown in the Experimental Section.

$$CH_3\overset{OH}{\overset{|}{C}}HCH_2OH + HBr \longrightarrow \underset{\mathbf{1}}{CH_3\overset{OH}{\overset{|}{C}}HCH_2Br} + \underset{\mathbf{2}}{CH_3\overset{Br}{\overset{|}{C}}HCH_2OH}$$

Thus it seemed to us that the only feasible method for obtaining "pure" optically active propylene oxide when starting with optically active 1,2-propanediol was to separate **1** and **2** (*via* preparative glpc) and then to form propylene oxide from each constitutional isomer.[4] By so doing, we could also determine the configuration and optical purity of **2**. Starting with (+)-(*S*)-propylene glycol and HBr we synthesized (+)-(*S*)-1-bromo-2-propanol (**1**) and (−)-(*R*)-2-bromo-1-propanol (**2**).[5] The results of this experiment are summarized in Scheme I. Since the formation of propylene oxide from **1** does not involve the asymmetric center, it is quite apparent from Scheme I

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

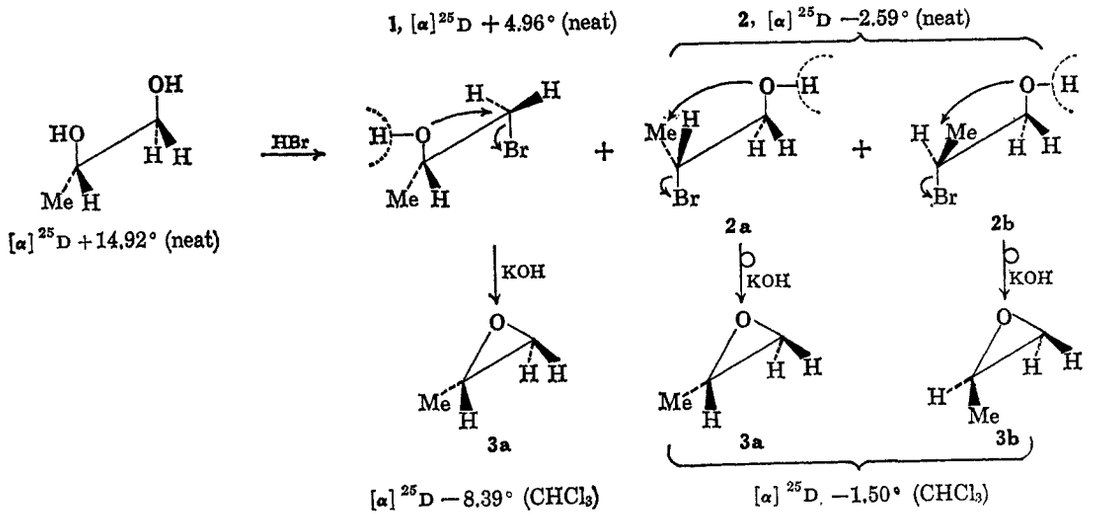
(2) C. C. Price and M. Osgan, *J. Am. Chem. Soc.*, **78**, 4787 (1956).

(3) N. Shieh and C. C. Price, *J. Org. Chem.*, **24**, 1169 (1959).

(4) Instead of "structural isomer" we are adopting the term "constitutional isomer" as used by K. Mislow. See K. Mislow "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1966, p 50.

(5) The absolute configuration of (+)-(*S*)-propylene glycol is based on the observation that the ethyl ester of (−)-(*R*)-lactic acid is reduced by sodium and ethanol to (−)-(*R*)-propylene glycol: P. A. Levene and H. L. Haller, *J. Biol. Chem.*, **67**, 329 (1926). See also E. Baer and H. O. L. Fischer, *J. Am. Chem. Soc.*, **70**, 609 (1948).

SCHEME I



that the optical rotation of (−)-(*S*)-propylene oxide (**3a**) is revised to at least −8.39° ($CHCl_3$)[1-3] (see Table I) and that of (+)-(*S*)-1-bromo-2-propanol (**1**) is revised to at least +4.96° (neat)[1-3] (see Table I). Furthermore, since the propylene oxide (**3a** plus **3b**) formed from 2-bromo-1-propanol (**2**) rotates polarized light in the same sense as the propylene oxide (**3a**) formed from 1-bromo-2-propanol (**1**), but is greatly diminished in magnitude, the formation of **2** from (+)-(*S*)-propylene glycol proceeds essentially with racemization accompanied by some inversion of configuration.[6] This latter conclusion is based on the assumption that conversion of **2** to **3a** plus **3b** proceeds with 100% inversion of configuration.[7] Since the optical purity of the **3a** plus **3b** mixture is 18% that of **3a** we therefore have 59% **3a** and 41% **3b** in the **3a** plus **3b** mixture. It follows then that the composition of **2** is 59% **2a** and 41% **2b**. From this result one can therefore calculate that the minimum specific rotation of pure **2a** or **2b** would be ∓14.4° (neat).

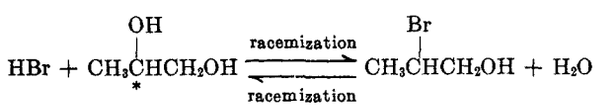
TABLE I

MINIMUM SPECIFIC OPTICAL ROTATIONS OF 1-BROMO-2-PROPANOL (1), 2-BROMO-1-PROPANOL, (2) AND PROPYLENE OXIDE

Compd	Lit $[\alpha]^{25}D$, deg	This work: 15.0° glycol $[\alpha]^{25}D$, deg	This work: 15.9° glycol $[\alpha]^{25}D$, deg
$CH_3CH(OH)CH_2Br$ (neat)	2.87[a]; 3.6[b]	4.96	5.3
$CH_3CH(Br)CH_2OH$ (neat)		14.4	15.3
$CH_3CH(O)CH_2$ ($CHCl_3$)	6.21[c]	8.39	8.9

[a] *Cf.* ref 1. [b] *Cf.* ref 2. [c] *Cf.* ref 3.

The specific optical rotations of 1-bromo-2-propanol (**1**), 2-bromo-1-propanol (**2**), and propylene oxide (**3a** or **3b**) are tabulated in Table I. The specific rotations are absolute based on the following assumptions: (i) propylene glycol undergoes no racemization[8] and (ii)



the formation of propylene oxide from the bromohydrin involves *only* inversion of configuration.[7] The rotations in the last column of Table I are calculated values based on a 15.9° glycol reported by Price and Osgan.[2]

Experimental Section

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Esso Research and Engineering Co., Analytical Division. Nmr analyses were obtained with a Varian A-60 spectrophotometer. A Perkin-Elmer Model 154 vapor fractometer was used for analytical glpc, and an Aerograph Autoprep Model A-700 was used as a preparative instrument. *dl*-1,2-propanediol, from Matheson Coleman and Bell, and *d*-1,2-propanediol, Aldrich Chemical Co., were used without further purification. Optical rotations were performed with an O. C. Rudolph and Sons Model 80 polarimeter.

Reaction of Hydrogen Bromide with *dl*-1,2-Propanediol.—In all experiments the glycol was weighed into a glass pressure tube fitted with a Fisher-Porter Teflon pressure valve. The tube was placed in an ice–water bath, and a slight excess (5–10%) of anhydrous hydrogen bromide was bubbled into the glycol. Approximately 4 hr was required to dissolve 20 g of hydrogen bromide, since the glycol became extremely viscous toward the end of the HBr addition. The tube was then placed in a bath of the desired temperature. The reaction mixture which became less viscous and much darker with time was analyzed periodically for bromide by removing a weighed sample, diluting to known volume with water, and titrating an aliquot with standard silver nitrate. Once the reaction was seen to have stopped (conversions of 70% maximum were attained), the reaction mixture was brought quickly to room temperature. After the tube contents were rinsed out with an equal volume of chloroform, an equal volume of 25% (by weight) aqueous sodium chloride was added with vigorous stirring. Next, 25% (by weight) aqueous sodium hydroxide was added until the pH of the aqueous phase was 5–6. After separation of the organic layer, the aqueous layer was extracted twice with chloroform. The chloroform layers were combined and dried over anhydrous sodium sulfate. The residue from the atmospheric distillation of chloroform was distilled to give a mixture of 1-bromo-2-propanol and 2-bromo-1-propanol in yields of 45–60%. The composition of this mixture

(6) (a) C. E. Wilson and H. J. Lucas, *J. Am. Chem. Soc.*, **58**, 2396 (1936); (b) S. Winstein and H. J. Lucas, *ibid.*, **61**, 1581 (1939).

(7) (a) J. D. Bartlett, *ibid.*, **57**, 224 (1935); (b) S. Winstein and H. J. Lucas, *ibid.*, **61**, 1576 (1939).

(8) The following reaction, for example, could lead to racemic propylene glycol.

was determined by (1) glpc analysis which showed two peaks with retention times of 14 (1-bromo-2-propanol) and 18 min (2-bromo-1-propanol) using a 2 m × 0.25 in. diethylene glycol succinate column at 100° with 160 ml/min helium flow and (2) nmr spectral analysis which showed two separate doublets for the methyl groups. Good correspondence was achieved in comparing the glpc peak area ratios with the nmr methyl area ratios.

Effect of Reaction Temperature.—The effect of reaction temperature on the relative yields of 1-bromo-2-propanol and 2-bromo-1-propanol is shown in Table II. It can be seen that in order to limit the formation of 2-bromo-1-propanol to negligible amounts, reduced reaction temperatures are required such that the reaction rate would be prohibitively slow.[9]

TABLE II

PRODUCT DISTRIBUTION WITH VARYING TEMPERATURE

Reacn temp, °C	1-Bromo-2-propanol (1), %	2-Bromo-1-propanol (2), %	Reacn time, hr
60	73	27	41
60	70	30	41
80[a]	60	40	4
100	52	48	2

[a] Tube was at 60° for 1 hr and then 80° for 4 hr.

Isolation of Optically Active Propylene Bromohydrins 1 and 2.—Using the method described above, 20.1 g (0.248 mole) of anhydrous hydrogen bromide was bubbled into 19.1 g (0.251 mole) of (+)-(*S*)-1,2-propanediol, $[\alpha]^{25}D$ +14.92° (neat). The reaction mixture was heated at 60° for 43 hr. Distillation yielded 19.3 g (0.139 mole, 56%) of propylene bromohydrins **1** and **2**, bp 53–58° (15 mm), $[\alpha]^{25}D$ +2.61° (neat), which analyzed 70/30 1-bromo-2-propanol (**1**) to 2-bromo-1-propanol (**2**) by glpc and 66/34 by nmr. Samples of 0.25 ml of the mixture were injected on a 12 ft × 3/8 in. preparative glpc column packed with 20% diethylene glycol succinate on Chromosorb P at 110°, and gave almost complete separation of the two peaks whose retention times were 20 and 39 min from air. Both components were collected in Dry Ice–acetone cooled traps in approximately 50% yield, and were checked for chromatographic purity *via* the analytical glpc column.

Fraction 1 with the shorter retention time, (+)-(*S*)-1-bromo-2-propanol (**1**), had $n^{25}D$ 1.4776, d^{25}_4 1.5589, $[\alpha]^{25}D$ +4.96° (neat), and an nmr spectrum which exhibited a methyl doublet (3 H) with center at δ 2.17 (J = 7.0 cps), another doublet (2 H, CH_2Br) centered at δ 4.2 (J = 6.0 cps), a multiplet (1 H, HCO) centered at δ 4.65, and a singlet (1 H, OH) centered at δ 5.2.

Anal. Calcd for C_3H_7BrO: C, 25.92; H, 5.08; Br, 57.49; MR, 25.34. Found: C, 25.74; H, 5.12; Br, 57.32; MR, 25.24.

Fraction 2 with the longer retention time, 2-bromo-1-propanol (**2**), had $n^{25}D$ 1.4791, d^{25}_4 1.558, $[\alpha]^{25}D$ −2.59° (neat), and an nmr spectrum which exhibited a methyl doublet (3 H) centered at δ 1.8 (J = 6.0 cps), another doublet (2 H, CH_2O) centered at δ 3.95 (J = 5.5 cps), a multiplet (1 H, HCBr) centered at δ 4.5, and a singlet (1 H, OH) centered at δ 5.1.

Anal. Calcd for C_3H_7BrO: C, 25.92; H, 5.08; Br, 57.49; MR, 25.34. Found: C, 25.99; H, 4.93; Br, 57.07; MR, 25.34.

Propylene Oxides.—To 4 ml of stirred, 50% (by weight) aqueous potassium hydroxide was added rapidly at 60°, 2.79 g (20.1 mmoles) of the (+)-(*S*)-1-bromo-2-propanol (**1**) isolated above. Propylene oxide distilled immediately, after which the reaction mixture was subjected briefly to reduced pressure (150–200 mm). The Dry Ice–acetone trapped condensate was redistilled from potassium hydroxide pellets to give 0.92 g (15.8 mmole, 79%), bp 35°, $[\alpha]^{25}D$ −8.39° ($CDCl_3$). Its glpc chromatogram and nmr spectrum were identical with those of authentic propylene oxide.

Treatment of 1.39 g (10.0 mmoles) of 2-bromo-1-propanol (**2**) with aqueous potassium hydroxide as above gave, on redistillation, 0.40 g (6.9 mmoles, 69%), bp 35°, $[\alpha]^{25}D$ −1.50° ($CDCl_3$). Again, its glpc chromatogram and nmr spectrum were identical with those of authentic propylene oxide.

(9) In a personal communication, Professor C. C. Price has informed us that their procedure for preparation of the bromohydrin (*cf.* ref 3) also involved addition of HBr at 0° followed by heating on a water bath for 1 hr. We are grateful to Professor Price for furnishing us with further experimental details.

Acknowledgment.—The authors are indebted to Mr. A. K. Russell for his very valuable technical assistance. We also wish to thank Dr. W. A. Thaler for his initial comments on our work when he, too, felt that exclusive primary carbon attack by HBr was highly suspect. In addition we also wish to acknowledge some very helpful comments by Dr. W. C. Baird, Jr., and Professor S. J. Cristol.

Structural Stabilities of the Trimethylsilylmethyl and Neopentyl Groups in the Preparation of Phosphonyl Dichlorides

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Several investigators have reported the preparation of the diesters of trimethylsilylmethylphosphonic acid, $(CH_3)_3SiCH_2PO(OR)_2$, (I) using the Michaelis–Arbuzov procedure.[1-3] This method is somewhat limited by the availability and reactivity of trialkyl phosphites (or dialkyl phosphonates) and often requires prolonged refluxing of reactants.

We have synthesized a number of these esters (Table I) by alcoholysis of trimethylsilylmethylphosphonyl dichloride (III), prepared by the reaction shown below. This is a modification of Clay's method[4]

$$(CH_3)_3SiCH_2Cl + PCl_3 + AlCl_3 \longrightarrow \underset{\text{II}}{[(CH_3)_3SiCH_2PCl_3]^+[AlCl_4]^-}$$

$$\text{II} + 7H_2O \longrightarrow \underset{\text{III}}{(CH_3)_3SiCH_2P(O)Cl_2} + AlCl_3\cdot 6H_2O + 2HCl$$

used to prepare alkylphosphonyl dichlorides from alkyl halides. Kinnear and Perren[5] investigated this reaction and showed that when propyl or higher primary or secondary alkyl chlorides are used, only rearranged products are obtained. We observed no rearrangement of the "neopentyl" structure of chloromethyltrimethylsilane in this reaction at or below room temperature, even though this compound undergoes a Wagner–Meerwein-type rearrangement to chlorodimethylethylsilane when warmed with aluminum chloride alone.[6]

The reaction does not appear to be applicable to chlorosilanes (≡SiCl) since we observed no evidence of complex formation between chlorotrimethylsilane and $AlCl_3$–PCl_3 at room temperature. This observation is in general agreement with Eaborn's[7] conclusion that the siliconium ion is not formed under conditions in which analogous carbonium ions exist.

(1) Gilbert and Precopio, Abstracts of Papers, 125th National Meeting of the American Chemical Society, Kansas City, Mo., 1954, p 16N.
(2) W. H. Keeber and H. W. Post, *J. Org. Chem.*, **21**, 509 (1956).
(3) A. E. Canavan and C. Eaborn, *J. Chem. Soc.*, 592 (1962).
(4) J. P. Clay, *J. Org. Chem.*, **16**, 892 (1951).
(5) A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).
(6) F. C. Whitmore, L. H. Sommer, and J. Gold, *J. Am. Chem. Soc.*, **69**, 1976 (1947).
(7) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, p 114.