

## STEREOSPECIFIC ALKYLATION OF BENZENE WITH (+)-PROPYLENE OXIDE BY LEWIS ACID CATALYST AND STEREOCHEMISTRY OF RING-OPENING<sup>1, 2</sup>

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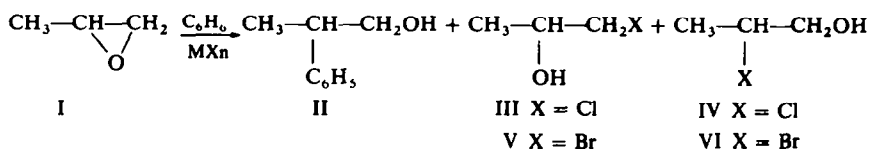
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**Abstract**—The alkylation of benzene with (+)-propylene oxide (I) in the presence of Lewis acid gave (+)-2-phenyl-1-propanol (II), and a mixture of (–)-1-halo-2-propanol (III or V) and (+)-2-halo-1-propanol (IV or VI) as the by-products. The reaction was conducted under various conditions. The magnitude of the optical yields of these products suggests that both the alkylation and ring opening proceed with complete inversion of configuration and the most probable mechanism is of the S<sub>N</sub>2 type, except for the cases of aluminum bromide catalyst and nitromethane solvent. When aluminum bromide was used as catalyst, about 50% racemization in the formation of (+)-II and (+)-VI was observed, and the reaction appears to proceed partially through a carbonium ion mechanism. Experiments showed that the formation of the racemic products was due neither to the racemization of the starting material nor to the racemization of the products. In the case of nitromethane solvent, the ring opening reaction proceeded with retention of configuration. This shows the possibility of S<sub>N</sub>i process.

IN THE presence of Lewis acid, the reaction between benzene and propylene oxide (I) gave 2-phenyl-1-propanol (II) and two halopropanols.<sup>3</sup> Recently, Hata<sup>4</sup> also reported



a similar result in the reaction of 1,2-epoxyoctane with benzene. This type of reactions has been believed to proceed via a carbonium ion mechanism involving formation of such an ion as  $\overset{\oplus}{\text{R}}\text{CHCH}_2\text{---O}^-\text{AlCl}_3$  formed by fission of secondary C—O bond in the epoxide.<sup>5</sup>

Price<sup>6, 7</sup> and Vandenberg<sup>8</sup> have found that the ring opening of epoxides occurs with complete inversion of configuration in the Lewis acid-catalyzed polymerization.

The stereochemical course of the Friedel–Crafts alkylation has been pointed out to proceed with almost complete racemization, e.g., *sec*-butylbenzene, produced by alkylation of benzene with optically active *sec*-butanol in the presence of boron trifluoride,<sup>9</sup> aluminum chloride,<sup>9, 10</sup> hydrogen fluoride, sulfuric acid or phosphoric

acid,<sup>10</sup> merely exhibited optical activities of less than 0.7%. In the boron trifluoride-catalyzed alkylation with optically active *sec*-butyl methyl ether, benzene was alkylated with a small net inversion as about 1.1–1.4%.<sup>11</sup>

The stereochemistry of Friedel–Crafts reaction with epoxide, however, has not been investigated. In this respect, we demonstrated previously that alkylation of benzene with (+)-propylene oxide (I) gave optically pure (+)-2-phenyl-1-propanol (II) in the presence of aluminum chloride or stannic chloride and proceeded with inversion of configuration at secondary carbon of the propylene oxide.<sup>2</sup> Such a high stereospecific example in the Friedel–Crafts alkylation has not been reported. Recently, Brauman *et al*<sup>12</sup> reported that the alkylation of benzene with optically active  $\gamma$ -valerolactone or 2-methyltetrahydrofuran in the presence of aluminum chloride proceeded with 47 and 35% net inversion of configuration respectively. They concluded that the reaction proceeded through ion pairs and that much of the stereospecificity was due to the cyclic nature of the substrate and the enforced proximity of the leaving group.

In the present paper, we have now undertaken a broader investigation of stereochemistry in Friedel–Crafts alkylation with (+)-propylene oxide (I) and its ring opening reaction under various conditions.

#### RESULTS AND DISCUSSION

(+)-Propylene oxide (I) and benzene were condensed at  $-5^\circ$  by means of various Lewis acid catalysts in various solvents. After 3.5 hr reaction period, the resulting mixture was worked up as mentioned in the previous paper<sup>3</sup> and gave 2-phenyl-1-propanol (II), together with a mixture of 1-halo-2-propanol (III or V) and 2-halo-1-propanol (IV or VI). The isomer compositions of the halopropanols were determined by gas chromatography and separated by means of preparative gas chromatography. The results under various conditions are shown in Tables 1 and 2.

*Alkylation.* The structure of II was identified by IR and NMR spectra and by the retention time of gas chromatography with those of an authentic sample prepared from hydratropic acid.

The absolute configurations of (+)-propylene oxide (I)<sup>13</sup> and (+)-2-phenyl-1-propanol (II)<sup>14</sup> have been established as R. Thus, it is apparent that the formation of (+)-II from (+)-I proceeds with the inversion of configuration.

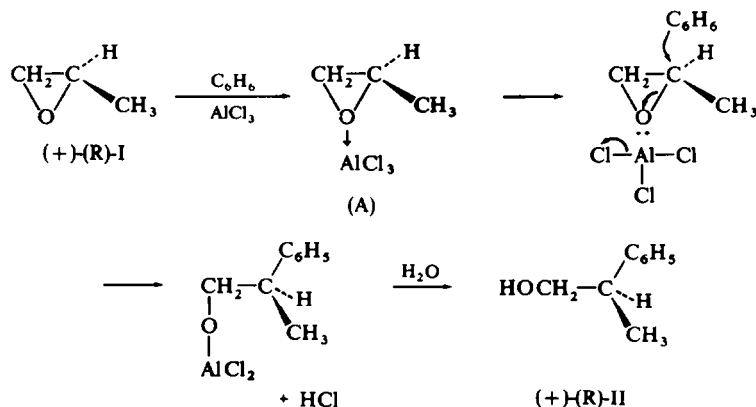


TABLE I. REACTION CONDITIONS AND RESULTS IN ALKYLATION

| Run             | (+)-PO (I)<br>[ $\alpha$ ] <sub>D</sub> <sup>20</sup> <sup>a</sup><br>(0.05 mole) | Lewis acid<br>(0.06 mole)           | Benzene<br>(mole) | Solvent<br>(ml)                      | Temp<br>(°C) | Yield (%) <sup>b</sup> | [ $\alpha$ ] <sub>D</sub> <sup>20</sup> (neat) | Inversion % <sup>c</sup> |
|-----------------|---|-------------------------------------|-------------------|--------------------------------------|--------------|------------------------|--|--------------------------|
| 1               | +7.23°  | AlCl <sub>3</sub>                   | 0.67              | CS <sub>2</sub>                      | -5           | 55.8                   | +15.96°  | 100                      |
| 2               | +8.29°  | SnCl <sub>4</sub>                   | 0.67              | CS <sub>2</sub>                      | -5           | 55.6                   | +16.58°  | 100                      |
| 3               | +8.25°  | TiCl <sub>4</sub>                   | 0.67              | CS <sub>2</sub>                      | -5           | 20.6                   | +16.47°  | 100                      |
| 4               | +8.05°  | BCl <sub>3</sub>                    | 0.67              | CS <sub>2</sub>                      | -5           | trace                  | —  | —                        |
| 5               | +7.39°  | AlCl <sub>3</sub>                   | 0.10              | CS <sub>2</sub>                      | -5           | 7.9                    | —  | —                        |
| 6               | +7.39°  | AlCl <sub>3</sub>                   | 0.25              | CS <sub>2</sub>                      | -5           | 21.2                   | +15.37°  | 100                      |
| 7               | +7.61°  | AlCl <sub>3</sub>                   | 0.25              | Cl(CH <sub>2</sub> ) <sub>2</sub> Cl | -5           | 45.9                   | +15.86°  | 100                      |
| 8               | +8.35°  | SnCl <sub>4</sub>                   | 0.25              | Cl(CH <sub>2</sub> ) <sub>2</sub> Cl | -5           | 49.3                   | +16.31°  | 100                      |
| 9               | +7.61°  | AlCl <sub>3</sub>                   | 0.25              | CHCl <sub>3</sub>                    | -5           | —                      | —  | —                        |
| 10              | +8.35°  | AlCl <sub>3</sub>                   | 0.25              | CH <sub>3</sub> NO <sub>2</sub>      | -5           | trace                  | —  | —                        |
| 11              | +7.81°  | AlCl <sub>3</sub> -HCl <sup>d</sup> | 0.67              | CS <sub>2</sub>                      | -5           | 11.0                   | +14.31°  | 93                       |
| 12              | +7.81°  | AlCl <sub>3</sub>                   | 0.67              | CS <sub>2</sub>                      | +10          | 45.1                   | +14.91°  | 97                       |
| 13              | +8.01°  | AlCl <sub>3</sub>                   | 0.67              | CS <sub>2</sub>                      | -20          | 42.7                   | +15.49°  | 98                       |
| 14 <sup>e</sup> | +7.96°  | AlBr <sub>3</sub>                   | 1.20              | CS <sub>2</sub>                      | -5           | 18.8                   | +7.42°   | 48                       |
| 15 <sup>e</sup> | +8.25°  | SnBr <sub>4</sub>                   | 1.20              | CS <sub>2</sub>                      | -5           | 30.3                   | +16.88°  | 100                      |
| 16 <sup>e</sup> | +8.06°  | AlBr <sub>3</sub> -HBr <sup>f</sup> | 1.20              | CS <sub>2</sub>                      | -5           | 14.0                   | +3.10°   | 20                       |

<sup>a</sup> Rotations taken in chloroform, concentration approximately 5.0%. The maximum rotation was estimated to be +8.49° (c 5.02, CHCl<sub>3</sub>) in run 24 (Table 4). Lit., <sup>26</sup> [ $\alpha$ ]<sub>D</sub><sup>25</sup> +7.05° (c 2, CHCl<sub>3</sub>).

<sup>b</sup> Based on (+)-propylene oxide used.

<sup>c</sup> Calculated from the reported rotation [ $\alpha$ ]<sub>D</sub><sup>25</sup> +16.7° (neat)<sup>16</sup> and corrected by the optical purity of (+)-propylene oxide used.

<sup>d</sup> The reaction was started after the addition of dry HCl to a mixture of benzene, CS<sub>2</sub> and AlCl<sub>3</sub> for 30 min.

<sup>e</sup> (+)-Propylene oxide: 0.10 mole, Lewis acid: 0.12 mole.

<sup>f</sup> The reaction was started after the addition of dry HBr to a mixture of benzene, CS<sub>2</sub> and AlBr<sub>3</sub> for 60 min.

TABLE 2. YIELDS AND SPECIFIC ROTATIONS OF PROPYLENE HALOHYDRINS

| Run <sup>a</sup> | Yield <sup>b</sup><br>(%) | Isomers % |      | Specific rotation <sup>c</sup> and Optical purity (OP %) <sup>d</sup> |                   |                      |                   |
|------------------|---------------------------|-----------|------|---|-------------------|----------------------|-------------------|
|                  |                           | III       | IV   | III   | (OP) <sup>e</sup> | IV                   | (OP) <sup>f</sup> |
| 1                | 21.1                      | 27.0      | 73.0 | -19.19°   | 100               | +17.54°              | 100               |
| 2                | 19.6                      | 6.0       | 94.0 | —   | —                 | +18.52° <sup>g</sup> | 94                |
| 3                | 34.7                      | 27.5      | 72.5 | -18.63°   | 96                | +19.51°              | 100               |
| 4                | 48.9                      | 51.3      | 48.7 | -19.31°   | 100               | +16.40°              | 86                |
| 5                | 25.3                      | 28.0      | 72.0 | -19.00°   | 100               | +18.07°              | 100               |
| 6                | 21.2                      | 26.1      | 73.9 | -18.69°   | 100               | +16.61°              | 95                |
| 7                | 23.3                      | 24.8      | 75.2 | —   | —                 | +14.95°              | 84                |
| 8                | 13.6                      | 11.1      | 88.9 | —   | —                 | +13.56°              | 69                |
| 9                | 36.8                      | 49.2      | 50.8 | -19.77°   | 100               | +18.28°              | 100               |
| 10               | 59.3                      | 7.6       | 92.4 | —   | —                 | -13.49°              | 65                |
| 11               | 48.3                      | 41.8      | 58.2 | -19.22°   | 98                | +16.75°              | 92                |
| 12               | 21.2                      | 26.1      | 73.9 | —   | —                 | +14.62°              | 80                |
| 13               | 16.8                      | 20.2      | 79.8 | —   | —                 | +18.78°              | 97                |
|                  |                           | V         | VI   | V   | (OP) <sup>h</sup> | VI <sup>i</sup>      | (OP)              |
| 14               | 26.5                      | 47.8      | 52.2 | -16.81°   | 100               | +1.77° <sup>j</sup>  | 30                |
| 15               | 18.0                      | 9.0       | 91.0 | —   | —                 | +5.86°               | 100               |
| 16               | 34.6                      | 49.6      | 50.4 | -16.38°   | 99                | +3.02° <sup>k</sup>  | 52                |

<sup>a</sup> See Table 1 for the reaction conditions.

<sup>b</sup> Based on (+)-propylene oxide used.

<sup>c</sup> Rotations taken in CHCl<sub>3</sub> at 25°, concentration approximately 5%.

<sup>d</sup> Corrected by the optical purity of (+)-propylene oxide used.

<sup>e</sup> Calculated from the rotation  $[\alpha]_D^{25} - 20.24^\circ$  in run 21 (Table 4). The optical rotation has not been reported.

<sup>f</sup> Calculated from the reported rotation  $[\alpha]_D^{25} + 17.39^\circ$  (neat).<sup>21</sup>

<sup>g</sup>  $[\alpha]_D^{25} + 15.9^\circ$  (neat).

<sup>h</sup> Calculated from the rotation  $[\alpha]_D^{25} - 17.42^\circ$  in run 24 (Table 4). Lit.,<sup>26</sup>  $[\alpha]_D - 10.53^\circ$  (in CHCl<sub>3</sub>).

<sup>i</sup> VI in run 15 was estimated to be optically pure material. The optical rotation has not been reported.

<sup>j</sup> Calcd. value from +0.84° of a mixture of V (5%) and VI (95%).

<sup>k</sup> Calcd. value from -0.08° of a mixture of V (16%) and VI (84%).

In the case of metal chloride catalysts, the specific rotation found for (+)-II was almost identical regardless of the kind of Lewis acid and solvent, and also of the reaction temperature, as shown in Table 1. In chloroform and nitromethane solvents, the yields of alkylated products were too low to permit the polarimetric measurement. Assuming that the optically pure materials of (+)-I and (+)-II exhibit  $[\alpha]_D^{20} + 8.49^\circ$  (chloroform)<sup>15</sup> and  $+16.7^\circ$  (neat)<sup>16</sup> respectively, the alkylation of benzene with epoxide in the presence of metal chloride catalysts suggests complete inversion of configuration. These results are elucidated as the bimolecular reaction between benzene and epoxide-metal chloride adducts.

The alkylation by aluminum bromide catalyst proceeded with 47% net inversion in contrast to that with aluminum chloride catalyst. In the case of stannic bromide, however, the alkylation proceeded with complete inversion. When hydrogen bromide

was added to aluminum bromide, the extent of racemization was much higher than with aluminum bromide alone. On the other hand, the addition of hydrogen chloride to aluminum chloride indicated no remarkable effects in the stereochemistry of the reaction.

In many cases of stereospecific reactions, it has been reported that the heterogeneity plays an important role.<sup>17</sup> In the present case, however, the reaction mixtures are homogeneous except in the case of aluminum chloride. Therefore the heterogeneity can not be responsible for the stereospecificity.

The possibility of racemization of the starting material in the course of reaction is excluded, which will be discussed later.

Brown *et al*<sup>18</sup> reported that disproportionation of isopropylbenzene readily occurred under the influence of aluminum bromide and hydrogen bromide at 0°. Since the racemization of the products in runs 14 and 16 could have resulted from a similar disproportionation, (+)-2-phenyl-1-propanol(II) was treated with aluminum or a mixture of aluminum bromide and hydrogen bromide under the same condition as that of alkylation. The specific rotation of (+)-II remained unchanged before and after the reaction as shown in Table 3.

TABLE 3. REACTION OF (+)-2-PHENYL-1-PROPANOL (II) WITH ALUMINUM BROMIDE\*

| Run             | Lewis acid             | [ $\alpha$ ] <sub>D</sub> <sup>25</sup> (neat) of (+)-2-Phenyl-1-propanol (II) |                |
|-----------------|------------------------|--|----------------|
|                 |                        | Before reaction  | After reaction |
| 17              | AlBr <sub>3</sub>      | + 15.96°   | + 15.93°       |
| 18 <sup>b</sup> | AlBr <sub>3</sub> -HBr | + 16.58°   | + 16.12°       |

\* The mole ratio of AlBr<sub>3</sub> to (+)-2-phenyl-1-propanol (II) is 1:5. Benzene (0.67 mole) and CS<sub>2</sub> (18 ml) are used.

<sup>b</sup> The reaction was started after the addition of dry HBr to a mixture of benzene, CS<sub>2</sub> and AlBr<sub>3</sub> for 30 min.

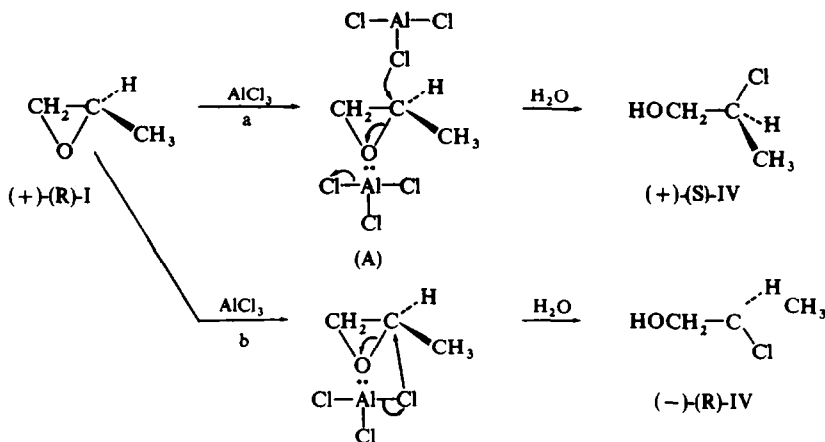
Consequently, the less stereospecificity in the aluminum bromide catalyzed alkylation does not depend on the racemization of the product. The racemization appears to be due to the partial formation of carbonium ion because of the stronger acidity of aluminum bromide.<sup>19\*</sup> The ring opening in the epoxide-aluminum bromide complex may bring a some extent of carbonium ion character along with the nucleophilic attack of benzene on the epoxide. The lesser stereospecificity due to the addition of hydrogen bromide to the system may be caused by its acidity strengthening effect. Recently, Price<sup>20</sup> concluded that the acid-catalyzed epoxide ring opening involving no molecular rearrangement must all proceed through oxonium intermediates; and carbonium ion intermediates, when formed, presumably rapidly rearranged to carbonyl isomers. In the present case, however, the carbonium ion or ion pairs must be considered as an intermediate for racemic products.

*Propylene halohydrins as by-products.* Along with the alkylation, halohydrins were obtained. The each isomer was identified by comparing with authentic samples prepared from propylene oxide with hydrogen halides.

\* On the acidity of aluminum chloride, the value of  $\Delta\nu_{CO} = 113 \text{ cm}^{-1}$  has been reported.

As the absolute configuration of the dextrorotatory 2-chloro-1-propanol (IV) has been established as  $S$ ,<sup>21</sup> it is apparent that the formation of the (+)-primary halo-hydrins also proceeds with inversion of configuration at the carbon atom undergoing ring opening.\*

As shown in Table 2, the observed optical purity of IV indicates that the reaction proceeds also with almost complete inversion of configuration except for the cases in runs 4, 7, 8 and 10. Thus the stereochemistry of the ring opening step excludes the possibility that the chlorine atom of the epoxide-aluminum chloride adduct (A) reacts with the asymmetric carbon intramolecularly to form the propylene chlorohydrin. The most probable mechanism is of the  $S_N2$  type as shown in path a. In the results of



run 4, however, the lower optical purity of the product appears to have resulted from the carbonium ion mechanism due to the strong acidity of boron trichloride.<sup>19</sup>

When nitromethane was used as solvent, the levorotatory product (IV) was obtained with 65% retention of configuration. This result suggests the possibility of  $S_Ni$  process through a four-centered transition state<sup>22</sup> (path b). Although the role of nitromethane in this reaction is ambiguous, the retention of configuration may be due to the high polarity of the solvent. The lower optical purity of (+)-2-chloro-1-propanol (IV) in runs 7 and 8 (in dichloroethane) may be interpreted by  $S_N2$  accompanying  $S_Ni$  mechanism. However, the carbonium ion mechanism can not be excluded in this stage of experiments.

Although maximum rotation of the primary bromohydrin (VI) has not been reported, the value of  $+5.86^\circ$  obtained in run 15 is considered to be maximal, since the alkylation proceeded completely stereospecific. In the cases with aluminum bromide and aluminum bromide-hydrogen bromide (runs 14 and 16), the primary bromohydrin (VI) had lower optical purity. In run 14, the extent of racemization corresponds to that of alkylation reaction, but in the results of run 16, there is some discrepancy between the two reactions. According to the literature, ring opening of epoxide with

\* Although the absolute configuration of (+)-2-bromo-1-propanol (VI) has not been established, it can be considered to be the same as that of (+)-2-chloro-1-propanol (IV).

TABLE 4. REACTION OF (+)-PROPYLENE OXIDE (I) WITH LEWIS ACID OR HYDROGEN HALIDE (HX)<sup>a</sup>

| Run | (+)-PO (I)<br>[ $\alpha$ ] <sub>D</sub> <sup>20</sup> <sup>b</sup><br>(0.05 mole) | Lewis acid<br>or HX<br>(0.05 mole) | Yield <sup>c</sup><br>(%) | Propylene halohydrins |      |   |     |                   |                   |
|-----|---|------------------------------------|---------------------------|-----------------------|------|---|-----|-------------------|-------------------|
|     |   |                                    |                           | Isomers %             |      | Specific rotation <sup>d</sup> and Optical purity (OP) % <sup>f</sup> |     |                   |                   |
|     |   |                                    |                           | III                   | IV   | III   | IV  | (OP) <sup>e</sup> | (OP) <sup>f</sup> |
| 19  | +8.03°  | AlCl <sub>3</sub>                  | 35.0                      | 53.3                  | 46.7 | -19.47°   | 100 | +19.70°           | 100               |
| 20  | +8.08°  | SnCl <sub>4</sub>                  | 27.5                      | 2.6                   | 97.4 | —   | —   | +14.19°           | 75                |
| 21  | +8.49°  | HCl                                | 67.8                      | 71.0                  | 29.0 | -20.24°   | 100 | —                 | —                 |
| 22  | +8.03°  | AlBr <sub>3</sub>                  | 79.1                      | 37.6                  | 62.4 | -16.67°   | 100 | +1.97°            | 34                |
| 23  | +8.06°  | SnBr <sub>4</sub>                  | 43.2                      | 31.4                  | 68.6 | -16.28°   | 99  | —                 | —                 |
| 24  | +8.49°  | HBr                                | 57.6                      | 80.1                  | 19.9 | -17.42°   | 100 | —                 | —                 |

<sup>a</sup> All reactions were carried out in CS<sub>2</sub> (75 ml) at -5°.<sup>b</sup> See footnote a in Table 1<sup>c</sup> c, d, e, f, g, h and i: See footnotes b, c, d, e, f, h and i in Table 2 respectively.

hydrogen halide proceeds with inversion,<sup>23</sup> and this may be the reason for this discrepancy.

The secondary halohydrins (III and V) obtained were almost optically pure in all runs. The absolute configurations of (-)-1-halo-2-propanols (III and V) are R in due course of that the asymmetric center of the epoxide (I) remains unchanged. This result shows that the racemization of the starting (+)-propylene oxide (I) does not occur in the course of reaction. If the racemization of the (+)-epoxide occurs, the secondary halohydrins (III and IV) obtained should not be optically pure.

In connection with this racemization, the reaction of the propylene bromohydrin with benzene was carried out in the presence of aluminum bromide, but phenylpropanol (II) was scarcely formed in this reaction. Thus it is ascertained that the racemization of (+)-VI and (+)-II in runs 14 and 16 is not due to the alkylation with the carbonium ion  $\text{CH}_3\overset{\oplus}{\text{C}}\text{HCH}_2\text{—OAlBr}_2$  from bromohydrin.

The results of the reaction of the epoxide with Lewis acid or hydrogen halide are presented in Table 4. The optical purity of propylene halohydrins produced were almost the same with the results in Table 2. In contrast with the fact that the reaction with hydrogen halide gave mainly secondary halohydrins (III and V), the primary halohydrins (IV and VI) predominated in the reaction with Lewis acid. Thus the halohydrin produced in the above alkylation can not be considered to have derived from the reaction of propylene oxide with the hydrogen halide formed in the course of alkylation. These two reactions, alkylation and formation of halohydrins, occur competitively.

Considering the isomer distribution of propylene halohydrins produced in the alkylation, it appears that the secondary propylene halohydrin tends to increase as the acidity of Lewis acid increase. For a better understanding of this problem, further study is needed.

## EXPERIMENTAL

All m.ps and b.ps are uncorrected. Rotations were taken on a Zeiss polarimeter using 1 and 0.5 dm tube, and on a REX photoelectric polarimeter using 1 dm tube. IR spectra were determined on a JASCO DS-301 spectrophotometer. NMR spectra were determined on a JEOL JNM-3H-60 instrument. Chemical shifts are given in ppm down field from internal TMS.

**Materials.** Benzene and chloroform were washed with conc  $\text{H}_2\text{SO}_4$  and treated as usual, after drying they were distilled.  $\text{CS}_2$  was agitated with Hg, dried over  $\text{P}_2\text{O}_5$  and distilled. Dichloroethane and nitromethane were used after distillation of commercial GR grade reagents.

$\text{AlCl}_3$  was prepared from high purity Al and dry HCl. Commercial GR grade  $\text{SnCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{TiCl}_3$  and  $\text{BCl}_3$  were used without further purification. Commercial GR grade  $\text{AlBr}_3$  and  $\text{SnBr}_4$  were distilled *in vacuo*. They were stored in ampules from which they could be transferred without coming into contact with moist air. HCl and HBr were prepared by usual method.

(+)-Propylene oxide (I) was prepared by the method of Levene<sup>13a</sup> and Price<sup>7</sup>: Acetol, prepared from  $\alpha$ -bromoacetone and potassium formate in methanol,<sup>24</sup> was reduced microbiologically by the reductase of baking yeast to (-)-propylene glycol<sup>25</sup>; b.p. 87–89°/15 mm,  $[\alpha]_D^{20} - 31.9^\circ$  (c 5.0,  $\text{CHCl}_3$ ) [lit.,<sup>26</sup>  $[\alpha]_D^{24} - 28.6^\circ$  ( $\text{CHCl}_3$ )]. The propylene glycol was converted to (-)-propylene bromohydrin with dry HBr at 0°; b.p. 64–67°/39 mm,  $[\alpha]_D^{20} - 13.5^\circ$ – $-16.1^\circ$  (c 5.0,  $\text{CHCl}_3$ ) [lit.,<sup>26</sup>  $[\alpha]_D^{24} - 10.53^\circ$  ( $\text{CHCl}_3$ )], the obtained fraction of (-)-propylene bromohydrin contained 25–15% of 2-bromo-1-propanol. The (-)-propylene bromohydrin was then cyclized to (+)-propylene oxide with 45% KOH aq. After distillation over KOH and then over  $\text{CaH}_2$ , (+)-propylene oxide (I) indicated b.p. 34–35°,  $[\alpha]_D^{20} + 7.23^\circ$ – $+ 8.49^\circ$  (c 5.0,  $\text{CHCl}_3$ ) [lit.,<sup>26</sup>  $[\alpha]_D^{21} + 7.05^\circ$  (c 2,  $\text{CHCl}_3$ )].

**A typical reaction procedure.** To a stirred mixture of benzene (32.8 g, 0.42 mole) containing  $\text{AlCl}_3$ ,



(8.1 g, 0.06 mole) and CS<sub>2</sub> (13 ml) was slowly added a soln of (+)-propylene oxide (2.9 g, 0.05 mole),  $[\alpha]_D^{20} + 7.23^\circ$  (c 5.0, CHCl<sub>3</sub>), in a mixture of benzene (19.5 g, 0.25 mole) and CS<sub>2</sub> (5 ml). The reaction temp was maintained at  $-5^\circ$  throughout the addition, which required 3.5 hr. After the addition the resulting mixture were allowed to stand at  $-5^\circ$  for 30 min and poured onto a mixture of crushed ice and 50 ml of conc HCl.

The benzene layer was separated and washed three times with water, and then dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was distilled *in vacuo* to give 3.8 g (55% yield) of II, b.p. 112–113°/19 mm. After purification by boric ester method,<sup>27</sup> II showed  $[\alpha]_D^{20} + 15.96^\circ$  (neat). IR (neat), 1000–1050 and 980 cm<sup>-1</sup> ( $\nu_{C-OH}$ ), which were characteristic for the primary alcohol; NMR (CDCl<sub>3</sub>),  $\delta$  7.2 (s, 5H, C<sub>6</sub>H<sub>5</sub>), 3.55 (d, 2H, —CH<sub>2</sub>—), 2.84 (sextet, 1H, =CH—), 1.8 (s, 1H, OH) and 1.2 ppm (d, 3H, —Me).

$\alpha$ -Naphthylurethane of (+)-II: m.p. 93–93.5°,  $[\alpha]_D^{25} + 25.55^\circ$  (c 4.99, CHCl<sub>3</sub>). (Found: C, 78.83; H, 6.38; N, 4.60. C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub> requires: C, 78.69; H, 6.23; N, 4.57%.)

The other results were presented in Table 1.

The water layer was extracted seven times with 70 ml-portions of ether. The combined extracts were washed with 10 ml NaHCO<sub>3</sub> aq and then dried over Na<sub>2</sub>SO<sub>4</sub>. After careful removal of ether, the residue was distilled *in vacuo* to give a mixture of III and IV, b.p. 61–64°/50 mm. The mixture was analyzed to contain III and IV in a ratio of 27:73 by gas chromatography and was separated by means of preparative gas chromatography. The specific rotations of III and IV were  $-19.19^\circ$  (c 5.0, CHCl<sub>3</sub>) and  $+17.54^\circ$  (c 5.0, CHCl<sub>3</sub>) respectively. The other results were presented in Table 2.

The determinations of isomer percentage of the propylene halohydrins were carried out on a 1 m 10% Carbowax 20M on Diasolid L column by Hitachi K-53 instrument (column temp: 75° for the chlorohydrins and 85° for the bromohydrins). The separation of propylene halohydrin isomers were carried out on a 3 m 30% Carbowax 20 M on C-22 column by Yanagimoto GCG-5DH instrument (column temp: 110° for the chlorohydrins and 130° for the bromohydrins).

*Reaction of (+)-2-phenyl-1-propanol (II) with aluminum bromide.* To a stirred soln of benzene (32.8 g, 0.42 mole) containing AlBr<sub>3</sub> (5.7 g, 0.22 mole) and CS<sub>2</sub> (13 ml) was added a soln of (+)-II,  $[\alpha]_D^{20} + 15.96^\circ$  (neat), (2.0 g, 0.015 mole) in a mixture of benzene (19.5 g, 0.25 mole) and CS<sub>2</sub> (5 ml). The reaction mixture was maintained at  $-5^\circ$  throughout the addition. The resulting mixture was worked up as mentioned above and 1.8 g (98%) of (+)-II was recovered. The data of specific rotation are presented in Table 3.

*Reaction of (+)-propylene oxide (I) with Lewis acid or hydrogen halide.* To a stirred mixture of CS<sub>2</sub> (55 ml) containing Lewis acid or hydrogen halide (0.06 mole) was added a soln of (+)-propylene oxide (2.9 g, 0.05 mole) in CS<sub>2</sub> (20 ml) at  $-5^\circ$ . The reaction mixture was treated as mentioned above. The results were presented in Table 4.

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