SHORT COMMUNICATIONS

Stereospecific Alkylation of Benzene with (+)-Propylene Oxide by Lewis Acid Catalyst

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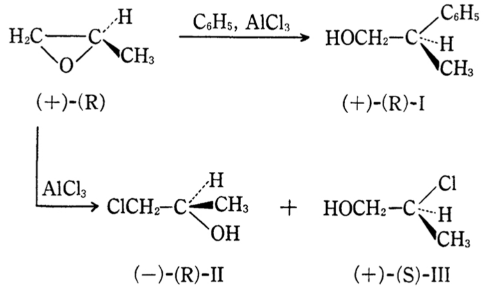
The reaction of propylene oxide with benzene in the presence of Lewis acids, such as aluminum chloride and stannic chloride, gives 2-phenyl-1-propanol and a mixture of 1-chloro-2-propanol and 2-chloro-1-propanol.[1] As a part of its mechanistic study, the same reaction has been carried out with optically active propylene oxide.

Into a benzene (32 g) solution containing aluminum chloride (8.1 g, 0.06 mol) and carbon disulfide (15 m*l*), was added a solution of (+)-propylene oxide (2.9 g, 0.05 mol),[2] $[\alpha]_D^{28}$ +7.23° (*c* 3.18, $CHCl_3$), in a mixture of benzene (20 g) and carbon disulfide (5 m*l*). The reaction temperature was maintained at −5°C throughout the addition, which required 3.5 hr. The resulting reaction mixture was worked up as mentioned in the previous paper[1] and gave 3.8 g (55.8% yield) of (+)-2-phenyl-1-propanol (I), bp 112—113°C/19 mmHg, $[\alpha]_D^{34}$ +13.28° (neat), and a mixture (1.0 g, 21.1% yield) of 1-chloro-2-propanol (II) and 2-chloro-1-propanol (III) (27 : 73 by gas chromatography), bp 61—64°C/ 50 mmHg, $[\alpha]_D^{34}$ +6.06° (*c* 1.62, $CHCl_3$). After the purification by boric ester method,[3] I showed $[\alpha]_D^{34}$ +14.83° (neat) (lit.[4] +16.7°); α-naphthylurethane, mp 93—93.5°C, $[\alpha]_D^{31}$ +25.55° (*c* 4.99, $CHCl_3$) (Found: C, 78.83; H, 6.38; N, 4.60%. Calcd for $C_{20}H_{19}NO_2$: C, 78.69; H, 6.23; N, 4.59%.). The mixture of II and III was separated by means of preparative gas chromatography. Specific rotation of II (containes 5% of III) and III (contains 5% of II) were −19.19° (*c* 5.17, $CHCl_3$) (not reported) and +13.22° (neat) (lit.[5] +17.39°), +15.74° (*c* 5.07, $CHCl_3$) respectively.

When stannic chloride was used in place of aluminum chloride, similar results were obtained. 2-Phenyl-1-propanol (I) (yield 36.9%) showed $[\alpha]_D^{34}$ +14.07° (neat), and the mixture of chloropropanols (yield 10.6%), $[\alpha]_D^{34}$ +15.75° (*c* 2.54, $CHCl_3$), was found to contain II and III in a ratio of 6 : 94.



The absolute configurations of (+)-propylene oxide,[6] (+)- I[7] and (+)-III[5] were established as R, R and S respectively. The stereochemical course for alkylation of Friedel-Crafts type reactions was pointed out to proceed accompanying racemization with slight inversion of configuration, in the case of alkylation of benzene with optically active 2-butanol employing aluminum chloride and boron trifluoride as catalysts.[8] In contrast, it is clear that the alkylation of benzene with (+)-propylene oxide proceeds with almost complete (more than 95%) inversion of configuration. Ring opening of the oxide also proceeds with 86% inversion of configuration. Thus, the carbonium ion mechanism cannot be applied to the ring opening as well as the alkylation. Combined with previous results, the most probable mechanism appears to be an S_N2 type.

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