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Reaction Behavior of Propylene Oxide in Various Solvents in the Presence of Boron Trifluoride

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Synopsis. The reaction behavior of propylene oxide with boron trifluoride was affected remarkably by solvent. In dioxane, the isomerization to propionaldehyde proceeded smoothly and selectively, while the reaction behavior in heptane, benzene, and tetrahydrofuran was quite different from that in dioxane.

Since Heusser et al. reported the use of boron trifluoride (BF_3) for the isomerization of substituted ethylene oxides,[1] BF_3 has been used widely as a Lewis acid in organic synthesis.[2] In the reaction of propylene oxide, boron trifluoride etherate ($BF_3 \cdot OEt_2$) was used as a polymerization catalyst but has not been reported as an isomerization catalyst.[3] Generally, $BF_3 \cdot OEt_2$ equilibrates in the exchange reactions with cyclic[4] and acyclic[5] ethers, while it dissociates to BF_3 and ether in CH_2Cl_2 to some extent.[6] It is hence expected that the acid strength of BF_3 may be adjusted by selection of solvent. In connection with our studies on epxides,[7,8] we observed an interesting solvent effect in the isomerization of propylene oxide (**1**) to propionaldehyde (**2**) and acetone (**3**) with $BF_3 \cdot OEt_2$. In heptane and benzene, polymerization of **1** occurred as expected, but the reaction behavior was greatly dependent on each solvent. In tetrahydrofuran (THF), the copolymerization of **1** and THF was observed as reported in the literature.[9,10] However, the isomerization to **2** proceeded smoothly and selectively in dioxane. To the best of our knowledge, such a behavior has not been previously described. The findings will be described herein.

Experimental

To a reaction solution (25 cm^3) of **1** (0.5 M)(1 M=1 mol dm^{-3}), a known amount of $BF_3 \cdot OEt_2$ was added and stirred magnetically at room temperature. The progress of the reaction was monitored with a Hitachi 163 model gas chromatograph (3 mmϕ×3 m stainless steel column: 15% PEG 4000 on Uniport B at 70 °C). After a given time, the reaction solution was treated with poly(4-vinylpyridine) (Aldrich; 7.6 mequiv g^{-1}) in order to remove the catalyst and filtered off. The filtrate was evaporated in vacuo at 50 °C until the weight of the residue became constant. In the reaction in THF, the reaction solution was directly analyzed by an IR spectrum . Solvents (Special Grade of Wako Co.), $BF_3 \cdot OEt_2$ (Tokyo Kasei Co.), and **1** (Tokyo Kasei Co.) were used without further purifications. No isomers were found in the commercial **1** gas chromatographically. The IR spectra of the polymers and the reaction solution were recorded as liquid film inserted between NaCl plates. A Shimadzu IR-400 spectrophotometer was used.

Results and Discussion

Solvent Effect. Figure 1 illustrates the solvent

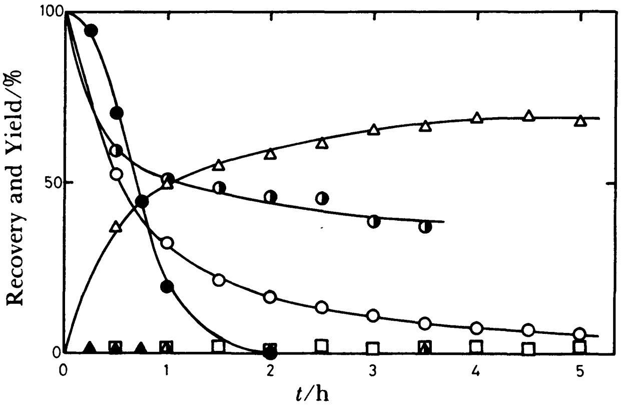

Fig. 1. Reaction behaviors of **1** with $BF_3 \cdot OEt_2$ in various solvents. ○: Recovery of **1**, △: yield of **2**, □: yield of **3**. Open symbols: in dioxane, half-filled symbols: in benzene, filled symbols: in THF.

Table 1. Relative Acid Strength of $BF_3 \cdot OEt_2$ in Various Solvents

Indicator[a]	A	B	C	Ref.
Acid range	Dilute HCl	56—75% H_2SO_4	77—94% H_2SO_4	
Sample				
Concd H_2SO_4	○	○	○	
$BF_3 \cdot OEt_2$	○	○	×	
$BF_3 \cdot OEt_2/Et_2O$	○	×	×	
$BF_3 \cdot OEt_2$/Dioxane	○	×	×	
$BF_3 \cdot OEt_2$/THF	○	×	×	
$BF_3 \cdot OEt_2$/Heptane[b]	○	×	×	Heptane Layer
	○	○	×	Etherate Layer
$BF_3 \cdot OEt_2$/Benzene	○	○	×	

○: Color change identical with that caused by concd H_2SO_4. a) A; 4-(Phenylazo)diphenylamine, B; benzylideneacetophenone, C; anthraquinone. b) Insoluble.

effect on the reaction behavior of **1** with a catalytic amount of $\mathrm{BF_3\cdot OEt_2}$ (30 mg, 0.21 mmol). In heptane, $\mathrm{BF_3\cdot OEt_2}$ did not dissolve completely but form fine oily drops. Immediately after the catalyst was added to a heptane solution of **1**, a brown oil separated and **1** was not detected in the reaction solution.

As shows in Fig. 1, **1** was consumed slowly in benzene during the reaction, but the isomers were scarcely formed. The product was identified as poly(propylene oxide) (PPO) by its IR spectrum,[3] which was in agreement with the spectrum of the product obtained in heptane [IR ν: 3400, 2850, 1440, 1380, and 1080 cm^{-1}]. In THF, a reverse S-type curve was observed and remarkable constriction of the volume (ca. 2 cm^3) of the reaction medium (25 cm^3) occured to give a viscous solution. The IR spectrum of the reaction solution indicated absorption due to alkyl ethers, overlapped with that of THF, and the absence of **1** [IR ν: 2850, 1450, 1360, 1060, and 900 cm^{-1}]. In the present case, copolymerization of **1** and THF by $\mathrm{BF_3\cdot OEt_2}$ proceeded.[9,10] In contrast, the isomerization of **1** to **2** proceeded smoothly and selectively in dioxane. In order to explain the present results, one should consider and an actual acid strength of $\mathrm{BF_3\cdot OEt_2}$ in each solvent. Table 1 lists the relative acid strength of $\mathrm{BF_3\cdot OEt_2}$ in each solvent (1:2 by mole ratio) estimated by Hammett indicators.[11]

In the case of oxygen-containing solvents, the acid strength of $\mathrm{BF_3\cdot OEt_2}$ was decreased due to equilibrated trapping of free $\mathrm{BF_3}$ from the etherate by the solvent. In benzene, the acid strength of $\mathrm{BF_3\cdot OEt_2}$ was high, because benzene interacts only weakly with $\mathrm{BF_3\cdot OEt_2}$. In heptane, a high acid strength must be held due to the low solubility of the etherate and the lack of Lewis basicity of the solvent. The polymerizatin of **1** therefore must need a relatively high acid strength as is shown in heptane and benzene solvents. The decrease in the reactivity of the polymerization in benzene is probably caused by a weak electron-donating character of benzene to decrease the acid strength of $\mathrm{BF_3\cdot OEt_2}$. In cyclic ether solvents, different reaction behavior was observed, although the acid strength of each, estimated by Hammett indicators, was almost the same. It is known that the order of Lewis basicity of ether is as follows.[12]

THF>dioxane>propylene oxide>dietheyl ether>epichlorohydrin

$\mathrm{BF_3}$-catalyzed copolymerization between ethers with different basicities such as THF-**1**[9,10] and THF-epichlorohydrin[10] has been reported. However, in the present study, the isomerization of **1** instead of copolymerization predominated in the presence of $\mathrm{BF_3\cdot OEt_2}$ in dioxane whose basicity is similar to that of **1**. $\mathrm{BF_3}$-catalyzed reactions seem to be remarkably affected by the Lewis basicities of the substrate and the solvent. In the isomerization of **1** to **2**, dioxane was found to be an effective solvent presumably due to the appropriate Lewis acidity arising from the exchange reactions between $\mathrm{BF_3\cdot OEt_2}$, **1**, and dioxane. One may expect that an active species in the $\mathrm{BF_3}$-catalyzed reaction is a neutral oxonium salt as shown in the reaction of $\mathrm{BF_3\cdot OEt_2}$, diethyl ether, and epichlorohydrin to give triethyloxonium tetrafluoroborate.[13,14] However, the participation of such a species was not described in the reports about $\mathrm{BF_3}$-catalyzed alkylation of benzene with ethers and alcohols,[15] $\mathrm{BF_3}$-catalyzed polymerization of cyclic ethers,[9,10] and $\mathrm{BF_3}$-catalyzed isomerization of epoxides in benzene and ether.[16] Our results can also be explained by an action of $\mathrm{BF_3}$ as described above. So we conclude that the present reaction of **1** in each solvent proceeds with $\mathrm{BF_3}$.

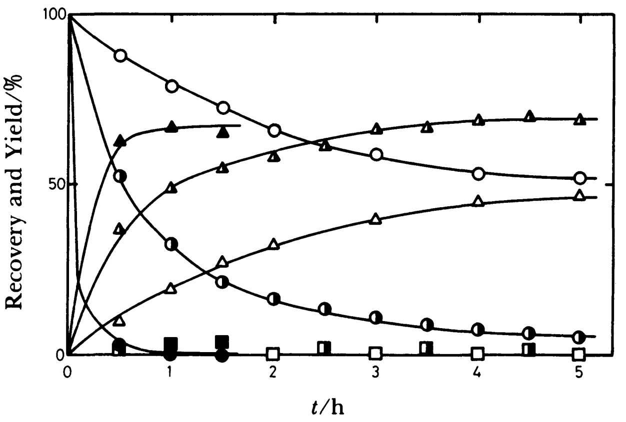

Fig. 2. Isomerization of **1** with $\mathrm{BF_3\cdot OEt_2}$ in dioxane. ○: Recovery of **1**, △: yield of **2**, □: yield of **3**. Open symbols: 0.12 mmol of $\mathrm{BF_3\cdot OEt_2}$, half-filled symbols: 0.21 mmol of $\mathrm{BF_3\cdot OEt_2}$, filled symbols: 0.85 mmol of $\mathrm{BF_3\cdot OEt_2}$.

Effect of Catalyst Amount. The isomerization behavior of **1** to **2** and **3** with different amounts of catalyst are shown in Fig. 2.

In each case, a major product was **2**. The results are reasonable and cosistent with a previous report.[17] On addition of 0.12 mmol of $\mathrm{BF_3\cdot OEt_2}$, the isomerization proceeded almost quantitatively, while the yield of **2** was 46% at 5 h. On addition of 0.21 mmol of the catalyst, the isomerization occurred more rapidly to give 68% yield within 5 h, but the selectivity was relatively poor, because of the polymerization of **1**. After 2 h, about 8% of **1** was isolated as PPO. In the case of 0.85 mmol, the substrate **1** disappeared completely within 30 min to yield 66% of **2**. The final yields of **2** were almost the same whenever 0.21 or 0.85 mmol of the catalyst was used. The addition of an excess of the catalyst in order to increase the yield of **2** thereby led to the polymerization of **1**, resulting in decrease in the selectivity without increase in the yield of **2**. In order to examine the possibility of the copolymerization of **1** and dioxane, the reaction of **1** (101 mmol) and dioxane (203 mmol) with $\mathrm{BF_3\cdot OEt_2}$ (0.21 mmol) was carried out. In this case, only PPO was obtained and no copolymerization occurred.

In conclusion, for the isomerization of **1** to **2**, dioxane was the most favorable solvent. On increasing the amounts of catalyst, the simultaneous polymerization of **1** occured to decrease the selectivity of **2**.

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