

CONTRIBUTION TO THE STUDY OF ALCOHOLYSIS OF OXIRANE COMPOUNDS

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Received October 8th, 1974

The reaction of cyclohexene oxide and styrene oxide with methanol, catalysed by an aluminosilicate catalyst or sulphuric acid, was studied. The reactions were carried out at 60°C in a discontinuous stirred reactor using an excess of methanol. An equimolecular mixture of both epoxides was also methanolysed. The activity and selectivity of both catalysts were compared.

The alcoholysis of olefin oxides belongs to the most advantageous methods in the preparation of 1,2-glycol ethers which are used in many organic syntheses. Several reviews on reactions of olefin oxides have been published¹⁻³. The reactions with alcohols are usually catalysed by sulphuric acid, boron trifluoride or the corresponding sodium alkoxide. Recently it was discovered⁴ that aluminosilicates can also catalyse this reaction. Consequently, it appeared desirable to compare the catalytic effect of the hitherto most frequently used sulphuric acid with that of aluminosilicate, first of all concerning the mechanism, catalytic activity and selectivity. These questions are the object of the present paper.

EXPERIMENTAL

Materials. Cyclohexene oxide was prepared by epoxidation⁵ of cyclohexene with cumene hydroperoxide using a catalyst on Mo-Si basis⁶. The measurements were carried out with the chromatographically pure product, b.p. 131.5°C, obtained by rectification of the crude reaction mixture. Styrene oxide was prepared by dehydrobromination⁷ of styrene bromohydrine. The pure product boiled at 191°C. Methanol was a commercial product of Analytical Grade (Lachema, Brno) and was dried with magnesium methoxide. Aluminosilicate catalyst (imported from the Soviet Union by CHZ ČSSP, Záluží u Mostu, Czechoslovakia), charge number 47001, content: 11% Al₂O₃, specific surface 351 m²/g, particle size 0.05–0.1 mm. Sulphuric acid was of Analytical Grade (Laborchemie, Apolda, GDR). 2-Phenyl-2-methoxyethanol, used as the chromatographic standard, was prepared by the reaction of methanol with styrene oxide, catalysed by the aluminosilicate catalyst, under the same conditions as described for the kinetic measurements. Rectification afforded the product, boiling at 236 to 237°C.

Apparatus and procedure. The reactions were carried out under normal pressure and at 60°C in an perfectly stirred isothermal discontinuous 100 ml glass reactor, equipped by reflux condenser and a device for withdrawal of samples by means of a syringe. The catalyst (0.1 g of the alu-

minosilicate) was added to a thermostated mixture of methanol (25 ml) and oxide (17 mmol) and in suitable time intervals the samples were withdrawn and analysed by gas-liquid chromatography. In the study of the competitive reaction, 17 mmol of each oxide and 0.2 g of aluminosilicate (or $5 \cdot 10^{-3}$ g of sulphuric acid) was used.

Analytical methods. The gas-liquid analyses were performed on a Chrom 4 instrument with flame-ionization detector, using a 2.5 m glass column, internal diameter 3 mm, packed with 15% Silicone SF 96 on Chromaton NAW HMDS, particle size 0.16–0.20 mm, at 150°C; the temperature of the vaporisation chamber was 165°C. The chromatograms were evaluated by means of standards of composition similar to that of the analysed samples. The initial reaction rate was determined as the slope of tangent at the time $t = 0$ to the curve resulting from plotting the oxide concentration (dimensionless) against time.

RESULTS AND DISCUSSION

The reaction of cyclohexene oxide with aliphatic alcohols can be under certain conditions accompanied by a side reaction leading to 2-alkoxy-2'-hydroxydicyclohexyl ether⁸. Its formation can be to a considerable extent suppressed by using an excess of the starting alcohol. The reaction of styrene oxide with aliphatic alcohols can lead in parallel reactions to two products, *i.e.* 1-phenyl-2-alkoxyethanol and 2-phenyl-2-alkoxyethanol. An acid-catalysed methanolysis affords about 90% of the latter product, whereas in the sodium methoxide catalysed reaction the product composition is shifted toward 1-phenyl-2-methoxyethanol⁹.

The rates of aluminosilicate catalysed methanolyses of cyclohexene oxide and styrene oxide were determined for the reaction of the individual compounds as well as for the reaction of an equimolecular mixture of both oxides. The methanolysis rates of an equimolecular mixture of oxides were measured using sulphuric acid as catalyst. The obtained reaction rates are given in Table I. A typical course of me-

TABLE I
Methanolysis of Cyclohexene Oxide and Styrene Oxide

No	Compound	Catalyst	Initial reaction rate mmol/min g_{cat}
1	Cyclohexene oxide	aluminosilicate	5.2
2	Styrene oxide	aluminosilicate	9.27
3	Cyclohexene oxide } Styrene oxide }	aluminosilicate	2.6 4.6
4	Cyclohexene oxide } Styrene oxide }	H ₂ SO ₄	$1.89 \cdot 10^3$ $3.37 \cdot 10^3$

thanalysis of cyclohexene oxide and styrene oxide in the presence of the aluminosilicate catalyst (under conditions given in Table I – No 1 and 2) is depicted in Fig. 1.

Using an excess of methanol (approximately 36 mol per 1 mol of the oxide) it was possible to suppress the formation of 2-methoxy-2'-hydroxycyclohexyl ether¹⁰ so that the methanolysis of cyclohexene oxide led practically selectively to 2-methoxycyclohexanol. In the methanolysis of styrene oxide the aluminosilicate catalyst proved to be more selective than sulphuric acid⁹. The amount of 1-phenyl-2-methoxyethanol was not greater than 2–3%, based on the reacted styrene oxide, and thus the reaction afforded practically selectively 2-phenyl-2-methoxyethanol.

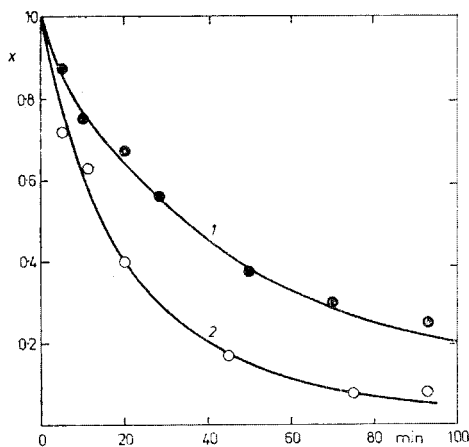


FIG. 1
The Course of Cyclohexene Oxide and Styrene Oxide Methanolysis in Individual Reactions
 x Dimensionless concentration ($C_{OX} : C_{OX}^0$), 1 cyclohexene oxide, 2 styrene oxide.

The ratio of the initial reaction rates of both oxides, as determined for the methanolysis of their equimolecular mixture in the presence of the aluminosilicate catalyst, was identical with the rate ratio, obtained from the reactions of the individual oxides. This ratio was the same also in the sulphuric acid catalysed methanolysis of this mixture of epoxides (Table I).

In all cases, the methanolysis of styrene oxide was faster. The found difference in the reactivity may be caused by the polar influence of the substituents on the oxirane ring. The proper catalytic effect of the aluminosilicate in the reaction of olefin oxides with alcohols rests obviously in its protonic acidity. The mechanistic considerations would be premature because there is not enough experimental material available.

As far as the reaction rate is based on the weight of the catalyst, sulphuric acid is by far more active in both reactions than the aluminosilicate used in this study.

REFERENCES

1. Parker R. E., Isaacs N. S.: *Chem. Rev.* 59, 737 (1959).
2. Eliel E. L. in the book: *Steric Effects in Organic Chemistry* (M. S. Newman, Ed.) p. 106. Wiley, New York 1956.
3. Winstein C., Henderson R. B. in the book: *Heterocyclic Compounds* (R. C. Elderfield, Ed). Vol. I, p. 1. Wiley, New York 1960.
4. Červený L., Marhoul A., Růžička V., Hora A., Novák J.: *Czech.* 158 516 (1974).
5. Červený L., Marhoul A., Strohal J., Růžička V.: *Chem. Prům.* 23, 17 (1973).
6. Červený L., Marhoul A., Růžička V.: *Chem. Prům.* 23, 299 (1973).
7. Chih Hai Huang, Ming-Ching Hsin: *Hua Kung Hsuet Pao* 1965, 87.
8. Červený L., Marhoul A., Růžička V.: *Chem. Prům.* 23, 357 (1973).
9. Reeve W., Christoffel J.: *J. Amer. Chem. Soc.* 72, 1480 (1950).
10. Červený L., Bartoň J., Růžička V.: *This Journal* 39, 2470 (1974).

Translated by M. Tichý.