EFFECT OF ALCOHOLIC STRUCTURES ON THE COURSE OF CYCLOHEXENE OXIDE ALCOHOLYSIS

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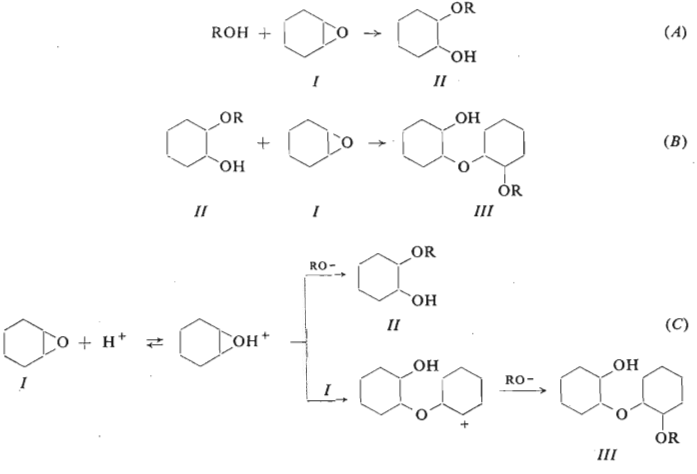
Received September 29th, 1973

Cyclohexene oxide alcoholysis was studied in the series of six aliphatic alcohols and in cyclohexanol. Reactions were catalysed by an alumosilicate catalyst (heterogeneous system). Initial reaction rates were measured of the main reaction (formation of 2-alkoxycyclohexanol) and the side reaction (formation of 2-alkoxy-2′-hydroxydicyclohexyl ether). The effect of the structure of the starting alcohol on the rate of these reactions was interpreted using the method of linear correlations of free enthalpies.

The alcoholysis of alkene oxides represents one of the most advantageous method in the preparation of 1,2-glycol ethers which are used in numerous organic syntheses. For reviews on reactions of alkene oxides see ref.[1-3]. Reactions with alcohols are



most frequently catalysed by sulfuric acid, boron trifluoride or the corresponding sodium alkoxide. In connection with discovery of a new alumosilicate catalyst[4] for this reaction, especially on the industrial scale, it appeared desirable to investigate the thus-catalysed alcoholysis in detail. It has been observed[5] that the alcoholysis of cyclohexene oxide (*I*) is accompanied by a side formation of 2-alkoxy-2′-hydroxydicyclohexyl ether (*III*). In the present paper we have now examined the structural effect of the particular alcohol on the rate of the two reactions, *i.e.* formations of 2-alkoxycyclohexanol (*II*) and the two isomeric 2-alkoxy-2′-hydroxydicyclohexyl ethers (*III*).

EXPERIMENTAL

Materials. Cyclohexene oxide (*I*) was prepared by epoxidation[6] of cyclohexene with cumene hydroperoxide using a catalyst[7] on the Mo—Si basis. Measurements were performed with the chromatographically homogeneous substance obtained by rectification (b.p. 131·5°C) of the crude reaction mixture. The alcohols were of commercial origin and were purified by distillation before use. Methanol, 1-propanol, and 2-propanol were of Analytical Grade (Lachema, Brno, Czechoslovakia); anhydrous ethanol (Kaučuk, Kralupy, Czechoslovakia), tert-butyl alcohol (Analytical Grade; Reanal, Hungary), 1-heptanol (pure; imported by Lachema), and cyclohexanol (pure; Spolana, Neratovice, Czechoslovakia). Alumosilicate (imported from Soviet Union by Chemical Works of Czechoslovak-Soviet Friendship, Záluží, Czechoslovakia), charge number 47001; content: 11·1% Al_2O_3, 83·3% SiO_2, 0·31% Fe_2O_3, 0·10% Na_2O, 0·07% K_2O, traces of CaO; specific surface 351 m^2 per gram; particle size 0·05—0·10 mm.

Apparatus and procedure. Reactions were performed in an efficiently stirred discontinuous reactor[5] at ordinary pressure and 60°C. Molar ratio of the alcohol to cyclohexene oxide, 5 : 1. Catalyst, $2{\cdot}5 \,.\, 10^{-2}$ g per 1 g of cyclohexene oxide. Samples of reaction mixtures were with-

TABLE I

Initial Reaction Rates (mol/min . g) of the Cyclohexene Oxide Alcoholysis

No	Alcohol	r_I^0	r_{II}^0	r_{III}^0	S^c
1	methanol	3·9	3·0	1·05	2·86
2	ethanol	3·5	2·7	0·80	3·38
3	1-propanol	2·9	2·5	0·52	4·81
4	2-propanol	1·16	0·84	0·23	3·65
5	1-heptanol	0·7	0·53	0·16	3·32
6	cyclohexanol	0·092	0·092	—[a]	—
7	tert-butyl alcohol	—[b]	—	—	—

[a] Compounds *III* were not detected in the reaction mixture; [b] the reaction did not proceed at a measurable rate; [c] selectivity.

drawn with the use of a syringe by a capillary equipped with a plug of glass wool, transferred into glass ampoules, and analysed by gas chromatography.

Analytical methods. Analyses were performed on a Chrom-2 apparatus (Czechoslovakia) with a flame-ionisation detector (glass column length, 2 m; internal diameter, 3 mm; packed with 5% Reoplex 400 on Chromaton N—AW, particle size 0·16—0·20 mm). Temperature was varied from 150°C (lower alcohols) up to 190°C (higher alcohols). The carrier gas (nitrogen) overpressure at the column inlet was 0·5—0·8 kp per cm^2. The column was equipped with direct injection to prevent decomposition of cyclohexene oxide due to contact with metallic parts of the commercial evaporator. Chromatograms were evaluated by means of standards, the composition of which was similar to that of analysed samples. Areas of chromatographic waves were processed by planimetry.

RESULTS AND DISCUSSION

Initial reaction rates were determined as slopes of *c vs t* (concentration *versus* time) curves (at $t = 0$); concentration c of components *I—III* was defined by equations (*1*) to (*3*):

$$c_{\mathrm{I}} = n_{\mathrm{I}}/n_{\mathrm{I}}^{0}\,, \tag{1}$$

$$c_{\mathrm{II}} = n_{\mathrm{II}}/n_{\mathrm{I}}^{0}\,, \tag{2}$$

$$c_{\mathrm{III}} = 2n_{\mathrm{III}}/n_{\mathrm{I}}^{0}\,. \tag{3}$$

To obtain the values of initial reaction rates, the curves were derived by means of the mirror method. Determination of initial reaction rates is accompanied by a relatively great error. It is technically difficult to obtain a greater amount of samples from the initial stage of the reaction. The greater relative error in determinations of compounds with a low concentration (compound *III*) might be the cause of the scattered data on Fig. 3. With respect to the discussion on the reaction mechanism, one of the most important observations consists in the relatively high concentration of compounds *III* in the first samples of all reaction mixtures. An inflex, if any, of the c_{III} *vs t* curve in the region of low concentrations would be impossible to observe under the present experimental conditions.

Fig. 1 shows a typical course of the cyclohexene oxide (*I*) alcoholysis. The kinetics of such a system are very complicated[5]. In this system, the catalyst is rapidly deactivated, obviously because of the strong adsorptivity of compounds *III*. These compounds may undergo subsequent reactions with further molecules of cyclohexene oxide with the formation of higher-molecular condensates, the role of which in deactivation of the catalyst is difficult to determine. The condensates were not taken into account in the mass balance, since their content is at least one order of magnitude lower[5] than that of compounds *III*. The influence of the structure of the particular alcohols on the rate of alcoholysis was consequently examined with the use of initial

reaction rate values (Table I) measured under the same experimental conditions free of the above mentioned effects. The last column of Table I contains *S* selectivity values as the ratio of initial rates in the formation of compounds *II* and *III*. The difference between rates of the uptake of compound *I* and formation of compounds *II* and *III* is due to experimental error.

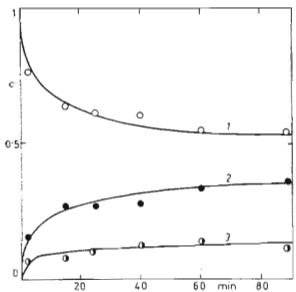


FIG. 1

The Course of Cyclohexene Oxide (*I*) Propanolysis

1 Cyclohexene oxide (*I*), *2* 2-propoxycyclohexanol (*II*), *3* 2-propoxy-2′-hydroxydicyclohexyl ether (*III*).

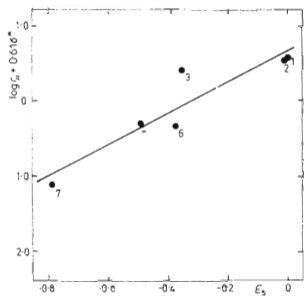


FIG. 2

Correlation of Formation Rates of Compounds *II* according to Equation (*4*)

Numbering of points corresponds to numbers of Table I.

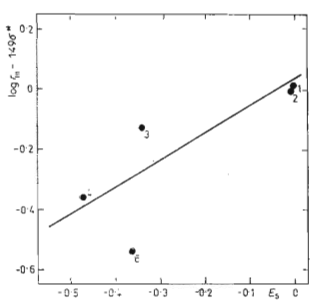


FIG. 3

Correlation of Formation Rates of Compounds *III* according to Equation (*5*)

Numbering of points corresponds to numbers of Table I.

The results were interpreted with the use of the Taft equation[8]. Its application leads to a considerable extent to a formal description of the system since in the present model series of alcohols the substituents of which are represented by alkyls only, there exists correlation between the σ^* and E_s constants[9] of the alkyl groups, but it is also possible to predict on the basis of this interpretation the reactivities of other alcoholic structures.

In correlations of formation rates of compound *II*, the use of the reported[10] σ^* and E_s values of alkyl substituents R is in accordance with equation (*A*). Formation of compounds *III* of unknown mechanism is more complicated. The high concentration of compounds *III* at the very begin of the reaction indicates that compounds *III* are not exclusively formed by the parallel-subsequent reaction (*B*) but that an equilibrium is involved from which compounds *II* and *III* are formed by two parallel reactions (*C*).

Some other explanations are presented in an earlier paper[5]. In the case of the reaction course according to equation (*B*), the use of steric and polar parameters of substituents R represents a rough approximation only since the corresponding values of the 2-alkoxycyclohexyl substituents (directly reacting with the OH group) are not known. In the case of the reaction course according to equation (*C*), the protonisation of the cyclohexene oxide probably represents the slowest process; the selectivity is not markedly influenced by the nature of the alcohol (see Table I). The structure of the alcohol should therefore markedly affect the rate of protonisation. The possibility of a quantitative description of this effect[5] by means of the Taft equation can not be predicted.

By the method of multiple regression there were determined (for the graphical representation see Figs 2 and 3) correlation equations of both systems except for tert-butyl alcohol in both cases and cyclohexanol in the case of compound *III*:

$$\log r_{II} = -0{\cdot}61\sigma^* + 2{\cdot}10E_s + 0{\cdot}66\,, \qquad (4)$$

$$\log r_{III} = 1{\cdot}48\sigma^* + 1{\cdot}137E_s + 0{\cdot}12\,. \qquad (5)$$

In view of the above mentioned relation between the σ^* and E_s parameters in the present series of structures, it is hardly possible to draw any conclusions on the extent of the involvement of polar or steric effects on the rate of the above reactions from the observed σ^* and δ values: compound *II*, $\sigma^* = -0{\cdot}61$ and $\delta = 2{\cdot}10$; compound *III*, $\sigma^* = 1{\cdot}48$ and $\delta = 1{\cdot}137$, *cf.* equations (*4*) and (*5*). As determined by regression analysis, the direction of the polar effect (as characterised by the sign of σ^*) on the rate of both reactions is opposite. Detailed analysis would require extension of the model series by alcohols with other functional groups than with alkyls but such an extension would exceed the original scope of the present work. The cor-

relation equations given above can serve for the reactivity estimation of the most frequent alcohols in alcoholyses of some additional oxirane compounds.

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Translated by J. Pliml.