2. Several laws governing the acid-catalyzed nucleophilic substitution of hydroxyl groups in 2-alkyl(aryl)thioethanols have been revealed. In particular, an increase in the selectivity of the process with decreasing strength of the nucleophilic reagent has been established.

LITERATURE CITED

1. A. V. Fokin and A. F. Kolomiets, The Chemistry of Thiiranes [in Russian], Nauka, Moscow (1978).
2. H. T. Clarke, J. Chem. Soc., 101, 1583 (1912).
3. German Patent No. 47,835 (1940); Chem. Abstr., 34, 6302 (1940).
4. W. Steinkopf, J. Herold, and J. Stohr, Ber., 53, 1006 (1920).
5. U. S. Patent No. 2,598,640 (1952); Chem. Abstr., 47, 2199 (1953).
6. A. V. Fokin, A. F. Kolomiets, and V. S. Shchennikov, Zh. Org. Khim., 7, 1406 (1971).
7. M. Kirner and H. Richter, J. Am. Chem., 51, 3413 (1929).

CLEAVAGE OF 4,4'-BIS(1-ACETOXYETHYL)DIPHENYL ETHER

B. A. Zaitsev, L. L. Dantsig,
I. O. Gusarova, M. B. Tennikov,
and B. G. Belen'kii

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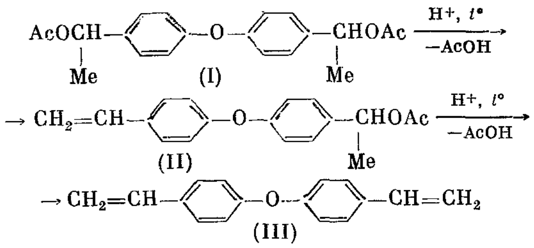
Cleavage of esters is often used for the synthesis of alkenes [1, 2]. However, there is no information on the use of this method to obtain vinyl- and divinylaromatic monomers, which are of significant interest for the preparation of crosslinked polymers.

In the present paper, we investigated the kinetics of thermal and catalytic cleavage of 4,4'-bis(1-acetoxyethyl)diphenyl ether (I) to 4-vinyl-4'-(1-acetoxyethyl)diphenyl ether (II) and 4,4'-divinyldiphenyl ether (III)



The reaction mixtures were analyzed by exclusion liquid chromatography and titration.

During heating in air or in an inert medium to ∿200°C, (I) retained its stability. In 3 h at 218°C, (I) underwent 7-10% cleavage, with (II) being formed (5% yield) together with a small amount of oligomeric products (IV) and (V). In 3 h at 230°C, 40% of (I) underwent conversion, being converted to (II) (4%) and (V), products of the oligomerization and co-oligomerization of ethers (II) and (III) (Fig. 1, curve 1). When the thermolysis time was increased to 5 h, the conversion of (I) increased to 50%.

If we assume that the acetate groups in (I) are independent and that their activities in (I) and (II) are identical, the rate of the reaction being investigated can be represented in the following integral form:

$$\ln \frac{C_0}{C} = kt \tag{1}$$

where C_0 and C are the concentrations of the acetate groups, k is the rate constant, and t is the reaction time.

Institute of Macromolecular Compounds, Academy of Sciences of the USSR, Leningrad.
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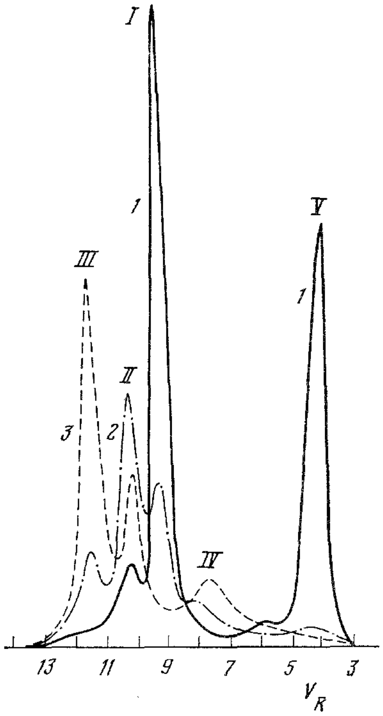

Fig. 1. Chromatograms: 1) pyrolysate of 4,4'-bis(1-acetoxyethyl)diphenyl ether (I) (230°C, 3 h); 2, 3) product of the catalytic cleavage of (I) (0.315 mole/liter) in the presence of p-toluenesulfonic acid (0.007083 mole/liter) in toluene at 98°C for 15 and 60 min, respectively. The peaks in the chromatograms correspond to the following: I) 4,4'-bis(1-acetoxyethyl)diphenyl ether; II) 4-vinyl-4'-(1-acetoxyethyl)diphenyl ether; III) 4,4'-diphenyl ether; IV) dimers and trimers; V) oligomers.

An investigation of the kinetics of cleavage at 218, 230, and 240°C showed that Eq. (1) is valid only for the initial steps of cleavage, for which the semilogarithmic anamorphoses of the kinetic curves retained their linearity. The activation energy calculated for these early cleavage steps was 160 ± 30 kJ/mole. With increasing conversion, the rate constant increased, apparently because of the catalytic effect of the resulting AcOH. A similar effect was observed previously in a study of the pyrolysis of poly(tert-butyl methacrylate) [3].

It should be noted that the thermolysis of (I) occurred at lower temperatures than in the case of many esters [4, 5]. Catalytic cleavage of (I) occurred under mild conditions: 60-100°C during catalysis of the reaction by p-toluenesulfonic acid (VI) (0.0017-0.004 mole/liter) and during its occurrence in toluene (see Fig. 1, curves 2 and 3).

The rate of abstraction of the acetate groups for the catalytic reaction can be represented in the form of the equation

$$\ln \frac{C_0}{C} = C_{\mathrm{cat}} k' t \qquad (2)$$

where C_{cat} is the concentration of the catalyst, and k' is the rate constant of the catalytic reaction.

The results of a kinetic investigation of the catalytic reaction at 60, 70, 80, and 90°C showed that the semilogarithmic anamorphoses of the kinetic curves of consumption (abstraction) of acetate groups were linear only along the initial segments. The deviation from linearity with increasing conversion of (I) was due to the formation and accumulation of AcOH in the reaction medium, as we confirmed experimentally. Thus, in the presence of 25-50 mole % AcOH, the rate of the cleavage of (I) decreased to 2/3-1/2 the original rate, apparently because of the effect of AcOH on the activity of (VI).

The activation energy E and the preexponential factor A, determined for the initial step of the catalytic cleavage of (I), when the effect of AcOH was still absent, were ∿50 kJ/mole and $4.4 \cdot 10^5$ sec^{-1}, respectively. Thus, the activation energy of catalytic cleavage of (I) was ∿1/3 the activation energy of thermal cleavage.

EXPERIMENTAL

Exclusion liquid chromatography was carried out under high-performance conditions on a 60 × 0.8-cm column on Sephadex LH-20 with an efficiency of 7000-8000 theoretical plates (with respect to toluene) with a KhZh-1307 chromatograph. The columns were filled with Sephadex by the procedure described in [6]. The eluate was $CHCl_3$, the elution rate was 20 ml/h, the detector was a refractometer, and the concentration of the specimens in the sample was 0.2-2%.

4,4'-Bis(1-acetoxyethyl)diphenyl Ether (I). To a solution of 60 g (0.23 mole) of 4,4-bis(1-hydroxyethyl)diphenyl ether in 105 ml of toluene and 56 ml of pyridine, 44.2 g (0.56 mole) of AcCl was added with stirring for 1 h. The mixture was kept at ∿20°C for 24 h, decomposed with dilute (1:10) HCl mixed with ice, the toluene layer was washed with water and dried with $MgSO_4$, and the toluene was distilled off. Obtained: 59 g (74%) of crude (I), which was purified by vacuum distillation, bp 170°C (∿0.1 mm), n_D^{20} 1.5378; d_4^{20} 1.135. Found: C 70.04; H 6.56%. $C_{20}H_{22}O_5$. Calculated: C 70.16; H 6.48%. IR spectrum (ν, cm^{-1}, thin layer): 1735 (C=O), 1600, 1505 (C_6H_4), 1370 (CCH_3), 1240 (COC).

Thermal Cleavage of (I). Compound (I) (0.2-0.3 g) was placed in ampuls, which were evacuated to a residual pressure of ∿0.1 mm, sealed, and kept at 218, 230, and 240°C for a specific time. Then the ampuls were cooled and opened; 1 ml of purified dioxane was added to the contents of the ampuls. The amount of AcOH was determined by titration with a 0.1 N solution of NaOH in the presence of phenolphthalein.

Catalytic Cleavage of (I). A mixture of 8.57 g of (I), 116 ml of toluene, 0.09 g of hydroquinone, 0.2 g of CuCl, and 0.0943 g of p-toluenesulfonic acid monohydrate (96% purity) was heated with stirring at 98°C with periodic withdrawal of samples, in which the content of AcOH was determined. The composition of the samples was analyzed by elution liquid chromatography. Experiments with withdrawal of samples at 80, 70, and 60°C were carried out similarly.

CONCLUSIONS

1. During thermal ($\geqslant$ 230°C) and p-toluenesulfonic acid-catalyzed (60-98°C) cleavage of 4,4'-bis(1-acetoxyethyl)diphenyl ether, a mixture of 4-vinyl-4'-(1-acetoxyethyl)diphenyl and 4,4'-divinyldiphenyl ethers and the products of their oligomerization were formed.

2. Thermolysis of 4,4'-bis(1-acetoxyethyl)diphenyl ether at 220-240°C had an autocatalytic nature, due to the abstracted AcOH. During catalytic cleavage of 4,4'-bis(1-acetoxyethyl)diphenyl ether, AcOH decreased the reaction rate.

LITERATURE CITED

1. C. H. Deluy and R. W. King, Chem. Rev., 60, 431 (1960).
2. D. H. Wertz and N. L. Allinger, J. Org. Chem., 42, 698 (1977).
3. D. M. Grant and N. Grassie, Polymer, 1, 445 (1960).
4. R. L. Burwell, Chem. Rev., 4, 615 (1954).
5. W. J. Bailey and J. J. Hewitt, J. Org. Chem., 21, 543 (1956).
6. V. V. Ulyashin, V. I. Deigin, V. T. Ivanov, and Yu. A. Ovchinnikov, J. Chromatogr., 215, 263 (1981).