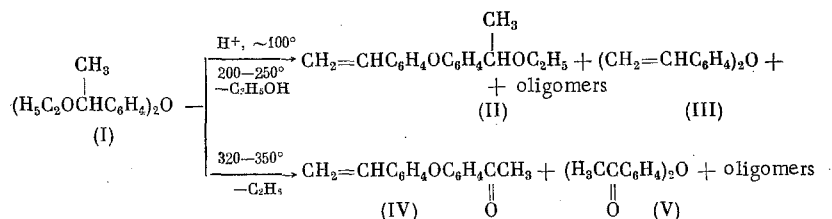


THERMAL AND CATALYTIC CLEAVAGE OF  
4,4'-DI(1-ETHOXYETHYL)DIPHENYL ETHER

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UDC 541.128:542.92:547.562

In the acid-catalyzed decomposition of ethers, alcohols and olefins can form [1]. 4,4'-Di(1-ethoxyethyl)-diphenyl ether is the first example of the ability of ethers of secondary aromatic diols to be converted upon heating to aromatic ketones or unsaturated aromatic compounds, depending on the reaction temperature:



Ether I was obtained by heating 4,4'-di(1-hydroxyethyl)diphenyl ether in toluene with excess ethanol in the presence of p-toluenesulfonic acid (VI) and azeotropic distillation of water. I, bp 125°C (~15 Pa)  $n_D^{20}$  1.5315. Found: C 76.48; H 8.27%.  $C_{20}H_{26}O_3$ . Calculated: C 76.40; H 8.33%. It was established by exclusion liquid chromatography, GLC, IR, and PMR spectroscopy, and mass spectrometry that when I is heated in vacuum ( $10^{-4}$ –15 Pa) at 200–250°C for 5–10 h or in toluene at 100°C in the presence of VI (0.0157 mole/liter) for 2–3 h, it undergoes cleavage to form principally ethanol, II, and III, and their oligomerization products. Heating of I at 320–350°C for 5 h yields, along with the above products, 30–50% of methyl ketone IV, diketone V, a significant amount of ethane, and oligomers. The IR spectrum of the pyrolysate shows a methyl ketone absorption band at  $1670\text{ cm}^{-1}$ ; the PMR spectrum shows the methyl proton signals of the acetyl group in the 7.5 ppm region; and the mass spectrum shows the peaks of the molecular ion of ethane.

## LITERATURE CITED

1. P. Sykes, *Guidebook to Mechanism in Organic Chemistry*, Wiley (1965).

Institute of High-Molecular-Weight Compounds, Academy of Sciences of the USSR, Leningrad. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 4, pp.959-960, April, 1983. Original article submitted December 28, 1982.