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REACTION OF 1,3-DIOXEPANE WITH ETHYL ACETATE

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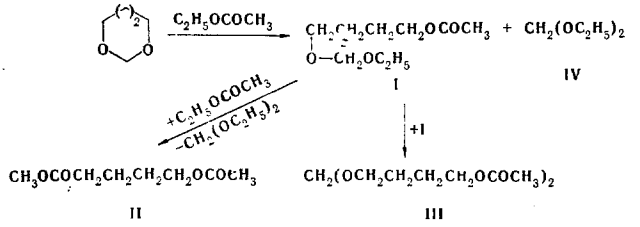
UDC 547.841+661.73

In a search for a reagent capable of cleaving cyclic formals at one of the ring C–O bonds to give a stable intermediate, we studied the reaction of 1,3-dioxepane with ethyl acetate [in a glass thermostatted reactor at 70°, a 1,3-dioxepane to ethyl acetate ratio of 1 : 2, 1% (of the charge) H_2SO_4 as the catalyst, and a reaction time of 3 h]. The primary reaction products – 5,7-dioxa-1-nonanol acetate (I) – and 1,4-butanediol diacetate (II), 5,7-dioxa-1,11-undecanediol diacetate (III), and diethoxymethane (IV) were isolated by means of preparative gas–liquid chromatography (GLC) (PAKhV-05, Apiezon L on Chromaton N-AW, at 160-220° and a helium flow rate of 12 liters/h). On the basis of a determination of the kinetic parameters, a separate study of the reaction of I with ethyl acetate, and its behavior in the absence of the ester, the most probable scheme for the formation of the isolated compounds is as follows:



The observed formation of unsymmetrical I and symmetrical III – linear formals that contain an ester group – is specific for 1,3-dioxacyclanes. Compounds of this sort cannot be obtained in the case of linear formals or oxygen-containing heterocyclic compounds with oxygen atoms separated by more than one carbon atom. Compound I, with bp 116° (6 mm), n_D^{20} 1.4390, and d_4^{20} 1.0350, was obtained in 21.1% yield. Compound II, with bp 225°, n_D^{20} 1.4189, and d_4^{20} 1.0620, was obtained in 48.6% yield. Compound III, with bp 147° (8 mm), n_D^{20} 1.4640, and d_4^{20} 1.1012, was obtained in 12.8% yield. The mass spectra of I and III contain CH_3CO^+ ions (m/e 43, 100%). The ^{13}C NMR spectra contain signals of CH_3 groups at 21.1-22.1 ppm and a singlet at 169.1-169.4 ppm (COO^-); the methyl groups resonate at 61.2-64.5 and 68.6-68.8 ppm, depending on the environment.

Ufim Petroleum Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1698-1699, December, 1976. Original article submitted June 7, 1976.