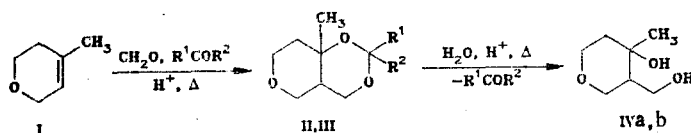


U. G. Ibatullin, R. F. Talipov,
I. S. Faizrahmanov, and M. G. Safarov

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It is known that the Prins reaction with ketones gives only 1,3-diones and unsaturated alcohols, [1], and the expected cyclic ketals do not form.

We have succeeded in obtaining 1,3-dioxane structures, viz., 3,3-dialkyl-1-methyl-2,4,8-trioxabicyclo[4.4.0]decane, from ketones under Prins reaction conditions by the reaction of 4-methyl-5,6-dihydro-2H-pyran (I) with formaldehyde and R^1COR^2 in aqueous sulfuric acid:



II $R^1=CH_3$, $R^2=C_2H_5$; cis-trans, 1:3; III $R^1=R^2=C_2H_5$; cis-trans, 2:1

The reaction product forms in about 30% yield as a mixture of thermally unstable cis and trans-isomers; the proportion was determined from the hydrolysis of compounds II and III to the known cis, trans-3-hydroxymethyl-4-hydroxy-4-methyltetrahydropyrans (IVa, b) [2]. Bicycles II and III were separated by chromatography on Al_2O_3 .

To 36.5 ml (0.34 mole) of olefin I, 0.34 mole of ketone, and 14.2 ml (0.17 mole) of CH_2O as 36% aqueous solution was added 3.4 ml (0.018 mole) of 96% sulfuric acid, and the mixture was boiled with stirring for 3 h. The mixture was cooled to room temperature and treated with gaseous NH_3 . An organic phase separated and the aqueous phase was extracted with ether. The combined extracts and the organic phase were dried with $MgSO_4$. Evaporation of solvent left about 30 g of material which was dissolved 1:1 in hexane and boiled with metallic Na for 1 h. The residue was filtered off and the filtrate was extracted with $NaHSO_3$ solution. The organic phase was separated, dried with $MgSO_4$, and chromatographed on an Al_2O_3 column.

1,3-Dimethyl-3-ethyl-2,4,8-trioxabicyclo[4.4.0]decane (II). n_D^{20} 1.4851; R_f 0.58 (Al_2O_3 , chloroform-hexane 4:1); PMR spectrum (CCl_4): 3.68 (6H, m, CH_2O); 2.08 (3H, m, CH, CH_2); 1.58 (6H, s, CH_3); 0.93 (3H, t, CH_3); 0.75-1.10 ppm (2H, m, CH_2).

3,3-Diethyl-1-methyl-2,4,8-trioxabicyclo[4.4.0]decane (III), n_D^{20} 1.4748; R_f 0.816 (Al_2O_3 , benzene-alcohol 9:1); PMR spectrum (CCl_4): 3.11-4.00 (6H, m, CH_2O); 1.19 (3H, s, CH_3); 0.90 (6H, m, CH_3); 0.83-1.68 ppm (7H, m, CH, CH_2).

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Bashkir State University, Ufa 450074. Translated from Khimiya Geterotsiklicheskih Soedinenii, No. 12, pp. 1688-1689, December, 1985. Original article submitted March 18, 1985.