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TERPENE ETHERS VII*. NEW PRODUCTS FROM THE REACTION OF 3-CARENE WITH FORMALDEHYDE

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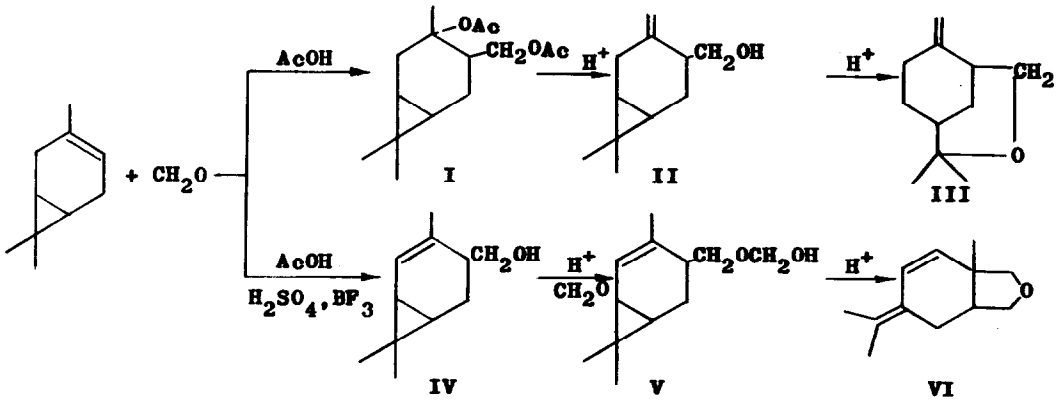
There are only few papers in the literature dealing with the reaction of 3-carens with formaldehyde.[1-4] Without catalysts this reaction yields 3-hydroxymethyl-4-carene /IV/ as main product together with small amount of 3-hydroxymethyl-4/10/-carene /II/.

Studying the reaction of 3-carene with formaldehyde in anhydrous acetic acid we found that two additional products were also formed: the diacatate of 3-hydroxymethylcaranol-4 /I/ and the bicyclic ether 2,2-dimethyl-6-methylene-3-oxabicyclo-[3.3.1.]-nonane /III/.[5]



* Part VI: Roczniki Chem.(in press)

The diacetate /I/ was isolated from the reaction mixture by fractional distillation. Pure compound has the following constants: b.p. 136°C (2 mm Hg), n_D^{20} 1.4802, d_4^{20} 1.0519, α_D^{20} +25.5°, Anal.Calcd for $C_{15}H_{24}O_4$: C, 67.13 ; H, 9.01; O, 23.86; MW, 268. Found: C, 67.05; H, 8.89; O, 24.06; MW, 270. Infrared spectra of the diacetate /I/ and of the corresponding glycol show bans at 1045 and 1136 cm^{-1} (-C-OH, ≥C-OH), 980 cm^{-1} (cyclopropane ring), 1384 and 1390 cm^{-1} (gem. dimethyl group). Pure bicyclic ether /III/ could not be isolated from the reaction mixture by distillation under reduced pressure. To isolate pure /III/ the corresponding fraction of the distilate was hydrolyzed with 10% ethanolic KOH and was chromatographed on a silica gel column. The compound has the following constants: b.p. 105° (10 mm Hg); n_D^{20} 1.5002 ; d_4^{20} 0.9870 ; α_D^{20} -1°, Anal. Calcd for $C_{11}H_{18}O$: C, 79.46 ; H, 10.91 ; O, 9.63; MW, 166. Found: C, 79.30; H, 10.85; O, 9.85; MW, 168, 169 (benzene).

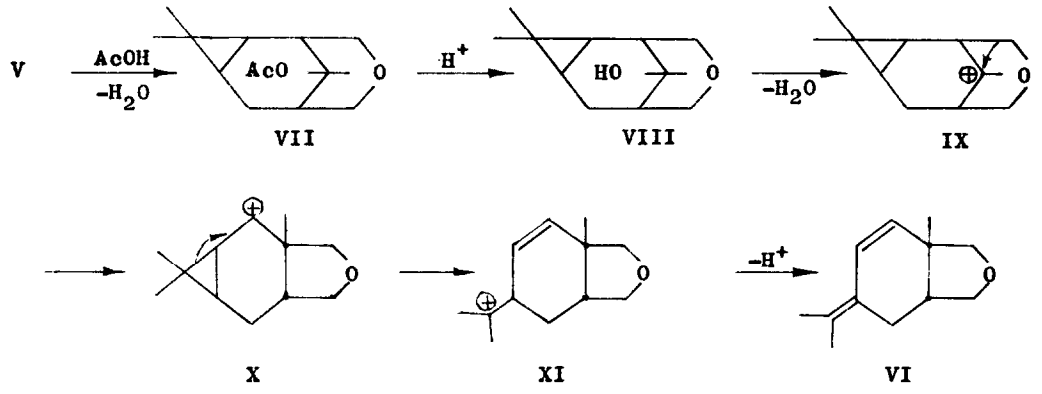
IR spectrum of the ether /III/ shows strong bands at 992 and 1100 cm^{-1} (cyclic -C-O-C-), 890 and 1664 cm^{-1} (≥C=CH_2), doublet at 1380 and 1392 cm^{-1}/≥C(CH_3)/. In the NMR spectrum there are two sharp bands at τ: 9.02 and 9.08 /≥C(CH_3)/ , 6.09 and 6.22 (-CH_2-O-), 5.43 (≥C=CH_2).

The ether /III/ is propably formed from the diacetate /I/ through the alcohol /II/. Such a reaction would be similar to the formation of pinol from pinandiol-2,3, observed by Schmidt and coworkers.[6]

With catalysts such as H_2SO_4 , H_3PO_4 , HCOOH, $BF_3 \cdot (C_2H_5)_2O$, $BF_3 \cdot CH_3COOH$, $SnCl_4$ and $ZnCl_2$ the reaction takes a different course. We found that in the presence of strong catalysts (H_2SO_4, BF_3) the reaction yields the unknown 1-methyl-7-isopropylidene-3-oxabicyclo-[4.3.0.]-8-nonene /VI/. This bicyclic ether, purified by column chromatography on silica gel, has the following constants: b.p. 95° (1 mm Hg); n_D^{20} 1.5242; d_4^{20} 0.9832; α_D^{20} -26.1°; MW, 178. Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.12; O, 9.04; MW, 178. Found: C, 80.72 ; H, 10.01; O, 9.27; MW, 179 (benzene).

In the IR spectrum of the ether /VI/ there are bands at 992 and 1070 cm^{-1}, dinstinctive for the cyclic ethers. A band at 3030 cm^{-1}, corresponding to the -CH=CH-group was also present. UV spectrum λ_{max}^{EtOH} 242 mμ is dinstinctive for conjugated double bonds. (E.g. 2,4/8/-p-menthadiene absorbs at λ 244 mμ). [7] NMR spectrum of /VI/ shows a strong band at τ 8.97 (CH_3), sharp singlets at 8.34, 8.37 ($>C=C(CH_3)_2$) and a multiplet between 6.22 and 8.86 ($-CH_2-O-CH_2-$). The protons at the double bond in the cyclohexane ring are shown as to sharp doublets at 4.77 and 4.90 (J = 5.3 cps) and 3.75 , 3.88 (J = 5.3 cps). Strong shift of the band for one of these protons is due to the presence of conjugated double bonds. [7,8]

A mechanism of the formation of a similar ether from cyclohexene and formaldehyde was reported by Blomquist and Wolinsky.[9] Basing on this mechanism we assume that the unsaturated alcohol /IV/ is formed as the first reaction product. In acid medium a molecule of formaldehyde is added to this alcohol with the formation of the hemiformal /V/. Subsequent cyclization and Wagner-Meerwein rearrangement yields a carbocation /X/ which is stabilized by a fission of the cyclopropane ring and loss of proton, thus giving the ether /VI/ as final product.



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