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FORMATION OF CYCLODIETHERS FROM 6-METHYL-5-HEPTEN-2-OL AND CITRONELLOL IN THE PRESENCE OF BORON TRIFLUORIDE ETHERATE

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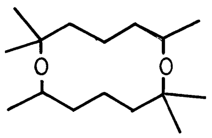
On treatment with boron trifluoride etherate at room temperature, 6-methyl-5-hepten-2-ol and citronellol dimerized to give dioxamonocyclic compounds in a good yield.

In a previous paper on action of boron trifluoride etherate (BF_3OEt_2) towards geranyl alcohol, formation of both digeranyl and linalyl geranyl ethers has been reported.[1)] In this paper, 6-methyl-5-hepten-2-ol[2)] and citronellol[3)] which contain one double bond in the δ or ζ-position for the hydroxyl group were respectively submitted to the action of BF_3OEt_2 to give monocyclic saturated diethers in a good yield. This method is interesting one for preparation of the cyclic diethers.

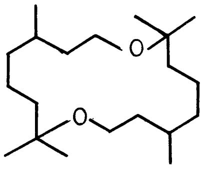
Formation of 2,2,6,8,8,12-Hexamethyl-1,7-dioxacyclododecane (I): 6-Methyl-5-hepten-2-ol (10 g), mixed with BF_3OEt_2 (5 ml), allowed to stand at room temperature for 6 days. The reaction mixture was subjected to fractional distillation followed by elution chromatography on silica gel with a hexane-ethyl acetate mixture to give I as a colorless oily substance, d_4^{20} 0.8695 and n_D^{19} 1.4251, in 80 % yield. The molecular formula of I was determined as $C_{16}H_{32}O_2$ (M^+ 256, molecular weight (Rast): 252). The IR spectrum exhibited the presence of ether bonds (1098 and 1069 cm^{-1}) and geminal dimethyl groups (1389 and 1372 cm^{-1}) and the absence of double bonds. The catalytic hydrogenation of I over Adams catalyst in acetic acid showed no hydrogen uptake. These evidences indicate I to be a saturated monocyclic diether. The NMR spectrum taken in a $CDCl_3$ solution exhibited the proton signals at δ 1.14 (6H, d, J=7Hz, $C\underline{H}_3\text{-}\overset{|}{C}H\text{-}O\text{-}$ X 2), 1.20 (12H, s, $(C\underline{H}_3)_2\overset{|}{C}\text{-}O\text{-}$ X 2), 3.47 (2H, q, J=7Hz, $\text{-}\overset{|}{\underset{|}{C}}\text{-}O\text{-}\overset{|}{C}\underline{H}\text{-}CH_3$ X 2) and 1.48 (12H, $\text{-}C\underline{H}_2\text{-}$ X 6), and the coupling between the methyl group at δ 1.14

and the methyne proton at δ 3.47 was confirmed by double-irradiation experiment. The mass spectrum contained several characteristic ions at m/e 69(base), 81(30%, C_6H_9), 107(20, C_8H_{11}), 109(26, C_8H_{13}), 129(11, $C_8H_{17}O$), 135(9, $C_{10}H_{15}$), 220(14, $M^+ -2H_2O$), 238(2, $M^+ -H_2O$), 241(1, $M^+ -15$), 256(trace, M^+). This ether was thus represented as 2,2,6,8,8,12-hexamethyl-1,7-dioxacyclododecane (I).

Formation of 2,2,6,10,10,14-Hexamethyl-1,9-dioxacyclohexadecane (II): When citronellol was subjected to reaction with BF_3OEt_2 (1 ml) at room temperature for 3 days, II was obtained as colorless needles, mp 61-62°C, in a yield of 32 %. The molecular formular of II was determined to be $C_{20}H_{40}O_2$ (M^+ 312, molecular weight (Rast): 317). The IR spectrum and no hydrogen uptake on catalytic hydrogenation showed the absence of a double bond. Thus it is certain that II was a saturated monocyclic diether. The IR and NMR spectra exhibited the presence of two methyl groups ($\delta^{CDCl_3}_{ppm}$: 0.85, 6H, J=6Hz, $\underline{CH_3}$-$\overset{|}{C}$H- X 2), two geminal dimethyl groups ($\nu^{CCl_4}_{max}$ 1380, 1362 cm^{-1}; δ 1.10, 12H, s, $(\underline{CH_3})_2\overset{|}{C}$-O- X 2) and two ether linkages (1085 cm^{-1}; δ 3.28, 4H, t, J=6Hz, -$\overset{|}{\underset{|}{C}}$-O-$\underline{CH_2}$-$CH_2$- X 2). When II (100 mg) was heated with 0.2 ml of hydroiodic acid (d=1.7) for 10 minutes, it was converted into $C_{10}H_{20}$ (M^+ 140) and $C_{10}H_{20}I$ (M^+ 267). These facts were reasonably explained by the structure of II, which was also supported by the mass spectrum containing m/e 81(29%), 83(base, C_6H_{11}), 138(25, $C_{10}H_{18}$), 140(50, $C_{10}H_{20}$), 157 (25, $C_{10}H_{21}O$), 199(11, $M^+ -C_8H_{17}$), 276(trace, $M^+ -2H_2O$), 297(11, $M^+ -15$) and 312(2, M^+) ions.



(I)



(II)

References

1) K.Nagai, Chem.Pharm.Bull.,18,2123(1970).

2) dl-6-Methyl-5-hepten-2-ol (bp 176°C, n_D^{17} 1.4401) was prepared from 6-methyl-5-hepten-2-one (n_D^{20} 1.4391) [R.F.Nystrom, and W.G.Brown, J.Amer.Chem.Soc., 69,1197(1947)].

3) Commercial citronellol was used after repeating the fractionation. Bp 109.0°C/4mmHg, d_4^{25} 0.8530, n_D^{25} 1.4539, $[\alpha]_D^{25} \pm 0°$ in $CHCl_3$.

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