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A NEW ROUTE TO 3,7-DIMETHYL-2,6-OCTADIEN-1-OL AND 3,7-DIMETHYL-2-OCTENE-1,7-DIOL FROM ISOPRENE

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A convenient synthetic method for 3,7-dimethyl-2,6-octadien-1-ol (1) (geraniol and nerol) and 3,7-dimethyl-2-octene-1,7-diol (2), involving the anionic telomerization of isoprene and the rearrangement of amine oxide was established. The overall yields of (1) and (2) (E/Z ratio=2) from isoprene were 61 and 44%, respectively.

The step-wise synthesis of polyisoprenoid alcohols has been well established¹⁾, but new preparations are still being described²⁾. To our knowledge, however, the selective synthesis of 3,7-dimethyl-2,6-octadien-1-ol (geraniol and nerol) (1) and 3,7-dimethyl-2-octene-1,7-diol (hydroxygeraniol and hydroxynerol) (2) by the telomerization or the oligomerization of isoprene has not been reported³⁾. We herein describe a new route to (1) and (2) from isoprene.



N,N-Diethylnerylamine $(3)^{4}$ was prepared by the butyllithium-initiated telomerization of isoprene with diethylamine (5 : 1) in a benzene-ether solution at 55°C for 30 hr in an 80% yield. To a methanol solution of (3) was added dropwise aqueous hydrogen peroxide (30%) under ice-cooling. The mixture was allowed to warm to room temperature and then left for 15 hr. The excess hydrogen peroxide was destroyed by the addition of a small amount of platinum oxide⁵⁾. After removal of the solvents under reduced pressure, the crude amine oxide was obtained quantitatively. A benzene solution of this amine oxide was heated at 115-125°C for 6 hr in a sealed tube and then the distillation of the products gave 0-(3,7-dimethyl-2,6-octadienyl)-N,N-diethylhydroxylamine (4) in an 81% yield. [(4); bp 95-97°C/2.0mmHg, ir(neat, cm⁻¹): 1660, 1015 and 823, nmr(CCl₄,δ): 1.07(6H,t,J=7.0Hz), 1.50-1.76(9H,m), 2.61(4H,q,J=7.0Hz), 4.08(2H,bd,J=7.0Hz), 4.82-5.42 (2H,m), 1.90-2.16(4H,m).].

Reductive N-O bond fission⁶⁾ of (4) with zinc dust in acetic acid at 27°C for 15 hr gave (1) (a ca. 2 : 1 mixture of geraniol and nerol)⁷⁾ in a 94% yield.

3,7-Dimethyl-2-octene-1,7-diol (2) was synthesized as follows; N,N-Diethylnerylamine (3) was hydrated by aqueous sulfuric acid at 45°C for 5 hr to give N,Ndiethyl(6,7-dihydro-7-hydroxyneryl)amine (5) in a 93% yield.

[(5); bp 115-117°C/3.0mmHg, ir(neat, cm⁻¹): 3380, 1660, 1190, 1155 and 830, nmr(CCl₄,δ): 0.91(6H,t,J=7.0Hz), 1.07(6H,s), 1.23-1.47(4H,m), 1.64(3H,bs), 1.72-2.12

(2H,m), 2.46(4H,q,J=7.0Hz), 2.24(1H,bs), 2.86(2H,d,J=7.0Hz), 5.13(1H,t,J=7.0Hz)]. The subsequent treatment of (5) as mentioned above afforded a ca. 2 : 1 mixture of hydroxygeraniol and hydroxynerol (2) in a combined yield of 59% from (5) through the hydroxylamine (6).

[(6); bp 120-125°C/1.5mmHg, ir(neat, cm⁻¹): 3390, 1660, 1145, 1015 and 825, nmr(CC1₄,δ): 1.08(6H,t,J=7.0Hz), 1.12(6H,s), 1.28-1.55(4H,m), 1.55-1.77(3H,m), 1.80-2.20(2H,m), 2.63(4H,q,J=7.0Hz), 4.09(2H,bd,J=7.0Hz), 5.00-5.42(1H,m)].

[(2); bp 105-109°C/0.45mmHg, ir(neat, cm⁻¹): 3350, 1660, 1145, 1000 and 830, nmr (CC1₄,δ): 1.13(6H,s), 1.27-1.52(4H,m), 1.62 and 1.69(3H,s), 1.80-2.20(2H,m), 3.29 (2H,s), 4.00(2H,bd,J=7.0Hz), 5.02-5.52(1H,m)].

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References and Notes

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- 3) It is well-known that the cationic telomerization of isoprene with carboxylic acid or prenyl chloride affords a mixture of geranyl, neryl, linalyl, lavandulyl and -terpinyl derivatives. [J. Tanaka, T. Katagiri and T. Takeshita, Nippon Kagaku Zasshi, 89, 65 (1968). K. V. Leets, Zh. Obshch. Khim., 28, 3096 (1958).].
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- 5) The platinum oxide was recovered by filtration.
- 6) V. Rautenstrauch, Helv. Chim. Acta, 56, 2492 (1973).
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