

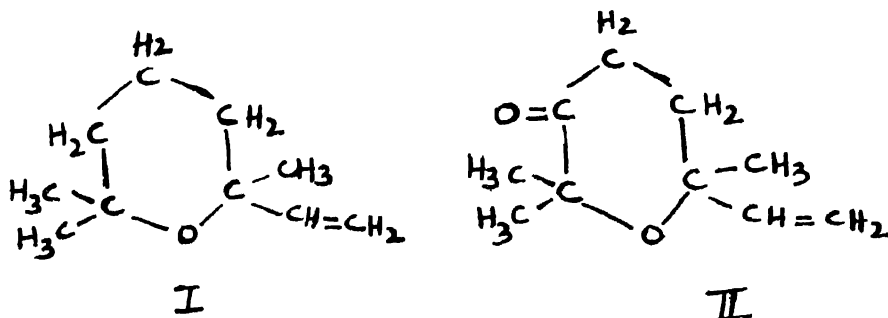
Terpenoids : Part. XXXVI.

A new synthesis of 2, 2, 6-trimethyl-6-vinyltetrahydropyran

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2-Methyl-6, 6-ethylenedioxy-2-heptanol, obtained through hydration of 2-methyl-6, 6-ethylenedioxy-2-heptene, after deketalisation when submitted to Grignard reaction with vinylmagnesium bromide followed by treatment with cold sulphuric acid (dilute) afforded 2, 2, 6-trimethyl-6-vinyl-tetrahydropyran.

2,2,6-Trimethyl-6-vinyltetrahydropyran (I) has been isolated from the oils of lime and geranium¹⁻³. The presence of this monoterpene oxide has been reported during dimerisation of isoprene with aqueous sulphuric acid⁴ and also among the products obtained from the Wolff-Kishner reduction of 2,6,6-trimethyl-2-vinyltetrahydropyran-5-one⁵⁻⁶ (II).

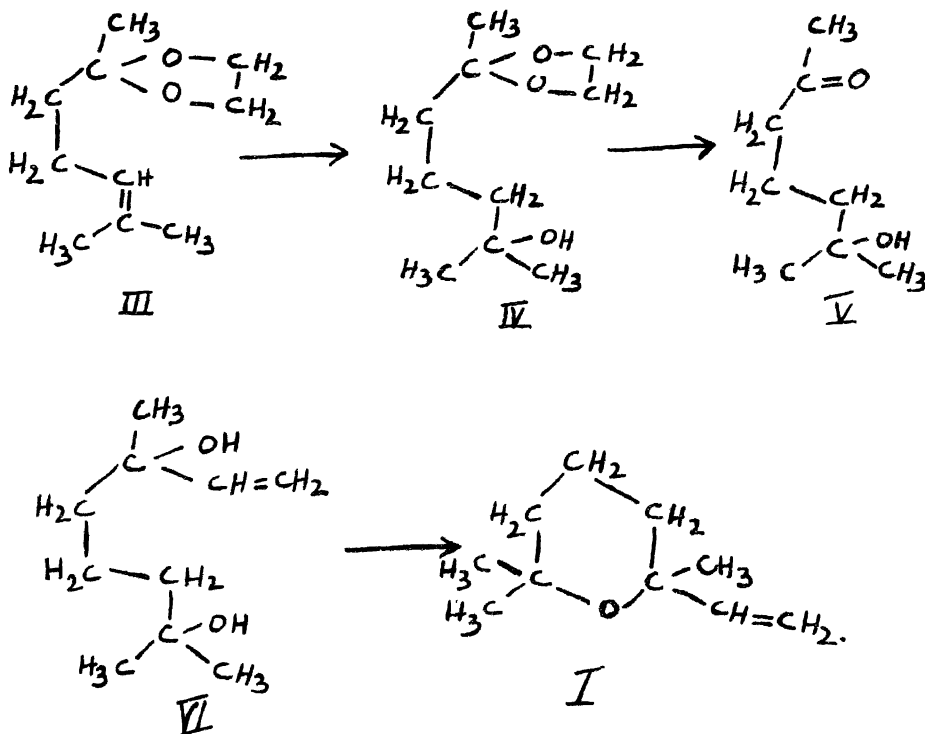


The formulation (I) has also been supported through its synthesis⁶. However, the present studies record a clean synthesis of this monoterpene oxide. The following chart depicts the sequence of the reactions employed :

2-Methyl-6,6-ethylenedioxy-2-heptene⁷ (III), the starting material, when hydrated through oxymercuration-demercuration procedure as described by Brown *et al.*,⁸ afforded 2-methyl-6,6-ethylenedioxy-2-heptanol (IV) in 85 per cent yield. The ketal carbinol (IV)

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thus obtained by dekatalisation under usual conditions⁹, furnished 2-methyl-6-keto-2-heptanol (V) in quantitative yields. The compound (V) on reaction with more than two moles of vinyl magnesium bromide in tetrahydrofuran gave the diol (VI) which directly on treatment with aqueous sulphuric acid at low temperature produced the desired monoterpeneoxide (I). The identity of the synthetic compound (I) was established through comparison of its I R absorption spectrum with that of the naturally occurring ether.



EXPERIMENTAL*

2-Methyl-6,6-ethylenedioxy-2-heptanol (IV): To mercuric acetate (12.76 g.), water (40 ml) and tetrahydrofuran (40 ml) was added slowly the ketal (III) (6.3 g). The reaction mixture was stirred at room temperature for 10 min. Then sodium hydroxide (12%, 40 ml) was introduced followed by sodium borohydride in sodium hydroxide (12%, 40 ml). The mercury thus formed was allowed to settle. The water layer was saturated with sodium chloride. The organic material was extracted with ether and dried (Na_2SO_4). After the removal of the solvent the residue on distillation under reduced pressure furnished the ketal carbinol (IV), (5.7 g.) in 85 per cent yield, b.p. $108^\circ/8$ mm n_D^{25} 1.4926 I.R. absorption peaks : 3450 (OH), and 1060 cm^{-1} (ketal). (Found : C, 63.74; H, 10.68; Calc for $\text{C}_{10}\text{H}_{20}\text{O}_3$, C, 63.79; H, 10.71%).

9. W. S. Johnson, J. D. Dass and K. L. Williamson, *Tetrahedron*, 1963, 19, 861.

*Boiling points are uncorrected. Analysis by B. N. Anand, and L. K. Khullar, Microanalysts, Panjab University, Chemistry Department, Chandigarh. I. R. absorption spectra were recorded on Perkin-Elmer infracord with sodium chloride optics using a thin liquid film.

2-Methyl-6-keto-2-heptenol (V): The ketal carbinol (IV), (5 g.), acetone (160 ml), paratoluene-sulphonic acid (1 g.) and water (10 ml) were stirred at room temperature for 2 hr. The reaction mixture was then diluted with saturated sodium chloride solution and extracted with ether. The ether-extract was washed with sodium bicarbonate solution (5 per cent) again with brine and dried (Na_2SO_4). The solvent was stripped off and fractionation of the residue under diminished pressure gave the keto-alcohol (V) (2.3 g.) 60 per cent yield, b.p. $98^\circ/\text{mm}$. n_D^{25} 1.4950 I.R. absorption peaks: 3450 (OH) and 1710 cm^{-1} ($-\text{C}=\text{O}$). (Found: C, 66.69; H, 11.16; $\text{C}_8\text{H}_{16}\text{O}_2$ requires C, 66.63; H, 11.18%).

2,2,6-Trimethyl-6-vinyltetrahydropyran (I): To the Grignard reagent prepared from magnesium metal (0.8 g.) and vinyl bromide (5.0 g.) in anhydrous tetrahydrofuran (70 ml.) was added dropwise, the keto alcohol (V) (2.2 g.) in 50 ml. tetrahydrofuran. The contents were stirred at room temperature for 6 hr. Thereafter, the reaction mixture was refluxed for 3 hr. It was cooled and decomposed with saturated solution of ammonium chloride and worked up in the customary manner. After the evaporation of the solvent, there was obtained, the diol (VI) (1.98 g.) which was not distilled. I.R. absorption peaks 3450 ($-\text{OH}$), 3060, 1645, 990 and 910 cm^{-1} ($-\text{CH}=\text{CH}_2$).

The above diol (1.9 g), ether (50 ml.) and dilute sulphuric acid (8%) (15 ml.), were stirred at 5° for 2 hr. The organic material was extracted with ether. The ethereal layer was washed with sodium bicarbonate solution, water and dried (Na_2SO_4). After the removal of the solvent the residue was passed over neutral alumina column (elution with petroleum ether $40-60^\circ$ (80 ml.). Distillation under reduced pressure afforded 2, 2, 6-trimethyl-6-vinyl-tetrahydropyran (I) (0.9 g.) b.p. $86^\circ/54\text{ mm}$., n_D^{20} 1.4490. Lit $1\eta_D^{20}$ 1.4492.

*I.R. absorption peaks 3080, 1827, 1645, 1415, 1375, 1366, 1350, 1290, 992 and 912 cm^{-1} . Lit.¹ reports I.R. peaks at 3080, 1827, 1641, 1410, 1381, 1366, 1350, 1295, 994 and 912 cm^{-1} . (Found C, 77.85, H, 11.66; Calc. for $\text{C}_{10}\text{H}_{18}\text{O}$, C, 77.86; H, 11.76%).

One of the authors (M.S.B.) is grateful to the C.S.I.R., New Delhi for the award of a Junior Research Fellowship.

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Received March 30, 1968.

*The superimposability of I.R. spectra of the synthesised and the natural product could not be checked as we could not procure the sample of the naturally occurring 2, 2, 6-trimethyl-6-vinyl-tetrahydropyran isolated by Y. Ohta² in spite of our request to them for the same.