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NOTES

Synthesis of Ethyl-4, 8, 12, Trimethyl-5-Oxa-7-11-Tridecadienoate-A New Oxirane

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A New oxirane ethyl-4, 8, 12-trimethyl-5-oxa-7, 11 tridecadienoate has been synthesised. It has been synthesised from geraniol and a levulinic acid derivative.

Various oxiranes have been synthesised. The natural $C_{18}J^H$ hormone Cecropia[1] has methyl substituent at C_3 position. Other oxiranes with and without methyl substituents has been tested for J^H activity. A new oxirane having a methyl substituent at C_4 position has been synthesised with levulinic acid derivative and geraniol as against 5-oxaoxirane synthesised by using costly chemicals such as BF_3, phosporane etc.[4]. Ethyl levulinate[2] was reduced by aluminium isopropoxide (M. P. V. reduction) to get ethyl-4-hydroxy valerate.[3] Ethyl-4-hydroxy valerate was treated with thionyl chloride in presence of pyridine to get 4-chlorovalerate which was directly treated with geraniolyl anion formed by geraniol with sodium to get ethyl-4,8,12-trimethyl-5-oxa-7,11-tridecadienoate.

A mixture of levuline acid (58 g.) absolute ethanol (50 ml.) and conc. H_2SO_4 (1 ml.) was refluxed for 20 hrs, and worked up as usual to give ethyl levulinate (b. pt. 133-35% 12 mm., yield 35 g.). A mixture of ethyl levulinate (8 g.) dry isopropanol and freshly prepared aluminium isopropoxide (3 g.) was slowly distilled until the distillate did not give test for acetone with 2,4-DNP (3 hrs.). Thereafter, excess propanol was distilled under reduced pressure, sufficient ether added and the mixture decomposed with 2N HCl while cooling under tap-water. The ether layer was washed with water, dried (anhyd. Na_2SO_4), solvent removed and the residue distilled under reduced pressure to give ethyl-4-hydroxyvalerate b. pt. 950/20 mm. IR: 3500 cm^{-1} (νOH). Ethyl 4-hydroxy valerate (7.3 g.) and pyridine (4.3 g.) were mixed together. Little benzene (15 ml.) was added to it and then thionyl chloride (6.25 g.) was added dropwise. The reaction was exothermic. The reaction mixture was refluxed for $\frac{1}{2}$ hr. The white precipitate initially formed, dissolved during refluxation. The contents were cooled and kept overnight when pyridine-hydrochloride formed a lower insoluble dark layer. The contents were separated, lower pyridine-hydrochloride layer was extracted twice or thrice with benzene

(10–15 ml. every time). The solution of ethyl 4-chloro valerate was used directly for further reaction.

Sodium (1.1 g.) was taken in absolutely dry benzene. Geraniol (8 g.) was added to it and the mixture was refluxed for about 35 hrs when all sodium had dissolved. A solution of ethyl 4-chloro valerate (prepared above) in benzene was added to it dropwise with constant stirring. Exothermic reaction occurred and insoluble sodium chloride was separated. The contents were refluxed (avoiding bumping due to sodium chloride) for 2 hrs. The reaction mixture was taken in separating funnel, washed nicely with excess of water to remove all unreacted ethyl 4-chloro valerate, sodium chloride formed in this reaction and pyridine (from previous reaction). The benzene layer was then dried over anhydrous sodium sulphate. Benzene was evaporated to get crude ethyl 4,8,12-trimethyl 5-oxa 7,11-tridecadienoate. The whole mass was kept overnight in alcoholic potassium hydroxide at room temperature. Ethyl alcohol was evaporated off. Ether was added to separate unreacted geraniol (neutral fraction). Fresh lot of ether was added to it and contents were acidified with dilute hydrochloric acid (2 N). Ether was evaporated and the acid obtained was further esterified by usual method to get pure ethyl 4,8,12-trimethyl 5-oxa 7,11-tridecadienoate, b. pt. 172°/6 mm. (10 g.).

Found %: C 72.13%, H 10.67%; $C_{17}H_{30}O_3$ requires %: C 72.34%, H 10.64%. IR(KBr.) : 2,900 cm^{-1} (C=C), 1.730 cm^{-1} (estertorbonyl) 1150 cm^{-1} (aliphatic ether linkage).

PMR ($CDCl_3$) : 1.25 (t 3H CH_3 for methyl), 1.41 (d 3H of C_4 methyl), 1.60–1.68 (s 9H, 3H each of C_8, $C_{12}(\times 2)$ methyls), 1.72–1.94 (m 2H of C_3), 2.21–2.65 (m 6H of C_2, C_9 & C_{10}), 3.58 (m 3H, 2H of C_6 and 1H of C_4), 4.66 (q 2H of CH_2 from ethyl), 5.13 (t 1H of C_{11}), 5.4 (t 1H of C_7).

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