

NOTES

SYNTHESIS OF 3-ETHYL-7,11-DIMETHYL-4-OXA-6,10-DODECADIENOIC ACID BY A NEW ROUTE

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The derivatives of 3-ethyl-7,11-dimethyl-4-oxa-6,10-dodecadienoic acid have enhanced J H activity (100%) against the nymphs of *Dysdercus Koenigii*. This acid has now been synthesised starting from levulinic acid.

The dodecadienoic acid referred in the present paper had been synthesised from geraniol and methyl ester of pentenoic acid. In the present study instead of methyl ester of pentenoic acid¹, levulinic acid has been used. Ethyl ester of levulinic acid was brominated to 3-bromo ethyl levulinate². It was refluxed with geraniol sodium to give acetyl-7, 11-dimethyl-4-oxa-6,10-dodecadienoic acid which on reduction with hydrazine hydrate by Huang Minlon modification³ of Wolf Kischner method gave 3-ethyl-7,11-dimethyl-4-oxa-6,10-dodecadienoic acid. The present route leads to the complete recovery of geraniol and pure acid is directly obtained and separated in a single step as against geranye-2-pentenoate and three other compounds formed in the original process¹.

Ethyl levulinate (14.4 g) was dissolved in ether (40 ml). The solution was cooled to 0°C with freezing mixture. Bromine (4 ml) was added to the ice cold solution dropwise, with constant stirring. The temperature of the reaction mixture was maintained at 0°C, for 2 hrs after addition of bromine was over. It was then allowed to attain room temperature when the colour of the reaction mixture was changed from red to colourless instantaneously. Hydrobromic acid gas was removed under water suction pump. The reaction mixture was then transferred to water (50 ml). The aqueous solution was then extracted several times with excess of ether every time since ethyl 3-bromo levulinate is highly soluble in water. The ethereal layer was dried over anhydrous sodium sulphate. Ether was evaporated to get ethyl 3-bromo levulinate (19.3 g). It was distilled at 107°C at 7 mm.

Sodium (2.3 g) was taken in absolutely dry benzene. Geraniol (16 g) was added to it and the mixture was refluxed for ca. 35 hrs, when all sodium had dissolved. A solution of ethyl 3-bromo levulinate (22 g) in benzene (40 ml) was added to it dropwise with constant stirring. Exothermic reaction occurred and sodium bromide was separated. The contents were refluxed for 2 hrs. Benzene was distilled partially and alcoholic solution of NaOH (5 g. in 50 ml.) was added to the residue and was kept overnight at room temperature. The reaction mixture was washed nicely with water to remove sodium bromide formed in the reaction and unreacted ethyl 3-bromo levulinate (if any). Benzene was evaporated and the whole mass was taken in ether. Neutral fraction was separated and then the

mass was acidified with dilute hydrochloric acid (2 N). The ether was separated and dried over anhydrous sodium sulphate. Ether was evaporated to get 3-acetyl-7,11-dimethyl 4-oxa-6,10-dodecadienoic acid (20 g)

IR (KBr) : $3,400\text{ cm}^{-1}$ (OH), 1730 cm^{-1} (CO), 1690 cm^{-1} (COOH).

PMR (CDCl_3) : 1.59 - 1.69 (s 9H C_7 and C_{11} Methyls), 2.2 (s 3H of CH_3 from acetyl), 2.26 - 2.83 (m, 6H C_2 , C_8 , C_9), 3.67 (d 2H of C_5), 4.8 (t 1H C_3), 5.02 (t 2H of C_6 and C_{10}) 7.28 (br.s 1H of COOH exchangeable.)

3-Acetyl 7,11-dimethyl-4-oxa 6,10-dodecadienoic acid (5.36 g) was taken in ethyl alcohol (20 ml.) and refluxed with hydrazine hydrate (85%, 3 ml.) for about 2 hrs. Solid sodium hydroxide (2 g) and triethylene glycol (40 ml) were added to it and heated strongly without condenser, when ethyl alcohol, water vapour and excess of hydrazine hydrate were allowed to evaporate completely. The temperature of the reaction mixture was increased to 190°C . The reaction mixture was further refluxed for 3 hrs. The contents were cooled and extracted with benzene after acidification with dilute hydrochloric acid (2 N). Benzene layer was separated washed with water and dried over anhydrous sodium sulphate. Benzene was evaporated to get 3-ethyl 7,11 dimethyl 4-oxa 6,10-dodecadienoic acid (4.7 g).

Found % C, 70.53, H, 10.37, $\text{C}_{15}\text{H}_{26}\text{O}_3$ required % C, 70.87, H, 10.24.

IR (KBr) : $3,200\text{ cm}^{-1}$ (OH of COOH), 1690 cm^{-1} (COOH).

PMR (CDCl_3) : 0.92 (t 3H CH_3 from ethyl), 1.08 - 1.28 (m 2H of CH_2 from ethyl), 1.6-1.68 (s, 9H of C_7 C_{11} ($\times 2$) methyls), 1.8 - 2.8 (m 6H of C_2 , C_8 , C_9), 3.65 (d 2H of C_5), 4.24 (m 1 H of C_3), 5.02 (t 2H of C_6 and C_{10}), 7.24 (br, s 1H of COOH exchangeable with D_2O).

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