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Synthesis of Tetrahydro Pseudionone by a New Route and Synthesis of 2:6 Dimethoxy Octane and Ethanethiol Ester of Levulinic Acid by Kolbe Electrosynthesis Process in Aprotic Medium and Dilute Condition

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Tetraphydropseudoionone and 2 : 6 dimenthoxy-octane have been synthesised by cross kolbe reaction between cirtronellic acid and levulinic acid and dimerisation of 4-methoxy valeric acid. This gives a new route for the syntheses of dihydropseudo ionine and rhodinolidol (similar to nerolidol). The work is in progress. Kolbe electrosynthesis of phenylthioacetic acid gives by radical and carboniumion, products such as $PhSCH_2SPh$ etc. It was thought interesting to study cross Kolbe reaction between levulic acid and ethanethiol to get a Ketone $CH_3COCH_2CH_2S.Et$ similar to the product $PhSCH_2S{\cdot}Ph$ referred above. However only the ester $CH_3COCH_2COSC_2H_5$ in 12 h at ambient temperature, in aprotic medium and dilution, due to intimate vicinity of the acid and thiol. Rapid removal of the water formed as 'H' and OH' ions from the sphere of action, has favoured esterification in 20% yield on the base of levulinic acid.

INTRODUCTION

Work on terpenes and Kolbe electrolysis is going on for a long time at Poona School of Sciences.[1, 2] Citronellic acid was electrolysed by cross Kolbe reaction with leuulinic acid and tetrahydropseudoione was obtained, which paved the new way for the syntheses of dihydropseudoionone and rhodinolidol (similar to nerolidol) both the synthesis are in progress.

EXPERIMENTAL

2:6 Dimethoxy octane has been synthesised by dimerisation of 4-methoxy-valeric acid by Kolbe electrolysis.

Phenylthioacetic acid gives by Kolbe electrosynthetic process products such as $Ph{\cdot}S{\cdot}CH_2S{\cdot}Ph$ etc. by radical and carbonium ion reaction. It was thought interesting to study reaction between levulinic acid and ethanethiol to get a ketone $CH_3COCH_2CH_2S$ Et, similar to the product $Ph{\cdot}S{\cdot}CH_2S{\cdot}Ph$ referred in the abstract. However only the ester $CH_3COCH_2CH_2$ COSPh has been obtained in 20% yield on levulinic acid at ambient temperature in aprotic medium in methanol at high dilution, due to intimate viscinity of levulinic acid and ethanethiol on the electrode. Rapid removal of the water formed as H and OH ions from the sphere of action, that has favoured esterification as it appears.

The chemicals used levulinic acid, ethanethiol, citronellal, methanol and sodium etc. were of C.p. quality silver nitrate and sodium hydroxide were of A.R. quality.

Citronellal was oxidised to citronellic acid by the method used by ping yuan yeh *et al*[3].

Citronellal (31.08 g) was mixed with silver nitrate (68.09 g) in water (600 mL), sodium hydroxide (29.0 g) in 85 mL water was slowly added and the mixture was stirred for 5 h. The mixture was filtered. The filtrate was acidified and extracted with ether, Ether layer was washed with distilled water and separated. Ether layer was dried over anhydrous sodium sulphate. Yield 27.0 g. The acid was distilled at 141–145°C (10 mm. Hg).

Citronellic acid (3.4 g) was mixed levulinic acid (7 g) in the molar proportion 1:2 in the electrolysis cell and electrolysis was carried out in dry methanol (50 mL.) and sodium (0.2 g). The electrolysis was carried out at 25–30°C, current density 0.3 to 0.4 amp/per sq. cm. and 35 to 40 volts. Electrolysis was carried out for 12 h and the solution was acidified with acetic acid, methanol was removed on water bath and the dimerised and electrolysed products were taken in ether. The ether layer was washed with sodium-bicarbonate (10%), distilled water and the ether layer was dried over anhydrous sodium sulphate, ether was distilled out on water bath and the residue was fractionated and three fractions were collected.

I fraction upto 115°C (10 mm. Hg.) of octanedione (reported b.p. 112°C at (10 mm).

II fraction 115–125°C (10 mm.) monoketone and III fraction above 125°C hydrocarbon.

The second fraction after due purification over alumina in petroleum ether was refractionated to give a yellow oily product 1.8 g, b.p. 118° (at 10 mm).

Infrared showed peaks at 2900 cm^{-1} for (C—H) stretching and at 1750 cm^{-1} for >C = 0 group.

% C obtained 78.84; reqd. 79.3

% H obtained 12.3; reqd 12.13 for ($C_{13}H_{24}O$)

2:4 D.N.P. derivative, m.p. 118°C

The nitrogen % of 2:4 DNP derivative was found out to be 14.6 by Kjeldahl's method against theoretical % for ($C_{19}H_{26}O_4N_4$) (14.88%).

Levulinic acid (30 g) was refluxed with super dry alcohol (50 mL) and conc. sulphuric acid (1.2 g) for to 5 h. The mixture was taken in ether and was washed with minimum amount of sodium bicarbonate solution to remove acids and water. Ether layer was separated and dried over anhydrous sodium sulphate. Ether was removed on water bath and residue was fractionated to give ethyllevulinate at 200–202°. Sap equivalent 3894 mg. Ethyllevulinate (12.9 g.), dry isoporpanol (60–80 mL) and freshly prepared aluminium isopropoxide were slowly distilled at the rate of 1 to 3 drops per minute till the distillate showed a negative test towards 2:4 D.N.P. excess; isopropanol was removed under reduced pressure. The mixture was taken in ether and the aluminium salt was decomposed with 2N HCl. Ether layer was washed with minimum amount of water. Ether layer was dried over sodium sulphate, ether removed on water bath and residues distilled under reduced pressure and collected at 105–110°C/20 mm.

RESULTS AND DISCUSSION

The structure was confirmed by its infrared spectrum which showed bands at 3500 cm^{-1} and 1750 cm^{-1} corresponding to ester carbonyl group. PMR ($CDCl_3$) = 1.25 (t, 3H of CH_3 from ethyl.) 1.41 (d, 3H of CH_3), 1.72 to 1.98 (m of 2H C—CH_2—C), 2.48 (t, 2H of CH_2—CO), 4.2 (broads, IH of OH exchangable with D_2O), 4.48–4.81 (m, 3H 1H of C—CH—C and 2H of O—CH_2).

γ-Hydroxy valerate (14.6 g) was taken in dry benzene (100 mL) and pyridine (8 g) and thionyl chloride (7.3 mL) were slowly added during 3 h. A white solid separated which partially dissolved as the reaction proceeded. The mixture was refluxed for 1 h after complete addition when the separated solid thoroughly dissolved. The top layer was removed, dried over sodium sulphate and benzene, pyridine and thionylchloride were removed by fractionation to give a crude product 10 g.

γ-Chloroethyl valerate (4.1 g) was mixed with sodium methoxide (1.359 g sodium) prepared by the action of sodium on dry methanol. The mixture was gently refluxed for 1 h. Sodium chloride was removed and γ-methoxy valerate was collected at 95–98°C (20 mm).

Infrared spectrum showing peaks at 1120 cm^{-1} and P.M.R. ($CDCl_3$), 1.2 (t, 3H of CH_3 from ethyl), 1.3 (d 3H of CH_3), 1.72–1.98 (m of 2H C—CH_2—C), 2.38 (t of CH_2 CO), 3.2 (S, of 3H of O—CH_3) 4.3–4.7 (m, 1H of C—CH—C and 2HO of O—CH_2 of ethyl).

γ-Methoxy-ethyl valerate (5 g) was refluxed with sodium hydroxide (4.2 g) in water (50 mL) for 2 h. The clear solution was cooled, acidified and extracted with ether. The ether extract was dried over sodium sulphate, ether evaporated to give γ-methoxy-valeric acid. (yield-4 g).

γ-Methoxy-valeric acid (4 g) was taken in electrolysis cell and dry methanol (30 mL) and sodium (0.25 g) were added to it. The solution was electrolysed at 25–30°C at the current density of 0.3 to 0.4 amp/sq. cm. and 35–40 V. The mixture was electrolysed for 12 h. Methanol was removed on water bath and the residue was acidified with acetic acid. It was taken in ether and washed with sodium bicarbonate (5%), Water and ether separated, evaporated to give dimethoxy octane 1.5 g. The C.H. analysis give following results.

Carbon observed 68.95, H-12.71%

Carbon required 68.98 H required 12.65%

PMR ($CDCl_3$) showed a singlet at 3.2 d corresponding to 6H:

Cross Kolbe electrolysis between ethane thiol and levulinic acid:

Levulinic acid (6 g) was taken in electrolysis cell and methanol (50 mL) and ethane thiol (9 g) were added to it the molar proportion 1:3, sodian hydroxide (0.4 g) was added to it and the solution was electrolysed at 25 to 30°C at the current density of 0.3 to 0.4 amp./sq. cm. and 30 to 40 volts for 10 h. Methanol was removed on water bath and the residue was acidified with acetic acid and taken in ether. Ether layer was washed with sodium bicarbonate solution (2%), then with water, separated and ether layer was dried over sodium sulphate. Ether was evaporated and the resudue was fractionated at 149°C to remove all disulphide. The remaining liquid was fractionated under vacuum to give a faction at 90°C/20 mm. 1.8 g sulphur % obtained was 20.2 required for thioketone 24.2 ($CH_3COCH_2CH_2SC_2H_5$). Though reported b.p. of thoketone is also 90°C at 20 mm as the sulphur percentage obtained was much less thus the derivative of 2:4 D.N.P. was attempted. The derivative melted at 131°C and could not be raised even after repeated crystallisation; 2:4 DNP derivative of thioketone reported is 163°C. The reported b.p. of ethanethiol ester is 90°C/20 mm and its 2:4 D.N.P. derivative is reported to melt at 131°C. The fraction collected at 90°C/20 mm was therefore subjected to hydrolysis with alkali.

The compound b.p. 90°C/20 mm (1 g) was taken in methanol (25 mL) and methanolic sodium hydroxide (15 mL, 5% solution) was added to it. The solution was kept for 24 h and methanol was allowed to be evaporated at room temperature in a shallow dish after wards. The residue was neutralised with dilute hydrochloric acid and was taken in ether. Ether layer was washed with water and the washing were added to the original water layer. Ether was distilled at 34°C on water bath and collected and no higher boiling point fraction could be collected, isolated and the flask was completely dry. Ether became completely free of ethane thiol when washed with little sodium hydroxide (10 mL 5%).

The water solution gave 2:4 D.N.P. mp. m.m.p. 214°C corresponding to levulinic acid.

No thioketone was formed in the electrolysis and only the ester with the same number of carbon atmos that is levulinic was formed 1.8 g from levulinic acid about 20% at ambient temperature. So no cross Kolbe process would be applied or the Hofer moist product could be isolated from cross Kolbe method and interestingly only the ester formation to the extent of 20% has been attained at such a dilution and at ambient temperature; though esterification of thiol with acid is not so easy as with alcohol. The esterification has taken place due to intimate vicinity of ethanethiol and levulinic acid on the electrode and water formed in the reaction being removed as hydrogen and oxygen from the sphere of action and that has favoured esterification as it appears.

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