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NOTES

Synthesis of an Isomer of Dihydro Citronellol and 7-Methyl-Octan-4-Ol.

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A synthesis of a C_{10} alcohol has been reported herewith.

Synthesis of a C_{10} alcohol an isomer of dihydrocitronellol has been reported herewith. Isobutyraldehyde was condensed with levulinic acid in alkaline medium. The condensate was stabilised by Parr hydrogenation[1] to 7-methyl-4-keto -octanoic acid. The acid was electrolysed with propionic acid to give a neutral ketone 8-methyl-nonane-5-one. b.p. 110°/6 mm having an odour similar to carvone. 8-Methyl-nonane-5-one on Meerwein reduction[2] gave an alcohol 8-methl-nonan-5 -ol a C_{10} alcohol b.p. 120°/6 mm having a comphoraceous odour hydroxyl group being secondary and in the middle of the chain.

7-Methyl-4-octanoic acid on electrolysis with acetic acid gave 7-methyl-octan-4 -one and 7-methyl-octan-4-ol on Meerwein reduction of the same[2].

In the process of photosynthesis carbohydrates are in variably formed and so many other compounds are formed when formaldehyde is treated with alkali. Terpenoids, flavonoids, benzenoids, naphthenoids, carotenoids occur in nature. When open chain terpenoids and isoprenoids are subjected to ozonolysis levulinic aldehyde is formed. When carbohydrates are treated with concentrated acids levulinic acids invariably formed. An isomer of dihydrocitronellol has been synthesised by cross Kolb's electrolysis of propionic acid with 7 methyl-4-keto -octanoic acid and reduction of the neutral product obtained. 7-Methyl-4-octanoic acid was obtained by hydrogenating the condensate of isobutyraldenyde and levulinic acid. A C_{10} alcohol referred above has an odour similar to camphor. The mannich product of 7-methyl-4-keto-octanoic acid is in hand and the reduced product of the above C_{10} acid is being examined.

Levulinic acid (22 ml) was added to sodium hydroxide solution (8.5 g) in (27 ml) water and alcohol (70 ml). Isobutyraldehyde (16.5 g) was added to the above solution. The mixture was kept overnight and transferred to a shallow dish to evaporate all alcohol and isobutyraldenyde (unreacted) for 24 h. The thick liquid was acidified with concentrated hydrochloric acid and extracted with ether. Ethereal layer was washed twice with saturated sodium chloride solution and then with little water. The ethereal layer was dried over anhydrous sodium sulphate and ether evaporated to get a crude acid condensate *i.e.*, *7-Methyl-4-keto-octanoic acid ethyl ester.*

The condensate (12 g) was taken in a flask, then absolute alcohol (80 ml) and Pd-C (0.5 gm, 10%) were added to the condensate. The mixture after usual care was hydrogenated at 60 lbs pressure. The pressure after 3 h reduced to 38 lbs. It was kept for further 2 h. No reduction in pressure was observed. Then solution was filtered; conc. H_2SO_4 (1.7 ml) was added and refluxed for 4 h, absolute alcohol (50 ml) was added twice and 100 ml distillate was collected. The residue was concentrated till 3/4 of alcohol added was distilled out. The concentrate was extracted with ether. Ether layer was washed with water, then with sodium bicarbonate solution, and again with water. Ethereal layer was dried over anhydrous sodium sulphate. Ether layer was evaporated and residue was distilled under reduced pressure b.p. 140°/6 mm.

4-Keto-7-Methyl-Octanoic acid

Hydrolysis of above product (ester) was carried out in cold alkali solution, by adding ester (2 ml) to the solution of sodium hydroxide (0.4 g) prepared in ethyl alcohol (40 ml) and keeping aside over night. The alcohol was evaporated at room temperature and water (25 ml) was added. The clear solution was acidified and extracted with ether. Ether layer was washed with water and then ether layer was dried over anhydrous sodium sulphate. Ether layer was evaporated and residue was collected for further process. Eq. wt. 172. 38, required 172.0.

8-Methyl-Nonane-5-one

Sodium hydroxide (0.3 g) was dissolved in methanol (30 ml) and C_9 acid referred above (2 g) was added to it. Propionic acid (2 ml) was transferred to above solution and electolysis was carried out at current density 0.3 amp/cm^2; temp. 30–35° and voltage 20 to 30 volts 4h. After 4h again 0.5 ml of propionic acid was added to the solution and electrolysis continued for another 1 h. Methanol was evaporated and contents were neutralised with acetic acid and extracted with ether. Ethereal layer was washed with sodium bicarbonate solution (5%), water and dried over anhydrous sodium sulphate and evaporated to get a neutral product b.p. 108–110°C at 6 mm pressure and odour is similar to carvone.

IR spectrum showed peak of 2950 cm^{-1} corresponding to CH and peak at 1725 cm^{-1} corresponding to carbonyl (C=O) group. Found % C–76.56, H–12.5%, required % C–76.92, H–12.8%.

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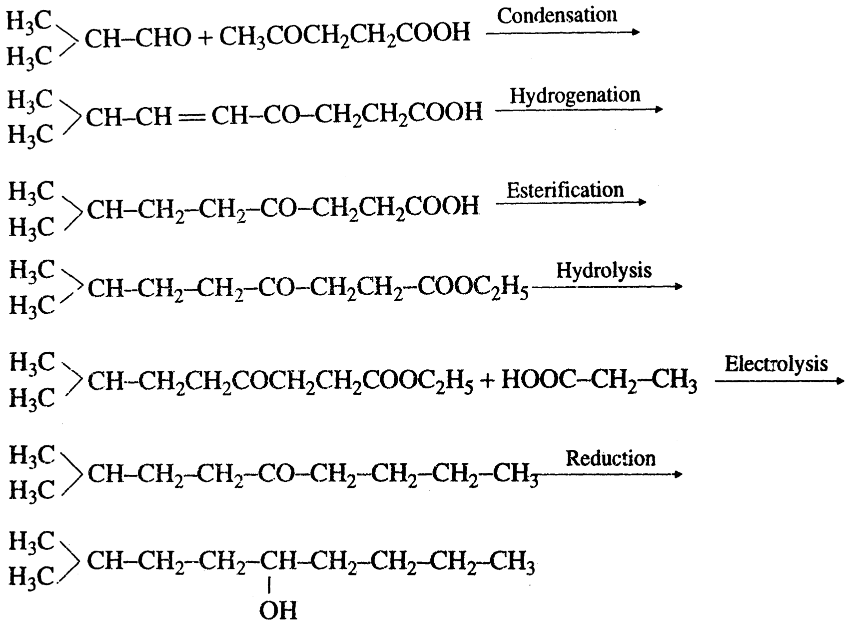

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH\text{–}CHO + CH_3COCH_2CH_2COOH \xrightarrow{\text{Condensation}}$$

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH\text{–}CH{=}CH\text{–}CO\text{–}CH_2CH_2COOH \xrightarrow{\text{Hydrogenation}}$$

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH\text{–}CH_2\text{–}CH_2\text{–}CO\text{–}CH_2CH_2COOH \xrightarrow{\text{Esterification}}$$

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH\text{–}CH_2\text{–}CH_2\text{–}CO\text{–}CH_2CH_2\text{–}COOC_2H_5 \xrightarrow{\text{Hydrolysis}}$$

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH\text{–}CH_2CH_2COCH_2CH_2COOC_2H_5 + HOOC\text{–}CH_2\text{–}CH_3 \xrightarrow{\text{Electrolysis}}$$

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH\text{–}CH_2\text{–}CH_2\text{–}CO\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_3 \xrightarrow{\text{Reduction}}$$

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH\text{–}CH_2\text{–}CH_2\text{–}\underset{\underset{OH}{|}}{CH}\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_3$$

C_{10}–Hydroxy compound

8-Methyl-Nonane-5-Ol

A mixture of electrolysed product (3.5 g) dry isopropanel (60–70 ml) and freshly prepared aluminium isopropoxide (3 g) was distilled using one foot fractionating column distilling condenser maintaining rate of 1–3 drops per minute using voltage control. Distillate was tested for 2, 4-dinitrophenyl hydrazine reagent. Reaction was carried out until distillate did not give test with reagent. After the reaction was over the mixture was refluxed for ten minutes cooled and excess propanol was removed under reduced pressure. Sufficient ether was added to aluminium salt and was decomposed with hydrochloric acid (2N) by cooling under tap water. Ethereal layer was washed twice with distilled water, dried with anhydrous sodium sulphate, ether was evaporated to get hydroxy compound. (Hydroxy compound distilled at 120°C/6 mm pressure).

IR Spectrum showed peak at 3500 cm^{-1} corresponding to OH group and peak at 2973 cm^{-1} corresponding to CH Found % C– 75.7, H–13.8%, required %C–75.95, H–13.92% PMR ($CDCl_3$) = 0.7 (m 3H of C_9), 1.1 (d 6H of C_1 and C_{10}), 1.6 (m 1H of C_2), 2.45 (t 4H of C_4 and C_6), 3.5 (m 1H of C_5) 3.7 (brs 1H of OH exchangable with D20).

7-Methyl-Octane-4-One

Sodium hydroxide (0.3 g) was dissolved in methanol (30 ml) and 7-methyl-octanoic acid (2 g) was added to it. Acetic acid (2 ml) was transferred to above solution and electrolysis was carried out at current density 0.2 amp/sq. cm, T–30–35° and voltage 20–30 volts for 4 h. After 4 h again acetic acid (0.5 ml) was added to the solution and electrolysis continued for another 1 h. Methanol was evaporated and contents were neutralised with acetic acid and extracted with ether. Ethereal layer was washed with sodium-bicarbonate solution (5%), water and dried over anhydrous sodium sulphate. Ether was evaporated to get a neutral product b.p. 101° at 6 mm.

Found % C–75.7, H–12.5; required % C–76.05%, H–12.67% (P'MR ($CDCl_3$: 0.8 (m 3H of C_1), 1.1 (d 6H of C_8 and C_9) 1.4 (m 2H of C_2), 1.6 (m 1H of C_7), 2.65 (t4 H of C_3 and C_5).

7-Methyl-Octane-4-Ol

A mixture of electrolysed neutral product b.p. 101°/6 mm, dry isopropanol (60 ml to 70 ml) and freshly prepared aluminium isopropoxide (3 g.) was distilled using one foot fractionating column maintaining distillation rate at 1 to 3 drops per minute using voltage control. After the reaction was over, the mixture was refluxed for ten minutes, cooled and excess propanol was removed under reduced pressure, sufficient ether was added to aluminium salt and was decomposed with hydrochloric acid (2N) by cooling under tap water, Ether layer was washed twice wth distilled water, dried over anhydrous sodium sulphate. Ether was evaporated to get 7-methyl-octan-4-ol b.p. 118/6 mm.

Found % C–74.8; H–13.6%, Required % C–75.0, H–13.98% PMR ($CDCl_3$)–0.8, (m 3H of C_1), 1.1 (d, 6 H of C_8 and C_9), 1.4 (m, 2H of C_2), 1.6 (m 1 H of C_7), 2.65 (t 4H of C_3 and C_5), 3.5 (m 1H of C_4), 3.9 (brs 1 H of OH exchangable with D20).

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