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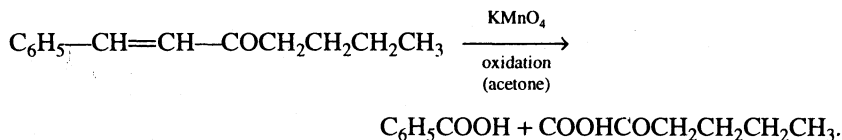
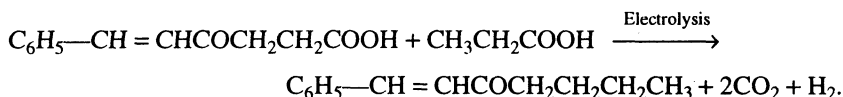
Syntheses of 7-Phenyl-5-Keto-Hepta-6-7-ene and 6-Phenyl-Hexa-4-Keto-5-6-ene the Intermediates in the Syntheses of Norleucine and Norvaline

P.A. LIMAYE*, M.S. NIMSE and S.M. GHATE
Poona School of Sciences
 339, Navi Peth, Pune-411 030, India

Syntheses of compounds which will serve as intermediates in the syntheses of norvaline and norleucine have been reported herewith. Kolbe process of electro organic synthesis has been used for the same.

Amino acid norvaline is present in casein, globin and steerhorn. Various methods for the syntheses of amino acids using different types of initial reagents such as malonic acid ester, L-bromoacids, hydantoin etc. have been used. During the syntheses of aminoacids keto acids were also used as basic materials¹.

These intermediate products were synthesized by using electro organic process. Cross Kolbe reaction was carried out between S-benzal levulinic acid² and acetic acid, and S-benzal levulinic acid and propionic acid. Ketones obtained can be oxidised to respective keto acids by KMnO₄ in presence of pure acetone.



The above keto acid can be used as intermediate in the synthesis of norleucine.

Levulinic acid, sodium hydroxide, benzaldehyde, acetic acid, propionic acid, methanol and isopropyl alcohol used were all of B.D.H. quality.

S-Benzal levulinic acid

S-benzal levulinic acid was prepared by condensing levulinic acid with benzaldehyde in alkaline medium. A mixture of levulinic acid (11.6 g in 200 mL of water), sodium hydroxide (8.9 g in 100 mL of water) and benzaldehyde (10.12 g in 100 mL of alcohol) was warmed on water bath at 50°C. After 10 min the solution became clear. It was rapidly cooled in ice-salt mixture and benzaldehyde separated and solution was acidified with concentrated hydrochloric acid (40 to

50 mL). Separated yellow oil layer was rapidly stirred and scratched to get crystalline mass. It was recrystallised from alcohol. (Yield 10 g), m.p. 124–25°C (literature m.p. 125°C). In order to get extra pure compound, the crude product was dissolved in sufficient alkali and decomposed with acid, extracted with ether to get crystalline material after evaporation, which exactly melted at 126°C.

6-Phenyl-4-keto-hexa-5-6-ene

Sodium hydroxide (0.3 g) was dissolved in methanol (30 mL) and S-benzal levulinic acid (2 g) referred above was added to it. Acetic acid (5 mL) was transferred to above solution and sodium hydroxide (0.3 g) was dissolved in methanol (30 mL) and S-benzal levulinic acid referred above (2 g) was added to it. Acetic acid (5 mL) was transferred to above solution and electrolysis was carried out at current density 0.3 amp/cm², T 30°–35° and voltage 20 to 30 volts for 4 h. After 4 h again 0.5 mL of acetic 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. Ether layer was washed with sodium bicarbonate solution (5%) in water and dried over anhydrous sodium sulphate and evaporated to get a neutral product, b.p. 140°/20 mm.

Infrared spectrum showed peaks at 3000 to 2900 cm⁻¹ corresponding to CH and peak at 1750 cm⁻¹ corresponding to carbonyl (C=O) group and peak at 1625 cm⁻¹ corresponding to aromatic ring. % Analysis, Found (Calcd.): C = 82.50 (82.62), H = 7.70 (8.00). PMR (CDCl₃) = 0.9 (t, 3H of CH₃ of Cl), 1–2 (m, 2H of CH₂ of C₂), 1.4 (t, 2H of CH₂ of C₃), 7.2–7.8 (s, 5H of phenyl ring), 7.9 (d, 2H of C₅ and C₆).

7-Phenyl-5-keto-hepta-6-7-ene

Sodium hydroxide (0.3 g) was dissolved in methanol (30 mL) and S-benzal levulinic acid (2 g) referred to above was added to it. Propionic acid (5 mL) was transferred to above solution and sodium hydroxide (0.3 g) was dissolved in methanol (30 mL) and S-benzal levulinic acid referred, above (2 g) was added to it. Propionic acid (5 mL) was transferred to above solution and electrolysis was carried out at current density 0.3 amp/cm², T 30°–35° and voltage 20 to 30 volts for 4 h. After 4 h 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 propionic acid and extracted with ether. Ether layer was washed with sodium bicarbonate solution (5%) water and dried over anhydrous sodium sulphate and evaporated to get a neutral product b.p. 140°/20 mm.

Infrared spectrum showed peaks at 2900 to 3000 cm⁻¹ corresponding to CH and peak at 1750 cm⁻¹ corresponding to carbonyl (C=O) group and peak at 1625 cm⁻¹ corresponding to aromatic ring. % Analysis, Found (Calcd.): C = 82.50 (82.97); H = 8.0 (8.5).

REFERENCES

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2. R.N. Sen and B.C. Roy, *J. Indian Chem. Soc.*, **15**, 40 (1930).

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