

STUDIES IN SESQUITERPENEŠ

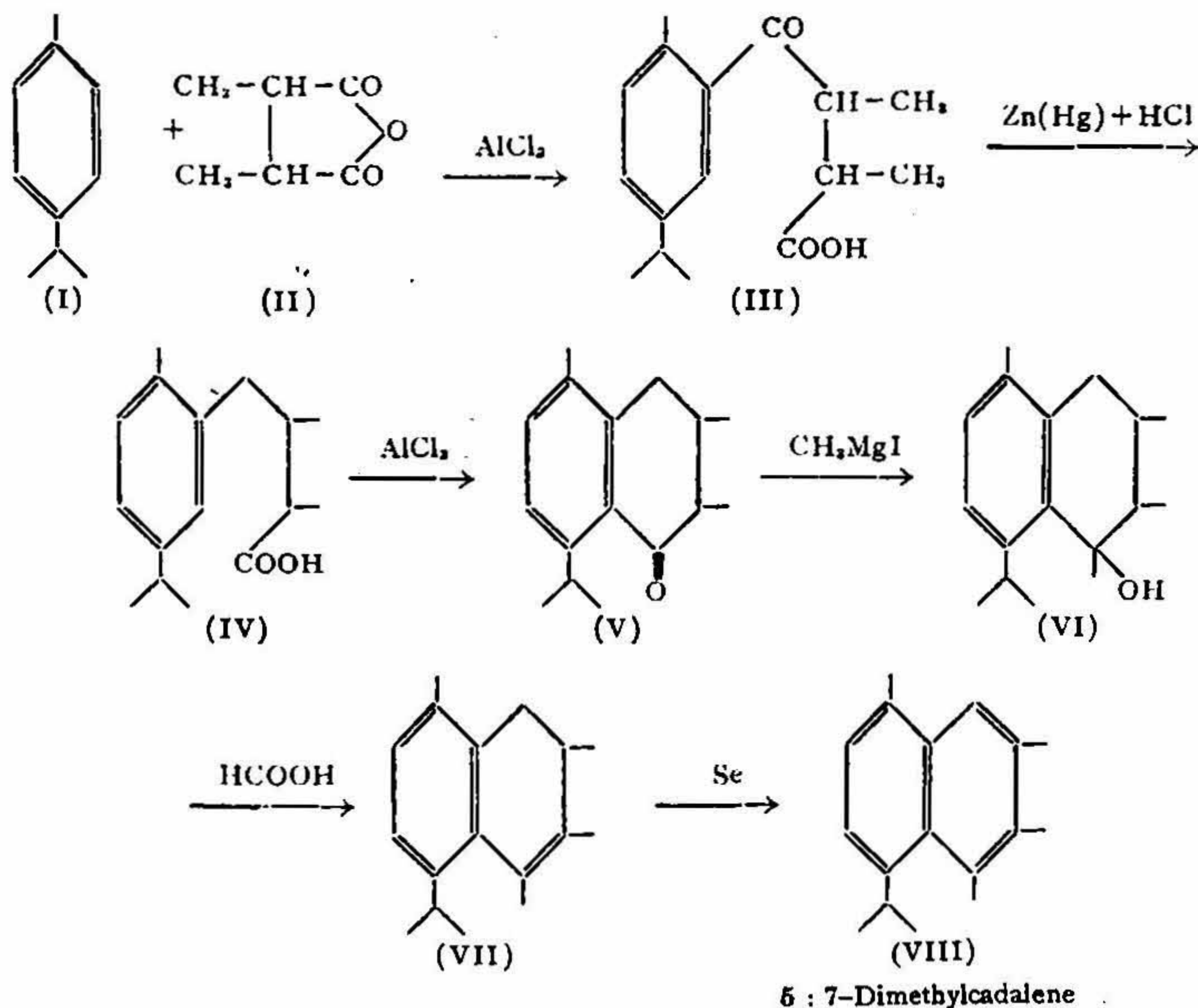
Part VII. Synthesis of 5 : 7-Dimethylcadalene (1 : 5 : 6 : 7-Tetramethyl 4-isopropylnaphthalene)

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In continuation of the studies in sesquiterpene series (Gupta and Muthana, *J. Indian Inst. Sci.*, 1953, 35, 259 *et seq.*), the present paper deals with the synthesis of 5:7-dimethyl cadalene, according to the following scheme:



p-Cymene (I), when condensed with α : β -dimethyl-succinic anhydride (II) in nitrobenzene solution in presence of anhydrous aluminium chloride, yielded β -(*p*-cymoyl-2)- α : β -dimethylpropionic acid (III), which on Clemmensen's reduction furnished γ -(*p*-cymoyl-2)- α : β -dimethylbutyric acid

(IV). The latter on cyclisation in presence of anhydrous aluminium chloride gave 2:3:5-trimethyl-8-isopropyl-tetralone-1 (V), which on treatment with methylmagnesium iodide and subsequent dehydration of the crude carbinol (VI) with formic acid, afforded 1:5:6:7-tetramethyl-4-isopropyl-dihydronaphthalene (VII). The hydrocarbon (VII) on dehydrogenation with selenium gave 5:7-dimethylcadalene.

EXPERIMENTAL

(i) β -(*p*-cymoyl-2-)- α : β -dimethylpropionic acid (III) has been prepared according to the method described by Gupta and Muthana, *Ibid.*, 1953, 35, 261).

(ii) γ -(*p*-cymyl-2-)- α : β -dimethylbutyric acid (IV).—Methyl ester of the acid III (5 g.), zinc amalgam (9 g.) concentrated hydrochloric acid (16 c.c.), water (15 c.c.) and toluene (10 c.c.) were refluxed together for 30 hours. Concentrated hydrochloric acid (6 c.c.) was added every 6 hours. After cooling the mixture, toluene layer was separated and washed with water. Toluene was removed on water-bath under suction and the residue purified by distillation. The acid was obtained as a colourless viscous liquid, b.p. 140–5° C./2 mm. Yield 3.9 g. (Found: C, 77.53; H, 9.38. $C_{16}H_{23}O_2$ requires C, 77.732; H, 9.31 per cent.).

(iii) 2:3:5-Trimethyl-8-isopropyltetralone-1 (V).—The acid (IV, 3.7 g.) was converted into acid chloride with phosphorus pentachloride (3.7 g.) in benzene solution, and the acid chloride, without further purification, was cyclised in presence of anhydrous aluminium chloride (*cf.* “preparation of 2:4:5-trimethyl-8-isopropyl tetralone,” Gupta and Muthana, *Ibid.*, 1953, 35 A, 263). The ketone was obtained as a colourless mobile liquid; b.p. 115° C./3 mm. Yield 1.1 g. (Found: C, 82.81; H, 9.37. $C_{18}H_{23}O$ requires C, 83.48; H, 9.564 per cent.).

2:4-Dinitrophenylhydrazone of the ketone was prepared by the sulphuric acid method, and crystallised from alcohol in scarlet red crystalline powder, m.p. 205° C. (Found: N, 13.61. $C_{22}H_{26}N_4O_4$ requires N, 13.658 per cent.).

(iv) 1:5:6:7-Tetramethyl-4-isopropyl-dihydronaphthalene (VII).—To a Grignard mixture, prepared from magnesium (0.21 g.; 2 mols.), methyl iodide (1.5 g.) and ether (10 c.c.), a solution of the ketone (VII, 1 g., 1 mol.) in ether (10 c.c.) was added. The contents were refluxed for 12 hours, and the complex decomposed with dilute sulphuric acid (10 c.c.) and ice (15 g.). The crude carbinol was dehydrated with formic acid (90%; 10 c.c.) and the hydrocarbon (VII) isolated, and purified by distilling over sodium; b.p.

115–16° C./3 mm. Yield 0.4 g. (cf. "Preparation of 1:5:6:8-tetramethyl 4-isopropylidihydronaphthalene, Synthesis of 5:8-dimethylcadalene," Gupta and Muthana, *Ibid.*, 1953, 35 A, 131).

(v) *5:7-Dimethylcadalene (VIII)*.—The hydrocarbon (VII, 0.4 g.) was dehydrogenated with selenium (0.2 g.) by heating at 300–330° C. for 40 hours. The dehydrogenated product was purified by distilling over sodium (twice), b.p. 118–20° C./2 mm. Yield 0.15 g. (Found: C, 89.86; H, 9.69; $C_{17}H_{22}$ requires C, 90.265; H, 9.735 per cent.).

Trinitrobenzene compound was prepared by mixing hot alcoholic solutions of trinitrobenzene and the hydrocarbon. Bright yellow needles thus obtained were crystallised from alcohol (twice), m.p. 160–61° C. (Found: N, 9.41. $C_{23}H_{25}N_3O_6$ requires N, 9.52 per cent.).

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