STUDIES IN SESQUITERPENES

Part IV. Synthesis of 2:3-Dimethyl Eudalene

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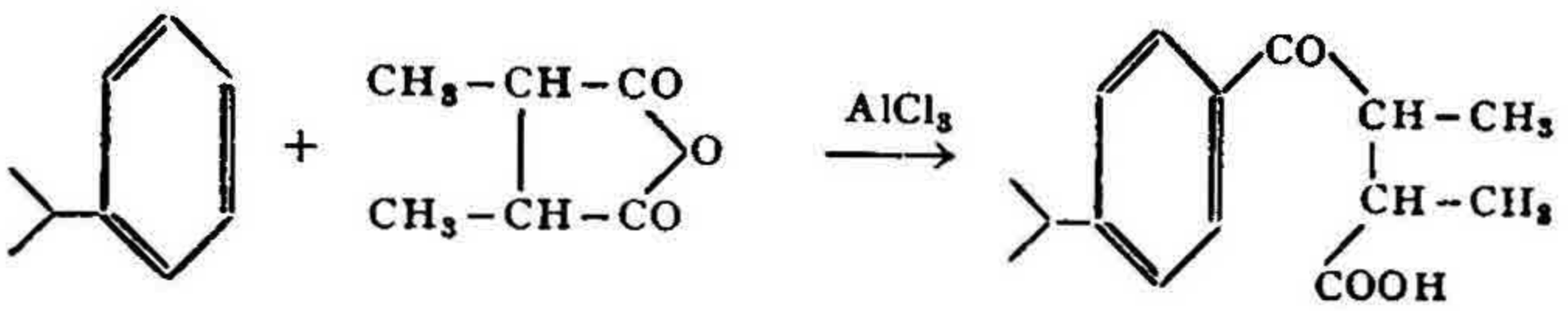
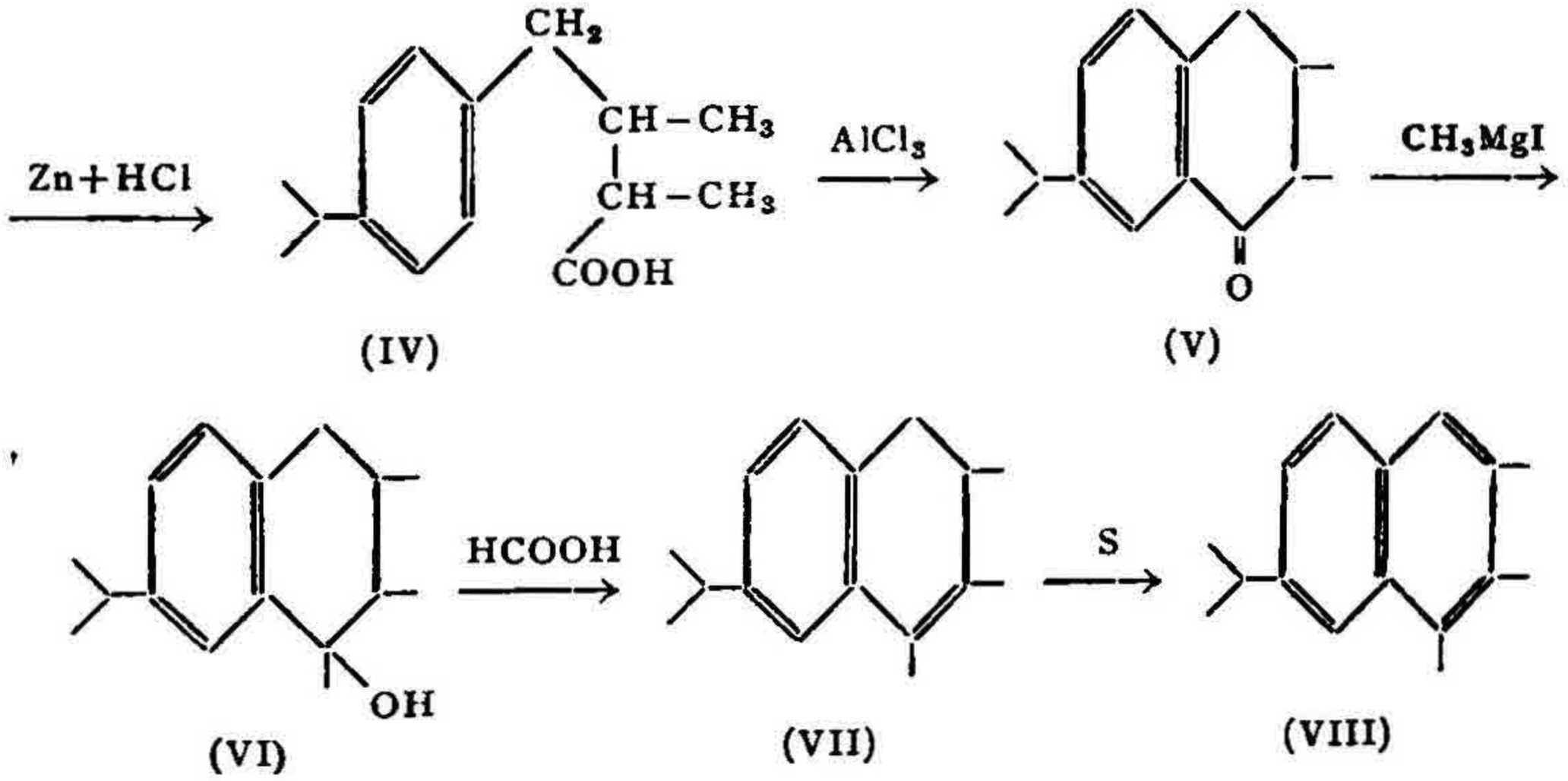
In continuation of the syntheses of dimethyl-cadalenes and dimethyl-eudalenes published in the earlier parts of this series of investigations (Gupta and Muthana, *J. Indian Inst. Sci.*, 1953, **35A**, 263) the synthesis of 2:3 dimethyl eudalene has been accomplished as outlined below:



(I) (II) (III)



(IV) (V) (VI) (VII) (VIII)

Isopropylbenzene (I) was condensed with α:β-dimethyl succinic anhydride (II) in nitrobenzene solution in the presence of anhydrous aluminium chloride, when β-(*p*-isopropyl benzoyl)-α:β-dimethyl-propionic acid (III) was obtained. The latter was reduced with zinc and hydrochloric acid and γ-(*p*-isopropyl-benzene)-α:β-dimethyl-butyric acid (IV), thus obtained, was cyclised in presence of anhydrous aluminium chloride to 1:2-dimethyl-7-isopropyl-tetralone-1 (V). The ketone (V) was treated with methyl magnesium iodide and the crude carbinol (VI), thus isolated, was dehydrated with formic acid

to yield 1 : 2 : 3-trimethyl-7-isopropyldihydronaphthalene (VII), which on dehydrogenation with sulphur furnished 2 : 3-dimethyleudalene.

EXPERIMENTAL

(i) *β-(p-Isopropyl benzoyl)-α : β-dimethyl propionic acid (III).*—Isopropylbenzene (I, 41 g., 1·1 mol.) was condensed with α : β-dimethyl-succinic anhydride (II, 40 g., 1 mol.) in nitrobenzene (150 c.c., dry and freshly distilled) in presence of anhydrous aluminium chloride (94·6 g., 2·2 mol.) [for details see Gupta and Muthana, Preparation of β-(*p*-isopropylbenzoyl)-α-methylpropionic acid (*Ibid.*, 1953, **35A,** 263)]. The orange red syrup obtained was decomposed with ice (250 g.) and concentrated hydrochloric acid (60 c.c.). After removing nitrobenzene by steam distillation, the oily layer was extracted with ether (4 times). The ethereal extract was washed with water (thrice) and extracted with dilute sodium carbonate solution (4 times). The alkaline extract was boiled to remove traces of nitrobenzene, treated with norite, filtered, cooled, and acidified with concentrated hydrochloric acid (congo red). The liberated viscous acid was extracted with ether (thrice), and the ethereal solution was washed with water and dried over anhydrous sodium sulphate. After removing three-fourth of ether, petroleum ether (30–60°) was added, and on keeping in ice-chest for 24 hours, the acid crystallised out in colourless needles, m.p. 88–9° C. Yield 13 g. (Found: C, 71·83; H, 7·6; $C_{15}H_{20}O_3$ requires C, 72·58; H, 8·063 per cent.).

(ii) *γ-(p-Isopropylbenzene)-α : β-dimethylbutyric acid (IV).*—The keto acid (III, 22 g.), concentrated hydrochloric acid (65 c.c.), toluene (35 c.c.), water (10 c.c.) and amalgamated zinc (35 g.) were heated under reflux for 40 hours, adding concentrated hydrochloric acid (15 c.c.) every 6 hours. The mixture was cooled and toluene layer separated and washed with water. After removing toluene on water-bath under suction, the acid was purified by distilling under reduced pressure; b.p. 155–60°C./1 mm. Yield 18 g. (Found: C, 76·93; H, 9·167; $C_{15}H_{22}O_2$ requires C, 76·93; H, 9·4 per cent.).

(iii) 2 : 3-*Dimethyl-7-isopropyl-tetralone-1* (*V*).—Acid chloride was prepared from the acid (IV, 17 g., 1 mol.) and phosphorus pentachloride (16·5 g., 1·1 mol.) and without further purification was cyclised in presence of anhydrous aluminium chloride (10·68 g.; 1·1 mol.) in benzene solution. (For details *cf.* Gupta and Muthana, Preparation of 2 : 4 : 5-trimethyl-8-isopropyl-tetralone-1, *ibid.*, 1953, **35A,** 263). The complex was decomposed with ice (100 g.) and concentrated hydrochloric acid (20 c.c.). The ethereal layer was separated, washed with dilute hydrochloric acid, water, dilute

sodium hydroxide and then with water. After drying over anhydrous sodium sulphate, ether was removed and the ketone purified by distillation. A colourless mobile liquid was obtained; b.p. 131–2° C./1 mm. Yield: 5 g. (Found: C, 82·7; H, 9·54; $C_{15}H_{20}O$ requires C, 83·33; H, 9·258 per cent.)

2:4-*Dinitrophenyl-hydrazone* of the ketone (IV) was prepared by sulphuric acid method and crystallised from alcohol in bright red needles, m.p. 157–8° C.

(iv) 1:2:3-*Trimethyl-7-isopropyldihydronaphthalene* (*VII*).—To Grignard solution, prepared from magnesium (1·2 g., 2·4 mol.), methyl iodide (7·5 g., 2·4 mol.) and ether (50 c.c.), a solution of the ketone (V, 5 g., 1 mol.) in ether (25 c.c.) was added in a thin stream under stirring and ice-cooling. The mixture was left overnight and refluxed for 3 hours next day. The complex was decomposed with a mixture of ammonium chloride (50 g.), water (25 c.c.) and ice (100 g.), and worked up in the usual manner (*cf.* Gupta and Muthana, Preparation of 1:2:4-trimethyl-7-isopropyldihydronaphthalene, *loc. cit.*). The crude carbinol (VI) was dehydrated with 85 per cent. formic acid (20 c.c.) by heating on water-bath for 6 hours. After working up the product, the hydrocarbon (VII) was purified by distilling over sodium under reduced pressure, b.p. 115–6° C./2 mm. Yield 3·6 g.

(v) 2:3-*Dimethyleudalene* (*VIII*).—The hydrocarbon (VII, 3 g.) was dehydrogenated in presence of sulphur (0·45 g.) by heating at 230° C. for half an hour and at 260° for further half an hour. The dehydrogenated product was purified by repeatedly distilling over sodium when 2:3-dimethyleudalene was obtained as a colourless liquid, b.p. 130–10° C./2 mm. Yield 2·5 g. (Found: C, 89·94; H, 9·31; $C_{16}H_{20}$ requires C, 90·57; H, 9·43 per cent.)

Picrate was prepared in the usual manner from alcohol and crystallised orange red needles, m.p. 104–5° C.

T. N. B. Compound was prepared by mixing hot alcoholic solutions of trinitrobenzene and the hydrocarbon. On crystallising from alcohol bright yellow needles were obtained, m.p. 115–6° C.

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