

STUDIES IN SESQUITERPENES

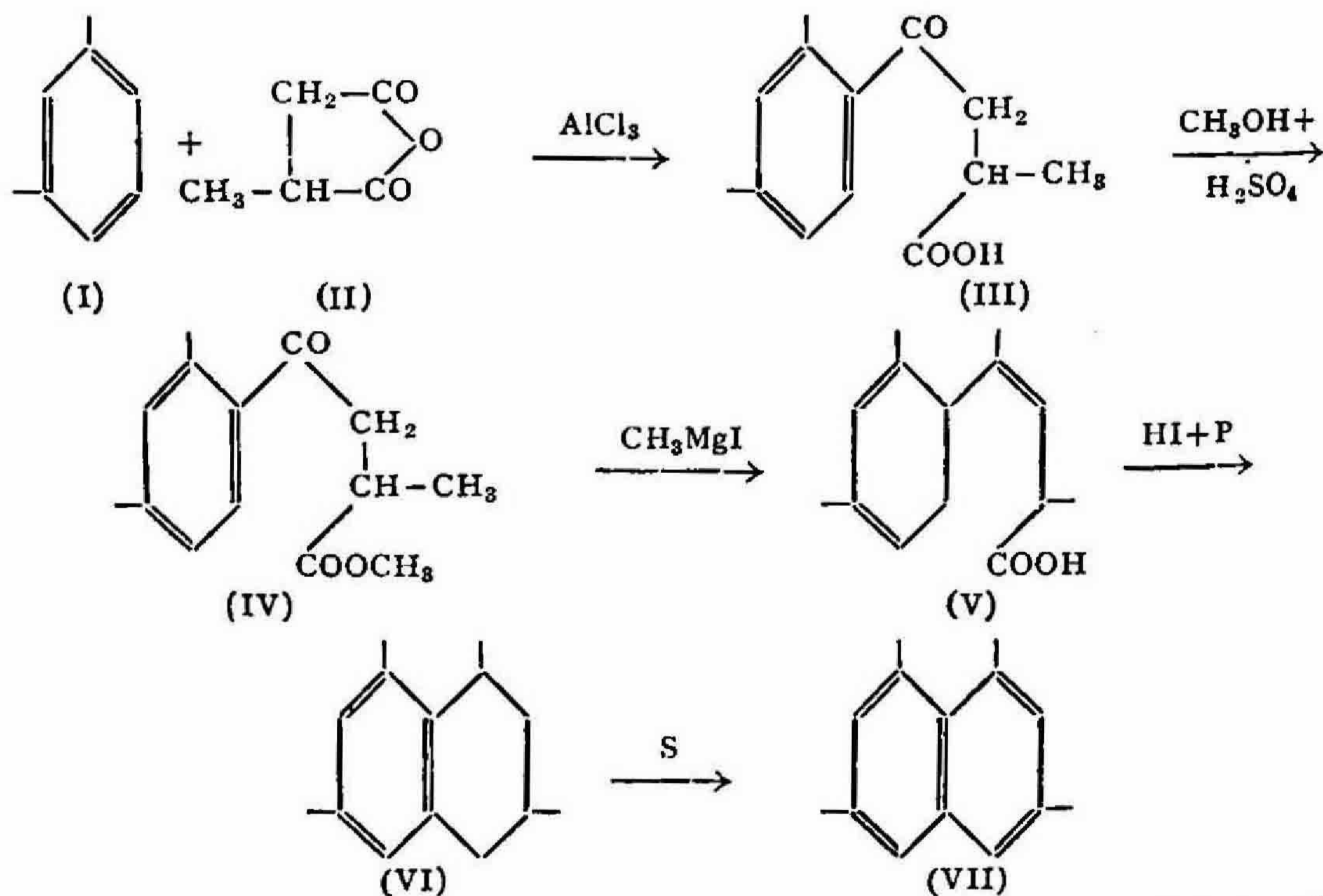
Part VI. Synthesis of 1 : 3 : 6 : 8-Tetramethylnaphthalene

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During the course of investigations in the alkylnaphthalene series (Gupta and Muthana, *J. Ind. Inst. Sci.*, 1953, 35, 259 *et. seq.*), it was observed that Tischenko (*Bull. Soc. Chim.*, 1930, (4) 47, 1137) while investigating the condensation of acetone in presence of sulphuric acid, isolated a pentamethylnaphthalenic compound which on dehydrogenation furnished a tetramethylnaphthalene, and the latter on oxidation yielded mellophanic acid, indicating the position of methyl groups at 1, 3, 6 and 8 carbon atoms. It was proposed to establish the identity of this compound beyond any doubt by synthesizing it by an unequivocal method, and the scheme that was followed is outlined below:



m -xylene (I) was condensed with methylsuccinic anhydride (II), in nitrobenzene in presence of anhydrous aluminium chloride to give β -(m -xyloyl-2)- α -methylpropionic acid (III), the identity of which has already been established in an earlier paper of this series, Part V (Gupta and Muthana,

“Synthesis of 1:3:6-trimethylnaphthalene,” *ibid.*, 1953, 35, 310). The ketoacid (III) was esterified and subjected to inverse Grignard reaction with methylmagnesium iodide to furnish γ -(*m*-xylyl-2-)- α : γ -dimethyl-vinyl-acetic acid (V). The latter was refluxed with a mixture of phosphoric acid, red phosphorus and iodine to effect the process of reduction, cyclisation and further reduction in one step and subsequently give rise to 1:3:6:8-tetra-methyltetralin (VI), which on dehydrogenation with sulphur furnished 1:3:6:8-tetra-methylnaphthalene (VII); m.p. 81° C., picrate; m.p. 151–2° C. T.N.B. compound; m.p. 175–6° C. Tischenko (*loc. cit.*) reports picrate, m.p. 151–2° C.

EXPERIMENTAL

(i) 1:3:6:8-Tetramethyltetralin (VI)

γ -(*m*-Xylyl-2-)- α : γ -dimethylvinylacetic acid (for preparation see “Synthesis of 3:8-dimethylcadalene,” Gupta and Muthana, *ibid.*, 1953, 35, 310) (VI, 15 g.; 1 part), phosphoric acid (syrupy, d. 1.75, 45 c.c., 3 parts), red phosphorus (15 g.; 1 part) and iodine (7.5 g.; 0.5 part), were heated together under reflux in an oil-bath at 170–80° C. for 60 hours. The mixture was cooled, diluted with water and extracted with ether (4 times). The ethereal extract was washed with water, sodium carbonate solution, water, sodium thiosulphate solution and water successively and dried over anhydrous sodium sulphate. Ether was removed and the residue purified by distillation. B.p. 110–3° C./2 mm. Yield, 7 g. (Found: C, 89.56; H, 10.24; C₁₄H₂₀ requires C, 89.35; H, 10.65 per cent.).

(ii) 1:3:6:8-Tetramethylnaphthalene (VII)

The hydrocarbon (VI; 7 g.) was dehydrogenated in presence of sulphur (2.4 g.) by heating in a metal-bath at 260° C. for one hour. The dehydrogenated product was purified by repeatedly distilling over sodium, b.p. 115–16° C./2 mm. Yield 2.5 g. On cooling the distilled product in ice-salt mixture a white solid separated which was crystallised from dilute alcohol (thrice); m.p. 81° C. (Found: C, 90.8; H, 8.55; C₁₄H₁₆ requires C, 91.31; H, 8.69 per cent.).

Picrate was prepared by mixing hot and saturated alcoholic solutions of picric acid and hydrocarbon, when orange red needles separated which were crystallised from alcohol twice; m.p. 151–2° C.

T.N.B. Compound was prepared in the usual manner and crystallised from alcohol (twice) in bright yellow needles, m.p. 175–6° C (Found: N, 10.60; C₂₀H₁₉N₃O₆ requires, N, 10.58 per cent.).

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