1 : 6-DIMETHYL-4-ETHYLNAPHTHALENE

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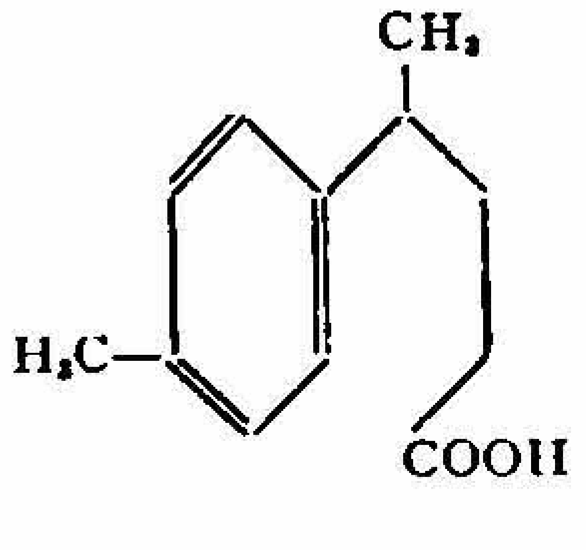
Summary

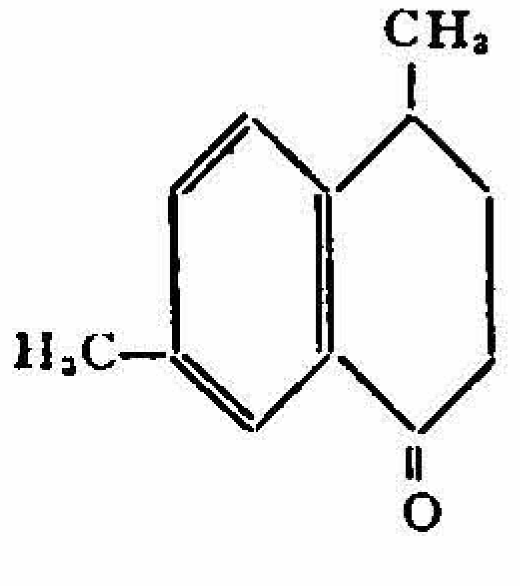
1 : 6-Dimethyl-4-ethylnaphthalene has been prepared by the succinic anhydride method.

A sesquiterpene isolated from the destructive distillation products of Black Damar resin (*Canarium strictum*, Roxb.) has been degraded to a naphthalene derivative, expected to be 1 : 6-dimethyl-4-ethylnaphthalene.[1] The present synthesis was undertaken to check the identity of the product.

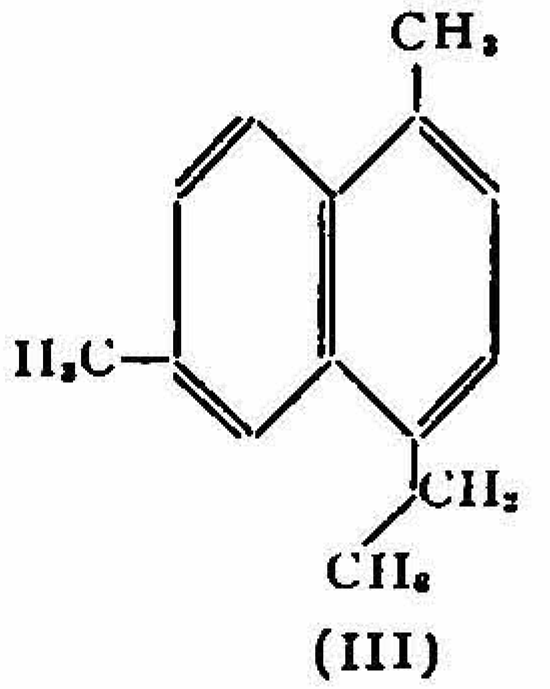
γ-Methyl-γ-(*p*-tolyl)-vinylacetic acid[2] was reduced by Raney-nickel alloy or by hydriodic acid to give γ-(*p*-tolyl)-valeric acid (I) (*cf.* Lit. [2–5]). This acid on cyclisation with polyphosphoric acid yielded the required 4 : 7-dimethyl-tetralone (II); this ketone has been obtained previously by other workers[3–5] by different procedures. Action of ethyl magnesium bromide on this ketone gave the corresponding carbinol, which was dehydrated with a trace of iodine in benzene. The resulting dihydronaphthalene was dehydrogenated with chloranil in boiling xylene to give the required 1 : 6-dimethyl-4-ethyl-naphthalene (III).



(I)



(II)



(III)

Experimental

γ-(p-*Tolyl*)-*valeric acid* (I).—γ-Methyl-γ-(*p*-tolyl)-vinylacetic acid, required for this purpose, was prepared by the method of Rupe and Steinbach[2] and was reduced by two different procedures.

(i) The unsaturated acid (6·5 gm.) was heated in an oil-bath at 130–40° for 18 hours with hydriodic acid (*d* 1·75, 35 gm.) and red phosphorus (4·5 gm.). The mixture was cooled, poured into water and extracted with ether. The extract was shaken with aqueous sodium carbonate solution, and the alkaline solution was clarified with Norit charcoal, filtered and acidified with hydrochloric acid

(Congo Red). The oily product was extracted with ether, washed with brine and dried ($MgSO_4$). Fractionation gave γ-(p-tolyl)-valeric acid as a thick, viscous liquid, b.p. 173°/9 mm. (Lit.[2] gives b.p. 173–74°/9 mm.) n_D^{25} 1·5123, yield 2·65 gm. (41%).

(ii) The unsaturated acid (13 gm.) was dissolved in sodium hydroxide solution (15 gm. in 110 c.c. of water) and reduced by the cautious addition of nickel aluminium alloy (— 40 mesh, 7·5 gm.) by following the procedure of Schwenk *et al.*[6] The acid was obtained as a thick, viscous oil, b.p. 156°/3 mm., n_D^{25} 1·5113, yield 9·02 gm. (69%).

4:7-*Dimethyl-tetralone* (II).—γ-(p-tolyl)-valeric acid (2 gm.) was heated for 2 hours on a water-bath with polyphosphoric acid[7] prepared from ortho-phosphoric acid (85%, 6 gm.) and phosphorus pentoxide (10 gm.). The mixture was poured into water, extracted with ether, extract washed with sodium carbonate solution and brine, and dried ($MgSO_4$). Fractionation gave the ketone as a colourless oil, b.p. 129°/6 mm. (Lit.[3] gives b.p. 145–52°/15 mm.) n_D^{25} 1·5524, yield 1·55 gm. (86%).

The 2:4 *dinitrophenylhydrazone* (HCl method) was obtained from benzene in short deep-red needles, m.p. 232–33° (Found: N, 15·96%; $C_{18}H_{18}O_4N_4$ requires N, 15·82%).

1:6-*Dimethyl-4-ethyl-*1:2-*dihydronaphthalene.*—A solution of the above ketone (II, 4·7 gm., 1 mol) in dry ether (25 c.c.) was added to a Grignard solution of ethyl magnesium bromide, prepared from ethyl bromide (4·36 gm., 1·6 mols) and magnesium (0·98 gm., 1·6 mols) in dry ether (25 c.c.) and worked up in the usual way. The crude carbinol (5·15 gm., 94 %) thus obtained was dehydrated by refluxing its benzene solution (50 c.c.) with iodine (0·5 gm.), removing the water of dehydration azeotropically (1 hour). The mixture was then diluted with petroleum ether (25 c.c.) and washed with sodium thiosulphate solution, water and then brine, and finally dried over activated silica gel powder (6 gm.). Fractionation gave the dihydronaphthalene as a colourless oil, b.p. 134°/13 mm., n_D^{25} 1·5443, yield 2·78 gm. (55% on the ketone) (Found: C, 90·3%, H, 9·7%; $C_{14}H_{18}$ requires C, 90·33%, H, 9·67%).

1:6-*Dimethyl-4-ethylnaphthalene* (III).—The above dihydronaphthalene (2·12 gm., 1 mol) was refluxed for 8 hours with chloranil (2·95 gm., 1·05 mol) in dry xylene (25 c.c.).[8] The mixture was cooled, filtered to remove chloranil hydroquinone formed, and then diluted with petroleum ether (25 c.c.). The solution was washed with 4% potassium hydroxide solution and water, and dried (silica gel powder). Fractionation gave the required hydrocarbon as a colourless oil, b.p. 123–26°/2–3 mm., n_D^{25} 1·5932, yield 1·11 gm. (53%) (Found: C, 92·26%, H, 7·7%; $C_{14}H_{16}$ requires C, 92·3%, H, 7·7%).

The *picrate* was obtained from alcohol as long orange-red needles, m.p. 99–100° (Found: N, 10·26%; $C_{20}H_{19}O_7N_3$ requires N, 10·17%).

The *trinitrobenzene complex* was obtained from alcohol as short yellow needles, m.p. 134·5–136° (Found: N, 10·23%; $C_{20}H_{19}O_6N_3$ requires N, 10·58%) (Vasishth[1] reports m.p. 124–26°).

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