## 39. 1-*Methyl and* 1 : 7-*Dimethyl*-4-iso*propylnaphthalene.*

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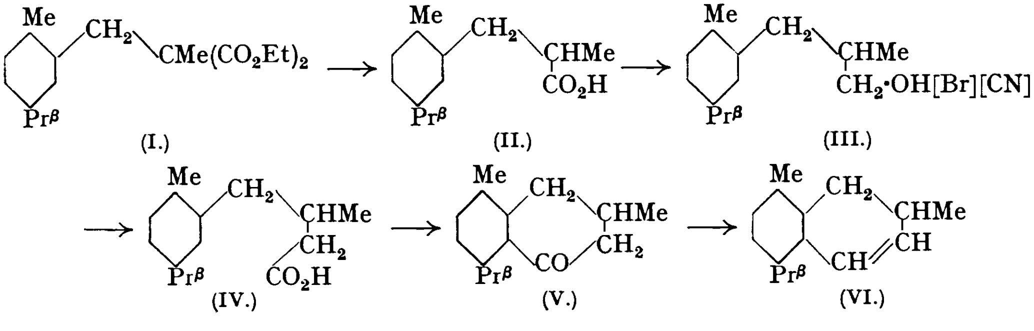
1-METHYL-2-CHLOROMETHYL-4-*iso*PROPYLBENZENE was condensed with ethyl sodiomalonate to yield ethyl (2-cymylmethyl)malonate. Methylation of the sodio-ester with methyl iodide (methyl sulphate cannot be employed) afforded ethyl (2-cymylmethyl)-methylmalonate (I) in satisfactory yield. Saponification of the ester and decarboxylation gave β-2-*cymyl*iso*butyric acid* (II), which was esterified and reduced by Bouveault's method to γ-2-cymyl*iso*butyl alcohol (III). This alcohol was converted, by way of the bromide and cyanide, into γ-2-cymyl-β-methylbutyric acid (IV), the chloride of which passed readily into 1-keto-3 : 5-dimethyl-8-*iso*propyl-1 : 2 : 3 : 4-tetrahydronaphthalene (V) on treatment with aluminium chloride. Reduction of the ketone by Clemmensen's method was unsatisfactory, but sodium and alcohol gave a mixture of the carbinol with the corresponding unsaturated hydrocarbon (VI). This mixture was dehydrogenated by sulphur to 1 : 7-*dimethyl*-4-iso*propylnaphthalene,* which, unlike the isomeric cadalene, is solid (m. p. 60°) at room temperature.



Repetition of the above synthetic process, but omitting the methylation stage, furnished 1-methyl-4-*iso*propylnaphthalene, already synthesised by Ruzicka and Mingazzini (*Helv. Chim. Acta*, 1922, **5**, 714) by a slightly different route.

## EXPERIMENTAL.

1-*Methyl*-2-*chloromethyl*-4-iso*propylbenzene*.—The 54% yield obtained by Blanc (*Bull. Soc. chim.*, 1923, **33**, 313) may be increased to 70% by the following modification. Paraform (18 g.), *p*-cymene (130 g.), and powdered $ZnCl_2$ (14·4 g.) at 60° were stirred so that a thick emulsion was produced, and dry HCl was passed for 7 hr. 57 G. of *p*-cymene were recovered and 77 g. of the chloromethyl compound, b. p. *ca.* 120°/12 mm., were obtained.

*Ethyl* (2-*Cymylmethyl*)*malonate*.—Ethyl sodiomalonate (1·2 mols.) and 1-methyl-2-chloromethyl-4-*iso*propylbenzene afforded a 66% yield of this ester (b. p. 197—200°/9·5 mm.) when boiled with dry $C_6H_6$ for 7—8 hr.

*Ethyl* (2-*Cymylmethyl*)*methylmalonate*.—MeI (1·2 mols.) was gradually added to a solution of Na (1·05 atoms) and the substituted malonic ester in abs. EtOH (16 c.c. per g. Na), and the mixture boiled for 3—4 hr. The product was obtained as a thick oil (yield, 76%), b. p. 181—185°/8 mm. Approximately the same yield resulted by conducting the condensation in $C_6H_6$.

(2-*Cymylmethyl*)*methylmalonic Acid*.—The ester was refluxed (3 hr.) with a solution of Na (4 atoms) in 95% EtOH (20 c.c. per g. Na). The *acid* obtained was insol. in the majority of solvents, but separated from 80% MeOH in colourless plates, m. p. 170° (Found : C, 68·1; H, 7·6; equiv. by titration, 134. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%; equiv., 132).

β-2-*Cymyl*iso*butyric Acid*.—The dibasic acid was decarboxylated at 180°, yielding the monocarboxylic *acid* as a thick colourless oil, b. p. 190—195°/14 mm. (yield, 87%) (Found : equiv. from Ag salt, 221. $C_{14}H_{20}O_2$ requires equiv., 220). The acid, 1·3*N*-$Na_2CO_3$ (1·5 mols.), and $Me_2SO_4$ (1 mol.) gave a 79% yield of ester, b. p. 142—148°/8 mm.

γ-2-*Cymyl*iso*butyl Alcohol*.—Reduction of the ester, dissolved in abs. EtOH [3 vols., dried over $Al(OEt)_3$], with Na (14 atoms) and abs. EtOH (8 c.c. per g. Na) at 140° (4 hr.) gave the alcohol as a colourless oil, b. p. 157—158°/14 mm. (average yield, 85%).

γ-2-*Cymyl*-β-*methylbutyric Acid*.—The above alcohol was heated with 50% HBr–AcOH (4 mols.) for 16 hr. at 140°, and the bromide converted into the cyanide by refluxing it (12—16 hr.) with KCN (2·5 mols.) and 95% EtOH (25 c.c. per g. KCN). The crude cyanide was boiled with 10*N*-alc. KOH (5 mols.) for 10—12 hr., most of the EtOH removed, and the residue poured into $H_2O$. An attempt to remove neutral impurities by extraction with $Et_2O$ resulted in solution of the potassium salt in the $Et_2O$ layer. The acid was obtained as a colourless oil, b. p. 182—188°/9 mm. (yield, *ca.* 30%).

The acid chloride, b. p. 150—151°/8 mm., was obtained by warming the acid at 60° for 2—3 hr. with $SOCl_2$ (1 mol.) and light petroleum (free from aromatic hydrocarbons; 3 c.c. per g. of acid). Yield, 92%.

1-*Keto*-3 : 5-*dimethyl*-8-iso*propyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—A solution of the acid chloride in dry light petroleum (3 vols.; b. p. 60—80°) was added to $AlCl_3$ (1·1 mols.) covered with the same solvent, and the mixture ultimately refluxed for 3 hr. The cyclic ketone was obtained as a colourless oil, b. p. 150—155°/8 mm. (yield, 94%).

1 : 7-*Dimethyl*-4-iso*propylnaphthalene*.—The ketone was reduced at 110° by means of Na (13 atoms) and abs. EtOH (12 c.c. per g. Na). The product, b. p. 140—155°/8 mm., consisting of the carbinol and the corresponding unsaturated hydrocarbon (yield, 80%), was heated with S (1·1 atoms) at 180° until evolution of $H_2O$ ceased and then at 230° for 5 hr. The crude product, b. p. 150—158°/12 mm., was redistilled from Na and converted into the *picrate*, which separated from EtOH in orange-red needles, m. p. 92° [Found : *M*, by titration with 0·025*N*-$Ba(OH)_2$ (lacmoid), 425. $C_{21}H_{21}O_7N_3$ requires *M*, 427]. On decomp. of the picrate with $NH_3$ the naphthalene *hydrocarbon* was obtained; it crystallised from 90% EtOH in plates, m. p. 60° (Found : C, 90·9; H, 9·1. $C_{15}H_{18}$ requires C, 90·9; H, 9·1%). The styphnate formed yellow needles, m. p. 120°.

β-2-*Cymylpropionic Acid*.—Saponification and decarboxylation of ethyl 2-cymylmethylmalonate gave the monocarboxylic *acid* as a viscous oil, b. p. 165—170°/4·5 mm., which slowly solidified to crystals : these were exceedingly sol. in the usual solvents, but separated from dil. AcOH in plates, m. p. 85° (Found : *M*, by titration, 206·1. $C_{13}H_{18}O_2$ requires *M*, 206·2). The methyl ester, b. p. 162—168°/11 mm., was obtained in 78% yield by the action of $Na_2CO_3$ and $Me_2SO_4$ as described above.

γ-2-*Cymylpropyl alcohol*, b. p. 152—158°/11 mm. (yield, 76%), γ-2-cymylbutyric acid, b. p.

173—180°/4 mm. (yield, 33%), and its acid chloride, b. p. 151—153°/7·5 mm. (yield, 91%), and 1-keto-5-methyl-8-*iso*propyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 140—145°/6 mm. (yield, 80%), were obtained by the methods described in the case of the methyl homologues.

Reduction of the ketone (11·2 g.) by Clemmensen's method gave a poor yield (2·85 g.) of the hydrocarbon, b. p. 135—140°/12 mm., but reduction with Na and abs. EtOH furnished a mixture, b. p. 135—160°/12 mm., of the carbinol with the unsaturated hydrocarbon in 64% yield.

1-*Methyl*-4-iso*propylnaphthalene*.—Dehydrogenation of either the dihydro-derivative or the crude carbinol and distillation of the product from Na gave the naphthalene hydrocarbon, which was purified by regeneration from the picrate and then had b. p. 145—148°/12 mm.; $d_{4^\circ}^{14\cdot5^\circ}$ 0·9934; $n_{\mathrm{D}}^{14\cdot5^\circ}$ 1·5907; $[R_L]_{\mathrm{D}}$ 62·50; $\mathrm{E}M_{\mathrm{D}}$ 2·39; $\mathrm{E}\Sigma_{\mathrm{D}}$ 1·30. The picrate separated from EtOH in orange needles, m. p. 99° (Ruzicka and Mingazzini, *loc. cit.*, give m. p. 99—100°) (Found: $M$, by titration, 413·5. Calc. for $C_{20}H_{19}O_7N_3$: $M$, 413).

The styphnate separated from EtOH in fine yellow needles, m. p. 102°.

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