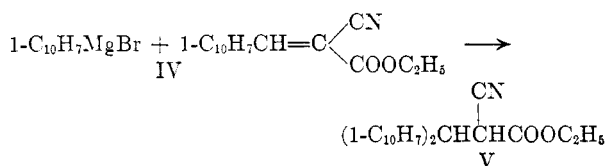


V, was obtained. Since the latter could be hydrolyzed to the corresponding malonic acid in 93% yield a distinct improvement in the synthesis of hexahelicene^{3c} has been attained.



EXPERIMENTAL

Diethyl 1-naphthylidenemalonate, II. In a flask fitted with a small packed column and a phase-separating head were placed 157 g. of 1-naphthaldehyde, 160 g. of diethyl malonate, 3 g. of benzoic acid, and 500 ml. of benzene. At reflux 5 ml. of piperidine was added. After 11 hr., during which four 2-g. additions of piperidine were made, slightly more than the theoretical amount of water had been collected. On distillation⁶ there was obtained 252 g. (85%) of II, b.p. 187–197° at 1.5–2.0 mm.

Diethyl phenyl-1-naphthylmethylmalonate, III. To a solution of 1-naphthylmagnesium bromide freshly prepared from 21 g. (0.1 mole) of 1-bromonaphthalene was added slowly with cooling 21 g. (0.085 mole) of diethyl benzylidenemalonate⁸ in 50 ml. of ether and the mixture was then stirred at room temperature for 6 hr. After treatment with saturated ammonium chloride solution and removal of ether from the washed and dried ether layer, there was obtained a crude solid mass which was heated with Skellysolve B (petroleum ether, b.p. 60–70°) and cooled. Filtration yielded 26.7 g. (84%) of III, m.p. 96–99°, good enough for further work. A sample recrystallized from absolute alcohol several times melted at 99.5–101.5°.⁷

When a solution of 21.5 g. of II in 50 ml. of ether was added to a solution of phenylmagnesium bromide freshly prepared from 17 g. of bromobenzene an insoluble complex separated. After stirring at room temperature for 6 hr., the reaction mixture was treated as above to yield 6.0 g. (22%)

(6) C. F. H. Allen and F. W. Spangler, *Org. Syntheses*, **25**, 42 (1945).

(7) G. A. Holmberg, *Acta Acad. Aboensis Math. et Phys.*, **16**, 138 (1948) gives the m.p. as 98–99°.

of III, m.p. 98–100°. In addition some biphenyl and a large quantity of tar were obtained.

Diethyl di-1-naphthylmethylmalonate. To a stirred mixture of 0.1 mole of freshly prepared magnesium bromide and 15 g. (0.05 mole) of II in ether was added 140 ml. of 0.5N (0.07 mole) 1-naphthylmagnesium bromide. After refluxing for 2 hr. the reaction mixture was treated with ammonium chloride solution and worked up as usual to yield 8.0 g. (38%) of III.⁵

To 3.0 g. (0.01 mole) of II in 20 ml. of dry ether was added under nitrogen 200 ml. of 0.1N di-1-naphthylmagnesium solution and 250 ml. of dry benzene. The mixture was heated and the ether distilled. After 40 hr. of refluxing, the mixture was decomposed by treating with ammonium chloride solution and worked up to yield 2.9 g. (97%) of II.

Ethyl 1-naphthylidenecyanoacetate, IV. A mixture of 100 g. of 1-naphthaldehyde, 74 g. of ethyl cyanoacetate, 6 g. of piperidine, 5 g. of benzoic acid, and 700 ml. of benzene was refluxed into a phase-separating head. After 1 hr. the theoretical amount of water had been collected. After the usual workup there was obtained 149 g. (92.8%) of crude IV, b.p. 180–195° at 1 mm. Recrystallization from alcohol afforded 142.6 g. (88.8%) of IV, m.p. 80.0–81.4°. The analytical sample melted at 81.0–81.4°.

Anal. Calcd. for C₁₈H₁₃O₂N: N, 5.6. Found: N, 5.3.

Ethyl di-1-naphthylmethylcyanoacetate, V. To the Grignard reagent prepared from 20.7 g. of 1-bromonaphthalene in ether-benzene and cooled to 0–5° was added 12.5 g. of IV in ether-benzene. After coming to room temperature the mixture was heated at reflux for 12 hr. and then poured into dilute hydrochloric acid. After the usual treatment 17.7 g. (94%) of V was isolated as a colorless solid, m.p. 189.8–191.0°, by crystallization from ethanol.

Anal. Calcd. for C₂₈H₂₁NO₂: C, 82.3; H, 5.6; N, 3.7. Found: C, 82.3; H, 5.6; N, 3.7.

Di-1-naphthylmethylmalonic acid. A mixture of 3.9 g. of V and 200 ml. of 50% aqueous alcoholic potassium hydroxide was refluxed for 31 hr., cooled, and poured into water. This aqueous solution was then poured into excess hydrochloric acid. The solid was collected and recrystallized from alcohol to yield 3.5 g. (92%) of the desired malonic acid,^{8c} m.p. 196° dec. Decarboxylation afforded the known 2,2-di-1-naphthylpropionic acid,^{8c} m.p. 248°.

COLUMBUS 10, OHIO

(8) Analyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Syntheses of 1'-Methyl- and 4'-Methyl-1,2-benzanthracenes¹

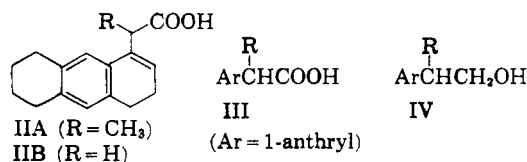
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The syntheses of 1'-methyl- and 4'-methyl-1,2-benzanthracene are described.

In a previous paper, the reasons for synthesizing relatively large amounts of all of the monomethyl-1,2-benzanthracenes were outlined and the syntheses of all but 1'-methyl- and 4'-methyl-1,2-benzanthracene were described.² In this paper are

described syntheses for the latter two compounds as outlined in the chart. More than 10 g. of each was made and is available for research workers.



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(2) M. S. Newman and R. Gaertner, *J. Am. Chem. Soc.*, **72**, 264 (1950).