atmosphere and at 100° for 1.5 hr. Crystallization did not occur after cooling; evaporation at reduced pressure under nitrogen left a sticky amber residue which was not purified.

Attempted cyclication of IV. A solution of IV in 21. of water was added, over a period of 9 hr., to 2.51. of 0.2N sodium hydroxide at about 50°, with stirring. Continuous extraction of the mixture for 2 days with ether, and evaporation of the ether gave 1.52 g. (68%) of light amber oil, n_D^{25} 1.5059, with a strong amine-like odor.

The product did not react with sodium iodide in acetone or with 2,4-dinitrophenylhydrazine reagent.

The infrared spectrum of a 20% solution of the product in carbon tetrachloride showed the following maxima (cm.⁻¹): 3390 (m) NH; 3030 (shoulder) CH=CH; 2960 (s) CH₂ and CH; 1759 (m) CO; 1655 (m) C=C; 1460 (m) CH₂; 1268 (m), 1163 (m), 1098 (m), 1038 (m), 677 (s), cis C=C.

Treatment of the product with benzoyl chloride or *p*nitrobenzoyl chloride, by the Schotten-Baumann method, gave brown gums which could not be crystallized. Both derivatives decolorized bromine in carbon tetrachloride; the dibromides were also noncrystalline. The picrate was a dark red oil which would not crystallize.

The chloroplatinate, prepared by addition of an excess of chloroplatinic acid in 95% ethanol to the amine, melted at $180-181^{\circ}$ with decomposition (preliminary darkening at 170°). Recrystallization could not be effected.

Anal. Calcd. for $(C_8H_{13}N)_{2}H_{2}PtCl_6$: C, 29.28; H, 4.30; N, 4.27; Pt, 29.74. Found: C, 30.55; H, 4.59; N, 4.20; Pt, 28.45.

UNIVERSITY OF MARYLAND COLLEGE PARK, MD.

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

Some Factors Influencing the 1,4-Addition of Grignard Reagents to Arylidenemalonic Esters

MELVIN S. NEWMAN AND HAROLD R. FLANAGAN¹

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The 1,4-addition of Grignard reagents to α , β unsaturated esters has long been known.² In this laboratory this type of reaction has often been used to build up compounds needed for the synthesis of polycyclic aromatic hydrocarbons.³ In each case the product was a compound of the symmetrical benzhydryl type, I.

 $\begin{array}{l} \operatorname{ArMgBr} + \operatorname{ArCH} = C(\operatorname{COOC}_2H_5)_2 \longrightarrow \\ & (\operatorname{Ar})_2 \operatorname{CHCH}(\operatorname{COOC}_2H_5)_2, \text{ I.} \end{array}$

yield.⁴ Thus, the yield is significantly better when the Grignard reagent with the larger steric requirement is added to the unsaturated ester with the lesser steric requirement, than in the reverse case. The greater tendency of 1-naphthylmagnesium bromide to add to α , β -unsaturated malonic ester is also apparent in the 45–53% yields obtained in the addition to II⁵, whereas the addition of phenylmagnesium bromide to II afforded at most a 22% yield.

$$C_{6}H_{5}MgBr + 1-C_{10}H_{7}CH = C(COOC_{2}H_{5})_{2}$$

$$II$$

$$1-C_{10}H_{7}MgBr + C_{6}H_{5}CH = C(COOC_{2}H_{5})_{2}$$

$$R_{4}\%$$

$$CHCH(COOC_{2}H_{5})_{2}$$

$$R_{4}\%$$

$$III$$

We became interested in the question of whether the yield of type I compound would vary significantly depending on the order of introduction of two different aryl groups. We have found that when phenylmagnesium bromide is added to diethyl 1naphthylidenemalonate, II, the yield of diethyl phenyl-1-naphthylmalonate, III, is 22%, whereas the addition of 1-naphthylmagnesium bromide to diethyl benzylidenemalonate affords III in 84% In an attempt to account for the erratic yields previously obtained^{3c} in the addition of 1-naphthylmagnesium bromide to II, we have found that the addition of excess magnesium bromide solution to the Grignard reagent prior to reaction with II had little effect on the yield. However, when di-1naphthylmagnesium was used, no addition reaction occurred and II was recovered in 97% yield.

When 1-naphthylmagnesium bromide was added to ethyl 1-naphthylidenecyanoacetate, IV, a 94% yield of ethyl di-1-naphthylmethylcyanoacetate,

⁽¹⁾ The work reported herein was part of a thesis presented by H. R. Flanagan to the Ohio State University, 1956, for the M.S. degree.

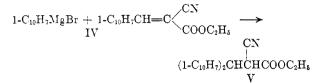
⁽²⁾ The first example was provided by E. P. Kohler, Am. Chem. J., 34, 132 (1905) who added phenylmagnesium iodide to diethyl benzylidenemalonate.

^{(3) (}a) M. S. Newman and M. Wolf, J. Am. Chem. Soc.,
74, 3225 (1952). (b) M. S. Newman and R. M. Wise, J. Am. Chem. Soc., 78, 450 (1956). (c) M. S. Newman and D. Lednicer, 78, 4765 (1956).

⁽⁴⁾ Inverse addition, *i.e.* addition of ester to Grignard reagent, was used in all cases since previous work had indicated no difference when direct addition was made. However, the results reported herein were not checked by direct addition experiments.

⁽⁵⁾ The yields of diethyl di-1-naphthylmethylmalonate were more consistently in the 45-53% range in the present work than in that reported previously.³⁰

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 distillation³⁰ 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 benzylidene-malonate⁶ 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. $180-195^{\circ}$ at 1 mm. Recrystallization from alcohol afforded 142.6 g. (88.8%) of IV, m.p. $80.0-81.4^{\circ}$. The analytical sample melted at $81.0-81.4^{\circ}$.

Anal. Calcd. for C₁₆H₁₃O₂N: N, 5.6. Found:⁸ 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 $0-5^{\circ}$ 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 $C_{26}H_{21}NO_2$: C, 82.3; H, 5.6; N, 3.7. Found 9 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,³⁰ m.p. 196° dec. Decarboxylation afforded the known 2,2-di-1-naphthylpropionic acid,³⁰ 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]

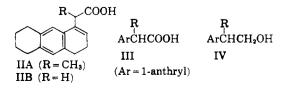
Syntheses of 1'-Methyl- and 4'-Methyl-1,2-benzanthracenes¹

MELVIN S. NEWMAN AND SEI OTSUKA

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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-1,2benzanthracene 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.



⁽¹⁾ The work herein reported was supported by a grant, C-2484, from the U. S. Public Health Service to whom grateful acknowledgment is made.

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