procedure similar to that for the preparation of 3,9-bis(1,1-dimethyl-3-cyanopropyl)-2,4,8,10-tetroxaspiro[5.5]undecane.

3,9-Bis(1,1-diethyl-3-carboxypropyl)-2,4,8,10-tetroxaspiro[5.5]undecane was prepared in a 93.8% yield by basic hydrolysis of the dinitrile in aqueous Cellosolve. It recrystallized very easily from methanol.

3,9-Bis(iodomethyl)-2,4,8,10-tetroxaspiro[5.5]undecane. A mixture of 102.4 g. (0.40 mol.) of 3,9-bis(chloromethyl)-2,4,8,10-tetroxaspiro[5.5]undecane, 240 g. (1.60 mol.) of sodium iodide, and 1 l. of ethyl Cellosolve was refluxed for 24 hr. The reaction product, obtained by dilution with water, weighed 153.5 g. (87.5%) and melted at 144.5–145.5°. Recrystallization from ethanol gave colorless flakes melting at 146.5–147.5°.

Anal. Calcd. for $C_9H_{14}I_2O_4$: C, 24.55; H, 3.21. Found: C, 24.4, 24.6; H, 3.22, 3.29.

Attempts to cyanate the above diiodide with a three-fold excess of potassium cyanide in refluxing ethyl Cellosolve yielded only tars which could not be characterized. Use of cuprous cyanide in pyridine gave similar results.

Attempts to replace the chlorine of *3,9-bis(chloromethyl)-2,4,8,10-tetroxaspiro[5.5]undecane.* (a) *Amination.* Heating the dichloride with a saturated methanolic ammonia solution at 130° resulted in intractable tars which could not be characterized.

(b) *Cyanation.* Refluxing a solution of the dichloride with sodium cyanide and a small amount of sodium iodide in either ethanol or ethyl Cellosolve resulted in quantitative recovery of starting material.

(c) *Gabriel reaction.* Heating a mixture of the dichloride with potassium phthalimide in dimethyl formamide on a steam bath for 1 hr. resulted in recovery of the starting material. Refluxing for 20 hr. gave an oil which could not be characterized nor hydrolyzed to the amine.

Attempts to replace the chlorine of *1,3-dichloro-2,2-dimethoxypropane.* (a) *Reaction with secondary amines.* Heating a methanolic solution of the dichloride with excess dimethyl amine at 100° for 8 hr. resulted in the recovery of the starting material.

(b) *Iodination.* Attempts to replace the chlorine with iodine, using conditions similar to those used in preparing 3,9-bis(iodomethyl)-2,4,8,10-tetroxaspiro[5.5]undecane, resulted in the recovery of starting halide.

Monopentaerythritol. 3,9-Dimethyl-2,4,8,10-tetroxapiro-[5.5]undecane (pentaerythritol bisacetal) was prepared from commercial pentaerythritol and acetaldehyde diethyl acetal according to the method of Mkhitaryan.[3] Three careful vacuum fractional distillations gave a product boiling at 113.0–113.5°/18 mm. The over-all yield was 56%. No hydroxyl groups could be detected in the infrared spectrum. Steam distillation of a weakly acidic (HCl) aqueous solution of the bisacetal resulted in complete hydrolysis to pentaerythritol. The pentaerythritol was isolated by evaporation of the reaction mixture to incipient crystallization, cooling thoroughly, and filtering. One recrystallization from the minimum amount of water gave 69% of product melting at 263–265°. The literature has reported melting points from 260°[11] to 269°.[12] Others[4,13] have reported intermediate values.

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(11) W. Friedrich and W. Brun, *Ber.*, **63B**, 6281 (1930).

(12) G. Desseigne, *Mem. des Poudres*, **33**, 169 (1951); *Chem. Abstr.*, **48**, 1954i (1954).

(13) P. Ebert, *Ber.*, **64**, 114 (1931); B. W. Lew, M. L. Wolfrom, and R. M. Goepp, *J. Am. Chem. Soc.*, **86**, 1449 (1946).

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

Synthesis of 6-Fluoro-, 7-Fluoro-, and 6-Methoxy-10-methyl-1,2-benzanthracenes[1]

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The syntheses of 6-fluoro-, 7-fluoro-, and 6-methoxy-10-methyl-1,2-benzanthracenes are described. The ratio of isomeric keto acids formed from reactions of 1,2-naphthalic anhydride with *p*-fluorophenylmagnesium bromide and with fluorobenzene in the Friedel-Crafts condensation were determined and the results are compared with those obtained with 3-methyl- and 3-chlorophthalic anhydrides. On hydrolysis of methyl 1-*p*-fluorobenzoyl-2-naphthoate with aqueous methanolic potassium hydroxide, an unexpectedly high yield of 1-*p*-methoxybenzoyl-2-naphthoic acid was obtained.

In continuation of a previously described program of synthesis designed to provide all of the monofluoro-10-methyl-1,2-benzanthracenes[2] for studies on carcinogenicity, we have prepared 6-fluoro-10-methyl-1,2-benzanthracene (III) and 7-fluoro-10-methyl-1,2-benzanthracene (IV) by routes essentially the same as those used for the synthesis of the corresponding 6- and 7-chloro analog.[3,4]

The condensation of *p*-fluorophenylmagnesium bromide with 1,2-naphthalic anhydride yielded 1-*p*-fluorobenzoyl-2-naphthoic acid (I) and 2-*p*-fluorobenzoyl-1-naphthoic acid (II) in the approximate ratio of 1 to 2.6. The ratio of product II, resulting from reaction at the unhindered carbonyl group, to that of I, arising from reaction of the hindered carbonyl group is thus similar to that ratio obtained in the reactions of *p*-chlorophenylmagnesium bromide[3] and of *m*-chlorophenylmagnesium bromide[4] with 1,2-naphthalic anhydride, and of phenylmagnesium bromide with 3-methylphthalic anhydride.[5] It appears then that in the

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(1) This work was supported by a grant from the National Institutes of Health.

(2) M. S. Newman, D. MacDowell, and S. Swaminathan, *J. Org. Chem.*, **24**, 509 (1959).

(3) M. S. Newman and M. Orchin, *J. Am. Chem. Soc.*, **61**, 244 (1939).

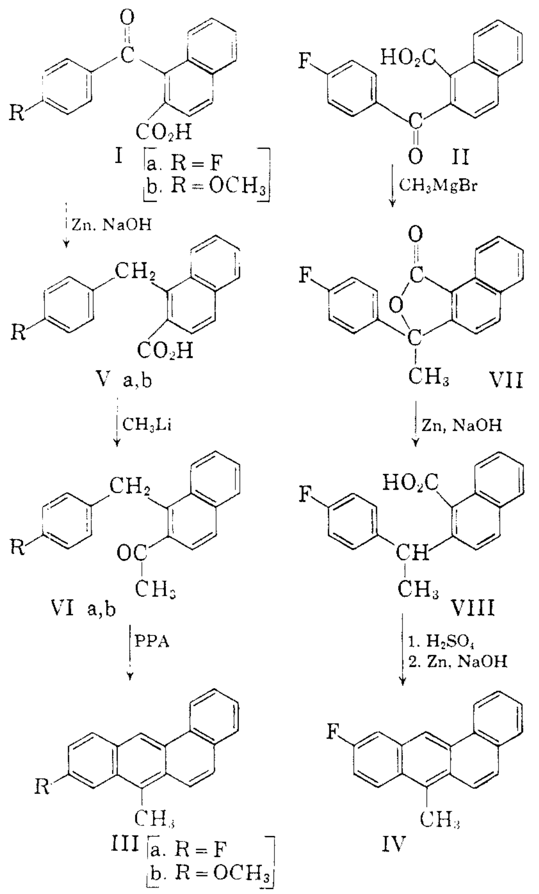
(4) M. S. Newman and M. Orchin, *J. Am. Chem. Soc.*, **60**, 586 (1938).

(5) M. S. Newman and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1542 (1941).

Grignard reaction the steric effect of a fused aromatic ring ortho to an anhydride grouping is about the same as that of an ortho methyl group.

The keto acids I and II were prepared also by a Friedel-Crafts condensation of 1,2-naphthalic anhydride on fluorobenzene, the yields of I and II being 48% and 19%, respectively.[6] In contrast, 3-methylphthalic anhydride yields approximately equal amounts of the two isomeric acids on condensation with benzene[5] whereas 3-chlorophthalic anhydride yields exclusively 2-benzoyl-3-chlorobenzoic acid, the product of reaction at the most hindered carbonyl.[7] It thus appears that an ortho fused aromatic ring is intermediate between *o*-methyl and *o*-chloro groups in its directive influence on Friedel-Crafts condensations of anhydrides with aromatic compounds.

The acids I and II were converted into 6-fluoro-10-methyl-1,2-benzanthracene (III) and 7-fluoro-10-methyl-1,2-benzanthracene (IV), respectively, by the reactions outlined below.



The separation of acids I and II (obtained by the Grignard or Friedel-Crafts method) was effected by the sulfuric acid method previously described.[5]

The alkaline hydrolysis of the methyl ester of Ia in aqueous methanolic potassium hydroxide for 24 hr. afforded in high yield an acid which was believed to be the expected fluoro acid, Ia. By steps analogous to those involved in the synthesis of 6-chloro-10-methyl-1,2-benzanthracene,[3] the acid thus obtained was converted into a compound believed to be IIIa. However, analysis showed that in the final compound a methoxy group was present instead of a fluorine atom. The replacement of fluorine by methoxyl was then proved to have taken place during the hydrolysis of the methyl ester of Ia in aqueous methanolic potassium hydroxide. The resulting acid was proved to be 1-*p*-methoxybenzoyl-2-naphthoic acid (Ib) and hence the final compound is 6-methoxy-10-methyl-1,2-benzanthracene (IIIb). The facile replacement of the fluorine by methoxyl in the treatment with aqueous methanolic potassium hydroxide is striking and merits further study.

When the hydrolysis of the methyl ester of Ia was carried out for 30 min. in aqueous ethanolic sodium hydroxide, the acid I was obtained in high yield. The synthesis of 6-fluoro-10-methyl-1,2-benzanthracene (IIIa) was then carried out as indicated on the chart.

EXPERIMENTAL[8]

Reactions of 1,2-naphthalic anhydride. a. Grignard reaction. The filtered Grignard reagent prepared from 22.0 g. of *p*-bromofluorobenzene[9] and 3 g. of magnesium in 150 ml. of dry ether was added during 10 min. to a warm stirred solution of 24.8 g. of 1,2-naphthalic anhydride in 275 ml. of benzene and 50 ml. of ether. After refluxing for 2 hr., the reaction mixture was cooled, treated with dilute acid, and the products were separated into a neutral and an acid fraction, 28.0 g. (76%), m.p. 138–146°. The acid fraction was separated into its components as described below.

b. *Friedel-Crafts reaction.* To a stirred mixture of 20.0 g. of fluorobenzene,[10] 40.0 g. of 1,2-naphthalic anhydride and 200 ml. of *o*-dichlorobenzene was added portionwise 65.0 g. of powdered aluminum chloride. The deep red mixture was heated at 80–90° for 4 hr. and was then cooled and decomposed with ice and 150 ml. of concentrated hydrochloric acid. An ether-benzene solution of the reaction mixture was well washed with dilute hydrochloric acid and water. Acidification of a potassium carbonate extract of the resulting solution afforded 31.5 g. (55%) of a mixture of acids (Ia and II), m.p. 140–175°, which was separated into its

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[6] H. Waldman, *J. prakt. Chem.*, **127**, 195 (1930); **131**, 71 (1931) reported that 1-benzoyl-2-naphthoic acid was the main product of the Friedel-Crafts reaction of 1,2-naphthalic anhydride with benzene but no accurate estimate of the amounts of isomeric acids was given.

[7] See M. S. Newman and P. G. Scheurer, *J. Am. Chem. Soc.*, **78**, 5004 (1956) for a discussion of Grignard and Friedel-Crafts reactions of β-substituted phthalic anhydrides.

[8] All melting points are corrected. Analyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Huffman Microanalytical Laboratories, Wheatridge, Colo. The term "treated in the usual manner" means that an ether-benzene solution of the organic matter was washed with saturated sodium chloride solution, filtered through a filter paper containing anhydrous magnesium sulfate, and concentrated by distillation at atmospheric pressure or under reduced pressure.

[9] Obtained from the Pierce Chemical Co., Box 117, Rockford, Ill.

[10] We are indebted to the Pennsylvania Salt Chemical Co. for a generous supply of fluorobenzene.

components as described[5] below. From the neutral fraction 8.0 g. of 1,2-naphthalic anhydride, m.p. 147–150°, was recovered.

Separation of acids, Ia *and* II. In a typical case, 28.0 g. of the acid mixture obtained from the Grignard reaction described above was esterified by refluxing for 2 hr. with methanolic hydrogen chloride solution. This ester fraction, 26.0 g., (over 1 g. of acid fraction, m.p. 140–145°, was recovered) was added slowly with cooling to 100 ml. of approximately 100% sulfuric acid (m.p. 10.4° on the less than 100% side of the f.p. maximum). The clear dark brown solution was kept at about 20–25° for 2.5 hr. and then poured on ice. The organic material was taken into ether-benzene and separated into neutral and acid fractions by extraction with potassium carbonate solution. From the acid fraction 16.0 g. (65%) of 2-*p*-fluorobenzoyl-1-naphthoic acid (II), m.p. 170–174°, was obtained. After three recrystallizations from benzene pure II, m.p. 175.0–175.8°, was obtained with little loss. The crude acid, m.p. 170–174°, was used for the next reaction.

Anal. Calcd. for $C_{18}H_{11}FO_3$: C, 73.5; H, 3.8. Found: C, 73.1; H, 3.8.

Crystallization of the neutral fraction isolated in the usual manner yielded 4.5 g. (17%) of methyl 1-*p*-fluorobenzoyl-2-naphthoate (Ia), m.p. 100–105°, sufficiently pure for the hydrolysis described below. The analytical sample, m.p. 110.5°, was obtained after three recrystallizations from methanol.

Anal. Calcd. for $C_{19}H_{13}FO_3$: C, 74.0; H, 4.3. Found: C, 74.2; H, 4.3.

Similar treatment of 44 g. of ester mixture obtained from the acid fraction resulting from the above Friedel-Crafts condensation of 1,2-naphthalic anhydride yielded 11.5 g. (27%) of II, m.p. 172–174°, and 31.6 g. (72%) of the methyl ester of Ia, m.p. 99–102°. On one crystallization from absolute methanol 28.6 g. (65%) of pure ester, m.p. 109–111°, was obtained, suitable for further reaction. In another run almost identical proportions of Ia and II were obtained.

Alkaline hydrolysis of methyl 1-p-fluorobenzoyl-2-naphthoate. Hydrolysis of 10.0 g. of the above methyl ester by heating for 30 min. in a solution containing 5 g. of sodium hydroxide, 100 ml. of water, and 100 ml. of alcohol yielded 9.2 g. of crude Ia. One recrystallization from 80% ethanol afforded 8.65 g. (90%) of Ia, m.p. 205–206°. Three crystallizations from 80% alcohol yielded the analytical sample of 1-*p*-fluorobenzoyl-2-naphthoic acid, Ia, m.p. 206.0–207.0°.

Anal. Calcd. for $C_{18}H_{11}FO_3$: C, 73.5; H, 3.8. Found: C, 73.4; H, 4.1.

On treatment with diazomethane, Ia yielded the methyl ester, m.p. 110.0–111.0°, alone and mixed with the purified sample obtained by the above described treatment with sulfuric acid. When the hydrolysis of 36.0 g. of the methyl ester of Ia was conducted for 24 hr. in a refluxing solution of 24 g. of potassium hydroxide in 180 ml. of methanol and 36 mg. of water, an almost quantitative yield of acid, m.p. 207–210°, was obtained. Recrystallization from benzene-Skellysolve B (petroleum ether, b.p. 65–70°) yielded colorless crystals of Ib, m.p. 214.5–216.5° with little loss. The analytical sample of 1-*p*-methoxybenzoyl-2-naphthoic acid, m.p. 216.0–217.0°, was obtained by two more such recrystallizations; a mixed m.p. with pure Ia, m.p. 206–207° was 175–180°.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.5; H, 4.6; OCH_3, 10.1. Found: C, 74.7, 74.5; H, 4.5, 4.6; OCH_3, 10.2.

When a solution of 2.0 g. of 1-*p*-fluorobenzoylnaphthalene in 40 ml. of methanol containing 2 ml. of water and 4 g. of potassium hydroxide was refluxed for one day a small yield (about 25%) of 1-*p*-methoxybenzoylnaphthalene, m.p. 100.0–101.0° alone and mixed with authentic 1-*p*-methoxybenzoylnaphthalene, was obtained. 1-*p*-Chlorobenzoylnaphthalene under similar conditions did not give 1-*p*-methoxybenzoylnaphthalene.

Proof of structure of acids, Ia, Ib, *and* II. A mixture of 1.0 g. of Ia and 0.12 g. of its copper salt[11] was heated at 240–250° for 30 min. Distillation yielded 0.5 g. of an oil which yielded an orange-red 2,4-dinitrophenylhydrazone, m.p. 230–231° alone and mixed with an authentic sample prepared from 1-*p*-fluorobenzoylnaphthalene. This ketone was prepared in 80% yield by the reaction of *p*-fluorophenylmagnesium bromide with 1-naphthonitrile. Since the ketone had a low m.p. of 32.8–33.5°, it was converted into the 2,4-dinitrophenylhydrazone, m.p. 230–231°, for identification and comparison purposes.

Anal. Calcd. for $C_{17}H_{11}FO$: C, 81.6; H, 4.4. Found: C, 81.4; H, 4.8. Calcd. for $C_{23}H_{15}FN_4O_4$: C, 64.2; H, 3.5; N, 13.0. Found: C, 64.2; H, 3.8; N, 13.2.

Similarly II was decarboxylated in high yield to 2-*p*-fluorobenzoylnaphthalene, m.p. 110.0–110.8°, alone and mixed with an authentic sample prepared from the Friedel-Crafts condensation of 2-naphthoyl chloride with fluorobenzene in 54% yield.

Anal. Calcd. for $C_{17}H_{11}FO$: C, 81.6; H, 4.4. Found: C, 81.4; H, 4.5.

In the same way, Ib was decarboxylated to 1-*p*-methoxybenzoylnaphthalene, m.p. 100.0–101.0°, m.p. alone and mixed with an authentic sample prepared in 66% yield by the reaction of *p*-methoxyphenylmagnesium bromide with 1-naphthonitrile. In addition, the 2,4-dinitrophenylhydrazones, m.p. 239.5–240.5° alone and mixed, were prepared and compared.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.4; H, 5.4. Found: C, 82.6; H, 5.2. Calcd. for $C_{24}H_{18}N_4O_5$: C, 65.2; H, 4.1; N, 12.7. Found: C, 64.8; H, 4.3; N, 12.4.

1-p-Fluorobenzyl-2-naphthoic acid, Va. A mixture of 22.0 g. of Ia, 50 g. of potassium hydroxide, 60 g. of zinc dust (activated with ammoniacal copper sulfate) and 300 ml. of water was refluxed for 34 hr. The alkaline solution was decanted and the zinc refluxed with 100 ml. of 5% potassium hydroxide for 0.5 hr. The filtered alkaline solutions were combined and acidified to yield 19.0 g. (90%) of acid, m.p. 140–146°. The analytical sample, obtained after three recrystallizations from aqueous alcohol, melted at 192.0–193.0°. Evidently polymorphic forms are present as the yields of desired product in further steps were almost as good when lower melting fractions were used as when high melting Va was used.

Anal. Calcd. for $C_{18}H_{13}FO_2$: C, 77.1; H, 4.7. Found: C, 77.3; H, 4.8.

6-Fluoro-10-methyl-1,2-benzanthracene, IIIa. To a stirred ethereal solution of 25 ml. of 0.8*N* methyllithium was added a solution of 1.6 g. of Va, m.p. 184–186°, in 150 ml. of dry ether under nitrogen. After stirring at room temperature for 1 hr. the reaction mixture was processed as usual to yield 1.4 g. of crude oily 1-*p*-fluorobenzyl-2-acetonaphthalene, VIa, and 0.2 g. of Va, m.p. 170–173°. The oily ketone was heated with 15 g. of PPA[2,12,13] at 120–130° for 5 hr. The reaction mixture was then poured into water and the organic portion treated in the usual way. Chromatography over activated alumina (heated to 170° until no more steam was evolved) afforded 0.61 g. (46%) of crude hydrocarbon, m.p. 113–115°. Further crystallization from benzene-Skellysolve B yielded 0.45 g. (35%) of almost colorless IIIa, m.p. 119.0–120.0°. The analytical sample, obtained after further recrystallization, melted at 120.0–121.0°.

Anal. Calcd. for $C_{19}H_{13}F$: C, 87.7; H, 5.0; F, 7.3. Found: C, 87.8; H, 5.1.; 7.1.

In similar runs using starting acid Va melting at 140–146° and varying the time of heating in PPA to 3 hr. and

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[11] See L. F. Fieser and M. S. Newman, *J. Am. Chem. Soc.*, **58**, 2376 (1936).

[12] Polyphosphoric acid, obtained from the Victor Chemical Co., to whom we are indebted for a generous gift.

[13] *Cf.* C. K. Bradsher and F. A. Vingiello, *J. Org. Chem.*, **71**, 1434 (1949). They used HBr-AcOH-H_2O mixture for this type of cyclization.

the temperature to 90–100° somewhat smaller yields (42% crude and 26% pure) of IIIa were obtained.

Lactone of 2-(α-hydroxy-α-methyl-p-fluorobenzyl)-1-naphthoic acid, VII. Reaction of 24.5 g. of II, m.p. 170–176°, with methylmagnesium bromide followed by treatment as described[4] yielded 14.2 g. (58%) of colorless VII, m.p. 105–107°, of sufficient purity for further work. An additional 6–8 g. of less pure product was obtained from the mother liquors but was not investigated further. The analytical sample, obtained after two recrystallizations from ethanol, melted at 108.0–108.5°

Anal. Calcd. for $C_{19}H_{13}FO_2$:C, 78.0; H, 4.5. Found: C, 77.7; H, 4.3.

2-(α-Methyl-p-fluorobenzyl)-1-naphthoic acid, VIII. Reduction of 13.7 g. of VII, m.p. 105–107° as described[4] yielded 12.7 g. (93%) of VIII, m.p. 174.5–175.5°. Recrystallization from benzene yielded pure VIII, m.p. 176.2–177.0°, with little loss.

Anal. Calcd. for $C_{19}H_{15}FO_2$: C, 77.6; H, 5.1. Found: C, 77.4; H, 5.1.

Reduction of crude lactone VII afforded crystalline VIII, m.p. 174.5–175.5°, in good yield also, so that it was possible to utilize noncrystalline VII directly in the preparation of VIII.

7-Fluoro-10-methyl-1,2-benzanthracene, IV. Cyclization of 13.1 g. of VIII, m.p. 174.5–175.5° with 150 ml. of concentrated sulfuric acid at 25° for 2 hr. followed by reduction of the authrone as described[4] afforded 6.3 g. (55%) of crude IV, m.p. 100–103°. The analytical sample, obtained by further chromatography and recrystallization from benzene–Skellysolve B, formed colorless needles, m.p. 102.5–103.2°.

Anal. Calcd. for $C_{19}H_{13}F$: C, 87.7; H, 5.0; F, 7.3. Found: C, 87.4; H, 5.2; F, 7.5.

1-p-Methoxybenzyl-2-naphthoic acid, Vb. In the best of several reductions, a mixture of 5.0 g. of Ib, 75 ml. of 20% potassium hydroxide solution and 15 g. of zinc dust (activated as above) was refluxed for 30 hr. After a procedure similar to that for Va, 1.4 g. (29%) of crude Vb, m.p. 150–159°, was obtained. The analytical sample, obtained by two recrystallizations from benzene, formed colorless needles, m.p. 165.5–166.5°. The remainder was used in the next step.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 77.8; H, 5.3.

6-Methoxy-10-methyl-1,2-benzanthracene, IIIb. To a stirred solution of 50 ml. of 0.4*N* methyllithium in ether was added during 10 min. a solution of 1.5 g. of Vb (the above crude product) in 100 ml. of ether and 50 ml. of pure dry tetrahydrofurane. A purple color developed. After 1 hr. at room temperature the reaction mixture was treated as usual and the neutral oily fraction, presumably containing 1-*p*-methoxybenzyl-2-acetonaphthalene, VIb, was heated on a steam bath with 99% PPA for 20 min. Dilution with water and the usual workup, including chromatography over alumina (activated as above) afforded 0.70 g. (50%) of crude IIIb, m.p. 169–174°. Recrystallizations from benzene afforded IIIb as pale yellow needles, m.p. 174.0–174.8°, with some loss.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.2; H, 5.9; OCH_3, 11.4. Found: C, 88.5, 88.4; H, 5.9, 6.0; OCH_3, 11.2.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

Unsymmetrical Tetraalkylmethanes. IV.[1] General Method of Synthesis of Tetraalkylmethanes

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A number of unsymmetrical tetraalkylmethanes, containing from 27 to 50 carbon atoms, have been prepared in relatively high over-all yields from unsymmetrical ketones. The latter were transformed into alkylidenecyanoacetates, which were then caused to undergo conjugate addition with Grignard reagents to give α-cyano-β,β,β-trialkylpropionates (I). These were hydrolyzed and decarboxylated to β,β,β-trialkylpropionitriles (III), which were converted through the branched ketones (IV) to the hydrocarbons (VII) which possessed the desired quaternary carbon atom structure.

The previous paper[1] in this series described a method for preparing unsymmetrical tetraalkylmethanes from β,β-disubstituted glutaric acids, which contained the desired center of asymmetry. In the present study it was found that the procedure failed when an attempt was made to apply it to the synthesis of high molecular weight hydrocarbons. Although the Guareschi reaction[5] affords good yields of α,α-dicyano-β,β-dialkylglutarimides with simple methyl and cyclic ketones, no condensation could be effected with 6-dodecanone. The amination reaction occurred exclusively and the ethyl cyanoacetate was converted to cyanoacetamide. Others[6] have reported limitations of the Guareschi condensation.

Alkylidenecyanoacetates, which can be obtained readily by Cope's procedure,[7] seemed to offer a general approach to the synthesis of molecules which possess quaternary carbon atoms. As the Michael addition of active methylene compounds to the alkylidene derivatives could lead to β,β-disubstituted glutaric acids of the type obtained

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[1] Paper III. N. Rabjohn and H. H. Farmer, *J. Org. Chem.*, **24**, 359 (1959).

[2] Abstracted in part from the Ph.D. thesis of L. V. Phillips, 1957.

[3] Supported in part by the Petroleum Research Fund of the American Chemical Society.

[4] Lubrizol Foundation Fellow, 1956–1958.

[5] I. Guareschi, *Gazz. chim. ital.*, **49**, 124 (1919).

[6] A. I. Vogel, *J. Chem. Soc.*, 1758 (1934); A. J. Birch and R. Robinson, *J. Chem. Soc.*, 488 (1942); and S. M. McElvain and D. H. Clemens, *J. Am. Chem. Soc.*, **80**, 3915 (1958).

[7] A. C. Cope, C. M. Hofmann, C. Wykoff, and E. Hardenbergh, *J. Am. Chem. Soc.*, **63**, 3452 (1941).