stable at room temperature on prolonged standing or on heating, turning green in color. The attempted preparation of the 2,4-dinitrophenylhydrazone, oxime and semicarbazone of IV yielded only the dihydrofuran XII.

2,2,5-Triphenyl-3-benzylidene-2,3-dihydrofuran (XII). To 1 g. (0.0025 mole) of IV was added 30 ml. of a saturated solution of sodium acetate in acetic anhydride. The solution was heated on a steam bath for 5 hr., then extracted with ether. The ether extract was washed several times with water, dried over magnesium sulfate and evaporated to yield a yellow-green solid. The crude product was crystallized from ethanol to yield 0.6 g. (62%) of dihydrofuran as fluorescent yellow-green needles, m.p. 150–151.5°.

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.14; H, 5.74. Found: C, 90.20; H, 5.87.

Acknowledgment. The authors are grateful to the National Science Foundation for financial support of this research (Grant No. NSF-G9985).

CHICAGO 16, ILL.

[CONTRIBUTION FROM THE UNIVERSITY OF NEW MEXICO AND BIOMEDICAL RESEARCH GROUP,[1] LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

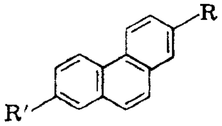
Liquid Scintillators. IX. Synthesis of Some Aryl Substituted Phenanthrenes and Dihydrophenanthrenes, and Related *p*-Terphenyls and *p*-Quaterphenyls[2]

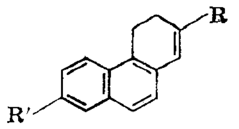
STEPHEN P. BIRKELAND,[3] GUIDO H. DAUB, F. NEWTON HAYES, AND DONALD G. OTT

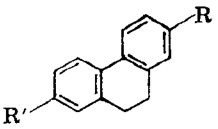
Received October 28, 1960

2-Phenylphenanthrene and 2-(4-biphenylyl)phenanthrene, synthesized *via* the corresponding 2-aryl-3,4-dihydrophenanthrenes, were converted to the related 2,2′-bis(hydroxymethyl)- and 2,2′-bis(methoxymethyl)-*p*-terphenyls and *p*-quaterphenyls as well as the 3-aryl-5,7-dihydrodibenz[c,e]oxepins and 2-aryl-9,10-dihydrophenanthrenes. Analogous 2″,3′-disubstituted *p*-quaterphenyls, 5,7-dihydro-3,9-diphenyldibenz[c,e]oxepin, 9,10-dihydro-2,7-diphenylphenanthrene, and 2,7-diphenylphenanthrene were prepared starting with *p*-quaterphenyl-2″,3′-dicarboxylic acid. Evaluation of these compounds as liquid scintillation solutes is reported in Paper X of this series.

In Paper VI of this series,[4] the synthesis of some aryl-substituted fluorenes was reported along with the evaluation of these compounds as liquid scintillators. We are herewith describing the synthesis of some related phenanthrene derivatives. The compounds of initial interest in this study were 2-phenylphenanthrene (Ia), 2-(4-biphenylyl)phenanthrene (Ib), and 2,7-diphenylphenanthrene (Ic) as well as their 9,10-dihydro derivatives (IIIa, IIIb, and IIIc). The 3,4-dihydrophenanthrenes, IIa and IIb, were also prepared for evaluation as liquid scintillator solutes.

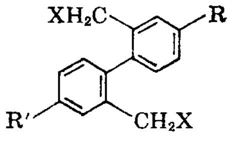




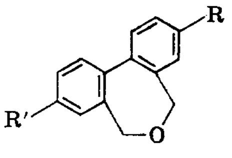


a. R′ = H, R = C_6H_5
b. R′ = H, R = 4-$C_6H_5C_6H_4$
c. R = R′ = C_6H_5

In the course of preparing the 9,10-dihydro derivatives, a number of interesting *p*-terphenyls (IVa, Va, and VIa) and *p*-quaterphenyls (IVb, IVc, Vb, Vc, VIb, and VIc) were synthesized from available intermediates.



IVa, b, c. X = OH
Va, b, c. X = OCH_3



VIa, b, c

2-Phenylphenanthrene (Ia) was prepared by the method described by Newman[5] and the 2-(4-biphenylyl) derivative Ib was obtained by a similar procedure, starting with phenylacetonitrile (series a) and 4-biphenylylacetonitrile (series b), respectively. The latter starting material was prepared in four steps from 4-biphenylcarboxylic acid which was reduced to 4-phenylbenzyl alcohol. This alcohol was converted to 4-phenylbenzyl bromide which, upon treatment with potassium cyanide, afforded 4-biphenylylacetonitrile. The alkylation of these arylacetonitriles was accomplished with 2-(1-naphthyl)ethyl bromide to give the corresponding 2-aryl-4-(1-naphthyl)butyronitriles, which were hydrolyzed to the substituted butyric acids. These were cyclized, *via* the acid chlorides, to the respective 2-aryl-1-oxo-1,2,3,4-tetrahydrophenanthrenes. Reduction of the ketones

---

(1) Work done in part under the auspices of the U. S. Atomic Energy Commission.

(2) From the dissertation presented by Stephen P. Birkeland to the graduate faculty of the University of New Mexico in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Graduate Research Assistant under Los Alamos Contract SC-5 with The University of New Mexico.

(4) M. D. Barnett, G. H. Daub, F. N. Hayes, and D. G. Ott, *J. Am. Chem. Soc.*, **81**, 4583 (1959).

(5) M. S. Newman, *J. Org. Chem.*, **9**, 518 (1944).

followed by dehydration afforded 3,4-dihydro-2-phenylphenanthrene (IIa) and 2-(4-biphenylyl)-3,4-dihydrophenanthrene (IIb), which, when heated with 10% palladium-charcoal, yielded 2-phenylphenanthrene (Ia) and 2-(4-biphenyl)phenanthrene (Ib), respectively.

Attempts to prepare 9,10-dihydro-2-phenylphenanthrene (IIIa) by selective reduction of the 9,10-double bond in Ia were unsuccessful. High pressure hydrogenation over copper chromite[6] and reduction using sodium in Dimethyl Cellosolve[7] or lithium in ether[8] gave the hydrocarbon Ia as the only isolable product.

Successful synthesis of the 2-aryl-9,10-dihydrophenanthrenes (IIIa and IIIb) were accomplished in several steps via *p*-terphenyl-2,2′-dicarboxylic acid and *p*-quaterphenyl-2,2′-dicarboxylic acid, respectively. Peroxide oxidation of either the hydrocarbons, Ia and Ib,[9] or their quinones[10] gave the corresponding dicarboxylic acids which were reduced *via* their methyl esters to 2,2′-bis(hydroxymethyl)-*p*-terphenyl (IVa) and 2,2′-bis(hydroxymethyl)-*p*-quaterphenyl (IVb), respectively. The diols were converted to the corresponding dibromides which were cyclized with phenyllithium[11,12] to 9,10-dihydro-2-phenylphenanthrene (IIIa) and 2-(4-biphenylyl)-9,10-dihydrophenanthrene (IIIb), respectively.

2,2′-Bis(bromomethyl)-*p*-terphenyl and 2,2′-bis(bromomethyl)-*p*-quaterphenyl were also treated with methanolic sodium methoxide to give 2,2′-bis(methoxymethyl)*p*-terphenyl (Va) and 2,2′-bis(methoxymethyl)*p*-quaterphenyl (Vb), respectively. Cyclization of the diols IVa and IVb by heating with potassium bisulfate[13] afforded 5,7-dihydro-3-phenyldibenz[c,e]oxepin (VIa) and 3-(4-biphenylyl)-5,7-dihydrodibenz[c,e]oxepin (VIb).

The preparation of *p*-quaterphenyl-2″,3′-dicarboxylic acid has previously been reported[4] and afforded the necessary starting material for synthesis of the compounds in series c. In like manner to the a and b series, this acid was readily converted to 2″,3′-bis(hydroxymethyl)-*p*-quaterphenyl (IVc), 2″,3′-bis(methoxymethyl)-*p*-quaterphenyl (Vc), 5,7-dihydro-3,9-diphenyldibenz[c,e]oxepin (VIc), and 9,10-dihydro-2,7-diphenylphenanthrene (IIIc). Dehydrogenation of IIIc over palladium-charcoal afforded 2,7-diphenylphenanthrene (Ic).

The evaluation of these compounds as liquid scintillation solutes, determination of their Kallmann parameters, and discussion of structural relationships to scintillation ability are reported in Paper X of this series.[14]

EXPERIMENTAL[15]

1-Hydroxy-2-phenyl-1,2,3,4-tetrahydrophenanthrene. A solution of 96.5 g. (0.356 mole) of 1-oxo-2-phenyl-1,2,3,4-tetrahydrophenanthrene,[5] m.p. 176–178° and 150 g. (0.75 mole) of technical aluminum isopropoxide in 1 l. of dry isopropyl alcohol was placed in a flask equipped with a mechanical stirrer and a Hahn condenser.[16] The reaction mixture was refluxed with stirring for 45 hr. during which time acetone and alcohol were allowed to distill slowly while an additional 500 ml. of dry isopropyl alcohol was added. The reaction mixture was hydrolyzed by the addition of dilute hydrochloric acid and extracted with a mixture of benzene and ether. The organic extracts were dried and the solvent removed to yield 89.5 g. (92%) of 1-hydroxy-2-phenyl-1,2,3,4-tetrahydrophenanthrene, m.p. 78–81°, after crystallization from cyclohexane.

3,4-Dihydro-2-phenylphenanthrene (IIa). Two g. (0.007 mole) of 1-hydroxy-2-phenyl-1,2,3,4-tetrahydrophenanthrene m.p. 78–81°, and 15 ml. of formic acid were heated on a steam bath with occasional shaking for 30 min. after which time the formic acid was removed under reduced pressure. The residue was taken up in benzene, washed well with water, and 5% sodium carbonate solution, and dried. The benzene solution was passed through a short alumina column and the solvent removed on a steam bath. The residual solid was crystallized from cyclohexane to give 1.5 g. (80%) of the hydrocarbon IIa, m.p. 153–155°, as shiny plates; reported[5] m.p. 150–151°. Maxima and (log ϵ) values for the ultraviolet absorption spectrum are: 345 mμ (4.265), 287 mμ (4.52), 278 mμ (4.53), and 225 mμ (4.45).

2-Phenylphenanthrene (Ia). An intimate mixture of 87.6 g. (0.32 mole) of 1-hydroxy-2-phenyl-1,2,3,4-tetrahydrophenanthrene, m.p. 78–81°, and 9.0 g. of 10% palladium on charcoal was heated at 290° for 4 hr. The cooled residue was pulverized and crystallized from toluene yielding 63 g. (78%) of 2-phenylphenanthrene (Ia) as shiny plates, m.p. 195–197°; reported[5] m.p. 196.6–197.2°. Maxima and (log ϵ) values for the ultraviolet absorption spectrum are: 294 mμ (4.45) and 268 mμ (4.86).

p-Terphenyl-2,2′-dicarboxylic acid. A mixture of 69 g. (0.272 mole) of finely powdered 2-phenylphenanthrene (Ia), m.p. 195–197°, 700 ml. of glacial acetic acid, and 150 ml. of 50% hydrogen peroxide (Becco Chemicals) was slowly heated with stirring.[9] The reaction mixture, which took on a pale red color, was refluxed for 2 hr. and then poured into 2 l. of cold water. The pale yellow solid which precipitated was crystallized from ethyl acetate to yield 39.4 g. (47%) of *p-terphenyl-2,2′-dicarboxylic acid,* m.p. 256–258°. An analytical sample, m.p. 258–259°, was prepared by recrystallization from 50% aqueous ethanol.

Anal. Calcd. for $C_{20}H_{14}O_4$: C, 75.48; H, 4.40. Found: C, 75.18; H, 4.38.

Methyl p-terphenyl-2,2′-dicarboxylate. To a solution of 60 g. of dry hydrogen chloride in 1 l. of C.P. methanol was added 39.4 g. (0.24 mole) of *p*-terphenyl-2,2′-dicarboxylic

---

(6) D. D. Phillips, *Org. Syntheses,* **34,** 31 (1954).

(7) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.,* **58,** 2442 (1936).

(8) E. Bergmann and F. Bergmann, *J. Am. Chem. Soc.,* **59,** 1443 (1937).

(9) W. F. O'Connor and E. J. Moriconi, *J. Am. Chem. Soc.,* **73,** 4044 (1951).

(10) R. P. Linstead and W. E. Doering, *J. Am. Chem. Soc.,* **64,** 1991 (1942).

(11) D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.,* 711 (1950).

(12) E. D. Bergmann and R. Ikan, *J. Am. Chem. Soc.,* **80,** 208 (1958).

(13) A. J. Weinheimer, S. W. Kantor, and C. R. Hauser, *J. Org. Chem.,* **18,** 801 (1953).

(14) S. P. Birkeland, G. H. Daub, F. N. Hayes, and D. G. Ott, *Z. Physik,* **159,** 516 (1960).

(15) Melting points are uncorrected. Ultraviolet absorption spectra were determined in cyclohexane or chloroform at concentrations cf *ca.* $3 \times 10^{-5}M$ in 1-cm. silica cells using a Beckman DK-1 recording spectrophotometer.

(16) A. L. Wilds, *Org. Reactions,* II, 178 (1944).

acid, m.p. 256–258°. The mixture was refluxed with stirring for 24 hr. after which time most of the methanol was removed by distillation and replaced by benzene. The benzene solution was washed with water and 5% sodium carbonate solution, and dried. Removal of the solvent afforded 40 g. (93%) of crude ester of suitable purity for the next step. A small sample purified by crystallization from cyclohexane yielded an analytical sample of *methyl p-terphenyl-2,2'-dicarboxylate* as bright shiny plates, m.p. 98–99°.

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.28· H, 5.24. Found: C, 76.51; H, 5.35.

2,2'-Bis(hydroxymethyl)-p-terphenyl (IVa) To a stirred slurry of 6.7 g. (0.175 mole) of lithium aluminum hydride in 500 ml. of anhydrous C.P. ether under a nitrogen atmosphere there was added as fast as refluxing permitted, a solution of 40 g. (0.119 mole) of crude methyl *p*-terphenyl-2,2'-dicarboxylate in 1 l. of anhydrous ether-benzene (10:1). The reaction mixture was refluxed with stirring for an additional 3 hr. after the addition was complete. After cooling in an ice bath, the reaction mixture was hydrolyzed by the cautious addition of water followed by cold 10% sulfuric acid. The ether layer was separated, washed with water, dried, and the solvent removed to yield a colorless residue. Crystallization of this solid from benzene yielded 28 g. (78% over-all from the acid) of the *diol IVa*, m.p. 144–146°. Recrystallization from benzene gave an analytical sample as colorless needles, m.p. 150–151°. Maximum and (log ε) values for the ultraviolet absorption spectrum are: 265 mμ (4.42).

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.89; H, 6.31.

2,2'-Bis(bromomethyl)-p-terphenyl. In the best of several experiments 2 g. (0.007 mole) of finely powdered diol IVa, m.p. 144–146°, was added in several small portions to a cold (4–5°) stirred solution of 100 ml. of 48% hydrobromic acid and 7 ml. of sulfuric acid.[17] The mixture was stirred at room temperature for 1 hr. and refluxed for 4 hr. The reaction flask was cooled in an ice bath and the gum which separated was dissolved in benzene, washed with water and 10% sodium bisulfite solution, and dried over calcium chloride. The solvent was removed and the viscous oily residue was crystallized with difficulty from petroleum ether (b.p. 60–90°), to yield 2.2 g. (77%) of solid material, m.p. 67–71°. Recrystallization from petroleum ether gave *2,2'-bis(bromomethyl)-p-terphenyl* as colorless needles, m.p. 75–77°.

Anal. Calcd. for $C_{20}H_{16}Br_2$: C, 57.72; H, 3.88. Found: C, 57.98; H, 4.02.

9,10-Dihydro-2-phenylphenanthrene (IIIa). A solution of 1.5 g. (0.004 mole) of 2,2'-bis(bromomethyl)-*p*-terphenyl, m.p. 71–73°, in 20 ml. of anhydrous C.P. benzene was added slowly over a period of 30 min. to a refluxing phenyllithium solution prepared from 0.05 g. (0.007 g.-atom) of lithium wire and 0.6 ml. (0.005 mole) of C.P. bromobenzene in 35 ml. of anhydrous C.P. ether.[18] The mixture was refluxed with stirring for an additional 4 hr. and poured into ice water. The organic layer was washed with water, dried, and the solvent was removed. The gummy residue was distilled and crystallized from methanol to give 0.15 g. (17%) of the hydrocarbon IIIa, m.p. 127–129°. A sample purified by recrystallization from methanol gave *9,10-dihydro-2-phenylphenanthrene* (IIIa) as shiny plates, m.p. 130–131°. Maximum and (log ε) values for the ultraviolet absorption spectrum are: 295 mμ (4.43).

Anal. Calcd. for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.55; H, 6.25.

2,2'-Bis(methoxymethyl)-p-terphenyl (Va). Two g. (0.004 mole) of 2,2'-bis(bromomethyl)-p-terphenyl, m.p. 71–73°, was added to a solution of methanolic sodium methoxide (prepared from 1 g. (0.043 g.-atom) of sodium and 200 ml. of anhydrous C.P. methanol), and the resulting mixture was refluxed overnight. Most of the methanol was removed and replaced by ether. The ether solution was washed with water, dried, and the solvent was removed to give a colorless solid which, upon crystallization from petroleum ether (b.p. 60–90°), afforded 1.0 g. (70%) of *2,2'-bis(methoxymethyl)-p-terphenyl* (Va), m.p. 87–89°. An analytical sample purified by recrystallization from petroleum ether (b.p. 60–90°) was obtained as shiny plates, m.p. 91–92°. Maximum and (log ε) values for the ultraviolet absorption spectrum are: 258 mμ (4.44).

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96. Found: C, 83.19; H, 6.76.

5,7-Dihydro-3-phenyldibenz[*c,e*]oxepin (VIa). An intimate mixture of 1.5 g. (0.005 mole) of 2,2'-bis(hydroxymethyl)-*p*-terphenyl (IVa), m.p. 144–146°, and 10 g. of freshly fused potassium bisulfate was heated at 190° for 30 min. in a nitrogen atmosphere. The cooled melt was pulverized and dissolved in a mixture of benzene and water. The benzene layer was dried, passed through a short alumina column, and the solvent was removed to yield 0.86 g. (61%) of the colorless oxepin VIa, m.p. 135–138°. A sample purified for analysis by crystallization from cyclohexane gave *5,7-dihydro-3-phenyldibenz*[*c,e*]*oxepin* (VIa) as colorless needles, m.p. 137–138°. Maximum and (log ε) values for the ultraviolet absorption spectrum are: 278 mμ (4.47).

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.19; H, 5.92. Found: C, 88.14; H, 5.93.

4-Phenylbenzyl alcohol. 4-Biphenylcarboxylic acid, m.p. 222-225° (Pilot Chemical Co.), was converted to methyl 4-biphenylcarboxylate, m.p. 118–120°, in 96% yield by refluxing for 2 hr. with methanol saturated with hydrogen chloride. A solution of 101 g. (0.477 mole) of the ester in 3 l. of anhydrous C.P. ether was added, as fast as refluxing would permit, to a slurry of 14.5 g. (0.380 mole) of lithium aluminum hydride in 200 ml. of anhydrous C.P. ether under dry nitrogen. After all of the ester had been added, the reaction mixture was refluxed with stirring for an additional hour. The reaction was worked up in the usual manner to give 79.5 g. (92% yield) of 4-phenylbenzyl alcohol, m.p. 101–102°, after crystallization from benzene; reported[19] m.p. 101–102°.

4-Phenylbenzyl bromide. A mixture of 20.7 g. (0.113 mole) of 4-phenylbenzyl alcohol, m.p. 101–102°, and 250 ml. of 48% hydrobromic acid was heated on a steam bath for 1 hr. The solid which appeared upon cooling was collected, dried, and crystallized from cyclohexane to give 25 g. (90%) of *4-phenylbenzyl bromide*, m.p. 84–85°. Recrystallization from cyclohexane provided an analytical sample as colorless crystals, m.p. 86–87°.

Anal. Calcd. for $C_{13}H_{11}Br$: C, 63.17; H, 4.49. Found: C, 63.35; H, 4.73.

4-Biphenylylacetonitrile. A solution of 10 g. (0.04 mole) of 4-phenylbenzyl bromide, m.p. 84–85°, in 100 ml. of acetone was added dropwise over 20 min. to a stirred refluxing solution of 10 g. of potassium cyanide in 80 ml. of 70% aqueous acetone. After refluxing for 20 hr., most of the aqueous acetone was removed by distillation and replaced with a 4 to 1 mixture of benzene and ether. The cooled organic phase was washed several times with water, dried, and the solvent was removed on a steam bath. The residue was crystallized from cyclohexane to yield 7 g. (90%) of 4-biphenylylacetonitrile, m.p. 93–95°; reported[20] m.p. 94–95°.

2-(4-Biphenylyl)-4-(1-naphthyl)-butyronitrile. A mixture of 166 g. (0.86 mole) of 4-biphenylylacetonitrile, m.p. 93–95°,

---

[17] C. W. Muth, W. Sung, and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, **77**, 3393 (1955).

[18] E. D. Bergmann and R. Ikan, *J. Org. Chem.*, **23**, 907 (1958).

[19] J. V. Braun and H. Engel, *Ann.*, **436**, 299–320 (1924).

[20] I. G. Farbenind. A-G. (Rudolf Lesser, Inventor), Ger. Patent **658,114** (1938); *Chem. Abstr.*, **32**, P4798 (1938).

34.5 g. (0.88 mole) of sodium amide (Farchan Laboratories), 1.5 l. of anhydrous C.P. ether, and 200 ml. of anhydrous C.P. benzene was refluxed with stirring for 1 hr. under a nitrogen atmosphere. Heating was discontinued and 210 g. (0.90 mole) of 2-(1-naphthyl)-ethyl bromide (b.p. 136–140° at 0.25 mm.) was added dropwise. After the addition was complete, the reaction mixture was brought to reflux and stirring was continued for 8 hr. After standing overnight, the organic solution was thoroughly washed with water, dried, and the solvent was removed to yield a viscous oil. Fractionation through a one foot Vigreux column gave 159.5 g. (53%) of *2-(4-biphenylyl)-4-(1-naphthyl)-butyronitrile*, b.p. 252–253° at 0.03 mm., which was hydrolyzed directly to the acid.

2-(4-Biphenylyl-4-(1-naphthyl)butyric acid. A mixture of 159.5 g. (0.46 mole) of 2-(4-biphenylyl)-4-(1-naphthyl)butyronitrile, b.p. 252–253° at 0.03 mm., 800 ml. of glacial acetic acid, and 150 ml. of 50% sulfuric acid was refluxed for 67 hr. At the end of this time, 500 ml. of water was added and the flask was cooled in an ice bath. The solid product was collected, air dried, and crystallized from ethyl acetate giving 125 g. (77%) of tan solid, m.p. 170–180°. Several recrystallizations from ethyl acetate afforded an analytical sample of *2-(4-biphenylyl)-4-(1-naphthyl)butyric acid* as colorless crystals, m.p. 200–201°.

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 85.51; H, 6.27.

2-(4-Biphenylyl)-1-oxo-1,2,3,4-tetrahydrophenanthrene. A mixture of 129 g. (0.352 mole) of crude 2-(4-biphenylyl)-4-(1-naphthyl)butyric acid, m.p. 170–180°, 78 g. (0.38 mole) of C.P. phosphorus pentachloride, and 2 l. of anhydrous C.P. benzene was heated with stirring under a nitrogen atmosphere until a clear tan solution resulted. The solution was cooled to just below room temperature and 133 g. (0.39 mole) of anhydrous technical aluminum chloride was added cautiously in small portions over a period of 10 min. The reaction mixture was refluxed for 3 hr., and at the end of this time the reaction mixture was poured into ice and 10% hydrochloric acid. The benzene was removed on a steam bath, and after cooling the solid was isolated and air dried. The crude product was dissolved in chloroform, and the hot solution was passed through a short alumina column. Concentration of the eluate afforded 100 g. (82%) of *2-(4-biphenylyl)-1-oxo-1,2,3,4-tetrahydrophenanthrene* as a colorless solid, m.p. 250–252°. Recrystallization from benzene gave an analytical sample, m.p. 252–253°.

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.44; H, 5.76.

2-(4-Biphenylyl)-1-hydroxy-1,2,3,4-tetrahydrophenanthrene. A stirred mixture of 176 g. (0.86 mole) of technical aluminum isopropoxide, 2 l. of dry C.P. toluene, and 91 g. (0.26 mole) of 2-(4-biphenylyl)-1-oxo-1,2,3,4-tetrahydrophenanthrene, m.p. 250–252°, was gently refluxed using a Hahn condenser. After 40 hr., the distillatd no longer gave a positive acetone test, and the reaction mixture was cooled to room temperature and washed well with 15% sulfuric acid. The toluene layer was concentrated, and the alcohol crystallized, yielding 70 g. (77%) of *2-(4-biphenylyl)-1-hydroxy-1,2,3,4-tetrahydrophenanthrene*, m.p. 203–206°. A sample purified for analysis gave colorless crystals, m.p. 200–201°.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.10; H, 6.33. Found: C, 89.36; H, 6.49.

2-(4-Biphenylyl)-3,4-dihydrophenanthrene (IIb). Two grams (0.006 mole) of 2-(4-biphenylyl)-1-hydroxy-1,2,3,4-tetrahydrophenanthrene, m.p. 203–206°, was dehydrated by heating with 15 ml. of formic acid as previously described for IIa. Crystallization from toluene gave 1.5 g. (80%) of the hydrocarbon IIb as pale yellow plates, m.p. 268–270°. An analytical sample of colorless *2-(4-biphenylyl)-3,4-dihydrophenanthrene* (IIb), m.p. 271–273°, was prepared by recrystallization from toluene. Maxima and (log ϵ) values for the ultraviolet absorption spectrum are: 359 mμ (4.55), 297 mμ (4.69), and 290 mμ (s) (4.66).

Anal. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 94.03; H, 6.14.

2-(4-Biphenylyl)phenanthrene (Ib). A mixture of 26 g. (0.074 mole) of 2-(4-biphenylyl)-1-hydroxy-1,2,3,4-tetrahydrophenanthrene, m.p. 203–206°, and 2.6 g. of 10% palladium on charcoal was heated for 2 hr. at 350°. The cooled residue was crystallized from toluene to give 22 g. (90%) of *2-(4-biphenylyl)phenanthrene* (Ib), m.p. 280–285°. Repeated crystallization from toluene gave an analytical sample as colorless plates, m.p. 298–299°. Maxima and (log ϵ) values for the ultraviolet absorption spectrum are: 310 mμ (4.61), 296 mμ (4.76), 284 mμ (4.79), and 255 mμ (s) (4.73).

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.23; H, 5.35.

2-(4-Biphenylyl)phenanthraquinone. A mixture of 46 g. (0.14 mole) of 2-(4-biphenylyl)phenanthrene (Ib), m.p. 298–299°, 350 g. of potassium dichromate, and 1.5 l. of glacial acetic acid was refluxed with stirring for 4 hr., and then poured into ice water. The product which was a mixture of the desired quinone and unchanged hydrocarbon Ib was collected, dried, and carried over to the next step without further purification. A sample purified for analysis by crystallization from toluene gave *2-(4-biphenylyl)phenanthraquinone* as red needles, m.p. 261–262°.

Anal. Calcd. for $C_{26}H_{16}O_2$: C, 86.64; H, 4.48. Found: C, 86.29; H, 4.58.

p-Quaterphenyl-2,2'-dicarboxylic acid. A mixture of 40 g. of crude quinone, 40 ml. of 30% hydrogen peroxide, 300 ml. of 3% hydrogen peroxide, and 1 l. of glacial acetic acid was refluxed with stirring for 4 hr. After cooling, the precipitated solid was collected and digested on a steam bath with several portions of 5% sodium carbonate solution. The acidic product was obtained by acidification of the basic filtrates, and the neutral residue was recycled through both oxidation steps. After three such cycles there was obtained a total of 24 g. (44%) of *p-quaterphenyl-2,2'-dicarboxylic acid*, m.p. 310–320°. Repeated crystallization from 95% ethanol afforded an analytical sample as colorless crystals, m.p. 321–322°.

Anal. Calcd. for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 79.20; H, 4.86.

Methyl p-quaterphenyl-2,2'-dicarboxylate. Esterification of 26 g. (0.066 mole) of *p*-quaterphenyl-2,2'-dicarboxylic acid, m.p. 310–320°, was accomplished in a manner similar to that used for the terphenyl derivative described earlier. The crude ester thus obtained was of suitable purity for the next step. Recrystallization from methanol gave an analytical sample of *methyl p-quaterphenyl-2,2'-dicarboxylate*, as colorless plates, m.p. 152–153°.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found: C, 79.59; H, 5.28.

2,2'-Bis(hydroxymethyl)-p-quaterphenyl (IVb). The crude ester from above was dissolved in a mixture of 1 l. of anhydrous C.P. ether and 300 ml. of anhydrous C.P. benzene, and reduced with lithium aluminum hydride as previously described in the preparation of IVa. Isolation of the alcohol IVb in the usual manner yielded 14.5 g. (60%) of *2,2'-bis(hydroxymethyl)-p-quaterphenyl* (IVb), m.p. 209–211°. Recrystallization from ethyl acetate gave the alcohol IVb as colorless crystals, m.p. 210–211°. Maximum and (log ϵ) values for the ultraviolet absorption spectrum are: 285 mμ (4.55).

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 84.96; H, 5.98.

2,2'-Bis(bromomethyl)-p-quaterphenyl. A mixture of 6.5 g. (0.017 mole) of 2,2'-bis(hydroxymethyl)-*p*-quaterphenyl (IVb), m.p. 209–211°, 20 ml. of phosphorus tribromide, and 400 ml. of anhydrous C.P. benzene containing 1 drop of dry pyridine was placed in a dried flask and, with stirring, heated to 50° for 6 hr. The flask was cooled and methanol, followed by water, was cautiously added. The organic phase was washed thoroughly with water, 10% sodium bisulfite solution, and dried. The solvent was removed, and the colorless residue was crystallized from cyclohexane to give 4.7 g. (54%) of the dibromide, m.p. 126–131°. Recrystallization from petroleum ether (b.p. 60–90°) afforded an analytical sample of *2,2'-bis(bromomethyl)-p-quaterphenyl* as colorless crystals, m.p. 140–141°.

Anal. Calcd. for $C_{26}H_{20}Br_2$: C, 63.43; H, 4.06. Found: C, 63.59; H, 4.17.

2-(4-Biphenylyl)-9,10-dihydrophenanthrene (IIIb). A solution of 2.0 g. (0.004 mole) of 2,2'-bis(bromomethyl)-*p*-quaterphenyl, m.p. 126–131°, in 20 ml. of anhydrous C.P. benzene was added slowly over a period of 1 hr. to a refluxing phenyllithium solution prepared from 0.056 g. (0.008 g.-atom) of lithium wire and 0.6 ml. (0.006 mole) of C.P. bromobenzene in 25 ml. of anhydrous C.P. ether. An additional 25 ml. of anhydrous C.P. benzene was added and the mixture was refluxed with stirring for 3 hr. The reaction mixture was poured into ice water and the organic layer was separated, washed with water, and dried. Removal of the solvent yielded a colorless solid which was crystallized from ethyl acetate affording 0.5 g. (37%) of *2-(4-biphenylyl)-9,10-dihydrophenanthrene* (IIIb) as bright plates, m.p. 203–208°. Recrystallization from ethyl acetate gave an analytical sample of the hydrocarbon IIIb, m.p. 220–221°. Maximum and (log ε) values for the ultraviolet absorption spectrum are: 317 mμ (4.59).

Anal. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found C, 93.69; H, 6.33.

2,2'-Bis(methoxymethyl)p-quaterphenyl (Vb). One gram (0.002 mole) of 2,2'-bis(bromomethyl)-*p*-quaterphenyl, m.p. 126–131°, was allowed to react with a methanolic sodium methoxide solution as described above in the preparation of Va. Crystallization of the crude product from methanol afforded 0.52 g. (70%) of colorless ether Vb, m.p. 96–98°. An analytical sample prepared by recrystallization from petroleum ether (b.p. 60–90°) gave *2,2'-bis-(methoxymethyl)-p-quaterphenyl* (Vb) as colorless crystals, m.p. 97–98°. Maximum and (log ε) values for the ultraviolet absorption spectrum are: 284 mμ (4.59).

Anal. Calcd. for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64. Found: C, 85.45; H, 6.58.

3-(4-Biphenylyl)-5,7-dihydrodibenz[c,e]oxepin (VIb). An intimate mixture of 1.0 g. (0.003 mole) of 2,2'-bis(hydroxymethyl)-*p*-quaterphenyl (IVb), m.p. 209–211°, and 8.0 g. of freshly fused potassium bisulfate was heated at 220° for 40 min. The reaction mixture was worked up as described for VIa and recrystallization from ethyl acetate provided 0.2 g. (21%) of analytically pure *3-(4-biphenylyl)-5,7-dihydrodibenz[c,e]oxepin* (VIb), m.p. 217–219°, as colorless needles. Maximum and (log ε) values for the ultraviolet absorption spectrum are: 300 mμ (4.69).

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.66; H, 5.74. Found: C, 89.10; H, 5.72.

Methyl p-quaterphenyl-2",3'-dicarboxylate. A mixture of 1 l. of C.P. methanol, 200 g. of dry hydrogen chloride, and 24 g. (0.06 mole) of *p*-quaterphenyl-2",3'-dicarboxylic acid,[4] m.p. 333–336°, was refluxed with stirring for 20 hr. and worked up in the manner previously described to give 19.3 g. (75%) of *methyl p-quaterphenyl-2",3'-dicarboxylate,* m.p. 196–198°. The ester was also prepared in similar yield by the reaction of excess diazomethane with a slurry of the acid in benzene.

2",3'-Bis(hydroxymethyl)-p-quaterphenyl (IVc). Reduction of 12.9 g. (0.0306 mole) of methyl *p*-quaterphenyl-2",3'-dicarboxylate, m.p. 195–196°, in 450 ml. of dry benzene with 2.35 g. of lithium aluminum hydride (suspended in 520 ml. of dry ether) was carried out as described for the previously prepared diols. After hydrolysis, the colorless diol which was suspended between the organic and aqueous layers was collected by filtration and was combined with that obtained from evaporation of the solvents from the organic layer. Recrystallization from 95% ethanol afforded 10.25 g. (91.5%) of pale yellow *2",3'-bis(hydroxymethyl)-p-quaterphenyl* (IVc), m.p. 223–225°. Recrystallization from absolute ethanol afforded an analytical sample as pale yellow crystals, m.p. 224–225°. Maximum and (log ε) values for the ultraviolet absorption spectrum are: 265 mμ (4.61).

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 85.05; H, 6.09.

2",3'-Bis(bromomethyl)-p-quaterphenyl. Treatment of 5.0 g. (0.013 mole) of the diol IVc with phosphorus tribromide as in the preparation of the 2,2'-bis(bromomethyl)-*p*-quaterphenyl afforded 5.8 g. (88%) of *2",3'-bis(bromomethyl)-p-quaterphenyl,* m.p. 169–171°, after crystallization from benzene. An analytical sample prepared by recrystallization from benzene was obtained as colorless crystals, m.p. 172–173°.

Anal. Calcd. for $C_{26}H_{20}Br_2$: C, 63.43; H, 4.06. Found: C, 63.03; H, 4.19.

9,10-Dihydro-2,7-diphenylphenanthrene (IIIc). A solution of 2.5 g. (0.005 mole) of 2",3'-bis(bromomethyl)-*p*-quaterphenyl, m.p. 168–171°, in 150 ml. of anhydrous C.P. benzene was added slowly over a period of 1 hr. to a refluxing phenyllithium solution prepared from 0.07 g. (0.01 g.-atom) of lithium wire and 0.6 ml. (0.005 mole) of C.P. bromobenzene in 50 ml. of anhydrous C.P. ether. The reaction mixture was refluxed with stirring for an additional 4 hr. and worked up in the usual manner. Crystallization from benzene gave 0.8 g. (50%) of the hydrocrbon IIIc as shiny plates, m.p. 241–243°. Recrystallization from benzene afforded an analytical sample of *9,10-dihydro-2,7-diphenylphenanthrene* (IIIc), m.p. 242–243°. Maximum and (log ε) values for the ultraviolet absorption spectrum are: 323 mμ (4.60).

Anal. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found C, 93.85; H, 6.11.

2,7-Diphenylphenanthrene (Ic). A mixture of 0.25 g. (0.007 mole) of 9,10-dihydro-2,7-diphenylphenanthrene (IIIc), m.p. 241–243°, and 0.03 g. of 10% palladium-charcoal was heated at 300° for 1 hr. The cooled melt was pulverized and dissolved in boiling toluene. Crystallization from toluene yielded 0.15 g. (60%) of the hydrocarbon Ic, m.p. 312–313°. An analytical sample prepared by recrystallization from toluene gave *2,7-diphenylphenanthrene* (Ic) as colorless plates, m.p. 314–315°. Maxima and (log ε) values for the ultraviolet absorption spectrum are: 316 mμ (4.49) and 283 mμ (4.85).

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.41; H, 5.58.

2",3'-Bis(methoxymethyl)-p-quaterphenyl (Vc). One gram (0.002 mole) of 2",3'-bis(bromomethyl)-*p*-quaterphenyl, m.p. 169–170°, was allowed to react with sodium methoxide in methanol as described earlier, and crystallization of the product from petroleum ether (b.p. 60–90°) gave 0.7 g. (86%) of the ether Vc, m.p. 136–138°. Recrystallization from petroleum ether (b.p. 60–90°) gave an analytical sample of *2",3'-bis(methoxymethyl)-p-quaterphenyl* (Vc), as colorless plates, m.p. 138–139°. Maximum and (log ε) values for the ultraviolet absorption spectrum are: 265 mμ (4.81).

Anal. Calcd. for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64. Found: C, 85.30; H, 6.53.

5,7-Dihydro-3,9-diphenyldibenz[c,e]oxepin (VIc). A mixture of 10.25 g. (0.028 mole) of 2",3'-bis(hydroxymethyl)-*p*-quaterphenyl (IVc), m.p. 223–225°, and 100 g. of freshly fused potassium bisulfate was heated at 200° for 1.5 hr. under a dry nitrogen atmosphere. The reaction mixture was worked up as described for VIa and 7.38 g. (76% yield) of *5,7-dihydro-3,9-diphenyldibenz[c,e]oxepin* (VIc) was obtained as shiny plates, m.p. 249–251°. Recrystallization from benzene afforded an analytical sample, m.p. 250–251°. Maximum and (log ε) values for the ultraviolet spectrum are: 298 mμ (4.64).

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.66; H, 5.74. Found: C, 89.94; H, 5.93.

Acknowledgment. The authors are indebted to Dr. Wright H. Langham of the Los Alamos Scientific Laboratory for making laboratory facilities available to them, and to Mr. Vernon N. Kerr, also of LASL, for technical assistance. Financial support from the Industrial Hygiene Laboratory of Sandia Corporation, as well as encouragement from Mr. William H. Kingsley of that Laboratory, were also greatly appreciated.

ALBUQUERQUE, N. M.
LOS ALAMOS, N. M.

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

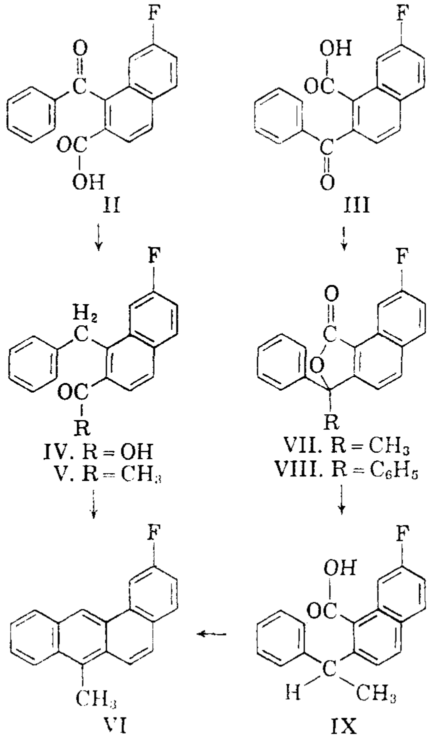
The Synthesis of 2′-Fluoro-10-methyl-1,2-benzanthracene[1]

MELVIN S. NEWMAN, RAMESH CHATTERJI, AND S. SESHADRI

Received December 19, 1960

The Friedel-Crafts condensation of 7-fluoro-1,2-naphthalic anhydride, I, with benzene affords about equal amounts of 1-benzoyl-7-fluoro-2-naphthoic acid (II) and 2-benzoyl-7-fluoro-1-naphthoic acid (III). Each of these acids is converted into 2′-fluoro-10-methyl-1,2-benzanthracene (VI), as shown in the charts.

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 2′-fluoro-10-methyl-1,2-benzanthracene by the routes outlined in the chart.



The keto acids, II and III, were prepared by the Friedel-Crafts condensation of 7-fluoro-1,2-naphthalic anhydride (I) with benzene. Although this condensation was not studied in great detail, it was shown that the acids II and III were formed in about equal amounts, in addition to a small but variable amount (5–17% in different runs) of the phthalide VIII. Thus, the overall condensation at the unhindered carbonyl group of I was slightly greater than the condensation at the hindered carbonyl of I. This result may be compared with those in the condensation of benzene with 3-methylphthalic anhydride[3] (about equal amount of condensation at the hindered and unhindered carbonyls) and with 3-chlorophthalic anhydride[4] (condensation entirely at the hindered (2-position) carbonyl). The condensation of 1,2-naphthalic anhydride with benzene has been reported[5] but the relative amounts of the isomeric acids produced were not determined.

As the main objective of this research program was to provide 2′-fluoro-10-methyl-1,2-benzanthracene (VI) for biological experimentation,[2] a minimum of developmental work was done. Acid II was converted into VI in about 13% overall yield and III into VI in about 12% overall yield as shown in the chart.

EXPERIMENTAL[6]

β-(p-Fluorobenzoyl)propionic acid. To a stirred solution of 50 g. (0.5 mole) of succinic anhydride in 300 ml. of *o*-dichlorobenzene and 55 ml. (0.6 mole) of fluorobenzene[7] held at 50–60° was added gradually 134 g. (1.0 mole) of powdered anhydrous aluminum chloride. The reaction mixture was held

---

[1] This research was supported by a Grant, C-4395, from the U.S. Public Health Service.

[2] M. S. Newman, D. MacDowell, and S. Swaminathan, *J. Org. Chem.*, **24**, 509 (1959). For a report on the biological activity of the fluorinated compounds prepared in this laboratory see H. A. Hartmann, E. C. Miller, and J. A. Miller, *Proceedings for Experimental Biology and Medicine*, **101**, 626 (1959), and E. C. Miller and J. A. Miller, *Cancer Research*, **20**, 133 (1960).

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

[4] M. S. Newman and P. G. Scheurer, *J. Am. Chem. Soc.*, **78**, 5004 (1956).

[5] H. Waldmann, *J. prakt. Chem.*, **127**, 195 (1930); **131**, 71 (1931).

[6] All melting points of pure compounds are corrected. Microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Schwarzkopf Microanalytical Laboratories,

[7] We acknowledge with thanks a generous gift of fluorobenzene from the Penn Salt Chemicals Corp., Three Penn Center, Philadelphia 2, Pa.