

acetic acid and hydrochloric acid were added in portions. The 1,2,2a,3,4,4a-hexahydrocyclopenta(cd)fluoranthene (VIII) obtained from the toluene layer crystallized from ethanol in colorless needles; yield 1.2 g. (61%). The hydrocarbon melted at 92–93°, and when the melted sample was allowed to cool and solidify it remelted at 82–83°.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.75; H, 7.07.

When a mixture of 1.3 g. of hydrocarbon VIII and 65 mg. of palladium-on-charcoal catalyst was heated to 320°, evolution of the theoretical volume of hydrogen was complete within thirty minutes. A benzene solution of the residue was decolorized with charcoal and alumina and the 1,2-dihydrocyclopenta(cd)fluoranthene (IX) was finally crystallized from a mixture of ethanol and acetone; yield, 1.0 g. (78%) of pale yellow needles, m. p. 154–155°.

Anal. Calcd. for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.92; H, 5.07.

The ultraviolet absorption spectrum of IX in 95%

ethanol, shown in Fig. 1, was obtained by employing a Beckman quartz spectrophotometer, model DU.

Summary

1,2-Dihydrocyclopenta(cd)fluoranthene, a stable hydrocarbon having a structure in which two five-membered rings are fused to the opposite *peri* positions of a naphthalene nucleus, has been synthesized from 3-keto-1,2,3,10b-tetrahydrofluoranthene by a sequence of unequivocal reactions.

The successful cyclization of 3-(1,2,3,10b-tetrahydrofluoranthyl)-acetyl chloride, with aluminum chloride in nitrobenzene, indicates that five-membered rings can be closed readily across both *peri* positions of the partially hydrogenated naphthalene nucleus.

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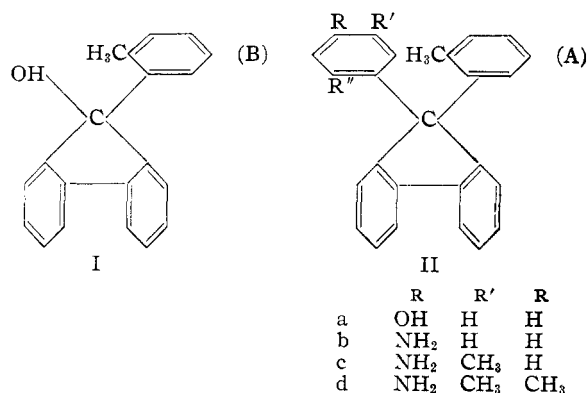
Hindered Tetraarylmethanes

BY ROGER ADAMS* AND JOHN CAMPBELL

An examination of scale models of the tetraphenylmethane molecule reveals a high degree of steric hindrance. It would appear quite difficult for one of the phenyl rings to rotate completely about its bond to the central carbon atom if the positions of the other three rings were fixed. Rotation of the phenyl rings in such a molecule should take place with greatest ease when all four rings rotate simultaneously in a coordinated manner. Fixing the positions of two of the four rings, by incorporating the fluorene nucleus in the molecule, should have a highly hindering effect on the rotation of the aryl groups, especially of *o*-substituted, about the central carbon atom. If the rotation is completely restricted, the molecule will become asymmetric or capable of existence in *cis-trans* forms. The present paper reports the synthesis of a number of tetraarylmethanes containing the fluorene nucleus and the attempted resolution of two such compounds.

Tetraarylmethanes may be prepared readily by the Friedel-Crafts type condensation of triarylcarbinols or triarylchloromethanes with phenols and aromatic amines, but very few are known which contain the fluorene nucleus.^{1,2} The tetraarylmethanes described herein were synthesized by the condensation of 9-hydroxy-9-*o*-tolylfluorene³ (I) with phenol and several aromatic amines.

The condensation of 9-hydroxy-9-*o*-tolylfluorene with phenol takes place in glacial acetic acid solution with sulfuric acid as a catalyst and



yielded 4-(biphenylene-*o*-tolylmethyl)-phenol (IIa). The latter was soluble in dilute ethanolic alkali and was reprecipitated by acidification, indicating that O-alkylation had not taken place. The condensation of I with *o*-cresol, resorcinol or β -resorcylic acid did not yield products from which pure entities could be obtained.

The condensation of 9-hydroxy-9-*o*-tolylfluorene (I) with aniline, *o*-toluidine and *p*-xylydine gave satisfactory yields of the corresponding 4-(biphenylene-*o*-tolylmethyl)-substituted anilines, IIb, IIc and IId, respectively. The reaction product of I and 2,5-dimethoxyaniline could not be obtained in a pure state. The condensations were effected by refluxing the reactants in glacial acetic acid solution with concentrated hydrochloric acid as a catalyst. The amines thus prepared were soluble in dilute hydrochloric acid solution upon the addition of a little ethanol. That they were primary amines, and not N-alkylation products, was shown by diazotization

* Harvard University Ph.D. 1912.

(1) Hardy, *J. Chem. Soc.*, 1000 (1929).

(2) Ullmann and v. Wursterberger, *Ber.*, **38**, 4105 (1905).

(3) Weiss and Knapp, *Monatsh.*, **61**, 61 (1932).

and coupling with β -naphthol. In addition, the corresponding phthalimide was prepared from 4-(biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline (II_d), the most hindered amine of those studied.

The scale models of 4-(biphenylene-*o*-tolylmethyl)-2-methylaniline (II_c) and 4-(biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline (II_d) indicated that they might be capable of resolution into optically active forms. If rings A and B (see II) were to interfere with each other and with the phenyl rings of the fluorene nucleus, such that rings A and B could not rotate about their bonds to the central carbon atom and become coplanar, then a plane of symmetry would be lacking in the molecule. However, attempts to resolve II_c and II_d have failed. The attempted resolution of II_c with *d*-camphorsulfonic acid afforded a crystalline salt but no separation was obtained. Reaction of II_c with succinic anhydride gave the corresponding amido acid, but no crystalline salts resulted from it and the common resolving agents for acids. No salts formed from II_d and the common optically active acids, nor could crystalline products be isolated from II_d and *d*-camphorsulfonyl chloride, *l*-methoxyacetyl chloride or *d*-diacetyltartaric anhydride.⁴ Upon reaction of II_d with *d*-camphoric anhydride, only one pure camphoramic acid could be obtained in poor yield. Reaction of II_d with phthalic anhydride afforded the corresponding phthalamic acid from which a crystalline quinine salt was prepared. No resolution, however, could be achieved.

Experimental

9-Hydroxy-9-*o*-tolylfluorene.—The compound was prepared by a modification of the method of Weiss and Knapp.³ To the Grignard reagent prepared from 42.0 g. of magnesium and 300 g. of *o*-bromotoluene in 850 ml. of dry ether was added 210 g. of fluorenone in 600 ml. of benzene. The resulting mixture was refluxed for nine hours, cooled and decomposed with 500 ml. of cold 20% aqueous hydrochloric acid. The ether-benzene layer was separated, the solvents removed and the residue steam distilled. The non-volatile product was collected on a filter, air dried and recrystallized from petroleum ether (b. p. 90–110°) to yield 249 g. (78%) of cream-colored crystals. Two further recrystallizations gave a nearly colorless product, m. p. 120.5–122° (cor.). Weiss and Knapp³ reported a 50% yield of pale rose crystals melting at 121–123°.

Anal. Calcd. for C₂₀H₁₆O: C, 88.20; H, 5.92. Found: C, 88.47; H, 6.22.

4-(Biphenylene-*o*-tolylmethyl)-phenol.—A solution of 1.0 g. of 9-hydroxy-9-*o*-tolylfluorene, 1.0 g. of phenol and 1.75 g. of concd. sulfuric acid in 12 ml. of glacial acetic acid was allowed to stand twenty-four hours at room temperature. The precipitate of small white crystals from the dark red solution was collected on a filter and washed with a few ml. of cold glacial acetic acid. After drying *in vacuo* over sodium hydroxide, the product weighed 1.05 g. (82%). The product was essentially pure as the melting point was unchanged by three recrystallizations from glacial acetic acid. After drying *in vacuo* at 100° for five hours, the melting point was 139–141° (cor.). The product dissolved in 10% aqueous sodium hydroxide upon the addition of an equal volume of ethanol.

Anal. Calcd. for C₂₈H₂₀O: C, 89.63; H, 5.79. Found: C, 89.77; H, 5.83.

4-(Biphenylene-*o*-tolylmethyl)-aniline.—A solution of 0.70 g. of 9-hydroxy-9-*o*-tolylfluorene, 1.0 g. of aniline and 1 g. of concd. hydrochloric acid (sp. gr. 1.19) in 4 ml. of glacial acetic acid was refluxed gently for three hours. The resulting dark red solution was poured into 20 ml. of ethanol-water (1:1) containing 2 g. of sodium hydroxide, whereupon a brown oil separated. Upon allowing the mixture to stand in the ice-box overnight, the oil solidified to a gum. The supernatant liquid was decanted and the gum washed by decantation with water. Recrystallization from absolute ethanol with the use of Darco gave 0.67 g. (75%) of cream-colored crystals. The product retained ethanol which caused its melting point to be under 100° with evolution of this solvent. After two more recrystallizations from absolute ethanol, it was crystallized from petroleum ether (b. p. 90–110°). It separated from the latter solvent as a gum which solidified on standing under the solvent. White crystals, m. p. 152.0–153.5° (cor.) were then obtained.

Anal. Calcd. for C₂₆H₂₁N: C, 89.87; H, 6.09; N, 4.03. Found: C, 90.07; H, 6.25; N, 4.26.

4-(Biphenylene-*o*-tolylmethyl)-2-methylaniline.—The condensation of 9-hydroxy-9-*o*-tolylfluorene with *o*-toluidine, in the same manner as with aniline, afforded a 70% yield of crude product, m. p. 166–170°. Three recrystallizations from absolute ethanol gave white crystals, m. p. 172–174° (cor.). No retention of solvent was observed.

Anal. Calcd. for C₂₇H₂₃N: C, 89.71; H, 6.41; N, 3.87. Found: C, 90.05; H, 6.67; N, 4.00.

N-Succinyl-4-(biphenylene-*o*-tolylmethyl)-2-methylaniline.—A solution of 11.0 g. of 4-(biphenylene-*o*-tolylmethyl)-2-methylaniline and 3.05 g. of succinic anhydride in 90 ml. of dry benzene was refluxed for twenty minutes. The resulting mixture was cooled and the flocculent white precipitate collected on a filter and washed with cold benzene. The yield was 13.0 g. (92%). Recrystallization from benzene-absolute ethanol (5:1) gave a pure product, m. p. 169–170° (cor.) with decomposition.

Anal. Calcd. for C₃₁H₂₇NO₄: C, 80.67; H, 5.90; N, 3.04. Found: C, 80.76; H, 6.04; N, 3.14.

Attempted Resolution of 4-(Biphenylene-*o*-tolylmethyl)-2-methylaniline.—A solution of 2.50 g. of 4-(biphenylene-*o*-tolylmethyl)-2-methylaniline in 75 ml. of ethyl acetate was added to a solution of 1.561 g. of *d*-camphorsulfonic acid in 75 ml. of hot ethyl acetate. The resulting yellow solution deposited a flocculent white precipitate upon standing one hour. The product was collected on a filter and dried *in vacuo* over phosphorus pentoxide; 3.87 g. (95.3%). The salt softened at 195° and slowly decomposed over the range 215–227°.

Rotation: 0.0888 g. made up to 5 ml. with 95% ethanol at 25° gave $\alpha_D + 0.027^\circ$; *l*, 1; $[\alpha]_D^{25} + 15^\circ$.

Recrystallization from 500 ml. of a mixture of 2:1 ethyl acetate and ethylene dichloride yielded fraction I, 2.18 g. Evaporation of the filtrate with a current of air to a volume of 300 ml., and then to 150 ml., gave fractions II and III, amounting to 0.80 g. and 0.55 g., respectively. Within experimental error, all fractions showed the same rotation as that of the original salt. Fraction I was recrystallized four times with no accompanying change in rotation. The product from the final recrystallization was hydrolyzed at 0°, by stirring with 5% aqueous ethanolic (1:1) sodium hydroxide solution. The resulting free amine was collected on a filter, washed with cold ethanol and dried; m. p. 172–174°. It showed no rotation in benzene.

Anal. Calcd. for C₂₇H₂₃NO₄S: C, 74.84; H, 6.62. Found: C, 74.66; H, 6.84.

4-(Biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline.—The condensation of 9-hydroxy-9-*o*-tolylfluorene with *p*-xylydine in the same manner as with aniline afforded a 66% yield of crude yellow product. Four recrystallizations from absolute ethanol with the use of Darco were necessary

(4) Lucas and Baumgarten, *THIS JOURNAL*, **68**, 1653 (1941).

to obtain white crystals of maximum m. p. 188–189° (cor.). No retention of solvent was observed.

Anal. Calcd. for $C_{28}H_{28}N$: C, 89.56; H, 6.71; N, 3.73. Found: C, 89.41; H, 6.56; N, 4.00.

N-Phthaloyl-4-(biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline.—A solution of 2.34 g. of 4-(biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline and 0.92 g. of phthalic anhydride in 150 ml. of dry benzene was refluxed for thirty minutes, cooled and the flocculent white precipitate collected on a filter. The yield was 2.59 g. (79%). The compound had no definite melting point; upon heating above 130° it slowly melted with the evolution of water vapor with ring closure to the imide structure taking place. The sample for analysis was recrystallized three times from benzene and dried *in vacuo* at 60° for three hours.

Anal. Calcd. for $C_{36}H_{32}NO_2$: C, 82.58; H, 5.58; N, 2.68. Found: C, 83.08; H, 5.66; N, 2.70.

N-[4-(Biphenylene-*o*-tolylmethyl)-2,5-dimethylphenyl]-phthalimide.—A mixture of equivalent amounts of 4-(biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline and phthalic anhydride was melted and maintained at 180° for thirty minutes. After cooling, the solidified melt was broken up and boiled with 20 ml. of 95% ethanol for ten minutes. After cooling, the cream-colored product was collected on a filter and dried. The yield was 90%. Two recrystallizations from a 3:1 mixture of absolute ethanol and benzene gave microscopic white crystals, m. p. 232–234° (cor.).

Anal. Calcd. for $C_{36}H_{32}NO_2$: C, 85.51; H, 5.38. Found: C, 85.27; H, 5.50.

Attempted Resolution of N-Phthaloyl-4-(biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline with Quinine.—A solution of 0.50 g. of N-phthaloyl-4-(biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline and 0.361 g. of quinine trihydrate in 7.5 ml. of hot benzene was allowed to stand at room temperature for thirty-six hours. The resulting precipitate of white "wart" crystals was collected on a filter and washed with a few ml. of benzene. The yield was 0.67 g. (83%). The salt decomposed with evolution of water vapor over the range 150–160°.

Rotation: 0.0270 g. made up to 2 ml. with 95% ethanol at 25° gave $\alpha_D - 0.92^\circ$; $l, 1$; $[\alpha]^{25}_D - 67^\circ$.

The salt was recrystallized four times from benzene to yield 0.19 g. of material. The rotation of the salt after each recrystallization was identical with that of the original salt within experimental error. The final product was hydrolyzed at 0° by stirring with 5 ml. of ethanol–water (1:1) containing a few drops of concd. hydrochloric acid.

The resulting free acid showed no rotation in ethanol. Both the quinine salt and the free acid dissolved too slowly to determine if immediate mutarotation occurred.

Anal. Calcd. for $C_{36}H_{32}NO_5$: C, 79.31; H, 6.30; N, 4.96. Found: C, 79.27; H, 6.59; N, 4.95.

N-Camphoryl-4-(biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline.—A mixture of 3.00 g. of 4-(biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline and 1.45 g. of *d*-camphoric anhydride was melted and the melt maintained at 150° for fifteen minutes. After cooling, the melt was taken up in 30 ml. of hot benzene and the resulting dark orange solution placed in the ice box overnight. The light tan precipitate was collected on a filter and washed with a few ml. of benzene; 2.75 g. (62%). The product decomposed with foaming over the range 155–185°. Twelve hours of drying *in vacuo* at 100° did not change the decomposition range.

Rotation: 0.0229 g. made up to 2 ml. with absolute ethanol at 25° gave $\alpha_D + 0.34^\circ$; $l, 1$; $[\alpha]^{25}_D + 30^\circ$. Three recrystallizations from benzene gave 0.70 g. of white product with a constant rotation, decomposing over the range 160–190°.

Rotation: 0.0400 g. made up to 3 ml. with absolute ethanol at 25° gave $\alpha_D + 0.32^\circ$; $l, 1$; $[\alpha]^{25}_D + 16^\circ$.

The initial filtrate was evaporated to dryness by a current of air and the brown gummy residue recrystallized from carbon tetrachloride with the use of Darco to afford 0.90 g. of light tan product.

Rotation: 0.0299 g. made up to 2 ml. with absolute ethanol at 25° gave $\alpha_D + 0.39^\circ$; $l, 1$; $[\alpha]^{25}_D + 26^\circ$. Three further recrystallizations from carbon tetrachloride gave a product identical with that obtained by recrystallization from benzene; $[\alpha]^{25}_D + 16^\circ$. The product dissolved too slowly to determine if immediate mutarotation occurred.

Anal. Calcd. for $C_{38}H_{38}NO_3$: C, 81.83; H, 7.05; N, 2.51. Found: C, 82.03; H, 7.30; N, 2.70.

Summary

1. A number of tetraarylmethanes containing the fluorene nucleus have been prepared by condensing 9-hydroxy-9-*o*-tolylfluorene with phenol, aniline, *o*-toluidine and *p*-xylydine.

2. The attempted resolutions of 4-(biphenylene-*o*-tolylmethyl)-2-methylaniline and 4-(biphenylene-*o*-tolylmethyl)-2,5-dimethylaniline failed.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Synthesis of Viridifloric Acid

BY ROGER ADAMS* AND WERNER HERZ

A program of research has been undertaken in this Laboratory to elucidate the structures of the acid moieties in the alkaloids of the type occurring in various *Senecio* species. These alkaloids are esters of retronecine, or of a closely related pyrrolizidine derivative, with dibasic acids usually containing ten carbon atoms. Alkaloids of this general type are not restricted, however, to the genus *Senecio*, but have been isolated from several other genera of plants. Monocrotaline¹ from *Crotalaria spectabilis* and *retusa* is an ester of retronecine with monocrotalic acid, a monobasic

acid of formula $C_8H_{12}O_5$. In the genera *Heliotropium*, *Trachelanthus*, *Cynoglossum* and *Lindelofia*, the alkaloids are esters of a pyrrolizidine derivative with various seven-carbon monobasic acids.

This communication concerns viridifloric acid obtained by hydrolysis of the alkaloid viridiflorine² found in *Cynoglossum viridiflorum*. It is a stereoisomer of trachelanthic acid obtained by hydrolysis of trachelanthamine found in *Trachelanthus korolkovi*³; more recently the latter was

(2) Menshikov, *Zhur. Obshchei Khim.*, **18**, 1736 (1948).

(3) (a) Menshikov, *ibid.*, **17**, 343 (1947); (b) Menshikov and Borodina, *ibid.*, **11**, 209 (1941); (c) **15**, 225 (1945); (d) Menshikov, *ibid.*, **16**, 1311 (1946); (e) Gurevitch and Menshikov, *ibid.*, **17**, 1714 (1947).

* Harvard University Ph.D. 1912.

(1) Adams and Rogers, *THIS JOURNAL*, **61**, 2815 (1939).