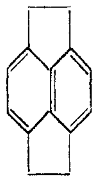
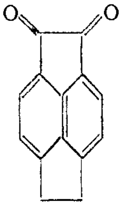
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

# A Synthesis of 1,2-Dihydrocyclopenta(cd)fluoranthene

BY MILTON C. KLOETZEL* AND FRANCIS L. CHUBB[1]

The feasibility of preparing compounds which have two five-membered rings fused to the opposite *peri* positions of a naphthalene nucleus has been tested by several investigators. Mayer and Kaufmann[2] attempted to prepare 1,2-dihydrocyclopenta(fg)acenaphthene (I) by distillation of 5-ethylacenaphthene from zinc dust but obtained only acenaphthylene. From the reaction of acenaphthene with oxalyl bromide in the presence of aluminum chloride, Fleischer and Wolff[3] obtained a product which they described as pyracene hemiquinone (II). However, analysis of the compound failed to confirm the suggested composition and no further evidence was adduced in support of structure II.


I

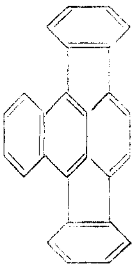


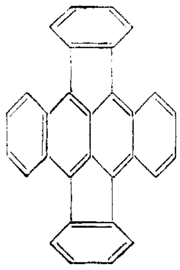
II

Fieser and Peters[4] attempted unsuccessfully to prepare a derivative of I by cyclization of β-(5-acenaphthoyl)-β-bromopropionic acid.

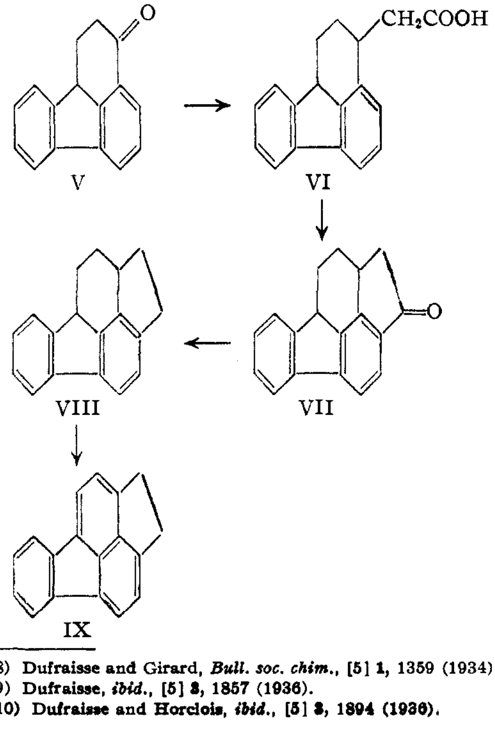
Further evidence of resistance to the closing of a second five-membered *peri* ring in the naphthalene nucleus is the observation that anthrahydroquinone-1,4-dicarboxylic acid forms only a monolactone while anthrahydroquinone-1,5-dicarboxylic acid forms a dilactone.[5]

Isorubicene (III), a hydrocarbon which presumably contains the fused ring skeleton of structure I, was first reported by Clar,[6] who claimed to have prepared it by heating 9,10-dichloro - 9,10 - dihydroanthracene - 9,10 - endo - α,β-succinic anhydride with benzene in the presence of aluminum chloride. Fedorov[7] has also reported the preparation of isorubicene by heating 1,4 - dichloro - 9,10 - dihydroxy - 9,10- diphenyl - 9,10-dihydroanthracene with oxalic acid, sodium formate, copper powder and aluminum powder. The hydrocarbon prepared by Fedorov was not identical with that prepared by Clar. Closely related to isorubicene is the hydrocarbon 5,6,11,12-diphenylenenaphthacene (IV), which was reported by Dufraisse and co-workers[8-10] to result from the oxidation of 5,12-diphenylnaphthacene and from the action of potassium hydroxide on 5,11-dichloro-6,12-diphenylnaphthacene or 5-chloro-6-phenyl-11,12-phenylenenaphthacene.


III


IV

In view of the conflicting evidence regarding the existence of naphthalene derivatives having two five-membered rings fused across the opposite *peri* positions, it appeared desirable to attempt the synthesis of such a compound by a new sequence which would leave no doubt as to the nature of the polycyclic skeleton. Herein is described a synthesis of 1,2-dihydrocyclopenta(cd)fluoranthene (transformations V to IX) which fulfils these requirements.



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* Harvard University Faculty 1938-1941.

[1] This work is abstracted from a portion of the thesis submitted by Francis L. Chubb to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Master of Science.

[2] Mayer and Kaufmann, *Ber.*, **53**, 289 (1920).

[3] Fleischer and Wolff, *ibid.*, **53**, 925 (1920).

[4] Fieser and Peters, THIS JOURNAL, **54**, 4347 (1932).

[5] Scholl and Böttger, *Ber.*, **63**, 2128 (1930).

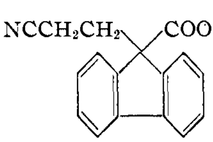
[6] Clar, *ibid.*, **64**, 2194 (1931).

[7] Fedorov, *Bull. Acad. Sci. U. S. S. R., Classe Sci. Chem.*, 397 (1947).

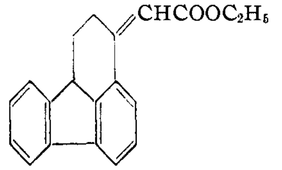
[8] Dufraisse and Girard, *Bull. soc. chim.*, [5] **1**, 1359 (1934).

[9] Dufraisse, *ibid.*, [5] **3**, 1857 (1936).

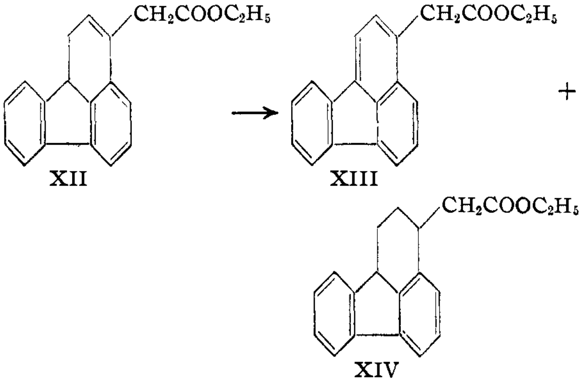
[10] Dufraisse and Horclois, *ibid.*, [5] **3**, 1894 (1936).



X



XI



Cyclization of β-(9-fluoryl)-propionyl chloride with aluminum chloride in nitrobenzene, adapting a procedure employed by Bachmann and Kloetzel[11] to cyclize phenanthrylpropionyl chlorides, afforded a 77% yield of 3-keto-1,2,3,10b-tetrahydrofluoranthene (V).[12] The requisite β-(9-fluoryl)-propionic acid was prepared by saponification and partial decarboxylation of ethyl 9-(β-cyanoethyl)-9-fluorenecarboxylate (X), which, in turn, resulted in 94% yield from a Michael-type condensation of acrylonitrile with ethyl 9-fluorenecarboxylate in the presence of pyridine and sodium hydroxide. Only 9,9-bis-(β-cyanoethyl)-fluorene was obtained when acrylonitrile was allowed to condense directly with fluorene in the presence of sodium hydroxide and pyridine,[13] conditions which have been employed by Pinck and Hilbert[14] for the condensation of benzalacetophenone with fluorene.

3-Keto-1,2,3,10b-tetrahydrofluoranthene (V) was subjected to a Reformatsky reaction with ethyl bromoacetate, under conditions similar to those employed by Bachmann and Edgerton[15] with 4 - keto - 1,2,3,4 - tetrahydrophenanthrene. Dehydration of the product yielded an oily mixture from which two solid esters were isolated. Analysis indicated that one of these was the ethyl 3 - (1,2,3,10b - tetrahydrofluoanthylidene)-acetate (XI) or its isomer (XII), and that the other was ethyl 3-fluoranthylacetate (XIII). Dehydrogenation of the oily ester mixture by heating with palladium-on-charcoal catalyst,[16] afforded a 90% yield of ethyl 3-fluoranthylacetate (XIII). This material and the ethyl 3-fluoranthylacetate isolated directly from the Reformatsky dehydration mixture were identical. It is not improbable that ethyl 3-fluoranthylacetate was formed by a disproportionation (XII → XIII + XIV) which occurred during dehydration of the Reformatsky reaction product, and that the unidentified liquid portion of the resulting mixture contained some ester XIV.

The mixture of acids obtained by saponification of the Reformatsky reaction dehydration product was hydrogenated over Adams catalyst to yield 3-(1,2,3,10b-tetrahydrofluoranthyl)-acetic acid (VI). A pure sample of 3-fluoranthylacetic acid was recovered 90% unchanged after long exposure to identical hydrogenation conditions. This clearly demonstrated that VI had the ascribed structure resulting from hydrogenation of the acid corresponding to XI or XII. It could not have been a different isomer produced by hydrogenation of 3-fluoranthylacetic acid which was present in the saponified Reformatsky reaction dehydration product.

Cyclization of the acid chloride of VI with aluminum chloride in nitrobenzene afforded a 59% yield of 1-keto-1,2,2a,3,4,4a-hexahydrocylopenta(cd)fluoranthene (VII). The successful synthesis of ketone VII indicates that five-membered rings can be closed readily across both *peri* positions of the partially hydrogenated naphthalene nucleus. In direct contrast were the results obtained when the naphthalene nucleus was completely aromatic. Attempted cyclization of 3-fluoranthylacetyl chloride yielded only polymeric material.

1,2,2a,3,4,4a-Hexahydrocyclopenta(cd)fluoranthene (VIII) was prepared by Clemmensen reduction of ketone VII. When this hydrocarbon was heated to 260–320° with palladium-on-charcoal catalyst, hydrogen equivalent to two moles per mole of hydrocarbon was evolved, and 1,2-dihydrocyclopenta(cd)fluoranthene (IX) was obtained in 78% yield. Comparison of the ultraviolet absorption spectrum of IX with that

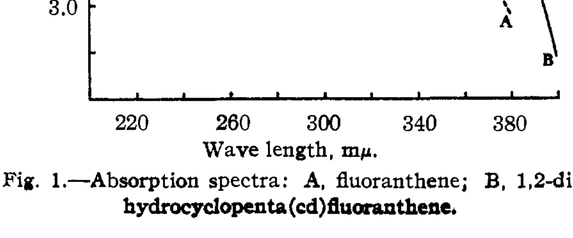


Fig. 1.—Absorption spectra: A, fluoranthene; B, 1,2-dihydrocyclopenta(cd)fluoranthene.

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(11) Bachmann and Kloetzel, THIS JOURNAL, **59**, 2207 (1937).

(12) Compare von Braun and Anton, *Ber.*, **62**, 145 (1929), whose conditions yielded only 33% of the ketone.

(13) A similar result was obtained by Bruson, THIS JOURNAL, **64**, 2457 (1942), who employed benzyltrimethylammonium hydroxide as catalyst.

(14) Pinck and Hilbert, *ibid.*, **68**, 2014 (1946).

(15) Bachmann and Edgerton, *ibid.*, **62**, 2970 (1940).

(16) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1292 (1925).

of fluoranthene[17] (Fig. 1) shows sufficient similarity to preclude any assumption of skeletal rearrangement during dehydrogenation of VIII. The fusion of two five-membered rings across the opposite *peri* positions of a naphthalene nucleus, once accomplished, evidently gives rise to a stable structural configuration.

## Experimental[18]

**3-Keto-1,2,3,10b-tetrahydrofluoranthene** (V).—To a solution of 14.3 g. of ethyl 9-fluorenecarboxylate[19] and 3.2 g. of acrylonitrile in 25 cc. of pyridine was added 5 cc. of 50% sodium hydroxide. Reaction began immediately, with evolution of heat, when the mixture was shaken. After being cooled and allowed to stand at room temperature for thirty minutes, the mixture was diluted with 300 cc. of water, acidified with hydrochloric acid and extracted with benzene. Evaporation of the washed benzene extract and distillation of the residue under reduced pressure yielded 16.4 g. (94%) of **ethyl 9-(β-cyanoethyl)-9-fluorenecarboxylate (X)**, b.p. 210-220° at 1-2 mm.

Hydrolysis of 16.4 g. of ester X was accomplished by refluxing for four hours with 200 cc. of 20% potassium hydroxide. The solid dibasic acid obtained by acidification of the resulting solution was heated to 250° until evolution of carbon dioxide ceased. Crystallization of the product from benzene-heptane yielded 12.8 g. (95%) of **β-(9-fluoryl)-propionic acid**, m. p. 141-145°. Two recrystallizations from aqueous acetic acid raised the m. p. to 146-148°. The purified sample gave no m. p. depression when mixed with a sample of the acid prepared from the sodio derivative of ethyl 9-fluorenecarboxylate and ethyl β-bromopropionate by the method of von Braun and Anton.[12]

Preparation and cyclization of β-(9-fluoryl)-propionyl chloride by methods analogous to those previously described[11] for phenanthrylpropionyl chlorides afforded a 77% yield of 3-keto-1,2,3,10b-tetrahydrofluoranthene (V), b. p. 180-190° at 2-3 mm., m. p. 99-100°. von Braun and Anton[12] reported a m. p. of 98° for this ketone.

**3-Fluoranthylacetic Acid and Derivatives.**—A Reformatsky reaction of 3-keto-1,2,3,10b-tetrahydrofluoranthene (V) with ethyl bromoacetate was effected under conditions similar to those employed by Bachmann and Edgerton[15] with 4-keto-1,2,3,4-tetrahydrophenanthrene. The crude hydroxy ester was dehydrated by heating to 200° at 1-2 mm. pressure, and the product (91% yield from ketone V) distilled at 210-220° at 1-2 mm. Upon standing for several days, the mixture slowly solidified.

Fractional crystallization of a sample of the ester mixture from petroleum ether yielded first **ethyl 3-fluoranthylacetate** (XIII), which eventually separated from alcohol in fluorescent, pale yellow plates, m. p. 111-112°.

*Anal.* Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.07; H, 5.70.

The second crop of crystals from petroleum ether eventually yielded **ethyl 3-(1,2,3,10b-tetrahydrofluoranthylidene)-acetate** (XI) or its isomer (XII), which separated from alcohol in non-fluorescent, colorless needles, m. p. 111-112°.

*Anal.* Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.69; H, 6.47.

A mixture of XIII with XI (or XII) melted at 90-110°.

Dehydrogenation of a 2.0 g. sample of the mixed esters from the Reformatsky reaction, by heating to 280-290° for one and one-quarter hours with 100 mg. of palladium-on-charcoal catalyst, yielded the calculated volume of hydrogen and 1.8 g. (90%) of **ethyl 3-fluoranthylacetate** (XIII). Admixture of a sample of this ester with the ethyl 3-fluoranthylacetate isolated directly from the Reformatsky reaction caused no depression of m. p.

Hydrolysis of 14.8 g. of XIII, by refluxing for twenty minutes with 150 cc. of 20% potassium hydroxide, yielded 11.5 g. (86%) of **3-fluoranthylacetic acid**, which separated from acetic acid in pale yellow plates, m. p. 233-234°.

*Anal.* Calcd. for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.92; H, 4.74.

No significant absorption of hydrogen occurred when a mixture of 5 g. of 3-fluoranthylacetic acid, 50 cc. of glacial acetic acid and 100 mg. of Adams catalyst was shaken for five hours with hydrogen at 30-lb. pressure. After removal of the acetic acid and catalyst, 4.5 g. (90%) of pure 3-fluoranthylacetic acid was recovered unchanged.

**3-Fluoranthylacetyl chloride** was prepared by warming a mixture of the acid and thionyl chloride (10 cc. thionyl chloride per g. of acid) on the steam-bath for fifteen minutes and evaporating excess thionyl chloride under reduced pressure. Crystallized from benzene, the compound formed yellow plates, m. p. 139-141°, which contained one molecule of solvent for each two of acid chloride.

*Anal.* Calcd. for $C_{42}H_{28}O_2Cl_2$: Cl, 11.16. Found: Cl, 11.18.

Removal of benzene of crystallization was effected by heating to 80° in vacuum: m. p. 140-141°.

*Anal.* Calcd. for $C_{18}H_{11}OCl$: Cl, 12.72. Found: Cl, 12.62.

A solution of 3-fluoranthylacetyl chloride, freshly prepared from 2 g. of the corresponding acid, in 15 cc. of nitrobenzene was added slowly to a solution of 2 g. of anhydrous aluminum chloride in 16 cc. of nitrobenzene. The temperature was maintained at 0° during the addition and for an additional period of four hours. Hydrolysis was effected by pouring the reaction mixture into a mixture of ice and hydrochloric acid. Steam distillation of the nitrobenzene left 1.8 g. of a yellow powder which was insoluble in boiling nitrobenzene, pyridine, dioxane, acetic acid or acetone. The powder, evidently polymeric, began to darken at 300° but did not melt even at 340°.

**Synthesis of 1,2-Dihydrocyclopenta(cd)fluoranthene IX.**—Hydrolysis of 26 g. of the mixture of dehydrated esters obtained from the aforedescribed Reformatsky reaction was accomplished by refluxing for fifteen minutes with 20% sodium hydroxide. The precipitated mixture of acids, once recrystallized from aqueous acetic acid (20 g., m. p. 180-186°), was hydrogenated at 23-31-lb. pressure in 200 cc. of glacial acetic acid over 400 mg. of Adams catalyst. The requisite volume of hydrogen was absorbed within three hours. Crystallization of the stereoisomeric mixture from acetic acid yielded 9.5 g. (47%) of **3-(1,2,3,10b-tetrahydrofluoranthyl)-acetic acid (VI)**, m. p. 151-155°. A sample recrystallized four times from acetic acid melted at 157-158°.

*Anal.* Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.69; H, 5.91.

Two grams of pure acid VI (m. p. 157-158°) was converted to the acid chloride and cyclized in the same manner as previously described for cyclization of β-(9-fluoryl)-propionyl chloride. **1-Keto-1,2,2a,3,4,4a-hexahydrocyclopenta(cd)fluoranthene (VII)** was isolated in 59% yield (1.1 g.). The ketone was dimorphic, crystallizing from ethanol in colorless needles which changed to hexagonal plates upon standing in contact with the solution. Both forms melted at 134-135°.

*Anal.* Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.81; H, 5.84.

The oxime of VII, prepared in pyridine according to the procedure of Shriner and Fuson,[20] separated from ethanol in colorless needles, m. p. 192-193°.

*Anal.* Calcd. for $C_{18}H_{15}NO$: N, 5.36. Found: N, 5.12.

Ketone VII was reduced by the Clemmensen method, employing 20 g. of amalgamated zinc, 24 cc. of concentrated hydrochloric acid, 20 cc. of glacial acetic acid, 20 cc. of toluene and 2.1 g. of the ketone. During the reflux period (forty-eight hours) an additional 20 cc. each of

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[17] Orchin and Reggel, THIS JOURNAL, **69**, 505 (1947).

[18] All m. p.'s are uncorrected. Analyses by Dr. Adalbert Elek, Elek Micro Analytical Laboratories, Los Angeles, California.

[19] Adickes, *J. prakt. Chem.*, **145**, 235 (1936).

[20] Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 167.

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.

LOS ANGELES, CALIFORNIA RECEIVED AUGUST 8, 1949

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

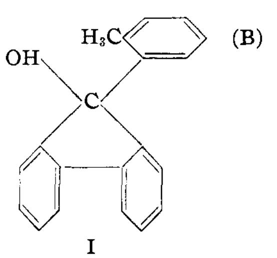
# Hindered Tetraarylmethanes

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 coördinated 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*-tolylfluorene[3] (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.



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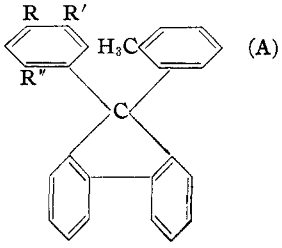

II

| | R | R′ | R |
|---|---|---|---|
| a | OH | H | H |
| b | $NH_2$ | H | H |
| c | $NH_2$ | $CH_3$ | H |
| d | $NH_2$ | $CH_3$ | $CH_3$ |

The condensation of 9-hydroxy-9-*o*-tolylfluorene (I) with aniline, *o*-toluidine and *p*-xylidine 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

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* Harvard University Ph.D. 1912.

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

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

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