The Acid-catalyzed Reaction of 9-Fluorenol with 9-Alkylidenefluorenes

By S. Wawzonek and E. Dufek[1]

The addition of Grignard reagents to fluorenone in benzene and ether formed, in addition to the desired carbinols, considerable amounts of 9-fluorenol. These mixtures, if not separated, gave on dehydration with acid 1,1-(9-fluorenyl-9-fluorenylidene)-alkanes in addition to the 9-alkylidenefluorenes. The structure of the former was demonstrated by reduction to the alkyl-bis-9-fluorenylmethane, oxidation to fluorenone and the alkyl 9-fluorenyl ketone and synthesis from 9-fluorenylmagnesium bromide and an ethyl ester.

The addition of Grignard reagents to fluorenone in benzene and ether forms in addition to the desired carbinols[2] considerable amounts of 9-fluorenol (I). These mixtures, if not separated, on dehydration with acid give in addition to the alkylidenefluorenes II high melting by-products. These products have now been identified as the 1,1-(9-fluorenyl-9-fluorenylidene)-alkanes (III) and result from an acid-catalyzed reaction between 9-fluorenol (I) and the alkylidenefluorene II.
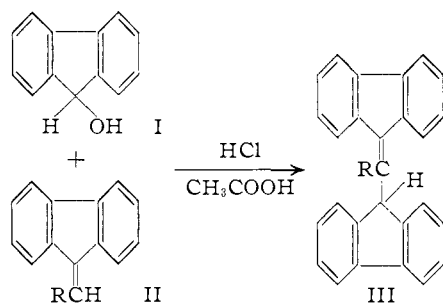
The unsaturated structure was indicated by reduction with hydrogen iodide and red phosphorus, oxidation with various agents and by the ultraviolet spectra. Catalytic hydrogenation had no effect on the double bond using platinum oxide as the catalyst.

Reduction with hydrogen iodide and red phosphorus of 1,1-(9-fluorenyl-9-fluorenylidene)-propane (III, R = C₂H₅) and 9-fluorenyl-9-fluorenylidenemethane (III, R = H) gave the corresponding saturated hydrocarbon IV. The simplest one (IV, R = H) was synthesized by alkylating lithium fluorenyl (V) with 9-fluorenylmethyl chloride (VI).
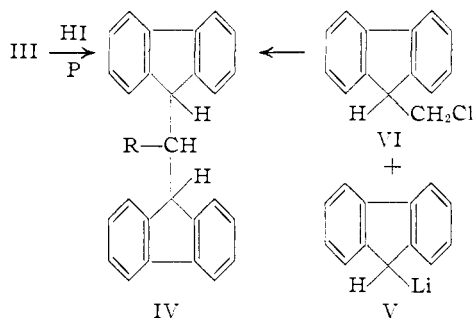

Ozonolysis of 1,1-(9-fluorenyl-9-fluorenylidene)-

propane (III, R = C₂H₅) gave in one run a small amount of ethyl 9-fluorenyl ketone (VII). In another such study fluorenone as the 2,4-dinitrophenylhydrazone was isolated together with 9-fluorenol since catalytic hydrogenation was used in the decomposition of the ozonide.

Oxidation of 1,1-(9-fluorenyl-9-fluorenylidene)-propane (III, R = C₂H₅) with potassium dichromate gave only fluorenone. A similar reaction using performic acid gave the pinacol rearrangement product, ethyl 9-(9,9'-bifluorenyl) ketone (VIII, R = C₂H₅), of the expected glycol. An analogous reaction occurred with 1,1-(9-fluorenyl-9-fluorenylidene)-ethane (III, R = CH₃). The structure of the resulting ketone (VIII, R = C₂H₅) was demonstrated by cleavage with alkali to 9,9'-bifluorenyl (IX, R = H) and synthesis from ethyl 9-fluorenyl ketone (VII, R = C₂H₅) and 9-
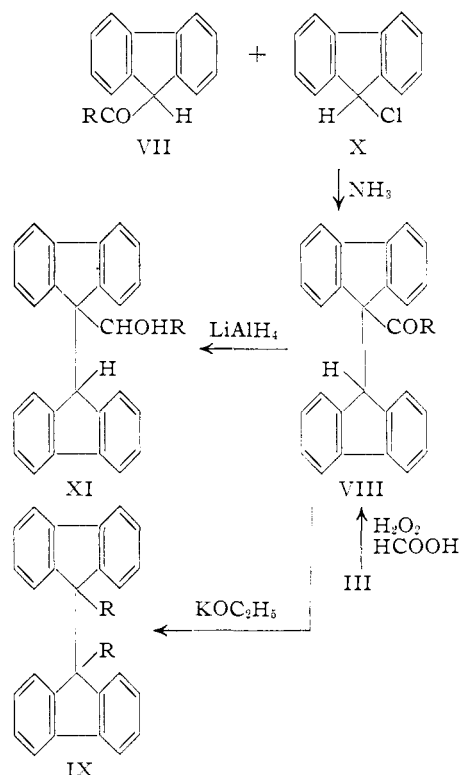
chlorofluorene (X) using conditions similar to those given for the preparation of 9-carbethoxy-9,9'-bifluorenyl.[3] Ethyl 9-(9,9'-bifluorenyl) ketone did not react with phenylhydrazine or 2,4-dinitrophenylhydrazine but was reduced by lithium

(1) Abstracted in part from the Ph.D. Thesis, June, 1956, of E. Dufek and presented before the Organic Division of the American Chemical Society at the Cincinnati Meeting, April, 1955.

(2) S. Wawzonek, E. Dufek and N. M. Sial, J. Org. Chem., 21, 276 (1956).

(3) L. A. Pinck and G. E. Hilbert, This Journal, 68, 377 (1946).

aluminum hydride to ethyl 9-(9,9'-bifluorenyl)-carbinol (XI, R = C_2H_5).

1,1-(9-Fluorenyl-9-fluorenylidene)-propane (III, R = C_2H_5) was synthesized by adding 9-fluorenyl-magnesium bromide to ethyl propionate. This product was accompanied by ethyl 9-fluorenyl ketone (VII) and an oil which gave an ultraviolet absorption spectrum similar to that for a mixture of 9-propylidenefluorene (II) and ethyl 9-fluorenyl ketone (VII). The former (II) could be formed by the reduction of ethyl 9-fluorenyl ketone (VII) in the Grignard reaction to the corresponding alcohol and a subsequent dehydration of this product during the course of the distillation.

The acid conditions used in the condensation of 9-fluorenol with a 9-alkylidenefluorene suggest the formation of a carbonium ion (XII) from 9-fluorenol (I) and the addition of this substance to the alkylidenefluorene (II). This addition can proceed in two ways and form the intermediate car-

bonium ions XIII and XIV. The ion XIII would give the desired product by a simple loss of a proton whereas ion XIV would require a rearrangement involving the migration of a fluorenyl group followed by a loss of a proton. Carbonium ion XIV, however, is similar to the intermediates postulated in the rearrangement of 9-fluorenylcarbinols to phenanthrenes[4] and could give the latter if the rearrangement to the phenanthrene were to proceed more readily than the migration of the fluorenyl group.
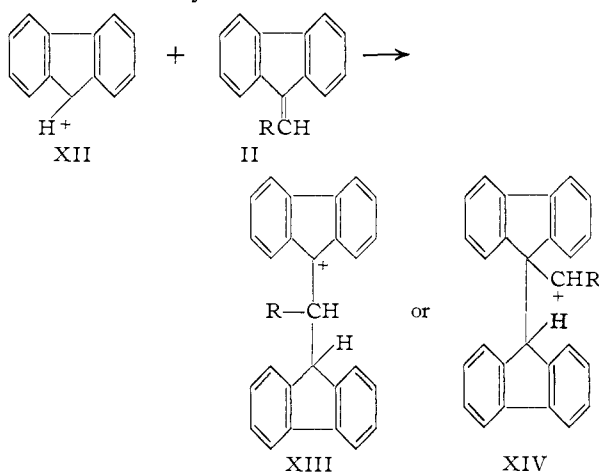
To distinguish between these two paths 9-(9,9'-bifluorenyl)-carbinol (XV) was prepared and treated with phosphorus pentoxide according to the directions given for the rearrangement of the
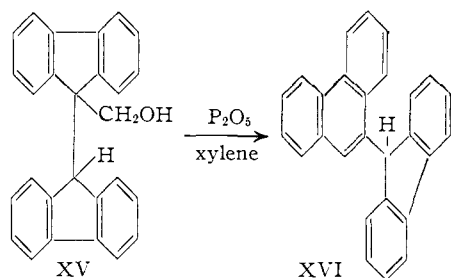
(4) E. J. Greenhow, D. McNeil and E. N. White, J. Chem. Soc., 987 (1952).

9-fluorenylcarbinol.[5] The formation of 9-fluorenyl-phenanthrene (XVI) under these conditions eliminated the possibility that ion XIV was an intermediate in the reaction. The 1,1-(9-fluorenyl-9-fluorenylidene)-alkanes must be formed, therefore, by the first mechanism outlined.

The ultraviolet spectra for these compounds, which were of help earlier in the work, are listed in Table I. Maxima in the region of 237, 247 and 311 mμ occur for both the 9-alkylidenefluorenes (II) and the 1,1-(9-fluorenyl-9-fluorenylidene)-alkanes (III) and are absent for the 9,9'-dialkyl-9,9'-bifluorenyls (IX, R = alkyl), 9-spirofluorenyl-cyclopropane[4] and the bis-fluorenylmethanes. These frequencies are associated therefore with the unsaturation in the 9-position of fluorene. This extension of the conjugation also destroys the fine structure of the fluorene system in the 260–270 mμ region in a manner similar to that found with other aromatic compounds.

The peak at 229 mμ which was found for a number of examples is related to the fluorene ring since it is also given by fluorene and the 9-alkylfluorenes.[4]

The dialkylbifluorenyls (IX) mentioned are formed by the bimolecular reduction of 9-alkyl-9-fluorenols (II) using stannous chloride and iodine[6] and possibly could have arisen in the decomposition of the Grignard mixture if traces of magnesium had been present. A cyclopropane derivative could arise from carbonium ion XIII by an intramolecular alkylation of the 9-position of the other fluorene ring.

Both of these possibilities were also excluded by the chemical behavior observed for the 1,1-(9-fluorenyl-9-fluorenylidene)-alkanes (III).

Experimental[7]

1,1-(9-Fluorenyl-9-fluorenylidene)-propane (III, R = C_2H_5). a.—Fluorenone (180 g.) in dry benzene (300 ml.) was added to a solution of n-propylmagnesium bromide (1 mole) in absolute ether (300 ml.) and dry benzene (300 ml.). The resulting solution after refluxing for 3 hr. was decomposed with ammonium chloride and gave crude 9-n-propyl-9-fluorenol (130 g.), m.p. 90–100°. This carbinol was heated for 2 hr. in glacial acetic acid (500 ml.) and concentrated hydrochloric acid (50 ml.) and then diluted with an equal amount of cold water. The oily layer was separated and the aqueous layer was extracted with three 75-ml. portions of petroleum ether (b.p. 30–60°). The ether extracts and oily layer were combined and after removal of acidic impurities were dried over magnesium sulfate. Removal of the solvent gave 9-n-propylidenefluorene, b.p. 150–155° at 1 mm.; yield, 56.1 g. The dark glassy distillation residue gave 7.5 g. of an orange solid when dissolved in ethyl acetate; successive recrystallizations from benzene, ethyl acetate and carbon tetrachloride, gave white hexagonal plates (2.5 g.) melting at 160–162°. An additional yield of this compound (16.5 g.), 1,1-(9-fluorenyl-9-fluorenylidene)-propane, was obtained from the magnesium sulfate used in drying by treating with water and extracting with benzene. The analytical sample after two recrystallizations from ethyl acetate melted at 162–164°.

Anal. Calcd. for $C_{29}H_{22}$: C, 94.05; H, 5.95; mol. wt., 370. Found: C, 93.94; H, 6.08; mol. wt., 365, 372.

A sample of the crude 9-n-propyl-9-fluorenol when recrystallized twice from methanol melted at 125–126°. The methanol filtrate upon dilution with water gave 9-fluorenol (11.7% yield), which after one crystallization from benzene melted at 149–151°.

(5) W. G. Brown and B. Bluestein, This Journal, 62, 3256 (1940).

(6) A. Wanscheidt and B. Moldavski, Ber., 64, 917 (1931).

(7) Melting points are not corrected.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED FLUORENES[a]

Compound	λ_{max}, mμ (log ϵ)
9-Fluorenyl-9-fluorenylidenemethane	229(4.80), 237(4.68), 247(4.75), 259(4.87), 275(4.51), 290(4.44), 302(4.47), 315(4.39)
1,1-(9-Fluorenyl-9-fluorenylidene)-ethane	232(4.71), 240(4.59), 249(4.59), 259(4.69), 275(4.44), 290(4.34), 302(4.34), 312(4.29)
1,1-(9-Fluorenyl-9-fluorenylidene)-propane	231(4.65), 239(4.53), 249(4.55), 259(4.66), 274(4.37), 288(4.30), 301(4.28), 318(4.23)
1,1-(9-Fluorenyl-9-fluorenylidene)-butane	231(4.49), 240(4.40), 250(4.42), 259(4.52), 275(4.24), 290(4.16), 302(4.15), 320(4.11)
9-n-Propylidenefluorene	230(4.59), 236(4.42), 247(4.44), 256(4.61), 273(4.03), 283(4.06), 298(3.94), 311(3.93)
9-n-Butylidenefluorene	229(4.57), 235(4.40), 246(4.44), 256(4.62), 273(4.15), 278(4.19), 301(4.10), 311(3.94)
9,9'-Bifluorenyl	258(4.39), 264(4.42), 267(4.42), 291(3.93), 302(4.05)
9,9'-Di-n-propyl-9,9'-bifluorenyl	262(4.61), 266(4.64), 270(4.64), 294(4.24), 305(4.34)
9,9'-Di-n-butyl-9,9'-bifluorenyl	262(4.53), 266(4.56), 270(4.56), 294(4.15), 305(4.26)
Bis-9-fluorenylmethane	258(4.50), 264(4.55), 266(4.56), 290(4.05), 302(4.18)
Ethyl-bis-9-fluorenylmethane	258(4.39), 264(4.41), 267(4.42), 291(3.93), 302(4.05)
9-Spirofluorenylcyclopropane[b]	226(4.30)　259(4.15), 268(4.20), 275(4.07), 292(3.90), 302(4.04)
Ethyl 9-fluorenyl ketone	258(4.40), 266(4.37), 290(3.75), 301(3.70)
Oil from reacn. of 9-fluorenylmagnesium bromide and ethyl propionate	233(4.57), 240(4.31), 249(4.39), 257(4.55), 266(4.26), 275(4.22), 285(4.09), 302(3.98), 317(3.83)

[a] Solvent 95% ethanol, Cary recording spectrophotometer, model 11; 1-cm. silica cells.　[b] Reference 4.

b. A mixture of 9-fluorenol (4.5 g.) and 9-n-propylidene-fluorene (5.5 g.) in glacial acetic acid (30 ml.) and concentrated hydrochloric acid (3 ml.) was refluxed for 1.25 hr. and after cooling treated with cold water (10 ml.). The yellow gummy mass formed was dissolved in ethyl acetate, washed with water and dried with magnesiun sulfate. The precipitate which formed and the magnesium sulfate were filtered, washed with water and a small amount of hot ethanol and then recrystallized from ethyl acetate; yield, 2.5 g., m.p. 160–162°. A mixture with the product isolated from the preparation of 9-n-propylidenefluorene melted at the same point.

c. Similar results were obtained using a mixture of 9-fluorenol and pure 9-n-propyl-9-fluorenol.

1,1-(9-Fluorenyl-9-fluorenylidene)-butane (III, R = C₃H₇).—Crude 9-n-butyl-9-fluorenol (30 g.) when treated as in part a for the corresponding propyl compound gave n-butylidenefluorene (21.8 g.) and 1,1-(9-fluorenyl-9-fluorenyl-idene)-butane (1 g.). Crystallization successively from benzene, a mixture of benzene and petroleum ether (b.p. 30–60°) and ethyl acetate gave white hexagonal plates melting at 158–160°.

Anal. Calcd. for C₃₀H₂₄: C, 93.75; H, 6.25. Found: C, 93.16; H, 6.32.

1,1-(9-Fluorenyl-9-fluorenylidene)-ethane (III, R = CH₃).—A mixture of 9-fluorenol (4.5 g.) and 9-ethyl-9-fluorenol (5.5 g.) when treated as in part c gave a product (8.0 g.) which after recrystallization successively from ethyl acetate, carbon tetrachloride and ethyl acetate melted at 139–141°.

Anal. Calcd. for C₂₈H₂₀: C, 94.38; H, 5.62. Found: C, 94.44; H, 5.60.

9-Fluorenyl-9-fluorenylidenemethane (III, R = H).—A mixture of 9-fluorenol (4.5 g.) and 9-methyl-9-fluorenol (5.5 g.) when treated according to part c gave a crude product (4.0 g.) which melted at 206–208° after successive recrystallizations from benzene–petroleum ether (b.p. 30–60°) and ethyl acetate.

Anal. Calcd. for C₂₇H₁₈: C, 94.74; H, 5.26. Found: C, 94.82; H, 5.33.

Ethyl-(bis-9-fluorenyl)-methane.—1,1-(9-Fluorenyl-9-fluorenylidene)-propane (1 g.) in glacial acetic acid (50 ml.) was refluxed with hydrogen iodide (47%, sp. gr. 1.50) (10 ml.) and red phosphorus (0.5 g.) for 1.75 hr. The hot solution gave white crystals after filtering through a sintered glass funnel to remove the phosphorus and cooling. Recrystallization from a mixture of benzene and petroleum ether (b.p. 30–60°) gave long white needles melting at 158–160°; yield 0.63 g.

Anal. Calcd. for C₂₉H₂₄: C, 93.55; H, 6.45. Found: C, 93.44; H, 6.60.

Catalytic reduction using acetic acid or ethyl acetate as the solvent and platinum oxide as the catalyst was not successful.

Bis-9-fluorenylmethane.—9-Fluorenyl-9-fluorenylidene-methane (0.20 g.) when treated with hydrogen iodide as above gave bis-9-fluorenylmethane (0.15 g.). Recrystallization from a mixture of benzene and petroleum ether (b.p. 30–60°) gave long white needles melting at 212–213°.

Anal. Calcd. for C₂₇H₂₀: C, 94.19; H, 5.81. Found: C, 94.01; H, 6.07.

A solution of 9-chloromethylfluorene (0.8 g.) in petroleum ether (b.p. 60–68°) was added to 9-fluorenyllithium,[8] prepared from 1 g. of lithium and fluorene and the mixture was refluxed for 12 hr. The excess fluorenyllithium was decomposed with absolute ethanol and the solution steam distilled to remove the solvent and excess fluorene. The dark brown residue was filtered and triturated with hot ethanol. The resulting gray solid was recrystallized from benzene and petroleum ether (b.p. 30–60°); yield, 0.6 g., m.p. 212–213°.

9-Chloromethylfluorene.—9-Fluorenylcarbinol (15 g.) was treated with thionyl chloride (45 ml.) and the resulting solution refluxed for 30 minutes. Removal of the excess thionyl chloride under reduced pressure was followed by a distillation of the product at reduced pressure, b.p. 140–145° (1–3 mm.). Three recrystallizations from ethanol gave a white solid (5.6 g.) melting at 66.5–67.5°.

Anal. Calcd. for C₁₄H₁₁Cl; C, 78.32; H, 5.17. Found: C, 78.10; H, 5.42.

If the crude product after removal of the thionyl chloride is dissolved in ether and washed with water, a quantitative yield of bis-9-fluorenylmethyl sulfite, m.p. 106–107°, is obtained.

Anal. Calcd. for C₂₈H₂₂SO₃: C, 76.50; H, 5.16. Found: C, 76.54; H, 5.06.

Oxidation of 1,1-(9-Fluorenyl-9-fluorenylidene)-propane a. Ozonolysis.—1,1-(9-Fluorenyl-9-fluorenylidene)-propane (1.0 g.) in ethyl acetate was treated at −40° with ozone. The resulting solution was treated with hydrogen (40 lb.) in the presence of platinum oxide. Removal of the solvent gave a small amount of ethyl 9-fluorenyl ketone (0.05 g.), which after one recrystallization from ethanol melted at 93–96°. This melting point was not depressed when mixed with an authentic sample.

In a similar run, but using palladium catalyst for the decomposition of the ozonide, only 9-fluorenol, m.p. 149–151°, and fluorenone as the 2,4-dinitrophenylhydrazone, m.p. 300° dec., were isolated.

b. Dichromate Oxidation.—A solution of 1,1-(9-fluo-renyl-9-fluorenylidene)-propane (0.20 g.) in glacial acetic acid (20 ml.) was refluxed with potassium dichromate (1.2 g.) and concentrated sulfuric acid (1 ml.) for 1 hr. The solution after cooling and dilution with cold water (50 ml.) gave fluorenone (0.15 g.) melting at 80–83°.

c. Performic Acid Oxidation.—A solution of 1,1-(9-fluorenyl-9-fluorenylidene)-propane (0.5 g.) in benzene (10 ml.) and formic acid (98–100%) (15 ml.) was treated with 30% hydrogen peroxide (2 ml.) and allowed to stand for 36–48 hr. Removal of the solvent under reduced pressure gave ethyl 9-(9,9'-difluorenyl) ketone, which was recrystallized three times from dilute ethanol; yield, 0.35 g., m.p. 211–212°.

Anal. Calcd. for C₂₉H₂₂O: C, 90.15; H, 5.70. Found: C, 89.38; H, 5.76.

Performic Acid Oxidation of 1,1-(9-Fluorenyl-9-fluorenyl-idene)-ethane.—1,1-(9-Fluorenyl-9-fluorenylidene)-ethane

(8) S. H. Tucker and M. Whalley, *J. Chem. Soc.*, 50 (1949).

when oxidized in the same manner as in part c gave methyl 9-(9,9'-bifluorenyl) ketone. Two crystallizations from 95% ethanol gave a product melting at 160–161°.

Anal. Calcd. for $C_{28}H_{20}O$: C, 90.32; H, 5.37. Found: C, 90.16; H, 5.06.

Cleavage of Ethyl 9-(9,9'-Bifluorenyl) Ketone.—Ethyl 9-(9,9'-bifluorenyl) ketone (0.3 g.) was refluxed with potassium ethoxide (3.3 g. of potassium) in 20 ml. of ethanol for 3 hr. Cooling the solution gave a solid (0.2 g.) which was recrystallized from benzene and petroleum ether (b.p. 30–60°). The long white needles formed, melted at 244–245° and did not depress the melting point of 9,9'-bifluorenyl when mixed with this compound.

Ethyl 9-(9,9'-Bifluorenyl) Ketone.—Liquid ammonia (15 ml.) was added to a solution of 9-chlorofluorene (1.9 g.) and ethyl 9-fluorenyl ketone (2.2 g.) in dry toluene (10 ml.) and the resulting mixture allowed to stand overnight. Removal of the solvent under reduced pressure and recrystallization from 95% ethanol gave ethyl 9-(9,9'-bifluorenyl) ketone (0.8 g.) melting at 212–213°. A mixture with the product from the performic acid oxidation of 1,1-(9-fluorenyl-9-fluorenylidene)-propane melted at the same point.

Ethyl 9-Fluorenyl Ketone.—The conditions used were similar to those given for the preparation of methyl 9-fluorenyl ketone.[9] A mixture of potassium methoxide (from 10.5 g. of potassium), fluorene (43 g.) and ethyl propionate (27.6 g.) was refluxed in ether (80 ml.) for 20 hr. The resulting mixture was poured into water (225 ml.) and acidified with 3 N hydrochloric acid. Extraction with ether gave a solid which was recrystallized twice from petroleum ether (b.p. 30–60°). The long white needles (24.6 g., 42.7% yield) melted at 101°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.48; H, 6.30. Found: C, 86.10; H, 6.42.

The 2,4-dinitrophenylhydrazone when recrystallized from ethanol melted at 170–170.5°.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.67; H, 4.43; N, 13.93. Found: C, 65.17; H, 4.69; N, 13.52.

Ethyl-9-(9,9'-bifluorenyl)-carbinol.—Ethyl 9-(9,9'-bifluorenyl) ketone (0.5 g.) in absolute ether (10 ml.) was added to a solution of lithium aluminum hydride (0.2 g.) in absolute ether (20 ml.). After decomposition of the excess lithium aluminum hydride with ethyl acetate and addition of dilute hydrochloric acid to dissolve the precipitated salts, the ether layer was separated and washed with water. Removal of the ether followed by two recrystallizations from benzene and petroleum ether (b.p. 30–60°) gave 0.3 g. of a product melting at 181–182°.

Anal. Calcd. for $C_{29}H_{24}O$: C, 89.65; H, 6.23. Found: C, 89.56; H, 6.47.

Reaction of 9-Fluorenylmagnesium Bromide[8] with Ethyl Propionate.—Fluorene (27.7 g.) in xylene (85 ml.) was added to a solution of ethylmagnesium bromide (0.42 mole) in ether (300 ml.), and the resulting solution was refluxed until the theoretical amount of ethane was evolved (3 hr.). During this time the ether was distilled off slowly. The resulting xylene solution was treated with a mixture of ether (50 ml.) and xylene (50 ml.) and then removed after the solid settled. To this solid in ether (50 ml.), ethyl propionate (4.8 g.) in ether (50 ml.) was added, and the resulting mixture was refluxed for 2.5 hr. Decomposition with ammonium chloride followed by extraction with ether gave an

(9) I. Von and E. C. Wagner, *J. Org. Chem.*, **9**, 155 (1944).

oil which upon cooling gave fluorene (3.2 g.). Distillation of the remaining oil gave a fraction (0.8 g.) boiling at 132–138° (1 mm.) and analyzing for a mixture of 9-propylidene-fluorene and ethyl 9-fluorenyl ketone. The ultraviolet spectra confirmed the presence of the unsaturated compound.

Anal. Calcd. for $C_{32}H_{28}O$: C, 89.64; H, 6.54. Found: C, 89.31; H, 6.84.

The next fraction boiling at 138–145° (1 mm.) gave ethyl 9-fluorenyl ketone (0.5 g.), m.p. 101°.

The dark red residue in the flask dissolved in ethyl acetate and gave a white crystalline compound (1.0 g.) which melted at 161–164° after crystallization from benzene and did not depress the melting point of 1,1-(9-fluorenyl-9-fluorenylidene)-propane.

9-(9,9'-Bifluorenyl)-carbinol.—Lithium aluminum hydride (1.2 g.) was added to a suspension of 9-carbethoxy-9,9'-bifluorenyl (2.2 g.)[3] in absolute ether (30 ml.), and the mixture was stirred for 1 hr. After adding excess ethyl acetate, the slurry was acidified with dilute hydrochloric acid. The ether layer was separated, washed thoroughly with water and evaporated to dryness. Two recrystallizations of the residue from a mixture of benzene and petroleum ether (b.p. 30–60°) gave 1.1 g. of white crystals melting at 174–175°.

Anal. Calcd. for $C_{27}H_{20}O$: C, 90.00; H, 5.55. Found: C, 89.31; H, 5.31.

9-(9'-Fluorenyl)-phenanthrene. Rearrangement of 9-(9,9'-Bifluorenyl)-carbinol.—A solution of 9-(9,9'-bifluorenyl)-carbinol (1.0 g.) in anhydrous xylene (20 ml.) and phosphorus pentoxide (5.0 g.) was refluxed for 4 hr. The solution was cooled and decanted, and the phosphorus pentoxide residue was extracted with a small amount of hot benzene. The combined benzene and xylene solutions were washed with water, filtered and evaporated to dryness at reduced pressure. Two recrystallizations of the residue from a mixture of benzene and petroleum ether (b.p. 30–60°) gave 9-(9'-fluorenyl)-phenanthrene (0.64 g.) melting at 196–198°. The melting point was the same for a mixture with an authentic sample.[10]

9,9'-Di-n-propyl-9,9'-bifluorenyl.—These directions are similar to those used for the dimethyl analog.[6] To a solution of 9-n-propyl-9-fluorenol (2.5 g.) in warm glacial acetic acid (40 ml.) a stannous chloride–iodine solution (80 ml.), prepared by adding a solution of stannous chloride (10 g.) in concentrated hydrochloric acid (20 ml.) to iodine (5 g.) in warm glacial acetic acid (80 ml.), was added. After stirring the mixture for 1.5 hr., the orange precipitate which formed was filtered, dissolved in ether and washed once with dilute sodium hydroxide and once with water. Removal of the ether and recrystallization of the residue three times from ethyl acetate gave 0.9 g. of white crystals melting at 208–209°.

Anal. Calcd. for $C_{32}H_{30}$: C, 92.70; H, 7.30. Found: C, 92.62; H, 7.51.

9,9'-Di-n-butyl-9,9'-bifluorenyl.—9-n-Butyl-9-fluorenol (2.5 g.) when treated with stannous chloride and iodine as above gave 9,9'-di-n-butyl-9,9'-bifluorenyl (0.8 g.) after recrystallization from ethyl acetate, m.p. 202°.

Anal. Calcd. for $C_{34}H_{34}$: C, 92.26; H, 7.74. Found: C, 92.04; H, 7.86.

Iowa City, Iowa

(10) W. E. Bachmann, This Journal, **56**, 1365 (1934).