mixture with lead tetraacetate in chloroform followed by strontium hypobromite, yielded partially racemized strontium D-methoxy-diglycolate, proving independently the presence and nature of the ring and showing the proportion of alpha and beta forms in the mixture used.

7. The rate of oxidation of methyl-*d*-arabinofuranoside by lead tetraacetate, as well as the amount of oxidant consumed, have been found to be in close agreement with the predictions previously made for a substance of this structure.

8. The rate of hydrolysis of *d*-erythrose diacetamide by 0.100 *N* sulfuric acid has been measured.

9. The rate of mutarotation of *d*-arabinose oxime has been measured.

CAMBRIDGE, MASS. RECEIVED JUNE 2, 1939

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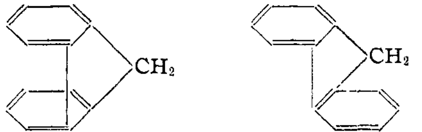
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

# The Structure of Fluorene

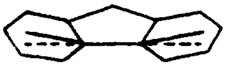
BY WARREN C. LOTHROP

Although fluorene has been a familiar compound for many years, it has not excited the interest which has so enlarged our knowledge of the comparable tricyclic hydrocarbons anthracene and phenanthrene. Indeed a recent review of the chemistry of fluorene[1] indicates how little is known of its reactions and how much uncertainty still attaches to its structure.

Since 1925 when Kuhn and Jacob[2] proposed a space formula for fluorene (I) based on Kaufler's formula for diphenyl, in order to explain their claimed separation of two forms of 9-aminofluorene, there has been extensive investigation of the possibility of stereoisomerism of 9-substituted fluorenes. All such attempts have failed or been disproved,[3] so that the existence of such extreme forms as pictured in (I) seems unlikely if not impossible. Whether or not the two aromatic rings are inclined at a slight angle to the plane of the five-membered ring[4] cannot be stated with certainty yet, but the evidence does seem to indicate that the rings are bent away from the coaxial diphenyl bond with a distortion of the valence angles from the benzene rings by 12°,[5] to give a planar structure (II) as pictured by Pinck and Hilbert[6] where the five-membered ring is a nearly regular pentagon



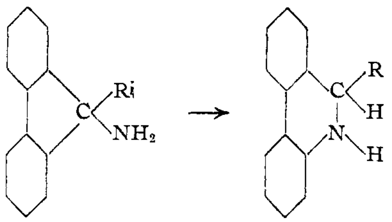
I



II

This formula is probable from dipole measurements[5,7] and X-ray studies[8] and is further supported by the failure of fluorenone-4-carboxylic acid to close a fourth ring,[4a] the distance being too great to be bridged.

That such a planar configuration as (II) would be in a condition of some strain is to be anticipated and has been used[6] to account for the ready enlargement of the five-membered ring in the Stieglitz rearrangement of amines of the type (III) to yield phenanthridines:



III

It has been suggested further[5] that this internal strain could be relieved at least partially by a preferred arrangement of the double bonds according to the argument of Mills and Nixon[9] so that a definitely preferred bond structure (IV) should most nearly represent fluorene

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[1] Rieveschl and Ray, *Chem. Rev.*, **23**, 287 (1938).

[2] Kuhn and Jacob, *Ber.*, **58**, 1432 (1925).

[3] Cook and Iball, *Chemistry & Industry*, 467 (1936), give a critical review of the stereochemistry of fluorene.

[4] (a) Mills, Palmer and Tomkinson, *J. Chem. Soc.*, **125**, 2365 (1924); (b) Iball, *Z. Krist.*, **94**, 397 (1936).

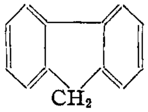
[5] Hughes, LeFèvre and LeFèvre, *J. Chem. Soc.*, 202 (1937).

[6] Pinck and Hilbert, THIS JOURNAL, **59**, 8 (1937).

[7] Bergmann, Engel and Hoffmann, *Z. physik. Chem.*, **17**, 92 (1932).

[8] Hengstenberg and Mark, *Z. Krist.*, **70**, 283 (1929).

[9] Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).



IV

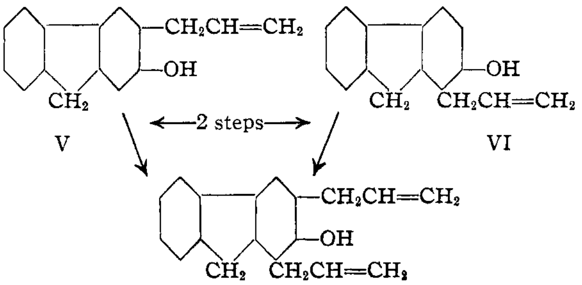
Auwers and co-workers[10] have given the only evidence as to the chemical nature of the double bonds and on the basis of refractive studies they declared that the aromatic rings of fluorene must be classed as similar to naphthalene and anthracene although they do not attempt a quantitative comparison. Others,[11] while not going as far, have distinguished fluorene from diphenyl by considering it as "quasi-aromatic" and more to be compared to dibenzocyclopentadiene. This view is disputed by Ruiz[12] and Mangini[13] with however little evidence aside from the special reactivity of fluorene at positions 2 and 7 which correspond to the active 4,4′-positions in diphenyl.

Evidence favoring formula IV is scant but may be found in the ring closures of $\gamma$-2-fluorylbutyric acid[14] and of *o*-(2-fluoryl)-benzoic acid[15] both of which take place into the 3-position. As similar ring closures in the case of 2-substituted naphthalene would be into the 1-position, analogy would seem to indicate that the double bond in fluorene is located entirely between positions 2 and 3 as shown in IV.

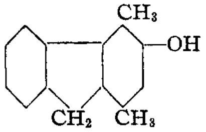
Another reaction indicating preference for position 3 may be found in the reported formation of 2,3-diacetofluorene,[16] while the special reactivity[17] of a bromine atom at 3 must have significance.

From the above discussion it is evident that the problem of the bond structure of fluorene is similar to that of naphthalene, anthracene, hydrindene and tetralin and like them should be susceptible to attack by the methods used by Fieser and Lothrop,[18] which depend on the Claisen rearrangement of allyl ethers and the diazo coupling of hydroxyl derivatives.

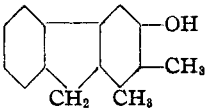
A preliminary investigation of the rearrangement of the allyl ethers of 2-hydroxyfluorene and 3-hydroxyfluorene gave ambiguous results. From the pyrolysis of the former, two isomeric substances were obtained corresponding undoubtedly to compounds V and VI, both of which yielded 1,3-diallyl-2-hydroxyfluorene on pyrolysis of their respective allyl ethers. This indicates apparently that the aromatic ring in fluorene is more benzenoid than naphthoid, for such behavior would be impossible in the latter case. Pyrolysis of the allyl ether of the previously unreported 3-hydroxyfluorene, however, yielded only an unworkable gum.



So that there might be no doubt regarding the chemical activity of a hydroxyl group in position 3, derivatives were synthesized by unambiguous methods in which both ortho positions were successively blocked by methyl groups. The allyl ethers of these test compounds (VII and VIII) rearranged smoothly and the free hydroxyfluorenes coupled readily in alkaline solution with diazotized aniline, proving conclusively that there is little or no fixation of the double bonds in the Mills–Nixon formulation (IV) and that fluorene is more like benzene, tetralin and hydrindene, than like naphthalene, anthracene and phenanthrene. The special reactivity of positions 2 and 7 is probably to be ascribed to the greater directive influence of the phenyl group as compared to the benzyl group, and the hydrocarbon is closely related to diphenyl although form IV may be favored slightly.



VII



VIII

The preparation of the needed derivatives of 3-hydroxyfluorene was accomplished by the method employed originally by Ullmann and co-workers[19] for the preparation of 3-methoxyfluorenone. This consisted of the internal coupling of diazotized *o*-aminobenzophenone derivatives obtained

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[10] Auwers and Frühling, *Ann.*, **422**, 220 (1920); Auwers and Krollpfeiffer, *ibid.*, **430**, 264 (1923).

[11] Goss and Ingold, *J. Chem. Soc.*, 1268 (1928); Anatakrishnan and Hughes, *ibid.*, 1607 (1935).

[12] Ruiz, *Añal. asoc. quim. argentina*, (a) **16**, 170 (1928), (b) **17**, 42 (1929).

[13] Mangini, *Ricerca sci.*, **7**, I, No. 5–6 (1936).

[14] Koelsch, THIS JOURNAL, **55**, 3885 (1933).

[15] Barnett, Goodway and Watson, *Ber.*, **66**, 1876 (1933).

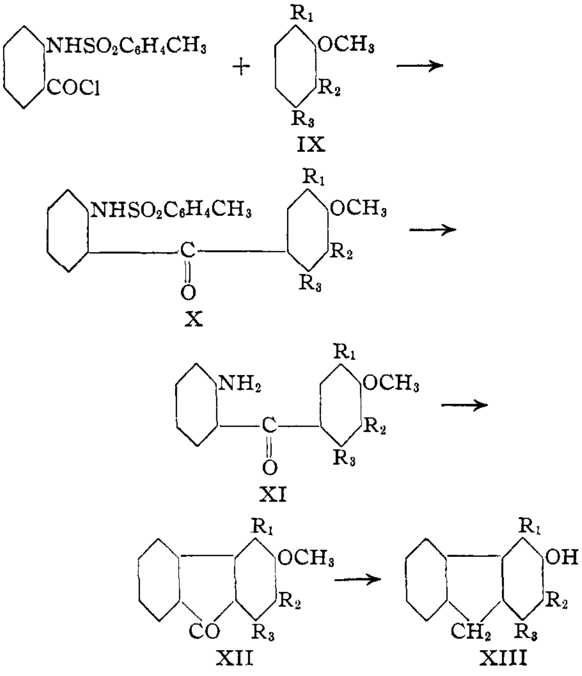
[16] Dziewonski and Kleszcz, *Roczniki Chem.*, **12**, 172 (1932); *cf.* ref. 1, p. 365.

[17] Miller and Bachman, THIS JOURNAL, **57**, 2443 (1935).

[18] Fieser and Lothrop, *ibid.*, (a) **57**, 1459 (1935); (b) **58**, 749, (c) 2050 (1936); (d) **59**, 945 (1937).

[19] Ullmann and Bleier, *Ber.*, **35**, 4273 (1902).

by sulfuric acid hydrolysis of the products formed in the Friedel–Crafts synthesis between the appropriate anisole derivative and the *p*-toluenesulfonamide of anthranilic acid chloride. Refluxing of acetic acid solutions of the resultant methoxyfluorenones with red phosphorus and hydriodic acid gave the desired hydroxyfluorenes directly, since demethylation and reduction were thus effected simultaneously. The general method is indicated below



## Experimental Part

**2-Hydroxyfluorene.**—This compound was obtained in 57% yield from 2-aminofluorene by diazotization and subsequent hydrolysis as described by Ruiz.[12a] After treatment of its alkaline solution with norite and precipitation with acid, it was crystallized in white plates from 50% acetic acid, m. p. 169°.

**2-Alloxyfluorene.**—A solution of 8.5 g. of 2-hydroxyfluorene in 150 cc. of anhydrous acetone was refluxed for twenty-four hours with 7.7 g. of allyl bromide and 9.25 g. of finely powdered anhydrous potassium carbonate. A white solid product, completely insoluble in 1 *M* sodium hydroxide, was precipitated when the reaction mixture was poured into water; it was crystallized in gleaming white plates from dilute alcohol, m. p. 95–96°. The yield was 10.3 g. or 99%.

*Anal.* Calcd. for $C_{16}H_{14}O$: C, 86.44; H, 6.34. Found: C, 86.30; H, 6.38.

**1-Allyl and 3-Allyl-2-hydroxyfluorene (VI and V).**—Pyrolysis of 6.0 g. of 2-alloxyfluorene at 235–238° for five minutes gave a solid product, m. p. 83–84°, which was soluble in alkali but only with great difficulty. It was separated into two products by repeated fractional crystallization from petroleum ether. Compound A crystallized in fine, cream-colored needles, m. p. 87–88°, and represented about 60% of the whole. Compound B crystallized in thick, pale-brown needles, m. p. 111–112°, and represented about 25% of the material recovered.

By analogy with the melting points of pseudo-cumenol (m. p. 70°) and hemi-mellitenol (m. p. 81°) it seemed likely that Compound A was 3-allyl-2-hydroxyfluorene (V) and Compound B was 1-allyl-2-hydroxyfluorene (VI). This is in agreement with the preferred reactivity of position 3 previously cited; however, no proof of structure was attempted.

*Anal.* Calcd. for $C_{16}H_{14}O$: C, 86.44; H, 6.34. Found for A: C, 86.30; H, 6.18. Found for B: C, 86.16; H, 6.03.

The allyl ethers of both A and B were prepared without difficulty in 70–75% yields and were crystallized from 80% alcohol in nearly colorless plates. The allyl ether of A melted at 44–45° while that of B melted at 82–83°.

*Anal.* Calcd. for $C_{19}H_{18}O$: C, 87.00; H, 6.90. Found for allyl ether of A: C, 87.30; H, 7.12. Found for allyl ether of B: C, 87.12; H, 7.16.

**1,3-Diallyl-2-hydroxyfluorene.**—Pyrolysis of the allyl ethers of either A or B gave the same dark oil, which was purified by vacuum distillation, b. p. 170° at 3 mm. The distillate solidified in small clumps of fine yellow needles and crystallized from petroleum ether in fine, cream-colored needles, m. p. 58°.

*Anal.* Calcd. for $C_{19}H_{18}O$: C, 87.00; H, 6.90. Found: C, 86.96; H, 7.09.

**3-Methoxyfluorenone** (XII where $R_1$, $R_2$ and $R_3$ are H atoms).—This compound, described by Ullmann and Bleier,[19] was obtained as an orange-yellow solid, m. p. 92–94°, which was not purified further.

**3-Hydroxyfluorene** (XIII where $R_1$, $R_2$ and $R_3$ are H atoms).—A solution of 8.5 g. of the crude 3-methoxyfluorenone in 75 cc. of glacial acetic acid was refluxed for eighty hours with 1.0 g. of red phosphorus and 60 cc. of constant boiling hydriodic acid. The crude product dissolved in ether and filtered to remove excess phosphorus was extracted with small portions of cold, dilute alkali containing a trace of sodium hydrosulfite to remove iodine and any unreduced hydroxyfluorenone. This method served to eliminate the impurities without apparently effecting any loss of the much less acidic hydroxyfluorene, which was recovered as a white solid. It was crystallized from dilute alcohol in cream-colored plates, m. p. 136–137°. The yield was 4.9 g. or 66%. The **benzoate** crystallized from dilute alcohol in fine plates, m. p. 128°.

*Anal.* Calcd. for $C_{13}H_{10}O$: C, 85.66; H, 5.54. Found: C, 85.36; H, 6.14. Calcd. for $C_{20}H_{14}O_2$ (benzoate): C, 83.89; H, 4.92. Found: C, 83.52; H, 5.27.

**2-(4-Toluenesulfonamido)-benzoyl Chloride.**—The acid chloride was prepared from anthranilic acid as described by Miller and Bachman.[17]

**2,5-Dimethyl-4-methoxy-2′-(4-toluenesulfonamido)-benzophenone** (X where $R_1$ and $R_3$ are $CH_3$ groups and $R_2$ is a H atom).—To a vigorously stirred mixture of 20.4 g. of powdered aluminum chloride and 45.5 g. of the above acid chloride in 200 cc. of carbon disulfide, 20.0 g. of the methyl ether of *p*-xylene[18c] was added dropwise at room temperature, and the resulting dark red complex gradually warmed on the steam-bath. Refluxing was continued for six hours and the reaction allowed to stand overnight. Treatment of the mixture in the usual manner gave 4.2 g. of unchanged methoxyxylene and a white product which crystallized well from 600 cc. of 95% alcohol after treatment with norite. The yield of thick, pale yellow blades, m. p. 140–141°, was 35.0 g. or 71%.

*Anal.* Calcd. for $C_{23}H_{23}O_4NS$: C, 67.45; H, 5.67; N, 3.42. Found: C, 67.03; H, 5.69; N, 3.52.

The corresponding **methylamine** derivative was prepared in 99% yield by treatment of an alkaline solution of the above compound with dimethyl sulfate. It crystallized in gleaming white plates from alcohol, m. p. 168–169°.

*Anal.* Calcd. for $C_{24}H_{25}O_4NS$: C, 68.08; H, 5.95; N, 3.31. Found: C, 68.55; H, 6.34; N, 3.16.

**2,5-Dimethyl-4-methoxy-2′-aminobenzophenone** (XI where $R_1$ and $R_3$ are $CH_3$ groups and $R_2$ is H).—When 12 g. of the above sulfonamide was mixed with 35 cc. of concentrated sulfuric acid a clear red solution resulted in a few hours but reaction was complete only after three days of standing at room temperature. The mixture was poured into excess ammonia and the product filtered and crystallized from dilute alcohol in bright yellow needles, m. p. 102–104°. The yield was 7.5 g. or 99%.

*Anal.* Calcd. for $C_{16}H_{17}O_2N$: C, 75.27; H, 6.70; N, 5.48. Found: C, 74.97; H, 6.46; N, 5.46.

**1,4-Dimethyl-3-methoxyfluorenone** (XII where $R_1$ and $R_3$ are $CH_3$ groups and $R_2$ is H).—Several trials indicated that while this compound could be obtained in one step by the diazotization of the diluted sulfuric acid hydrolysis solution of the above amine in the manner described by Ullmann and Bleier,[19] the yields were low (36%) and the product difficult to purify. The most satisfactory results were obtained when the crude aminobenzophenone (7.5 g.) was dissolved in 1 liter of cold water containing 260 cc. of concentrated hydrochloric acid and treated with 8.0 g. of sodium nitrite. The clear orange solution was filtered, warmed on the steam-bath for five hours, and the bright yellow product which separated was recovered by filtration. It was three times extracted by suspension at 100° in 50-cc. portions of 3 *N* potassium hydroxide and after thorough washing with water crystallized from dilute alcohol in bright yellow needles, m. p. 140–141°. The yield was 5.85 g. or 84%.

*Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.78; H, 6.12.

**2,5-Dimethyl-4-methoxy-2′-hydroxybenzophenone.**—Acidification of the alkaline extracts above gave a substance which crystallized from alcohol in yellow prisms, m. p. 94–95°, and which weighed 0.1 g. Its **acetate** crystallized from alcohol in white prisms, m. p. 81–82°.

*Anal.* Calcd. for $C_{16}H_{16}O_3$: C, 74.99; H, 6.28. Found: C, 75.17; H, 6.65. Calcd. for $C_{18}H_{18}O_4$(acetate): C, 72.50; H, 6.07. Found: C, 72.45; H, 6.34.

**1,4-Dimethyl-3-hydroxyfluorenone.**—This compound was a product of incomplete reduction in the reaction described below, or could be obtained directly by the demethylation of its methyl ether with 48% hydrobromic acid. It crystallized from glacial acetic acid in fine, brilliant yellow needles, m. p. 223–224°, and gave an intensely red solution in alkali. The **acetate** separated from dilute acetic acid in pale yellow needles, m. p. 133–134°.

*Anal.* Calcd. for $C_{15}H_{12}O_2$: C, 80.36; H, 5.40. Found: C, 80.62; H, 5.75. Calcd. for $C_{17}H_{14}O_3$(acetate): C, 76.67; H, 5.29. Found: C, 76.72; H, 5.69.

**1,4-Dimethyl-3-hydroxyfluorene** (VII).—A solution of 3.9 g. of 1,4-dimethyl-3-methoxyfluorenone in 125 cc. of glacial acetic acid was refluxed for sixteen hours with 30 cc. of hydriodic acid (b. p. 127°) and 0.5 g. of red phosphorus. The product was recovered and purified in the manner already described for 3-hydroxyfluorene, being finally crystallized from ligroin in long, flesh colored needles, m. p. 180–181°. The yield was 2.58 g. or 87%. The acetate crystallized from alcohol in cream-colored plates, m. p. 100°.

*Anal.* Calcd. for $C_{15}H_{14}O$: C, 85.70; H, 6.71. Found: C, 85.69; H, 6.72. Calcd. for $C_{17}H_{16}O_2$(acetate): C, 80.94; H, 6.38. Found: C, 81.28; H, 6.45.

**1,4-Dimethyl-2-benzeneazo-3-hydroxyfluorene.**—When an alkaline solution of 0.1 g. of the hydroxyfluorene above in 10 cc. of 2 *N* sodium hydroxide and 5 cc. of water was treated at 0° with a slight excess of a freshly prepared solution of benzene diazonium chloride, an orange-brown precipitate immediately appeared. It was crystallized from glacial acetic acid in fine brown needles, m. p. 183–184°.

*Anal.* Calcd. for $C_{21}H_{18}ON_2$: C, 80.24; H, 5.76. Found: C, 80.34; H, 5.59.

**1,4-Dimethyl-3-alloxyfluorene.**—A mixture of 1.1 g. of (VII), 1.0 g. of powdered anhydrous potassium carbonate and 0.7 g. of allyl bromide in 25 cc. of acetone, was refluxed for forty-five hours and poured into water. The oily product was recovered by ether extraction and crystallized from dilute alcohol in fine white needles, m. p. 54–55°. The yield was 1.06 g. or 82%.

*Anal.* Calcd. for $C_{18}H_{18}O$: C, 86.40; H, 7.23. Found: C, 86.68; H, 7.29.

**1,4-Dimethyl-2-allyl-3-hydroxyfluorene.**—This compound was obtained in 62% yield by the pyrolysis of the above alloxyfluorene under nitrogen at 215°. It was difficultly soluble in alkali and crystallized from glacial acetic acid in nearly colorless plates, m. p. 150–151°.

*Anal.* Calcd. for $C_{18}H_{18}O$: C, 86.40; H, 7.23. Found: C, 86.66; H, 7.34.

**vic-*o*-Xylenol Methyl Ether** (IX where $R_1$ is H and $R_2$ and $R_3$ are $CH_3$ groups).—Several different attempts showed that this compound may be prepared best from 2-amino-3-methylanisole[20] by its conversion into 2-bromo-3-methylanisole[21] and subsequent treatment of the Grignard reagent of the latter with dimethyl sulfate. The yields for the last two procedures, however, were improved materially. In the Sandmeyer reaction the cuprous bromide solution was added at 0° instead of 60° and the diazonium complex allowed to decompose by standing at room temperature for two hours. The yield of product, b. p. 122–127° at 18 mm., m. p. 37–38°, was 80% compared with the reported 44%.[21]

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[20] Gibson, *J. Chem. Soc.*, **123**, 1269 (1923); Hodgson and Beard, *ibid.*, **127**, 498 (1925).

[21] Short, Stromberg and Wiles, *ibid.*, 319 (1936).

The conversion of the bromide into the desired xylenol methyl ether was effected in 79% yield by the use of two moles of dimethyl sulfate instead of one[21] and subsequent treatment as described elsewhere.[22] The over-all yield from 118 g. of *m*-cresol was 26.3 g. of vic-*o*-xylenol methyl ether.

The preparation of the compounds listed below was accomplished by procedures exactly like those recorded above; therefore repetition of details is omitted.

**2,3 - Dimethyl - 4 - methoxy - 2′ - (4 - toluenesulfonamido)-benzophenone** (X where $R_2$ and $R_3$ are $CH_3$ groups and $R_1$ is H).—Was obtained from alcohol in 33% yield as nearly colorless needles, m. p. 136–138°.

*Anal.* Calcd. for $C_{23}H_{23}O_4NS$: C, 67.45; H, 5.67; N, 3.42. Found: C, 67.43; H, 5.90; N, 3.50.

The corresponding **methylamine** derivative was prepared with difficulty due to the great insolubility of the above sulfonamide in alkali. It crystallized from dilute alcohol in white needles, m. p. 160°.

*Anal.* Calcd. for $C_{24}H_{25}O_4NS$: C, 68.08; H, 5.95; N, 3.31. Found: C, 68.05; H, 6.25; N, 3.37.

**2,3 - Dimethyl - 4 - methoxy - 2′ - aminobenzophenone** (XI where $R_2$ and $R_3$ are $CH_3$ groups and $R_1$ is H).—This was obtained in 95% yield and crystallized from dilute alcohol in pale yellow needles, m. p. 144–145°.

*Anal.* Calcd. for $C_{16}H_{17}O_2N$: C, 75.27; H, 6.70; N, 5.48. Found: C, 75.58; H, 7.05; N, 5.29.

**1,2-Dimethyl-3-methoxyfluorenone** (XII where $R_2$ and $R_3$ are $CH_3$ groups and $R_1$ is H) was obtained in 63% yield by the use of much larger volumes of solutions due to the extreme insolubility of the amine hydrochloride. It crystallized from glacial acetic acid in brilliant yellow needles, m. p. 178–179°.

*Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.90; H, 6.22.

**2,3-Dimethyl-4-methoxy-2′-hydroxybenzophenone** was formed as a by-product in the above reaction to the extent of 10%. It separated from dilute alcohol in yellow prisms, m. p. 135–136°. Its **acetate** also crystallized from dilute alcohol in white prisms m. p. 97–98°.

*Anal.* Calcd. for $C_{16}H_{16}O_3$: C, 74.99; H, 6.28. Found: C, 74.79; H, 6.50. Calcd. for $C_{18}H_{18}O_4$(acetate): C, 72.50; H, 6.07. Found: C, 72.80; H, 6.35.

**1,2 - Dimethyl - 3 - hydroxyfluorenone.**—This compound separated from acetic acid in orange needles, m. p. 258–259° dec. The **acetate** was obtained from the same solvent in long yellow needles, m. p. 137–138°.

*Anal.* Calcd. for $C_{15}H_{12}O_2$: C, 80.36; H, 5.40. Found: C, 80.36; H, 5.59. Calcd. for $C_{17}H_{14}O_3$(acetate): C, 76.67; H, 5.29. Found: C, 76.99; H, 5.48.

**1,2-Dimethyl-3-hydroxyfluorene (VIII),** formed in 74% yield was obtained in fine white needles from benzene-ligroin, m. p. 212–213° dec. The **acetate** separated from dilute acetic acid in white needles, m. p. 146–147°.

*Anal.* Calcd. for $C_{15}H_{14}O$: C, 85.70; H, 6.71. Found: C, 85.82; H, 6.98. Calcd. for $C_{17}H_{16}O_2$(acetate): C, 80.94; H, 6.38. Found: C, 81.22; H, 6.68.

**1,2 - Dimethyl - 4 - benzeneazo - 3 - hydroxyfluorene.**—The extreme insolubility of the hydroxyfluorene in alkali at 0° necessitated the addition of 5 cc. of dioxane. The coupling product crystallized from glacial acetic acid in fine clusters of brown needles, m. p. 201° dec.

*Anal.* Calcd. for $C_{21}H_{18}ON_2$: C, 80.24; H, 5.76. Found: C, 80.32; H, 6.02.

**1,2-Dimethyl-3-alloxyfluorene** was obtained in 76% yield from alcohol as white plates, m. p. 102–103°.

*Anal.* Calcd. for $C_{18}H_{18}O$: C, 86.40; H, 7.23. Found: C, 86.62; H, 7.56.

**1,2-Dimethyl-4-allyl-3-hydroxyfluorene.**—Pyrolysis of the above allyl ether at 230° gave a yield of 78% of pale yellow needles, m. p. 135–136°, from glacial acetic acid.

*Anal.* Calcd. for $C_{18}H_{18}O$: C, 86.40; H, 7.23. Found C, 86.44; H, 7.53.

## Summary

Methods which have been useful for the location of double bonds in other aromatic hydrocarbons have been applied to fluorene, with the result that the latter may be said to be benzenoid rather than naphthoid. Fluorene has been found to possess no considerable fixation of bonds as might be expected if the Mills–Nixon effect were operating and it is suggested that the special reactivity of positions 2 and 7 may be ascribed to the superior directive properties of the phenyl group.

HARTFORD, CONNECTICUT RECEIVED JUNE 10, 1939

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(22) *Org. Syntheses*, **11**, 66 (1931).