238. *Reaction of 2-Nitrofluorenone with Potassium Hydroxide, Aniline, and Sodium Anilide.*

By WILLIAM BRADLEY and F. P. WILLIAMS.

With potassium hydroxide in pyridine 2-nitrofluorenone gives 3-hydroxy-2-nitrofluorenone and a dicarboxylic acid of 4 : 4′-azoxydiphenyl. With aniline and potassium hydroxide the products are 6-hydroxyquinoxalino-[2,3-*a*]fluorenone and a 4-phenylazodiphenylcarboxylic acid. Sodium anilide at 20° gives the anil of 2-phenylazofluorenone, also prepared from 2-aminofluorenone. At 40—45° sodium anilide gives two compounds $C_{24}H_{15}N_3$ and $C_{24}H_{15}ON_3$, considered to be the anils of 13-oxofluoreno[1,2-*b*]quinoxaline and a monoxide of this. 13-Oxofluoreno[2,3-*b*]quinoxaline was prepared for comparison. The mechanism of the reactions involved is discussed.

IN earlier publications [1,2] the direct replacement of hydrogen in nitrobenzene and α-nitronaphthalene by amines was described and the present is an extension of the work to 2-nitrofluorenone [3] (I).

On being heated with potassium hydroxide in " AnalaR " pyridine, the compound (I) gave 3-hydroxy-2-nitrofluorenone (II) (17%) and 4 : 4′-azoxydiphenyldicarboxylic acid (III). When a good laboratory grade of pyridine was used the main product isolated was

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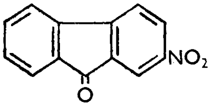
[1] Bradley and Robinson, *J.*, 1932, 1254.

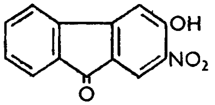
[2] Bradley and Williams, *J.*, 1959, 360.

[3] Diels, *Ber.*, 1901, **34**, 1758.

2 : 2′-azoxyfluorenone (20%). The constitution of the phenol (II) was established by (*a*) nitration of 3-methoxyfluorenone and demethylation of the resulting 3-methoxy-2-nitrofluorenone with aluminium chloride, and (*b*) methylation of the phenol to 3-methoxy-2-nitrofluorenone identical with that obtained in (*a*).



(I)



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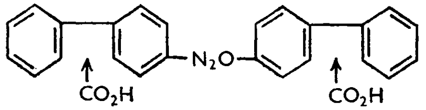
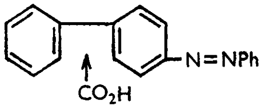


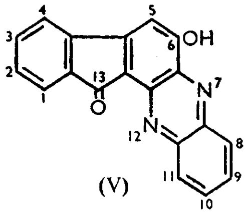
(III)

Under comparable conditions 2-nitrofluorene [4] was not hydroxylated by potassium hydroxide in pyridine. The effect of the carbonyl group of 2-nitrofluorenone in facilitating substitution by hydroxyl ions is analogous to other instances,[5, 6] and in this case as in the others substitution occurs *para* to the carbonyl group.

With potassium hydroxide and aniline at 175—180° 2-nitrofluorenone gave a 4-phenylazodiphenylcarboxylic acid (IV) and 6-hydroxy-13-oxofluoreno[1,2-*b*]quinoxaline (V).



(IV)



(V)

The acid was identical with that obtained on heating 2-phenylazofluorenone with potassium hydroxide. The hydroxy-azine structure (V) rests on the following considerations. The compound forms an alkali-metal salt, a non-phenolic monomethyl ether, a cupric derivative, and a sulphate, $C_{19}H_{10}O_2N_2,H_2SO_4$. It is reduced with difficulty to an unstable, deeply coloured product. The boroacetic anhydride test was negative. It is identical with the derivative obtained on heating 2-*o*-nitroanilinofluorenone with potassium hydroxide in pyridine. In its behaviour on reduction it resembled 13-oxofluoreno[2,3-*b*]-quinoxaline (VI), prepared from 2 : 3-diaminofluorenone and *cyclo*hexane-1 : 2-dione with dehydrogenation of the tetrahydro-azine so formed with iodine.

With potassium hydroxide and aniline under reflux fluorenone gave diphenyl-2-carboxylic acid and fluorenone anil.

With sodium anilide in aniline at the room temperature 2-nitrofluorenone gave 2-phenylazofluorenone anil (VIII) and a small amount of the anil of (X).

On hydrolysis, the anil (VIII) gave 2-phenylazofluorenone (IX) and aniline. The same compound (VIII) was also formed by the action of aniline and zinc chloride on 2-phenylazofluorenone, suggesting that in the reaction between 2-nitrofluorenone and sodium anilide 2-phenylazofluorenone is formed first and is then further converted into the anil. Fluorenone itself reacted with sodium anilide to form fluorenone anil identical with the compound prepared by condensation of aniline with fluorenone in the presence of zinc chloride.

With sodium anilide in aniline at 40—45° two compounds $C_{24}H_{15}N_3$ and $C_{24}H_{15}ON_3$ were formed, both of which gave aniline and 13-oxofluoreno[1,2-*b*]quinoxaline (X) on hydrolysis. The last resembled but was distinct from its isomer (VI). The compound $C_{24}H_{15}N_3$ was probably the anil of (X), and the compound $C_{24}H_{15}ON_3$ one of the two related oxides.

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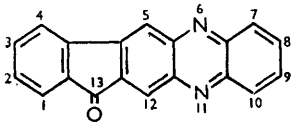
[4] *Org. Synth.*, Coll. Vol. II, p. 447.

[5] Bradley and Waller, *J.*, 1953, 3778.

[6] Backhouse and Bradley, *J.*, 1954, 4506.

It is clear from these results that the effect of potassium hydroxide alone, in the presence of pyridine, is to hydroxylate 2-nitrofluorenone in the 3-position and, in part, to open the fluorenone ring. In the presence of aniline, and without pyridine, a more complicated reaction ensues. The main result is conversion of the nitro-group into phenylazo, by reaction with aniline, accompanied by ring fission; at the same time a hydroxylated azine is formed. Separate experiments showed that the azine was not derived by the further action of alkali on 2-phenylazofluorenone. A more likely route to its formation is the direct introduction of an anilino-group *ortho* to the nitro-group, giving (VII), followed by cyclisation to an azine and hydroxylation. This is the reaction involved in Wohl and Aue's synthesis of phenazine from nitrobenzene, aniline, and potassium hydroxide.[7] With sodium anilide in aniline at the room temperature the conversion of the nitro-group into phenylazo again occurs; at the same time a new reaction appears, conversion of the carbonyl group into an anil. At 40—45° the sodium anilide reaction is more complicated: anil formation occurs and at the same time the anilide ion substitutes the nucleus *ortho* to the nitro-group, and there is then cyclisation to an azine and its oxide.



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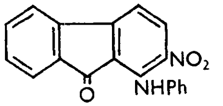
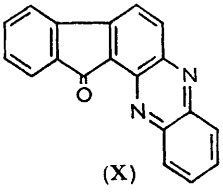
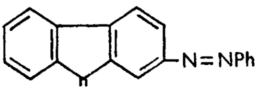


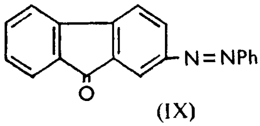
(VII)



(X)



(VIII)



(IX)

EXPERIMENTAL

3-Hydroxy-2-nitrofluorenone.—3-Methoxyfluorenone[8] (3 g.) was refluxed for 4 hr. with aluminium chloride (5·7 g.) in chlorobenzene (100 ml.). The 3-hydroxy-derivative which was formed was purified by dissolution in 5% aqueous sodium hydroxide; on being recrystallised from chlorobenzene it afforded yellow needles, m. p. 227—228° (2·2 g.) (Ullmann[8] records m. p. 228—229°). Nitric acid (0·3 ml.; *d* 1·5) in glacial acetic acid (2 ml.) was added dropwise at 50—60° to a stirred suspension of finely divided 3-hydroxyfluorenone (1 g.) in acetic acid (20 ml.) and acetic anhydride (4 ml.). Stirring was continued for 30 min. and the solid which separated was crystallised from alcohol and then toluene. *3-Hydroxy-2-nitrofluorenone* forms pale yellow needles, m. p. 248—249° (Found: C, 64·9; H, 2·9; N, 5·9. $C_{13}H_7O_4N$ requires C, 64·7; H, 2·9; N, 5·8%). It dissolves in dilute aqueous potassium hydrogen carbonate with a yellow colour; the solution in concentrated sulphuric acid is orange-red. It sublimes readily under reduced pressure at 180—190°.

3-Methoxy-2-nitrofluorenone.—(*a*) Potassium hydroxide (0·2 g.) in methanol (2 ml.) was added to a solution of the above hydroxynitro-derivative (0·6 g.) in pyridine (5 ml.). An orange-yellow precipitate of the potassium salt was separated, dried, and then heated with methyl sulphate (7 ml.) at 100° for an hour. *3-Methoxy-2-nitrofluorenone* which separated on addition to water was crystallised from toluene and then chromatographed on alumina from chlorobenzene. Elution with toluene containing 1% of acetone gave greenish-yellow needles, m. p. 271—278° (Found: C, 66·4; H, 3·6; N, 5·1. $C_{14}H_9O_4N$ requires C, 65·9; H, 3·5; N, 5·5%), indistinguishable from the product obtained by nitration of 3-methoxyfluorenone.

(*b*) Finely ground 3-methoxyfluorenone (1 g.) was shaken for 12 hr. at the room temperature with nitric acid (10 ml.; *d* 1·42). The product obtained on addition to water was chromatographed on alumina from chlorobenzene and then crystallised from 95% alcohol, toluene, and

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[7] Bradley and Leete, *J.*, 1951, 2136.

[8] Ullmann, *Ber.*, 1902, **35**, 4273.

chlorobenzene in turn. 3-Methoxy-2-nitrofluorenone obtained in this way had m. p. 278—281° (Found: C, 66·4; H, 3·8; N, 5·1%). The products from (*a*) and (*b*) both gave reddish-pink solutions in concentrated sulphuric acid and the same absorption spectrum in " AnalaR " pyridine.

Action of Potassium Hydroxide on 2-Nitrofluorenone.—2-Nitrofluorenone (15 g.) and finely ground potassium hydroxide (13·2 g.) were refluxed with stirring in " AnalaR " pyridine (150 ml.). The colour of the reactants changed from yellow through dark red and deep green to brown. After 3 hr. the mixture was added to water and acidified, and the solid collected. This was dried (16·5 g.), powdered, and then extracted with cold 15% aqueous potassium hydrogen carbonate (2 × 150 ml.); a residue (2·7 g.) remained. Acidification of the filtered solution gave a brown solid (13·1 g.) which was dried and then sublimed *in vacuo* at 180—190°. A yellow crystalline sublimate (2·75 g.) was formed which crystallised from benzene in slender, pale yellow needles, m. p. 247—248° (Found: C, 64·8; H, 3·0; N, 5·6%), not depressed by 3-hydroxy-2-nitrofluorenone obtained by the nitration of the 3-hydroxy-derivative. The portion (8 g.) of the alkali-soluble material which did not sublime was extracted twice with 20% aqueous potassium hydrogen carbonate (100 ml.). The filtered extract gave yellow crystals on being kept and these were collected, acidified, and then crystallised from alcohol. Pale yellow needles (0·7 g.), m. p. 292—293° (Found: C, 71·4; H, 4·1; N, 6·8. $C_{26}H_{18}O_5N_2$ requires C, 71·4; H, 3·9; N, 6·4%), were obtained. The absorption spectrum in 95% alcohol showed the absence of typical fluorenone bands and a similarity to 4-phenylazodiphenyl-2(or 2′)-carboxylic acid. Reduction with stannous chloride in hydrochloric acid gave a primary amine.

There was no corresponding hydroxylation when 2-nitrofluorene was used instead of 2-nitrofluorenone in this experiment.

Fluorenone Anil.—A solution of sodium anilide was prepared by refluxing sodium (2·5 g.), copper bronze (0·05 g.), and nickel oxide (0·05 g.) in " AnalaR " aniline (65 ml.) until reaction ceased. The solution was cooled to 50° and a solution of fluorenone (4 g.) in " AnalaR " aniline (10 ml.) was added dropwise with stirring during 30 min. Dilute sodium hydroxide was added and the product obtained as a brown residue after distillation in steam. The acetone-soluble part was chromatographed on alumina from benzene. Elution with benzene–light petroleum (b. p. 60—80°) and recrystallisation from light petroleum (b. p. 40—60°) gave large yellow prisms, m. p. 86—87° (Found: C, 89·5; H, 5·0; N, 5·3. Calc. for $C_{19}H_{13}N$: C, 89·4; H, 5·3; N, 5·5%), which on being heated with aqueous-alcoholic hydrochloric acid gave fluorenone and aniline.

2-Phenylazofluorenone.—Nitrosobenzene (2·7 g.) and 2-aminofluorenone (5 g.) in acetic acid (10 ml.) were heated at 80° for 4 hr. The acid-insoluble portion of the product was chromatographed on alumina from chlorobenzene, the main zone eluted with toluene, and the *2-phenylazofluorenone* so obtained crystallised from benzene–ligroin as orange prisms, m. p. 159—160° (Found: C, 79·9; H, 3·9; N, 10·1. $C_{19}H_{12}ON_2$ requires C, 79·9; H, 4·2; N, 9·9%), which dissolved in concentrated sulphuric acid with an orange-brown colour. Reduction with stannous chloride and hydrochloric acid gave 2-aminofluorenone and aniline.

2-Phenylazo-9-phenyliminofluorene.—Aniline (0·5 ml.), 2-phenylazofluorenone (0·5 g.), and zinc chloride (0·05 g.) were heated at 170° for 30 min. and then added to water. The resulting suspension was made just alkaline, unchanged aniline was distilled in steam, and the residue chromatographed on alumina from benzene. The main zone was eluted with 95% alcohol, and the solid so obtained crystallised (0·4 g.) from benzene–light petroleum (b. p. 60—80°). *2-Phenylazo-9-phenyliminofluorene* forms orange-yellow prisms, m. p. 172—173° (Found: C, 83·4; H, 4·9; N, 11·7. $C_{25}H_{17}N_3$ requires C, 83·5; N, 4·7; N, 11·7%).

Hydrolysis. On being heated on a steam-bath for 10 min. with a mixture of 95% alcohol (3 ml.), water (1·5 ml.), and concentrated hydrochloric acid (1·5 ml.) the above anil (0·2 g.) gave 2-phenylazofluorenone and aniline.

2-o-Nitroanilinofluorenone.—(*a*) 2-Chlorofluorenone [9] (2 g.), *o*-nitroaniline (1·54 g.), potassium carbonate (1·3 g.), copper bronze (0·02 g.), and cupric acetate (0·06 g.) were refluxed in nitrobenzene (10 ml.) for 3 hr. After addition to water and steam-distillation a solid remained, and this was chromatographed on alumina from chlorobenzene. Elution of the main zone with 95% alcohol and concentration of the eluate gave *2-o-nitroanilinofluorenone* as orange-red needles (0·25 g.), m. p. 207—208° (Found: C, 71·8; H, 3·9; N, 8·9. $C_{19}H_{12}O_3N_2$ requires C,

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[9] Courtot, *Compt. rend.*, 1927, **184**, 1179.

72·2; H, 3·9; N, 8·9%), which disolved in pyridine with a yellow colour rendered deep blue-violet on the addition of a drop of methanolic potassium hydroxide. (*b*) The same compound, m. p. 206—207° (Found: C, 71·8; H, 3·8; N, 8·8%), was obtained by refluxing 2-aminofluorenone (2 g.), *o*-chloronitrobenzene (1·9 g.), potassium carbonate (1 g.), copper bronze (0·01 g.), and cupric acetate (0·02 g.) in *o*-dichlorobenzene (15 ml.) for 10 hr.

13-*Oxofluoreno*[2,3-b]*quinoxaline and* 13-*Oxodibenzo*[f,h]*fluoreno*[2,3-b]*quinoxaline*.—2 : 3-Diaminofluorenone was prepared by Eckert's method [10] and obtained as brown prisms, m. p. 175—177° (Eckert [10] gives m. p. 185°) (Found: C, 74·6; H, 4·9; N, 13 3. Calc. for $C_{13}H_{10}ON_2$: C, 74·3; H, 4·8; N, 13·3%).

Solutions of the above diamine (0·2 g.) and phenanthraquinone (0·2 g.) in the minimum volume of acetic acid were mixed. A yellow precipitate was formed immediately and this was separated, chromatographed on alumina from chlorobenzene, eluted with toluene, and recovered, and the solid so obtained crystallised from 95% alcohol. Yellow crystals (0·3 g.) of 13-*oxodibenzo*[f,h]*fluoreno*[2,3-b]*quinoxaline*, m. p. 342—344° (Found: N, 7·4. $C_{27}H_{14}ON_2$ requires N, 7·3%), were obtained which dissolved in concentrated sulphuric acid with a red-violet colour. The *sulphate* formed orange-yellow needles (Found: N, 5·7. $C_{27}H_{16}O_5N_2S$ requires N, 5·8%).

13-*Oxofluoreno*[2,3-b]*quinoxaline*.—The above diamine (0·45 g.) and *cyclo*hexane-1 : 2-dione (0·25 g.) were refluxed for 2 hr. in acetic acid (15 ml.). The product was isolated as in the preceding preparation and 7 : 8 : 9 : 10-*tetrahydro*-13-*oxofluoreno*[2,3-b]*quinoxaline* obtained as straw-coloured needles (0·18 g.), m. p. 202—203° (Found: C, 79·9; H, 4·8; N, 9·7. $C_{19}H_{14}ON_2$ requires C, 79·7; H, 4·9; N, 9·8%), which gave an orange-red colour in concentrated sulphuric acid. Addition of zinc dust to the greenish-yellow solution in acetic acid caused a slow change to green and finally on being warmed to brownish-red. The tetrahydroazine (0·1 g.) was refluxed with iodine (0·35 g.) in acetic acid for 8 hr. The product was chromatographed on alumina from chlorobenzene, eluted with toluene, and crystallised first from 95% alcohol and then from benzene. 13-*Oxofluoreno*[2,3-b]*quinoxaline* was obtained (0·06 g.) as pale greenish-yellow needles, m. p. 239—241° (Found: C, 80·2; H, 3·2. $C_{19}H_{10}ON_2$ requires C, 80·8; H, 3·6%), which dissolved in concentrated sulphuric acid with a dark violet colour. On being heated with zinc in acetic acid the yellow solution changed through green to reddish-brown. The colour faded on cooling but was restored on heating.

Action of Sodium Anilide on 2-Nitrofluorenone.—(a) *At the room temperature*. Sodium anilide was prepared from sodium (7·5 g.), copper bronze (0·1 g.), nickel oxide (0·1 g.) and "AnalaR" aniline (190 ml.) under reflux in nitrogen until the metal had dissolved. The resulting solution was cooled to 15° and a suspension of 2-nitrofluorenone (15 g.) in "AnalaR" aniline (30 ml.) added in portions during 30 min. The colour changed through red to brown. After being stirred for 30 min. longer the solution was added to water and steam-distilled, and the acetone-soluble part of the black solid (24·5 g.) so obtained was chromatographed on alumina from benzene. One of the zones was orange in colour and this was eluted with benzene. Concentration of the benzene solution gave a solid and this was crystallised from benzene–ligroin, then from ligroin, and re-chromatographed on alumina from benzene. The main band, eluted and crystallised from benzene–light petroleum (b. p. 60—80°), gave 2-phenylazo-9-phenyliminofluorene, m. p. 171—172°, undepressed by the authentic compound. The two samples had the same absorption spectrum in 95% alcohol.

(b) *At* 45—50°. This experiment was identical with (a) except that the reaction temperature was 45—50°. Two orange zones were formed. The lower was eluted with benzene, the eluate was concentrated and light petroleum (b. p. 60—80°) added; orange-red needles (0·6 g.), m. p. 217—218° (Found: C, 83·1; H, 5·1; N, 11·1%) (product B), were obtained. The upper zone eluted with 95% alcohol afforded after concentration of the eluate orange-red needles (0·5 g.), m. p. 181—182° (Found: C, 79·8; H, 4·6; N, 11·1%) (product C).

Hydrolysis of B and C. Formation of 13-*oxofluoreno*[1,2-b]*quinoxaline*. A solution of product B (0·2 g.) in 95% alcohol (4 ml.), water (2 ml.), and concentrated hydrochloric acid (4 ml.) was heated on a steam-bath for 3 hr. Water (90 ml.) was then added and the precipitated solid collected; the filtrate contained a diazotisable amine. Crystallisation of the solid from benzene–light petroleum (b. p. 60—80°) gave pale yellow needles (0·12 g.), m. p. 276—277° (Found: C, 80·7; H, 3·5; N, 10·0. $C_{19}H_{10}ON_2$ requires C, 80·8; H, 3·6; N, 9·9%). 13-*Oxofluoreno*[1,2-b]*quinoxaline* gives a violet solution in concentrated sulphuric acid. On being

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[10] Eckert, *J. prakt. Chem.*, 1928, **118**, 263.

heated with zinc dust the yellow solution in acetic acid changed to green, and on being warmed to magenta. On cooling, the colour faded but was restored on heating.

Similar hydrolysis of product C (0·2 g.) gave again a diazotisable amine and the same yellow needles (0·12 g.), m. p. 276—277° (Found: C, 80·8; H, 3·5; N, 10·0%), as resulted from B. A mixture of the two products showed no m. p. depression.

Action of Aniline and Potassium Hydroxide on 2-*Nitrofluorenone. Formation of* 6-*Hydroxy*-13-*oxofluoreno*[1,2-b]*quinoxaline and* 4-*Phenylazodiphenyl*-2(*or* 2′)-*carboxylic Acid.*—Finely powdered potassium hydroxide (18·75 g.) was added in small successive amounts during 30 min. to a stirred solution of 2-nitrofluorenone (15 g.) in " AnalaR " aniline (80 ml.) at 175—180°. Stirring was continued for 30 min., then the resulting dark melt was cooled, added to water, and distilled in steam. The non-volatile product consisted of an alkali-insoluble residue (R) (8·3 g.) and a solution from which brown material (P) (7·7 g.) was precipitated after filtration and acidification. The residue (R) was first extracted hot with chlorobenzene and then alcohol and finally crystallised from acetic acid and then pyridine. Pale yellow needles, m. p. 303—304° (Found: C, 76·5; H, 3·5; N, 9·2. $C_{19}H_{10}O_2N_2$ requires C, 76·5; H, 3·4; N, 9·4%), were obtained. This 6-*hydroxy*-13-*oxofluoreno*[1,2-b]*quinoxaline* formed a red sodium salt with alcoholic sodium sulphide but no reduction occurred even on heating. Addition of a solution of stannous chloride in concentrated hydrochloric acid to a solution in hot acetic acid changed the colour from yellow to magenta and finally to brown. No aniline was formed in this reaction and the original compound was recovered after the product had crystallised from chlorobenzene. It dissolved in concentrated hydrochloric with a dark orange colour and gave a violet solution in concentrated sulphuric acid. The boroacetic anhydride test was negative.

Addition of concentrated sulphuric acid (0·5 ml.) drop by drop to a solution of the 6-hydroxy-compound (0·4 g.) in hot acetic acid (150 ml.) precipitated orange-red prisms of a *sulphate* (Found: C, 57·3; H, 2·9; N, 6·6; S, 7·8. $C_{19}H_{10}O_2N_2,H_2SO_4$ requires C, 57·6; H, 3·0; N, 7·1; S, 8·1%) after concentration and cooling. The sulphate was hydrolysed on addition to water. It dissolved in concentrated sulphuric acid with a violet colour.

Solutions containing cupric acetate (0·25 g.) in pyridine (5 ml.) and the 6-hydroxy-compound (0·25 g.) in water (4 ml.) and pyridine (12 ml.) were mixed and refluxed for 3 hr. A brown solid separated on cooling and this was collected and washed with a solution of ammonium chloride in aqueous ammonia (Found: C, 69·5; H, 3·2; Cu, 8·7. $C_{38}H_{18}O_4N_4Cu$ requires C, 69·4; H, 2·7; Cu, 9·7%). On being dissolved in concentrated sulphuric acid and then added to water the *cupric derivative* gave the original 6-hydroxy-derivative, m. p. 302—303°.

Methyl toluene-*p*-sulphonate (1·0 g.) was added in 0·2 g. portions at intervals of 2 hr. to a refluxing solution of the 6-hydroxy-derivative (0·5 g.) in *o*-dichlorobenzene (20 ml.) containing anhydrous potassium carbonate (1·0 g.). Then refluxing was continued for 7 hr., the suspension was filtered, and the residue extracted with hot *o*-dichlorobenzene. The combined solutions were made up to 50 ml. with addition of more *o*-dichlorobenzene and then chromatographed on alumina. The main yellow zone was eluted with toluene containing acetone (1%) and the 6-*methoxy-derivative* crystallised from benzene as pale yellow needles, m. p. 243—244° (Found: C, 77·25; H, 3·9; N, 8·6. $C_{20}H_{12}O_2N_2$ requires C, 76·9; H, 3·9; N, 9·0%). It did not form a salt with sodium hydroxide solution.

Preparation of 6-*hydroxy*-13-*oxofluoreno*[1,2-b]*quinoxaline from* 2-o-*nitroanilinofluorenone.* Potassium hydroxide (0·15 g.) and 2-*o*-nitroanilinofluorenone (0·15 g.) were ground together, refluxed in pyridine (4 ml.) for 36 hr. with stirring, and added to water. The solution was acidified, and the resulting precipitate was collected, dried, and sublimed at 0·01 mm. from a bath at 275—280°. The sublimate crystallised from chlorobenzene as pale yellow needles (0·07 g.), m. p. 302—303° (Found: C, 76·2; H, 3·7; N, 9·4%), which did not depress the m. p. of the authentic 6-hydroxy-compound.

4-*Phenylazodiphenyl*-2(*or* 2′)-*carboxylic acid.* The precipitate (P) obtained from the action of aniline and potassium hydroxide on 2-nitrofluorenone was stirred for 2 hr. with 20% aqueous potassium hydrogen carbonate (100 ml.). The bright orange solid formed was stirred with dilute hydrochloric acid, and the orange solid obtained crystallised from chlorobenzene as needles (2·5 g.), m. p. 204—205° (Found: C, 75·5; H, 4·7; N, 9·2. $C_{19}H_{14}O_2N_2$ requires C, 75·5; H, 4·6; N, 9·3%), of 4-*phenylazodiphenyl*-2(*or* 2′)-*carboxylic acid.* This derivative gave a yellow solution in concentrated sulphuric acid. The ultraviolet absorption spectrum in 95% alcohol showed the absence of characteristic fluorenone bands. On being reduced with stannous chloride (2 g.) in concentrated hydrochloric acid (5 ml.) and acetic acid (5 ml.) 4-phenylazodiphenyl-2(or 2′)-carboxylic acid (0·4 g.) gave aniline, characterised as 1-phenylazo-2-naphthol, m. p. and mixed m. p. 129—131°.

The carboxylic acid (0·4 g.) was refluxed for 4 hr. with 3% methanolic hydrogen chloride (10 ml.). The crystals which separated on cooling recrystallised from methanol as orange-yellow prisms, m. p. 70—71° (Found: C, 76·3; H, 4·8; N, 9·1. $C_{20}H_{16}O_2N_2$ requires C, 76·0; H, 5·1; N, 8·9%).

Action of Potassium Hydroxide in Aniline on 2-Phenylazofluorenone.—2-Phenylazofluorenone (3 g.) was intimately ground with potassium hydroxide (3 g.) and refluxed in " AnalaR " aniline (15 ml.) for 1 hr. with stirring. After being cooled the resulting suspension was added to water and acidified. The precipitate was dried and extracted with ligroin (b. p. 100—120°), and the filtered extract concentrated to yield crystals, m. p. 180—195° (0·14 g.). On being stirred for 2 hr. with 20% aqueous potassium carbonate (50 ml.) these gave a bright orange-yellow solid. This was treated with dilute hydrochloric acid, and the orange solid which was formed was crystallised from chlorobenzene to give prisms, m. p. 204—205° (Found: C, 74·8; H, 4·7; N, 9·0%), not depressed by the 2-phenylazodiphenylcarboxylic acid, m. p. 204—205°, obtained on reaction of aniline and potassium hydroxide with 2-nitrofluorenone.

3-Bromo-2-phenylazofluorenone.—2-Amino-3-bromofluorenone[11] (4 g.) in the minimum volume of acetic acid was stirred with nitrosobenzene (1·4 g.) in the same solvent (10 ml.) at 80—90° for 9 hr. After being crystallised from chlorobenzene, chromatographed on alumina, and crystallised from toluene *3-bromo-2-phenylazofluorenone* formed orange-yellow needles, m. p. 231—232° (Found: C, 62·5; H, 3·0; N, 7·7; Br, 22·3. $C_{19}H_{11}ON_2Br$ requires C, 62·8; H, 3·0; N, 7·7; Br, 22·0%). This derivative gave a reddish-orange solution in concentrated sulphuric acid.

2 : 2′-Azoxyfluorenone.—Zinc dust (10 g.) and a solution of calcium chloride (3·4 g.) in water (5 ml.) were added to a suspension of 2-nitrofluorenone (10 g.) in water (240 ml.) and alcohol (260 ml.). After being refluxed for 2 hr. the suspension was cooled and filtered, and the filtrate was concentrated to yield a further precipitate. The combined solids were dried and extracted with trichlorobenzene (500 ml.), and the solution so obtained was cooled. Yellow needles separated and were chromatographed on alumina from trichlorobenzene. Development with chlorobenzene and then with toluene containing 1% of acetone gave two main bands. The upper orange-yellow zone on extraction with aqueous pyridine gave yellow needles (0·08 g.) of *2 : 2′-azoxyfluorenone*, m. p. 331—332° (Found: C, 78·7; H, 3·6; N, 7·2. $C_{26}H_{14}O_3N_2$ requires C, 77·6; H, 3·5; N, 7·0%). It dissolves in concentrated sulphuric acid with an orange-red colour. A similar product, m. p. 329—331° (Found: C, 78·0; H, 3·8; N, 6·8%), was obtained by the action of alkaline stannous chloride on 2-nitrofluorenone.

2 : 2′-Azofluorenone.—A solution of the above azoxy-derivative (0·4 g.) in hot pyridine (50 ml.) was added in 15 min. to a vigorously stirred solution of sodium hydroxide (6 g.) and sodium dithionite (3 g.) in water (60 ml.) at 80—90°. Stirring was continued for 15 min. longer, then the solution was cooled; it formed two layers. The reddish-brown pyridine layer was added to water (200 ml.), and the resulting *2 : 2′-azofluorenone* was collected, dried, and crystallised several times from pyridine to give yellow needles, m. p. 338—340° (Found: C, 81·0; H, 3·6; N, 7·1. $C_{26}H_{14}O_2N_2$ requires C, 80·8; H, 3·6; N, 7·3%). The mixed m. p. with 2 : 2′-azoxyfluorenone was 311—324°. The solution in concentrated sulphuric acid was deep blue, tinged red.

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[11] Fletcher and Pan, *J. Amer. Chem. Soc.*, 1956, **78**, 4812.