

*Substituted Fluoren-9-ols.*

By C. L. ARCUS and M. M. COOMBS.

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The synthesis of 3-nitrofluorenone reported by Ray and Barrick (*J. Amer. Chem. Soc.*, 1948, **70**, 1493) has been revised. 2-Methyl-, 3-methyl-, 2-methoxy-, 3-methoxy-, 2-hydroxy-, 2-amino-, and 3-nitro-fluoren-9-ol have been prepared by reduction of the corresponding fluorenones with aluminium isopropoxide. A form of 9-phenylfluoren-9-ol having m. p. 85° (lit., 107°) has been obtained.

A NUMBER of fluoren-9-ols, substituted with groups of different electronic characteristics, have been prepared for use in the syntheses of phenanthridines to be described (Arcus and Coombs, *J.*, 1954, in the press).

*Fluorenones.*—2-Methyl-, 3-methyl-, and 3-methoxy-fluorenones have been obtained by known procedures.

The reduction of 2-nitro- to 2-amino-fluorenone is conveniently effected by stannous chloride. This amine was converted into 2-hydroxy- and hence into 2-methoxy-fluorenone by known methods.

A synthesis of 3-nitrofluorenone has been described by Ray and Barrick (*J. Amer. Chem. Soc.*, 1948, **70**, 1493); it consists of six stages: (i) conversion of 2-aminodiphenyl into its toluene-*p*-sulphonyl derivative; (ii) nitration of this at position 5; (iii) hydrolysis of the toluene-*p*-sulphonyl group; (iv) conversion of the amine into 2-cyano-5-nitrodiphenyl by a Sandmeyer reaction; (v) hydrolysis to 5-nitrodiphenyl-2-carboxylic acid; (vi) ring closure with sulphuric acid, yielding 3-nitrofluorenone. Ray and Barrick's procedures are effective for stages (i), (iii), (iv, modified), and (vi); those for stages (ii) and (v) proved unsatisfactory. Nitration, with fuming nitric-acetic acid according to these authors, gave an explosive reaction from the product of which the 5-nitro-derivative could not be isolated. Further, contrary to Ray and Barrick's statement, nitration with dilute nitric acid by Bell's method (*J.*, 1928, 2774) proceeds satisfactorily; 5-nitro-2-toluene-*p*-sulphonamidodiphenyl was obtained in 79% yield. Hydrolysis in stage (v) with 50% sulphuric acid according to Ray and Barrick gave much tar and poor yields of the carboxylic acid; hydrolysis with aqueous acetic-sulphuric acid (Jones and Braker, U.S.P. 1,922,205) is effective.

*Fluoren-9-ols.*—Reduction of the corresponding fluorenones with aluminium isopropoxide in hot isopropanol gave the following fluoren-9-ols in the stated yields: 2-methyl-

(80%), 3-methyl- (84%), 2-methoxy- (71%), 3-methoxy- (71%), 2-hydroxy- (50%), 2-amino- (69%), 3-nitro- (86%). The new fluorenols have been converted into the corresponding 9-acetoxyfluorenes; 9-chloro-2-methoxy-, 9-chloro-2-nitro-, and 9-chloro-3-nitrofluorene have been prepared.

9-Methyl- and 9-benzyl-fluoren-9-ol were obtained from the known reaction of fluorenone with, respectively, methylmagnesium iodide and benzylmagnesium chloride; the interaction of phenylmagnesium bromide with fluorenone added (*a*) in benzene-ether solution, (*b*) as the powdered solid according to the original preparation by Ullmann and von Wurstemberger (*Ber.*, 1904, **37**, 73), yielded in each instance 9-phenylfluoren-9-ol, m. p. 85°. The above authors, also Williamson, Anderson, and Watts (*J. Amer. Chem. Soc.*, 1943, **65**, 49), record m. p. 107°. On reaction with hydrazoic and sulphuric acids, the fluorenol, m. p. 85°, gave 9-phenylphenanthridine in 94% yield (Arcus and Coombs, *loc. cit.*); further, it yielded 9-chloro-9-phenylfluorene having m. p. 78°, a value identical with that recorded by Ullmann *et al.* and by Williamson *et al.* for this compound prepared from the higher-melting fluorenol. The two forms of the fluorenol appear, therefore, to be structurally identical; no geometrical isomers (due, *e.g.*, to folding) were apparent on inspection of a C.R.L.-Catalin model of 9-phenylfluoren-9-ol. The compound is concluded to be dimorphic.

#### EXPERIMENTAL

M. p.s are corrected.

*Fluorenones.*—By the use of Ritchie's procedures (*J. Proc. Roy. Soc., N.S.W.*, 1946, **80**, 33) there have been prepared, successively, 5-methyl-2:3-diphenylindole (49.5 g.), m. p. 155—156°, 1-acetyl-5-methyl-2:3-diphenylindole (46 g.), m. p. 175—177°, 2-amino-5-methylbenzophenone (22 g.), m. p. 60—61°, and 2-methylfluorenone [9.2 g., from light petroleum (b. p. 40—60°)], yellow needles, m. p. 91—92°. For these compounds, respectively, Ritchie records m. p. 156°, 176°, 63°, 92°.

2-Amino-4'-methylbenzophenone (10.7 g., m. p. 92°; *Org. Synth.*, 1952, **32**, 8) was converted into 3-methylfluorenone [4.5 g., from light petroleum (b. p. 40—60°)], yellow prisms, m. p. 68°, by the method of Ullmann and Mallet (*Ber.*, 1898, **31**, 1694), who record m. p. 66.5°.

2-Nitrofluorene (30 g.; m. p. 157—158°; *Org. Synth.*, 1933, **13**, 74) yielded 2-nitrofluorenone (27 g., from xylene), yellow leaflets, m. p. 220—221°, on oxidation according to Diels (*Ber.*, 1901, **34**, 1760), who records m. p. 222—223°. 2-Nitrofluorenone (100 g.), stannous chloride (SnCl<sub>2</sub>·2H<sub>2</sub>O; 400 g.), concentrated hydrochloric acid (400 ml.), and ethanol (200 ml.) were boiled together under reflux for 6 hr., and then cooled. The insoluble tin complex was collected and decomposed with an excess of 2*N*-sodium hydroxide. Crystallisation of the base from hot xylene gave permanganate-coloured needles of 2-aminofluorenone (68 g.), m. p. 158°. Diels (*loc. cit.*), who used ammonium sulphide as the reducing agent, records m. p. 160°.

2-Aminofluorenone (66 g.) was converted into 2-hydroxyfluorenone (61 g.), red needles, m. p. 206—208°, by the procedure of Diels (*loc. cit.*), who records m. p. 206—207°.

2-Hydroxyfluorenone (55 g.) gave 2-methoxyfluorenone (53.5 g.), orange needles, m. p. 75—76°, on methylation according to Werner and Gross (*Annalen*, 1902, **322**, 168), who record m. p. 77—78°.

By the use of Ullmann and Bleier's procedures (*Ber.*, 1902, **35**, 4273), *N*-toluene-*p*-sulphonylanthranilic acid (45 g.) was successively converted into 4-methoxy-2'-toluene-*p*-sulphonamidobenzophenone, 2-amino-4'-methoxybenzophenone sulphate, and 3-methoxyfluorenone [11.1 g., from light petroleum (b. p. 60—80°)], yellow prisms, m. p. 99—100°. The above authors record m. p. 99°.

A suspension of 2-toluene-*p*-sulphonamidodiphenyl (200 g.; m. p. 99—100°) in water (2 l.) and concentrated nitric acid (200 ml.) was stirred at 100° for 9 hr.; the yellow oil became converted into a flocculent orange solid which was collected and crystallised from glacial acetic acid (750 ml.); it yielded 5-nitro-2-toluene-*p*-sulphonamidodiphenyl (160 g., 79%), orange needles, m. p. 168—169°. The procedure is adapted from that applied to 1 g. of sulphonamide by Bell (*loc. cit.*), who records m. p. 169°. Nitration of the sulphonamide (78 g.) by Ray and Barrick's method (*loc. cit.*) was at first tried: when the temperature reached 70° a reaction of explosive violence occurred. Reaction was again violent in an experiment on one-third the scale. No pure compound was isolated.

5-Nitro-2-toluene-*p*-sulphonamidodiphenyl (570 g.) was hydrolysed to 2-amino-5-nitrodiphenyl (240 g.), m. p. 125°, which (220 g.) was converted into 2-cyano-5-nitrodiphenyl (120 g.), m. p. 133—135°, by Ray and Barrick's procedures, except that sodium cuprocyanide was prepared according to *Org. Synth.*, Coll. Vol. I, 2nd Edn., pp. 170, 514. This nitrile (118 g.), hydrolysed by Jones and Braker's method (*loc. cit.*), gave 5-nitrodiphenyl-2-carboxylic acid (89 g.), m. p. 180°. Ring closure of this compound by the procedure of Ray and Barrick yielded 3-nitrofluorenone (60.5 g., from glacial acetic acid), yellow needles, m. p. 235°. Recrystallisation from glacial acetic acid, from pyridine, and from ethanol did not raise the m. p.; the above authors record m. p. 235—236°, 239—240° (corr.), and Nunn, Schofield, and Theobald (*J.*, 1952, 2797) record m. p. 232—233° (uncorr.).

*Fluoren-9-ols.*—*Aluminium isopropoxide reductions.* The fluorenone was heated, under reflux for the stated time, with a solution of aluminium isopropoxide prepared from aluminium turnings and isopropanol (0.4 g. and 12 ml., respectively, to 1 g. of fluorenone). The mixture

Fluorenone	2-Me	3-Me	2-MeO	3-MeO	2-HO	2-NH <sub>2</sub>	3-NO <sub>2</sub>
Weight (g.) .....	5.0	4.5	40.0	7.7	2.0	16.0	20.0
Time (min.) .....	180	120	120	180	45 *	5 *	30 *

\* Longer reaction times gave lower yields.

was poured into ice-cold *N*-sulphuric acid (20 ml. to 3 ml. of isopropanol), and the solid product was collected, washed, dried, and recrystallised.

9-Acetoxyfluorenes were prepared by heating the fluorenols with acetic anhydride and dry pyridine (respectively 1 ml. and 5 ml. to 1 g. of fluorenol) for 3 hr. on a steam-bath.

9-Chlorofluorenes were prepared by warming the fluorenols with thionyl chloride (5 ml. to 1 g. of fluorenol) until evolution of hydrogen chloride was complete; excess of thionyl chloride was removed *in vacuo*, and the product was recrystallised.

Exceptions to these procedures are recorded below. There were obtained:

2-Methylfluoren-9-ol [4.0 g., from light petroleum (b. p. 60—80°)], needles, m. p. 143—144° (Found: C, 85.65; H, 6.25. C<sub>14</sub>H<sub>12</sub>O requires C, 85.7; H, 6.15%). It (1.0 g.) yielded 9-acetoxy-2-methylfluorene (1.0 g., from ethanol), needles, m. p. 114—115° (Found: C, 80.95; H, 6.2. C<sub>16</sub>H<sub>14</sub>O<sub>2</sub> requires C, 80.65; H, 5.9%).

3-Methylfluoren-9-ol [3.8 g., from light petroleum (b. p. 60—80°)], needles, m. p. 144—145° (admixture with 2-methylfluoren-9-ol depressed the m. p. by 20°) (Found: C, 85.8; H, 6.0%). It (1.0 g.) gave 9-acetoxy-3-methylfluorene (0.75 g., from ethanol), plates, m. p. 90° (Found: C, 80.6; H, 6.1%).

2-Methoxyfluoren-9-ol [28.5 g.; from benzene; the solution was boiled with charcoal (1 g.)], buff prisms, m. p. 160° (Found: C, 79.4; H, 5.95. C<sub>14</sub>H<sub>12</sub>O<sub>2</sub> requires C, 79.25; H, 5.7%). It (1.5 g.) gave 9-acetoxy-2-methoxyfluorene (1.6 g., from ethanol), orange tablets, m. p. 82—83° (Found: C, 75.75; H, 5.8. C<sub>16</sub>H<sub>14</sub>O<sub>3</sub> requires C, 75.6; H, 5.55%). The fluorenol (10.0 g.) yielded 9-chloro-2-methoxyfluorene [8.0 g., from light petroleum (b. p. 40—60°)], yellow platelets, m. p. 98.5—99.5° (Found: C, 72.6; H, 4.85; Cl, 15.25. C<sub>14</sub>H<sub>11</sub>OCl requires C, 72.9; H, 4.8; Cl, 15.4%).

3-Methoxyfluoren-9-ol [5.5 g., from light petroleum (b. p. 100—110°)], leaflets, m. p. 120° (Found: C, 78.6, 78.6; H, 5.75, 5.8%). It (0.5 g.) gave 9-acetoxy-3-methoxyfluorene (0.4 g., from ethanol), m. p. 126—127° (Found: C, 75.55; H, 5.7%).

2-Hydroxyfluoren-9-ol (1.0 g.; the product from the reduction was reprecipitated from its filtered solution in 2*N*-sodium hydroxide, and crystallised from glacial acetic acid), golden needles, m. p. 188—189° (Found: C, 78.5; H, 5.15. C<sub>13</sub>H<sub>10</sub>O<sub>2</sub> requires C, 78.75; H, 5.1%). It (0.15 g.) was heated for 4 hr. with a treble quantity of reagents and yielded 2:9-diacetoxyfluorene (0.1 g., from 50% ethanol), prisms, m. p. 106° (Found: C, 72.35; H, 4.95. C<sub>17</sub>H<sub>14</sub>O<sub>4</sub> requires C, 72.35; H, 5.0%).

The solution from the reduction of 2-aminofluorenone was poured into ice-cold 2.5*N*-sodium hydroxide (1 l.); the product was reprecipitated from its solution in *N*-hydrochloric acid. It yielded 2-aminofluoren-9-ol (11 g., from ethanol), leaflets, m. p. 197—198°; Diels (*Ber.*, 1901, 34, 1767) obtained this compound, m. p. 196°, by reducing 2-nitrofluorenone with zinc dust.

2-Nitrofluorenone (22.4 g.) gave 2-nitrofluoren-9-ol (18.7 g.), m. p. 128—129°, on reduction with aluminium isopropoxide according to Friedler (Ph.D. Thesis, London, 1952), who records the same m. p. for this compound; it (13.2 g.) yielded 9-chloro-2-nitrofluorene (10.5 g., from benzene), yellow columns, m. p. 141° (Found: C, 63.6; H, 3.25; N, 5.4; Cl, 14.45. C<sub>13</sub>H<sub>8</sub>O<sub>2</sub>NCl requires C, 63.55; H, 3.3; N, 5.7; Cl, 14.45%).

3-Nitrofluorenone was added in suspension in benzene (200 ml.) to the reagent prepared from 100 ml. of isopropanol; there was obtained 3-nitrofluoren-9-ol (17.3 g., from benzene), needles, m. p. 156° (Found: C, 68.45; H, 4.1; N, 6.2.  $C_{13}H_9O_3N$  requires C, 68.7; H, 4.0; N, 6.2%). It (1.0 g.), heated under reflux for 5 hr. with acetic anhydride (20 ml.) and glacial acetic acid (20 ml.), gave 9-acetoxy-3-nitrofluorene (0.9 g., from ethanol), yellow needles, m. p. 130° (Found: C, 66.95; H, 3.85; N, 5.45.  $C_{15}H_{11}O_4N$  requires C, 66.9; H, 4.1; N, 5.2%). The fluorenol (1.2 g.) yielded 9-chloro-3-nitrofluorene (0.55 g., from benzene), needles, m. p. 150—151° (Found: C, 63.5; H, 3.3; Cl, 14.8%).

9-Methylfluoren-9-ol (7.2 g., from benzene-ether), needles, m. p. 175°, and 9-benzylfluoren-9-ol [2.7 g., from benzene-light petroleum, b. p. 40—60°], tablets, m. p. 140—141°, were prepared by the interaction of fluorenone (8.0 g. for each) with methylmagnesium iodide and benzylmagnesium chloride by the method described below. For these fluorenols Ullmann (*Ber.*, 1905, 38, 4107) records m. p. 174.5° and m. p. 139°.

To a stirred solution of phenylmagnesium bromide (from magnesium, 1.5 g., bromobenzene, 6.6 ml., and ether, 40 ml.) was added, during  $\frac{1}{2}$  hr., a solution of fluorenone (10.0 g.) in benzene-ether (20 ml. each). The mixture was heated for an hour on a steam-bath and added to ice and ammonium chloride; the benzene-ether solution was dried ( $Na_2SO_4$ ) and concentrated to 30 ml., and light petroleum (b. p. 40—60°; 100 ml.) was added. There separated rhombs (11.1 g.), m. p. 73—75°, which (2.00 g.) lost solvent and attained constant weight (1.74 g.) during 30 min. at 120°; the resulting colourless melt solidified on cooling, to crystalline 9-phenylfluoren-9-ol, m. p. 85° (Found: C, 88.0; H, 5.4. Calc. for  $C_{19}H_{14}O$ : C, 88.35; H, 5.45%). This compound, on recrystallisation from benzene, gave rhombs, m. p. 74—75° alone or when mixed with the substance of m. p. 73—75°, above. On recrystallisation from carbon tetrachloride, the fluorenol, m. p. 85°, gave prisms m. p. 80—84°, which effloresced in air; after 24 hr. the white powder again melted at 85°, alone or in admixture with the analysed specimen. 9-Phenylfluoren-9-ol was also prepared by Ullmann and von Wursterberger's method (*loc. cit.*); it separated from light petroleum (b. p. 60—80°), containing benzene, as rhombs, m. p. 75° alone or when mixed with the similar material from the above preparation. Solvent was removed by heating the substance at 120° for 1 hr.; the product then had m. p. 85—86° alone and when mixed with the analysed specimen. The above authors obtained 9-phenylfluoren-9-ol, m. p. 107°, which, when recrystallised from carbon tetrachloride, formed solvated crystals, m. p. 85—88°; they also obtained a solvated fluorenol from benzene (m. p. unstated).

Phosphorus pentachloride (2.2 g.) was added to a solution of 9-phenylfluoren-9-ol (2.6 g.; m. p. 85°) in benzene (25 ml.); after 10 min. the solution was boiled under reflux for 5 min., then cooled and shaken with ice. The product (2.8 g.) from the benzene layer yielded 9-chloro-9-phenylfluorene [0.5 g., from light petroleum (b. p. 40—60°)], tablets, m. p. 78°. Ullmann and von Wursterberger (*loc. cit.*), also Williamson, Anderson, and Watts (*loc. cit.*), obtained 9-chloro-9-phenylfluorene, m. p. 78—79°, from 9-phenylfluoren-9-ol having m. p. 107°.

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