zene and petroleum ether to give pure white crystals, m.p. 187–188°. Two more recrystallizations from 65% ethanol gave beautiful golden-flecked crystals m.p. 194–195°. The crystals showed moderate yellow fluorescence and in strong ethanol solutions showed moderate green fluorescence. The yield of highly purified acid was 4.5 g. (12%); experimental equivalent weight 274 (calcd. 276).

Anal. Calcd. for $C_{14}H_{12}SO_4$: C, 60.90; H, 4.35. Found: C, 60.97; H, 4.49.

The structure of the 2′-methylsulfonylbiphenyl-2-carboxylic acid (II) was confirmed as follows. 2′-Methyl-2-nitrobiphenyl was prepared[24] and reduced to 2-amino-2′-methylbiphenyl.[24] The latter was diazotized and upon treatment with potassium iodide produced 2-iodo-2′-methylbiphenyl[24] in fair yield. The Grignard of 2-iodo-2′-methylbiphenyl upon treatment with sulfur and subsequent acidification (see above preparation of 2-biphenylthiol) produced 2′-methylbiphenyl-2-thiol in 51% yield, b.p. 110–113° (1 mm.), n_D^{20} 1.6272.

2′-Methylbiphenyl-2-thiol treated with sodium ethoxide in ethanol and then methyl iodide produced 2′-methyl-2-methylmercaptobiphenyl as a noncrystallizable oil. Oxidation of the latter sulfide with 30% hydrogen peroxide in glacial acetic acid produced waxy low melting 2′-methyl-2-methylsulfonylbiphenyl which could not be readily recrystallized for analysis. Oxidation with strong sodium dichromate and sulfuric acid in aqueous acetic acid produced fair yields of the desired 2′-methylsulfonylbiphenyl-2-carboxylic acid upon diluting with water and standing for 10 days at 0°. From about 3 g. of starting 2′-methylbiphenol-2-thiol about 0.6 g. of crude acid was obtained. After recrystallization from benzene-petroleum ether mixture and then from 56% ethanol, the material melted at 192–194°; the material failed to depress the melting point of the acid obtained from the mixed Ullman reaction, confirming the structure of the latter.

Two grams of the above highly purified 2′-methylsulfonylbiphenyl-2-carboxylic acid were refluxed for 16 hr. with 5 ml. of thionyl chloride to convert it to the acid chloride. The excess thionyl chloride was distilled *in vacuo* at 100° and the cooled residual acid chloride was then cautiously treated with 6 ml. of ethanol under reflux. After refluxing for 15 min., the resulting solution was poured into ice and the oil shaken first with 5% sodium bicarbonate solution and then water. The oil spontaneously crystallized to form white crystals of ethyl 2′-methylsulfonylbiphenyl-2-carboxylate which was recrystallized from petroleum ether (b.p. 70–90°); yield was 2.0 g. (91%), m.p. 70.5–72°.

Anal. Calcd. for $C_{16}H_{16}SO_4$: C, 63.1; H, 5.26. Found: C, 62.96; H, 5.23.

6,7-Dihydro-2,3-4,5-dibenzothiapin-6-one-1-dioxide (I). Two grams (0.0066 mole) of ethyl 2′-methylsulfonyl-biphenyl-2-carboxylate, 11 ml. of toluene, and 0.30 g. (0.0132 g.-atom) of sodium metal were refluxed with stirring for 18 hr. After cooling, the toluene layer was decanted cautiously into 4*N* aqueous ammonia and shaken. The ammoniacal layer, containing the desired compound, was decolorized by boiling with 0.3 g. of activated charcoal, filtered, and acidified with hydrochloric acid. After standing at 0° for 24 hr., the resulting 6,7-dihydro-2,3-4,5-dibenzothiapin-6-one-1-dioxide was filtered and recrystallized from a minimum of 70% ethanol to give white crystals; yield 1.3 g. (76%), m.p. 167–168°.

The material was stable to hot hydrochloric acid and was reprecipitated unchanged upon acidifying a hot sodium hydroxide solution of the material.

Anal. Calcd. for $C_{14}H_{10}SO_3$: C, 65.1; H, 3.88. Found: C, 65.27; H, 3.86.

The infrared absorption spectrum shows characteristic bands at 5.95μ (6.26μ) (benzoyl type aryl ketone bands); 7.57μ, 8.66μ, and 8.85μ (sulfone bands); and 12.88μ, 13.16μ, and 13.81μ (apparently, substituted phenyl bands). Compare with significant bands in ethyl 2′-methylsulfonylbiphenyl-2-carboxylate at 5.88μ, (aryl ester band), 7.68–7.76μ, 8.69μ (8.79 and 8.86μ) (12.63–12.74μ), 13.09μ, and 13.24μ; and also the significant bands in 2-methylsulfonylbiphenyl at 7.71μ, 8.71μ, 8.90μ, 12.77μ, 13.19μ, and 13.33μ. Planar, aromatic, seven-membered ring, tropone displays carbonyl band at *ca.* 6.1μ while dibenzotropones (believed to contain nonplanar, nonaromatic seven-membered rings) have bands at *ca.* 6.0μ.

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[24] R. G. Shuttleworth, W. S. Ropson, E. T. Stewart, *J. Chem. Soc.*, 1944, 71–73.

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH LABORATORY OF THE DEPARTMENT OF SURGERY, UNIVERSITY OF WASHINGTON SCHOOL OF MEDICINE]

Derivatives of Fluorene. IX. 4-Hydroxy-2-fluorenamine; New 3,4-Benzocoumarin Derivatives[1]

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Synthesis of 4-hydroxy-2-fluorenamine, 4-hydroxyfluorene, and related compounds is described. New 7- and 6-substituted 3,4-benzocoumarins were synthesized; the first series was obtained in an alternate attempt to synthesize 4-hydroxy-2-fluorenamine. Ultraviolet and infrared spectral data for several of these new compounds are reported.

Although several ring-hydroxylated metabolites of the carcinogen, *N*-2-fluorenylacetamide have been identified,[3] *N*-2-(4-hydroxyfluorenyl)acetamide has not been reported, nor is there any recorded synthesis. The following describes the preparation of this substance and of 4-hydroxyfluorene, also new to the literature, and of several related derivatives. One approach failed to give the fluorene nucleus when facile splitting of the methoxyl group

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[3] E. K. Weisburger and J. H. Weisburger in J. P. Greenstein and A. Haddow (eds.), *Advances in Cancer Research, Vol. V*, Academic Press, Inc., New York, N.Y., 1958, pp. 409–418.

in 2-carboxy-2′-methoxy-4′-nitrobiphenyl, led to lactonization giving a new 3,4-benzocoumarin derivative.

Selective monoacetylation of 2,4-fluorenediamine had given us excellent yields[4] of the 2-acetylated derivative. Diazotization of the latter in fluoboric acid followed by treatment with acetic anhydride gave *N*-2-(4-acetoxyfluorenyl)acetamide. Mild and more drastic hydrolysis led respectively to *N*-2-(4-hydroxyfluorenyl)acetamide and 4-hydroxy-2-fluorenamine. Treatment of the phenolic amine with 100% formic acid yielded *N*-2-(4-hydroxyfluorenyl)formamide which was acetylated giving the *O*-acetyl derivative.

Deamination of 4-hydroxy-2-fluorenamine was not successful. The expected product, 4-hydroxyfluorene, was obtained by diazotization and hydrolysis of 4-aminofluorene.

Reaction of *N*-2-(4-acetoxyfluorenyl)acetamide and dimethyl sulfate in the presence of potassium hydroxide gave *N*-2-(4-methoxyfluorenyl)acetamide, which, upon hydrolysis and deamination gave 4-methoxyfluorene. The latter compound was also obtained from reduction of the known 4-methoxyfluorene.

Ullmann coupling, with methyl *o*-bromobenzoate, of 2-iodo-5-nitroanisole and of 2-iodo-4-nitroanisole followed by hydrolysis of the reaction product in a mixture of acetic acid and 64% sulfuric acid gave, respectively 7-nitro-3,4-benzocoumarin and 6-nitro-3,4-benzocoumarin. Raney nickel and hydrazine hydrate reduction[5] of the nitro compounds followed by deamination gave 3,4-benzocoumarin. Methylation of 7-nitro-3,4-benzocoumarin with dimethyl sulfate in an excess of alkali led to the formation of 2-methoxy-4-nitrodiphenyl-2′-carboxylic acid. The latter was also obtained by mild alkaline hydrolysis (to avoid ether-splitting and lactonization) of methyl 2-methoxy-4-nitrodiphenyl-2-carboxylate in the Ullmann reaction mixture. Attempted cyclization of 2-methoxy-4-nitrodiphenyl-2′-carboxylic acid to a fluorenone in polyphosphoric acid gave, instead, the lactone which had been obtained from acid hydrolysis.

Table I gives data from the ultraviolet spectra[6] of some of these compounds. Infrared spectral data[6] for some of the 3,4-benzocoumarin derivatives are included in Table II.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA[a]

Compound (molarity)	λ max, mμ	Log ε
4-Hydroxyfluorene (2.67 × 10^{-5})	258	4.37
	268	4.42
	287	4.02
	294	4.06
	306	3.83
4-Hydroxyfluorenone (2.5 × 10^{-5})	249	4.42
4-Hydroxy-2-fluorenamine (5 × 10^{-5})	297	3.96
	213[b]	
	283[b]	
N-2-(4-Hydroxyfluorenyl)formamide (2.35 × 10^{-5})	217	4.56
	281	4.41
	294	4.39
	300[b]	
	318[b]	
N-2-(4-Acetoxyfluorenyl)formamide (2.5 × 10^{-5})	281	4.51
	289	4.55
	303	4.45
N-2-(4-Acetoxyfluorenyl)acetamide (1.86 × 10^{-5})	282	4.47
	290	4.52
	303	4.43
	220[b]	
2-Methoxy-4-nitrodiphenyl-2′-carboxylic acid (8 × 10^{-5})	293	3.96
	338	3.81
7-Nitro-3,4-benzocoumarin (2.5 × 10^{-5})	261	4.57
	278	4.57
	325[b]	
7-Amino-3,4-benzocoumarin (2.5 × 10^{-5})	229	4.38
	296	4.18
	317	4.19
6-Nitro-3,4-benzocoumarin (2.5 × 10^{-5})	226	4.41
	243	4.35
	258	4.38
6-Amino-3,4-benzocoumarin (2.5 × 10^{-5})	232	4.53
	238	4.52
	271[b]	

[a] Determined in absolute ethanol. [b] Shoulder.

EXPERIMENTAL[6]

N-2-(4-Acetoxyfluorenyl)acetamide. *N*-2-(4-Aminofluorenyl)acetamide[4] (2.1 g., 0.009 mole) was stirred in a mixture of 48% fluoboric acid (25 ml.) and water (10 ml.). To the suspension sodium nitrite (0.62 g., 0.009 mole) in water (3 ml.) was added dropwise at 0° (10 min.). The reaction mixture was stirred at −10–0° for 30 min., then filtered, washed successively with cold 5% fluoboric acid, methanol and ether, and dried over phosphorus pentoxide giving 2.9 g. of 4-(2-acetamidofluorenyl)diazonium fluoborate.

The fluoborate was suspended in acetic anhydride (15 ml.) and heated under reflux at 90–95° (bath) until evolution of gas ceased. The mixture was then distilled under reduced pressure and the residue treated with dilute sodium acetate solution, and the residual acetic anhydride destroyed with sodium carbonate solution. The solid was filtered, washed with water, and recrystallized twice from ethanol-water and once from acetone-methanol giving glistening crystals, 1.1 g. (44% from the amine), m.p. 230.5–231.5°. One more crystallization from acetone-methanol gave an analytical sample, m.p. 231–232°.

Anal. Calcd. for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.74; H, 5.42; N, 5.09.

4-Hydroxy-2-fluorenamine. *N*-2-(4-Acetoxyfluorenyl)acetamide (0.3 g.) was dissolved in boiling absolute ethanol (50 ml.). To the solution, concd. hydrochloric acid (10 ml.) was added. The mixture was refluxed for 16.5 hr. with occasional agitation. The alcohol was distilled and the precipitate filtered (0.25 g.) and refluxed for 15 min. in 2*N* sodium hy-

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(4) T. L. Fletcher, W. H. Wetzel, M. J. Namkung, and H. L. Pan, *J. Am. Chem. Soc.*, **81**, 1092 (1959).

(5) T. L. Fletcher and M. J. Namkung, *J. Org. Chem.*, **23**, 680 (1958).

(6) All melting points were taken on a Fisher-Johns apparatus and were corrected to standards. Microanalyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The ultraviolet absorptions were measured with a Beckman model DK-1 Recording Spectrophotometer and the infrared spectra were run on a Beckman IR-5 (potassium bromide disks).

TABLE II

Selected Infrared Absorption Bands of Some 3,4-Benzocoumarins[a]

Compound	$\lambda_{C=O}$, μ	λ_{C-O}, μ	λ_{NH_2}, μ	$\lambda_{C_6H_5-N}$, μ	$\lambda_{C_6H_5-NO_2}$, μ
3,4-Benzocoumarin	5.80	7.90 8.29(?)			
6-Amino-3,4-benzocoumarin	5.88	7.85 8.27(?)	2.91[b] 2.98[b] 3.09[c]	7.59	
6-Nitro-3,4-benzocoumarin	5.75	7.92 8.20(?)			7.42
7-Amino-3,4-benzocoumarin	5.89	7.88 8.44(?)	2.90[b] 2.97[b] 3.07[c]	7.62	
7-Nitro-3,4-benzocoumarin	5.75	7.91 8.29(?)			7.43

[a] Potassium bromide disk. [b] Free. [c] Bonded.

droxide (10 ml.). After cooling to room temperature, the *p*H was adjusted to 6 and the precipitate collected by filtration, 0.2 g. Recrystallization from methanol-water (Darco) gave white bars which started blackening at 225° and melting at 230–234° dec., 0.15 g. (76%). Two crystallizations from methanol-water gave an analytical sample, m.p. 234.5–236.5° dec.

Anal. Calcd. for $C_{15}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 78.98; H, 5.74; N, 7.06.

N-2-(4-Hydroxyfluorenyl)acetamide. *N*-2-(4-Acetoxyfluorenyl)acetamide (0.1 g.) was refluxed for 1 hr. in a mixture of ethanol (10 ml.) and 10% sodium carbonate solution (10 ml.). The mixture was distilled to 50% of the original volume and acidified with dilute hydrochloric acid to *p*H 5. The precipitate was filtered, washed with water, and dried. The material started darkening at 255° and melted at 265° dec., 0.07 g. (83%). Two crystallizations from methanol-water gave an analytical sample, m.p. 270–272.5° dec.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.13; H, 5.70; N, 6.14.

N-2-(4-Hydroxyfluorenyl)formamide. 4-Hydroxy-2-fluorenamine (0.1 g.) was dissolved in 98–100% formic acid (1 ml.) and the solution heated on a steam bath for 30 min. and then cooled. The precipitate was filtered, washed with water, and dried giving shiny flakes, 0.11 g., m.p. 250–253° dec. Recrystallization from ethanol-water raised the m.p. to 256.5–258° dec.

Anal. Calcd. for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.46; H, 4.83; N, 6.33.

N-2-(4-Acetoxyfluorenyl)formamide. *N*-2-(4-Hydroxyfluorenyl)formamide (0.06 g.) was mixed with acetic anhydride (0.5 ml.) and warmed. Pyridine was added dropwise until a solution was obtained which was heated in a water bath at 70–80° for 20 min. and the volatile material removed in a vacuum. The crystalline solid was stirred in 10% sodium acetate solution, which was then made alkaline to *p*H 8 with sodium bicarbonate, and the solid was filtered off, washed with water, and dried. Crystallization from ethanol-water and then from benzene–carbon tetrachloride gave lustrous prisms (0.04 g.), m.p. 189.5–191°. Recrystallization from benzene–carbon tetrachloride gave an analytical sample, m.p. 190–191°.

Anal. Calcd. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.76; H, 5.05; N, 5.12.

N-2-(4-Methoxyfluorenyl)acetamide. *N*-2-(4-Acetoxyfluorenyl)acetamide (1.5 g.) was suspended in boiling acetone (25 ml.) and 66% potassium hydroxide (1.5 ml.) was added, (a modification of a reported method[7]). The mixture was shaken, boiled briefly and shaken at room temperature for 10 min. Dimethyl sulfate (1.5 ml.) was then added dropwise over a period of 25 min. with occasional heating and constant agitation, which was continued for another hour. The mixture was then cooled and diluted with 5% sodium acetate solution (200 ml.), and the precipitate filtered, washed with water, and dried (1.3 g.). Chromatographic separation on neutral alumina gave 0.6 g. (45%), m.p. 192.5–194.5°. Crystallization from benzene-ligroin gave an analytical sample, m.p. 195.5–196.5°.

Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.90; H, 6.12; N, 5.77.

4-Methoxy-2-fluorenamine. *N*-2-(4-Methoxyfluorenyl)acetamide (0.67 g.) was dissolved in hot absolute ethanol (25 ml.) and concd. hydrochloric acid (10 ml.) was added. This solution was refluxed for 7 hr. and then distilled. The residue (0.55 g.) was filtered, washed with absolute ethanol, and dried.

The amine hydrochloride (0.25 g.) was treated with dilute ammonium hydroxide (1:3) and the free amine was collected and crystallized from methanol-water, 0.2 g. (95%), m.p. 148.5–149.5°.

Anal. Calcd. for $C_{14}H_{13}NO$: N, 6.63; $-OCH_3$, 14.69. Found: N, 6.56; $-OCH_3$, 15.02.

4-Methoxyfluorene. (a) 4-Methoxy-2-fluorenamine hydrochloride (0.3 g., 0.0012 mole) was diazotized in dilute hydrochloric acid (2:3) with sodium nitrite (0.1 g., 0.0015 mole) at 0°. The solution was then treated at 0–3° with 50% hypophosphorous acid (6 ml.) for 16 hr. and the product isolated and purified, 0.08 g. (30%), m.p. 72.5–76°; mixture melting point of this material with the analytical sample obtained below, 74–77°. Infrared spectra of these two compounds are identical.

(b) 4-Aminofluorenone was converted to 4-hydroxyfluorenone by a standard procedure, m.p. 250–251.5° (reported[8] m.p. 250–251°), and methylated with dimethyl sulfate to give 4-methoxyfluorenone, m.p. 114–115° (reported[8] m.p. 114.5–115.5°). The methoxy ketone (4.2 g., 0.02 mole) was mixed with 85% hydrazine hydrate (15 ml.) and a solution of sodium hydroxide (4 g., 0.1 mole) in 2,2′-oxydiethanol (80 ml.). The mixture was refluxed at 170–180° (bath) for 2.5 hr. then at 200° (bath) for another 2.5 hr. and cooled. The reaction solution was diluted with water and extracted with ether. By evaporation of the ether there was obtained 2.6 g. of an oil which crystallized upon refrigeration. The crystalline solid was extracted with ligroin (*d.* 0.67–0.69), and recrystallized from methanol giving 1.4 g. of the product, m.p. 73.5–76°. A second crop was obtained from the ligroin extract (0.4 g.). The combined crops were recrystallized again from methanol giving 1.5 g. (39%), m.p. 76.5–77.5°.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.38; H, 6.01.

4-Hydroxyfluorene. This hydroxy compound was prepared from 4-aminofluorene by hydrolyzing the diazonium salt (35% from the amine), m.p. 108–109°.

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(7) H. M. Duvall and E. Mosettig, *J. Am. Chem. Soc.*, **60**, 2409 (1938).

(8) R. Huisgen and H. Rist, *Ann.*, **594**, 137 (1955).

Anal. Calcd. for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.51; H, 5.64.

7-Nitro-3,4-benzocoumarin. To a stirred mixture of 2-iodo-5-nitroanisole[9] (21 g.), activated copper powder[10] (10 g.), and methyl *o*-bromobenzoate (32.3 g., 2 equiv.), activated copper powder (60 g.) was added in small portions over a period of 1 hr. while the mixture was heated at 210–215° (bath) then at 220° for 30 min. with occasional addition of activated copper powder (10 g.). The reaction mixture was cooled, extracted with boiling chloroform, and the residual oil from the chloroform extract was hydrolyzed by refluxing for 6 hr. in a mixture of acetic acid (300 ml.), concd. sulfuric acid (200 ml.) and water (100 ml.).[11] After water dilution of the hydrolysis solution the precipitate was filtered and extracted with hot 20% sodium carbonate solution. The insoluble solid was recrystallized from toluene giving 3.5 g. (18.5%), m.p. 203–205°. Thinking at first that the carbonate extract contained the desired carboxylic acid, it was acidified and the precipitate filtered, dried (15 g.) and heated in polyphosphoric acid (150 g.) at 150–160° (oven) for 2 hr. Upon water dilution and extraction of the solid with hot 20% sodium carbonate solution there was obtained 8.5 g. of the crude carbonate insoluble product, which, after recrystallization from benzene gave 3.9 g. (20%) of the pure substance supposedly a fluorenone, m.p. 203.5–204.5°.

This, however, was identical with the carbonate insoluble product and did not appear to be a fluorenone (infrared spectrum) and is described in the following procedure.

Anal. Calcd. for $C_{13}H_7NO_4$: C, 64.73; H, 2.93; N, 5.81. Found: C, 64.61; H, 3.07; N, 6.07.

2-Methoxy-4-nitrodiphenyl-2′-carboxylic acid. The above product (2 g.) was refluxed in a solution of sodium hydroxide (1 g.) in water (20 ml.) until all the solid had gone into solution. It was cooled in an ice bath and dimethyl sulfate (1 g., 2 equiv.) were added dropwise with rapid stirring (10 min.). The ice bath was removed and the reaction mixture was stirred at room temperature for 30 min., then refluxed for 10 hr. The mixture was filtered and the filtrate carefully neutralized with concd. hydrochloric acid with rapid stirring. The solid was removed by filtration and the filtrate acidified. The precipitate was separated, recrystallized from glacial acetic acid (rhombic crystals, 0.75 g.), m.p. 225–227.5°. Two crystallizations from acetic acid–water gave an analytical sample, m.p. 229.5–230.5°.

Anal. Calcd. for $C_{14}H_{11}NO_5$: C, 61.54; H, 4.06; N, 5.13; —OCH_3, 11.36. Found: C, 61.59; H, 4.33; N, 4.91; —OCH_3 11.17.

Heating this compound in polyphosphoric acid at 150° for 2 hr. gave the compound obtained previously, 7-nitro-3,4-benzocoumarin, m.p. and mixture m.p. 203–204°.

7-Amino-3,4-benzocoumarin. 7-Nitro-3,4-benzocoumarin (5 g.) was dissolved in a boiling mixture of toluene (200 ml.) and 95% ethanol (200 ml.) and reduced in the usual way[5] with Raney nickel and hydrazine hydrate. The product amounted to 3.8 g. (86%), m.p. 239.5–240.5°. Recrystallization from chloroform gave the analytical sample.

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.92; H, 4.30; N, 6.63. Found: C, 74.11; H, 4.35; N, 6.47.

7-Acetamido-3,4-benzocoumarin. Acetylation of the above amine with acetic anhydride in glacial acetic acid gave a quantitative yield of the acetamido compound, m.p. 298–299°.

Anal. Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.37; N, 5.53. Found: C, 71.13; H, 4.46; N, 5.76.

3,4-Benzocoumarin. Deamination of 1 g. of 7-amino-3,4-benzocoumarin was effected with hypophosphorous acid giving 0.9 g. of the crude product which was extracted with ligroin (d. 0.67–0.69). After evaporation of the ligroin the residue was recrystallized from methanol-water yielding 0.7 g. This melted at approximately 85°, resolidified and remelted at 91.5–92.5°. A mixture with the authentic material[12] showed no melting point depression and the infrared spectrum of the product is identical with that of 3,4-benzocoumarin.

6-Nitro-3,4-benzocoumarin. Ullmann reaction of 2-iodo-4-nitroanisole[13] and methyl *o*-bromobenzoate at 210–220° (bath) for 2 hr. gave an oil which was hydrolyzed in a mixture of acetic acid and 64% sulfuric acid. The solid obtained from the hydrolysis was extracted with sodium carbonate solution, giving 9.5% of the product as insoluble solid. The carbonate extract was acidified and the precipitate heated in polyphosphoric acid at 150–160° (oven) for 2 hr. giving another 16% of the benzocoumarin, m.p. 261.5–262.5°.

Anal. Calcd. for $C_{13}H_7NO_4$: C, 64.73; H, 2.93; N, 5.81. Found: C, 64.78; H, 3.13; N, 5.89.

6-Amino-3,4-benzocoumarin. Raney nickel and hydrazine hydrate reduction[5] of the nitro compound gave a 94% yield of the amine, m.p. 190–191°.

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.92; H, 4.30; N, 6.63. Found: C, 74.09; H, 4.05; N, 6.56.

Deamination of the amine gave 3,4-benzocoumarin,[12] as shown by melting point, mixture melting point, and infrared spectrum.

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[9] W. E. Hanford and R. Adams, *J. Am. Chem. Soc.*, **57**, 1592 (1935).

[10] E. C. Kleiderer and R. Adams, *J. Am. Chem. Soc.*, **55**, 4219 (1933).

[11] When the oil was hydrolyzed by refluxing for 7 hr. in an equal mixture of ethanol and 20% sodium carbonate solution, there was obtained a compound melting at 228–229°. A mixture melting point with 2-methoxy-4-nitrodiphenyl-2′-carboxylic acid was not depressed.

[12] C. Graebe and P. Schestakow, *Ann.*, **284**, 306 (1895).

[13] G. M. Robinson, *J. Chem. Soc.*, **109**, 1083 (1916).