lation with toluene was used to remove the water, b.p. 105–107° at 2 mm., n_D^{25} 1.5806. The Grignard reagent was made by the general procedure and carbonated by passing dry carbon dioxide over the surface. Extraction of the ether layer with aqueous sodium hydroxide, followed by acidification of the alkaline layer gave *m*-carboxyacetophenone, m.p. 161–162°, 0.002 mole, 4%. The ether layer yielded crude acetophenone, b.p. 50° at 2 mm., 26%, n_D^{25} 1.5325, reported n_D^{25} 1.5310. A duplicate run gave 40% acetophenone of approximately the same quality.

NASHVILLE 5, TENN.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

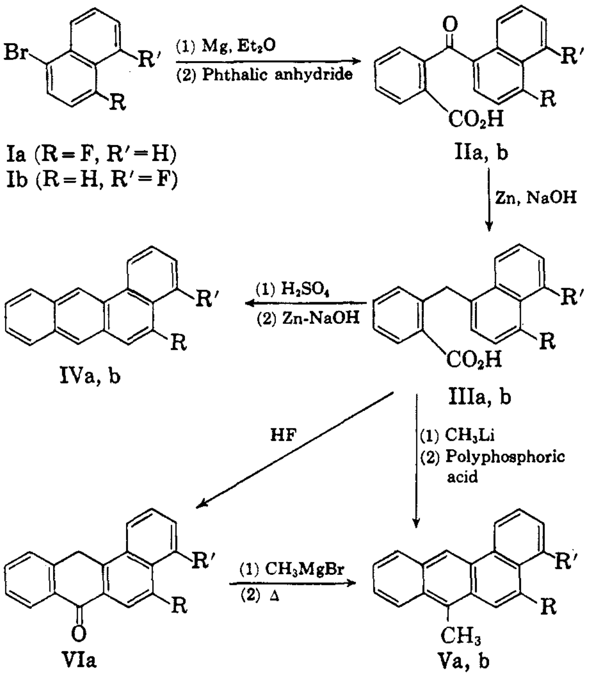
The Synthesis of Some Monofluoro-1,2-benzanthracenes[1]

MELVIN S. NEWMAN, DENIS MACDOWELL, AND SAMBASIÑA SWAMINATHAN

Received November 3, 1958

The syntheses of 3- and 4′-fluoro-1,2-benzanthracenes and of 3-fluoro- and 4′-fluoro-10-methyl-1,2-benzanthracenes are described.

Substitution of the rings in a number of aromatic carcinogens can profoundly alter their carcinogenic activity. Of the various groups available,[2] the fluoro group has several advantages, *viz*, the small size of the fluorine atom, its strong bond with carbon, and its resistance to metabolism *in situ* as contrasted with other groups. Miller, Miller, and Finger[3,4] have shown that most of the fluoro derivatives of the rat liver carcinogen 4-dimethylaminoazobenzene are as active as, or more active than, the parent dye and have further proposed that tests of the biological activity of various fluoro derivatives of biologically active molecules could be used to indicate the positions directly involved in the activity in question. If a fluoro derivative is inactive, then the position blocked may be involved in the biological activity of the nonfluorinated parent concerned. If the fluoro derivative is active, the substituted position is probably unimportant in the biological activity under study. With a view of extending this concept to a study of the carcinogenic polycyclic aromatic hydrocarbons, we have undertaken the synthesis of the various monofluoro derivatives of the carcinogens, 10-methyl-1,2-benzanthracene and 9,10-dimethyl-1,2-benzanthracene. The syntheses of the 3-fluoro- and 4′-fluoro-10-methyl-1,2-benzanthracenes as well as the corresponding parent fluoro-1,2-benzanthracenes have been carried out by the sequence of reactions outlined below:



The syntheses involved the use of 1-bromo-4-fluoronaphthalene (Ia) and 1-bromo-5-fluoronaphthalene (Ib) as starting materials. The former was obtained by standard methods involving the bromination of 1-formamidonaphthalene followed by replacement of the amino group, obtained by hydrolysis, with fluorine.[5] Ib was obtained from 1-nitronaphthalene by bromination, reduction with

---

[1] This work was supported by a grant from the National Institutes of Health.

[2] J. L. Hartwell, "Survey of Compounds Which Have Been Tested for Carcinogenic Activity," 2nd ed., 1951, U. S. Public Health Service Publication No. 149, Washington, D. C.

[3] J. A. Miller, E. C. Miller, and G. C. Finger, *Cancer Research*, **13**, 93 (1953).

[4] J. A. Miller, E. C. Miller, and G. C. Finger, *Cancer Research*, **17**, 387 (1957).

[5] A. Roe, *Org. Reactions*, V, 193 (1949).

iron and hydrochloric acid[6] and replacement of the resultant amino group with fluorine.[5]

The Grignard reagents corresponding to Ia and Ib reacted smoothly with phthalic anhydride to give the ketoacids IIa and IIb, respectively. Zinc alkali reduction of IIa and IIb afforded the acids IIIa and IIIb. IIIa was converted to the anthrone VIa with anhydrous hydrofluoric acid. This anthrone was treated with methylmagnesium bromide and crude product pyrolyzed to give a low yield (1% based on VIa) of 3-fluoro-10-methyl-1,2-benzanthracene (Va). However, a better yield (40%) of Va was obtained by reacting IIIa with excess methyllithium to give the corresponding methyl ketone and cyclizing the latter (without purification) by heating with polyphosphoric acid. The use of a mixture of hydrobromic and acetic acids, which has been employed for similar cyclizations[7] did not effect cyclization of the above methyl ketone. The acid (IIIb) was similarly converted to the corresponding methyl ketone which could be cyclized either with a mixture of hydrobromic and acetic acids (27% yield) or polyphosphoric acid (33% yield) to give 4′-fluoro-10-methyl-1,2-benzanthracene (Vb). Polyphosphoric acid does not seem to have been previously employed to cyclize the type of methyl ketones referred to above to *meso* substituted anthracenes, though other reagents have been reported.[7,8]

The acids IIIa and IIIb were treated with concentrated sulfuric acid and the resulting anthrones subsequently reduced to give 68.7% and 42.5% yields, respectively, of 3-fluoro and 4′-fluoro-1,2-benzanthracenes (IVa and IVb).

EXPERIMENTAL[9]

1-Formamidonaphthalene. Treatment of 1-naphthylamine with 90% formic acid under reflux for 2 hr. afforded the formulated amine, m.p. 135–137° (lit.[10] 138.5°) in 84% yield.

1-Bromo-4-formamidonaphthalene. Bromination of this product in glacial acetic acid and pyridine afforded the bromo compound in 93% yield, m.p. 169–172° (lit.[11] 172°).

1-Amino-4-bromonaphthalene. Saponification of the bromo compound using methanolic potassium hydroxide proceeded smoothly and gave 1-amino-4-bromonaphthalene in 81% yield, m.p. 100–103° (lit.[11] 94–95°).

1-Bromo-4-fluoronaphthalene (Ia). The above bromoamine (100 g., 0.45 mole) was diazotized in aqueous hydrochloric acid solution with sodium nitrite. Addition of 48–50% fluoboric acid caused the immediate formation of the diazonium fluoborate. The mixture was stirred at −5° for 30 min. and was then filtered, the precipitate being washed with water and cold acetone. Drying over phosphorus pentoxide crude dry diazonium fluoborate as a dark green solid, 127 g. (88%) m.p. 151–155° (dec.) (lit.[12] 151.5°).

Decomposition of a 400-g. portion of the crude diazonium fluoborate was effected by heating the solid under reflux at 160° for 10 min. The residue was then taken up in benzene and distilled, affording a yellow-brown distillate of crude bromofluoronaphthalene. This was shaken with cold concentrated sulfuric acid and redistilled to yield the desired product, 134 g. (51%), b.p. 110–115° (2 mm.), m.p. 33.9° by a time-temperature cooling curve (lit.[12] m.p. 36°).

o-(4-Fluoro-1-naphthoyl)benzoic acid (IIa). To a stirred suspension of 5.35 g. of magnesium in 50 ml. of anhydrous tetrahydrofuran and 30 ml. of anhydrous ether was added a solution of 50 g. of Ia in 60 ml. of tetrahydrofuran. Formation of the Grignard reagent proceeded steadily, and after the reaction had reached completion, it was forced by dry nitrogen into a solution of 33 g. of phthalic anhydride in 150 ml. of tetrahydrofuran. The mixture was stirred under reflux for about 2 hr. Tetrahydrofuran and ether were removed by distillation and were replaced by benzene. Decomposition of the complex was effected with cold dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether benzene and combined with the main benzene extract. Acidic material was removed from the organic extracts by repeated extraction with aqueous potassium carbonate. These alkaline extracts afforded impure ketoacid, 61 g. m.p. 155–160°, on acidification. Recrystallization from acetonitrile gave 49.5 g. (76%) of a colorless product, m.p. 161–163°. An analytical sample obtained by several recrystallizations from acetonitrile melted at 163.0–164.9°.

Anal. Calcd. for $C_{18}H_{11}FO_3$: C, 73.5; H, 3.8. Found: C, 73.8; H, 3.6.

The alkali insoluble material obtained from the organic extracts yielded 1.8 g. of a brown oil which, on trituration with cold Skellysolve C (petroleum ether, b.p. 90–97°) gave impure 4,4′-difluoro-1,1′-binaphthyl. An analytical sample recrystallized from Skellysolve C melted at 176.0–177.0°.

Anal. Calcd. for $C_{20}H_{12}F_2$: C, 82.7; H, 4.2. Found: C, 82.7; H, 4.1.

o-(4-Fluoro-1-naphthylmethyl)benzoic acid (IIIa). A mixture of 20 g. of the ketoacid (IIa), 100 ml. of ammonium hydroxide, 50 ml. of water, and 60 g. of zinc dust activated by the addition of 3 ml. of ammoniacal copper sulfate solution, was heated under reflux of 22 hr. The mixture was cooled and filtered and the solids were extracted with an additional 100 ml. of ammonium hydroxide. After removal of neutral material from the viscous layer by extraction with ether benzene, acidification afforded 16.0 g. of impure acid (IIIa), m.p. 173.0–175.5°. Recrystallization from Skellysolve C–benzene gave 14.0 g. (74%) of IIIa, m.p. 175.0–177.0°. An analytical sample, m.p. 176.0–177.0°, was obtained as colorless needles from the same solvent.

Anal. Calcd. for $C_{18}H_{13}FO_2$: C, 77.1; H, 4.7. Found: C, 77.4; H, 4.8.

3-Fluoro-10-oxo-9,10-dihydro-1,2-benzanthracene (VIa). The acid (IIIa), (7 g.) was treated with excess anhydrous hydrofluoric acid in a polyethylene bottle. After 1 hr. the solution was poured onto ice and the yellow impure anthrone (6.0 g.) on crystallization from benzene-ethanol melted at 165–170° (4.5 g.).

Anal. Calcd. for $C_{18}H_{11}FO$: C, 82.4; H, 4.2. Found: C, 82.9; H, 4.3.

3-Fluoro-10-methyl-1,2-benzanthracene (Va). (a) To a solution of 12 g. of VIa in a solution of 300 ml. of benzene and 100 ml. of tetrahydrofuran was added excess methylmag-

---

[6] J. B. Shoesmith and H. Rubli, *J. Chem. Soc.*, 3104 (1927).

[7] C. K. Bradsher and S. T. Webster, *J. Am. Chem. Soc.*, **79**, 343 (1957).

[8] F. A. Vingiello and A. Bořkoveć, *J. Am. Chem. Soc.*, **78**, 3205 (1956).

[9] All melting points are corrected, all boiling points are uncorrected. Analyses were performed by Clark Laboratories, Urbana, Illinois, and Galbraith Laboratories, Knoxville, Tennessee. All fluorine analyses by the Huffman Microanalytical Laboratories, Denver, Colorado.

[10] G. Tobias, *Ber.*, **15**, 2447 (1882).

[11] G. T. Morgan, F. M. G. Micklethwait, and H. B. Winfield, *J. Chem. Soc.*, **85**, 750 (1904).

[12] G. Schiemann, W. Guffroy, and W. Winkelmuller, *Ann.*, **487**, 270 (1931).

nesium bromide. The mixture was heated under reflux for 16 hr., decomposed with ammonium chloride and hydrochloric acid and was then thoroughly extracted with ether benzene. Removal of the solvents afforded an oil which was heated at 190–200° for 10 min. Chromatography over alumina in benzene yielded 1.8 g. of a green solid, m.p. 125–130°. A boiling solution of this in ethanol was treated with an ethanolic solution of 1,3,5-trinitrobenzene. The red solution on cooling gave a complex which was purified by recrystallization from methanol. A benzene solution of the purified trinitrobenzene complex was passed through a column of alumina and the eluted solid was recrystallized three times from Skellysolve B to yield 130 mg. (1%) of analytically pure Va, m.p. 141.0–142.0°.

Anal. Calcd. for $C_{19}H_{13}F$: C, 87.7; H, 5.0; F, 7.3. Found: C, 87.7; H, 5.2; F, 7.2.

(b) To a stirred solution of 115 ml. of 0.8*N* methyllithium in ether, was added gradually over 15 min. a solution of 7.8 g. of IIIa in a mixture of 500 ml. of ether and 100 ml. of tetrahydrofuran. As the acid was added, a deep purple color developed. After the addition was over, the mixture was stirred for 1 hr. and then decomposed with iced water. The organic layer was separated, washed with saturated sodium chloride solution, and dried over magnesium sulfate. After removal of solvents 7.5 g. of crude oily methyl ketone was obtained as brown liquid. The alkaline aqueous layer furnished little starting material when acidified. The above liquid (6.18 g.) was added to 30 g. of polyphosphoric acid[13] at 60° and the mixture heated with frequent stirring on a steam bath for 20 min. and kept overnight at room temperature. The heated mixture was then diluted with water and the yellow solid which precipitated was collected and air-dried. Extraction of the solid with two 100-ml. portions of refluxing benzene furnished, after treatment with charcoal and concentration, two successive crops of 1.66 g. and 0.48 g. of crystals with m.p. 140–141° and m.p. 136–139°, respectively. The filtrate from the second crop was freed of benzene and the residue crystallized from Skellysolve B to give an additional 0.6 g. of crude product. By chromatography in benzene over alumina there was obtained 2.3 g. (40% yield based on the crude methyl ketone) of pale yellow Va, m.p. 141.5–142.0°, undepressed by the product obtained by method (a) above.

3-Fluoro-1,2-benzanthracene (IVa). Finely powdered IIIa (3 g.) was dissolved in 30 ml. of concd. sulfuric acid at room temperature to give a clear orange solution. After 6 hr., the solution was poured on ice and the anthrone which separated was collected and refluxed for 14 hr. with a mixture of 10 g. of zinc dust (activated with copper sulfate), 150 ml. of water, and a solution of 22 g. of sodium hydroxide in 120 ml. of water. The mixture was cooled, acidified with 60 ml. of concd. hydrochloric acid, and the solids were collected and dried. Extraction with 150 ml. of refluxing benzene followed by concentration of the extract gave 0.61 g. of pale yellow almost colorless crystals, m.p. 131–132° and a second crop of 1.04 g., m.p. 128–129°. Recrystallization of the second crop (after treatment with charcoal) afforded 0.95 g. of colorless needles, m.p. 130.5–131.0°. An additional 0.25 g. of pure product was obtained by passing the filtrate from the second crop through alumina. The total yield of pure material amounted to 1.81 g. (68.7%). The analytical sample, m.p. 131.5–132.5°, was obtained after two crystallizations from a mixture of benzene and Skellysolve B (petroleum ether, b.p. 60–70°).

Anal. Calcd. for $C_{18}H_{11}F$: C, 87.8; H, 4.5; F, 7.7. Found: C, 88.2; H, 4.5; F, 8.0.

1-Bromo-5-nitronaphthalene. To 300 g. of 1-nitronaphthalene in a 3 l. three necked flask fitted with a stirrer and condenser, was added dropwise 125 ml. of bromine. The mixture was stirred vigorously with external cooling. After 10 min., the mixture had set to a hard cake which was allowed to stand overnight at room temperature. On recrystallization from alcohol containing a little chloroform, there was obtained 336 g. (76%) of 1-bromo-5-nitronaphthalene, m.p. 118–122° (lit.[14] m.p. 121°).

1-Amino-5-bromonaphthalene. To a refluxing mixture of 1-bromo-5-nitronaphthalene (268 g., 1.06 mole), 95% ethanol (800 ml.), and hydrochloric acid (15 ml.) was added powdered iron (180 g.) in three equal portions over a period of 3 hr. The reaction was refluxed for 1 hr. after the final addition, about half of the ethanol was removed by distillation, and the residual solution was made alkaline by the addition of 20% potassium hydroxide solution. The crude oily amine solidified on cooling and was removed by filtration, powdered, and dried. The yield was 241 g. of a dark red solid m.p. 64–69° (lit.[14] 69°).

1-Bromo-5-fluoronaphthalene (Ib). The crude 1-amino-5-bromonaphthylamine (100 g., 0.45 mole) was diazotized with sodium nitrite and hydrochloric acid in a polyethylene beaker. Fluoboric acid (48–50%) (160 ml.) was added in one portion, and the thick mixture was stirred at 0–5° for 30 min. The fluoborate was removed by filtration, washed with dilute fluoboric acid, and dried over phosphorus pentoxide *in vacuo.* Yield 145 g. (100%) of a gray-green solid. This crude diazonium fluoborate (100 g.) was heated at 160° for 15 min. After evolution of boron trifluoride had ceased, the residue was repeatedly extracted with benzene and ether, the solvents were removed, and the residue was distilled under reduced pressure. The impure bromofluoronaphthalene (49 g.) b.p. 95–100° (1 mm.) thus obtained was shaken with cold concd. sulfuric acid and redistilled. Pure Ib, b.p. 85–90° at 0.5 mm., was obtained in 60% yield. A time-temperature cooling curve indicated a m.p. of 18–19°.

Anal. Calcd. for $C_{10}H_6BrF$: C, 53.4; H, 2.7. Found: C, 53.5; H, 2.7.

o-(5-Fluoro-1-naphthoyl)benzoic acid (IIb). The Grignard reagent prepared in ether from 34 g. of Ib was forced by dry nitrogen into a stirred solution of 22 g. of phthalic anhydride in 100 ml. of benzene and 100 ml. of ether. The mixture was heated under reflux for 2 hr. and was then decomposed with saturated ammonium chloride solution. The aqueous layer was thoroughly extracted with ether benzene and the combined organic extracts were extracted with aqueous potassium carbonate. The alkaline extract was boiled for a short period with decolorizing carbon and was then poured onto ice and hydrochloric acid. The precipitated acid, m.p. 174–180°, was obtained in 64% yield. An analytical sample, m.p. 181.0–182.5°, was obtained by repeated crystallization from benzene.

Anal. Calcd. for $C_{18}H_{11}FO_3$: C, 73.5; H, 3.8. Found: C, 73.5; H, 3.9.

o-(5-Fluoro-1-naphthylmethyl)benzoic acid (IIIb). A mixture of the ketoacid (IIb) (10 g., 0.034 mole), water (150 ml.), potassium hydroxide (28 g.), zinc dust (30 g.), and a few drops of ammoniacal copper sulfate was heated under reflux with stirring for 16 hr. The mixture was cooled, filtered, and extracted with an ether benzene mixture to remove any nonacidic material. Acidification of the alkaline extract afforded 8.4 g. (88%) of IIIb as a light tan solid, m.p. 173–176°. An analytical sample recrystallized from benzene–Skellysolve C melted at 176.0–177.9°.

Anal. Calcd. for $C_{18}H_{13}FO_2$: C, 77.1; H, 4.7. Found: C, 77.3; H, 4.7.

4′-Fluoro-10-methyl-1,2-benzanthracene (Vb). (a) To a stirred solution of methyllithium prepared from 3.5 g. of lithium and 23 g. of methyl iodide in ether was added dropwise a solution of 7.0 g. of IIIb in 100 ml. of ether. As the acid was added, a purple color developed. After the addition was complete, the mixture was stirred for 5 min. and then poured on ice. The methyl ketone was extracted with an ether benzene mixture and was obtained as a dark brown oil (6.4 g.) on removal of the solvents. This oil was heated

---

(13) Supplied by the Victor Chemical Works, Box 603, Chicago 90, Ill.

(14) G. Lock, *Monatsh.*, **81**, 850 (1950).

under reflux with 150 ml. of glacial acetic acid 20 ml. of 40% hydrobromic acid for 20 hr. and the solution was poured on ice, made alkaline with aqueous potassium hydroxide, and the hydrocarbon was extracted with ether benzene. The crude oily product was taken up in Skellysolve C and was chromatographed over alumina to yield 3.6 g. of a yellow solid which after several recrystallizations from Skellysolve B afforded 1.57 g. (27%) of pure Vb, m.p. 142.5–143.5°, as very pale yellow needles.

Anal. Calcd. for $C_{19}H_{13}F$: C, 87.7; H, 5.0; 7.3. Found: C, 87.5; H, 5.3; F, 7.1.

(b) Cyclization of 2.6 g. of the crude methyl ketone obtained in the previous experiment with 23 g. of polyphosphoric acid as described for Va, followed by chromatographic purification of the crude hydrocarbon furnished 0.80 g. (33%) of Vb, m.p. 142.2–143.0° undepressed by the product obtained above.

4′-Fluoro-1,2-benzanthracene (IVb). A solution of 8.1 g. of finely ground IIIb in 81 ml. of concd. sulfuric acid was kept at room temperature for 2 hr. and then poured on ice. The anthrone was collected and refluxed for 7.5 hr. with a mixture of 40 g. of zinc dust (activated with copper sulfate), 500 ml. of water, and a solution of 66 g. of sodium hydroxide in 200 ml. of water. After cooling and acidifying with 180 ml. of concentrated hydrochloric acid, the solids were collected, dried, and extracted with 250 ml. of refluxing benzene. The benzene extract on cooling furnished 3.85 g. of crystalline product, m.p. 169.5–172.0°. Crystallization from benzene after treatment with charcoal furnished 2.07 g. of a I crop of very pale yellow crystals m.p. 171.5–172.0° and 1.3 g. of product, m.p. 170–172°. The latter after chromatographic purification afforded 0.95 g. pure hydrocarbon, m.p. 171.5–172°, the total yield of pure hydrocarbon amounting to 3.02 g. (42.5%). The analytical sample, m.p. 171.5–172.0°, was obtained by recrystallization from a mixture of benzene and Skellysolve B.

Anal. Calcd. for $C_{18}H_{11}F$: C, 87.8; H, 4.5; F, 7.7. Found: C, 87.9; H, 4.6; F, 7.6.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE TECHNICAL RESEARCH DEPARTMENT OF MATSUSHITA ELECTRIC WORKS, LTD.]

Synthetic Products from Methylolphenols, Formaldehyde, and Primary Aromatic Amines

MIYOSHI NODA, HIROSHI SHIMAOKA, AND SUSUMU NAGASE

Received October 27, 1958

Reaction of 2,6-dimethylol-*p*-cresol with aromatic primary amines resulted in the formation of *N*-(2-hydroxy-3-methylol-5-methylbenzyl)arylamines (I). Nitroso compounds (II) were obtained upon nitrosation of I, indicating that they were secondary amines. Benzoxazine compounds (III) were prepared by reaction of I with formaldehyde. In the same manner *N*-(4-hydroxybenzyl)arylamines (IV) and their nitroso compounds (V) were obtained from 4-methylolphenol. Twenty-six new compounds, and two compounds obtained by two new methods were prepared and studied.

Aromatic amine-phenol-formaldehyde resins which are formed by the condensation of amine, phenol, and formaldehyde are noted for their high electric resistance.[1] However, it is rarely reported whether they are simple mixtures of aromatic amine-formaldehyde and phenol-formaldehyde resins or copolymers of the three constituents.

This work is a study of the initial condensation products of amines, phenols, and formaldehyde.

The condensation of phenols with formaldehyde and primary[2] or secondary[3] aliphatic amines has been studied in several laboratories. *o*-Alkylaminomethyl-*p*-substituted phenol, *N*,*N*-bis-(2-hydroxybenzyl)alkylamines and a new series of 3,4-dihydro-3,6-disubstituted-1,3,2*H*-benzoxazine were obtained directly from three reactants in the presence of alcoholic potash in certain instances.[4]

The condensation of phenols with formaldehyde and primary aromatic amines has also been studied[5] by several workers, the following products being obtained: *N*-(2-hydroxybenzyl)aniline,[6,7] *N*-(2-hydroxybenzyl)-*p*-toluidine,[6] *N*-(4-hydroxybenzyl)-aniline,[6] *N*-(4-hydroxybenzyl)-*p*-toluidine[6] and *N*-nitroso-*N*-(4-hydroxybenzyl)aniline.[8] 3,4-Dihydro-3-*p*-tolyl-6-*t*-butyl-1,3,2*H*-benzoxazine and 3,4-dihydro-3-*p*-tolyl-6-bromo-1,3,2*H*-benzoxazine were also prepared by Burke and co-workers.[9]

---

(1) (a) L. Helm, Brit. Patent **25,216** (1907); (b) A. Gams and G. Widmer, U. S. Patent **2,199,155** (1940); (c) F. E. Calvert and P. A. Bury, U. S. Patent **2,449,876** (1948); (d) P. C. Schroy, J. Grabowski, and M. J. Scott, U. S. Patent **2,523,333** (1950).

(2) (a) H. A. Bruson, U. S. Patent **2,031,557** (1936); **2,114,122** (1938); (b) J. Harmon and F. M. Meigs, U. S. Patent **2,098,869** (1937); (c) H. A. Bruson, *J. Am. Chem. Soc.*, **58**, 1741 (1936).

(3) (a) W. T. Caldwell and T. R. Thompson, *J. Am. Chem. Soc.*, **61**, 765 (1939); (b) H. A. Bruson and C. W. MacMullen, *J. Am. Chem. Soc.*, **63**, 270 (1941).

(4) (a) W. J. Burke and C. W. Stephens, *J. Am. Chem. Soc.*, **71**, 609 (1949); (b) W. J. Burke, R. P. Smith, and C. Weatherbee, *J. Am. Chem. Soc.*, **74**, 602 (1952); **74**, 1518 (1952).

(5) (a) H. Franzen, *J. prakt. Chem.*, **72** (2), 217 (1905); (b) A. Hantzsch and E. Wechsler, *Ann.*, **325**, 248–9 (1902); (c) Farbwerke Höchst AG, Ger. Patent **109,488** (1855); (d) C. A. Bischoff and E. Fröhlich, *Ber.*, **39**, 3967–76 (1906).

(6) (a) O. Emmerich, *Ann.*, **241**, 344–56 (1887).

(7) (a) C. Paal and H. Senninger, *Ber.*, **27**, 1802–4 (1894); (b) C. Paal, *Arch. Pharm.*, **240**, 681–90 (1902).

(8) E. Bamberger and J. Müller, *Ann.*, **313**, 104–16 (1900).

(9) W. J. Burke, K. C. Murdock, and Grace Ec, *J. Am. Chem. Soc.*, **76**, 1677 (1954).