yield 1.6 g. of 1,5-naphthyridine methiodide, m.p. 254–255° dec.; λ_{max} 288 mμ (5500), 319 (10,100), 326 (10,100); in acid, 268 (6250), 311 (11,900), 318 (12,100), 362 (2500).

Anal. Calcd. for $C_9H_9N_2I$: C, 39.7; H, 3.3; N, 10.3; I, 46.6. Found: C, 39.4; H, 3.3; N, 10.0; I, 46.4.

1-Methyl-1,5-naphthyridin-2(1*H*)-one (XIX).—To a stirred solution of 2.0 g. (7.7 mmoles) of 1,5-naphthyridine methiodide in 20 ml. of water, cooled in an ice–methanol bath, was added dropwise a solution of 1.3 g. (32 mmoles) of sodium hydroxide in 2.5 ml. of water during 5 min. and 5.3 g. (16 mmoles) of potassium ferricyanide in 10 ml. of water during 30 min., both additions starting at the same time. After 1.5 hr., the ice bath was removed and stirring was continued for an additional 5 hr. at room temperature. Continuous extraction of the reaction mixture with chloroform and evaporation of the chloroform led to 0.8 g. of residue which was dissolved in 5 ml. of chloroform and applied to 30 g. of alumina packed in benzene. The fractions eluted with chloroform–benzene (2:1) were combined and sublimed at 95° (5 μ) to give 685 mg. (56% yield) of 1-methyl-1,5-naphthyridin-2(1*H*)-one, m.p. 104–105°; λ_{max} 220 mμ (ε 39,900), 335 (11,000), 350 (7500); in acid, 223 (28,000), 261 (6200), 345 (11,700).

Anal. Calcd. for $C_9H_8ON_2$: C, 67.5; H, 5.0; N, 17.5. Found: C, 67.4; H, 5.0; N, 17.0.

1-Methyl-1,5-naphthyridin-2(1H)-one methiodide was prepared by heating under reflux for 2 days a solution of the naphthyridinone XIX and methyl iodide in benzene. Cooling and filtering gave a precipitate of methiodide which was crystallized from methanol–ether as orange needles, m.p. 216° dec.

Anal. Calcd. for $C_{10}H_{11}N_2OI$: C, 39.8; H, 3.7; N, 9.3; I, 42.0. Found: C, 39.9; H, 3.8; N, 9.0; I, 42.3.

1,5-Dimethyl-1,5-naphthyridine-2,6(1*H*,5*H*)-dione (XX).—To a stirred solution of 3.0 g. (10 mmoles) of 1-methyl-1,5-naphthyridin-2(1*H*)-one methiodide in 25 ml. of water, cooled in an ice bath, were added a 5-ml. portion of a solution of 2.8 g. (70 mmoles) of sodium hydroxide in 25 ml. of water and a solution of 10 g. (30 mmoles) of potassium ferricyanide in 50 ml. of water. The remaining 20 ml. of alkali solution was added portionwise over a 5 min. period and the suspension was stirred for 15 min. Continuous extraction with chloroform and evaporation of the chloroform afforded 1.8 g. of crystalline material which was sublimed [190° (10 μ)] and recrystallized from methanol–acetone as yellow needles, m.p. 220–222° dec.; λ_{max} 233 mμ (ε 66,000), 387 (13,000), 405 (11,400).

Anal. Calcd. for $C_{10}H_{10}N_2O_2$: C, 63.1; H, 5.3; N, 14.7. Found: C, 63.2; H, 5.1; N, 14.7.

1-Methyl-3-ethyl-1,5-naphthyridin-2(1*H*)-one (XXI) and 1,5-Dimethyl-3-ethyl-1,5-naphthyridine-2,6(1*H*,5*H*)-dione (XXII).—A solution of 2.0 g. (13 mmoles) of 3-ethyl-1,5-naphthyridine (V) in 25 ml. of dry benzene and 10 ml. of methyl iodide was heated on the steam bath for 2 days. The benzene and excess methyl iodide were removed *in vacuo*, and to the residue was added 6 g. (50 mmoles) of potassium ferricyanide in 25 ml. of water. This solution was cooled to 5° in an ice bath, and 13 g. (0.33 mole) of sodium hydroxide in 20 ml. of water was added slowly with stirring. After an hour, the solution was extracted with chloroform, the chloroform was evaporated, and the residue taken up in 3 *N* hydrochloric acid. Extraction with chloroform and evaporation of the chloroform led to the isolation of a yellow solid which was sublimed at 150° (10 μ) to give 479 mg. (17% yield) of 1,5-dimethyl-3-ethyl-1,5-naphthyridine-2,6(1*H*,5*H*)-dione, m.p. 261–262°; λ_{max} 234 mμ (ε 47,000), 383 (15,000), 402 (12,000).

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.0; H, 6.5; N, 12.8. Found: C, 66.1; H, 6.5; N, 12.8.

The acid solution was made alkaline and extracted with methylene chloride which was filtered through alumina. Evaporation of the filtrate gave a white solid which was sublimed at 80° (50 μ) to give 335 mg. (14% yield) of 1-methyl-3-ethyl-1,5-naphthyridin-2(1*H*)-one, m.p. 107–108°; λ_{max} 221 mμ (ε 37,000), 248 (5000), 330 (13,000), 343 (9400); in acid, 219 (25,000), 262 (5900), 343 (16,500), 355 (15,900).

Anal. Calcd. for $C_{11}H_{12}N_2O$: C, 70.2; H, 6.4; N, 14.9. Found: C, 70.3; H, 6.4; N, 14.8.

Determination of pK_a values was carried out by partitioning the base between an organic solvent (hexane or ether) and aqueous phosphate buffer at various pH values. Concentrations were determined spectrophotometrically, and the pK_a values were calculated from the equation

$$\frac{P}{P'} = 1 + \frac{(H^+)}{K_a}$$

where P is the true partition coefficient and P' is the apparent partition coefficient at the specific pH.

New Heteroaromatic Compounds. XVII.[1] Fluoro Derivatives of 10-Methyl-10,9-borazarophenanthrene[2]

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Four monofluoro derivatives of 10-methyl-10,9-borazarophenanthrene have been synthesized in the hope that their fluorine n.m.r. chemical shifts may provide information concerning the π-electron distribution. In the course of this work a number of new derivatives of biphenyl have been prepared.

The chemical shifts shown by the fluorine nuclear magnetic resonance in derivatives of fluorobenzene seem to reflect the π-electron density of the ring atom adjacent to fluorine.[3] It occurred to us that the corresponding chemical shifts in monofluoro derivatives of heteroaromatic systems might be used to prepare π-electron density maps of the rings and so used to check the predictions of current MO treatments.

One particularly interesting system from this point of view is 10,9-borazarophenanthrene,[4] and, therefore, we decided to synthesize as many as possible of its eight monofluoro derivatives. For convenience we included a methyl substituent in the 10-position since the parent compounds, being in effect boron hydrides, tend to oxidize rather easily in air. Unfortunately these compounds proved unexpectedly recalcitrant and we were able to obtain only four of the isomers, with fluorine in the 2-, 3-, 6-, and 7-positions.

The fluorine n.m.r. spectra of these compounds, together with those of a number of other fluoro derivatives of various aromatic systems, will be reported elsewhere and discussed. Here we describe the synthesis of the four fluoroborazarophenanthrenes, and of various new derivatives of biphenyl which we obtained as intermediates.

In order to obtain the various fluoroborazarophenanthrenes, we needed[4] the corresponding fluoro derivatives of 2-aminobiphenyl, and the most obvious route

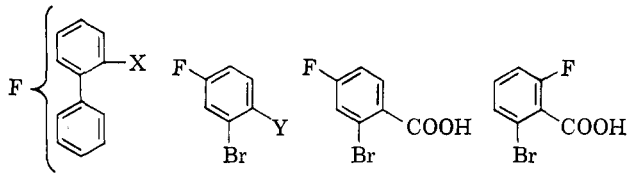
(1) Part XVI, M. J. S. Dewar, C. Kaneko, and M. K. Bhattacharjee, *J. Am. Chem. Soc.*, **84**, 4884 (1962).

(2) This work was supported by a grant (G-346) from the Office of Ordnance Research.

(3) *Cf.* R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959).

(4) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

to them involved reduction of the corresponding nitro compounds. Only three of the isomeric fluoro-2-nitrobiphenyls had been previously reported. Van Hove[5] isolated 4- and 4′-fluoro-2-nitrobiphenyl by fractional crystallization of the nitration product from 4-fluorobiphenyl and 2-fluoro-2′-nitrobiphenyl has also been described.[6] We now have prepared these and the remaining fluoro-2-nitrobiphenyls (I) (except the 3-fluoro isomer) by improved routes. The 2-, 3-, and 4-fluoro-2′-nitrobiphenyls were made by Ullmann condensations from the corresponding fluoroiodobenzene and *o*-bromonitrobenzene, and 4- and 5-fluoro-2-nitrobiphenyl by a similar reaction from iodobenzene and the corresponding fluoro-2-bromonitrobenzene; 2-bromo-4-fluoronitrobenzene (IIa), which had not been described previously, was obtained by nitration of *m*-fluorobromobenzene and characterized by reduction and acetylation to 2-bromo-4-fluoroacetanilide (IIb). The remaining isomer, 2-fluoro-6-nitrobiphenyl, was prepared from 2,6-dinitrobiphenyl by partial reduction to 2-amino-6-nitrobiphenyl followed by a Schiemann reaction.



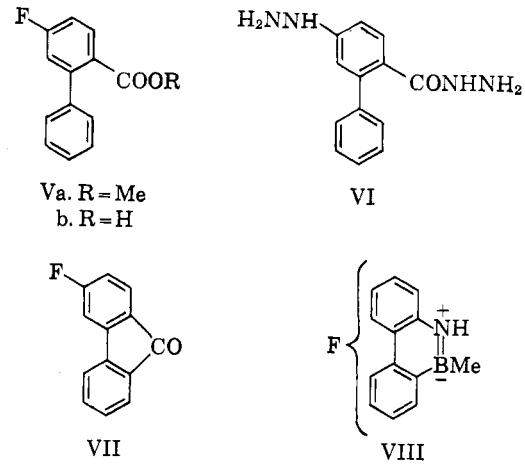
Ia. X = NO_2 IIa. Y = NO_2 III IV
b. X = NH_2 b. Y = NHAc

The nitro compounds were reduced to the corresponding aminofluorobiphenyls by the method of Marler and Turner.[7] Only the 2-amino-2′-fluoro[6] and 2-amino-4′-fluoro[5] isomers had been reported previously. The amines were characterized by their acetyl derivatives.

An alternative route to these amines would have involved replacement of the carboxyl group in a fluorobiphenyl-2-carboxylic acid by amino. We accordingly prepared 2-bromo-4-fluorobenzoic acid (III) by oxidation of 2-bromo-4-fluorotoluene, and 2-fluoro-6-bromobenzoic acid (IV) by oxidation of 2-fluoro-6-bromobenzyl bromide, itself prepared by bromination of 2-fluoro-6-bromotoluene. The methyl ester of III condensed with iodobenzene in presence of copper to give methyl 5-fluorobiphenyl-2-carboxylate (Va), but all attempts to convert this to the corresponding aminofluorobiphenyl by well established methods[8] failed. Thus Va on boiling with hydrazine hydrate gave the hydrazinobiphenylcarbohydrazide (VI). Similar replacement of fluorine by hydrazine in analogous compounds has been noticed by Dewar and Marr.[9]

Attempts to replace the carboxyl group in the corresponding acid (Vb) by amino *via* a Schmidt reaction also failed since the acid underwent cyclization in concentrated sulfuric acid to 3-fluorofluorenone (VII).

The conversion of fluoro-2-aminobiphenyls to the corresponding fluoro - 10 - methyl - 10,9 - borazarophenanthrenes was carried out by the method of Dewar, Kubba, and Pettit.[4] In this way the 2-, 6-, and 7-fluoro derivatives (VIII) were obtained. Similar treatment of 2-amino-3′-fluorobiphenyl gave a single product which must surely have been the 3-isomer; for the Friedel–Crafts ring closure is an electrophilic process and for such processes fluorine is very strongly *para*-directing.



Va. R = Me VI
b. R = H

VII VIII

Numerous attempts to cyclize 2-amino-2′-fluorobiphenyl to a 4-fluoroborazarophenanthrene failed, presumably because of steric hindrance to coplanarity in the biphenyl. The failure cannot be ascribed merely to the deactivating effect of fluorine *meta* to the point of ring closure since we encountered no difficulty in cyclizing 2-amino-4′-fluorobiphenyl to a product where the fluorine is also *meta* to boron.

The fluoro - 10 - methyl - 10,9 - borazarophenanthrenes were as stable as the parent compound, except for the 3-isomer; this darkened slowly on exposure to air.

Experimental

2-Bromo-4-fluoronitrobenzene.—Fuming nitric acid (80 g., *d* 1.5) was added slowly to a mixture of *m*-bromofluorobenzene (200 g.) and concentrated sulfuric acid (400 ml.), shaken vigorously at 30–35°. The mixture was then poured on ice, extracted with dichloromethane, and the organic layer dried and distilled. **2-Bromo-4-fluoronitrobenzene** was collected at 70–75° (0.4 mm.) as a yellow oil (75 g., 30%), $n^{25}D$ 1.5710, which crystallized on standing, m.p. 42°, not raised by recrystallization from petroleum ether.

Anal. Calcd. for $C_6H_3BrFNO_2$: C, 32.7; H, 1.36; N, 6.35. Found: C, 32.6; H, 1.29; N, 6.23.

Reduction and acetylation gave 2-bromo-4-fluoroacetanilide, identical (mixture melting point) with a sample prepared by bromination of *p*-fluoroacetanilide (see following text).

2-Bromo-4-fluoroacetanilide.—A solution of bromine (3.1 g.) in acetic acid (10 ml.) was added dropwise to one of *p*-fluoroacetanilide (10 g.) in acetic acid (50 ml.) at 60°. After 1 hr. the mixture was poured into water. The precipitate of **2-bromo-4-fluoroacetanilide** crystallized from aqueous ethanol in colorless needles (14.1 g., 94%), m.p. 119–120°.

Anal. Calcd. for C_8H_7BrFNO: C, 41.4; H, 3.02; N, 6.09. Found: C, 41.8; H, 3.31; N, 6.07.

2-Bromo-4-fluorotoluene.—A solution of sodium nitrite (55 g.) in water (200 ml.) was added slowly at 0.5° to 4-amino-2-bromotoluene[10] (124 g.) dissolved in concentrated hydrochloric acid (200 ml.) and water (200 ml.). The corresponding diazonium fluoborate, precipitated by adding excess fluoboric acid, was dried and decomposed by heating over a naked flame. The crude distillate was dissolved in ether, washed with dilute hydrochloric acid, water, dilute sodium hydroxide, then again with water, dried, and distilled. **2-Bromo-4-fluorotoluene** was collected at 170–172° as a colorless liquid (82 g., 67%), $n^{25}D$ 1.5265.

Anal. Calcd. for C_7H_6BrF: C, 44.5; H, 3.17. Found: C, 44.4; H, 3.21.

(5) T. Van Hove, *Bull. soc. chim. Belges*, **32**, 52 (1953).
(6) A. Roe and H. L. Fleishman, *J. Am. Chem. Soc.*, **69**, 509 (1947).
(7) E. E. J. Marler and E. E. Turner, *J. Chem. Soc.*, 1362 (1931).
(8) R. Labriola, *J. Org. Chem.*, **5**, 329 (1950); K. G. Rutherford and M. S. Newman, *J. Am. Chem. Soc.*, **79**, 213 (1957).
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(10) R. H. Nevile and A. Winther, *Ber.*, **14**, 417 (1881).

TABLE I

YIELDS AND PHYSICAL DATA FOR THE AMINOFLUOROBIPHENYLS

Amine	M.p. or b.p., °C.	Lit. m.p. or b.p. °C.	Calcd. C	Calcd. H	Found C	Found H	Yield, %
2-Amino-4-fluorobiphenyl	102–105 (0.2 mm.)	...	77.0	5.35	77.4	5.62	59
2-Amino-5-fluorobiphenyl	92–96 (0.1 mm.)	...	77.0	5.35	77.3	5.22	48
2-Amino-6-fluorobiphenyl	52–55	...	77.0	5.35	See acetyl derivative		30
2-Amino-2′-fluorobiphenyl	91.5–92	91[a]	77.0	5.35	Well characterized		72
2-Amino-3′-fluorobiphenyl	106–110 (0.5 mm.)	...	77.0	5.35	77.0	5.42	53
2-Amino-4′-fluorobiphenyl	42–43	42–42.5[b]	77.0	5.35	Well characterized		68

[a] Ref. 5. [b] Ref. 4.

TABLE II

PHYSICAL DATA FOR THE ACETYLAMINOFLUOROBIPHENYLS

Compound	M.p., °C.	Lit. m.p., °C.	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
2-Acetylamino-4-fluorobiphenyl	90–91°	98[a]	73.4	5.24	6.12	72.9	5.23	6.42
2-Acetylamino-5-fluorobiphenyl	136–137	...	73.4	5.24	6.12	73.6	5.16	6.31
2-Acetylamino-6-fluorobiphenyl	102–103	...	73.4	5.24	6.12	73.7	5.40	6.10
2-Acetylamino-2′-fluorobiphenyl	103–104	102[b]	73.4	5.24	6.12	Well characterized		
2-Acetylamino-3′-fluorobiphenyl	102–103	...	73.4	5.24	6.12	73.5	5.16	6.50
2-Acetylamino-4′-fluorobiphenyl	125	120[a]	73.4	5.24	6.12	73.4	5.40	6.10

[a] Ref. 6. [b] Ref. 7.

TABLE III

DATA FOR THE PREPARATION OF THE FLUORO-10-METHYL-10,9-BORAZAROPHENANTHRENES

Yield, %	Position of F	M.p., °C.	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
33	2	80–81	74.0	5.21	6.64	74.0	5.21	6.35
12	3	52–55	74.0	5.21	6.64	73.7	5.20	...
28	6	54–55	74.0	5.21	6.64	73.9	5.41	6.72
52	7	89–90	74.0	5.21	6.64	73.6	5.38	6.41

2-Bromo-6-fluorotoluene.—Prepared likewise from 2-amino-6-bromotoluene,[11] **2-bromo-6-fluorotoluene** was obtained in 58% yield, b.p. 177–180°, $n^{25}D$ 1.5305.

Anal. Found: C, 44.5; H, 3.36.

2-Bromo-4-fluorobenzoic Acid.—Oxygen was bubbled through a boiling solution of 2-bromo-4-fluorotoluene (148 g.) and cobaltic acetate (0.05 mole) in acetic acid (500 ml.) until a permanent green color appeared. After half the solvent had been distilled, the residue was poured into dilute hydrochloric acid and the **2-bromo-4-fluorobenzoic acid** then collected, washed, and dried. The crude acid (140 g., 82%) had m.p. 168–171°, raised by recrystallization from dilute ethanol to 171–172.5°.

Anal. Calcd. for $C_7H_4BrFO_2$: C, 38.4; H, 1.83. Found: C, 38.6; H, 2.1.

Methyl 2-Bromo-4-fluorobenzoate.—Crude 2-bromo-4-fluorobenzoic acid was esterified by the Fischer Speier method and the **methyl ester** (125 g., 87%) isolated by distillation, b.p. 122° (10 mm.), $n^{25}D$ 1.5372.

Anal. Calcd. for $C_8H_6BrFO_2$: C, 41.2; H, 2.58. Found: C, 40.9; H, 2.46.

2-Bromo-6-fluorobenzyl Bromide.—2-Bromo-6-fluorotoluene (30 g.) in carbon tetrachloride (250 ml.) was heated under reflux for 4 hr. with N-bromosuccinimide (5–8 g.) and a trace of benzoyl peroxide. The solution was cooled, filtered, and the filtrate freed from solvent by distillation. Distillation of the residue gave the pure **benzyl bromide** (29.4 g., 69%), b.p. 128–131 (25 mm.), $n^{25}D$ 1.5912.

Anal. Calcd. for $C_7H_5Br_2F$: C, 31.3; H, 1.87. Found: C, 31.7; H, 2.09.

2-Bromo-6-fluorobenzoic Acid.—2-Bromo-6-fluorobenzyl bromide (10 g.) was heated overnight under reflux with potassium permanganate (20 g.) in water (100 ml.). After cooling, the solution was decolorized with sulfur dioxide and the precipitated *acid* (6.1 g., 74%) filtered, washed, and dried. A sample crystallized from dilute ethanol in white needles, m.p. 155°.

Anal. Calcd. for $C_7H_4BrFO_2$: C, 38.4; H, 1.83. Found: C, 38.8; H, 2.14.

Synthesis of the Biphenyls.—A mixture containing equimolecular quantities of the two halides used in the biphenyl synthesis was heated to 120° and vigorously stirred while copper powder (3 g.-atoms) (Venus National Copper, U. S. Bronze Powder Works) was added over 20 min. The mixture was held at 120° for 20 hr., then cooled, extracted several times with dichloromethane, and the filtered solution evaporated to yield the crude product. The following compounds were prepared by this general method.

2′-Fluoro-2-nitrobiphenyl was prepared from 2-bromonitrobenzene (82 g.), 2-fluoroiodobenzene (90 g.), and copper powder (77 g.). Chromatography of the crude mixture on alumina (Merck) with petroleum ether (b.p. 60–68°) and dichloromethane (gradient elution) gave a major very pale yellow band after a colorless forerun containing some difluorobiphenyl. Evaporation of the eluent containing the major band gave 2′-fluoro-2-nitrobiphenyl which crystallized from petroleum ether (b.p. 30–35°) in pale yellow prisms (53 g., 57%), m.p. 72.5–73°, (lit.[8] m.p. 71–72°).

3′-Fluoro-2-nitrobiphenyl was prepared from 2-bromonitrobenzene (13.3 g.), 3-iodofluorobenzene (14.7 g.), and copper powder (12.5 g.). Distillation of the crude product gave the partially purified biphenyl derivative, b.p. 95–9 8°(0.05 mm.) (7.6 g.). Chromatography as described previously yielded pure **3′fluoro-2-nitrobiphenyl** which crystallized from petroleum ether (b.p. 30–35°) in pale yellow needles (6.5 g., 45%), m.p. 47.5–48°.

Anal. Calcd. for $C_{12}H_8FNO_2$: C, 66.5; H, 3.69; N, 6.45. Found: C, 66.3; H, 3.79; N, 6.84.

4′-Fluoro-2-nitrobiphenyl was prepared from 2-bromonitrobenzene (11 g.), 4-fluoroiodobenzene (12 g.), and copper powder (10.3 g.). Distillation and chromatography as before gave pure 4′-fluoro-2-nitrobiphenyl, b.p. 90–92° (0.05 mm.), which crystallized from petroleum ether (b.p. 30–35°) in very pale yellow needles (3.1 g., 36%), m.p. 60–60.5° (lit.[5] m.p. 59–60°).

4-Fluoro-2-nitrobiphenyl was prepared from 2-bromo-5-fluoronitrobenzene[12] (32 g.), iodobenzene (33 g.), and copper powder (28 g.). Distillation and chromatography gave pure 4-fluoro-2-nitrobiphenyl, b.p. 108–110° (0.05 mm.), which crystallized from petroleum ether (b.p. 30–35°) in pale yellow prisms (13.6 g., 43%), m.p. 72.5–74° (lit. m.p. 53–54°).

Anal. Calcd. for $C_{12}H_8FNO_2$: C, 66.5; H, 3.69; N, 6.45. Found: C, 66.2; H, 4.06; N, 6.75.

5-Fluoro-2-nitrobiphenyl was prepared from 2-bromo-4-fluoronitrobenzene (50 g.), iodobenzene (51 g.), and copper powder (43 g.). Distillation gave **5-fluoro-2-nitrobiphenyl** as a liquid (28.9 g., 58.5%), b.p. 114–118° (0.6 mm.), $n^{24}D$ 1.5954.

Anal. Calcd. for $C_{12}H_8FNO_2$: C, 66.5; H, 3.69; N, 6.45. Found: C, 66.1; H, 3.89; N, 6.70.

(11) E. Noelting, *Ber.*, **37**, 1015 (1904).

(12) E. Berliner and K. C. Monack, *J. Am. Chem. Soc.*, **74**, 1574 (1954).

5-Fluoro-2-methoxycarbonylbiphenyl.—Prepared from methyl 2-bromo-4-fluorobenzoate (103 g.), iodobenzene (91 g.), and copper powder (82 g.), **5-fluoro-2-methoxycarbonylbiphenyl** was collected at 110–118° (0.2 mm.), and redistilled (53 g., 52%), b.p. 108–110° (0.1 mm.), $n^{25}D$ 1.5662. Vapor phase chromatography analysis showed only one peak.

Anal. Calcd. for $C_{14}H_{11}FO_2$: C, 73.0; H, 4.79. Found: C, 73.1; H, 5.10.

2-Amino-6-nitrobiphenyl.—2,6-Dinitrobiphenyl[13] (24 g.) in ethanol (350 ml.) was boiled under reflux for 3 hr. during the addition of a solution of sodium sulfide (28 g.) and sulfur (6.9 g.) in water (85 ml.). The ethanol was mostly removed by distillation and the product poured into water and isolated with dichloromethane. Three recrystallizations from dilute ethanol gave **2-amino-6-nitrobiphenyl** as yellow needles (7.5 g., 35.5%), m.p. 74–75°.

Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.3; H, 4.67. Found: C, 67.5; H, 4.99.

2-Fluoro-6-nitrobiphenyl.—2-Amino-6-fluorobiphenyl (6 g.) in concentrated hydrochloric acid (30 ml.) and water (30 ml.) was diazotized at 0.5°. Fluoboric acid (60 ml.) was added and the diazonium fluoborate filtered, washed with cold methanol and ether, and dried overnight in a vacuum desiccator. The solid was decomposed by heat and the residue extracted with petroleum ether (b.p. 30–35°, six 50-ml. portions). Evaporation of this ether gave an oil which solidified on scratching. Recrystallization from petroleum ether (b.p. 30–35°) gave pure **2-fluoro-6-nitrobiphenyl** as very pale yellow needles (3.5 g., 60%), m.p. 67–68°.

Anal. Calcd. for $C_{12}H_8FNO_2$: C, 66.5; H, 3.69; N, 6.45. Found: C, 66.7; H, 3.99; N, 6.82.

2-Carboxy-5-fluorobiphenyl.—A mixture of the methyl ester of 5-fluorobiphenylcarboxylic acid (2.1 g.), sodium hydroxide (10 ml. of 1 *N*), and ethanol (20 ml.) was kept overnight at 40° and then acidified. The **2-carboxy-5-fluorobiphenyl** was isolated with ether and then crystallized from petroleum ether (b.p. 60–68°) in white needles (1.5 g., 76%), m.p. 110°.

Anal. Calcd. for $C_{13}H_9FO_2$: C, 72.2; H, 4.17. Found: C, 72.0; H, 4.47.

3-Fluorofluorenone.—2-Carboxy-5-fluorobiphenyl (0.5 g.) was allowed to stand in concentrated sulfuric acid (10 ml.) at room temperature for 1 hr. The solution turned deep violet. Pouring into water gave an almost theoretical yield of **3-fluorofluorenone** which crystallized from petroleum ether (b.p. 90–100°)–benzene in yellow needles, m.p. 129–130°.

Anal. Calcd. for $C_{13}H_7FO$: C, 78.8; H, 3.54. Found: C, 79.0; H, 4.00.

5-Hydrazinobiphenyl-2-carboxylic Acid Hydrazide.—2-Carboxy-5-fluorobiphenyl (1 g.) and hydrazine (1 g.) were treated under reflux overnight. Addition of ethanol gave an almost theoretical yield of the **hydrazide** which crystallized from ethanol in cream-colored plates, m.p. 140°.

Anal. Calcd. for $C_{13}H_{14}N_4O$: C, 64.5; H, 5.78; N, 23.2. Found: C, 64.6; H, 6.18; N, 22.9.

Reductions of the Fluoronitrobiphenyls to the Corresponding Amines.—The reductions of the fluoronitrobiphenyls to the corresponding amines were carried out using the method of Marler and Turner.[6] The amines were characterized as their acetyl derivatives. 2-Amino-6-fluorobiphenyl had been characterized previously only by its acetyl derivative. The yields, melting points, and analysis data are shown in Tables I and II.

Synthesis of the Fluoro-10-methyl-10,9-borazarophenanthrenes.—The method of Dewar, Kubba, and Pettit[4] was used to prepare the boron–nitrogen heterocycles. The 10-methyl group was introduced by the action of methylmagnesium iodide on the fluoro-10-chloro-10,9-borazarophenanthrenes. The crude methyl compounds were purified by chromatography on alumina (Merck) with petroleum ether (b.p. 30–35°) as eluent. Sublimation and one or more crystallizations from petroleum ether (b.p. 30–35°) gave the pure compounds. The yields in Table III refer to analytical samples.

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The Reaction of Trimethyl Thioborate with Diazoalkanes[1]

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The interaction of trimethyl thioborate with several diazoalkanes has been studied. Trimethyl thioborate and diazomethane leads only to polymethylene; trimethyl thioborate reacts with phenyldiazomethane to give methyl benzyl sulfide and *trans*-stilbene; trimethyl thioborate reacts with ethyl diazoacetate to give ethyl S-methylmercaptoacetate and diethyl S-methylmercaptosuccinate; trimethyl thioborate reacts with phenylbenzoyldiazomethane to give methyl diphenylthioacetate. These several products are rationalized in terms of the alternate pathways illustrated in Fig. 1.

Numerous examples of the interaction of diazoalkanes, principally diazomethane, with inorganic compounds have been reported in the literature.[3] In some cases the inorganic compound undergoes methylenation with diazomethane as, for example, stannic chloride which reacts to form various chloromethyl derivatives; *e.g.*, $ClCH_2SnCl_3$.[4] In other cases the inorganic material acts as a polymerization catalyst as, for instance, the trialkylborons, the trialkyl borates, and the boron halides,[5] the main action on diazomethane being to form polymethylene.[6] The present work extends the list of boron compounds reactive toward diazo compounds to include trimethyl thioborate Although, in common with the boron compounds just mentioned, it induces polymerization of diazomethane, it reacts with substituted diazomethanes in several other ways, the nature of which depends upon the particular diazoalkane.

Trimethyl Thioborate and Diazomethane.—This reaction leads to the production of polymethylene, the catalytic action of trimethyl thioborate being rationalized in terms of pathway A–A_1 (see Fig. 1) according to a recent suggestion.[7] The tendency for the first-formed complex to react further with diazomethane rather than to undergo internal rearrangement must derive from the very great reactivity of the $-CH_2N_2^{\oplus}$ moiety. If groups hindering the intermolecular reaction with additional molecules of diazo compound are attached to the diazonium center, the reaction may then take

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