In a trial run omitting deuterated reagents, the material from the chloroform extract which failed to dissolve in warm water was thoroughly dried and shown by nmr spectroscopy to be mostly *N*-(4-bromobenzyl)isoquinolone (1.29 g, 78%).

B. 1-Deuterio Salt in Aqueous Alkaline Dioxane–Carbon Disulfide.—A stirred mixture of *N*-(4-bromobenzyl)-1-deuterioisoquinolinium bromide (93% d_1), 5.5 ml of water, 5.5 ml of dioxane, and 3.7 ml of carbon disulfide was heated to 72°, and 5.5 ml of 11 *N* sodium hydroxide was added in one portion. After 4 min, the reaction mixture was quenched in an ice bath with stirring, made just acidic at temperatures below 16° with concentrated sulfuric acid, and diluted with water (100 ml) and chloroform (50 ml). The aqueous layer was concentrated, the remaining water was removed with benzene as the azeotrope, and the dry salts obtained were extracted with chloroform. The isoquinolinium salt obtained from the chloroform extract (357 mg) had 60% hydrogen at C_1, according to nmr analysis.

Reactions of Deuterium Labeled *N*-(4-Bromobenzyl)isoquinolinium Bromides with Carbon Disulfide in Alkaline Aqueous Dioxane. A. *N*-(4-Bromobenzyl-α-d_2)isoquinolinium Bromide.—A 100-ml three-necked flask was charged with 2.00 g of this isoquinolinium salt, 5.5 ml of water, 5.5 ml of purified dioxane, and 3.7 ml of carbon disulfide. The mixture was stirred mechanically, heated, and diluted with 5.5 ml of 11 *N* sodium hydroxide; the red mixture obtained was stirred at 72° for 8 hr, cooled to room temperature with stirring, stored at −15° for 2 days, and filtered on a sintered glass funnel. The crude products were washed on the funnel with three 6-ml portions of warm water and dried in the air. The red solid obtained (1.07 g) was chromatographed in the usual way on 50 g of neutral Woelm II alumina. The yellow band was isolated and concentrated to give *N*-(4-bromo-α-d_2-benzyl)isoquinolone. No benzyl hydrogens were detected by nmr analysis. The dark material at the top of the column was extracted with hot *N*,*N*-dimethylformamide; concentration of the extract gave a dark red solid, mp 197–201°. Recrystallization of the solid from DMF–acetonitrile gave 100 mg of adduct, mp 202°, having a mass spectrum indicative of the α-d_2-benzyl moiety.

B. *N*-(4-Bromobenzyl)-1-deuterioisoquinolinium Bromide.—Following the given reaction procedure, 2.0 g of the isoquinolinium salt gave rise to 1.04 g of red solid. A slurry of the solid in chloroform was delivered to the top of a column of alumina, which was eluted with more chloroform. The residue in the sand at the top of the column was extracted with hot DMF. The red solid isolated, mp 190–260°, was extracted in a Soxhlet with chloroform for 23 hr. The residue in the thimble, 83 mg, mp 200–202°, was recrystallized to give a sample for mass spectrometric analysis, 52 mg of bright red crystals, mp 202–204°. Most, but not all, of the deuterium in the starting material had been lost (Table I).

C. *N*-(4-Bromobenzyl)-8-deuterioisoquinolinium Bromide.—The reaction of 208 mg of the isoquinolinium bromide was carried through in the normal manner. The crude product was extracted in a micro Soxhlet with 10 ml of chloroform for 16 hr. The residue from the thimble, 10.4 mg, mp 200°, was analyzed mass spectrometrically; the adduct retained the deuterium present in the starting material (Table I).

D. *N*-(4-Bromobenzyl)-4-deuterioisoquinolinium Bromide.—The crude product from 1.0 g of the isoquinolinium salt, amounting to 312 mg, was continuously extracted with chloroform for 22.5 hr. The residue was thoroughly dried; it had mp 198–205° and a mass spectrum showing no deuterium label (Table I).

Attempted Exchange in *N*-(4-Bromobenzyl)isoquinolinium 4-Dithiocarboxylate Adduct.—To 50 mg of the $C_{17}H_{12}BrNS_{12}$ adduct was added 5.5 ml each of deuterium oxide, dioxane, and 11 *N* sodium deuterioxide, and 3.7 ml of carbon disulfide. The stirred mixture was heated at 72° for 9.5 hr, cooled, and filtered to give 37 mg of starting material. Recrystallization from DMF–acetonitrile gave red crystals, mp 202–204°, having no deuterium incorporation detectable by mass spectrometric analysis.

Registry No.—1 H, 23277-04-5; 1 3-CH_3, 27415-57-2; 1 4-CH_3O, 27415-58-3; 1 3-NO_2, 27410-57-7; 1 3-Br, 27410-58-8; 1 4-Br, 27371-56-8; 2 3-F, 27371-57-9; 2 4-Cl, 27371-58-0; 2 4-Br, 27371-59-1; 2 H, 27371-60-4; 2 3-CH_3, 27371-61-5; 2 4-CH_3, 27371-62-6; 2 4-CN, 27410-59-9; 2 3-CH_3O, 27410-60-2; 2 4-CH_3O, 27410-61-3; 2 3-^{35}Cl, 27410-62-4; 2 3-NO_2, 27410-63-5; 2 4-NO_2, 27410-64-6; 2 3-CF_3, 27410-65-7; 2 3-^{79}Br, 27410-66-8; 2 4-^{79}Br, 27410-67-9; 4 3-F, 27410-68-0; 4 3-Cl, 27410-69-1; 4 3-Br, 27410-70-4; 4 H, 27371-63-7; 4 3-CH_3, 27371-64-8; 4 4-CH_3, 27410-71-5; 4 3-CH_3O, 27410-72-6; 4 4-CH_3O, 27410-73-7; 4 4-^{35}Cl, 27410-74-8; 4 3-CF_3, 27410-75-9; 4 3-^{79}Br, 27410-76-0; 4 4-^{79}Br, 27410-77-1; 4 3-^{81}Br, 27371-65-9; 4 4-^{81}Br, 27410-78-2; *N*-(4-bromobenzyl-α-d_2)isoquinolinium bromide, 27410-79-3; *N*-(4-bromobenzyl)-1-deuterioisoquinolinium bromide, 27410-80-6; *N*-(4-bromobenzyl)-4-deuterioisoquinolinium bromide, 27410-81-7; *N*-(4-bromobenzyl)-8-deuterioisoquinolinium bromide, 27410-82-8; carbon disulfide, 75-15-0.

Synthesis of Fluoroarenes by Photolysis of Aryldiazonium Salts in the Solid State[1a]

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Photolysis of crystalline aryldiazonium fluoroborates and fluorophosphates gives the corresponding fluoroarenes. In some cases yields are much better than those obtained by pyrolysis.

The photochemistry of aryldiazonium salts in the solid state seems to have been ignored except for one study[2] of gas evolution from slurries in which the organic products were not identified. As the first step in a mechanistic study of this phenomenon, the principal products formed upon irradiation of crystalline films of a number of aryldiazonium salts have been determined.

In the photolysis of diazonium tetrafluoroborates and hexafluorophosphates, the corresponding fluoroarenes were usually the only volatile product as in pyrolysis. In some cases the yields of fluoroarenes were higher than those obtained by pyrolysis of these salts (the Balz–Schiemann reaction), which remains the most generally used means of introducing a fluorine substituent into an aromatic ring.[3] The Balz–Schiemann reaction fails

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[1] (a) Part of this work has been described by R. C. P. and A. D. in U. S. Patent 3,481,850 (1969); (b) Fellow of the Cancer Association of Greater New Orleans, Inc., summer 1966; (c) National Science Foundation Undergraduate Research Participant; (d) taken in part from the B.S. Thesis of J. P. Mykytka, Loyola University, New Orleans, 1968.

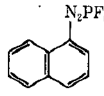
[2] G. Gavlin, "Increased Light-Sensitivity of a Diazotype Substance," Report of Armour Project No. 90-595C, Armour Research Institute, Department of Army Project, 3-99-04-052.

[3] K. O. Christe and A. E. Pavlath, *J. Org. Chem.*, **30**, 3170 (1965).

TABLE I

PHOTOLYSIS OF SOLID ARYLDIAZONIUM FLUOROBORATES AND FLUOROPHOSPHATES

$$RN_2{}^+BF_4{}^-(PF_6{}^-) \xrightarrow{h\nu} RF + N_2 + BF_3(PF_5)$$

Diazonium compd	Registry no.	Light source	Scale, g	Time, hr	Yield of RF, %
4-$(C_2H_5)_2NC_6H_4N_2BF_4$	347-46-6	3500 Å	1	4.5–49	53–55
			10	39	66
4-$(C_2H_5)_2NC_6H_4N_2PF_6$	733-51-7	3500 Å	1	4	72
			10	94	74
4-$(CH_3)_2NC_6H_4N_2BF_4$	24564-52-1	3500 Å	2	17	55
4-$CH_3OC_6H_4N_2BF_4$	18424-07-2	3500 Å	1	19	69[a]
4-$C_6H_5NHC_6H_4N_2BF_4$	2367-19-3	3500 Å	0.6	24	37
$C_6H_5N_2BF_4$	369-57-3	3000 Å	0.5	2	34
		Uviarc	0.5	48	25
4-$ClC_6H_4N_2BF_4$	673-41-6	Uviarc[b]	0.1	8	10[a]
3-$C_6H_5C_6H_4N_2BF_4$	323-96-6	3500 Å	0.1	2	29
	27388-25-6	3500 Å	1	12	40
	27388-19-8	3500 Å	1	54	19

[a] Product distilled as formed. [b] Quartz vessel.

completely or gives low yields occasionally. We have made a preliminary investigation of the generality and utility of the photolytic variation for small scale synthesis of fluoroarenes, the results of which are summarized in Table I. The best results by far were in making fluorobenzenes with electron-donating substituents, particularly three N-substituted fluoroanilines.

Pure 4-fluorodiphenylamine was isolated in 37% yield on the first attempt when the corresponding diazonium fluoroborate was irradiated as a solid film at 30° with 3500-Å light, although pyrolysis of this salt has been reported[4] to give only a "carbonaceous mass."

Schiemann and Winkelmüller[5] converted *p*-*N*,*N*-dimethylaminobenzenediazonium fluoroborate to 4-fluoro-*N*,*N*-dimethylaniline by heating in only 17% yield, and later workers[6] have preferred other methods for preparing the compound. By pyrolyzing a mixture of the diazonium salt with sand we improved the yield to 36%, but photolysis gave a 56% yield. Both methods also produced a small amount of the reduction product, *N*,*N*-dimethylaniline.

The synthesis of 4-fluoro-*N*,*N*-diethylaniline was studied more extensively. Pyrolysis of the corresponding diazonium fluoroborate gave a poor yield (20%) of the fluoro amine in agreement with Schiemann's report.[5] Worse, the ir spectrum of the product indicated that a significant amount of reduction product had been formed. The fluoro compound was produced by photolysis of 1 g of the fluoroborate in higher yield (55%) and, surprisingly, was uncontaminated by *N*,*N*-diethylaniline. On a 10-g scale the yield was better (66%). We have not tried any of these reactions on a scale over 10 g.

Hexafluorophosphates sometimes give better yields than tetrafluoroborates in the Balz–Schiemann reaction.[7] This is also true for the photoreaction, at least for the preparation of 4-fluoro-*N*,*N*-diethylaniline, the yields being over 70% on both a 1-g and a 10-g scale. The photolysis method is the method of choice in this case for reasons of both purity and yield.

With 4-methoxybenzenediazonium fluoroborate a new complication arose: the product is somewhat unstable to the 3500-Å light used for photolysis. The yield of 4-fluoroanisole was only 6% using the normal photolysis method. However, by vacuum distilling the product into a cold trap as it formed the yield was raised to 69%. 4-Fluorochlorobenzene was also unstable to the light used and had to be removed in the same way.

Photolysis of aryldiazonium salts substituted with electron-withdrawing groups gave much lower yields of fluoroarenes, perhaps because with the light sources available the products absorbed light about as well as the starting material and competing reactions destroyed them.

An ionic intermediate or transition state of some sort appears to be implicated in the photolysis of solid aryldiazonium fluoroborates and fluorophosphates. If aryl radicals were intermediates, they would be expected to abstract hydrogen atoms from other molecules of starting material, especially when side chains with alkyl groups are present. However, little or no reduction product was produced in the photolysis of even the dimethyl- and diethylamino compounds. In contrast, when crystalline *N*,*N*-dimethylaminobenzenediazonium *chloride* was irradiated, reduction to *N*,*N*-dimethylaniline (25%) competed strongly with conversion to 4-chloro-*N*,*N*-dimethylaniline (33%).

These observations are in accord with the results of studies of isomer distribution in the phenylation products formed when solid benzenediazonium chloride and various haloborates are pyrolyzed[8] or photolyzed[9] in the presence of substituted benzenes. The solid chlorides react as if they possessed the covalent structure ArN=NCl and lose nitrogen to give radicals, although their

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(4) J. Lichtenberger and R. Thermet, *Bull. Soc. Chim. Fr.*, 318 (1951).

(5) G. Schiemann and W. Winkelmüller, *Ber.*, **66**, 727 (1933).

(6) N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, **70**, 1564 (1948).

(7) K. G. Rutherford, W. Redmond, and J. Rigamonti, *J. Org. Chem.*, **26**, 5149 (1961).

(8) G. A. Olah and W. S. Tolgyesi, *ibid.*, **26**, 2053 (1961); R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc. B*, 497 (1968).

(9) R. C. Petterson and J. P. Mykytka, unpublished work.

ir and uv spectra are very much like those of other aryldiazonium ions.

The lack of parallelism between fluoroarene yields for photolysis *vs.* pyrolysis makes it unlikely that these reactions proceed exclusively through a common intermediate. Lewis and his coworkers[10] compared photochemical with thermal reactions of diazonium salts in aqueous solution and concluded definitely that there was no single intermediate common to both.

Experimental Section

Starting Materials.—Aryldiazonium fluoroborates were generally prepared by diazotizing the corresponding amines in fluoboric acid.[11] 4-*N*,*N*-Dialkylaminobenzenediazonium fluoroborates were purchased,[12] and the 4-chloro- and 4-phenylamino compounds were made by reaction of 48% fluoboric acid with the corresponding diazonium chlorides which happened to be available from another study.

4-*N*,*N*-Diethylaminobenzenediazonium Fluorophosphate.—To 20 g of the commercial fluoroborate in water (700 ml) was added 35 ml of 65% hexafluorophosphoric acid. The yellow crystals which formed were filtered off, washed with a 1:1 methanol–ether solution, and dried *in vacuo*. The fluorophosphate (22.6 g) melted at 129.5–130.5°.

Anal. Calcd for $C_{10}H_{14}F_6N_3P$: C, 37.40; H, 4.39; F, 35.50; N, 13.09; P, 9.65. Found: C, 37.75; H, 4.11; F, 35.40; N, 13.20; P, 9.71.

8-Quinolinediazonium fluoroborate was prepared but not characterized by Roe and Hawkins.[13] It melts at 138° dec and is converted by irradiation to 8-fluoroquinoline (see Table I), the picrate of which melted at 170° (lit.[13] 170–172°).

Anal. Calcd for $C_9H_6BF_4N_3$: C, 44.71; H, 2.48. Found: C, 44.92; H, 2.70.

4-*N*,*N*-Dimethylaminobenzenediazonium chloride was prepared from 4-*N*,*N*-dimethylaminoaniline monohydrochloride (1.7 g) by reaction with isoamyl nitrite (1.4 g) in absolute ethanol (8 ml) at 0°, a variation of Knoevenagl's method.[14] After recrystallization from an ethanol–ether mixture, the melting point was 210° (slow dec above 135°): ν_{max}^{Nujol} 2152, 2240 cm^{-1}; ($-N^+\equiv N$) $\lambda_{max}^{H_2O}$ 375 nm (log ϵ 4.52).

Anal. Calcd for $C_8H_{10}ClN_3$: N, 22.88. Found: N, 23.01.

The zinc chloride double salt was yellow, mp 151° dec, $\lambda_{max}^{H_2O}$ 375 nm (log ϵ 4.53).

Anal. Calcd for $C_8H_{10}ClN_3 \cdot {}^1/_2ZnCl_2$: C, 38.14; H, 3.97; Cl, 28.2. Found: C, 38.33; H, 3.95; Cl, 27.85.

Methods.—Diazonium salts were irradiated as crystalline films on the inner surfaces of borosilicate glass test tubes or round-bottomed flasks of 50 ml to 3 l. capacity, except for the 4-chloro compound, which was irradiated in a quartz tube. The films were deposited by evaporation of solutions of the salts in acetonitrile or methanol at room temperature or below using a rotary evaporator. Most irradiations were done in a Rayonet photochemical chamber reactor (So. New England Ultraviolet Co.) equipped with 16 8-W F8T5/BLB lamps (3500 Å) or RPR 3000 "erythemal" lamps. In two experiments (see Table I), we used a 500-W high-pressure mercury lamp (General Electric "Uviarc") mounted in a reflector, similar to a Gates Model 420-U1.

Except for 4-fluoroanisole and 4-chlorofluorobenzene, which were produced at a pressure of 1 Torr in a tube connected to a dark trap cooled to −78°, into which they distilled as they formed, the products were isolated by conventional extractive techniques. In most cases, it was advantageous to first make the reaction mixture basic and then steam distil the fluoro compound. The products were identified by comparing their ir spectra and glc retention times with those of authentic specimens, which were either available commercially or were made by the Balz–Schiemann method.

Crystalline 4-*N*,*N*-dimethylaminobenzenediazonium chloride (0.5 g) was irradiated (3500 Å) for 7 hr in a 50-ml Pyrex test tube. Base was added and the organic products extracted with ether. Glc analysis of the concentrated extracts with an internal standard showed that the yield of 4-chloro-*N*,*N*-dimethylaniline was 33% and that of *N*-*N*-dimethylaniline was about 25%.

Registry No.—4-*N*,*N*-Dimethylaminobenzenediazonium chloride, 100-04-9, 6023-44-5 (zinc chloride salt).

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