TABLE I
N-POLYFLUOROACYLAMINO DERIVATIVES

Compound	M.P., °C	Cryst. Solvent	Empirical Formula	Analyses Carbon Calc'd	Analyses Carbon Found	Analyses Hydrogen Calc'd	Analyses Hydrogen Found
2-Dfa[a] dibenzofuran	170–171	Heptane	$C_{14}H_9F_2NO_2$	64.4	64.2	3.44	3.50
2-Dfa fluorene	162–162.5	Heptane	$C_{15}H_{11}F_2NO$	69.5	69.4	4.25	4.36
2-Dfa-7-nitrofluorene	232–233	Xylene	$C_{15}H_{10}F_2N_2O_3$[b]				
2-Ppa[c] biphenyl	89–90	Hexane	$C_{15}H_{10}F_5NO$	57.1	57.0	3.17	3.31
2-Ppa fluorene	196–197	Benzene	$C_{16}H_{10}F_5NO$	58.7	58.7	3.05	3.00
2-Ppa dibenzofuran	184–185	Heptane	$C_{15}H_8F_5NO_2$	54.7	54.8	2.43	2.55
2-Ppa-9-fluorenone	240–241	Benzene	$C_{16}H_8F_5NO_2$	56.3	56.4	2.34	2.28
2-Ppa-7-acetylfluorene	215–216	Methanol	$C_{18}H_{12}F_5NO_2$	58.5	58.4	3.25	3.39
2-Ppa-7-nitrofluorene	220–221	Methanol	$C_{16}H_9F_5N_2O_3$	51.6	51.7	2.43	2.47
2-Pba[d] fluorene	190–191	Benzene	$C_{17}H_{10}F_7NO$	54.1	54.2	2.65	2.71
2-Pba biphenyl	93–94	Aq. Methanol	$C_{16}H_{10}F_7NO$	52.6	52.7	2.74	2.88
2-Pba dibenzofuran	178–179	Hexane	$C_{16}H_8F_7NO_2$	50.7	50.8	2.11	2.24
2-Pba naphthalene	122–123	Hexane	$C_{14}H_8F_7NO$	49.6	49.8	2.36	2.68
2-Pba-7-nitrofluorene	206	Xylene	$C_{17}H_9F_7N_2O_3$[e]	48.3	48.6	2.13	2.30

[a] Dfa = Difluoroacetylamino. [b] *Anal.* Calc'd: N, 9.21. Found: N, 9.11. [c] Ppa = Perfluoropropionylamino. [d] Pba = *n* Perfluorobutyrylamino. [e] *Anal.* Calc'd: N, 6.63. Found: N, 6.40.

Polyfluoroacyl Derivatives of Carcinogenic and Allied Amines[1]

EUGENE SAWICKI

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In connection with a study of the physical properties of carcinogenic amines a number of difluoroacetyl, perfluoropropionyl, and perfluorobutyryl derivatives of carcinogenic and related amines have been synthesized, Table I. The study of the effect of fluoroacyl groups on the physiological properties of various types of biologically useful amines should prove of value.

EXPERIMENTAL[2]

Difluoroacetic anhydride. A mixture of 10.5 g. of difluoroacetic acid[3] and 7.8 g. of phosphorus pentoxide was refluxed for 2–3 hours, 2 g. of phosphorus pentoxide was added, and then the mixture was distilled. The yield of product, b.p. 125–127° was 80–90%.

Anal. Calc'd for $C_4H_2F_4O_3$: C, 27.6; H, 1.2. Found: C, 27.7; H, 1.4.

Perfluoropropionic anhydride. Perfluoropropionic acid[4] and phosphorus pentoxide were similarly allowed to react. The product was obtained in 75–85% yield, b.p. 70°. Lit. b.p. 69.8–70° at 735 mm.[5]

Perfluorobutyric anhydride. Perfluorobutyric acid[4] and phosphorus pentoxide treated as above gave the anhydride in 90–95% yield, b.p. 107–108°. Lit. b.p. 106–108°.[6]

General procedure for the preparation of the fluorinated acylamino derivatives. To a solution of 0.01 mole of the aromatic amine in 10 ml. of hot benzene was added 0.011 mole of the anhydride. For 7-acetyl- and 7-nitro-2-aminofluorene 10 ml. of hot xylene was used as the solvent. The mixture usually solidified in several minutes. Excess water was added and the benzene or xylene was steam-distilled. The crude product was crystallized from the appropriate solvent, Table I. Yields ranged from 80–95%.

CANCER RESEARCH LABORATORY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

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[2] All melting points are uncorrected. Analyses were performed by the Peninsular ChemResearch, Inc., Gainesville, Florida.

[3] Difluoroacetic acid was obtained from the Peninsular ChemResearch, Inc.

[4] Perfluoropropionic acid and perfluorobutyric acid were obtained from the Minnesota Mining and Manufacturing Company, St. Paul 6, Minnesota.

[5] Husted and Ahlbrecht, *J. Am. Chem. Soc.*, **75**, 1605 (1953).

[6] Kirshenbaum, Streng, and Hauptschein, *J. Am. Chem. Soc.*, **75**, 3141 (1953).

Synthesis of Several Aromatic Isocyanides

DAVID SAMUEL, B. WEINRAUB, AND DAVID GINSBURG

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Although a number of aromatic isocyanides are known, there are no published syntheses of such compounds containing, in addition, functional groups which would increase their solubility in various body fluids. In view of the potential biological interest in such compounds, the synthesis of *p*-isocyanobenzoic acid and *p*-isocyanobenzenesulfonamide was attempted.

The problem was primarily one of isolation. It is necessary to remove the unstable product as soon as possible after acidification of the reaction mixture. This was accomplished with more success in the case of *p*-isocyanobenzoic acid. This product was sent to Professor L. Pauling whose interest in the type of compound described initiated this work.

EXPERIMENTAL

p-Isocyanobenzoic acid. To a refluxing mixture of *p*-aminobenzoic acid (27.4 g.), chloroform (13 ml.), and methanol (100 ml.), 20 alternate additions of powdered sodium hydroxide (3 g. each) and of a 60:40 mixture of