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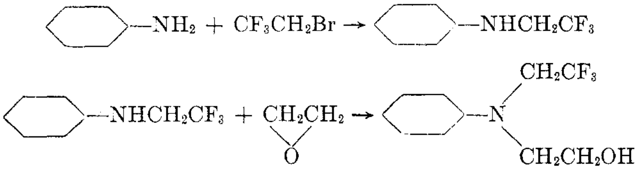
N-Fluoroalkylanilines and Their *N*-Hydroxyalkyl Derivatives

PREPARATION AND PROPERTIES

J. B. DICKEY, E. B. TOWNE, M. S. BLOOM, G. J. TAYLOR[1], H. M. HILL,
R. A. CORBITT[2], M. A. McCALL, AND W. H. MOORE
Tennessee Eastman Co., Division of Eastman Kodak Co., Kingsport, Tenn.

THIS paper describes the preparation and properties of a number of *N*-fluoroalkylanilines and *N*-fluoroalkyl-*N*-hydroxyalkylanilines which have proved to be valuable coupling constituents for a series of gas- and light-fast azo dyes for cellulose acetate. The effect of these fluorinated couplers on the color and fastness properties of azo dyes has been described in another paper (*3*).

The *N*-fluoroalkylanilines are a new class of compounds which were disclosed in recent patents from this laboratory (*2*, *21*). The *N*-fluoroalkyl-*N*-hydroxyalkylanilines were prepared by first treating aniline or a substituted aniline with a fluoroalkyl halide, then treating the resulting *N*-fluoroalkylaniline with a hydroxyalkylating agent. For example, *N*-[2,2,2-trifluoroethyl]-*N*-[2-hydroxyethyl]aniline was prepared as follows:



The various fluoroalkyl halides used, with their methods of preparation, physical constants, and references, are listed in Table I.

1-Bromo-2-fluoroethane (*9*), 2-bromo-1,1-difluoroethane (*8*), and 2-chloro-1,1,1-trifluoroethane (*11*, *15*) were prepared as described in the references. 2-Chloro-1,1-difluoroethane was obtained from the General Chemical Division, Allied Chemical and Dye Corp. 2-Bromo-1,1,1-trifluoroethane was obtained in the best yields by treating 1,2-dibromo-2,2-dichloroethane with a mixture of hydrogen fluoride, antimony trifluoride, and antimony pentachloride and venting the hydrogen chloride formed (*21*). It was also obtained by adding hydrogen fluoride to 2-bromo-1,1-difluoroethylene, a method not previously described.

1-Bromo-2,2-difluoropropane was prepared more readily and in better yield by treating 1,2-dibromo-2-chloropropane with mercuric fluoride than by treating with antimony trifluoride and using bromine as a catalyst (*10*). 1-Chloro-2,2-difluoropropane was prepared in 60% yield by treating 2,3-dichloropropene with hydrogen fluoride at 120° C. for 15 hours. The reported yield at 60° C. by this method was only 4% (*6*, *12*).

The new compound, 3-bromo-1,1-difluoropropane, was prepared by the reaction of mercuric fluoride with 1,1,3-tribromopropane, as described in a patent from this laboratory (*2e*). 1,1,3-Tribromopropane, also not previously described, was prepared in good yield by the free radical reaction of bromoform with ethylene in the presence of acetyl or benzoyl peroxide.

$$CHBr_3 + CH_2{=}CH_2 \xrightarrow{\text{Peroxide}} CHBr_2CH_2CH_2Br$$

$$CHBr_2CH_2CH_2Br + HgF_2 \rightarrow CHF_2CH_2CH_2Br$$

3-Chloro-1,1,1-trifluoropropane was prepared in 50% yield by the thermal chlorination of 1,1,1-trifluoropropane at 380° C., as described in the literature (*16*). A 2.8:1 ratio of 3-chloro-1,1,1-trifluoropropane to 2-chloro-1,1,1-trifluoropropane was obtained.

1-Chloro-3,3-difluorobutane was prepared in 45% yield by chlorinating 2,2-difluorobutane (*19*) in a Muskat apparatus (*18*) as described in the literature (*17*). A 3:2 ratio of 1-chloro-3,3-difluorobutane to 3-chloro-2,2-difluorobutane was obtained. It

Table I. Fluoroalkyl Halides

Compound	Boiling Point, ° C.	n_D^{20}	Method of Preparation	Lit. Cited
CH_2FCH_2Br	69–73	...	$CH_2BrCH_2Br + HgF_2$	(*9*)
CHF_2CH_2Cl[a]	35–36	...	.....	
CHF_2CH_2Br	57–60	...	$CHBr_2CH_2Br + HgF_2$	(*8*, *20a*)
CF_3CH_2Cl	6–8	...	$CCl_3CH_2Cl + SbF_3$ ($SbCl_5$); $CCl_2{=}CHCl + HF$ ($SbCl_5$)	(*1*, *11*, *15*)
CF_3CH_2Br[b]	29–33	...	$CCl_2BrCH_2Br + HF$ (SbF_3, $SbCl_5$); $CF_2{=}CHBr + HF$	(*11*, *15*, *21*)
$CH_3CF_2CH_2Cl$[b]	55–56	...	$CH_2{=}CClCH_2Cl + HF$	(*5*, *6*)
$CH_3CF_2CH_2Br$[b]	76–77	1.3890	$CH_3CClBrCH_2Br + HgF_2$	(*10*)
$CHF_2CH_2CH_2Br$[b]	92–94	1.4050	$CHBr_2CH_2CH_2Br + HgF_2$	(*21*)
$CF_3CH_2CH_2Cl$	47–49	1.3350	$CF_3CH_2CH_3 + Cl_2$ (380° C.)	(*13*, *16*)
$CH_3CF_2CH_2CH_2Cl$[b]	91–93	1.3709	$CH_3CF_2CH_2CH_3 + Cl_2$ (10° C., light)	(*7*, *17*)
$CH_3CF_2CH_2CH_2CH_2Cl$[b]	127–128	1.3848	$CH_3CCl{=}CHCH_2CH_2Cl + HF$	(*7*, *14*)

[a] Obtained from General Chemical Division, Allied Chemical and Dye Corp.
[b] See Experimental.

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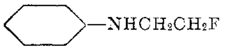
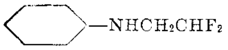
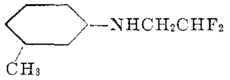
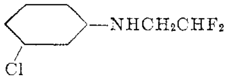
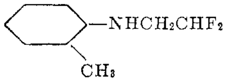
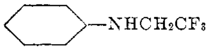
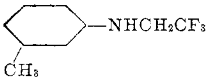
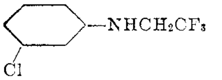
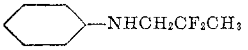
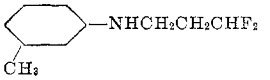
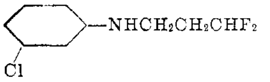
[1] Present address, Eastman Chemical Products, Inc., 260 Madison Ave., New York 16, N. Y.
[2] Present address, Eastman Kodak Co., Rochester, N. Y.

Table II. *N*-Fluoroalkylanilines[a]

Compound	Boiling Point[b]		n_D^{20}	C, %		H, %		N, %		Yield, %	Reaction Temp., ° C.
	° C.	Mm.		Calcd.	Found	Calcd.	Found	Calcd.	Found		
	87–90	5	1.5435	...	...	...	...	10.07	10.02	54	100[c]
	104–106	19	1.5142	61.15	61.70	5.73	6.14	8.92	8.72	75	150[c]
	96–99	7	1.5121	63.16	63.97	6.44	6.45	8.19	8.40	76	120[c]
	115–116	7	1.5333	50.13	50.18	4.18	4.35	7.31	7.36	46	170[c]
	113–117	23	...	63.16	64.13	6.44	6.57	8.19	8.58	10	130–140[c]
	84–85	15	1.4825	54.9	55.4	4.6	4.8	8.0	7.7	47	255[d]
	96–97	15	1.4797 (25°)	57.1	56.8	5.3	5.5	7.4	7.7	71	220[c]
	73	2	...	45.	46.0	3.4	3.7	6.7	6.9	6	185[c]
	103–107	12	1.5092	63.16	64.05	6.43	6.67	8.19	8.36	55	170[c]
	125–126	16	1.5127 (26°)	63.3	63.0	6.4	6.8	8.2	8.3	53	100[c]
	146–147	27	...	64.86	64.36	7.03	6.83	7.57	7.46	59	100[c]
	110–114	4	...	52.55	52.88	4.87	4.89	6.81	6.92	..	100[c]

was found, however, that the chlorination of 2,2-difluorobutane at 10° C. in the presence of ultraviolet light gave an improved yield (53.5%) and ratio (2:1) of 1-chloro-3,3-difluorobutane to 3-chloro-2,2-difluorobutane. The preparation of the necessary intermediates, 2,3-dichlorobutane and 2-chloro-2-butene, in improved yields is given in the Preparations section. These reactions are shown in the following equations:

$$CH_3CH{=}CHCH_3 + Cl_2 \rightarrow CH_3CHClCHClCH_3$$

$$CH_3CHClCHClCH_3 + NaOH \xrightarrow{CH_3OH} CH_3CCl{=}CHCH_3$$

$$CH_3CCl{=}CHCH_3 + 2HF \rightarrow CH_3CF_2CH_2CH_3$$

$$CH_3CF_2CH_2CH_3 + Cl_2 \rightarrow CH_3CF_2CH_2CH_2Cl + CH_3CF_2CHClCH_3$$

1-Chloro-4,4-difluoropentane was prepared in good yield by the following reactions:

$$CH_3COCH_2CH_2Cl + PCl_5 \rightarrow CH_3CCl{=}CHCH_2CH_2Cl + CH_3CCl_2CH_2CH_2CH_2Cl$$

$$CH_3CCl{=}CHCH_2CH_2Cl + 2HF \rightarrow CH_3CF_2CH_2CH_2CH_2Cl$$

While this work was in progress, the preparation of 1-chloro-4,4-difluoropentane from the corresponding acetylene compound and hydrogen fluoride was reported (*14*).

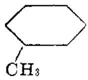
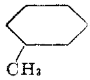
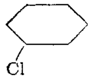
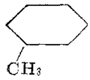
N-FLUOROALKYLANILINES

The *N*-fluoroalkylanilines (Table II) were prepared by treating aniline or substituted anilines with various fluoroalkyl halides. The temperature required to effect alkylation varied considerably and depended upon the reactivity of the fluoroalkyl halide as well as the basicity of the aniline used. The fluoroalkyl halides which contain fluorine on the beta carbon atom, with the exception of 1-bromo-2-fluoroethane, have relatively low reactivity; therefore they were treated at temperatures up to 250° C. in a rocking autoclave with two equivalents of the aniline for 12 to 30 hours. The fluoroalkyl chlorides required somewhat higher temperatures than the corresponding bromides. 2-Chloro-1,1,1-trifluoropropane is so inert that reaction with aniline was not effected even at 250° C., and at higher temperatures decomposition products resulted. 1-Chloro-4,4-difluoropentane, 1-chloro-3,3-difluorobutane, and 1-bromo-2-fluoroethane, which are more reactive and higher-boiling halides, were treated with the aniline and sodium bicarbonate on a steam bath.

In the reaction of 1-bromo-2,2-difluoropropane with aniline, the temperature is especially critical. At 165° C. the *N*-2,2-difluoropropyl derivative was obtained in good yield, but at higher temperatures a secondary reaction occurs to yield indoles. With 1-chloro-2,2-difluoropropane, temperatures effecting reaction yielded only indole-containing tars.

Unlike the other *N*-fluoroalkylanilines, *N*-(1*H*,1*H*-hepta-

TABLE II (*Continued*)

Compound	B.P.[b]		n_D^{20}	C, %		H, %		N, %		Yield,	Reaction
	° C.	Mm.		Calcd.	Found	Calcd.	Found	Calcd.	Found	%	Temp., ° C.
—$N(CH_2CH_2CHF_2)_2$	109–110	3	1.4898	57.83	58.27	6.02	5.86	5.62	5.86	..	...[c]
—$NHCH_2CH_2CF_3$	101–103	15	1.4847	57.1	58.4	5.3	5.7	7.4	8.0	50	180–190[d]
—$NHCH_2CH_2CF_3$	114–116	15	1.4848	59.1	60.2	6.0	6.2	6.9	6.9	43	180–190[d]
—$NHCH_2CH_2CF_2CH_3$	122–123	10	1.5087	64.9	65.6	7.1	7.1	7.6	7.7	56	160[d]
—$NHCH_2CH_2CF_2CH_3$	135–136	10	1.5054	...	...	...	...	7.0	7.4	74	160[d]
—$NHCH_2CH_2CF_2CH_3$	149–151	8	1.5330	54.7	54.6	5.5	5.5	6.4	6.8	30	160[d]
—$N(CH_2CH_2CF_2CH_3)_2$	149–150	10	1.4825	60.7	60.7	6.9	7.2	5.1	5.2	25	160[d]
—$NH(CH_2)_3CF_2CH_3$	101–102	2	1.5052 (19°)	66.2	65.8	7.5	7.6	7.0	6.9	55	100[d]
—$NH(CH_2)_3CF_2CH_3$	153–155	11	...	67.6	67.6	8.0	7.9	6.6	6.5	61	100[d]
—$N[(CH_2)_3CF_2CH_3]_2$	136–137	2	...	62.9	66.2	7.5	7.8	4.6	4.9	...[e]	100[d]

[a] The following aniline derivatives also were prepared: *m*-ethyl-*N*-(2,2-difluoroethyl)-, b.p. 106–108° C. (7 mm.); *N*-(2,2-difluoroethyl)-2-methoxy-5-methyl-, b.p. 122–125° C. (10 mm.); 5-acetamido-2-ethoxy-*N*-(2,2-difluoroethyl)-, m.p. 124–125° C.; *N*-(2,2-difluoropropyl)-*m*-methyl-, b.p. 115–117° C. (12 mm.), n_D^{20} 1.5135; *m*-chloro-*N*-(2,2-difluoropropyl)-, b.p. 115–120° C. (7 mm.); *m*-ethyl-*N*-(3,3-difluoropropyl)-, b.p. 108° C. (1 mm.); *m*-*tert*-butyl-*N*-(3,3-difluoropropyl)-, b.p. 115–120° C. (1 mm.); *N*-(1*H*,1*H*-heptafluorobutyl)-, b.p. 62–66° C. (1.5 mm.), n_D^{20} 1.4409; *N*,*N*-bis(3,3-difluorobutyl)-*m*-methyl-, b.p. 153–157° C. (10 mm.).

[b] Boiling points are uncorrected.

[c] Fluoroalkyl bromide used.

[d] Fluoroalkyl chloride used.

[e] Obtained as by-product (12.0%) in preparing —$NH(CH_2)_3CF_2CH_3$.

fluorobutyl)aniline was prepared by reducing heptafluorobutyranilide with lithium aluminum hydride.

The influence of fluorine substitution in these compounds is graphically displayed by the relative basicity of the *N*-fluoroalkylanilines. Those which are highly substituted with fluorine on the beta carbon atom, such as *N*-(2,2,2-trifluoroethyl)aniline, *N*-(2,2-difluoroethyl)aniline and *N*-(1*H*,1*H*-heptafluorobutyl)-aniline, are very weak bases, being insoluble in 5% hydrochloric acid solution. This property proved to be valuable in the preparation of *N*-(2,2,2-trifluoroethyl)aniline. Since the boiling point of *N*-(2,2,2-trifluoroethyl)aniline is very close to that of aniline itself, separation by distillation was difficult; however, extraction with 5% hydrochloric acid solution effected an easy separation. The *N*-fluoroalkylanilines in which the fluorine atoms are farther removed from the nitrogen atom more closely resemble their unfluorinated analogs in basicity.

The influence of fluorine atoms on the basicity of these *N*-fluoroalkylanilines is further demonstrated by their chemical reactivity. Thus the conditions required for hydroxyalkylation of the *N*-fluoroalkylanilines by alkylene oxides or hydroxyalkyl halides vary with the basicity of the *N*-fluoroalkylanilines.

In addition to characterizing the *N*-fluoroalkylanilines by analysis and the preparation of the *N*-hydroxyalkyl derivatives, the *N*,*N*-bis(fluoroalkyl) derivatives were prepared from *N*-(3,3-difluoropropyl)aniline and *N*-(3,3-difluorobutyl)aniline. In the case of *N*-(4,4-difluoropentyl)-*m*-toluidine, the hydrochloride was prepared and analyzed. In attempting to prepare the benzenesulfonyl derivative of *N*-(2,2,2-trifluoroethyl)aniline, heating for 4 hours on a steam bath with benzenesulfonyl chloride yielded only unreacted starting material. This very weakly basic behavior of *N*-(2,2,2-trifluoroethyl)aniline provided also an unusual route to the separation of the pure *N*-fluoroalkyl compound from aniline, similar to the separation by dilute hydrochloric acid described above.

The *N*-fluoroalkylanilines have a sweet, pleasant odor unlike that of their unfluorinated analogs.

Figure 1 shows the effect of fluorine substitution on the boiling points of *N*-alkylanilines. The boiling point is affected by both position and degree of fluorine substitution. As the number of fluorine atoms is increased, the boiling point is lowered in a regular manner. A similar lowering of boiling point is noted when the fluorine atoms are moved nearer the nitrogen atom—for example, from the gamma to the beta position in the propyl series.

Figure 2 shows the effect of fluorine substitution on the refractive indices of *N*-alkylanilines. The lowering of refractive index is dependent on the position and degree of substitution.

The ethyl series shows the pronounced and regular decrease in refractive index as the number of fluorine atoms is increased. The propyl series shows the decrease in refractive index caused by moving fluorine atoms from the gamma to the beta position.

N-FLUOROALKYL-*N*-HYDROXYALKYLANILINES

The preparation of *N*-fluoroalkyl-*N*-hydroxyalkylanilines by reaction of the *N*-fluoroalkylanilines with ethylene oxide or propylene oxide was usually conducted in a rocking autoclave at 180° C. for 6 to 8 hours. However, those *N*-fluoroalkylanilines which are highly substituted with fluorine on the beta carbon atom, such as *N*-(2,2,2-trifluoroethyl)aniline, required heating at 220° C. for 30 hours. Similarly, the *N*-fluoroalkyl-*m*-chloroanilines, all of which are weak bases, required the higher reaction temperature.

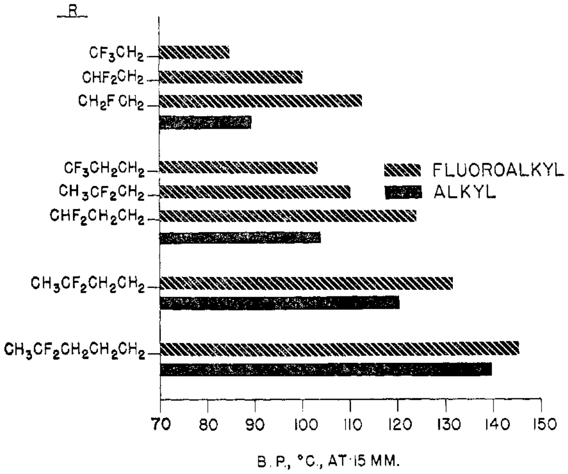
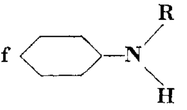


Figure 1. Effect of Fluorine Substitution on Boiling Points of



Hydroxyalkylation of the *N*-fluoroalkylanilines by 3-bromo-1-propanol and 3-chloro-1,2-propanediol was conducted at atmospheric pressure in the presence of sodium bicarbonate. Reaction temperatures ranged from 145° to 175° C., depending on the reactivity of the *N*-fluoroalkylaniline.

Most of these *N*-fluoroalkyl-*N*-hydroxyalkylanilines (Table III) are viscous liquids that were distilled at reduced pressure. A few are solids. They become discolored only on long standing in the presence of air.

PREPARATION OF FLUOROALKYL HALIDES

Only preparations of new compounds or improved preparations of known compounds are described for the fluoroalkyl halides listed in Table I (boiling and melting points are uncorrected). Representative examples are given of the different procedures used for alkylation and hydroxyalkylation.

2-Bromo-1,1,1-trifluoroethane. For this work, 2-bromo-1,1,1-trifluoroethane was usually prepared by fluorinating 1,2-dibromo-2,2-dichloroethane (*21*). However, it was also obtained by adding hydrogen fluoride to 2-bromo-1,1-difluoroethylene, a method not previously described:

Sixty-two grams (0.43 mole) of 2-bromo-1,1-difluoroethylene (*20*) and 77 grams (3.83 moles) of hydrogen fluoride, both cooled to dry ice–acetone temperature, were introduced into an autoclave cooled to −10° C. in an ice-salt mixture. After the autoclave was sealed, the temperature rose to 25° C. during 1 hour. The temperature was then raised to 60° C. during 1 hour. The autoclave was cooled in an ice-salt bath, then connected in series to cold water (10° C.) and dry ice–acetone receivers. The ice-salt bath was then removed and the autoclave was vented. When the temperature rose to 15° C., 2 grams of starting material was collected in the dry ice receiver, and a few drops were collected in the cold water receiver. The bomb was then cooled in an ice-salt bath. After the bomb was cold, a considerable amount of fine ice was added. The organic, bottom layer which separated was washed and dried. It was then distilled to obtain 11 grams (16%) of 2-bromo-1,1,1-trifluoroethane, b.p. 29–33° C.

1-Chloro-2,2-difluoropropane (*6*). Five grams of diphenylamine, 333 grams (3 moles) of 2,3-dichloropropene, and 200 grams (10 moles) of anhydrous hydrogen fluoride were placed in a rocking autoclave. The reactants were heated at 122° C. for 15 hours. The autoclave was then cooled, and the hydrogen halides were vented through a scrubber. The residual crude product was poured onto ice, then steam-distilled. The organic distillate was washed with sodium carbonate solution and dried over Drierite. Rectification yielded 165 grams (60.0%) of 1-chloro-2,2-difluoropropane, b.p. 55–56° C. A higher-boiling residue of 78 grams (19.8%) consisted mainly of 1,2-dichloro-2-fluoropropane.

1-Bromo-2,2-difluoropropane (*10*). Three hundred seventy-three grams (1.58 moles) of 1,2-dibromo-2-chloropropane was placed in a 1-liter, round-bottomed flask fitted with an upright, water-cooled condenser bearing a still head and a cooled receiving flask. Then 434 grams (1.81 moles) of mercuric fluoride was added portionwise during 45 minutes. A vigorous reaction occurred and the mixture refluxed gently. After refluxing for 1.5 hours, the water was removed from the jacket of the upright condenser. The reaction flask was then heated in an oil bath just hot enough to maintain distillation. The distillate, boiling at 70° to 84° C., was collected during 5 hours, and by this time the bath temperature had risen to 200° C. The crude product was washed with sodium bicarbonate solution, then with water and dried. Rectification yielded 123 grams (48.8%) of 1-bromo-2,2-difluoropropane, b.p. 76–77° C., n_D^{20} 1.3890.

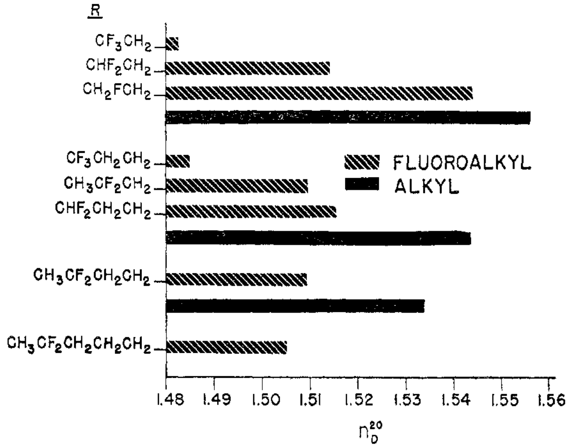
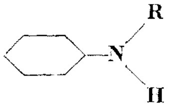


Figure 2. Effect of Fluorine Substitution on n_D^{20} of



3-Bromo-1,1-difluoropropane. (*a*) A mixture of 152 grams (0.6 mole) of bromoform and 12 grams (5 mole %) of a 30% solution of acetyl peroxide in dimethyl phthalate was placed in a rocking autoclave. Then ethylene was added until the pressure reached 400 pounds per square inch. The reactants were shaken for 8 hours at 95° to 105° C., then cooled. The reaction mixture was steam distilled, and the organic layer was dried over Drierite. Fractionation yielded considerable unreacted bromoform and 98 grams (58.1%) of 1,1,3-tribromopropane, b.p. 106–107° C. (30 mm.), n_D^{20} 1.5700.

Calculated for $C_3H_5Br_3$: C, 12.8; H, 1.8; Br, 84.4. Found: C, 12.9; H, 1.9; Br, 85.1.

(*b*) In a 200-ml., round-bottomed flask, fitted with a 12-inch still head with side arm and receiver, was placed 98 grams (0.035 mole) of 1,1,3-tribromopropane and 109 grams (0.42 mole) of mercuric fluoride. The mixture was heated gently with a flame to start a vigorous reaction which was then moderated by an ice-water bath. The reaction mixture was then heated moderately as the product distilled over at 80° to 95° C. The liquid distillate was washed successively with sodium bicarbonate solution and water, then dried over calcium chloride. The products from six such runs were combined and rectified. The total yield was 125 grams (37.0%) of 3-bromo-1,1-difluoropropane, b.p. 92–94° C., n_{D}^{20} 1.4050. There was a forerun of 36 grams and a higher boiling fraction (95° to 165° C.) of 31 grams from which a small amount of product was obtained.

Calculated for $C_3H_5BrF_2$: C, 22.7; H, 3.2; Br, 50.3. Found: C, 23.3; H, 3.4; Br, 50.1.

1-Chloro-3,3-difluorobutane. (*a*) The apparatus for preparing 2,3-dichlorobutane consisted of two flowmeters, a reactor consisting of an upright, water-cooled spiral condenser painted black, a receiver at the bottom of the condenser, a water scrubbing tower to remove hydrogen chloride, and a dry ice–cooled trap to recover unreacted 2-butene. Air (to inhibit chlorine substitution) was injected into the chlorine stream through a bubble counter.

During a 3-hour period, 128 grams (1.83 moles) of chlorine and 144 grams (2.57 moles) of 2-butene were passed through the flowmeters and mixed at the top of the condenser. Reaction took place readily, and the liquid product was collected in a receiver. After completion of the run, air was passed through the product to remove hydrogen chloride and to recover 48.5 grams of 2-butene. Rectification of the product gave 193 grams of 2,3-dichlorobutane (59.0% conversion, 89.0% yield from 2-butene; 84.0% conversion from chlorine) and a residue of 19 grams of polychlorobutanes.

(*b*) Preparation of 2-chloro-2-butene was conducted in a 2-liter, three-necked flask fitted with a vapor-tight stirrer, a dropping funnel, and a 14-mm. by 14-inch rectifying column.

A mixture of 508 grams (4 moles) of 2,3-dichlorobutane and 100 ml. of methanol was placed in the flask and heated to reflux. To this mixture was added a solution of 176 grams (4.4 moles) of sodium hydroxide in 900 ml. of hot methanol at such a rate that a good reflux was maintained at the top of the column. When the temperature at the top of the column had dropped to 51° C., the minimum-boiling mixture of 2-chloro-2-butene and methanol was removed slowly. Rectification was continued until the head temperature reached 59° C. This fraction, which weighed 431 grams, was diluted with two volumes of water, then the upper layer was separated and dried with calcium chloride. The weight of the dry product was 325 grams. By further distillation of the reaction mixture until no oil formed upon dilution of the distillate with water, 71.5 grams of distillate was obtained. When this was processed as above, 13.5 grams of dry product containing 10 grams of 2-chloro-2-butene was obtained. The total yield of product was 335 grams (3.7 moles) (92.5%). It was a mixture of cis and trans isomers and boiled at 60° to 69° C., n_{D}^{20} 1.4205.

(*c*) The chlorination of 2,2-difluorobutane, which was prepared by the method of Renoll (*19*) from 2-chloro-2-butene, was run in the liquid phase using a flask equipped with a sealed stirrer, an ultraviolet immersion light, a dry ice condenser, and a fritted-glass, gas-dispersion disk. Chlorine was bubbled into 205 grams (2.18 moles) of 2,2-difluorobutane at 10° C. at the rate of 0.35 gram per minute for 3 hours. Rectification of the product gave 110 grams of recovered 2,2-difluorobutane; 34.3 grams of 3-chloro-2,2-difluorobutane (26.5%), b.p. 72–76° C., n_{D}^{20} 1.3630; 68.6 grams of 1-chloro-3,3-difluorobutane (53.0%), b.p. 91–94° C., n_{D}^{20} 1.3709; and 7 grams of residue.

1-Chloro-4,4-difluoropentane. (*a*) In a 2-liter, three-necked flask, fitted with a stirrer and reflux condenser, was placed 735 grams (6.1 moles) of freshly distilled 5-chloro-2-pentanone (Eastman Kodak Co., P5560); 1270 grams (6.1 moles) of phosphorus pentachloride was added portionwise while stirring, during 2 hours. The temperature rose immediately to 70° to 80° C., and each addition caused vigorous evolution of hydrogen chloride. After addition, heating was continued for 2 hours at 80° C. A still head and a downward condenser were attached to the flask, and 500 grams of phosphorus oxychloride was then removed at 30° C. and 60 mm. The residue in the flask was run fairly rapidly, but dropwise, into hot water and then allowed to stand. Steam distillation of the lower layer gave 590 grams of crude product. Rectification yielded 288 grams (34.0%) of 2,5-dichloro-2-pentene, b.p. 151–153° C., n_{D}^{20} 1.4663, and 141 grams (13.1%) of 1,4,4-trichloropentane, b.p. 100–102° C. (40 mm.), n_{D}^{20} 1.4681.

(*b*) Two hundred eighty-nine grams (2.1 moles) of 2,5-dichloro-2-pentene was sealed in a rocking autoclave, then 300 grams of hydrogen fluoride was added by closed-system distillation. The mixture was shaken for 8 hours at 70° C., then cooled. After venting the gases through a scrubber containing alkali, the contents of the autoclave were poured over ice and then steam-distilled. Rectification of the organic distillate yielded 176 grams (59.4%) of 1-chloro-4,4-difluoropentane, b.p. 127–128° C., n_{D}^{20} 1.3848, and starting material (16.0%).

Calculated for $C_5H_9ClF_2$: C, 42.1; H, 6.3; Cl, 24.9. Found: C, 42.4; H, 6.6; Cl, 24.8.

PREPARATION OF *N*-FLUOROALKYLANILINES

The *N*-fluoroalkylanilines and *N*-fluoroalkyl-*N*-hydroxyalkylanilines prepared are listed in Tables II and III, respectively. One example of each method of preparing the fluoroalkylanilines is given. The method used in preparing others is shown in Table II.

***N*-(2,2,2-Trifluoroethyl)aniline.** A mixture of 34 grams (0.287 mole) of 2-chloro-1,1,1-trifluoroethane and 60 grams (0.645 mole) of aniline was heated in a Carius tube inside a rocking autoclave for 30 hours at 250° to 255° C. The reaction mixture obtained was shaken twice with dilute hydrochloric acid (70 ml. of concentrated hydrochloric acid in 490 ml. of water, used in two portions). The excess aniline dissolved to leave an insoluble layer which was separated by extraction and distilled. The yield of *N*-(2,2,2-trifluoroethyl)aniline, b.p. 84–85° C. (15 mm.), n_{D}^{20} 1.4825, was 23.5 grams (46.8%).

Calculated for $C_8H_8F_3N$: C, 54.9; H, 4.6; N, 8.0. Found: C, 55.4; H, 4.8; N, 7.7.

***N*-(1*H*,1*H*-Heptafluorobutyl)aniline.** A solution of 4.5 grams (0.149 mole) of lithium aluminum hydride in 150 ml. of anhydrous ether was prepared. Then a solution of 70 grams (0.254 mole) of crude heptafluorobutyranilide in 200 ml. of ether was added dropwise with stirring. Heptafluorobutyranilide was prepared from aniline and heptafluorobutyryl chloride. After our work was completed, this compound was described (*4*). Stirring was continued for 1 hour after addition was complete, then the mixture was treated with dilute sulfuric acid. The ether layer was separated and concentrated. The residue was washed with dilute potassium hydroxide solution. The oil which separated was dried with potassium hydroxide pellets and vacuum-distilled to yield 3.5 grams of product, b.p. 62–66° C. (1.5 mm.), n_{D}^{20} 1.4409.

***N*-(4,4-Difluoropentyl)-*m*-toluidine.** A mixture of 42.8 grams (0.3 mole) of 1-chloro-4,4-difluoropentane and 64.2 grams (0.6 mole) of *m*-toluidine was refluxed with stirring on a steam bath for 32 hours. The reaction mixture was diluted with ether, shaken with excess dilute alkali, then dried. Rectification yielded 39 grams (61.0%) of *N*-(4,4-difluoropentyl)-*m*-toluidine, b.p. 153–155° C. (11 mm).

Calculated for $C_{12}H_{17}F_2N$: C, 67.6; H, 8.0; N, 6.6. Found: C, 67.6; H, 7.9; N, 6.5.

TABLE III. *N*-FLUOROALKYL-*N*-HYDROXYALKYLANILINES[a]

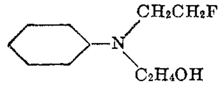
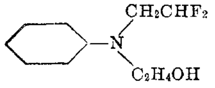
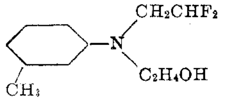
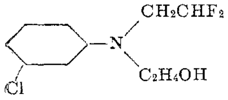
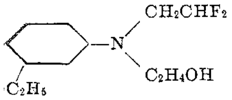
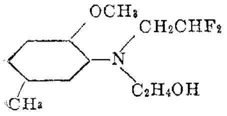
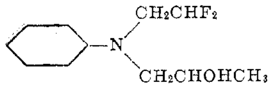
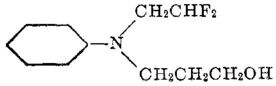
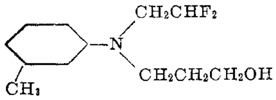
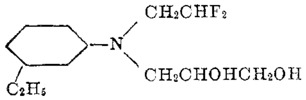
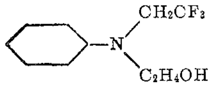
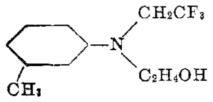
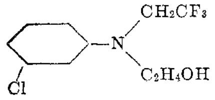
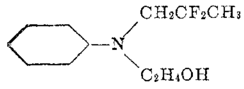
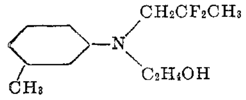
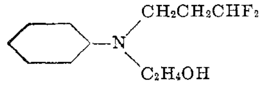
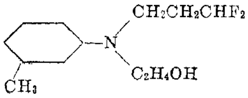
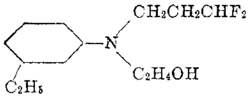
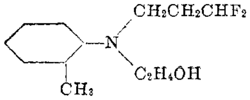
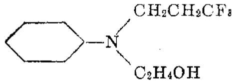
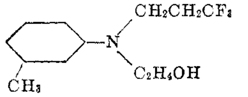
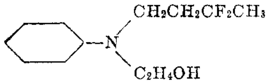
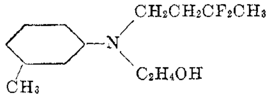
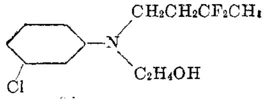
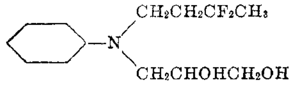
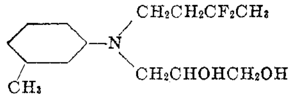
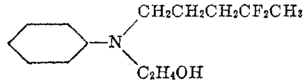
Compound	B.P.[b]		n_D^{20}	C, %		H, %		N, %		Yield, %	Reaction Temp., ° C.
	° C.	Mm.		Calcd.	Found	Calcd.	Found	Calcd.	Found		
	136–139	4	1.5512	65.57	65.49	7.65	7.91	7.65	7.83	44	145
	129–134	3	1.5273	59.70	59.50	6.42	6.65	6.97	6.91	83	195
	123–124	1	1.5238	61.40	60.89	6.98	7.01	6.51	6.47	82	195
	180–182	14	1.5448	50.96	51.42	5.10	5.07	5.94	6.04	65	200
	155–158	7	1.5199	62.88	62.19	7.42	7.33	6.11	6.24	53	200
	155–161	10	...	...	...	...	...	5.7	5.8	25	180
	135–137	6	1.5187	61.40	61.05	6.98	6.99	6.51	6.54	63	200
	117–121	1.5	1.5234	61.40	61.05	6.98	6.81	6.51	6.50	20	140
	133–138	1.5	...	...	...	...	...	6.1	5.9	29	145
	Viscous oil		...	60.23	60.83	7.34	7.64	5.41	5.46	45	155
	102–103	1.5	1.4996	54.8	54.8	5.5	5.6	6.4	6.2	66	200
	103–104	1.5	...	56.6	56.9	6.1	6.1	6.0	5.9	61	200
	115–120	1	...	47.5	46.7	4.4	4.3	4.5	5.1	13	195
	155–160	11	1.5227	61.4	61.9	7.0	6.9	6.5	6.4	84	190
	120–123	1	...	...	...	...	...	6.1	6.4	41	180
	135–136	2	1.5250 (28°)	61.4	61.2	7.0	7.0	6.5	6.6	78	210

TABLE III (*Continued*)

Compound	B.P.[b] ° C.	B.P.[b] Mm.	n_D^{20}	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found	Yield, %	Reaction Temp., ° C.
	130	1	...	62.88	62.21	7.42	7.34	6.11	5.52	44	210
	131–132	1	1.5185	64.20	64.30	7.82	7.52	5.76	5.81	60	220
	...	..	1.5031	62.88	62.75	7.42	7.18	6.11	6.18	..	180
	119–120	2	1.5018	56.6	56.5	6.1	6.2	6.0	6.4	84	180
	128–129	2	1.4992	58.3	58.0	6.5	6.6	5.7	5.5	80	185
	140–143	1.5	1.5142	62.9	62.7	7.5	7.8	6.1	5.9	84	180
	135	1	1.5165	64.2	64.5	7.9	8.0	5.8	5.8	86	180
	170–172	2.5	1.5300	54.8	54.4	6.1	6.0	5.3	5.3	78	180
	[c]		1.5230	60.2	60.1	7.4	7.3	5.4	5.3	95	145
	[d]; m.p., 79°		...	61.5	62.2	7.8	7.9	5.1	5.3	58	145
	170		1.5146	64.20	65.19	7.82	8.11	5.76	5.56	82	200

[a] The following aniline derivatives also were prepared: 2-ethoxy-5-ethyl-*N*-(2,2-difluoroethyl)-*N*-(2-hydroxyethyl)- , viscous oil; *N*-(2,2-difluoroethyl)-*N*-(2,3-dihydroxypropyl)- , m.p. 46–53° C.; *N*-(2,2-difluoroethyl)-*N*-(2,3 -dihydroxypropyl)-*m*-methyl- , viscous oil; *N*-(2,2-difluoroethyl)-*N*-(2,3-dihydroxypropyl)-2-methoxy-5-methyl- , viscous oil; *N*-2,2-difluoroethyl-*N*-methyl- , b.p. 85° C. (7 mm.); *m*-chloro-*N*-(2,2-difluoropropyl)-*N*-(2-hydroxyethyl)- , b.p. 165–170° C. (6 mm.); *N*-(3,3-difluoropropyl)-*N*-(2,3-dihydroxypropyl)-*m*-methyl- , viscous oil; *N*-(3,3-difluoropropyl)-*N*-(2,3-dihydroxypropyl)-*m*-methyl- , viscous oil; *m*-*tert*-butyl-*N*-(3,3-difluoropropyl)-*N*-(2-hydroxyethyl)- , b.p. 125–130° C. (1 mm.); *N*-(3,3-difluoropropyl)-*N*-(2,3-dihydroxypropyl)-*m*-methyl- , viscous oil; *m*-chloro-*N*-(3,3-difluoropropyl)-*N*-(2,3-dihydroxypropyl)- , viscous oil; *N*-(1*H*, 1*H*-heptafluorobutyl-*N*-(2-hydroxyethyl)- , b.p. 58–70° C. (1 mm.); *N*-(4,4-difluoropentyl)-*N*-(2-hydroxyethyl)-*m*-methyl- , b.p. 159–161° C. (2 mm.); *N*,*N*-bis(4,4-difluoropentyl)-*m*-methyl-, b.p. 153–157° C. (10 mm.).

[b] Boiling and melting points are uncorrected.

[c] Distilled in a molecular still at 22 μ; bath temperature 110–125° C.

[d] Distilled in a molecular still at 11–14 μ; bath temperature 110° C.

The hydrochloride melted at 167–169° C.

Calculated for $C_{12}H_{18}ClF_2N$: C, 57.8; H, 7.2; N, 5.6. Found: C, 57.7; H, 7.5; N, 5.4.

***N*,*N*-Bis(3,3-difluorobutyl)aniline.** A mixture of 35.8 grams (0.19 mole) of *N*-(3,3-difluorobutyl)aniline and 13 grams (0.10 mole) of 1-chloro-3,3-difluorobutane was heated in a rocking autoclave for 24 hours at 160° C. The reaction product was washed until neutral, then dried and rectified to yield considerable starting material and 4.4 grams (25% yield) of *N*,*N*-bis(3,3-difluorobutyl)aniline, b.p. 149–150° C. (10 mm.); n_D^{20} 1.4825.

Calculated for $C_{14}H_{19}F_4N$: C, 60.7; H, 6.9; N, 5.1. Found: C, 60.7; H, 7.2; N, 5.2.

PREPARATION OF *N*-FLUOROALKYL-*N*-HYDROXYALKYL-ANILINES

Examples are given for preparation of some of these products:

***N*-(2,2,2-Trifluoroethyl)-*N*-(2-hydroxyethyl)aniline.** A mixture of 13.5 grams (0.077 mole) of *N*-(2,2,2-trifluoroethyl)aniline and 4.4 grams (0.1 mole) of ethylene oxide dissolved in 10 ml. of ethanol was placed in a Carius tube cooled to 0° C. The sealed tube was fastened in a rocking autoclave and agitated at 200° C. for 18 hours. Rectification of the reaction product yielded 11.2 grams (65.5%) of the desired product, b.p. 102–103° C. (1.5 mm.).

Calculated for $C_{10}H_{12}F_3NO$: C, 54.8; H, 5.5; N, 6.4. Found: C, 54.8; H, 5.6; N, 6.2.

N-(2,2-Difluoroethyl)-N-(2-hydroxypropyl)aniline. A mixture of 23.5 grams (0.15 mole) of N-(2,2-difluoroethyl)aniline and 10.3 grams (0.15 mole) of propylene oxide dissolved in 10 ml. of ethanol was sealed in a Carius tube. The mixture was then agitated at 200° C. for 18 hours in a rocking autoclave. The mixture was distilled to obtain 18 grams (63.0%) of the desired product, b.p. 135–137° C. (6 mm.), n_D^{20} 1.5187.

Calculated for $C_{11}H_{15}F_2NO$: C, 61.40; H, 6.98; N, 6.51. Found: C, 61.05; H, 6.99; N, 6.54.

N-(3,3-Difluorobutyl)-N-(2,3-dihydroxypropyl)aniline. A mixture of 9 grams (0.049 mole) of N-(3,3-difluorobutyl)aniline and 4.6 grams (0.055 mole) of sodium bicarbonate was placed in a three-necked flask fitted with a mechanical stirrer. The mixture was stirred and heated at 145° C. while 6.1 grams (0.055 mole) of 1-chloro-2,3-propanediol was added dropwise during 30 min. and carbon dioxide was evolved. Heating was continued for 6 hours more. The reaction mixture became very viscous and dark. The product was treated with 50 ml. of water and 50 ml. of benzene, then stirred. The benzene layer was separated, and the aqueous layer was extracted with three 25-ml. portions of benzene. The benzene extracts were combined and steam distilled to obtain 12.1 grams (95.3%) of a viscous, brown liquid. This crude product was distilled in a molecular still at 22 μ with the bath temperature at 110° to 125° C. to obtain an oil, n_D^{20} 1.5230.

Calculated for $C_{13}H_{19}F_2NO_2$: C, 60.2; H, 7.4; N, 5.4. Found C, 60.1; H, 7.3; N, 5.3.

N-(2,2-Difluoroethyl)-N-(3-hydroxypropyl)aniline. A mixture of 47 grams (0.3 mole) of N-(2,2-difluoroethyl)aniline and 30.5 grams (0.36 mole) of sodium bicarbonate was stirred and heated at 135° C. while adding 46.4 grams (0.36 mole) of 3-bromo-1-propanol during one half hour. After the addition, stirring and heating at 140° C. were continued for 6 hours. The product distilled at 117° to 121° C. (1.5 mm.), n_D^{20} 1.5234. The yield was 9.5 grams (15.0%).

Calculated for $C_{11}H_{15}F_2NO$: C, 61.40; H, 6.98; N, 6.51. Found: C, 61.05; H, 6.81; N, 6.50.

SUMMARY

A new class of compounds, *N*-fluoroalkylanilines, was prepared by treating anilines with various fluoroalkyl halides. Some of these fluoroalkyl halides are new compounds; others are known compounds, and some were prepared by improved methods. The fluoroalkyl groups introduced into the anilines by alkylation were 2-fluoroethyl; 2,2-difluoroethyl; 2,2,2-trifluoroethyl; 2,2-difluoropropyl; 3,3-difluoropropyl; 3,3,3-trifluoropropyl; 3,3-difluorobutyl; and 4,4-difluoropentyl. *N*-(1*H*, 1*H*-heptafluorobutyl)aniline, however, was prepared by lithium aluminum hydride reduction of heptafluorobutyranilide.

These *N*-fluoroalkylanilines were hydroxyalkylated with ethylene oxide, propylene oxide, 3-bromo-1-propanol, and 3-chloro-1,2-propanediol to obtain the corresponding *N*-fluoroalkyl-*N*-hydroxyalkylanilines.

The properties of the *N*-fluoroalkylanilines and of the *N*-fluoroalkyl-*N*-hydroxyalkylanilines are greatly influenced by the introduction of fluorine. The effect is dependent on the degree of fluorine substitution and on the position of this substitution in the alkyl group. The effect appears in both the chemical and the physical properties.

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Catalysis by Complexes

DRYING OF LINSEED OIL

A. C. ZETTLEMOYER AND RAYMOND R. MYERS
National Printing Ink Research Institute, Lehigh University, Bethlehem, Pa.

EVER since the first accidental inclusion of oxides of lead in linseed oil, metal salts have been employed as drying catalysts in the paint, varnish, and ink industry. In the form of soluble salts of organic acids, the divalent ions of manganese, cobalt, and lead have dominated drier technology for decades.

The supremacy of these conventional catalysts was challenged first by the discovery that certain complex compounds of iron were of biological importance because of their ability selectively to catalyze oxidations under mild conditions—the role of hemoglobin in animal metabolism (*7*) is an example. In view of the fact that iron normally is an oxidation catalyst only at high temperature, the conclusion that the type of bond peculiar to these complex molecules was responsible for the greater activity led early experimenters to a study of related compounds as driers for inks.

Because of the similarity between biochemical oxidations and the drying of linseed oil, the use of hemin in the oxidation of drying oils was tried as early as thirty years ago by Robinson (*9*) in a