Fluorinated Aminoanthraquinone Dyes

J. B. DICKEY, E. B. TOWNE, M. S. BLOOM, G. J. TAYLOR¹, D. J. WALLACE, JOHN SAGAL, JR.², M. A. McCALL, and D. G. HEDBERG

Research Laboratories, Tennessee Eastman Co., Division of Eastman Kodak Co., Kingsport, Tenn.

A S PART of a program of preparing superior light- and gasfast dyes for cellulose acetate, a considerable number of azo and anthraquinone dyes which contain fluorine have been prepared. The effect of fluorine substitution on the color and fastness of monoazo dyes and the synthesis of their intermediates have been described (14, 15).

This paper describes the synthesis of two series of dyes which illustrate the effect of fluorine atoms in the alkylamino group of alkylaminoanthraquinones and of a trifluoromethyl group in the 2- position on the nucleus of aminoanthraquinones. In general, substituted aminoanthraquinones are excellent dyes for cellulose acetate, giving bright, pink to blue colors. Many of these fluorinated aminoanthraquinone dyes have much better fastness to gas and light than the corresponding unfluorinated compounds. However, this property is not so general as to warrant the conclusion that all fluorinated anthraquinone dyes have excellent gas and light fastness. The dyes discussed have been described in patents from this laboratory (4–8, 11–13).

Other types of anthraquinone dyes containing trifluoromethyl groups were developed by I. G. Farbenindustrie in the late 1930's. These included vat dyes derived from indanthrone, indanthrene, dibenzanthrone, and dibenzopyrenequinone, as well as the trifluorobenzoyl and trifluoroethoxybenzoyl derivatives of aminoanthraquinones (16, 17, 19, 24).

First series was made by reaction of fluoroalkylamines with leucoquinizarin

The first series comprises medium-bright, pink to violet dyes containing fluoroalkylamino groups. They were prepared by reaction of leucoquinizarin (1,4,9,10-anthratetrol) with several fluoroalkylamines and oxidizing the resulting leuco dyes to 1-fluoroalkylamino-4-hydroxyanthraquinones. For example:



The use of excess amine and higher temperatures yields the 1,4bis(fluoroalkylamino)anthraquinones, which are bluer dyes but have poorer dyeing and fastness properties. The fluoroalkylamines used in preparing this series of dyes were $CF_3CH_2NH_2$, $CHF_2CH_2NH_2$, $CF_3(CH_3)CHNH_2$, $CHF_2CH_2CH_2NH_2$, $CH_3CF_2 CH_2NH_2$, and $CH_3CF_2(CH_2)_3NH_2$. Another amine, $CF_3CH_2 CH_2NH_2$, was prepared but not converted to the dye.

The effect of these various fluoroalkyl groups on the color and fastness properties of the dyes is shown in Table I. The general formula of the dyes is given at the top of the table. The fluoroalkyl groups are listed in the order that the color of the corresponding dye shifts from pink to violet—that is, shifts the ab-

¹ Present address, Eastman Chemical Products, Inc., 260 Madison Ave., New York 16, N. Y.

² Present address, Eastman Kodak Co., Rochester, N. Y.

sorption maximum to a longer wave length. The groups R=H, C_2H_5 , and CH_2CH_2OH are included for comparison with the groups containing fluorine.



These fluorinated dyes vary in fastness to gas and light, being generally superior in these respects to the unfluorinated dyes in the case of 2-fluoroalkyl groups and about equal when fluorine substitution is on the 3- or 4- carbon of the alkyl group. They also have good exhaustion, give level dyeing, and are resistant to crocking and sublimation. Like all anthraquinone dyes, they discharge to a brown color rather than white.

From a study of the series of Table I the following observations can be made.

1. As the number of fluorine atoms on a single carbon atom is increased (2,2-difluoroethyl to 2,2,2-trifluoroethyl), the color shifts from red-violet to pink-violet.

2. As the distance from fluorine to nitrogen is increased for example, from 2,2-difluoroethyl to 4,4-difluoropentyl—the color shifts from red-violet toward blue, the color of unfluorinated alkylaminoanthraquinone dyes.

3. Dyes containing the ethyl or 2-hydroxyethyl group are bluer than those containing the 3,3-difluoropropyl or 4,4-difluoropentyl group.

4. The 2,2,2-trifluoroethyl, 2,2-difluoroethyl, and 1-(trifluoromethyl)ethyl groups confer excellent light and gas fastness upon the dyes, being decidedly superior to the unfluorinated ethyl group in this respect. The 2,2-difluoropropyl and 3,3difluoropropyl groups are about equal to the ethyl group in effect of light fastness, whereas the 4,4-difluoropentyl group is inferior.

Fluoroalkylamines. Some of the fluoroalkylamines used in preparing the N-fluoroalkylaminoanthraquinone dyes are new compounds, but the others have been described. 2,2,2-Trifluoroethylamine has been prepared by reducing trifluoroacetonitrile over a platinum catalyst (18) and by reaction of 2-chloro-1,1,1trifluoroethane with ammonium hydroxide in an autoclave (3).

PRODUCT AND PROCESS DEVELOPMENT

2,2-Difluoroethylamine has been prepared by reaction of 1,1difluoro-2-iodoethane with alcoholic ammonia in a sealed tube (25).

In general, the fluoroalkylamines which are new compounds were prepared by reaction of a fluoroalkyl bromide or chloride with 28% ammonium hydroxide in a rocking autoclave at temperatures ranging from 100° to 195° C., depending on the reactivity of the fluoroalkyl halide. The necessary fluoroalkyl halides were prepared as described in a previous paper (14).

$$CHF_{2}CH_{2}CH_{2}Br + NH_{4}OH \rightarrow CHF_{2}CH_{2}CH_{2}NH_{2}$$
(2)

The fluoroalkyl bromides reacted with ammonia at lower temperatures or in less time than the chloride, and those halides with fluorine in the 2- position were made less reactive than those with fluorine in the 3- or 4- position. 3,3,3-Trifluoropropylamine was prepared by direct amination of 3-chloro-1,1,1-trifluoropropane and by hydrolysis of N-(3,3,3-trifluoropropyl)phthalimide. 2,2,2-Trifluoro-1-(methyl)ethylamine was prepared by the Raney nickel reduction of the corresponding oxime, a known compound prepared from trifluoroacetone (26).

The fluoroalkylamines are low-boiling, mobile, colorless liquids with typical amine odors. Increasing the number of fluorine atoms from two to three in a fluoroalkylamine lowers the boiling point 25° to 30° C., even though the molecular weight is increased. This effect of the number and position of fluorine substitution on the boiling points of the fluoroalkylamines is shown in Figure 1.

Second series contains trifluoromethyl group in the anthraquinone nucleus

Dyes containing a trifluoromethyl group in the 2- position of the anthraquinone nucleus were prepared by refluxing 1-amino-4bromo-2-trifluoromethylanthraquinone (12) with an o- or p-(hydroxypolyethoxy)aniline in amyl alcohol in the presence of potassium acetate and a little cupric sulfate for 1.5 hours. For example:



These dyes give bright shades of blue on cellulose acetate and have excellent light fastness and good gas fastness. The (hydroxypolyethoxy)anilines contribute to good affinity and to depth and brightness of dyeing, being superior to aniline and *N*-alkylanilines, which give dull and weak dyes for cellulose acetate. The CF₃ group contributes to light and gas fastness, the dyes being superior to the corresponding dyes having a CN, CONH₂, or SO₂CH₃ group in the 2- position.

The depth and brightness of these dyes are influenced greatly by the (hydroxypolyethoxy)aniline used, being at a maximum for p-(hydroxytetraethoxy)aniline. The depth and brightness decrease regularly as the hydroxytriethoxy-, hydroxydiethoxy-, and hydroxyethoxy-substituted anilines are used.

The effect of the CF_3 group in the 2- position compared with that of $CONH_2$, CN, SO_2CH_3 , SCH_3 , and CH_3 groups on fastness properties is shown in Table II. Also shown is the effect on depth and brightness of varying the hydroxypolyethoxy group.



The following observations can be made concerning the dyes listed in Table II.

1. Dyes containing the CF_s group are comparable to the dye containing the CONH₂ group in brightness of color and are superior in fastness to light and gas.

2. Dyes containing the CF_3 group are generally superior to those containing the CN, SO_2CH_3 , SCH_3 , and CH_3 groups in depth and brightness of color and in fastness.

3. The dye containing both the CF_3 and a *p*-(hydroxytetraethoxy)anilino group is a much brighter and deeper blue than the corresponding dyes containing a *p*- or *o*-(hydroxytriethoxy)anilino group.

The intermediates leading to 1-amino-4-bromo-2-trifluoromethylanthraquinone were made in good yields from 2-methylanthraquinone. The latter was first chlorinated in the 1-position of the ring and then in the side chain to yield 1-chloro-2-trichloromethylanthraquinone, which was fluorinated to form 1-chloro-2-trifluoromethylanthraquinone (23). Amination of the latter, followed by bromination, yielded 1-amino-4-bromo-2-trifluoromethylanthraquinone (12).

The corresponding intermediates for dyes with groups other than CF₃ in the 2-position were prepared by similar methods. 1-Amino-4-bromo-2-methylanthraquinone was obtained by brominating 1-amino-2-methylanthraquinone (20). 1-Amino-4bromo-2-(methylthio)anthraquinone was prepared by brominating 1-amino-2-(methylthio)anthraquinone (22), and 1-amino-4bromo-2-methylsulfonylanthraquinone was prepared by oxidizing the 2-methylthio compound.

The dyes with a cyano group in the 2- position were made from the corresponding 2-bromo dyes (10) by treating them with cuprous cyanide (9). The dyes with an amide group in the 2position were made by hydrolyzing the corresponding cyano compound (21).

The o- and p-(hydroxypolyethoxy)anilines were prepared by first making 1-chloro-2(or 4)-nitrobenzene react with the monosodium salt of the desired polyethylene glycol $[NaO(C_2H_4O)_xH]$ in excess glycol as previously described, then reducing the nitro compound (6, 13).

Preparation of N-Fluoroalkylaminoanthraquinone Dyes. 1-HYDROXY-4-(2,2,2-TRIFLUOROETHYLAMINO)ANTHRAQUINONE. A mixture of 35.8 grams (0.14 mole) of quinizarin, 14.5 grams (0.26 mole) of leucoquinizarin, and 24.8 grams (0.25 mole) of 2,2,2trifluoroethylamine in 400 ml. of butyl alcohol was placed in a stainless steel, rocking autoclave and heated at 150° to 160° C. for 8 hours.

The reaction mixture was transferred to a flask and any excess amine was removed by heating. Then 200 ml. of butyl alcohol was added, and the leuco dye was oxidized by passing in air while refluxing the mixture for 6 hours. About half of the butyl alcohol was distilled off, and the residue was poured into about 12 volumes of water. The dye was collected on a filter and washed with hot water. The yield of crude dye was 62 grams (97%), melting point 135–143° C. Crystallization from xylene yielded 40.7 grams (63%) of dye, melting point 158–160° C.

The leuco dye can also be oxidized by adding 40 ml. of water to the reaction mixture in butyl alcohol, adding 61.6 grams (0.4 mole) of sodium perborate tetrahydrate portionwise, and finally heating on a steam bath with stirring for 3 hours.

Analysis. Calculated for $C_{16}H_{10}F_3NO_3$: N, 4.3. Found: 4.2. 1-(2,2-DIFLUOROETHYLAMINO)-4-HYDROXYANTHRAQUINONE. A mixture of 2.42 grams (0.01 mole) of leucoquinazarin and 0.85 gram (0.0105 mole) of 2,2-diffuoroethylamine in 15 ml. of ethyl alcohol was refluxed for 20 hours. A few drops of piperidine and a few crystals of cupric acetate were added, then air was bubbled into the solution for 7 hours during heating on a steam bath. The reaction mixture was then cooled and filtered to yield 2.7 grams (89%) of dye, melting point 131–135° C. Crystallization from butyl alcohol raised the melting point to 141–142° C.

Analysis. Calculated for $C_{16}H_{11}F_2NO_3$: N, 4.6. Found: 4.8. 1,4-BIs(2,2-DIFLUOROETHYLAMINO)ANTHRAQUINONE. A mixture of 2.42 grams (0.01 mole) of leucoquinizarin and 2.03 grams (0.025 mole) of 2,2-difluoroethylamine in 20 ml. of amyl alcohol was heated in a sealed tube at 125° to 135° C. for 6 hours. The reaction product was then placed in a flask, treated with a few drops of piperidine and a few crystals of cupric acetate, and oxidized with air for 7 hours while being heated on a steam bath. The mixture was cooled and filtered to obtain 2.8 grams (77%) of product melting at 185° to 210° C.

The crude product was successively extracted with boiling ethyl alcohol, amyl alcohol, and carbon tetrachloride to remove 1-(2,2-difluoroethylamino)-4-hydroxyanthraquinone. The residue of 1,4-bis(2,2-difluoroethylamino)anthraquinone melted at 242-243°C.

Analysis. Calculated for $C_{18}H_{14}F_4N_2O_2$: N, 7.7. Found: 7.6. 1-(2,2-DIFLUOROPROPYLAMINO)-4-HYDROXYANTHRAQUINONE. A mixture of 2.42 grams (0.01 mole) of leucoquinizarin and 1.14 grams (0.012 mole) of 2,2-difluoropropylamine in 40 ml. of butyl alcohol was refluxed for 7 hours, then cooled and treated with 5 ml. of water and 2.31 grams (0.015 mole) of sodium perborate tetrahydrate. The reaction mixture was then heated for 2 hours, cooled, and poured into 600 ml. of hot water. The aqueous mixture was heated to remove part of the butyl alcohol, then cooled and filtered. The yield of crude, air-dried dye was 1.9 grams (60%), melting point 112–130° C. Crystallization from ethyl alcohol gave 0.75 gram of purified dye, melting point 135–138° C.

Analysis. Calculated for $C_{17}H_{13}F_2NO_3$: N, 4.4. Found: 4.2. 1 - HYDROXY - 4 - [2,2,2 - TRIFLUORO - 1 - (METHYL)ETHYL-AMINO]ANTHRAQUINONE. A mixture of 2.42 grams (0.01 mole) of leucoquinazarin and 1.41 grams (0.0125 mole) of 2,2,2-trifluoro-1-(methyl)ethylamine in 20 ml. of butyl alcohol was heated in a sealed tube for 24 hours at 150° C. The reaction mixture was then placed in a three-necked flask, treated with 3 ml. of water and 2.31 grams (0.015 mole) of sodium perborate tetrahydrate portionwise, and stirred at 90° to 95° C. for 3 hours. The mixture was poured into 400 ml. of hot water, stirred until cold, then filtered. The product was washed with water and dried. The yield was 2.5 grams (75%) of dye which, after crystallization from xylene, melted at 143-145° C.

1-(3,3-DIFLUOROPROPYLAMINO)-4-HYDROXYANTHRAQUINONE. A mixture of 1.2 grams (0.005 mole) of leucoquinizarin and 0.5 gram (0.0053 mole) of 3,3-difluoropropylamine in 50 ml. of butyl alcohol was refluxed for 18 hours. Then 5 ml. of water and 1.2 grams of sodium perborate tetrahydrate were added. The mixture was refluxed for 1 hour, then poured into 1 liter of dilute (5 to 10%) hydrochloric acid. The product was filtered and

washed with water. The crude dye was crystallized from butyl alcohol

1-(4,4-DIFLUOROPENTYLAMINO)-4-HYDROXYANTHRAQUINONE. A mixture of 1.4 grams (0.0058 mole) of leucoquinizarin and 0.75 gram (0.006 mole) of 4,4-diffuoropentylamine in 20 ml. of butyl alcohol was refluxed with stirring on a steam bath for 17 hours. The mixture was cooled somewhat, treated with 3 ml. of water and 1.34 grams (0.0087 mole) of sodium perborate tetrahydrate in portions, then heated for 3 hours with stirring. The reaction mixture was poured with stirring into hot water, stirred for about an hour, then filtered. The somewhat tacky product was crystallized from 50 ml. of ethyl alcohol to yield 0.85 gram (43%) of dye, melting point 128–130° C.

Analysis. Calculated for C₁₉H₁₇F₂NO₃: N, 4.1. Found: 3.8.



Figure 1. Boiling points of fluoroalkylamines

Preparation of Fluoroalkylamines. 2,2,2-TRIFLUOROETHYL-AMINE (3, 18). A rocking autoclave containing 450 grams (7.4 moles) of 28% ammonium hydroxide and 1 gram of Nacconol NR was cooled to -20° C. in a dry ice bath. To this solution was added 134 grams (1.13 moles) of 2-chloro-1,1,1-trifluoroethane (boiling point 6° C.), similarly cooled. The autoclave was shaken and heated at 185–190° C. for 29 hours. It was then cooled to room temperature and finally in ice to 0° to 5° C.

The reaction mixture was transferred to a cooled, 2-liter, roundbottomed flask, using a little ice water for rinsing. The flask was fitted with a 2-foot packed column and a still head which led in turn to a water-jacketed condenser and receiver, a large, icecooled test tube, and a dry ice-cooled condenser and receiver. The crude amine was collected at 28° to 50° C., the major part distilling at 33° to 38° C. The distillate consisted of 48 grams in the water-cooled receiver, 5 grams in the ice-cooled test tube, and 75 grams in the dry ice-cooled receiver. Of the 75 grams, two thirds was liquid ammonia, which was evaporated at 0° C. to leave 26 grams of residue. The combined 79 grams of crude amine, containing some ammonia and water, was dried over potassium hydroxide, then fractionated over potassium hydroxide through a packed column. There was no forerun or residue, and 59 grams (53%) of 2,2,2-trifluoroethylamine, boiling point 35–36° C., was obtained.

A similar experiment using 2-bromo-1,1,1,1-trifluoroethane (14) and heating for 31 hours at 185° C. gave a 55% yield of amine.

2,2-DIFLUOROETHYLAMINE (25). A mixture of 173 grams (1.72 moles) of 2-chloro-1,1-difluoroethane (14) and 630 grams (10.1 moles) of 28% ammonium hydroxide was heated in a rocking autoclave at 135° to 140° C. for 31 hours. The autoclave was cooled, and the contents were removed and filtered. The ammonia-amine filtrate was then carefully distilled through a 10-plate, helix-packed column with an efficient condenser and water-jacketed receiver. The receiver in turn led to an ice-salt trap to condense any amine that was carried over by entrainment with ammonia. The distillate (104 grams), which

PRODUCT AND PROCESS DEVELOPMENT

contained considerable ammonia and some water, was then dried over solid sodium hydroxide and redistilled. The yield of 2,2-difluoroethylamine, boiling point $68-69^{\circ}$ C., was 91.7 grams (65%).

Similar experiments heating 223 grams (1.54 moles) of 2bromo-1,1-diffuoroethane with 560 grams (9.2 moles) of 28% ammonium hydroxide at 125° C. for 24 hours yielded 65 to 82 grams (52 to 65%) of 2,2-diffuoroethylamine, boiling point 68-69° C., and 4 to 6 grams (5%) of 2,2,2',2'-tetraffuorodiethylamine, boiling point 122-123° C.

3,3-DIFLUOROPROPYLAMINE. A mixture of 130 grams (0.82 mole) of 1-bromo-3,3-diffuoropropane (14) and 295 grams (4.8 moles) of 28% ammonium hydroxide was heated in a rocking autoclave at 110° to 120° C. for 24 to 26 hours. The reaction mixture was then neutralized by pouring into 500 ml. of a mixture of ice and concentrated hydrochloric acid. The strongly acid solution was filtered, and the filtrate was evaporated to dryness under vacuum on a steam bath.

The dried residue was extracted with eight 200-ml. portions of boiling absolute ethyl alcohol and the hot solutions were decanted through a suction filter to remove the soluble amine hydrobromide from the ammonium bromide. The combined filtrates were concentrated to dryness under vacuum. The residue of amine hydrobromide was cooled in an ice bath and neutralized with an excess of 50% potassium hydroxide solution. This mixture was then extracted with four 250-ml. portions of ether to dissolve the liberated amine. The ether solution was dried over potassium hydroxide and the solvent was distilled.

Fractionation of the crude amine through a packed column yielded 19.9 grams (26%) of 3,3-difluoropropylamine, boiling point 92–94° C., n_D^{20} 1.3650, and 12.8 grams (18%) of 3,3,3',3'-tetrafluorodipropylamine, boiling point 91–94° C. (50 mm.), n_D^{20} 1.3744.

Analysis. Calculated for $C_8H_7F_2N$; C, 37.9; H, 7.4: N, 14.7. Found: C, 36.8; H, 7.9; N, 13.7. Calculated for $C_6H_{11}F_4N$: C, 41.6; H, 6.4; N, 8.1. Found: C, 42.0; H, 6.6; N, 7.9.

2,2-DIFLUOROPROPYLAMINE. A mixture of 79.5 grams (0.5 mole) of 1-bromo-2,2-diffuoropropane (14), 180 grams (3.0 moles) of 28% ammonium hydroxide, and 200 ml. of ethyl alcohol was heated in a rocking autoclave at 135° C. for 19 hours, then at 150° C. for 29 hours. The contents were poured into an excess of a mixture of ice and concentrated hydrochloric acid. The ethyl alcohol and hydrochloric acid were removed under reduced pressure from the residue of ammonium bromide and amine hydrobromide. The amine hydrobromide was extracted from the ammonium bromide with absolute ethyl alcohol.

The solution of the amine hydrobromide in ethyl alcohol was evaporated to dryness under reduced pressure. The dry salt was treated with a solution of 200 grams of potassium hydroxide in 170 ml. of water dropwise and then the flask was heated in an oil bath to distill off the free amine. The amine distilled at 45° to 83° C., mainly at 65° to 75° C. The crude product (11 grams) was dried over potassium hydroxide and redistilled to yield 8.2 grams (17%) of 2,2-diffuoropropylamine, boiling point 76-77° C., $n_{\rm D}^{25}$ 1.3622.

2,2,2-TRIFLUORO-1-(METHYL)ETHYLAMINE. A. In a rocking autoclave, cooled in dry ice, was placed a precooled mixture of 30 grams (0.27 mole) of trifluoroacetone, 18.8 grams (0.27 mole) of hydroxylamine hydrochloride, and a solution of 22 grams (0.27 mole) of sodium acetate in 100 ml. of water. The autoclave was heated at 90° to 100° C. for 6 hours. The reaction mixture, which consisted of an aqueous and an oily phase, was cooled and extracted with ether. The ether extract was dried over Drierite and distilled. The product consisted of 24 grams (70%) of the oxime, boiling point 90° to 106° C. [This wide boiling range was due to inadequate drying; Swarts (26) reported a boiling point of 102.5–103° C. for the pure, dry oxime.]

B. The oxime (24 grams, 0.189 mole) was hydrogenated in

ether solution in a rocking autoclave with Raney nickel at 60° C. for 15 hours at 2000 pounds per square inch. The pressure drop was 117 pounds per square inch (calculated 132 pounds per square inch). The ether solution was dried over Drierite and filtered. Treatment of the filtrate with a solution of hydrogen chloride in ether yielded 8 grams (30%) of amine hydrochloride, which was crystallized from an ethyl alcohol-ether mixture. The salt sublimed but did not melt.

Analysis. Calculated for $C_3H_6ClF_3N$: C, 24.4; H, 4.7; N, 9.4. Found: C, 24.3; H, 4.6; N, 9.3.

The crystallized amine hydrochloride (5.9 grams, 0.039 mole) was treated in a distillation apparatus with 50 grams of cold 50% sodium hydroxide solution. Distillation yielded a fraction, boiling point 46–48° C., which was redistilled over sodium hydroxide to obtain 3.3 grams (75%) of 2,2,2-trifluoro-1-(methyl)-ethylamine, boiling point 46–47° C., $n_{\rm D}^{20}$ 1.3210.

3,3,3-TRIFLUOROPROPYLAMINE. A. A mixture of 24.3 grams (0.18 mole) of 3-chloro-1,1,1-trifluoropropane (14) and 37.0 grams (0.20 mole) of potassium phthalimide was heated in a sealed tube in a rocking autoclave at 180° to 200° C. for 20 hours. The brown, crystalline solid obtained was washed with hot water and dried.

A portion of the N-(3,3,3-trifluoropropyl)phthalimide which was recrystallized twice from ligroin melted at 112–113° C.

Analysis. Calculated for $C_{11}H_8F_3NO_2$: C, 54.3; H, 3.3; N, 5.8. Found: C, 54.5; H, 3.3; N, 5.9.

The crude product was heated with concentrated hydrochloric acid in a sealed tube in a rocking autoclave for 24 hours at 200° C. The resulting mixture of brown needles and liquid was treated with warm water and filtered. The filtrate was evaporated to dryness, and the resulting amine hydrochloride was covered with ether and treated with 50% potassium hydroxide solution. Distillation of the ether solution yielded a small amount of 3,3,3-trifluoropropylamine, boiling point 67° C., n_D^{20} 1.3316.

Analysis. Calculation for $C_3H_6F_3N$: N, 12.4. Found: N, 11.7.

B. A mixture of 19.9 grams (0.15 mole) of 3-chloro-1,1,1trifluoropropane (14) and 54 grams (0.9 mole) of 28% ammonium hydroxide was heated in a sealed tube in a rocking autoclave at 175° C. for 24 hours. The reaction mixture was then acidified and evaporated to dryness. The residue was extracted several times with ethyl alcohol, and the alcohol was then removed to obtain the amine hydrochloride. The salt was covered with ether and treated with 50% potassium hydroxide solution. Distillation of the ether solution yielded a small amount of 3,3,3trifluoropropylamine, boiling range 55° to 75° C., n_{20}^{20} 1.3378.

4,4-DIFLUOROPENTYLAMINE. A mixture of 99.8 grams (0.7 mole) of 1-chloro-4,4-diffuoropentane (14) and 252 grams (5 moles) of 28% ammonium hydroxide was placed in a rocking autoclave and heated at 110° to 120° C. for 22 hours. The reaction mixture was filtered and then distilled through a packed column. The distillate (23 grams) collected from 60° to 100° C. was saturated with potassium hydroxide. The upper layer which separated was distilled over barium oxide to obtain 15 grams (18%) of 4,4-difluoropentylamine, boiling range 125° to 130° C., n_D^{25} 1.3864. Further distillation of the original aqueous reaction mixture caused the steam distillation of 3 grams of a heavy, yellow oil. This oil was dried over potassium hydroxide and distilled over barium oxide. A forerun, boiling range 131° to 170° C., and a fraction, boiling range 190° to 240° C., n_D^{25} 1.3920, were obtained. The latter was presumably 4,4,4',4'-tetrafluorodipentylamine.

Preparation of 2-Trifluoromethylanthraquinone Intermediates and Dyes. 1-CHLORO-2-METHYLANTHRAQUINONE (23). A mixture of 1200 grams (5.4 moles) of 2-methylanthraquinone, 1250 grams (9.2 moles) of sulfuryl chloride, and 37.5 grams of iodine in 1660 ml. of dry nitrobenzene was heated with stirring on a steam bath for 18 hours under an efficient condenser. The condenser was then removed and the excess sulfuryl chloride was evaporated on the steam bath using a stream of air. The reaction mixture was cooled, and the solid was collected on a vacuum filter. The crude product was purified by stirring with 12 liters of 3% sodium hydroxide solution, filtering, washing with methanol, and then crystallizing from 7 liters of glacial acetic acid. The yield of 1-chloro-2-methylanthraquinone was 778 grams (56%), melting point 158–159.5°C.

1-CHLORO-2-TRICHLOROMETHYLANTHRAQUINONE (23). A solution of 1735 grams (6.7 moles) of 1-chloro-2-methylanthraquinone in 1700 ml. of anhydrous o-dichlorobenzene was chlorinated at 170° to 175° C. for 56 hours using illumination from a 200-watt incandescent bulb. Chlorination was considered complete when a sample of the crude product, washed once with methanol, melted at 185° to 195° C. The hot reaction mixture was transferred to a 4-liter beaker and allowed to stand overnight at room temperature. The solid product was crystallized from 4.5 liters of chlorobenzene, washed with 2 to 2.5 liters of methanol, and dried at 100° C. The yield of 1-chloro-2-trichloromethylanthraquinone was 1360 grams (55%), melting point 203-205° C.

1-Chloro-2-Trifluoromethylanthraquinone (23). A mixture of 153 grams (0.45 mole) of 1-chloro-2-trichloromethylanthraquinone and 400 grams of anhydrous hydrogen fluoride was heated with shaking in a stainless steel autoclave at 150° C. for 18 hours. The hydrogen chloride and excess hydrogen fluoride were vented into a caustic solution when the bomb had cooled to 80° C. The autoclave was then cooled to room temperature and the contents were removed. The reaction mixture was heated on the steam bath for 30 minutes and then allowed to crystallize overnight. The solid was collected on a filter, washed with methanol, and dried at 100° C. The yield of 1chloro-2-trifluoromethylanthraquinone was 92 grams (70%), melting point 208° C.

1-AMINO-2-TRIFLUOROMETHYLANTHRAQUINONE (12). A mixture of 172 grams (0.55 mole) of 1-chloro-2-trifluoromethylanthraquinone and 500 ml. of 28% ammonium hydroxide was heated in a rocking autoclave at 140° to 150° C. for 10 hours. The solid product was collected on a filter, washed with water, and dried at 100° C. The yield of 1-amino-2-trifluoromethylanthraquinone was 155 grams (97%), melting point 144-146° C.

1-Amino-4-bromo-2-trifluoromethylanthraquinone (12). A solution of 50 grams (0.17 mole) of 1-amino-2-trifluoromethylanthraquinone in 300 ml. of 96% sulfuric acid was poured into a well stirred solution of 2.5 grams of ferrous sulfate and 2.5 grams of ferric chloride in 2.5 liters of water. The solution was treated with 30 grams of bromine at 50° to 55° C., and the temperature was then held at 60° to 70° C. for 18 hours. The solid was collected on a filter, washed with water, and dried at 100° C. Crystallization from 700 ml. of butyl alcohol yielded 38 grams (60%) of product, melting point $175-177^{\circ}$ C.

1 - Amino - 4 - $(p - \{2 - \{2 - [2 - (2 - Hydroxyethoxy)ethoxy]\}$ ETHOXY } ETHOXY } ANILINO) - 2 - TRIFLUOROME1HYLANTHRA-QUINONE. A mixture of 6.4 grams (0.017 mole) of 1-amino-4bromo-2-trifluoromethylanthraquinone, 5.6 grams (0.02 mole) of $p - (2 - \{2 - [2 - (2 - hydroxyethoxy)ethoxy]ethoxy\}ethoxy)$ aniline, 2.0 grams of fused potassium acetate, and 0.2 gram of cupric sulfate in 32 ml. of amyl alcohol was refluxed with stirring for 1.5 hours. The reaction mixture was then cooled, poured into 1 liter of water, and stirred for 1 hour. The product was collected on a filter, washed with water, and then dried in a vacuum desiccator. Crystallization from 75 ml. of xylene vielded 5.5 grams (67%) of dye, melting point 110-115° C.

Dyeing and Testing. The dyes were applied in the desired concentration to 10-gram samples of cellulose acetate jersey fabric from an aqueous dispersion by standard procedures. Dyed fabrics were tested for light fastness (2) and gas fastness (1) by the standard procedures of the American Association of Textile Chemists and Colorists.

Summary

A new series of pink to violet, fluorinated aminoanthraquinone dyes has been prepared by replacing one hydroxyl group of quinizarin with a fluoroalkylamino group.

On cellulose acetate some of these dyes show exceptional fastness to light and gas. The following list shows the order in which the N-fluoroalkyl groups enhance the fastness of the dyes and shift their color from violet toward pink:

$CH_3CF_2CH_2CH_2CH_2-$, $CHF_2CH_2CH_2- <$ $CH_3CF_2CH_2 - \langle CHF_2CH_2 -, CF_3CH_2 -, (CF_3)(CH_3)CH_2 - \rangle$

Thus, the number and the position of the fluorine atoms in the fluoroalkylamino group are both involved in the color shift and fastness properties.

The 1,4-bis(fluoroalkylamino)anthraquinone dyes are bluer but poorer in fastness and dyeing properties than the 1-fluoroalkylamino-4-hydroxyanthraquinone dyes.

Of the fluoroalkylamines prepared, 2,2-difluoropropylamine, 3,3-difluoropropylamine, 3,3,3-trifluoropropylamine, 2,2,2-trifluoro-1-(methyl)ethylamine, and 4,4-difluoropentylamine are compounds.

Another new series of fluorinated aminoanthraquinone dves has been prepared by introducing a CF_3 group in the 2- position of the nucleus. These dyes were prepared by the reaction of 1-amino-4-bromo-2-trifluoromethylanthraquinone with a series of o- and p-(hydroxypolyethoxy)anilines. They dye cellulose acetate bright blue shades, and some have excellent fastness to light and good fastness to gas. In general, they are superior to the corresponding dyes having a CN, CONH₂, SO₂CH₃, SCH_{3} , or CH_{3} group in the 2- position.

Literature cited

- (1) Am. Assoc. Textile Chemists and Colorists, "Technical Manual and Year Book," vol. 27, p. 91, Howes Publishing Co., New York, 1951. Ibid., p. 101. (2)
- (3) Benning, A. F., and Park, J. D. (to Kinetic Chemicals, Inc.), U. S. Patent 2,348,321 (1944).
- (4) Dickey, J. B. (to Eastman Kodak Co.), Ibid., 2,466,008 (1949).
- (5) Ibid., 2,466,009 (1949).
- (6) Ibid., 2,537,975 (1951).
- (7) Ibid., 2,543,767 (1951).
 (8) Ibid., 2,624,746 (1953).
- (9) Dickey, J. B., and Loria, A. (to Eastman Kodak Co.), Ibid., 2,510,088 (1950).
- Dickey, J. B., Loria, A., and Towne, E. B. (to Eastman Kodak Co.), *Ibid.*, 2,487,045 (1949).
- Dickey, J. B., and Towne, E. B. (to Eastman Kcdak Co.), *Ibid.*, 2,451,478 (1948).
- (12) Ibid., 2,537,976 (1951).
- (13) Ibid., 2,539,406 (1951).
- (14) Dickey, J. B., Towne, E. B., Bloom, M. S., Taylor, G. J., Hill,
 H. M., Corbitt, R. A., McCall, M. A., and Moore, W. H.,
 IND. ENG. CHEM. 46, 2213 (1954).
- (15) Dickey, J. B., Towne, E. B., Bloom, M. S., Taylor, G. J., Hill, H. M., Corbitt, R. A., McCall, M. A., Moore, W. H., and Hedberg, D. G., Ibid., 45, 1730 (1953).
- (16) FIAT Final Report No. 1114, p. 46; BIOS Report 987; PB Report 75,860, U.S. Dept. Commerce.
- (17) Fox, M. R., J. Soc. Dyers Colourists 65, 515 (1949).
- (18) Gilman, H., and Jones, R. G., J. Am. Chem. Soc. 65, 1458 (1943)
- (19) I. G. Farbenindustrie, Brit. Patents 480,749, and 493,211 (1938).
- (20) Locher, A., and Fierz, H. E., Helv. Chim. Acta 10, 642 (1927).
- (21) Nawiasky, P., and Krause, A. (to General Aniline Works), U.S. Patent 1,894,191 (1933).
- (22) Ruggli, P., and Heitz, W., Helv. Chim. Acta 14, 257 (1931)
- (23) Scherer, O. (to I. G. Farbenindustrie), German Patent 713,745 (1941).
- (24) Schlichenmaier, H., and Berlin, L. (to I. G. Farbenindustrie), Ibid., 693,610 (1940); Brit. Patent 495,375 (1938).
- (25) Swarts, F., Bull. classe sci., Acad. roy. Belg. 762, 955 (1904).
- (26) Ibid., 13, 175 (1927).

RECEIVED for review August 8, 1955. ACCEPTED December 2, 1955. Presented before the Chemistry Section, Tennessee Academy of Science, Nashville, Tenn., November 26, 1954.