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2,3-Difluorostyrene and 2-Chloro-5-fluorostyrene. The Preparation of Aromatic Fluorine Compounds

ERNST D. BERGMANN AND S. BERKOVIC

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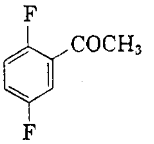
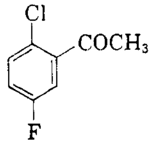
2,5-Difluorostyrene and 2-chloro-5-fluorostyrene have been prepared by conventional methods. The structure of the intermediate 2-chloro-5-fluoroacetophenone, prepared from *p*-chlorofluorobenzene and acetyl chloride, has been proven unambiguously. Polymers of the new styrene derivatives and co-polymers with styrene and methyl methacrylate has been prepared. In correction of a previous publication, it has been shown that the preparation of aromatic fluoro compounds by decomposition of diazonium fluoroborates in aqueous acetone in the presence of cuprous chloride or cupric fluoride is only possible if the aromatic amine contains no strongly polar substituent groups (e.g. hydroxyl, nitro, carboxyl). Fourteen cases are described in which this modification of Schiemann's method has been successful, and the mechanism of the reaction is discussed briefly.

2,5-Dichlorostyrene is known to have useful properties as a material for potting compositions[1-4]: In spite of the presence of the chlorine atoms its polymer has about the same dielectric constant and dielectric loss factor as polystyrene, as the dipole moments of the two C—Cl bonds in *para*-position to each other give an overall dipole moment of zero. On the other hand, Brooks[5] has pointed out that the polymer of 2,6-difluorostyrene is superior to polystyrene in many respects; it has a high softening point (as 2,5-dichlorostyrene), is thermally very stable, and, in spite of a higher dielectric constant, shows very small dielectric losses. It seemed, therefore, interesting to synthesize and study the hitherto unknown 2,5-difluorostyrene, which should electrically resemble the 2,5-dichloro compound and thermally the 2,6-difluoro isomer.

Two synthetic routes were employed, following our previous observations in the synthesis of 2,5-dichlorostyrene.[6,7] *p*-Difluorobenzene was converted by the Friedel-Crafts reaction into 2,5-difluoroacetophenone (I) which was converted by means of aluminum isopropoxide to the corresponding secondary alcohol and by dehydration over activated alumina at 310° into 2,5-difluorostyrene. The over all yield in these three steps was 47%. Alternatively, *p*-fluorobenzene was ethylated with gaseous ethylene and the 2,5-difluoroethylbenzene obtained brominated and dehydrobrominated. In this case, the overall yield was only 20%. In neither of these two syntheses was an isomerization of *p*-difluorobenzene observed as occurs when *p*-dichloro- or dibromobenzene are subjected to reactions involving aluminum chloride.[6]



I



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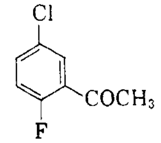

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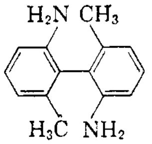

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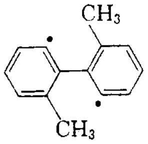

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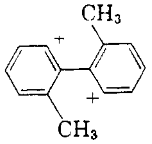

VIII

Analogously, 2-chloro-5-fluorostyrene was obtained *via* 2-chloro-5-fluoroacetophenone (II), which in turn was formed from *p*-chlorofluorobenzene and acetyl chloride in the presence of aluminum chloride. The product of the Friedel-Crafts reaction was homogeneous; only an insignificant amount of by-product was obtained which may have been the isomeric 5-chloro-2-fluoroacetophenone (III). The structure of II was established by hypobromite oxidation to the corresponding chlorofluorobenzoic acid. This acid was compared with 2-chloro-5-fluoro- (IV) and 5-chloro-2-fluorobenzoic acid (V) and was found identical with the first one. The synthesis of the two acids is illustrated in the accompanying chart.

It is somewhat surprising that in acetylation of *p*-chlorofluorobenzene the acetyl group enters the position *ortho* to the chlorine, and not to the fluorine atom. However, in the halobenzene series, nitration attacks more extensively the *ortho*-position, the larger the halogen atom, an effect that has been attributed by Ingold[8] to the selec-

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(1) A. von Hippel and L. G. Wesson, *Ind. Eng. Chem.*, **38**, 1121 (1946).

(2) E. B. McMillan, U. S. Patent Appl. **715,138** [*Chem. Abstr.*, **46**, 5227 (1952)].

(3) P. J. Franklin and M. Weinberg, *Plastics*, **7**, No. 1, 57 (1947) [*Chem. Abstr.*, **41**, 6765 (1947)].

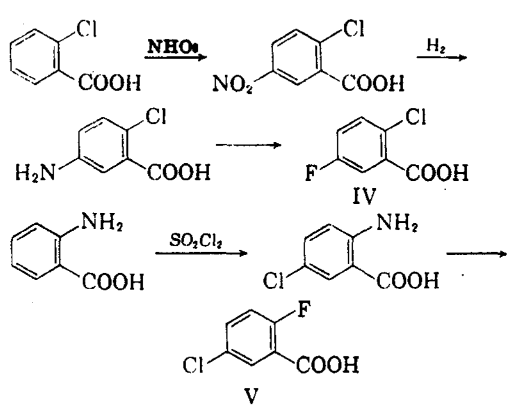
(4) P. J. Franklin, D. M. French, and W. C. Nyberg, *Chem. Abstr.*, **45**, 384 (1951).

(5) L. A. Brooks, *J. Am. Chem. Soc.*, **66**, 1295 (1944). *Cf.* J. C. Michalek, U. S. Patent 2,916,523 [*C.A.*, **54**, 8726 (1960)].

(6) S. Berkovic, *J. Org. Chem.*, **20**, 1322 (1955).

(7) For other fluorine-substituted styrenes, see: L. A. Brooks, *J. Am. Chem. Soc.*, **66**, 1295 (1944); G. B. Bachman and L. L. Lewis, *J. Am. Chem. Soc.*, **69**, 2022 (1947); C. S. Marvel and D. W. Hein, *J. Am. Chem. Soc.*, **70**, 1895 (1948).

(8) C. K. Ingold, *Structure and Mechanism in Organic Chemistry* (Cornell University Press, Ithaca, 1953), p. 260.



tive polar deactivation of the *ortho*-positions by halogen in accordance with the order of their electronegativities, which overrides the effect of the sizes of the atoms.

The polymers of the two new disubstituted styrenes[9] and their copolymers[10] with styrene and methyl methacrylate have been prepared, using benzoyl peroxide as catalyst, and their properties have been studied. The polymers had dielectric constant of 2.40 and 2.60 and the expectedly low loss factors 0.0005 and 0.0015, respectively (polystyrene 2.5–2.6 and 0.0002–0.0003; poly-2,5-dichlorostyrene 0.0002–0.0004 and 2.62).

For the preparation of *p*-difluorobenzene and *p*-chlorofluorobenzene, we used the method described by us some time ago,[11] *viz.* the decomposition of the diazonium fluoroborates, derived from *p*-phenylenediamine and *p*-chloroaniline, respectively, in acetone and in the presence of cuprous chloride or cupric fluoride at low temperature (20–56°). In studying this handy modification of the Schiemann reaction further, we have however found that it is not as reliable as indicated in our previous publication. Catalytic factors of unknown nature appear to play an important role and lead to erratic and often irreproducible results. A renewed study has led to the following conclusion which has been substantiated by many repetitive experiments. By the modified procedure, only aromatic amines can be converted into the corresponding fluoro compounds which either carry no additional substituents or only alkyl groups and/or halogen atoms. When the molecule contains strongly polar groups (*e.g.*, hydroxyl, nitro, carboxyl), the method is not reliable. In the Experimental of this paper, a number of cases are described in which results were consistently positive.[12]

In our previous paper, it had been suggested tentatively that the reaction described for the decomposition of diazonium fluoroborates at low temperature and in solution proceeds through a *radical* mechanism. This hypothesis appears to be supported by the observation that the application of the method to optically active ($[\alpha]_D^{20}$ −33.1°) 2,2′-diamino-6,6′-dimethylbiphenyl (VI) gave an almost inactive ($[\alpha]_D^{20}$ −0.45°) 2,2′-difluoro-6,6′-dimethylbiphenyl. Bell[13] has shown that decomposition at 100° gives a still more racemized product, $[\alpha]_D$ −0.14°. One would assume that only a free radical like VII, but, for electrostatic reasons, not a carbonium ion like VIII will be able to racemize under the above conditions by rotation around the central bond as axis. It may be recalled that the radical mechanism for the decomposition of fluoroborates has also been postulated by Nesmeyanov[14] on the basis of the observation that in the decomposition of benzenediazonium fluoroborate in benzene and in the presence of lead, tetraphenyl lead is formed. Contrary to the observations with the above diazonium fluoroborate, transformation of the diazonium hydrochloride into the diiodo analog is not accompanied by racemization.

EXPERIMENTAL

2,5-Difluoroacetophenone (I). To a mixture of 114 g. of *p*-difluorobenzene[11] and 320 g. of aluminum chloride, 120 g. of acetyl chloride was added slowly at 60°. The product was heated at 95° for 90 min. with continued agitation and poured onto a mixture of 2 kg. of ice and 500 ml. of concd. hydrochloric acid. Extraction with ether and distillation gave the desired ketone (88 g.; 57%) which boiled at 61° (5 mm.); n_D^{22} 1.4863; d_{22}^{22} 1.2099; $\lambda_{max}^{C_2H_5OH}$ 234 mμ (4.20); 288 mμ (3.48); ν_{max} 1689 (carbonyl); 907, 894 cm.$^{-1}$(1,2,4-trisubstituted benzene).

Anal. Calcd. for $C_8H_6F_2O$: C, 61.5; H, 3.8. Found: C, 61.5; H, 3.8.

The *2,4-dinitrophenylhydrazone* melted after recrystallization from alcohol at 157°.

Anal. Calcd. for $C_{14}H_{10}F_2N_4O_4$: C, 50.0; H, 3.0. Found: C, 50,3; H, 3.3.

2,5-Difluorophenylmethylcarbinol. A mixture of 85 g. of I, 170 g. of aluminum isopropoxide, and 650 ml. of ixopropyl alcohol was heated in a column until no more acetone appeared in the distillate (6.5 hr.). After cooling, the mixture was treated with 650 ml. of dilute (10%) hydrochloric acid and extracted with benzene. The secondary alcohol (80 g., 92%) boiled at 84° (10 mm.); 71° (3.5 mm.). The compound loses water easily; n_D^{20} 1.4720; d_{20}^{20}1.1683.

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(9) For other polymers of fluorinated styrenes, see L. A. Brooks and M. Nazzewski, U. S. Patent 2,406,319 [*Chem. Abstr.*, **41**, 314 (1947)], and W. C. Wooten and H. W. Coover, *J. Polymer Sci.*, **37**, 560 (1959).

(10) For other copolymers of fluorinated styrenes, see L. A. Brooks and M. Nazzewski[9]; C. S. Marvel, G. E. Inskeep, R. Deanin, D. W. Hein, P. V. Smith, J. D. Young, A. E. Juve, C. H. Schroeder, and M. M. Goff, *Ind. Eng. Chem.*, **40**, 2371 (1948); C. S. Marvel, G. E. Inskeep, R. Deanin, A. E. Juve, C. H. Schroeder, and M. M. Goff, *Ind. Eng. Chem.*, **39**, 1486 (1947).

(11) E. D. Bergmann, S. Berkovic, and R. Ikan, *J. Am. Chem. Soc.*, **78**, 6037 (1956).

(12) In the previous paper,[11] the preparations of 1- and 2-fluoroanthraquinone were not pure. The two quinones, prepared by Schiemann's method, have m.p. 193–194° and 203–204°, respectively. *Cf.* F. C. Hahn and E. E. Reid, *J. Am. Chem. Soc.*, **46**, 1645 (1924).

(13) F. Bell, *J. Chem. Soc.*, 835 (1934).

(14) A. N. Nesmeyanov, L. G. Makarova, and T. P. Tolstaya, *Tetrahedron*, **1**, 145 (1957). *Cf.* L. G. Makarova and M. K. Matveeva, *Chem. Abstr.*, **52**, 19994 (1958); L. G. Makarova and E. A. Gribchenko, *Chem. Abstr.*, **52**, 20002 (1958); L. G. Makarova, M. K. Matveeva, and E. A. Gribchenko, *Chem. Abstr.*, **53**, 8057 (1959).

Anal. Calcd. for $C_8H_8F_2O$: C, 60.8; H, 5.1. Found: C, 60.7; H, 5.1.

2,5-Difluoroethylbenzene. into a well agitated mixture of 34 g. of *p*-difluorobenzene and 40 g. of aluminum chloride, which was heated at 90°, 6.7 l. of ethylene was passed at the rate of 0.2 l./min. The stirring was continued for 30 min. at room temperature and the mixture decomposed with 200 g. of ice and 70 ml. of concd. hydrochloric acid and extracted with ether. Fractionation yielded some unchanged *p*-difluorobenzene, and 8 g. (32%) of 2,5-difluoroethylbenzene, b.p. 60–61° (45 mm.); n_D^{23} 1.4557; d_{23}^{23} 1.1003. MR, calcd. 35.22; MR, fd. 35.06.

Anal. Calcd. for $C_8H_8F_2$: C, 67.6; H, 5.6. Found: C, 67.4; H, 5.5. A small, higher boiling fraction (75–76°/17 mm.) was, according to the analysis, 2,5-difluoro-1,4(?)-diethylbenzene.

Anal. Calcd. for $C_{10}H_{12}F_2$: C, 70.6; H, 7.1. Found: C, 70.0; H, 6.7.

2,5-Difluoro-α-bromoethylbenzene. To a mixture of 7 g. of the foregoing compound, 0.1 g. of benzoyl peroxide, and 70 ml. of carbon tetrachloride, 16 g. of bromine was added slowly at water bath temperature. When the addition of the halogen was complete, the mixture was heated for another 30 min., washed with 1% sodium bicarbonate solution and water, dried, and distilled; b.p. 79–80° (10 mm.); yield, 9. g. (85%); n_D^{22} 1.5170; d_{22}^{22} 1.5402; MR, calcd. 42.93; MR, fd. 43.41.

Anal. Calcd. for $C_8H_7BrF_2$: C, 43.4; H, 3.2. Found: C, 43.5; H, 3.3.

2,5-Difluorostyrene. (a) 2,5-Difluorophenylmethylcarbinol (115 g.) was passed through a vertical column filled with alumina at a temperature of 310°, a pressure of 70 mm., and a rate of 1 drop per sec. The reaction product was collected in a trap cooled with acetone and Dry Ice; it was separated from the water formed, washed with water, dried, and distilled. Thus, 82 g. (90%) of 2,5-difluorostyrene, b.p. 52–53° (23 mm.); 43–44° (14 mm.), and 16 g. of unchanged starting material were obtained. n_D^{26} 1.4910; d_{26}^{26} 1.1266. MR, calcd., 34.77; MR, found, 35.99.

The infrared spectrum showed the vinyl bands at 910 and 970 cm.$^{-1}$

Anal. Calcd. for $C_8H_6F_2$: C, 68.7; H, 4.3. Found: C, 69.0; H, 4.5.

(b) At 170° and a pressure of 70 mm, 16.0 g. of 2,5-difluorophenylmethylcarbinol was added dropwise to a mixture of 2 g. of powdered potassium hydrogen sulfate and 2 g. of hydroquinone. Under these conditions, the 2,5-difluorostyrene distilled as soon as it was formed. It was separated by means of a short column; yield, 9.1 g. (65%).

(c) At 200° and a pressure of 60 mm, 7 g. of 2,5-difluoro-α-bromoethylbenzene was added dropwise to 4 g. of potassium hydroxide, so that the product formed distilled at once. It was washed with water, dried, and distilled; yield, 3.2 g. (75%).

p-Chlorofluorobenzene. A mixture of 127 g. of *p*-chloroaniline, 350 ml. of fluoroboric acid (55%), and 150 ml. of water was cooled to −5° and diazotized with a solution of 69 g. of sodium nitrite in 150 ml. of water. The diazonium fluoroborate crystallized. It was filtered off, washed with dilute fluoroboric acid, methanol, and ether and dried; yield, 181 g. (80%); dec. pt. 121–124°. A solution of 50 g. of the diazonium salt in 300 ml. of acetone was refluxed in the presence of 0.5 g. of cuprous chloride for 3 hr. Distillation gave 4.5–5.0 g. (16%) of the desired product, b.p. 130–131°.

Anal. Calcd. for C_6H_4ClF: C, 55.3; H, 3.1. Found: C, 55.8; H, 3.0.

2-Chloro-5-fluoroacetophenone (II). To a well agitated mixture of 82.5 g. of the foregoing substance and 240 g. of aluminum chloride, heated on a boiling water bath, 85 g. of acetyl chloride was added slowly. The reaction mixture was agitated for one more hour, and poured into a mixture of 500 g. of ice and 300 ml. of concd. hydrochloric acid. The product was washed with sodium bicarbonate and water, dried, and distilled; it boiled at 81–82° (5 mm.); 77–78° (4 mm.); yield, 57.5 g. (54%). n_D^{23} 1.5250; d_{23}^{23} 1.2884; MR, calcd., 40.28; MR, fd., 41.03. $\lambda_{max}^{C_2H_5OH}$ 235 mμ (3.78); 277 mμ (3.40); $\tilde{\nu}_{max}$ 1689 cm.$^{-1}$ (carbonyl).

Anal. Calcd. for C_8H_6ClFO: C, 55.7; H, 3.4. Found: C, 54.9; H, 3.8.

It is noteworthy that both in 2,5-difluoro- and in 2-chloro-5-fluoroacetophenone the substitution has a hypsochromic effect on the spectrum of acetophenone (λ_{max} 243 mμ; 296mμ).[15]

The *2,4-dinitrophenylhydrazone* was recrystallized from a mixture of ethanol and ethyl acetate and melted at 199–200°.

Anal. Calcd. for $C_{14}H_{10}ClFN_4O_4$: C, 47.7; H, 2.8. Found: 48.0; H, 3.1.

2-Chloro-5-fluorobenzoic acid (IV) from (II). With vigorous stirring, 8 g. of II was added to 50 ml. of a 1.3 *N* solution of sodium hypobromite at room temperature (24°). When the addition was complete, the stirring was continued for 2.5 hr. and the excess of hypobromite destroyed by addition of sodium bisulfite solution. The acid formed was precipitated from the alkaline solution with dilute hydrochloric acid and recrystallized from water, yield, 1.5 g. (19%); m.p. 125°.

Anal. Calcd. for $C_7H_4ClFO_2$: C, 48.3; H, 2.3. Found; C, 48.6; H, 2.1.

2-Chloro-5-fluorophenylmethylcarbinol. A solution of 30.5 g. of II in 200 ml. of isopropyl alcohol was reduced in the usual manner with 54 g. of aluminum isopropoxide. The reaction took 6.5 hr., during which period most of the solvent distilled with the acetone formed. The product was decomposed with 300 ml. of cold 10% hydrochloric acid and extracted with benzene. It boiled at 98–100° (7 mm.); yield, 28 g. (95%); n_D^{24} 1.5200; d_{24}^{24} 1.2635. MR, calcd., 41.77; MR, fd., 42.40.

Anal. Calcd. for C_8H_8ClFO: C, 55.2; H, 4.6. Found: C, 55.1; H, 4.8.

2-Chloro-5-fluorostyrene. In the manner described for the preparation of 2,5-difluorostyrene, the foregoing compound (28 g.) was dehydrated over activated alumina at 340° and 70 mm. pressure. The product boiled at 67–68° (13 mm.); yield, 20 g. (78%); n_D^{23} 1.5365; d_{23}^{23} 1.2098; MR, calcd., 39.77; MR, fd., 40.34. The infrared spectrum showed the vinyl bands at 910 and 970 cm.$^{-1}$

Anal. Calcd. for C_8H_6ClF: C, 61.6; H, 3.8. Found: C, 61.7; H, 4.0.

2-Chloro-5-fluorobenzoic acid (IV). (a) At 0°, a mixture of 16 g. of nitric acid (80%) and 40 g. of concd. sulfuric acid was added, with stirring, to 32 g. of *o*-chlorobenzoic acid in 160 g. of concd. sulfuric acid. After 12 hr. at room temperature and a few minutes at 60°, the reaction product was poured onto 400 g. of ice and the solid which precipitated, filtered, and recrystallized from boiling water. 2-Chloro-5-nitrobenzoic acid (37.5 g.; 92%) melted at 164° (literature,[16] m.p. 164–165°).

(b) A solution of 34 g. of the foregoing acid in 150 ml. of glacial acetic acid was reduced catalytically at room temperature and atmospheric pressure (Parr bomb) in the presence of palladium-charcoal (10%) as catalyst. 5-Amino-2-chlorobenzoic acid melted, after recrystallization from alcohol, at 185–188° (literature,[17] m.p. 185°); yield, 18 g. (69%).

(c) At −10°, a solution of 18 g. of 5-amino-2-chlorobenzoic acid in 95 ml. of fluoroboric acid (60%) was diazotized with a mixture of 7.5 g. of sodium nitrite in 30 ml. of water. The diazonium fluoroborate which is fairly soluble in water, crystallized on cooling; it was filtered, washed with water, cold methanol, and ether, and dried. It was then decomposed thermally according to Schiemann's method and the product extracted with ether. The solid ether residue was reprecipitated from its solution in sodium carbonate with dilute hydrochloric

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(15) M. Stamper and B. F. Aycock, *J. Am. Chem. Soc.*, **76**, 2786 (1954).

(16) H. Fierz-David and L. Blangey, *Fundamental Processes of Dye Chemistry*, Interscience Publ. Co., New York, 1949, p. 169.

(17) H. Huebner and R. Biedermann, *Ann.*, 147, 257 (1868); H. Huebner, *Ann.*, **222**, 166, especially 198 (1884), m.p. 185°, 188–188.5°.

acid and recrystallized from benzene. Melting point and mixed melting point with the oxidation product of II was 124°; yield, 6 g. (30%).

5-Chloro-2-fluorobenzoic acid (V). (a) During 10 min., 20 g. of anthranilic acid was added in small portions to a solution of 26 g. of sulfuryl chloride in 350 ml. of anhydrous ether. The ether and the excess of sulfuryl chloride were removed *in vacuo* and the residue heated at 60–70° for 1 hr. with 400 ml. of 8% hydrochloric acid. The solid was filtered off and the filtrate made just alkaline. The precipitation of 5-chloroanthranilic acid was completed by addition of a concentrated sodium acetate solution and the product recrystallized from aqueous alcohol (1:1); yield, 8 g. (32%); m.p. 204° (lit.,[18] m.p. 204°).

(b) At −6°, a solution of 7 g. of the foregoing acid in 10 ml. of fluoroboric acid (60%) and 50 ml. of water was diazotized with 3.0 g. of sodium nitrite in 25 ml. of water. As the diazonium fluoroborate did not crystallize, 0.5 g. of cuprous chloride was added, and the aqueous solution refluxed for 1 hr. on the water bath. The reaction product was isolated by extraction with ether and purified by reprecipitation from alkali and recrystallization from benzene; yield, 2.9 g. (36%); m.p. 151–152°.

Anal. Calcd. for $C_7H_4ClFO_2$: C, 48.3; H, 2.3. Found: C, 47.9; H, 2.3.

In the following paragraphs, the preparation of some fluoroaromatics by the variation of Schiemann's method is described briefly.

p-Fluorobromobenzene. *p*-Bromoaniline, 50 g., 300 ml. of fluoroboric acid (30%), and 21 g. of sodium nitrite in 50 ml. of water at −5° gave 67 g. (50%) of the diazonium fluoroborate (dec. pt. 118–122°). From 45 g. of the salt in 250 ml. of boiling acetone (4.5 hr.) and 0.3 g. of cuprous chloride, 10.5 g. (30%) of b.p. 150–152° was obtained.

Anal. Calcd. for C_6H_4BrF: C, 41.1; H, 2.3; F, 10.9. Found: C, 40.8; H, 2.5; F, 10.6.

o-Fluorotoluene. *o*-Toluidine, 107 g., 450 ml. of 47% fluoroboric acid, and 69 g. of sodium nitrite in 150 ml. of water at −5° gave 165 g. (81%) of the diazonium fluoroborate (dec. pt. 105°). A 60-g. sample of this salt in 350 ml. of boiling acetone (3.5 hr.) and 0.5 g. of cupric fluoride yielded 7.4 g. (21%) of material, b.p. 114° (760 mm.).

Anal. Calcd. for C_7H_7F: C, 76.4; H, 6.4; F, 17.3. Found: C, 76.4; H, 6.3; F, 17.4.

m-Fluorotoluene. The above quantities gave 152 g. (75%) of the diazonium fluoroborate (dec. pt. 103–105°) and 7.4 g. (21%) of b.p. 116° (760 mm.). (Found: C, 76.3; H, 6.2).

p-Fluorotoluene. The above quantities gave 165 g. (82%) of the diazonium fluoroboate (dec. pt. 106–110°) and 6.0 g. (17%) of material, b.p. 119° (760 mm.). In this case, careful fractionation was necessary, in order to remove a small quantity of toluene.

2,3-Dimethylfluorobenzene. Diazotization of 72.5 g. of 2,3-dimethylaniline in 500 ml. of 28% fluoroboric acid with 41.5 g. of sodium nitrite in 100 ml. of water gave 116 g. (85%) of the diazonium salt (dec. pt. 90–92°). From 70 g. of this salt in 300 ml. of boiling acetone (3 hr.) and 0.5 g. of cupric fluoride, 11.5 g. (30%) of material, b.p. 148–152° (760 mm.) was obtained.

Anal. Calcd. for C_8H_9F: C, 77.4; H, 7.2; F, 15.4. Found: C, 77.8; H, 6.9; F, 15.5.

2,3-Dimethylnitrobenzene[19] was synthesized from 100 g. of *o*-xylene by addition of a mixture of 100 g. of nitric acid and 200 g. of concd. sulfuric acid at a temperature between −10° and 0°. The product was diluted with 1 l. of water and the organic layer distilled twice *in vacuo,* after it had been washed with 5% sodium hydroxide solution; b.p. 127–130° (15 mm.); yield, 122 g. (86%). Catalytic reduction in the presence of palladium-charcoal (10%) in glacial acetic acid as solvent gave 2,3-dimethylaniline[20], b.p. 98–100° (11 mm.); yield, 113 g. (93%).

2,4-Dimethylfluorobenzene. 2,4-Dimethylaniline, 67.5 g., in 400 ml. of 40% fluoroboric acid and 35 g. of sodium nitrite in 180 ml. of water gave 38 g. (35%) of the diazonium salt (dec. pt. 107–109°). The latter was refluxed with 250 ml. of acetone and 0.5 g. of cupric fluoride (4 hr.). Simultaneously, the mother liquor of the diazonium salt which was quite soluble in water, was heated on the water bath with 1 g. of copper powder. The combined products yielded, upon distillation, 7.5 g. (17%) of b.p. 143–144°.

Anal. Calcd. for C_8H_9F: F, 15.4 Found: F, 15.3.

2,4-Dimethylnitrobenzene[21] was prepared by nitration of 106 g. of *m*-xylene with 320 g. of fuming nitric acid at 0°; it boiled at 244° (760 mm.); yield, 140 g. (93%). Hydrogenation in the presence of 10% palladium-charcoal gave in quantitative yield *2,4-dimethylaniline*[22], b.p. 76–78° (3 mm.).

2,5-Dimethylfluorobenzene. Diazotization of 84 g. of 2,5-dimethylaniline in 500 ml. of 36% fluoroboric acid with 98 g. of sodium nitrite in 100 ml. of water gave 127 g. (82%) of the diazonium salt (dec. pt. 99–100°). From 60 g. of the salt and 0.5 g. of cupric fluoride in 300 ml. of boiling acetone (3.5 hr.), 2,5-dimethylfluorobenzene was obtained after careful fractionation from a small quantity of *p*-xylene in a yield of 6.5 g. (19%); b.p. 145–147° (760 mm.).

Anal. Calcd. for C_8H_9F: C, 77.4; H, 7.2. Found: C, 77.7; H, 7.9.

2,5-Dimethylnitrobenzene[23] was synthesized from 150 g. of *p*-xylene and 370 g. of fuming nitric acid at 5–7°; yield, 191 g. (90%); b.p. 64–65 (0.35 mm.). Catalytic hydrogenation as above gave *2,5-dimethylaniline,*[24] b.p. 217° (760 mm.). in 95% yield.

1-Fluoronaphthalene. The solutions of 14.5 g. of 1-naphtylamine in 200 ml. of 15% fluoroboric acid and of 6.9 g. of sodium nitrite in 60 ml. of water were added slowly to 150 ml. of 60% fluoroboric acid at −5°. The diazonium salt (22 g., 92%) (dec. pt. 110°) was decomposed with 10 g. of cuprous chloride in 200 ml. of boiling acetone (2 hr.); b.p. 212° (760 mm.); yield, 6.5 g. (46%).

Anal. Calcd. for $C_{10}H_7F$: C, 82.2; H, 4.8; F, 13.0. Found: C, 82.0; H, 5.1; F, 12.8%.

2-Fluoronaphthalene. The diazonium fluoroborate (dec. pt. 115°) was obtained in 93%, the fluoronaphthalene in 57% yield, using the same quantities and procedure as in the previous example. The product was purified by steam distillation and melted at 59°.

Anal. Found: C, 82.3; H, 5.0; F, 13.1.

2-Fluorobiphenyl.[25] 2-Aminobiphenyl, 170 g., in 650 ml. of 27% fluoroboric acid gave at −5° with 69 g. of sodium nitrite in 100 ml. of water 202 g. (75%) of the fluoroborate (dec. pt. 75–77). An 80-g. sample of this salt was decomposed in the presence of 0.5 g. of cuprous chloride in 350 ml. of boiling acetone (3.5 hr.). Purification by steam distillation gave 12 g. (24%); m.p. 70–71°.

Anal. Calcd. for $C_{12}H_9F$: C, 83.7; H, 5.2; F, 11.1. Found: C, 83,3; H, 5.6; F, 11.4.

4,4'-Difluorobiphenyl.[26] Simultaneously, 142.5 g. of benzidine dihydrochloride in 150 ml. of water and 33.5 g. of sodium nitrite in 130 ml. of water were added at 0° to 350 ml. of 43% fluoroboric acid; yield of tetrazonium bisfluoroborate was 176 g. (90%) (dec. pt. 140°). From 50 g. of the salt and 1 g. of cuprous chloride in 250 ml. of boiling acetone (3 hr.), 17.5 g.

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(18) D. H. Shirley, *Preparation of Organic Intermediates,* John Wiley and Sons, New York, 1951, p. 8.

(19) D. A. Shirley, *loc. cit.*, p. 222.

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(21) W. Hansen, *Ber.*, **13**, 1558 (1880).

(22) Beilstein, XII, 1111.

(23) H. R. Snyder and F. J. Pilgrim, *J. Am. Chem. Soc.*, **70**, 3787 (1948).

(24) Beilstein, XII, 1135.

(25) *Cf.* A. Roe and H. L. Fleishmann, *J. Am. Chem. Soc.*, **69**, 509 (1947). G. Schiemann and M. Roselius, *Ber.*, **62**, 1805 (1929).

(26) *Cf.* G. Schiemann and W. Winkelmueller, *Org. Syntheses*, Coll. Vol. II, 188 (1943).

(72%) of 4,4′-difluorobiphenyl, m.p. 86° (after steam distillation) was obtained.

Anal. Calcd. for $C_{12}H_8F_2$: C, 75.7; H, 4.2; F, 20.1. From: C, 75.9; H, 4.5; F, 19.2.

2,2′-Difluoro-6,6′-dimethylbiphenyl. *dl*-2,2′-Diamino-6,6′-dimethylbiphenyl (VI) was prepared according to Dethloff;[27] it melted after recrystallization from alcohol at 133–134°. The resolution, carried out according to Meisenheimer,[28] gave the (+) −form, m.p. 153–155°; $[\alpha]_D^{20}$ −34.0°, and the (−) −form, m.p. 152°, $[\alpha]_D^{20}$ +33.1° (both in dilute (3.5%) hydrochloric acid, *c* = 0.995 and 1.006, respectively).

At −10°, a solution of 9 g. of the (−)-form in 40 ml. of concd. hydrochloric acid and 90 ml. of water was diazotized with 7.0 g. of sodium nitrite in 15 ml. of water. Addition of 40 ml. of 55% fluoroboric acid precipitated the tetrazonium bisfluoroborate, 13 g. (75% yield) (dec. pt. 93–96°). At this stage, no appreciable racemization had taken place. $[\alpha]_D^{25}$ −38.5° (acetone; *c* 0.3).

A solution of 13 g. of the salt in 150 ml. of acetone was refluxed for 3 hr. in the presence of 0.25 g. of cupric fluoride. The acetone was distilled and the residue, after addition of 50 ml. of water, subjected to steam distillation. The product (1.6 g.; 20.5%) had m.p. 40°. $[\alpha]_D^{20}$ −0.45° (in chloroform, *c*, 1.940).

Anal. Calcd. for $C_{14}H_{12}F_2$: F, 17.4. Found: F, 16.8.

1-Fluoroanthraquinone. A solution of 11.2 g. of 1-aminoanthraquinone in 20 ml. of concd. sulfuric acid was diluted with 40 ml. of water and at 10° diazotized with a solution of 8 g. of sodium nitrite in 12 ml. of water. The product was filtered and cooled to 0° and 20 ml. of fluoroboric acid (60%) added. The diazonium fluoroborate was filtered and washed with water, methanol and ether; yield, 14 g. (87.5%); dec. pt. 142°. By normal decomposition of 8 g. of this salt, 4.0 g. (71%) of 1-fluoroanthraquinone was obtained. It was purified by sublimation and melted at 193–194°.

Anal. Calcd. for $C_{14}H_7FO_2$: C, 74.3; H, 3.1; F, 8.4. Found: C, 73.7; H, 3.1; F. 8.3.

2-Fluoroanthraquinone. To a solution of 11.2 g. of 2-aminoanthraquinone in a mixture of 40 ml. of glacial acetic acid, 35 ml. of concd. hydrochloric acid, and 10 ml. of water, a solution of 8 g. of sodium nitrite in 20 ml. of water was added at 20°. The solution was cooled to 0° and the diazonium fluoroborate (13.5 g.; 84%; dec. pt. 188–200°) precipitated by addition of 20 ml. of 60% fluoroboric acid. Thermal decomposition of 8 g. of this salt gave 2.7 g. (47%) of 2-fluoroanthraquinone, m.p. 203–204° after sublimation. A mixture of the two quinones melted at 184–186°.

Anal. Calcd. for $C_{14}H_7FO_2$: C, 74.3; H, 3.1; F, 8.4. Found: C, 74.6; H, 3.4; F, 8.3.

ADDED IN PROOF: While this paper was in press, a similar synthesis of 2,5-difluorostyrene was reported by T. V. Talalaeva, G. V. Kazennikova and K. A. Kocheshkov, *Fhur. Obshchei Klim.*, **29**, 1593 (1959) [*C.A.*, **54**, 8677 (1960)].

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[CONTRIBUTION FROM ALCHEM]

Preparation of Trifluoroacetic Acid

DONALD RAE ALLEN

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Trifluoroacetic acid has been prepared by the direct oxidation of 1,1,1-trifluoroethane with air and water vapor in a high voltage electric discharge. The reaction was uncomplicated by any side reactions.

The compound 1,1,1-trifluoroethane is readily prepared from vinylidene chloride and hydrogen fluoride (Equation 1). Oxidation of 1,1,1-trifluoroethane is thermodynamically spontaneous but attempts to produce trifluoroacetic acid using oxygen and vanadium oxide were without success (Equation 2). It was decided that oxidation of trifluoroethane might take place readily in a high voltage electric discharge. A reactor of Pyrex glass in the shape of a Dewar cylinder was fabricated and aluminum foil electrodes were wrapped on the outside of the glass (Fig. 1). Electrical power for the reactor was furnished by an Acme neon sign transformer (Model 4611397–484393) using 110 volts a.c. primary and delivering 15,000 volts a.c. open circuit at its secondary terminals. Initial experiments of passing air and trifluoroethane through the operating reactor at atmospheric pressures did not produce any trifluoroacetic acid, but rather de-

$$CH_2{=}CCL_2 + 3HF \longrightarrow CF_3CH_3 + 2HCL \qquad (1)$$

$$CF_3CH_3 + 1^1/_2O_2 \longrightarrow CF_3CO_2H + H_2O \qquad (2)$$

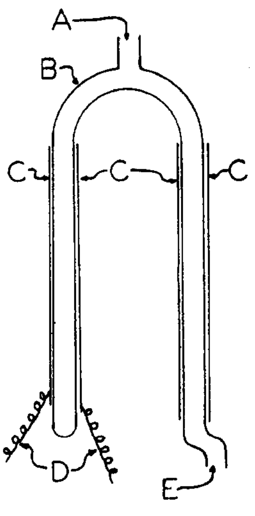

Fig. 1. Reactor used to prepare trifluoroacetic acid. *A*. Port of entry for gaseous mixture of air, 1,1,1-trifluoroethane, and water vapor. *B*. Reactor vessel having the shape of a Dewar cylinder and constructed of Pyrex glass tubing. *C*. Aluminum foil wraps for electrodes. *D*. Electrical leads for application of 15,000 volts a.c. to electrodes. *E*. Exit port for gaseous mixture leaving reactor.