have been prepared by the addition of aromatic thiols or sulfinic acids to β-nitrostyrene and some of its derivatives. Some of the sulfides and sulfones have been reduced to the corresponding β-(arylmercapto)- or β-(arylsulfonyl)-phenethylamines by zinc and acetic acid or stannous chloride and alcoholic hydrochloric acid.

The preparation of N,N-dimethyl-β-(*p*-tolylmercapto)-phenethylamine is described.

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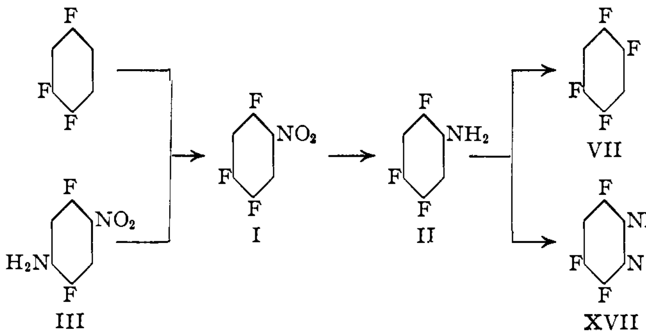
[CONTRIBUTION FROM THE GEOCHEMICAL SECTION OF THE ILLINOIS STATE GEOLOGICAL SURVEY]

Aromatic Fluorine Compounds. II. 1,2,4,5-Tetrafluorobenzene and Related Compounds[1,2]

BY G. C. FINGER, F. H. REED, D. M. BURNESS, D. M. FORT AND R. R. BLOUGH

The synthesis of a complete series of fluorinated benzenes would reveal the effect of progressive fluorine substitution upon the physical and chemical properties of benzene and benzenoid structures. A tetra- and pentafluorobenzene are needed to complete such a series. In addition, a study of the effect on properties of other substituents in the polyfluorobenzenes would lead to generalizations of theoretical and practical value.

1,2,4,5-Tetrafluorobenzene has been synthesized and the properties of its intermediates were studied in detail. For comparative purposes, a number of chlorofluorobenzenes possessing the 1,2,4,5-structure are reported. Flash points and other physical data accumulated thus far on the fluoro- and chlorofluorobenzenes are summarized. It was discovered that 1,2,4,5-tetrafluorobenzene gave a quinone rather than a nitro derivative under nitration conditions. The anomalous behavior of 2-nitro-3,4,6-trifluoroaniline under diazotization conditions was studied.



The nitration of 1,2,4-trifluorobenzene gave 2,4,5-trifluoronitrobenzene (I) as expected by analogy to the trichloro compound. A Schiemann reaction on 4-nitro-2,5-difluoroaniline (III) produced the same compound, and the position of the nitro group was established by the identity of the acetyl derivatives at II. Reduction gave 2,4,5-trifluoroaniline (II) and a Schiemann conversion formed 1,2,4,5-tetrafluorobenzene (VII), and a small amount of 2-chloro-1,4,5-trifluorobenzene (VIII) as a by-product.[3]

1,2,4,5-Tetrafluorobenzene resisted photochemical chlorination to a remarkable degree and the only reaction product isolated was a trace of a cyclohexane derivative, $C_6H_2Cl_6F_4$ (X). In other words, any chlorination that took place did not involve hydrogen substitution, but chlorine addition across the double bonds to form a saturated ring system. This is hardly comparable to the tetrachlorobenzene analog. In contrast, 1,4-difluoro- and 1,2,4-trifluorobenzene halogenated normally, thus making available bromo and chloro derivatives with a 1,2,4,5 structure. The 2-bromo (XI) and 2,5-dibromo (XII) derivatives of 1,4-difluorobenzene were obtained by bromination; likewise, the 2-bromo (IX) derivative of 1,4,5-trifluorobenzene. Sulfuryl chloride[4] chlorination of 1,4-difluorobenzene gave such derivatives as 2-chloro- (XIII), 2,5-dichloro- (XIV) and a small amount of 2,6-dichloro- (XV) and 2,3,5-trichloro-1,4-difluorobenzene (XVI). A trace of hexachlorobenzene was isolated. Apparently the aluminum chloride catalyst caused substitution of fluorine with chlorine in the formation of the hexachloro compound.

The behavior of 1,2,4,5-tetrafluorobenzene with such acids as nitric, sulfuric and their mixtures is unique and in sharp contrast to the chlorine analog. Attempts to form a nitro derivative were unsuccessful. The tetrafluoro compound appeared to be inert to concentrated or fuming nitric and sulfuric acids; with fuming nitric acid in a glass-sealed tube at 125° for four hours, a slight etching of the tube was the only evidence of reaction. There was no reaction with nitric–sulfuric acid mixtures if (1) both components were concentrated, or (2) if one component was fuming and the other concentrated. A nitric–sulfuric acid mixture of fuming reagents reacted with avidity, at times almost uncontrollable even at 5°; 2,5-difluoro-1,4-benzoquinone was identified in the decomposition products. This implies a fluorine displacement–oxidation mechanism involving a pair of fluorine atoms para to each other.

Since it was not feasible to obtain a nitro derivative of 1,2,4,5-tetrafluorobenzene by direct nitra-

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(1) Presented in part before the Organic and Industrial and Engineering Divisions at the 109th (April, 1946) and 116th (September, 1949) Meetings of the American Chemical Society, Atlantic City, N. J. The material in this paper is based on reports submitted to the Office of Scientific Research and Development under Contract OEMsr-469 (1942–43), and the Office of Naval Research under Contract N6ori-71; Task XIV (1946–50). The financial assistance of these agencies is gratefully acknowledged.

(2) Published with the permission of the Chief of the Illinois State Geological Survey.

(3) The formation of chloro by-products in Schiemann reactions is quite common if diazotization is effected in strong hydrochloric acid solutions.

(4) Cutter and Brown, *J. Chem. Ed.*, **21**, 443 (1944).

tion, the possibility of an alternate synthesis was investigated. The proposed method involved the formation of a 2-nitro derivative of 3,4,6-trifluoroaniline and a subsequent Schiemann reaction to 3-nitro-1,2,4,5-tetrafluorobenzene. Nitration of the acetyl derivative of II gave a 50% yield of 2-nitro-3,4,6-trifluoroaniline (XVII). The Schiemann reaction, however, on the weakly basic nitroamine was unsuccessful, due to failure to obtain an insoluble diazonium fluoborate and the multiplicity of anomalous reactions extent at the diazo stage.

The perverseness of 2-nitro-3,4,6-trifluoroaniline (XVI) to normal diazo reactions led to a study of the anomalous reaction products of diazotization. Depending upon conditions, evidence was obtained for the formation of two diazo oxides (XIX and XX), nitrodifluorophenol (XXI), iodonitrodifluorophenol (XXII), 2,3-dichloro-1,4,5-trifluorobenzene (XXIII)[5] and dichlorodifluorophenol (XXIV). The formation of these compounds revealed the operation of several mechanisms at the diazo stage such as (1) displacement of fluorine, ortho or para to the diazo group, to form a diazo oxide or phenol, (2) replacement of the nitro group with chlorine in hydrochloric acid solutions, and (3) a combination of these reactions. The ortho or para displacement is supported by the isolation of two apparently isomeric diazo oxides (XIX and XX). Diazotization in hydrochloric acid gave one form (XIX), whereas hydrofluoric gave the other (XX) which, in contrast to the former, could be repeatedly recrystallized from methanol to a definite melting point. Both isomers were light orange in color, exploded on heating or flame ignition, and impact detonation gave a powerful concussion. No structural assignments were made to the diazo oxides or the aforementioned phenols because of the uncertainty of the position of the labilized fluorine atom.

Counterparts of these separate mechanisms in fluorine chemistry are found in Hodgson's[6] diazo oxide from 3-nitro-4-fluoroaniline, and Schiemann's[7] 1-chloro-2-fluoronaphthalene from 1-nitro-2-aminonaphthalene. In other words, the fluorinated nitroamine in question fulfils all the structural conditions necessary to demonstrate the separate findings of Hodgson and Schiemann. As a further test of these findings, 2-nitro-4-chloro-3,6-difluoroaniline has been synthesized and will be reported later. These findings are consistent also with the discussion of Saunders[8] on similar reactions with non-fluorine containing compounds.

Table I is a summary of some of the physical properties of the fluoro- and chlorofluorobenzenes. The boiling point of 1,2,4,5-tetrafluorobenzene is not significantly different than the other fluorobenzenes, but its freezing point is close to that of benzene. The flash point and surface tension data of the fluoro- and chlorofluorobenzenes are significant in view of the increasing interest in organic fluorine compounds. It is almost inconceivable that the flash point of tetrafluorobenzene is 4°; likewise, the low values for the other fluorinated benzenes. The introduction of one chlorine atom in the fluorinated benzenes elevated the boiling and flash points to the vicinity of chlorobenzene. Progressive fluorine substitution in the benzene molecule caused a progressive decrease in surface tension. This is in contrast to an increase characterized by chlorine or the other halogens. The data also indicate that a decrease in surface tension by fluorine is somewhat compensated for by the introduction of chlorine into the molecule.

TABLE I

PHYSICAL PROPERTIES OF SOME FLUORINATED BENZENES

Compound	F. p., °C.	B. p., °C.	Flash point, °C. (open cup)	Surface tension dynes/cm., 20°
C_6H_6	5.5[a,b]	80[b]	−11[b,c]	28.9[b]
C_6H_5F	−41.9[d]	84.8[d]	−15	27.71[e]
$C_6H_4F_2$-1,4	−13[f]	88.5[f]	− 5.5	27.05[e]
$C_6H_3F_3$-1,2,4	−35[g]	88[g]	− 5	26.2
$C_6H_2F_4$-1,2,4,5	4	88	4	24.9
C_6H_5Cl[b]	−45	132	32[c]	33.2
$C_6H_4(F)(Cl)$-1,4	−27[b]	130[b]	32	31.3
$C_6H_3(F)_2(Cl)$-1,4,2	−24.6	127	31	29.9

[a] Melting point. [b] Data taken from Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio. [c] Closed cup. [d] Timmermans and Hennaut-Roland, *J. chim. phys.*, **32**, 501 (1935). [e] Desreux, *Bull. soc. chim. Belg.*, **44**, 249 (1935). [f] Schiemann and Pillarsky, *Ber.*, **62**, 3035 (1929). [g] Schiemann, *J. prakt. Chem.*, 40, 97 (1934).

Experimental[9-11]

2,4,5-Trifluoronitrobenzene (I).—To a mixture of 200 g. of concd. nitric and 736 g. of concd. sulfuric acids, 264 g. of 1,2,4-trifluorobenzene[12] was added with stirring. The reaction temperature was maintained at 20° and the time was three hours. Steam distillation of the crude material gave a yield of 307 g. or 87% of practically pure nitro compound. Pure 2,4,5-trifluoronitrobenzene has a mild nitrobenzene odor, but is somewhat lachrymatory, f. p. *ca.* −11°, b. p. 93.5° (20 mm.) or 192° (atm.), $n^{20}D$ 1.49384.

Anal. Calcd. for $C_6H_2F_3NO_2$: C, 40.69; H, 1.14; N, 7.91. Found: C, 40.73; H, 1.15; N, 8.19.

The same nitro compound was obtained by a Schiemann reaction on 4-nitro-2,5-difluoroaniline (III), thus proving its structure.

2,4,5-Trifluoroaniline (II).—This compound was obtained in a 90% yield by an iron reduction of I. Steam distillation gave a colorless oil which solidified to a white solid on cooling. Recrystallization from high boiling petroleum ether gave white needles, m. p. 58.5–60°.

Anal. Calcd. for $C_6H_4F_3N$: C, 48.99; H, 2.74; N, 9.52. Found: C, 48.90; H, 2.95; N, 9.45.

The acetyl derivative was recrystallized from aqueous ethanol as white microcrystals, m. p. 129–130°. A mixed melting point of the acetyl derivatives of the amines derived from the two routes proved them to be identical.

Anal. Calcd. for $C_8H_6F_3NO$: C, 50.80; H, 3.20; N, 7.41. Found: C, 50.80; H, 3.28; N, 7.46.

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(5) A Sandmeyer reaction gave a 40% yield of this compound. Frequent use of this reaction has been made in this Laboratory to convert fluorinated ortho nitroamines to the corresponding fluorinated ortho dichloro derivatives.

(6) Hodgson and Nixon, *J. Chem. Soc.*, 2272 (1931).

(7) Schiemann and Ley, *Ber.*, **69**, 960 (1936).

(8) K. H. Saunders, "The Aromatic Diazo-Compounds and Their Technical Applications," Edward Arnold & Co., London, 2nd ed., 1949.

(9) Analyses by H. S. Clark, microanalyst for the Survey.

(10) Melting and boiling points are uncorrected. Freezing points were determined with a toluene thermometer.

(11) The assistance of Messrs. J. L. Finnerty, E. W. Maynert, R. E. Oesterling, H. G. Schneider, A. M. Weiner and O. F. Williams is gratefully acknowledged.

(12) Schiemann, *J. prakt. Chem.*, **140**, 97 (1934).

4-Nitro-2,5-difluoroaniline (III).—To a solution of 116 g. of 2,5-difluoroacetanilide[13] in 500 cc. of concd. sulfuric acid and 50 cc. of acetic acid, a mixture of 57.5 cc. of concd. nitric and 75 cc. of concd. sulfuric acids was added in 75 minutes, and the temperature maintained below 10°. The crude nitroacetylamino compound, obtained in a quantitative yield, was hydrolyzed in 150 cc. of concd. sulfuric acid by heating for ten minutes on a steam-bath. A yield of 105 g. or 89% of crude nitroamine was obtained. Recrystallization from ethanol gave pure 4-nitro-2,5-difluoroaniline as golden needles, m. p. 153–153.5°. The mother liquor was reserved for the isolation of an isomer (IV).

Anal. Calcd. for $C_6H_4F_2N_2O_2$: C, 41.40; H, 2.32; N, 16.10. Found: C, 41.63; H, 2.14; N, 16.31.

Recrystallization of the acetyl derivative from ethanol gave cream-colored crystals, m. p. 189–189.5°.

Anal. Calcd. for $C_8H_6F_2N_2O_3$: N, 12.96. Found: N, 12.77.

6-Nitro-2,5-difluoroaniline (IV).—This compound, an isomer of III, was isolated in a very small amount from the mother liquor obtained in the purification of III. A combination of sublimation and recrystallization from ethanol gave pure 2-nitro-3,6-difluoroaniline as orange needles, m. p. 80–80.5°.

Anal. Calcd. for $C_6H_4F_2N_2O_2$: C, 41.40; H, 2.32; N, 16.10. Found: C, 41.57; H, 2.38; N, 16.10.

Sublimation gave the acetyl compound as a white solid, m. p. 160–161°.

Anal. Calcd. for $C_8H_6F_2N_2O_3$: N, 12.96. Found: N, 12.90.

The structure of this nitroamine was proven by reduction to the diamine (V) and the subsequent formation of a quinoxaline.

3,6-Difluoro-1,2-phenylenediamine (V).—The diamine was prepared from IV by the usual stannous chloride reduction. It was quite soluble in water and was extracted with ether. Vacuum sublimation gave the pure diamine as fine white needles, m. p. 80.8–81.1°.

Anal. Calcd. for $C_6H_6F_2N_2$: C, 50.00; H, 4.20; N, 19.45. Found: C, 50.15; H, 4.22; N, 19.60.

The 2,3-diphenyl-5,8-difluoroquinoxaline derivative was prepared by condensation of the diamine with benzil. Recrystallization from ethanol gave fine white crystals, m. p. 191–191.5°.

Anal. Calcd. for $C_{20}H_{12}F_2N_2$: C, 75.45; H, 3.80; N, 8.80. Found: C, 75.55; H, 3.80; N, 8.75.

2,5-Difluoro-1,4-phenylenediamine (VI).—This diamine was prepared from III by the same procedure described for V. Vacuum sublimation gave white crystals, m. p. 129–129.6°.

Anal. Calcd. for $C_6H_6F_2N_2$: C, 50.00; H, 4.20; N, 19.45. Found: C, 49.91; H, 4.28; N, 19.52.

The diacetate derivative upon recrystallization from acetic acid gave white microneedles, m. p. 304.5–305.5°.

Anal. Calcd. for $C_{10}H_{10}F_2N_2O_2$: N, 12.28. Found: N, 12.00.

1,2,4,5-Tetrafluorobenzene (VII).—A well-stirred mixture of 294 g. of 2,4,5-trifluoroaniline and 1100 cc. of commercial hydrochloric acid (18° Bé.) was heated until complete solution was obtained and then rapidly cooled to −5° to precipitate the amine hydrochloride. The resulting mixture was diazotized by the submerged addition of a solution of 140 g. of sodium nitrite in 210 cc. of water, and the temperature not allowed to go above 0°. After completion of the diazotization, a solution of 660 g. of sodium fluoborate in 940 cc. of water was added rapidly. The heavy slurry was stirred for 30 minutes, cooled to −15°, filtered and the light yellow fluoborate salt was dried. The yield of dry salt was over theory. After thermal decomposition by the usual procedure,[14] the crude reaction product was made alkaline with sodium carbonate solution and steam distilled. Distillation through a packed column gave a fraction boiling at 89–90.5°, yield 113–137 g. or 38–46% based on the amine. Pure 1,2,4,5-tetrafluorobenzene has a faint sweet odor. f. p. *ca.* 4°, b. p. 88°, d^{20}_{4} 1.4256, n^{20}_{D} 1.4074.

Anal. Calcd. for $C_6H_2F_4$: C, 48.01; H, 1.34. Found: C, 47.93; H, 1.42.

2-Chloro-1,4,5-trifluorobenzene (VIII).—This compound was obtained in a 60% yield from 2,4,5-trifluoroaniline by a Sandmeyer reaction or as a by-product from the tetrafluorobenzene synthesis, f. p. *ca.* −24.5°, b. p. 124–125°.

Anal. Calcd. for $C_6H_2ClF_3$: C, 43.27; H, 1.21. Found: C, 43.65; H, 1.19.

2-Bromo-1,4,5-trifluorobenzene (IX).—Bromination of 1,2,4-trifluorobenzene with iron as a catalyst gave a 76% yield of 2-bromo-1,4,5-trifluorobenzene, f. p. *ca.* −19°, b. p. 144°, d^{20}_{4} 1.8022, n^{20}_{D} 1.4862, γ^{20} 25.6 dynes/cm.

Anal. Calcd. for $C_6H_2BrF_3$: C, 34.15; H, 0.95; Br, 37.88. Found: C, 34.07; H, 0.95; Br, 37.87.

1,2,3,4,5,6-Hexachloro-1,2,4,5-tetrafluorocyclohexane (X).—A small amount of high-boiling material was the only evidence of the effect of exhaustive chlorination on 1,2,4,5-tetrafluorobenzene. A combination of vacuum distillation, recrystallization from ethanol, and sublimation gave a very small amount of white crystals, m. p. 79–80°, as the only isolable product. According to the analytical data, the white solid is a hexachlorotetrafluorocyclohexane.

Anal. Calcd. for $C_6H_2Cl_6F_4$: C, 19.85; H, 0.55; Cl, 58.64. Found: C, 19.84; H, 0.70; Cl, 58.38.

Halogenation of *p*-Difluorobenzene.—Bromination of *p*-difluorobenzene with bromine in the presence of iron gave the mono and dibromo derivatives with the latter being in largest amount. Both derivatives were removed from the reaction mixture by steam distillation, and then separated by vacuum distillation.

2-Bromo-1,4-difluorobenzene (XI).—This compound has a mild bromobenzene odor, f. p. *ca.* −31.5°, b.p. 58–58.5° (20 mm.), n^{20}_{D} 1.5086.

Anal. Calcd. for $C_6H_3BrF_2$: C, 37.34; H, 1.56; Br, 41.41. Found: C, 37.43; H, 1.62; Br, 41.06.

2,5-Dibromo-1,4-difluorobenzene (XII).—This is a crystalline solid, sublimes slowly on standing, and is recrystallizable from ethanol, m. p. 64.5–65.5°, b. p. 96° (20 mm.).

Anal. Calcd. for $C_6H_2Br_2F_2$: C, 26.50; H, 0.74; Br, 58.78; F, 13.98. Found: C, 26.61; H, 0.74; Br, 58.91; F, 13.48.

Chlorination of *p*-difluorobenzene was effected by the sulfuryl chloride–sulfur monochloride method with aluminum chloride as a catalyst.[4] A moderate excess of reagent gave the monochloro derivative, but this in turn chlorinated readily to the 2,5-dichloro compound. Chlorination beyond the dichloro stage was much slower. A large excess of chlorinating agent formed a complex mixture which gave a 60–70% yield of the 2,5-dichloro-1,4-difluorobenzene, a small amount of what may be 2,6-dichloro-1,4-difluorobenzene, 15–20% of 2,3,5-trichloro-1,4-difluorobenzene, and a trace of hexachlorobenzene. Separation of the components was by steam and vacuum distillations, and recrystallizations.

2-Chloro-1,4-difluorobenzene (XIII).—In addition to the direct chlorination, this compound was obtained as a by-product from the synthesis of 1,2,4-trifluorobenzene or by a Sandmeyer reaction on 2,5-difluoroaniline in a 60% yield, f. p. *ca.* 24.6°, b. p. 128°, d^{20}_{4} 1.3561, n^{20}_{D} 1.4772.

Anal. Calcd. for $C_6H_3ClF_2$: C, 48.51; H, 2.04; Cl, 23.87. Found: C, 48.46; H, 2.07; Cl, 28.86.

2,5-Dichloro-1,4-difluorobenzene (XIV).—The reaction product (177 g.) from exhaustive chlorination was divided arbitrarily into three volatile fractions, and a small non-volatile fraction by steam distillation. The order of volatile fractions was (1) a condensate (87 g.) which solidified on cooling, (2) an oil (86 g.) which remained a liquid at room temperature, and (3) a white solid. The residue (1.2 g.) and the last fraction (2.6 g.) was essentially hexachlorobenzene.

The first volatile fraction was almost pure 2,5-dichloro-1,4-difluorobenzene. As a result of processing the second fraction, an additional 25 g. of this dichloro derivative was accumulated from this source. It was identified by a mixed melting point with a known sample obtained from 4-nitro-2,5-difluoroaniline (III).

The synthesis of this compound from III was accomplished in one step by the simultaneous replacement of a nitro group with chlorine while a cuprous chloride Sandmeyer reaction was operating on the amino group. Fre-

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[13] Swarts, *Bull. classe sci., Acad. roy. Belg.*, 241 (1913); 186 (1914).

[14] Finger and Reed, THIS JOURNAL, **66**, 1972 (1944).

quent use of this reaction has been made with ortho-nitroamines to form dichlorides. Ten grams of III was diazotized as the amine hydrochloride at 40–45°, and then poured into a cuprous chloride solution. The crude reaction product was a mixture of the dichloro and chloronitro derivatives; a vacuum sublimation gave 3.2 g. of practically pure dichloro compound as the most volatile component.

Recrystallization from ethanol gave 2,5-dichloro-1,4-difluorobenzene as white crystals, m. p. 48–49°, b. p. 64° (20 mm.) or 164° (atm.).

Anal. Calcd. for $C_6H_2Cl_2F_2$: C, 39.38; H, 1.10; Cl, 38.75. Found: C, 39.44; H, 1.08; Cl, 38.78.

2,6-Dichloro-1,4-difluorobenzene (XV).—The second volatile fraction described under XIV was processed by fractional distillation into various cuts. In general, material boiling above 180° was reserved for the isolation of the trichloro derivative. Fractions boiling up to 180° were processed by repeated distillations and freezing of fractions to eliminate the 2,5-dichloro compound. The end result was several grams of oil, f. p. 3.5 to −10°, b. p. 65–66° (20 mm.), n^{20}_{D} 1.50750.

Anal. Calcd. for $C_6H_2Cl_2F_2$: C, 39.38; H, 1.10; Cl, 38.75. Found: C, 39.36; H, 1.17; Cl, 38.63.

There is little doubt that this material essentially is 2,6-dichloro-1,4-difluorobenzene. A synthetic sample prepared recently by a Sandmeyer reaction on 3-chloro-2,5-difluoroaniline[15] had practically the same properties, f. p. *ca.* −1.5 to 2.5°, b. p. 165°, n^{20}_{D} 1.50405.

Anal. Calcd. for $C_6H_2Cl_2F_2$: C, 39.38; H, 1.10. Found: C, 39.40; H, 1.06.

2,3,5-Trichloro-1,4-difluorobenzene (XVI).—The fraction boiling above 180° as indicated under XV and the higher cuts obtained from the isolation of the 2,6-dichloro compound were combined. This composite sample was redistilled to give about 30 g. of a middle fraction, b. p. 180–207°. Repeated fractional distillation and freezing of the fractions removed the hexachlorobenzene as a solid and with the elimination of the lower boiling fractions, an enriched trichloro fraction, b. p. 190–205°, was obtained. Redistillation of the enriched fraction gave about 25 g. of fairly pure material. Approximately 20 g. of pure 2,3,5-trichloro-1,4-difluorobenzene was finally isolated, f. p. *ca.* −11.5 to −12°, b. p. 94–95° (20 mm.) or 200° (atm.), n^{20}_{D} 1.5340.

Anal. Calcd. for $C_6HCl_3F_2$: C, 33.14; H, 0.46; Cl, 48.92. Found: C, 33.43; H, 0.56; Cl, 48.94.

Quinone Formation.—All attempts to prepare a nitro derivative of 1,2,4,5-tetrafluorobenzene (VII) by nitration failed. The unusual stability of this compound to nitric-sulfuric acid mixtures was discussed previously, and for the sake of brevity the isolation of the quinone intermediate will be described.

To a well-stirred mixture of 30 g. of 1,2,4,5-tetrafluorobenzene (VII) and 13.9 g. of fuming sulfuric acid (30% SO_3), 20 cc. of fuming nitric acid (1.49–1.5) was added dropwise and the reaction temperature maintained at 25–30°. The mixture became orange-red in color, a yellow solid formed, and a slow evolution of hydrogen fluoride was observed. After pouring the reaction mixture over ice, the yellow solid was removed by filtration, washed with water, dried, yield 8–10 g. It was purified by recrystallization from carbon disulfide or by sublimation, m.p. 171.5–172°. A mixed melting point with a known sample of 2,5-difluoro-1,4-benzoquinone[16] proved its identity.

2-Nitro-3,4,6-trifluoroaniline (XVII).—To a solution of 500 g. of 2,4,5-trifluoroacetanilide in 445 cc. of glacial acetic and 1550 cc. of concentrated sulfuric acids, a mixture of 200 cc. of fuming nitric acid (1.49–1.5) in 55 cc. of acetic and 195 cc. of concd. sulfuric acids was added slowly, and the temperature maintained at 20°. Stirring was continued for 30 minutes after addition, and some hydrogen fluoride evolution was observed during the nitration. After removal of the precipitate by filtration, the aqueous filtrate was extracted with ether for maximum recovery. The entire crude product (425 g.) was hydrolyzed with 300 cc. of concd. hydrochloric acid in 2700 cc. of water by refluxing for two hours. Steam distillation gave 267 g. (53%) of nitroamine, sufficiently pure for subsequent reactions. Vacuum sublimation gave pure 2-nitro-3,4,6-trifluoroaniline as a bright orange solid, m.p. 57.3–57.8°.

Anal. Calcd. for $C_6H_3F_3N_2O_2$: C, 37.52; H, 1.57; N, 14.59. Found: C, 37.78; H, 1.44; N, 14.51.

The acetyl derivative was purified by recrystallization from carbon tetrachloride and by vacuum sublimation, m.p. 124.5–124.8°.

Anal. Calcd. for $C_8H_5F_3N_2O_3$: N, 11.97. Found: N, 11.81.

3,4,6-Trifluoro-1,2-phenylenediamine (XVIII).—This diamine was prepared in an 82% yield by an iron reduction from the preceding nitroamine. Vacuum sublimation gave white needles, m.p. 74.6–75.2°.

Anal. Calcd. for $C_6H_5F_3N_2$: C, 44.45; H, 3.11; N, 17.28. Found: C, 44.65; H, 2.95; N, 17.06.

The quinoxaline derivative was prepared by the usual reaction with benzil in a 75% yield, and purified by passage through an aluminum oxide chromatograph in addition to recrystallization from ethanol. The pure 2,3-diphenyl-5,6,8-trifluoroquinoxaline was obtained as white needles, m.p. 169.5–170°.

Anal. Calcd. for $C_{20}H_{11}F_3N_2$: N, 8.33: Found: N, 8.26.

Diazotization of 2-Nitro-3,4,6-trifluoroaniline.—A variety of products was obtained by diazotization of 2-nitro-3,4,6-trifluoroaniline, depending upon the acid media and reagents used. Since a fluorine atom in the 4- or 6-position could be replaced, the structures of the diazo oxides or the phenolic compounds were not determined. In general, the phenolic compounds were converted to a benzoyl derivative in order to obtain a satisfactory analysis.

Diazo Oxides (XIX and XX).—Two apparently different diazo oxides of the same chemical composition were obtained, one was derived from diazotization in hydrochloric acid (XIX) and the other from hydrofluoric acid (XX). It is conceivable that one represents a fluorine replacement at the 4-position and the other at the 6-position.

The hydrochloric acid diazotization involved 5 g. of the nitroamine, 10 cc. of concd. hydrochloric acid and 3 g. of sodium nitrite in 5 cc. of water. The bright orange-colored precipitate was removed by filtration; the filtrate gave no precipitate with sodium fluoborate solution, thus negating a Schiemann reaction. After drying the precipitate, it melted near 80°, and burned explosively in a flame; one recrystallization from methanol gave orange colored crystals (XIX), which darkened upon heating but not melting up to 350°, and exploding violently on impact.

Anal. Calcd. for $C_6HF_2N_3O_3$: C, 35.83; H, 0.50; N, 20.90. Found: C, 35.95; H, 0.55; N, 20.71.

The hydrofluoric acid diazotization was similar to the above except 48% aqueous acid was used, and the reaction was performed in a rubber beaker. Due to the presence of insoluble salts, the dried orange precipitate was extracted with ether in a Soxhlet, and evaporation of the ether extract gave a crude red product. Repeated recrystallization from methanol gave a bright orange powder (XX), m.p. 119.3–120° (dec.), with the same characteristics as the preceding compound.

Anal. Calcd. for $C_6HF_2N_3O_3$: C, 35.83; H, 0.50; N, 20.90. Found: C, 35.75; H, 0.43; N, 20.80.

Nitrodifluorophenol (XXI).—Diazotization of the nitroamine (25 g.) in concd. sulfuric acid and application of the hypophosphorous deamination method gave a small amount (one gram) of a steam distillable solid. Recrystallization of the solid from chloroform and vacuum sublimation gave yellow crystals, m.p. 105–105.5°. A benzoyl derivative was prepared by the Schotten–Baumann reaction; recrystallization from ethanol gave white plates, m.p. 88–89°.

Anal. Calcd. for $C_{13}H_7F_2NO_4$: C, 55.92; H, 2.53; N, 5.02. Found: C, 56.31; H, 2.27; N, 5.01.

Iodonitrodifluorophenol (XXII).—This compound was obtained in very small amount by diazotization of the nitroamine in sulfuric acid followed by treatment with potassium iodide. A Schotten–Baumann reaction gave the benzoyl derivative, recrystallizable from ethanol to cream-colored needles, m.p. 135–136°.

Anal. Calcd. for $C_{13}H_6F_2INO_4$: C, 38.54; H, 1.49; N, 3.46. Found: C, 39.14; H, 1.46; N, 3.12.

2,3-Dichloro-1,4,5-trifluorobenzene (XXIII).—A suspension of 25 g. of powdered nitroamine in 50 cc. of concd. hy-

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(15) Finger, Reed and Finnerty, unpublished results.

(16) Finger, Finnerty and Schneider, Abstracts of 116th A. C. S. Meeting, September, 1949, Atlantic City, N. J., p. 17K.

drochloric acid was diazotized at -5° with the slow addition of 15 g. of powdered sodium nitrite. The resulting mixture was poured into a solution of 25 g. of cuprous chloride in 100 cc. of concd. hydrochloric acid. Steam distillation removed the dichloro compound as an oil, and the aqueous layer was reserved for the isolation of the dichlorodifluorophenol. The crude product, yield 10.6 g. or 40%, on distillation gave pure 2,3-dichloro-1,4,5-trifluorobenzene, f.p. *ca.* -3 to -4°, b.p. 153°, $n^{20}\text{D}$ 1.48866.

Anal. Calcd. for $C_6HCl_2F_3$: C, 35.85; H, 0.50; Cl, 35.28. Found: C, 35.92; H, 0.57; Cl, 34.90.

The cloudy supernatant liquid from steam distillation on chilling gave a few drops of oil, with a phenolic odor (XXIV), which was converted to a benzoyl derivative. Recrystallization from ethanol and a subsequent vacuum sublimation gave the derivative as a white powder, m.p. 84.5–85°.

Anal. Calcd. for $C_{13}H_6Cl_2F_2O_2$: C, 51.51; H, 2.00; Cl, 23.40. Found: C, 51.48; H, 1.74; Cl, 23.40.

Flash Points and Surface Tension.—The flash points were determined by the Pensky–Martens closed tester.[17]

Surface tension was determined by H. S. Clark using the micro-capillary tube method.[18]

Summary

The synthesis and properties of 1,2,4,5-tetrafluorobenzene and a group of bromofluoro and chlorofluorobenzenes with a predominating 1,2,4,5-structure are described. Flash point and surface tension data for the fluorinated benzenes and the influence of chlorine substitution upon these values were studied.

Under nitration conditions, 1,2,4,5-tetrafluorobenzene will not form a nitro derivative, but will undergo a preferential 1,4-fluorine displacement–oxidation mechanism to give 2,5-difluoro-1,4-benzoquinone.

Diazotization reactions on 2-nitro-3,4,6-trifluoroaniline reveal that the nitro group or a fluorine atom in the 4- or 6-position may become labilized, under certain conditions, and undergo replacement.

URBANA, ILLINOIS RECEIVED JUNE 9, 1950

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[17] "1949 Book of A. S. T. M. Standards," A. S. T. M. Designation: D93-46, American Society for Testing Materials, Philadelphia, Pa.

[18] Natelson and Pearl, THIS JOURNAL, **57**, 1520 (1935).

[CONTRIBUTION FROM THE GEOCHEMICAL SECTION OF THE ILLINOIS STATE GEOLOGICAL SURVEY]

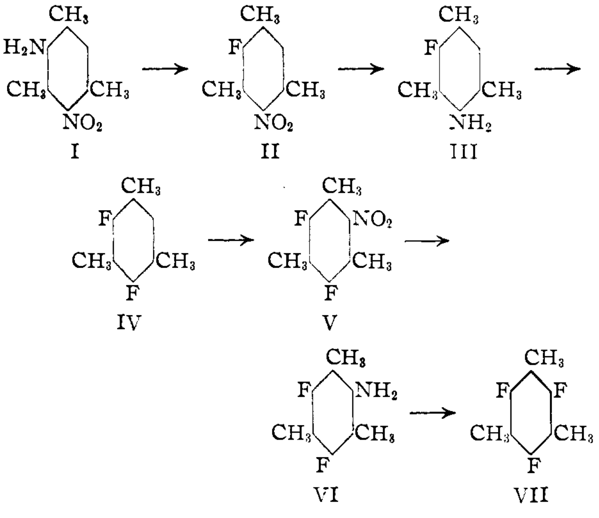
Aromatic Fluorine Compounds. III. The Fluoromesitylenes and Derivatives[1]

BY G. C. FINGER, F. H. REED, E. W. MAYNERT AND A. M. WEINER

As part of a study in this Laboratory on aromatic fluorides, 2,4-difluoro- and 2,4,6-trifluoromesitylene, and various fluorinated mesitylene derivatives were synthesized. Monofluoromesitylene was synthesized by Töhl[2] as early as 1892. Of special note is the synthesis of 2,4,6-trichloro-1,3,5-trifluorobenzene.

Dinitromesitylene was prepared in quantitative yields by the nitration of mesitylene in anhydrous hydrofluoric acid by the Fredenhagen process.[3] This method has much in its favor over the Fittig[4] red fuming nitric acid procedure. A sodium polysulfide reduction of the dinitro compound gave nitromesidine (I), and by means of a diazotization–Schiemann transformation 2-fluoro-4-nitromesitylene (II) was obtained. An iron reduction of II gave fluoromesidine (III), and a Schiemann reaction on the amine gave a 80–90% yield of 2,4-difluoromesitylene (IV).

A 90% yield of 2,4-difluoro-6-nitromesitylene (V) was obtained by the above hydrogen fluoride nitration process on IV. Difluoromesidine (VI), prepared by an iron reduction of V, was converted in an 86% yield to 2,4,6-trifluoromesitylene (VII) by a Schiemann reaction. The yields of difluoromesitylene and trifluoromesitylene from their respective amines are among the highest recorded for a Schiemann reaction.[5]



The chlorination of trifluoromesitylene readily gave a "hexachloro" derivative, probably 2,4,6-tris-(dichloromethyl)-1,3,5-trifluorobenzene, and this was converted slowly at a higher temperature to 2,4,6-tris-(trichloromethyl)-1,3,5-trifluorobenzene. The latter was complicated by chlorinolysis which gave rise to 2,4,6-trichloro-1,3,5-trifluorobenzene and carbon tetrachloride. Similar results had been reported for mesitylene and the chloromesitylenes.[6,7] Trifluoromesitylene with its chlorinated derivatives, and trichlorotrifluoroben-

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[1] Presented in part before the Organic Division at the 109th Meeting of the American Chemical Society, Atlantic City, N. J., April 1946. The material in this paper is based, primarily, on reports submitted to the Office of Scientific Research and Development under Contract OEMsr-469(1942-43) and on data obtained after the expiration of the contract. Published with the permission of the Chief of the Illinois State Geological Survey.

[2] Töhl, *Ber.*, **25**, 1525 (1892).

[3] (a) Fredenhagen, German Patent 529,538 (Aug. 2, 1930); *C. A.*, **25**, 5175 (1931). (b) "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 340-343.

[4] Fittig, *Ann.*, **141**, 133 (1867).

[5] "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1949, Vol. V, Ch. 4, pp. 217-222.

[6] I. G. Farbenind. A.-G., French Patent 798,727 (May 25, 1936); *C. A.*, **30**, 7121 (1936).

[7] McBee and Leech, *Ind. Eng. Chem.*, **39**, 393 (1947).