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}_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.

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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]

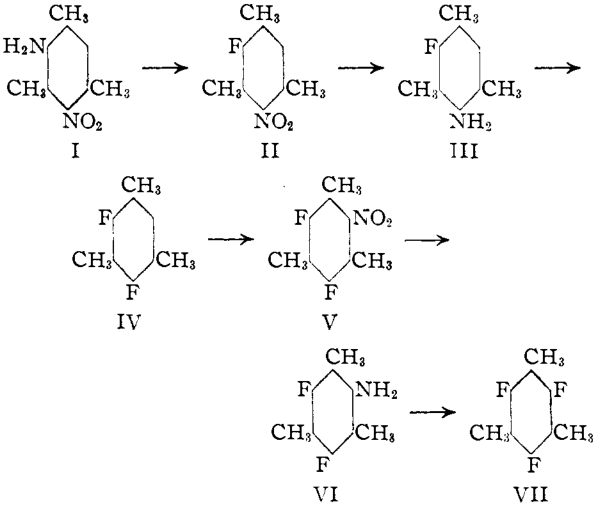
Aromatic Fluorine Compounds. III. The Fluoromesitylenes and Derivatives[1]

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).

zene possess the characteristic structure of symmetrical trifluorobenzene.

Mesitylene with trifluoroacetic anhydride undergoes the Friedel–Crafts acylation reaction to form the trifluoroaceto derivative. Various aceto derivatives of difluoromesitylene were prepared and, presumably, the same reactions could be applied to monofluoromesitylene. Sodium hypobromite converted the acetodifluoromesitylene to the tribromoaceto derivative which was degraded to *eso*-difluoro-β-isodurylic acid. Attempts to produce the same acid by the hydrolysis of 2-cyano-4,6-difluoromesitylene failed because of the stability of the amide intermediate.

The boiling points of mono-, di- and trifluoromesitylene, 167,[7] 169 and 169°, respectively, are slightly higher than mesitylene, b. p. 164°. The trifluoro compound is a solid, m. p. 68° in contrast to mesitylene and the other fluoromesitylenes which are liquids; it is quite volatile, sublimes slowly on standing, and exhibits thixotropic properties.

Experimental[8,9]

Nitrations in Anhydrous Hydrogen Fluorine.—The reaction vessel for nitrations in liquid anhydrous hydrofluoric acid was either an iron retort or a copper beaker. An anchor-shaped stirrer was used to ensure efficient agitation at all times. A thermometer well extended down to the center of the reaction vessel close to the stirrer shaft. The reaction temperature was controlled by an external Dry Ice–acetone cooling bath.

A. **Dinitromesitylene.**—To a cooled, well-stirred mixture of 2 kg. (100 moles) of liquid anhydrous hydrofluoric acid and 500 g. (4.17 moles) of mesitylene, 708 g. (8.34 moles) of powdered sodium nitrate was added at such a rate that the reaction temperature was held below 5°. Stirring was continued for 15–30 minutes. The dinitromesitylene precipitated as a yellow solid, and the final reaction mixture was a heavy sludge.

After pouring the reaction mixture over 5 kg. of crushed ice with vigorous stirring, the dinitromesitylene was removed and washed with water on a Buchner funnel, and dried. Yield was 805–840 g. or 94–98%, m. p. 84–85° (Fittig reported 86°). This product was sufficiently pure for the sodium polysulfide reduction to nitromesidine.

B. **2,4-Difluoro-6-nitromesitylene** (V).—Difluoromesitylene (0.77 mole) was nitrated in liquid anhydrous hydrofluoric acid (50 moles) by the addition of sodium nitrite (0.8 mole) according to the above procedure except that external cooling was not necessary. Yield of crude nitro compound was 90–92%, m. p. 53°.

Anal. Calcd. for $C_9H_9O_2NF_2$: C, 53.73; H, 4.51; N, 6.96. Found: C, 53.93; H, 4.49; N, 7.10.

A "mixed" acid nitration with concd. nitric and sulfuric acids gave the same nitro compound but in a slightly lower yield. Steam distillation gave a fairly pure product.

2-Fluoro-4-nitromesitylene (II).—A mixture of 400 g. of crude, powdered nitromesidine[10] and 1150 cc. of concd. hydrochloric acid was heated to form the amine hydrochloride, and then chilled rapidly to 0°. A solution of 190 g. of sodium nitrite in 350 cc. of water was added slowly while the reaction temperature was maintained at −5 to 0°. The clear diazonium chloride solution, after skimming off any tar-like material floating on the surface, was cooled to −10°, and a solution of 360 g. of sodium fluoborate in 430 cc. of water was added to form the insoluble diazonium fluoborate. In general, a yield of 95% was obtained.

The fluoborate salt was decomposed by careful heating in a large round-bottom flask equipped with a large bore, air reflux condenser, and allowing the exit gases to escape in a hood. After gas evolution had ceased, an ether extraction removed the crude product from the black, solid residue. The ether extract, after the usual water and 5% sodium hydroxide solution washings, drying and evaporation, gave a crude yield ranging from 210–270 g. or 53–67% based on the mesidine. Vacuum distillation gave pure 2-fluoro-4-nitromesitylene as a pale yellow, crystalline solid, m. p. 43–44°, b. p. 97–99° (10 mm.).

Anal. Calcd. for $C_9H_{10}O_2NF$: C, 59.00; H, 5.50; N, 7.64. Found: C, 58.73; H, 5.52; N, 7.63.

2-Fluoro-4-aminomesitylene (III).—This amine was prepared from the preceding nitro compound by the usual iron reduction[11] in an 88% yield. Steam distillation gave a product sufficiently pure for the subsequent reactions. Recrystallization from low boiling petroleum ether gave pure 2-fluoro-4-aminomesitylene as a white solid, m. p. 38.5–39.5°.

Anal. Calcd. for $C_9H_{12}NF$: C, 70.56; H, 7.90; N, 9.15. Found: C, 70.68; H, 7.75; N, 9.21.

Recrystallization of the acetyl derivative from aqueous ethanol gave white needles, m. p. 181–182°.

Anal. Calcd. for $C_{11}H_{14}ONF$: N, 7.18. Found: N, 7.22.

2,4-Difluoromesitylene (IV).—This compound was prepared from 2-fluoro-4-aminomesitylene (III) by the usual procedure.[11] The yield of diazonium fluoborate salt was 90–100%, and the crude yield of difluoromesitylene was 80–90% based on the amine.

Pure 2,4-difluoromesitylene is a colorless liquid, f. p. *ca.* −18.5°, b. p. 69.5° (20 mm.) or 168–169° (atm.), $d^{20}{}_4$ 1.183, $n^{20}{}_D$ 1.4682, γ^{20} 30.94 dynes/cm.

Anal. Calcd. for $C_9H_{10}F_2$: C, 69.21; H, 6.46. Found: C, 69.36; H, 6.20.

2,4-Difluoro-6-aminomesitylene (VI).—Crude 2,4-difluoro-6-nitromesitylene (V) was reduced to the amine with iron filings as described previously. The crude amine was removed from the reaction mixture by steam distillation, yield 83%. Recrystallization from aqueous ethanol gave white, granular crystals, m. p. 51–51.5°.

Anal. Calcd. for $C_9H_{11}NF_2$: C, 63.13; H, 6.48. Found: C, 63.31; H, 6.28.

The acetyl derivative upon recrystallization from ethanol gave white needles, m. p. 185–186°.

Anal. Calcd. for $C_{11}H_{13}ONF_2$: C, 61.96; H, 6.14. Found: C, 62.21; H, 6.07.

2,4,6-Trifluoromesitylene (VII).—Approximately 349 g. (2.04 moles) of powdered crude difluoromesidine was digested in 635 cc. of hot concd. hydrochloric acid to form the amine hydrochloride, and then chilled rapidly to 0° with stirring. To the thick pasty mass, a solution of 170 g. of sodium nitrite in 230 cc. of water was added slowly and the temperature not allowed to rise above 0°. The diazonium chloride solution with its precipitate of sodium chloride was cooled to −10°, and a solution of 560 g. of sodium fluoborate in 675 cc. of water was added. A heavy white magma of the diazonium fluoborate was obtained. The fluoborate salt was removed by filtration and dried in cool air (below 20°). A cool drying temperature was necessary as the damp salt had a tendency to liquefy at 25–30° until the moisture content had been reduced below a certain limit. Yield of dry salt was 533 g. or 97%; other experiments gave a yield range of 90–100%.

The fluoborate salt was decomposed thermally by low, continuous heating in a large flask equipped with a reflux condenser. Air was passed through the condenser jacket, but periodically some steam was used to melt down the solid condensate and thereby avoid condenser plugging. Vacuum distillation of the crude product gave a colorless main fraction, b. p. 91–94° (65 mm.), which solidified upon cooling. Purification may be effected also by sublimation. The yield data based on amine was (1) crude, 308 g. or 86%, and (2) distilled, 278 g. or 78%. Pure 2,4,6-trifluoromesitylene, m. p. 68°, b. p. 169°, is a white solid, quite volatile, sublimes slowly on standing to long, slender crystals, and it exhibits thixotropic properties in that the crystals appear to partially melt on mechanical working.

Anal. Calcd. for $C_9H_9F_3$: C, 62.03; H, 5.14. Found: C, 61.84; H, 5.16.

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[8] The authors are indebted to Mr. H. S. Clark, microanalyst of the Survey, for the analyses given in this investigation. Acknowledgment is made also of the assistance of Messrs. D. M. Burness, D. M. Fort, J. L. Finnerty and R. E. Oesterling.

[9] All melting and boiling points are uncorrected, and freezing points were determined with a toluene thermometer.

[10] Morgan and Davies, *J. Chem. Soc.*, **123**, 231 (1923).

[11] Finger and Reed, This Journal, **66**, 1973 (1944).

Chlorination of 2,4,6-Trifluoromesitylene.—The chlorination apparatus and procedure was similar to that described by McBee, *et al.*[12] No yield data were obtained due to the complexity of the reaction products and the difficulties encountered in isolating pure components.

Trifluoromesitylene was dissolved in a large excess of carbon tetrachloride and chlorinated below the boiling point of the solvent. The chlorination was strongly exothermic and rapid up to a "hexachloro" stage, whereupon it became very slow and the solvent was removed by distillation. This sluggish condition prevailed even at the higher temperatures (<200°). At the elevated temperatures, chlorinolysis of the methyl groups also took place since carbon tetrachloride in an appreciable amount and 2,4,6-trichloro-1,3,5-trifluorobenzene were found in the complex mixture of products. The yield of 2,4,6-tris-(trichloromethyl)-1,3,5-trifluorobenzene was rather low and it is quite conceivable that the chlorinolysis reaction was largely responsible for it. Fractional distillations and recrystallizations were used in isolating the various products.

The "hexachloro" compound was dissolved in petroleum ether and chromatographed through an aluminum oxide column with benzene as an eluant. A final recrystallization from ethanol gave white needles, m. p. 116–116.5°. It is quite likely that this compound is 2,4,6-tris-(dichloromethyl)-1,3,5-trifluorobenzene.

Anal. Calcd. for $C_9H_3Cl_6F_3$: C, 28.38; H, 0.79. Found: C, 28.49; H, 0.79.

2,4,6-Tris-(trichloromethyl)-1,3,5-trifluorobenzene upon recrystallization from ethanol gave white needles, m. p. 125–126°.

Anal. Calcd. for $C_9Cl_9F_3$: C, 22.32; Cl, 65.90. Found: C, 22.36; Cl, 66.03.

2,4,6-Trichloro-1,3,5-trifluorobenzene is a white solid, m. p. 62–63°, b. p. 79.5° (12 mm.).

Anal. Calcd. for $C_6Cl_3F_3$: C, 30.61. Found: C, 30.34, 30.45.

Aceto Derivatives: Trifluoroacetomesitylene.—Trifluoroacetic anhydride reacts with mesitylene in carbon disulfide with anhydrous aluminum chloride as a catalyst. A 16% yield of impure trifluoroacetomesitylene was obtained, b. p. 95–96.5° (25 mm.), and it was identified by nitration in red, fuming nitric acid to a dinitro derivative, m. p. 82.5° (ethanol).

Anal. Calcd. for $C_{11}H_9F_3O_5N_2$: C, 43.14; H, 2.96. Found: C, 43.26; H, 3.04.

Acetodifluoromesitylene.—Difluoromesitylene was converted to the aceto derivative by the usual Friedel–Crafts reaction with acetic anhydride, 85% yield. Pure acetodifluoromesitylene distils as a colorless product m. p. 23–24°, b. p. 120° (20 mm.) or 202–205° (atm.).

Anal. Calcd. for $C_{11}H_{12}OF_2$: C, 66.65; H, 6.10. Found: C, 66.65; H, 5.98.

Tribromoacetodifluoromesitylene.—The Hofmann hypobromite reaction[13] on acetodifluoromesitylene gave an 88% yield of the tribromoaceto derivative. Recrystallization from ethanol gave long, white needles of pure tribromoacetodifluoromesitylene, m. p. 81.5°.

Anal. Calcd. for $C_{11}H_9Br_3F_2O$: C, 30.38; H, 2.09. Found: C, 30.35; H, 2.10.

Trichloroacetodifluoromesitylene.—This compound was obtained in a 74% yield from acetodifluoromesitylene by the Hofmann hypochlorite reaction.[13] The pure compound is a heavy viscous oil, f. p. *ca.* −20.5°, b. p. 123° (5 mm.).

Anal. Calcd. for $C_{11}H_9Cl_3F_2O$: C, 43.81; H, 3.01. Found: C, 43.91; H, 2.95.

***eso*-Difluoro-β-isodurylic Acid.**—Ten grams of the tribromoacetodifluoromesitylene was hydrolyzed with difficulty to the β-isodurylic acid derivative by the Fuson and Walker[13] method. Recrystallization from benzene and sublimation gave the pure acid as white needles, m. p. 156–157°.

Anal. Calcd. for $C_{10}H_{10}F_2O_2$: C, 60.00; H, 5.04. Found: C, 60.25; H, 4.81.

***eso*-Difluoro-β-isodurylamide.**—A small sample of difluoromesidine was diazotized in hydrochloric acid and a Sandmeyer cuprous cyanide reaction gave the crude nitrile as a solid. The nitrile after recrystallization from ethanol and sublimation gave white needles, m. p. 67.5–68°, but an analysis indicated that it was slightly impure.

Hydrolysis of the impure nitrile by warming in concentrated sulfuric acid gave the isodurylamide derivative. Attempts to convert the amide to the acid failed even with a nitrosyl sulfuric acid mixture. Recrystallization from ethanol followed by sublimation gave the pure amide as a white powdery material, m. p. 196–197°.

Anal. Calcd. for $C_{10}H_{11}F_2NO$: C, 60.29; H, 5.57; N, 7.02. Found: C, 60.37; H, 5.61; N, 7.39.

Miscellaneous Derivatives

4,6-Dinitro-2-fluoromesitylene.—This compound was prepared by the nitration of fluoromesitylene or 4-nitro-2-fluoromesitylene in red, fuming nitric acid. Recrystallization from aqueous ethanol gave white needles, m. p. 95–96.5°.

Anal. Calcd. for $C_9H_9O_4N_2F$: C, 47.37; H, 3.97; N, 12.27. Found: C, 47.40; H, 3.96; N, 12.23.

4-Amino-6-nitro-2-fluoromesitylene.—A sodium polysulfide reduction on the preceding dinitro compound gave a quantitative yield of 4-amino-6-nitro-2-fluoromesitylene. An aqueous ethanol recrystallization gave yellow crystals, m. p. 72°. The acetyl derivative was obtained as almost colorless needles, m. p. 204.5–206°.

Anal. Calcd. for $C_{11}H_{13}O_3N_2F$: C, 54.99; H, 5.45; N, 11.66. Found: C, 54.88; H, 5.42; N, 11.69.

4,6-Diamino-2-fluoromesitylene.—Reduction of the preceding dinitro- or nitroaminofluoromesitylene gave the corresponding diamine. Recrystallization from high boiling petroleum ether gave long, white needles, m. p. 134–135°.

Anal. Calcd. for $C_9H_{13}N_2F$: C, 64.14; H, 7.78. Found: C, 64.50; H, 7.61.

2-Chloro-4-fluoromesitylene.—This compound was obtained in a very small amount as a by-product in the synthesis of 2,4-difluoromesitylene. It is a colorless liquid, f. p. −8°, b. p. 203–204°, n^{20}D 1.51046.

Anal. Calcd. for $C_9H_{10}ClF$: C, 62.61; H, 5.84. Found: C, 62.61; H, 5.82.

Summary

Nitration of mesitylene and difluoromesitylene in anhydrous hydrofluoric acid gave near quantitative yields of dinitromesitylene and 2,4-difluoro-6-nitromesitylene, respectively. Difluoro- and trifluoromesitylene were synthesized by the Schiemann reaction in record yields reported for this type of reaction. Various intermediates and derivatives are reported for the fluoromesitylenes.

Among the products of exhaustive chlorination of trifluoromesitylene, 2,4,6-tris-(trichloromethyl)-1,3,5-trifluorobenzene and 2,4,6-trichloro-1,3,5-trifluorobenzene were identified.

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[12] McBee, *et al.*, *Ind. Eng. Chem.*, **39**, 395 (1947).

[13] Fuson and Walker, THIS JOURNAL, **52**, 3274 (1930).