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Diazotization of Tetrafluoroanthranilic Acid and Several Reactions of Related Compounds

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Diazotization of tetrafluoroanthranilic acid with nitrosylsulfuric acid in acetic acid gave a ring-hydroxylated, stable diazonium salt **4**, which was isolated in high yield. Several reactions on this diazo compound were carried out. Replacement of the diazonium group with hydrogen, chlorine, or bromine was accomplished with the usual reagents. The reaction of diazo compound with diazomethane afforded a benzoxadiazine compound **13**. Other related polyfluoroaromatic compounds were prepared.

Tetrafluoroanthranilic acid (**1**) is a valuable precursor of tetrafluorobenzyne through the diazotized intermediate, tetrafluorobenzenediazonium-2-carboxylate (**2**).[1] Since an unsubstituted benzenediazonium-2-carboxylate is known as a stable, isolable compound,[2] we intended to isolate the analogous stable diazonium compound from **1**. When **1** was diazotized with sodium nitrite in dilute hydrochloric acid in the usual

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[1] S. Hayashi and N. Ishikawa, *Nippon Kagaku Zasshi*, **91**, 1000 (1971).

[2] M. Stiles, R. G. Miller, and U. Burckhardt, *J. Amer. Chem. Soc.*, **85**, 1792 (1963).

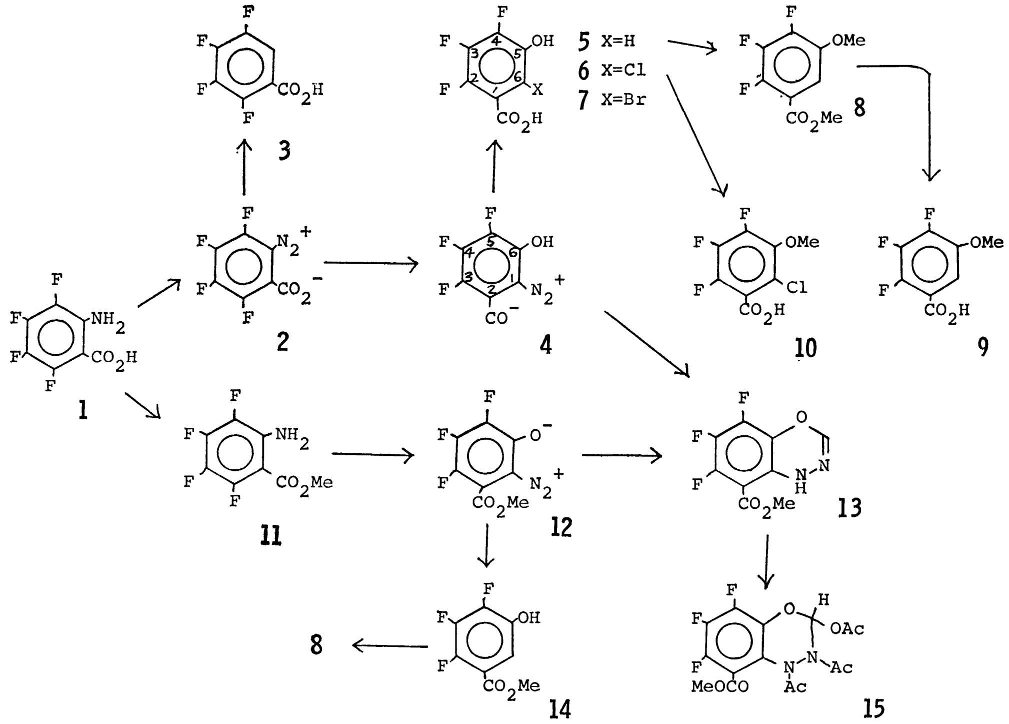

Chart A

manner, only a clear diazo solution was obtained, from which any attempted isolation of the diazonium compound was unsuccessful.

When the reaction was carried out with nitrosylsulfuric acid in acetic acid, however, a very stable diazonium compound of mp 187°C (decomp.) was obtained in good yield, and the structure of this compound was proved to be 3,4,5-trifluoro-6-hydroxybenzenediazonium-2-carboxylate (**4**) by ^{1}H and ^{19}F NMR and mass spectra. In this case, it was evident that the fluorine atom *ortho* to diazo group had been nucleophilically replaced with hydroxyl group during the course of the diazotization. This is not peculiar since a halogen substituent in *para* or *ortho*, especially the latter, to diazonium group is known readily replaceable by nucleophile.[3,4] As for polyfluoroaromatic compounds, it was reported that pentafluoroaniline gave *p*-hydroxytetrafluorobenzenediazonium salt exclusively when it was diazotized with sodium nitrite in hydrochloric acid or in 70% sulfuric acid.[5]

For the purpose of clarifying the structure and reactivity of a exceptionally stable diazonium compound **4**, we examined several reactions on this material. On heating with aqueous hypophosphorous acid it was reduced into 2,3,4-trifluoro-5-hydroxybenzoic acid (**5**) with evolution of nitrogen gas. The same reaction occurred when the diazonium compound was warmed with copper powder in either water, or ethanol, or dimethylformamide.

The diazonium group was also readily replaced with halogens affording 2,3,4-trifluoro-6-halogeno-5-hydroxybenzoic acid, **6** and **7**, in good yields when **4** was treated with the corresponding cuprous halides in aqueous hydrogen halides. However, the replacement of the diazonium group with iodine was unsuccessful. With aqueous potassium iodide alone there was no reaction, whereas in the presence of copper powder diazonium group was split off to give 2,3,4-trifluoro-5-hydroxybenzoic acid (**5**). This might be attributed to the steric effect on the attack of the bulky iodide ion. The NMR spectra of the compound **5**—**10** served for the determination for the positions of substituents (*loc. cit.*).

When diazomethane was allowed to react with 3,4,5-trifluoro-6-hydroxybenzenediazonium-2-carboxylate, an interesting heterocyclic compound, 6,7,8-trifluoro-5-methoxycarbonyl-4H-1,3,4-benzoxadiazine (**13**), was obtained. The yield was rather good (83%), and the structure was derived from its mass, NMR, and IR spectra. In the course of this reaction diazomethane should have attacked 3,4,5-trifluoro-2-methoxycarbonylbenzenediazonium-6-oxide (**12**), and this was confirmed preparatively.

Thus, the diazo oxide **12**, obtained from tetrafluoroanthranilic acid by methylation with methanol–sulfuric acid and subsequent diazotization of the resulting ester **11** with nitrosylsulfuric acid, was similarly converted to the oxadiazine **13** on treating with diazomethane. An analogous reaction between a diazo oxide and a substituted diazomethane was reported by R. Huisgen *et al.*[6] who observed the formation of 5,6,7,8-tetrachloro-2-phenyl-4*H*-1,3,4-benzoxadiazine from 3,4,5,6-tetrachlorobenzenediazonium-2-oxide and phenyldiazomethane.

The structure of the trifluoromethoxycarbonylben-

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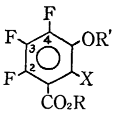
[3] K. H. Saunders, "The Aromatic Diazo Compounds", Edward Arnold & Co., London (1964), p. 117.

[4] J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).

[5] G. M. Brooke, E. J. Forbes, R. D. Richardson, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, **1965**, 2088.

[6] R. Huisgen and R. Fleischman, *Ann.*, **623**, 47 (1959).

Table 1. NMR spectra of **5**—**10**



Compd	^{1}H (τ)			^{19}F					
				δ ppm$^{a)}$			*J* (Hz)		
	R	X	R′	2-F	3-F	4-F	2-3	3-4	4-2
5	H	H 2.63$^{b)}$	H	66.2	82.1	72.5	21.8	21.8	4.8
6	H	Cl	H	71.3	83.3	75.0	22.1	19.6	~0
7	H	Br	H	70.8	82.2	74.8	22.0	19.6	~0
8	Me 6.17 (s)	H 2.90$^{c)}$	Me 6.17 (s)	60.4	78.2	67.7	16.8	16.8	
9	H	H 2.57$^{d)}$	Me 6.00 (s)	64.7	89.7	78.1	20.0	20.0	
10	H	Cl	Me 6.02 (d) J_{F-OMe} 1.5Hz	65.3	85.4	71.1	20.0	20.0	

a) From ext. CF_3CO_2H in Me_2CO or CCl_4.
b) J^m_{HF} 6.5, 9.0, J^p_{HF} 2.8 Hz.
c) J^m_{HF} 7.5, 7.8, J^p_{HF} 2.5 Hz.
d) J^m_{HF} 7.2, 8.1, J^p_{HF} 2.6 Hz.

zenediazonium oxide (**12**) was easily deduced by converting it to methyl 2,3,4-trifluoro-5-methoxybenzoate (**8**). Thus, treatment of **12** with 50% hypophosphorous acid afforded the phenol **14**, which gave **8** with diazomethane, indicating the validity of the assignment of structure **12** to the diazo oxide.

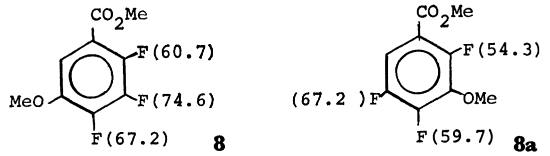
Benzoxadiazine **13** reacted with acetic anhydride to give 2-acetoxy-3,4-diacetyl-6,7,8-trifluoro-5-methoxycarbonyl-2*H*-3,4-dihydro-1,3,4-benzoxadiazine (**15**). The structure was confirmed by ^{1}H NMR spectrum.

For the generation of tetrafluorobenzyne, tetrafluoroanthranilic acid was diazotized with *n*-butyl nitrite in organic solvent.1) No hydroxylation or other nucleophilic reaction seemed to occur in this case. To confirm this we carried out the above diazotization in the presence of copper powder. As a result 2,3,4,5-tetrafluorobenzoic acid (**3**) was obtained in 62% and no other product was detected. Formation of **3** could be rationalized by the reductive decomposition of tetrafluorobenzenediazonium-2-carboxylate, which had not been hydroxylated in the absence of water.

NMR Spectra. In NMR spectra of polyfluoroaromatic compounds, it is generally known that the hydrogen nucleus in XCH_3 (X=O, N, S *etc.*) couple with both fluorine nuclei in *ortho* positions,7) but if one *ortho* position is unsubstituted such a coupling is not observed.8) This rule played an important role in the determination of positions of substituents in our compounds. Thus, in trifluoromethoxybenzoic acid **9** which was derived from **4**, *via* **5** and **8**, the signal of OCH_3 appeared as a sharp singlet. This means that the methoxyl group has one *ortho* fluorine atom and the other *ortho* position is unsubstituted. Among four trifluoromethoxybenzoic acids which can be considered in this case, only 2,3,4-trifluoro-5-methoxybenzoic acid is suited for this limitation (Table 1).

As for chlorotrifluoromethoxybenzoic acid (**10**), the NMR signal of OCH_3 protons appeared as a doublet (J=1.5 Hz). This also supports the assignment of structure of **10** as 6-chloro-2,3,4-trifluoro-5-methoxybenzoic acid, because it means one *ortho* position to methoxyl group is occupied with fluorine and the other with chlorine.

The structure of the methyl trifluoromethoxybenzoate (**8**) was deduced from the ^{19}F NMR spectrum. Utilizing Bruce's substituent shielding parameter,9) the chemical shifts of the various fluorine atoms for two possible structures, methyl 2,3,4-trifluoro-5-methoxybenzoate (**8**) and methyl 2,4,5-trifluoro-3-methoxybenzoate (**8a**) were calculated. The observed fluorine chemical shifts are in agreement with those expected for the former (**8**) (Fig. 1).



8 **8a**

Fig. 1. Calculated ^{19}F NMR chemical shift for **8** and **8a**.

Regarding ^{19}F NMR spectra of polyfluoroaromatic compounds it is also known that the signal of fluorine atom lying between two *ortho* fluorine atoms shift considerably to the upper field.10) In the spectra of the polyfluorodiazo compounds **4** and **12**, however, a shift to lower field of the 4-F signal was observed. This was probably caused by the strong electron-withdrawing effect of diazo group. A similar observation in the case of 3,4,5,6-tetrafluorobenzenediazonium-2-oxide was reported recently.11)

The structure for the acetoxy compound **15** was

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7) J. Burdon, *Tetrahedron*, **21**, 1101 (1965).

8) J. Burdon and W. B. Hollyhead, *J. Chem. Soc.*, **1965**, 6326.

9) M. I. Bruce, *J. Chem. Soc.*, *A*, **1968**, 1459.

10) J. W. Emsley, J. Feeney, and L. H. Sutchliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon Press (1966), Vol. 2, p. 905.

11) J. B. Birchall, R. N. Haszeldine, J. Nikokavouras, and E. S. Wilks, *J. Chem. Soc.*, *C*, **1971**, 562.

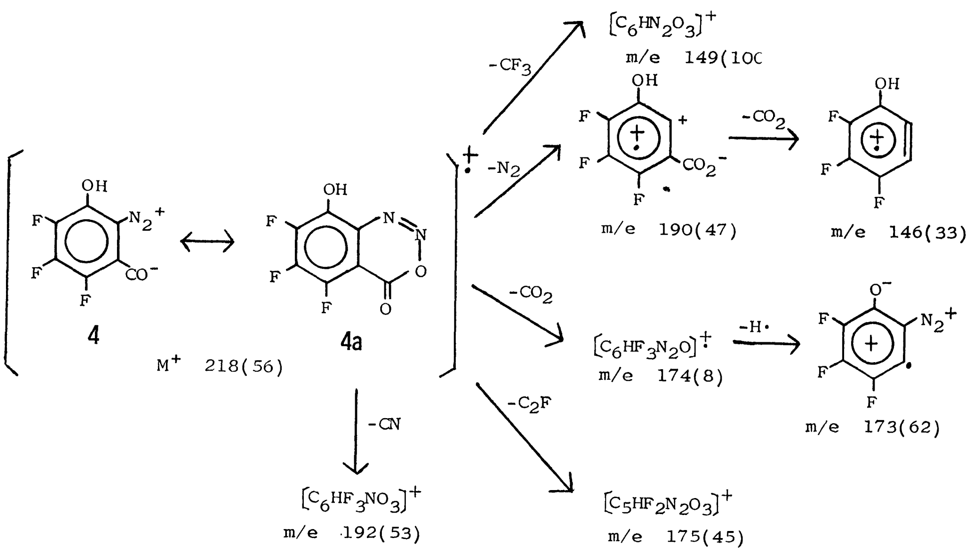

Fig. 2. MS fragmentation of **4**.

deduced from a consideration of the ^{1}H NMR spectrum. It showed five singlet signals, namely 7.88, 7.74, 7.65, 6.07, and 1.77 at τ-value. Signals, each integrating for three protons, at 7.88 and 7.74 were assigned to =N-COCH$_3$, while those at 7.65 and 6.07 were attributed to COCH$_3$ and CO$_2$Me respectively. Since it is well-known that methyl shift of acetamide is 7.85—8.25, usual acetic compounds 7.65—8.05 and methyl ester 5.8—6.6,[12] a signal at 1.77 was assigned to a methine proton.

Mass Spectra. The spectrum of 3,4,5-trifluoro-6-hydroxybenzenediazonium-2-carboxylate (**4**) was explained by the various fragments shown in Fig. 2. The intensity of the molecular ion (*m/e* 218) was unexpectedly strong. As anticipated, loss of N$_2$ (*m/e* 190) and then of CO$_2$ gave the ion of mass number 146, which was ascribed to ionized trifluorohydroxybenzyne. The ions of *m/e* 149 (base peak) and 175 could be rationalized by elimination of CF$_3$ and C$_2$F respectively, since such fragmentations are characteristic of polyfluorinated aromatic compounds.[13] Aside from the expected fragmentations, loss of CN (*m/e* 192) is interesting, as this ion could be considered to have been derived only from the structure (**4a**).

In the spectrum of 2,3,4-trifluoro-5-hydroxybenzoic acid (**5**), a strong molecular ion, also the base peak, was observed at *m/e* 192. Besides the expected decompositions, namely loss of OH, CO$_2$H, and (CO$_2$H+CO), peaks corresponding to *m/e* 149 and 69 were also observed. These could similarly be rationalized, as in the case of **4**, by eliminations of C$_2$F or CF$_3$ ion itself.

For 6,7,8-trifluoro-5-methoxycarbonyl-4*H*-1,3,4-benzoxadiazine (**13**), the spectrum showed a peak *m/e* 214 which corresponded to an ion formed by elimination of CH$_3$OH from the molecular ion (*m/e* 246), thus suggesting the presence of a H-containing group located on an *ortho* position to the methoxycarbonyl group[14] (Fig. 3). Other significant decompositions observed were loss of OMe (*m/e* 215), followed by eliminations of CO and HCN to give ions of *m/e* 187 and 160 respectively, the last process being charac-

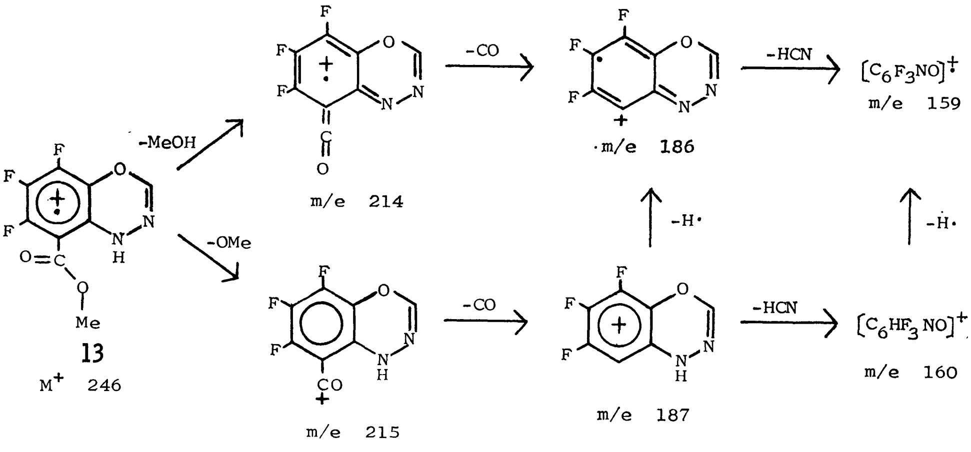

Fig. 3. MS fragmentation of **13**.

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[12] N. Nakagawa, "Interpretation of NMR Spectra" Kyoritsu, (1966), pp. 30—31.

[13] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, Inc. (1967), p. 441.

[14] *Ibid.*, pp. 199—200, 220.

teristic of nitrogen heterocycles.[15]

Experimental

3,4,5-Trifluoro-6-hydroxybenzenediazonium-2-carboxylate (4). Nitrosylsulfuric acid, prepared from sodium nitrite (7.6 g; 110 mmol) and concentrated sulfuric acid (60 m*l*), was added to a vigorously stirred solution of tetrafluoroanthranilic acid (20.9 g; 100 mmol) in glacial acetic acid (100 m*l*) during 15 min, the temperature of the reaction mixture being maintained below 40°C. The mixture was further stirred for 2 hr at room temperature and then poured onto crushed ice. After stirring for a further 1 hr, the mixture was left overnight in a refrigerator. The orange precipitate (15.4 g) was filtered, washed successively with cold water, cold ethanol-ether (1: 1 v/v) and dried. The filtrate was saturated with sodium chloride and extracted with ethyl ether. The ether extract was washed with saturated aqueous sodium chloride, dried and the solvent was removed under reduced pressure. After rinsing with a small amount of ether, the residue (2.4 g) was combined with the initial crop to give 3,4,5-trifluoro-6-hydroxybenzenediazonium-2-carboxylate (17.8 g, 81.5%), which crystallized from dioxane as orange crystals, mp 187°C (decomp.).

Found: C, 38.5; H, 0.40; F, 26.2; N, 13.2%. Calcd for $C_7HF_3N_2O_3$: C, 38.6; H, 0.46; F, 26.1; N, 12.8%. IR (KBr): 2800 (OH), 2180 ($-N_2^+$), 1710 (CO), 1630, 1474 (Ar). 1550, 1415 (CO_2^-) cm^{-1}. ^{19}F NMR: (δ ppm from ext. CF_3CO_2H in DMF) +61.8 (5-F, dd, J_{54} 21.3, J_{53} 4.2 Hz), +68.2 (4-F, dd, J_{43} 15.4 Hz), +71.0 (3-F, dd).

2,3,4-Trifluoro-5-hydroxybenzoic Acid (5). *a) With Hypophosphorous Acid*: A mixture of 3,4,5-trifluoro-6-hydroxybenzenediazonium-2-carboxylate (5.0 g; 22.9 mmol) and 50% hypophosphorous acidd (50 m*l*) was refluxed for 1 hr. After cooling to room temperature, the reaction mixture was extracted with ethyl ether. The ether extract was washed with water, dried and evaporated to give 2,3,4-trifluoro-5-hydroxybenzoic acid (3.0 g, 68%), which crystal lized from chlorobenzene, mp 163—165°C.

Found: F, 30.2%. Calcd for $C_7H_3F_3O_3$: F, 29.7%. IR (KBr): 3208 (OH), 1681 (CO), 1618, 1489 (Ar) cm^{-1}.

b) With Copper in Ethanol: A mixture of copper powder (0.5 g) and diazoniumcarboxylate **4** (0.5 g; 2.29 mmol) in ethanol (5 m*l*) was heated on a steam-bath for 1 hr. After cooling to room temperature, the copper was filtered and the filtrate was evaporated to dryness. The solid was treated with 2% aqueous sodium hydroxide and insoluble matter was removed by filtration. The filtrate was acidified and then extracted with ethyl ether. Evaporation of the dried ether extract afforded a residue (0.18 g, 41%) which was recrystallized from toluene to give **5**, mp 163—165°C, undepressed on admixture with a sample from *a*).

c) With Copper in Water: Diazoniumcarboxylate **4** (1.0 g; 4.58 mmol) was added in small portions to a mixture of copper powder (1.0 g) and water (10 m*l*) at 60°C. After the evolution of gas had subsided the mixture was refluxed for 10 min. The reaction mixture was treated as described in *b*) to give **5** (0.73 g, 83%), mp 163—165°C.

d) With Copper in Dimethylformamide: A solution of diazoniumcarboxylate **4** (1.0 g; 4.58 mmol) in dimethylformamide (5 m*l*) was added dropwise to a mixture of copper powder (1.0 g) and dimethylformamide (5 m*l*) at room temperature during 20 min. The reaction mixture was stirred for 40 min, then heated on the steam-bath for 30 min, and similarly treated as in *b*) to give **5** (0.31 g; 35%), mp 163—165°C.

5-Acetoxy-2,3,4-trifluorobenzoic acid. 2,3,4-Trifluoro-5-hydroxybenzoic acid (**5**) (1.0 g; 5.21 mmol) was heated with acetic anhydride (92 m*l*) and a trace of concentrated sulfuric acid at 60—65°C for 10 min. The mixture was poured onto ice and stirred. The acetoxyl compound was collected (0.98 g; 80%) and recrystallized from cyclohexane. mp 154°C.

Found: F, 24.2%. Calcd for $C_9H_5F_3O_4$: F, 24.3%. IR: 3080 (Ar-H), 2840 (OH), 1782, 1682 (CO), 1616, 1476 (Ar) 1190, 1110 (C–F) cm^{-1}.

Methyl 2,3,4-Trifluoro-5-methoxybenzoate (8). An ethereal solution of diazomethane was added dropwise to hydroxybenzoic acid **5** (1.0 g; 5.21 mmol) in ether (10 m*l*) and then stirred for 2—3 hr at room temperature. Evaporation of the ether, followed by recrystallization from *n*-hexane gave **8** (1.06 g, 92%), mp 60—62°C.

Found: F, 25.5%. Calcd for $C_9H_7F_3O_3$: F, 25.9%.

2,3,4-Trifluoro-5-methoxybenzoic Acid (9). Methyl ester **8** was refluxed with 5% sodium hydroxide solution for 0.5 hr to give **9** (86%), mp 161—162°C (from benzene).

Found: F, 27.6%. Calcd for $C_8H_5F_3O_3$: F, 27.7%.

6-Chloro-2,3,4-trifluoro-5-hydroxybenzoic Acid (6). 3,4,5-Trifluoro-6-hydroxybenzenediazonium-2-carboxylate (**4**) (2.0 g; 9.16 mmol) was added in small portions to a stirred solution of cuprous chloride (5.0 g) in concentrated hydrochloric acid (20 m*l*) at 60—70°C during 10 min. The mixture was refluxed for 0.5 hr and worked up as described for the compound **5** (Method *b*) to give chlorotrifluorohydroxybenzoic acid **6** (2.09 g; quantitatively). The acid has mp 131—132°C after sublimation followed by recrystallization from dichloroethane.

Found: Cl, 15.6; F, 25.5%. Calcd for $C_7H_2ClF_3O_3$: Cl, 15.6; F, 25.2%. IR: 3227 (OH), 1720 (CO), 1611, 1485 (Ar), 1119, 1049 (C–F), 858 (C–Cl) cm^{-1}.

6-Chloro-2,3,4-trifluoro-5-methoxybenzoic Acid (10). Excess ethereal diazomethane was added dropwise to a stirred solution of the acid **6** (0.77 g; 3.40 mmol) in ether and the reaction mixture was stirred for 2 hr at room temperature. After the solvent was evaporated the residual solid was refluxed with 5% aqueous sodium hydroxide (20 m*l*) for 40 min, then acidified with hydrochloric acid. The precipitate (0.53 g; 65%) was recrystallized from cyclohexane, and after sublimation the pure product showed mp 99—100°C.

Found: F, 23.2%. Calcd for $C_8H_4ClF_3O_3$: F, 23.7%.

6-Bromo-2,3,4-trifluoro-5-hydroxybenzoic Acid (7). Diazoniumcarboxylate (**4**) (2.0 g; 9.16 mmol) was treated similarly with cuprous bromide (5.0 g) in 47% hydrobromic acid (20 m*l*) as described for **6** gave bromotrifluorohydroxybenzoic acid **7** (1.18 g; 73%) which was purified by crystallization from cyclohexane-benzene followed by sublimation, mp 146—147°C.

Found: Br, 29.8; F, 20.7%. Calcd for $C_7H_2BrF_3O_3$: Br, 29.5; F, 21.0%. IR: 3240 (OH), 1718 (CO), 1620, 1475 (Ar), 1194, 1038 (C–F) cm^{-1}.

5-Acetoxy-6-bromo-2,3,4-trifluorobenzoic Acid. The acid **7** (0.50 g; 1.84 mmol) heated with acetic anhydride (1 m*l*) and concentrated sulfuric acid (2 drops) at 60—80°C for 10 min gave the acetate (0.50 g, 87%), mp 192—194°C (from 1,2-dichloroethane).

Found: F, 18.8%. Calcd for $C_9H_4BrF_3O_4$: F, 18.2%.

2,3,4,5-Tetrafluorobenzoic Acid (3). A solution of tetrafluoroanthranilic acid (4.2 g; 20 mmol) in dioxane (15 m*l*) was added dropwise to a mixture of *n*-butyl nitrite (2.6 g; 25 mmol), copper powder (6.8 g) and dioxane (20 m*l*) during 1 hr at 50°C. Stirring was continued for a further 5 hr at 90—93°C, the mixture was then cooled, filtered and the

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15) Q. N. Porter and J. Baldas, "Mass Spectrometry of Heterocyclic Compounds", Wiley-Interscience, (1971), Chap. 11—14.

filtrate was made alkaline by adding 2% aqueous sodium hydroxide solution. The aqueous layer was then acidified with hydrochloric acid, and the separated matter extracted with ether. The ether extract was washed with water, dried and then evaporated to give 2,3,4,5-tetrafluorobenzoic acid (**3**) (2.4 g; 62%), which was purified by sublimation followed by recrystallization from *n*-hexane, mp 90—92°C (lit,[16] mp 92—92.5°C).

Found: F, 39.2%. Calcd for $C_7H_2F_4O_2$: F, 39.2%. NMR (CCl_4): ^1H: τ -0.43 (s, CO_2H), 2.15—2.65 (m, Ar-H), ^{19}F (δ ppm from ext. CF_3CO_2H) $+59.2$ (2-F), $+59.6$ (5-F), $+72.8$ (4-F), $+74.9$ (3-F).

*6,7,8-Trifluoro-5-methoxycarbonyl-4*H*-1,3-benzoxazine (**13**).*

*a) From 3,4,5-trifluoro-6-hydroxybenzenediazonium-2-carboxylate (**4**)*: An excess of ethereal diazomethane was added dropwise to the diazoniumcarboxylate **4** (1.00 g; 4.58 mmol) in ether (20 m*l*) with stirring. Evolution of gas was observed immediately and the reaction mixture changed to a reddish solution. After further stirring for 2 hr at room temperature the solvent was evaporated, 2% aqueous solution of sodium hydroxide was added and the mixture kept overnight in a refrigerator. The yellowish green solid (0.94 g, 83%) was filtered, washed successively with dilute hydrochloric acid and water then recrystallized from cyclohexane to give the benzoxadiazine **13**, mp 153—154°C.

Found: C, 44.3; H, 1.99; F, 22.8; N, 11.0%. Calcd for $C_9H_5F_3N_2O_3$: C, 43.9; H, 2.05; F, 23.2; N, 11.4%. IR: 3289 (NH), 1695 (CO), 1650 (C=N), 1603, 1470 (Ar), 1218 (–O–), 1110, 1073 (C–F) cm^{-1}. NMR (in acetone at 50—60°C): ^1H, τ 1.63 (br, =NH), 3.55 (s, CH), 6.10 (s, CO_2Me). ^{19}F (δ from ext. CF_3CO_2H), $+60.6$ (6-F), $+71.4$ (8-F), $+89.9$ (7-F).

*b) From 3,4,5-trifluoro-2-methoxycarbonylbenzenediazonium-6-oxide (**12**)*: Instead of the diazoniumcarboxylate **4** in the above reaction, diazo oxide **12** (1.00 g) in acetone (10 m*l*) was used. The reaction was run similarly and the solid (0.91 g, 86%) obtained was recrystallized to give **13**, mp 151—152°C, which was identified with that prepared in *a*) by IR and mixed mp.

*2-Acetoxy-3,4-diacetyl-6,7,8-trifluoro-5-methoxycarbonyl-2*H-3,4-dihydro-*1,3,4-benzoxadiazine (**15**).* A mixture of the benzoxadiazine **14** (0.50 g; 2.03 mmol), acetic anhydride (5 m*l*) and concentrated sulfuric acid (3 drops) was refluxed for 5 min, then cooled and poured onto ice-water. The precipitate (0.60 g, 76%) was recrystallized from ethanol to give the triacetate **15**, mp 152—153.5°C.

Found: C, 46.2; H, 3.29; N, 6.88%. Calcd for $C_{15}H_{13}F_3N_2O_7$: C, 46.2; H, 3.36; N, 7.18%. NMR ($CDCl_3$): ^1H τ 7.88 (s), 7.74 (s), 7.65 (s), 6.07 (s), 1.77 (s), relative intensity, 3:3:3:3:1.

*Methyl Tetrafluoroanthranilate (**11**).* A mixture of tetrafluoroanthranilic acid (20.9 g; 100 mmol), methanol (200 m*l*) and concentrated sulfuric acid (50 m*l*) was refluxed for 5 hr. The excess methanol was evaporated under reduced pressure, and the mixture poured onto ice-water. The precipitate (17.4 g, 73%) was filtered, washed with water, dried, and recrystallized from methanol to give the methyl ester **11**, mp 104—105°C.

Found: F, 33.9; N, 6.28%. Calcd for $C_8H_5F_4NO_2$: F, 34.1; N, 6.28%.

*3,4,5-Trifluoro-2-methoxycarbonylbenzenediazonium-6-oxide (**12**).* Methyl tetrafluoroanthranilate (**11**) (16.25 g; 73 mmol in glacial acetic acid (70 m*l*) was treated similarly with nitrosylsulfuric acid [prepared from sodium nitrite (5.54 g; 80 mmol) and concentrated sulfuric acid (50 m*l*)] as described for the compound **4** to give the diazonium oxide **12** (11.85 g, 70%), mp 117—117.5°C.

Found: C, 41.3; H, 1.22; N, 12.4%. Calcd for $C_8H_3F_3N_2O_3$: C, 41.4; H, 1.30; N, 12.1%. IR: 2144 ($-N_2^+$), 1720 (CO), 1656, 1477 (Ar), 1141, 1078 (C–F) cm^{-1}. NMR ($CDCl_3$): ^1H; τ 6.00 (s, CO_2Me). ^{19}F; δ $+58.6$ (4-F), $+67.9$ (5-F), $+68.3$ (3-F).

*Methyl 2,3,4-Trifluoro-5-hydroxybenzoate (**14**).* A mixture of the diazo oxide **12** (2.0 g; 8.62 mmol) and 50% hypophosphorous acid (20 m*l*) was refluxed for 2 hr, then cooled to room temperature, and the precipitate (0.90 g) was filtered. The filtrate was extracted with ether which was then evaporated, and the solid residue (0.57 g) was crystallized from chlorobenzene. The purified product (0.43 g) was combined with the precipitate obtained earlier to give the hydroxybenzoate **14** (1.33 g, 77%), mp 154—156°C after recrystallization from chlorobenzene.

Found: F, 27.3%. Calcd for $C_8H_5F_3O_3$: F, 27.6%.

The hydroxy benzoate **14** (0.88 g; 4.27 mmol) was methylated with ethereal diazomethane to give methyl 2,3,4-trifluoro-5-methoxy benzoate, **8** (0.91 g, 97%), mp 61—62°C.

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[16] R. J. Harper, E. J. Solosky, and C. Tamborski, *J. Org. Chem.*, **29**, 2385 (1964).