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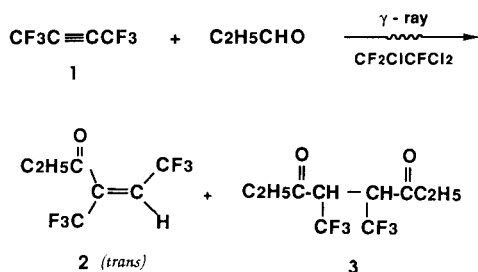
The addition reaction of propionaldehyde to hexafluoro-2-butyne (**1**) under γ -ray irradiation gave *trans*-6,6,6-trifluoro-4-trifluoromethyl-4-hexen-3-one (**2**) and 4,5-bis(trifluoromethyl)octa-3,6-dione (**3**). The latter compound was treated with sulfuric acid to give 2,5-diethyl-3,4-bis(trifluoromethyl)furan (**4a**). Several reactions, such as bromination, dehydrobromination and oxidation, were carried out to prepare derivatives of **4a**.

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Since heterocyclic compounds containing trifluoromethyl groups have attracted much attention, various synthetic methods have been proposed [1]. Though several papers have been reported on the syntheses of trifluoromethyl substituted furans [2a-f], to our knowledge, only a few 2,5-disubstituted 3,4-bis(trifluoromethyl)furans have been synthesized [3]. Previously, we reported the radical addition reaction of aldehydes to fluoroolefins [4a,b]. In this paper, the synthesis of 2,5-diethyl-3,4-bis(trifluoromethyl)furan from the 1:2 addition product obtained in the radical addition of propionaldehyde to hexafluoro-2-butyne was examined.

γ -Ray irradiation of a mixture of hexafluoro-2-butyne (**1**) and propionaldehyde in 1,1,2-trichloro-1,2,2-trifluoroethane (F-113) afforded ethyl 6,6,6-trifluoro-4-trifluoromethyl-4-hexen-3-one (**2**) and 4,5-bis(trifluoromethyl)octa-3,6-dione (**3**) in 21 and 76% yields, respectively (Scheme 1). The bis(trifluoromethyl)octadione **3**, having two asymmetric carbons, consisted of two diastereomers, *meso* and *dl* in a ratio of about 3:2. The *dl* diastereomer gradually changed to the *meso* upon standing.

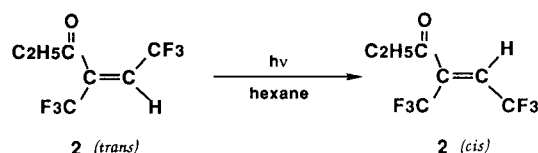
Scheme 1



To determine the geometrical structure of **2**, it was irradiated with a high pressure mercury lamp to give a mixture of *trans* and *cis* isomers in the ratio of 4:1 (Scheme 2). The isomers were isolated using a preparative gas chromatograph and their structures were identified from their ^1H and ^{19}F nmr spectra. Their chemical shifts of hydro-

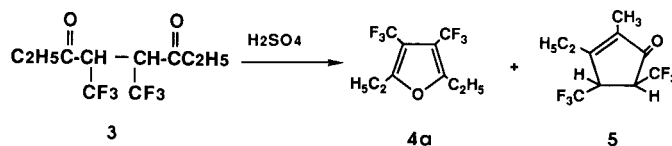
gens in the vinyl groups (*trans*: 6.28 ppm, *cis*: 6.58 ppm) and coupling constants of fluorines on adjacent CF_3 groups (*trans*: 1.7 Hz, *cis*: 10.5 Hz) indicated that the 1:1 addition product **2** was the *trans* form.

Scheme 2



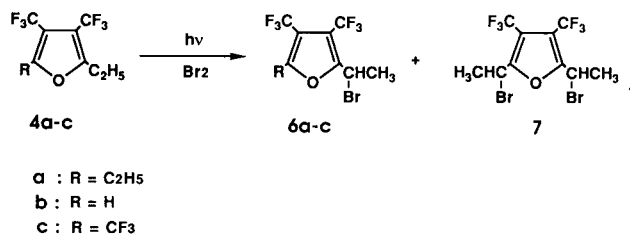
Treatment of **3** with sulfuric acid gave 2,5-diethyl-3,4-bis(trifluoromethyl)furan (**4a**) in 94% yield, together with a small amount of 3-ethyl-2-methyl-4,5-bis(trifluoromethyl)-2-cyclopenten-1-one (**5**) (Scheme 3).

Scheme 3



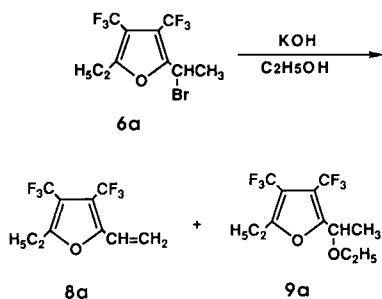
When a molar equivalent of bromine was added to **4a** in carbon tetrachloride, 2-(1-bromoethyl)-5-ethyl-3,4-bis(trifluoromethyl)furan (**6a**) and 2,5-bis(1-bromoethyl)-3,4-bis(trifluoromethyl)furan (**7**) were obtained in 59 and 13% yields, respectively (Scheme 4). While excess amounts of bromine was added to **4a**, only **7** was obtained in 93% yield.

Scheme 4



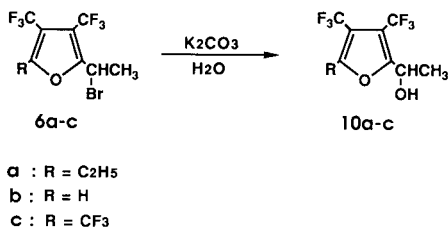
Dehydrobromination of **6a** with potassium hydroxide in ethanol afforded 5-ethyl-3,4-bis(trifluoromethyl)-2-vinylfuran (**8a**) in 23% yield, which easily polymerized upon standing, together with 2-(1-ethoxyethyl)-5-ethyl-3,4-bis(trifluoromethyl)furan (**9a**) in 18% yield (Scheme 5).

Scheme 5

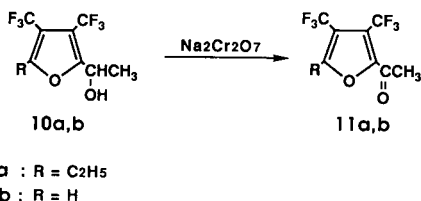


Hydrolysis of **6a** with aqueous potassium carbonate solution afforded 5-ethyl-2-(1-hydroxyethyl)-3,4-bis(trifluoromethyl)furan (**10a**) in 60% yield (Scheme 6), which was then oxidized with sodium bichromate to give 2-acetyl-5-ethyl-3,4-bis(trifluoromethyl)furan (**11a**) in 29% yield (Scheme 7).

Scheme 6

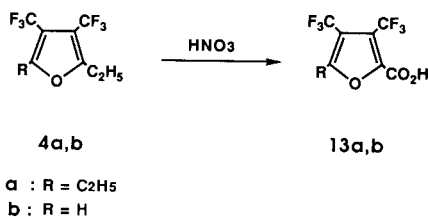


Scheme 7



Oxidation of **4a** with nitric acid in acetic acid at 135-140° gave 45% yield of 5-ethyl-3,4-bis(trifluoromethyl)-2-furancarboxylic acid (**13a**) along with a small amount of 5-ethyl-2-formyl-3,4-bis(trifluoromethyl)furan (**12a**, 1%) (Scheme 8).

Scheme 8

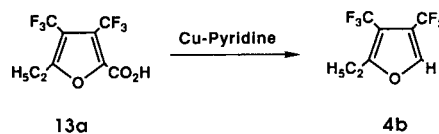


2-Ethyl-3,4-bis(trifluoromethyl)furan (**4b**) was obtained in 69% yield by decarboxylation of **13a** upon treatment with copper in pyridine at 100° (Scheme 9).

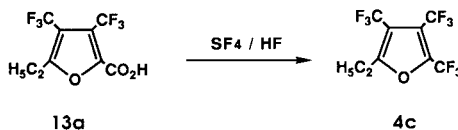
Bromination of **4b** gave 2-(1-bromoethyl)-3,4-bis(trifluoromethyl)furan (**6b**) in 79% yield (Scheme 4), whose hydrolysis with potassium carbonate afforded 2-(1-hydroxyethyl)-3,4-bis(trifluoromethyl)furan (**10b**) in 76% yield (Scheme 6). The oxidation of **10b** with sodium bichromate yielded 2-acetyl-3,4-bis(trifluoromethyl)furan (**11b**) in 50% yield (Scheme 7). Oxidation of **4b** with nitric acid gave only 2% yield of the corresponding furancarboxylic acid **13b**, showing **4b** less reactive than **4a** (Scheme 8).

In order to introduce an additional trifluoromethyl group, **13a** was treated with sulfur tetrafluoride in the presence of anhydrous hydrogen fluoride in an autoclave to give 2-ethyl-3,4,5-tris(trifluoromethyl)furan (**4c**) in 76% yield (Scheme 10) [2d]. Though the bromination of **4c** produced 78% yield of 2-(1-bromoethyl)-3,4,5-tris(trifluoromethyl)furan (**6c**) together with 4% yield of 2-(1,2-dibromoethyl)-3,4,5-tris(trifluoromethyl)furan (**14c**) (Scheme 4), the hydrolysis of **6c** gave only 6% yield of 2-(1-hydroxyethyl)-3,4,5-tris(trifluoromethyl)furan (**10c**) with starting material recovered (Scheme 6). An attempt to oxidize **4c** with nitric acid to prepare the tris(trifluoromethyl)furan-carboxylic acid was unsuccessful.

Scheme 9



Scheme 10



EXPERIMENTAL

General.

The ir spectra were taken on a Hitachi EPI-2 spectrometer. The ¹H and ¹⁹F nmr spectra were measured in carbon tetrachloride with Hitachi R-22 (¹H, 90 MHz) and R-20B (¹⁹F, 56.45 MHz) spectrometers, respectively. The ¹H nmr spectra were indicated in ppm downfield from tetramethylsilane. The ¹⁹F nmr spectra were expressed in ppm downfield from trifluoroacetic acid as an external reference. The mass spectra were measured with a Hitachi RMU-7 spectrometer.

Addition Reaction of Propionaldehyde to Hexafluoro-2-butyne (**1**).

Freshly distilled propionaldehyde (197 g, 3.39 moles) was dissolved in Freon 113 (259 g) in an ampoule. Hexafluoro-2-butyne (**1**) (259 g, 1.8 moles) was then introduced into the am-

poule using a vacuum line. The mixture was degassed by a freeze-thaw cycle and sealed in an ampoule. The γ -ray irradiation was carried out at $2.0 \times 10^5 \text{ r h}^{-1}$ by ^{60}Co for 101 hours at ambient temperature (total irradiation 20 Mr). After the reaction, precipitates which formed were separated by filtration to give *meso*-4,5-bis(trifluoromethyl)octa-3,6-dione (**3**, 211 g, 46%). The distillation of the filtrate gave *trans*-6,6,6-trifluoro-4-trifluoromethyl-4-hexen-3-one (**2**, 74.5 g, 21%) and *dl*-4,5-bis(trifluoromethyl)octa-3,6-dione (**3**, 126 g, 30%).

Compound *trans* **2** had bp 106° ; n_D^{20} 1.3382; d_4^{20} 1.318; ^1H nmr: δ 1.13 (t, $J = 7.4 \text{ Hz}$, CH_3), 2.68 (q, $J = 7.4 \text{ Hz}$, CH_2), 6.28 (qq, $J = 7.5$ and 1.5 Hz , CH); ^{19}F nmr: δ 12.9 (quintet, $J = 1.7$ and 1.5 Hz) 17.2 (dq, $J = 1.7$ and 1.5 Hz).

Anal. Calcd. for $\text{C}_7\text{H}_6\text{OF}_6$: C, 38.19; H, 2.75. Found: C, 38.14; H, 2.80.

Compound *meso* **3** had mp 123° ; ^1H nmr: δ 1.05 (t, $J = 7.2 \text{ Hz}$, CH_3), 2.82 (dq, $J = 7.2$ and 3.3 Hz , CH_2), 4.13 (m, CH); ^{19}F nmr: δ 13.9 (m).

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{F}_6$: C, 43.17; H, 4.35. Found: C, 43.47; H, 4.55.

Compound *dl* **3** had bp $121^\circ/75 \text{ mm Hg}$; n_D^{20} 1.3678; d_4^{20} 1.281; ^1H nmr: δ 1.01 (t, $J = 6.5 \text{ Hz}$, CH_3), 2.4-2.8 (m, CH_2), 4.12 (m, CH); ^{19}F nmr: δ 14.7 (m).

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{F}_6$: C, 43.17; H, 4.35. Found: C, 42.91; H, 4.49.

Isomerization of *trans* **2** under UV Irradiation.

In an ampoule made of quartz and equipped with a Dimroth condenser was placed a hexane solution of **2** (23.4 g, 0.106 mole), which was irradiated with a 1 kW high-pressure mercury lamp for 8 hours. After the reaction, the products were distilled to afford *trans*- and *cis*-**2** in a ratio of 3:1. The *cis*-6,6,6-trifluoro-4-trifluoromethyl-4-hexen-3-one (**2**) was isolated using a preparative gas chromatograph.

Compound *cis* **2** had bp 121° ; ^1H nmr: δ 1.13 (t, $J = 7.4 \text{ Hz}$, CH_3), 2.71 (q, $J = 7.4 \text{ Hz}$, CH_2), 6.58 (q, $J = 8.3 \text{ Hz}$, CH); ^{19}F nmr: δ 18.4 (q, $J = 10.5 \text{ Hz}$), 19.7 (dq, $J = 10.5, 8.3 \text{ Hz}$).

Anal. Calcd. for $\text{C}_7\text{H}_6\text{OF}_6$: C, 38.19; H, 2.75. Found: C, 38.31; H, 2.87.

Synthesis of 2,5-Diethyl-3,4-bis(trifluoromethyl)furan (**4a**).

To **3** (79.9 g, 0.287 mole) was added dropwise sulfuric acid (80 ml) with moderate stirring for 30 minutes. The resultant yellow oil was poured into a mixture of ice and ether. The ether layer was separated, washed with water, and dried over sodium sulfate. After evaporation of ether, the residual liquid was distilled to give 2,5-diethyl-3,4-bis(trifluoromethyl)furan (**4a**, 70.1 g, 94%). From the residue, 3-ethyl-2-methyl-4,5-bis(trifluoromethyl)-2-cyclopenten-1-one (**5**) was isolated in 1% yield using a preparative gas chromatograph.

Compound **4a** had bp $86-87^\circ/90 \text{ mm Hg}$; n_D^{20} 1.3820; d_4^{20} 1.276; ^1H nmr: δ 1.25 (t, $J = 7.5 \text{ Hz}$, CH_3), 2.80 (q, $J = 7.5 \text{ Hz}$, CH_2); ^{19}F nmr: δ 20.8 (s).

Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{OF}_6$: C, 46.16; H, 3.87. Found: C, 46.21; H, 3.76.

Compound **5** had bp 184° ; n_D^{20} 1.3994; d_4^{20} 1.276; ^1H nmr: δ 1.22 (t, $J = 7.5 \text{ Hz}$, CH_3), 1.82 (s, CH_3), 2.68 (q, $J = 7.5 \text{ Hz}$, CH_2), 3.20 (m, H), 3.70 (m, H); ^{19}F nmr: δ 9.34 (m), 9.50 (m).

Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{OF}_6$: C, 46.16; H, 3.87. Found: C, 46.33; H, 4.07.

Bromination of **4**.

To a carbon tetrachloride solution of **4a** (38.0 g, 0.15 mole), was added carbon tetrachloride solution of bromine (24.3 g, 0.15 mole) under ultraviolet irradiation with stirring. After the irradiation (30 minutes), the reaction mixture was poured into dichloromethane. The organic layer was washed with water, 10% aqueous sodium hydroxide solution, and dried over sodium sulfate. Distillation of the organic layer gave 2-(1-bromoethyl)-5-ethyl-3,4-bis(trifluoromethyl)furan (**6a**) (32.3 g, 59%) and 2,5-bis(1-bromoethyl)-3,4-bis(trifluoromethyl)furan (**7**, 7.6 g, 13%) respectively, together with starting material (**4a**, 7.0 g). When excess amounts of bromine (3.14 molar equivalents) was added to **4a**, followed by ultraviolet irradiation for 16.5 hours, **7** was obtained in 93% yield along with a small amount of **6a** (0.7%).

In a similar procedure, the bromination of **4b** and **4c** gave 2-(1-bromoethyl)-3,4-bis(trifluoromethyl)furan (**6b**) and 2-(1-bromoethyl)-3,4,5-tris(trifluoromethyl)furan (**6c**) in 79 and 78% yields, respectively. In the case of **4c**, 2-(1,2-dibromoethyl)-3,4,5-tris(trifluoromethyl)furan (**14c**) was also detected in 4% yield and identified by gc-mass analysis.

Compound **6a** had bp $98-99^\circ/20 \text{ mm Hg}$; n_D^{20} 1.4248; d_4^{20} 1.547; ^1H nmr: δ 1.33 (t, $J = 7.5 \text{ Hz}$, CH_3), 2.03 (d, $J = 7.2 \text{ Hz}$, CH_3), 2.88 (q, $J = 7.5 \text{ Hz}$, CH_2), 5.33 (q, $J = 7.2 \text{ Hz}$, CH); ^{19}F nmr: δ 21.8 (m).

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{OF}_6\text{Br}$: C, 35.42; H, 2.68. Found: C, 35.20; H, 2.68.

Compound **7** (diastereomer) had bp $84-85^\circ/3.5 \text{ mm Hg}$; n_D^{20} 1.4619; d_4^{20} 1.779; ^1H nmr: δ 2.07 (d, $J = 7.2 \text{ Hz}$, CH_3), 2.14 (d, $J = 7.2 \text{ Hz}$, CH_3), 5.38 (q, $J = 7.2 \text{ Hz}$, CH), 5.42 (q, $J = 7.2 \text{ Hz}$, CH); ^{19}F nmr: δ 21.8 (s), 22.0 (s).

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{OF}_6\text{Br}_2$: C, 28.74; H, 1.93. Found: C, 28.76; H, 2.01.

Compound **6b** had bp $97-99^\circ/61 \text{ mm Hg}$; n_D^{20} 1.4140; d_4^{20} 1.667; ^1H nmr: δ 2.04 (d, $J = 7.0 \text{ Hz}$, CH_3), 5.30 (q, $J = 7.0 \text{ Hz}$, CH), 7.77 (q, $J = 1.2 \text{ Hz}$, CH); ^{19}F nmr: δ 19.2 (dq, $J = 6.1$ and 1.2 Hz), 21.7 (q, $J = 6.1 \text{ Hz}$).

Anal. Calcd. for $\text{C}_8\text{H}_5\text{OF}_6\text{Br}$: C, 30.89; H, 1.62. Found: C, 30.87; H, 1.69.

Compound **6c** had bp $65-66^\circ/18 \text{ mm Hg}$; n_D^{20} 1.3887; d_4^{20} 1.730; ^1H nmr: δ 2.08 (d, $J = 7.2 \text{ Hz}$, CH_3), 5.35 (q, $J = 7.2 \text{ Hz}$, CH); ^{19}F nmr: δ 16.7 (m), 21.3 (m).

Anal. Calcd. for $\text{C}_9\text{H}_4\text{OF}_6\text{Br}$: C, 28.52; H, 1.06. Found: C, 28.53; H, 0.99.

Compound **14c** had n_D^{20} 1.4209; ir: ν 1642, 1622, 1598 (C=C); ^{19}F nmr: δ 17.0 (m), 21.6 (m); ms: m/z 379, 377 ($\text{M}^+\text{-Br}$, 72), 359, 357 ($\text{M}^+\text{-H-F-Br}$, 17), 298 ($\text{M}^+\text{-H-2Br}$), 279 ($\text{M}^+\text{-H-F-2Br}$, 34).

Dehydrobromination of **6a**.

To an ethanol solution (10 ml) of 8.97 g (26 mmoles) of monobromide **6a** containing a small amount of hydroquinone as a polymerization inhibitor, was added dropwise an ethanol solution (30 ml) of 2.26 (40 mmoles) of potassium hydroxide. The reaction mixture was heated to reflux for 1 hour and poured into water, then extracted with ether. The ethereal extract was washed with water, dried over sodium sulfate and distilled to provide 1.59 g (23%) of 5-ethyl-3,4-bis(trifluoromethyl)-2-vinylfuran (**8a**) and 1.44 g (18%) of 2-(1-ethoxyethyl)-5-ethyl-3,4-bis(trifluoromethyl)furan (**9a**). The vinyl compound **8a** polymerized easily at ambient temperature without addition of an inhibitor.

Compound **8a** had bp $140-142^\circ$ (with hydroquinone); ir: ν 1612, 1560 (C=C); ^1H nmr: δ 1.31 (t, $J = 7.5 \text{ Hz}$, CH_3), 2.82 (q, $J = 7.5 \text{ Hz}$, CH_2), 5.38-6.98 (m, CH=CH₂); ^{19}F nmr: δ 21.6 (q, $J =$

7.0 Hz), 22.4 (q, J = 7.0 Hz); ms: m/z 258 (M⁺, 34), 243 (M⁺-CH₃, 100), 239 (M⁺-F, 16).

Compound **9a** had bp 191-192°; n²⁰D 1.3933; d²⁰ 1.308; ¹H nmr: δ 1.17 (t, J = 7.5 Hz, CH₃), 1.28 (t, J = 7.4 Hz, CH₃), 1.50 (d, J = 6.8 Hz, CH₃), 2.86 (q, J = 7.5 Hz, CH₂), 3.40 (q, J = 7.4 Hz, OCH₂), 4.72 (q, J = 6.8 Hz, CH); ¹⁹F nmr: δ 21.4 (q, J = 7.3 Hz), 22.2 (q, J = 7.3 Hz).

Anal. Calcd. for C₁₂H₁₄O₂F₆: C, 47.37; H, 4.64. Found: C, 47.23; H, 4.25.

Hydrolysis of **6** with Potassium Carbonate.

2-(1-Bromoethyl)-5-ethyl-3,4-bis(trifluoromethyl)furan (**6a**, 17.3 g, 51.0 mmoles) was refluxed in 10% aqueous potassium carbonate solution (100 ml) for 7 hours. After cooling, the mixture was acidified with dilute sulfuric acid and extracted with ether, which was dried over sodium sulfate. The distillation of the ethereal solution gave 5-ethyl-2-(1-hydroxyethyl)-3,4-bis(trifluoromethyl)furan (**10a**, 8.43 g, 60%).

In a similar procedure, the hydrolyses of **6b** and **6c** gave 2-(1-hydroxyethyl)-3,4-bis(trifluoromethyl)furan (**10b**) and 2-(1-hydroxyethyl)-3,4,5-tris(trifluoromethyl)furan (**10c**) in 76 and 6% yields, respectively.

Compound **10a** had bp 105-106°/17 mm Hg; n²⁰D 1.4010; d²⁰ 1.361; ¹H nmr: δ 1.25 (q, J = 7.6 Hz, CH₃), 1.46 (d, J = 6.6 Hz, CH₃), 2.84 (q, J = 7.6 Hz, CH₂), 3.67 (s, OH), 5.02 (q, J = 6.6 Hz, CH); ¹⁹F nmr: δ 21.6 (q, J = 7.3 Hz), 22.2 (q, J = 7.3 Hz).

Anal. Calcd. for C₁₀H₁₀O₂F₆: C, 43.49; H, 3.65. Found: C, 43.47; H, 3.60.

Compound **10b** had bp 92-93°/14 mm Hg; n²⁰D 1.3863; d²⁰ 1.474; ¹H nmr: δ 1.48 (d, J = 6.7 Hz, CH₃), 3.72 (s, CH), 5.05 (q, J = 6.7 Hz, CH), 7.73 (s, OH); ¹⁹F nmr: δ 19.1 (dq, J = 6.2 and 1.4 Hz), 22.3 (q, J = 6.2 Hz).

Anal. Calcd. for C₈H₆O₂F₆: C, 38.72; H, 2.44. Found: C, 38.57; H, 2.58.

Compound **10c** had mp 34-36°; ir: ν 3620, 3350 (OH), 1641, 1621, 1597 (C=C); ¹H nmr: δ 1.61 (d, J = 6.3 Hz, CH₃), 2.11 (s, OH), 5.20 (q, J = 6.3 Hz, CH); ¹⁹F nmr: δ 17.0 (q, J = 8.2 Hz), 21.6 (heptet, J = 8.2 and 7.4 Hz), 22.5 (q, J = 7.4 Hz); ms: m/z 316 (M⁺, 3), 301 (M⁺-CH₃, 28), 281 (M⁺-H-F-CH₃, 100), 253 (M⁺-4H-F-2C-O, 27).

Oxidation of **10** with Sodium Dichromate.

To a dilute sulfuric acid solution of sodium dichromate (2.81 g, 9.41 mmoles) was added 2-(1-hydroxyethyl)-5-ethyl-3,4-bis(trifluoromethyl)furan (**10a**, 3.70 g, 13.4 mmoles). The reaction mixture was heated at ca. 60° for 2 hours and poured into water. The products were extracted with ether and washed with 5% aqueous potassium hydroxide solution. The distillation of ethereal solution gave 2-acetyl-5-ethyl-3,4-bis(trifluoromethyl)furan (**11a**) together with unchanged **10a**. The 2-acetyl-furan, **11a** (0.70 g, 29%) was isolated using a preparative gas chromatograph.

In a similar procedure, 2-acetyl-3,4-bis(trifluoromethyl)furan (**11b**) was obtained in 40% yield from **10b** by sodium dichromate oxidation.

Compound **11a** had bp 215°; n²⁰D 1.4109; d²⁰ 1.383; ¹H nmr: δ 1.35 (t, J = 7.5 Hz, CH₃), 2.50 (s, COCH₃), 2.96 (q, J = 7.5 Hz, CH₂); ¹⁹F nmr: δ 21.9 (s).

Anal. Calcd. for C₁₀H₈O₂F₆: C, 43.81; H, 2.94. Found: C, 43.76; H, 2.90.

Compound **11b** had bp 57-58°/2 mm Hg; n²⁰D 1.3930; d²⁰ 1.508; ¹H nmr: δ 2.54 (s, COCH₃), 7.88 (s, CH); ¹⁹F nmr: δ 19.3 (q,

J = 7.6 Hz), 21.7 (q, J = 7.6 Hz).

Anal. Calcd. for C₈H₄O₂F₆: C, 39.04; H, 1.64. Found: C, 38.92; H, 1.63.

Nitric Acid Oxidation of **4**.

A mixture of 2,5-diethyl-3,4-bis(trifluoromethyl)furan (**4a**, 47.8 g, 0.18 mole) and nitric acid (d 1.38, 140 ml) in acetic acid (400 ml) was refluxed for 50 hours. The reaction mixture was poured into water and extracted with dichloromethane (200 ml). The organic layer was dried over sodium sulfate. Evaporation of dichloromethane yielded white precipitates, which were separated by filtration and recrystallized from hexane to give 5-ethyl-3,4-bis(trifluoromethyl)-2-furancarboxylic acid (**13a**, 23 g, 45%). The filtrate was washed with 5% aqueous sodium bicarbonate solution, extracted with dichloromethane and dried. Distillation of the extract gave 5-ethyl-2-formyl-3,4-bis(trifluoromethyl)furan (**12a**, 0.57 g, 1%).

Compound **12a** had bp 186°; n²⁰D 1.4110; d²⁰ 1.433; ¹H nmr: δ 1.38 (t, J = 7.6 Hz, CH₃), 2.98 (qq, J = 7.6 and 1.3 Hz, CH₂), 9.72 (s, CHO); ¹⁹F nmr: δ 21.5 (tq, J = 7.4 and 1.3 Hz), 22.8 (q, J = 7.4 Hz).

Anal. Calcd. for C₉H₆O₂F₆: C, 41.55; H, 2.33. Found: C, 41.49; H, 2.63.

Compound **13a** had mp 93°; ¹H nmr: δ 1.36 (t, J = 7.5 Hz, CH₃), 2.09 (q, J = 7.5 Hz, CH₂), 11.64 (s, COOH); ¹⁹F nmr: δ 22.1 (m).

Anal. Calcd. for C₉H₆O₃F₆: C, 39.14; H, 2.19. Found: C, 38.99; H, 2.27.

In a similar procedure, a mixture of 2-ethyl-3,4-bis(trifluoromethyl)furan (**4b**, 11.9 g, 51.4 mmoles) and nitric acid (d 1.38, 30 ml) was refluxed in acetic acid for 45 hours. The reaction mixture was poured into water (700 ml) and extracted with dichloromethane (150 ml). The organic layer was washed with water and dried over sodium sulfate. After the distillation of the solvent, the products were isolated using a preparative gas chromatograph. 2-(1-Hydroxyethyl)-3,4-bis(trifluoromethyl)furan (**10b**, 0.53 g, 4%), 3,4-bis(trifluoromethyl)-2-furancarboxylic acid (**13b**, 0.27 g, 2%), and 2-(1-acetoxyethyl)-3,4-bis(trifluoromethyl)furan (**15b**, 0.77 g, 5%) were isolated.

Compound **13b** had mp 126-127°; ¹H nmr: δ 8.19 (s, CH), 10.38 (s, COOH); ¹⁹F nmr: δ 19.2 (dq, J = 7.8 and 1.2 Hz), 22.1 (q, J = 7.8 Hz).

Anal. Calcd. for C₇H₂O₃F₆: C, 33.89; H, 0.81. Found: C, 33.84; H, 1.13.

Compound **15b** had bp 186°; n²⁰D 1.3922; ¹H nmr: δ 1.59 (d, J = 6.6 Hz, CH₃), 2.04 (s, COCH₃), 6.03 (q, J = 6.6 Hz, CH), 7.79 (s, CH); ¹⁹F nmr: δ 22.2 (m).

Anal. Calcd. for C₁₀H₈O₃F₆: C, 41.39; H, 2.78. Found: C, 41.01; H, 2.79.

Decarboxylation of **13a**.

5-Ethyl-3,4-bis(trifluoromethyl)-2-furancarboxylic acid (**13a**, 48.8 g, 0.148 mole) and copper powder (22.0 g) were heated in pyridine (170 ml) at 100° for 4 hours. After the reaction, the solution was acidified with 50% sulfuric acid and extracted with ether. The distillation of the extract gave 2-ethyl-3,4-bis(trifluoromethyl)furan (**4b**, 23.7 g, 69%).

Compound **4b** had bp 129°; n²⁰D 1.3625; d²⁰ 1.353; ¹H nmr: δ 1.29 (t, J = 6.7 Hz, CH₃), 2.87 (qq, J = 6.7 and 1.3 Hz, CH₂), 7.63 (q, J = 1.3 Hz, CH); ¹⁹F nmr: δ 19.1 (dq, J = 6.2 and 1.3 Hz), 22.3 (tq, J = 6.2 and 1.3 Hz).

Anal. Calcd. for C₈H₆OF₆: C, 41.39; H, 2.61. Found: C, 41.22; H, 2.60.

Fluorination of 5-Ethyl-3,4-bis(trifluoromethyl)-2-furancarboxylic Acid (**13a**) with Sulfur Tetrafluoride.

In an autoclave (100 ml) made of Hastelloy was placed **13a** (5.03 g, 18.2 mmoles) and anhydrous hydrogen fluoride (5.64 g), then cooled with liquid nitrogen. Sulfur tetrafluoride (13.7 g, 126 mmoles) was introduced into the autoclave using a vacuum line. The autoclave was heated at 100° for 2 hours and then at 130° for 10 hours. After cooling, gaseous products were removed. The product was poured into a mixture of ice and 10% aqueous potassium hydroxide solution, and extracted with dichloromethane, and dried over sodium sulfate. Distillation of the extract gave 2-ethyl-3,4,5-tris(trifluoromethyl)furan (**4c**, 4.15 g, 76%).

Compound **4c** had bp 110°; n²⁰_D 1.3470; d²⁰₄ 1.477; ¹H nmr: δ 1.35 (t, J = 7.5 Hz, CH₃), 2.92 (q, J = 7.5 Hz, CH₂); ¹⁹F nmr: δ 16.8 (q, J = 7.6 Hz), 21.2 (m), 21.5 (m).

Anal. Calcd. for C₉H₈OF₆: C, 36.01; H, 1.68. Found: C, 35.89; H, 1.53.

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