The data of Table I indicate that the chemical shifts of the oxo oxygens are almost unaffected by the nature of the peroxo compounds, either neutral or anionic, the basicity of the coordinated ligands, and the nature of the associated cation, either H_3O^+ or Bu_4N^+. Moreover there is a very little effect by varying the nature of the solvent, e.g. from DCE to CH_3CN.

The chemical shifts reported in Table I fit the correlation, established in 1979 by Miller and Wentworth,[7] between ^{17}O chemical shifts of oxygen bound to Mo and Mo–O bond length, respectively. In fact for all the complexes analyzed, either neutral or anionic, the ^{17}O oxo resonance falls in the range 830–860 ppm in agreement with the 1.6-Å bond length as it is measured in the solid state.[1,5,16] Therefore, we can be quite confident that the negative charge of the anionic compounds investigated should not be localized on the oxo oxygen. As discussed above, it is also unlikely that the charge is on the peroxo oxygen. Consequently, we are left with the suggestion that the negative charge has to be located on the ligand.

Recently we have shown[19] that, in aqueous solution at pH 3, $[MoO_5 \cdot nH_2O]$ is in equilibrium with its monoanion which can be extracted into a chlorinated solvent by a phase transfer agent such as a tetraalkylammonium salt.[20] The oxo resonance of the peroxo molybdenum anion extracted with this procedure is found at 791 ppm. Therefore in this case, where no bidentate ligands are present and, hence, the negative charge has to be localized on the peroxo molybdenum ion, the oxo resonance is markedly shifted upfield (56 ppm) with respect to the average of the other signals reported in Table I. This could either mean that the M=O bond is longer[7] or that the complex has a different spatial arrangement.

The significance of this result is confirmed by the following control experiment. After extraction from an aqueous solution at pH 1.2, with the neutral lipophilic ligand hexaethylphosphoric triamide,[21] of the neutral peroxo species, an oxo resonance of 837 ppm has been measured, i.e. the same value found for $MoO(O_2)_2HMPT$, first entry of the Table I.

As far as the oxidation chemistry is concerned, it is worthy of notice that the extracted anionic peroxo complexes, where no bidentate ligands are present, behave differently from the anionic picolinate and picolinate *N*-oxido analogues.[20] In fact the latter are much more efficient than the former in the oxidation of primary alcohols to aldehydes.[1,20]

A correlation between the localization of the negative charge, as indicated by the spectroscopic evidence reported here, and the oxidative behavior might be envisaged. This could be useful in the understanding of the mechanism of alcohol oxidations currently under investigation.

Experimental Section

The ^{17}O NMR spectra were obtained with a Bruker WP 200 SY multinuclear spectrometer operating at 27.1 MHz for ^{17}O. No field/frequency locking system was used, and the spectra were obtained at about 30 °C. Chemical shifts were measured relative to acetone as external reference. The acetone chemical shift (+572 ppm from water) was previously determined in a separate experiment.

A sweep width of 62.5 kHz was used; the number of scans accumulated varied from 2×10^4 to 10^6 depending on the concentration and on the enrichment of the sample. The data were acquired as 4K data points in the time domain and transformed as 2K. No relaxation delay was used and, before FT, about 40 points were zeroed and exponential multiplication (LB 50Hz) was performed. It was estimated that the limit error for the chemical shifts reported in Table I is ±5 ppm.

Commercially available solvents were purified according to standard procedures.

All peroxo complexes were synthesized and purified by known literature methods.[1,4,5] The peroxidic oxygen content was always ≥98%.

The extraction of the peroxo complexes both neutral or anionic from the aqueous phase into the organic one was carried out via procedures described elsewhere.[14,20]

Acknowledgment. We thank Prof. V. Lucchini, University of Venezia, and Prof. R. Curci, University of Bari, for helpful discussions. We also thank R. Salmaso, CMRO, University of Padova, for technical assistance.

Registry No. $MoO(O_2)_2HMPT$, 25377-12-2; $MoO(O_2)_2PyO$, 115406-87-6; $MoO(O_2)_2Py$, 67228-13-1; $[MoO(O_2)_2PIC]^-Bu_4N^+$, 105177-38-6; $[MoO(O_2)_2PICO]^-Bu_4N^+$, 105194-63-6; $[MoO(O_2)_2PIC]^-H_3O^+$, 72074-55-6.

(20) Bortolini, O.; Conte, V.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1986**, *51*, 2661–2663.

(21) Bortolini, O.; Di Furia, F.; Modena, G.; Seraglia, R. *J. Org. Chem.* **1985**, *50*, 2688–2690.

Direct Perfluoroalkylation Including Trifluoromethylation of Aromatics with Perfluoro Carboxylic Acids Mediated by Xenon Difluoride

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It is now recognized that the regioselective replacement of hydrogen in an aromatic or heterocyclic system by a perfluoroalkyl group may have profound influence on the physical and biological properties of such molecules.[2] As a result, considerable effort has been devoted to the introduction of perfluoroalkyl units in such systems, as exemplified by the reactions of the reactive perfluoroalkyl cationic or radical species.[3] However, these processes often required careful preparation of the reactive intermediates[4] and were not available to conduct both perfluoroalkylation ($\geq C_2$) and trifluoromethylation.

We now describe a facile and general perfluoroalkylation procedure of electron-poor aromatic and heterocyclic systems by a common (both perfluoroalkylation ($\geq C_2$) and trifluoromethylation) and simple one-pot procedure.

Our method is based on the observation of several groups which reported that the commercially available reagent xenon difluoride[5] reacts with trifluoroacetic acid

(1) Present address: Takatsuki Research Laboratory, Sumitomo Chemical Co., Ltd., Takatsuki, Osaka 569, Japan.

(2) (a) Filler, R., Ed. ACS Symposium Series 28; American Chemical Society: Washington, DC, 1976. (b) Filler, R.; Kobayashi, Y. *Biomedicinal Aspects of Fluorine Chemistry*; Kodansha/Elsevier: New York, 1982. (c) Bancs, R. E. *Organofluorine Compounds and Their Applications*; Ellis Horwood Ltd.: Chichester, 1979. (d) Fuchikami, T. *Yuki Gosei Kagaku Kyokaishi* **1984**, *42*, 775. (e) Yoshioka, H.; Takayama, C.; Matsuo, N. *Yuki Gosei Kagaku Kyokaishi* **1984**, *42*, 809.

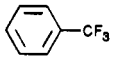
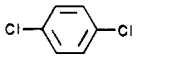
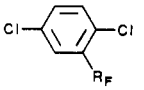
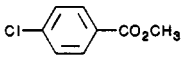
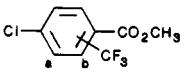
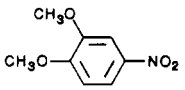
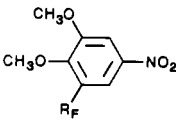
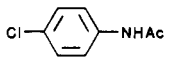
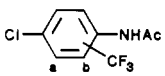
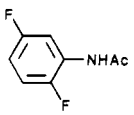
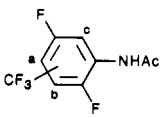
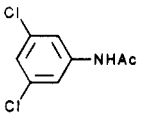
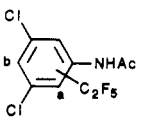
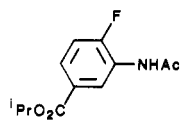
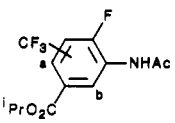
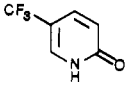
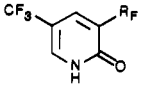
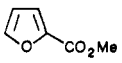
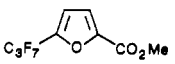
(3) For recent studies, see the following: (a) Perfluoroalkylation: Fuchikami, T.; Ojima, I. *Tetrahedron Lett.* **1984**, *25*, 303. (b) Trifluoromethylation: Wiemers, D. M.; Burton, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 832. Other examples are cited therein.

(4) (a) Umemoto, T.; Kuriu, Y.; Shuyama, H. *Chem. Lett.* **1981**, 1663. (b) Umemoto, T.; Miyano, O. *Tetrahedron Lett.* **1982**, *23*, 3929. (c) Umemoto, T.; Ando, A. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 447. (d) Yoshida, M.; Amemiya, H.; Kobayashi, M.; Sawada, H.; Higai, H.; Aoyama, A. *J. Chem. Soc., Chem. Commun.* **1985**, 234.

(5) Xenon difluoride is generally known and widely used as a fluorinating reagent. For a review, see: Filler, R. *Isr. J. Chem.* **1978**, *17*, 71. Commercially available from PCR Research Chemicals. Easily handled white crystals.

0022-3263/88/1953-4582$01.50/0

Table I. Perfluoroalkylation of Various Substituted Benzenes and Heterocycles[a]

entry	substrate	XeF_2 (equiv)	$R_F(CO_2H)$ (equiv)	product[b]	isomer ratio	yield (%)
1		1.5	CF_3 (2.0)			33[d]
2A		2.0	CF_3 (3.0)			72[e]
2B		2.0	C_2F_5 (3.0)			62[e]
2C		2.0	C_3F_7 (3.0)			55[e]
3		2.0	CF_3 (3.5)		a:b = 3:1	45[f]
4A		2.0	CF_3 (3.0)			52[f]
4B		2.0	C_2F_5 (3.0)			43[f]
5		2.0	CF_3 (3.0)		a:b = 1.5:1	47[f]
6		2.0	CF_3 (3.0)		a:b:c = 8:1:4	53[f]
7		2.0	C_2F_5 (3.0)		a:b = 1.2:1	49[f]
8		2.0	CF_3 (3.0)		a:b = 1.2:1	33[f]
9A		1.1	CF_3 (3.0)			40[f]
9B		1.3	C_2F_5 (1.5)			25[f]
10		2.0	C_3F_7 (2.0)			33[f]

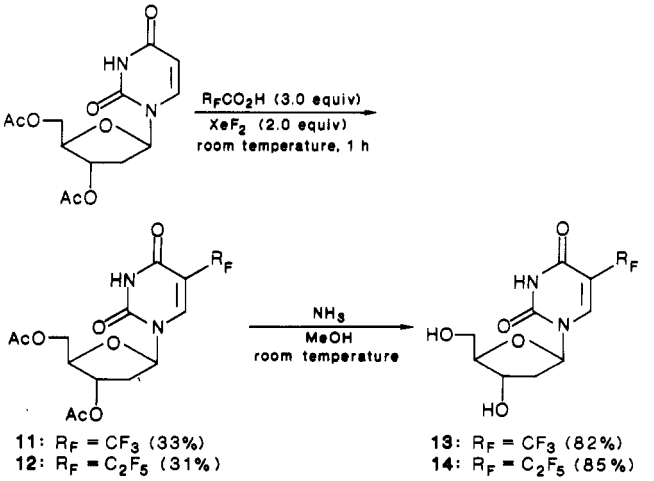
[a] These reactions were carried out in dichloromethane at room temperature. [b] All the compounds gave satisfactory spectral data (^1H and ^{19}F NMR and MS). [c] Large excess amount. [d] ^{19}F NMR yield based on trifluoroacetic acid. [e] GLC yield. [f] Isolated yield. The isomers separated by means of chromatography.

to produce an intermediate, xenon(II) trifluoroacetate, which undergoes decomposition to yield carbon dioxide and hexafluoroethane.[6,7] On the basis of this mechanism and the known reactivity of the intermediate trifluoromethyl radical with aromatics, it was anticipated that the action of xenon difluoride and a perfluoro carboxylic acid on an aromatic substrate would lead to perfluoroalkylation by way of a perfluoroalkyl radical. In fact, it was found that a series of aromatic compounds were perfluoroalkylated with the corresponding perfluoro carboxylic acids (2.0–3.5 equiv) on treatment with xenon difluoride (1.0–2.0 equiv)[8] in dichloromethane at room temperature (Scheme I). Of note is its applicability to various electron-poor aromatics. But unfortunately, when anisole or toluene is employed as a substrate, fluorination predominated over the perfluoroalkylation.[5]

Scheme I

$$ArH + R_FCO_2H + XeF_2 \rightarrow ArR_F + CO_2 + Xe + 2HF$$

Scheme II



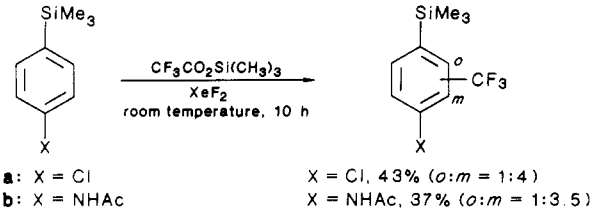
11: $R_F = CF_3$ (33%)
12: $R_F = C_2F_5$ (31%)
13: $R_F = CF_3$ (82%)
14: $R_F = C_2F_5$ (85%)

(6) (a) Eisenberg, M.; Desmarteau, D. D. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 29. (b) Gregoric, A.; Zupan, M. *J. Org. Chem.* **1979**, *44*, 4120.

(7) It was also reported that several aliphatic carboxylic acids underwent fluorodecarboxylation with xenon difluoride in the presence of hydrogen fluoride. (a) Patrick, T. B.; Johli, K. K.; White, D. H. *J. Org. Chem.* **1983**, *48*, 4159. (b) Patrick, T. B.; Johli, K. K.; White, D. H.; Bertrand, W. S.; Mokhtar, R.; Kilboourn, M. R.; Welch, M. J. *Can. J. Chem.* **1986**, *64*, 138.

(8) To compensate the loss of perfluoroalkyl radicals to form these dimers, excess XeF_2 (within 2-fold) and R_FCO_2H were required. The side reaction is supposed to occur due to low reactivity of the electron-deficient substrates. XeF_2 is known to react with active hydrogen of hydroxy or amino groups,[5] but in this reaction, it is supposed that the reaction of perfluoro carboxylic acids with XeF_2 precede that of the amide group.

Scheme III



4a: X = Cl — X = Cl, 43% (*o*:*m* = 1:4)
b: X = NHAc — X = NHAc, 37% (*o*:*m* = 1:3.5)

In the case of heterocycles such as 2-pyridone and 2-substituted furan, perfluoroalkylation proceeded regioselectively as shown in Table I. This new reaction is sufficiently mild so that 5-(perfluoroalkyl)-2′-deoxyuridine could be easily prepared. 5-(Trifluoromethyl)-2′-deoxyuridine (**13**)[9] is well-known as an antiviral active substance (Scheme II).

As a further extension, trifluoromethylation of arylsilane by the present method was investigated, because arylsilanes have often been used as substrates for regioselective introduction of various kinds of electrophiles into the benzene ring via ipsodesilylation.[10] Then trifluoromethylation of two 4-(trimethylsilyl)benzenes (**4**) under the same conditions (using 2.0 equiv of CF_3CO_2H and 1.5 equiv of XeF_2) was tried. The reaction gave mainly protodesilylation by the acidic medium. In order to overcome the problem, we found that trimethylsilyl trifluoroacetate was effective as a neutral trifluoromethylating agent[11] in place of CF_3CO_2H for the (trimethylsilyl)benzenes. It is noteworthy that proto- or ipsodesilylation was not observed in this reaction. When *p*-chloro(trimethylsilyl)benzene (**4a**) and *p*-acetamido(trimethylsilyl)benzene (**4b**) were subjected to the reaction using $CF_3CO_2SiMe_3$ (2.0 equiv) and XeF_2 (1.5 equiv), trifluoromethylation mainly occurred meta to the trimethylsilyl groups as shown in Scheme III.[12]

The above chemistry demonstrates the reactivity pattern expected of perfluoroalkyl radical. In conclusion, our method provides the first simple and general entry to a wide variety of perfluoroalkyl aromatics and heterocycles in one step from commercial reactants. The scope of this powerful reaction is now under investigation.

Experimental Section

Melting points were determined on a hot-stage microscope apparatus (Yanagimoto) and were uncorrected. ^1H NMR spectra were recorded on a Hitachi R-24 B spectrometer (60 MHz) using TMS as an internal standard in $CDCl_3$. ^{19}F NMR spectra (ϕ chemical shift) used trichlorofluoromethane as an internal standard in $CDCl_3$.

General Procedure for Perfluoroalkylation. To a stirred solution of aromatic substrate (10 mmol) and perfluoro carboxylic acid or trimethylsilyl trifluoroacetate (20–35 mmol) in dichloromethane (20 mL) was added a small piece of xenon difluoride at room temperature. After a few minutes, volatile gas was evolved (initiation), and the xenon difluoride (10–20 mmol) was added successively to the reaction mixture portion by portion, the reaction temperature being controlled below 35 °C. The reaction mixture was stirred at room temperature for 2 h and was poured into water (20 mL). The aqueous layer was extracted with dichloromethane (10 mL × 2). The combined extracts were dried (Na_2SO_4) and concentrated to leave crude products, which were purified by bulb-to-bulb distillation (method A) or column chromatography (method B).

α,α,α-Trifluorotoluene[12] **(1).** The yield (33%) was based on measurement of the crude compound (^{19}F NMR) with an authentic sample.

2,5-Dichlorobenzotrifluoride[13] **(2A). Method A.** The reaction of 1,4-dichlorobenzene (1.47 g, 10 mmol) with XeF_2 (3.38 g, 20 mmol) and CF_3CO_2H (3.48 g, 30 mmol) gave 1.51 g of distilled material (bulb-to-bulb distillation; oven temp 150 °C (20 mmHg)). The material contained 75% of **2A** and 18% of 1,4-dichlorobenzene checked by GLC analysis (SE-30, 1.6 m × 3 mm, column temp 80 °C): net yield 72%; MS, *m/e* 215 (M^+); ^1H NMR δ 7.30–7.40 (m, 2 H), 7.55–7.65 (m, 1 H); ^{19}F NMR ϕ 63.0 (s, 3 F).

1,4-Dichloro-2-(pentafluoroethyl)benzene (2B). Method A: bp 150 °C (oven temp) (18 mmHg); net yield 62%; MS, *m/e* 265 (M^+); ^1H NMR δ 7.30–7.50 (m, 2 H), 7.50–7.70 (m, 1 H); ^{19}F NMR ϕ 113.0 (s, 2 F), 83.5 (s, 3 F).

1,4-Dichloro-2-(heptafluoropropyl)benzene (2C). Method A: bp 150 °C (oven temp) (18 mmHg); net yield 55%; MS, *m/e* 315 (M^+); ^1H NMR δ 7.30–7.50 (m, 2 H), 7.50–7.70 (m, 1 H); ^{19}F NMR ϕ 125.5 (s, 2 F), 107.5 (m, 2 F), 81.0 (t, 3 F, J = 8.0).

Methyl 4-Chloro-3-(trifluoromethyl)benzoate (3a) and Methyl 4-Chloro-2-(trifluoromethyl)benzoate (3b). Method A: bp 200 °C (oven temp) (20 mmHg); net yield 27% (**3a**) and 18% (**3b**) checked by GLC analysis (OV-17, 2.0 m × 3 mm, column temp 150 °C); structures were determined after column chromatographic purification (hexane/ether, 10:1). Compound **3a**: MS, *m/e* 224 (M^+); ^1H NMR δ 3.80 (s, 3 H), 7.30–8.00 (m, 3 H); ^{19}F NMR ϕ 63.0 (s, 3 F). Compound **3b**: MS, *m/e* 224 (M^+); ^1H NMR δ 3.90 (s, 3 H), 7.40–7.80 (m, 2 H), 8.10 (d, 1 H, J = 10 Hz); ^{19}F NMR ϕ 60.0 (s, 3 F).

3,4-Dimethoxy-5-(trifluoromethyl)-1-nitrobenzene (4a). Method B (hexane/EtOAc, 4:1): yield 52%; mp 115–118 °C; MS, *m/e* 251 (M^+); ^1H NMR δ 3.95 (s, 6 H), 7.15–7.50 (m, 2 H); ^{19}F NMR ϕ 62.5 (s, 3 F). Anal. Calcd for $C_9H_8F_3NO_4$: C, 43.04; H, 3.21; N, 5.58. Found: C, 43.33; H, 3.18; N, 5.37.

3,4-Dimethoxy-5-(pentafluoroethyl)-1-nitrobenzene (4b). Method B: yield 43%; mp 105–108 °C; MS, *m/e* 319 (M^+); ^1H NMR δ 3.95 (s, 6 H), 7.15–7.50 (m, 2 H); ^{19}F NMR ϕ 113.5 (s, 2 F), 83.5 (s, 3 F). Anal. Calcd for $C_{10}H_8F_5NO_4$: C, 39.88; H, 2.68; N, 4.65. Found: C, 38.45; H, 2.61; N, 4.53.

***N*-[4-Chloro-3-(trifluoromethyl)phenyl]acetamide**[14] **(5a) and *N*-[4-Chloro-2-(trifluoromethyl)phenyl]acetamide**[15] **(5b). Method B ($CHCl_3$/AcOEt, 20:1).** Compound **5a**: yield 28%; ^1H NMR δ 2.20 (s, 3 H), 7.30–8.00 (m, 3 H), 8.05 (br s, 1 H); ^{19}F NMR ϕ 61.0 (s, 3 F). Compound **5b**: yield 19%; ^1H NMR δ 2.20 (s, 3 H), 7.30–7.60 (m, 3 H), 8.20 (d, 1 H, J = 10 Hz); ^{19}F NMR ϕ 63.0 (s, 3 F). All spectral data were coincident with the authentic samples.

***N*-[2,5-Difluoro-4-(trifluoromethyl)phenyl]acetamide (6a), *N*-[2,5-Difluoro-3-(trifluoromethyl)phenyl]acetamide (6b), and *N*-[3,6-Difluoro-2-(trifluoromethyl)phenyl]acetamide (6c). Method A.** A mixture of trifluoromethylated *N*-phenylacetamides **6a**, **6b**, and **6c** (40%, 5%, and 20%, respectively, on GLC analysis (XE-60, 1.6 m × 3 mm, column temp 200 °C)) and *N*-(2,5-difluorophenyl)acetamide (35% on GLC analysis) were gained after short column chromatography ($CHCl_3$/AcOEt, 10:1). Net yields of **6a**, **6b**, and **6c** were 33%, 4%, and 16%, respectively. The mixture was separable by using silica gel (Merck Art. No. 9335) flash column chromatography ($CHCl_3$/AcOEt, 20:1), which gave the pure products. Compound **6a**: mp 138–139 °C; MS, *m/e*

(9) For an example, see: (a) Heidelberger, C. *Cancer Res.* **1970**, *30*, 1549. A direct trifluoromethylation of triacetyluridine was shown in ref 3c, and trifluoromethylation of 5′-iodouridine derivatives with trifluoromethyl iodide/copper was also known: (b) Kobayashi, Y.; Yamamoto, K.; Asai, T.; Nakano, M.; Kumadaki, M. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2755.

(10) (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1980; pp 126. (b) Weber, P. E. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 114.

(11) In the hope that $CF_3CO_2Si(CH_3)_3$ was also expected to react with XeF_2, successful results were obtained, and the reaction proceeded probably according to the following equation. The time required for complete reaction was rather long (several hours) compared with that for reaction of CF_3CO_2H with XeF_2.

$$2CF_3CO_2Si(CH_3)_3 + XeF_2 \xrightarrow[\text{temp}]{\text{room}} 2CF_3^{\bullet} + 2CO_2 + 2FSi(CH_3)_3 + Xe$$

(12) The meta major orientation of the trifluoromethylation would be explained due to the steric bulkiness of a trimethylsilyl group compared with a chloro atom or an acetamido group, and/or to the stabilization of the intermediary aryl radical by the β-effect of silicon.[10]

(13) Yagupolskii, L. M.: Troitskaya, V. L. *Chem. Abstr.* **1960**, *54*, 11002c.

(14) Mp 115–116 °C. Caldwell, T. W.; Sayin, A. N. *J. Am. Chem. Soc.* **1951**, *73*, 5125.

(15) Mp 148 °C. Whalley, W. B. *J. Chem. Soc.* **1949**, 3016.

239 (M^+); ^1H NMR δ 2.25 (s, 3 H), 7.20 (s, dd, 1 H, J = 6 Hz, J = 10 Hz), 7.70–8.20 (br s, 1 H), 8.20 (dd, 1 H, J = 6 Hz, J = 12 Hz); ^{19}F NMR ϕ 60.0 (s, 3 F), 115.0 (s, 1 F), 132.5 (s, 1 F). Anal. Calcd for $C_9H_6F_5NO$: C, 45.20; H, 6.05; N, 5.86. Found: C, 45.12; H, 2.52; N, 5.77. Compound **6b**: mp 117–119 °C; MS, m/e 239 (M^+); ^1H NMR δ 2.25 (s, 3 H), 7.15–8.00 (m, 2 H), 8.20 (m, 1 H); ^{19}F NMR ϕ 60.5 (s, 3 F), 115.0 (s, 1 F), 134.5 (s, 1 F). Compound **6c**: mp 137–139 °C; MS, m/e 239 (M^+); ^1H NMR δ 2.25 (s, 3 H), 6.90–7.50 (m, 3 H); ^{19}F NMR ϕ 56.0 (s, 3 F), 114.0 (s, 1 F), 134.5 (s, 1 F).

***N*-[3,5-Dichloro-4-(pentafluoroethyl)phenyl]acetamide (7a) and *N*-[3,5-Dichloro-2-(pentafluoroethyl)phenyl]acetamide (7b). Method B ($CHCl_3$/AcOEt, 20:1).** Compound **7a**: yield 22%; mp 163–164 °C; MS, m/e 321; ^1H NMR (CD_3OD) δ 2.10 (s, 3 H), 7.70 (br s, 2 H); ^{19}F NMR ϕ 84.5 (s, 3 F), 105.0 (s, 2 F). Anal. Calcd for $C_{10}H_6Cl_2F_5NO$: C, 37.29; H, 1.88; N, 4.35. Found: C, 37.19; H, 1.77; N, 4.26. Compound **7b**: yield 27%; mp 154–157 °C; MS, m/e 321; ^1H NMR (CD_3OD) δ 2.10 (s, 3 H), 7.05 (d, 1 H, J = 2 Hz), 7.80 (d, 1 H, J = 2 Hz); ^{19}F NMR ϕ 84.0 (s, 3 F), 104.0 (s, 2 F). Anal. Calcd for $C_{10}H_6Cl_2F_5NO$: C, 37.29; H, 1.88; N, 4.35. Found: C, 37.10; H, 1.65; N, 4.25.

Isopropyl 5-Acetamido-4-fluoro-2-(trifluoromethyl)benzoate (8a) and Isopropyl 3-Acetamido-4-fluoro-2-(trifluoromethyl)benzoate (8b). Method B ($CHCl_3$). Compound **8a**: yield 18%; mp 114–117 °C; MS, m/e 303 (M^+); ^1H NMR δ 1.35 (d, 6 H), 2.25 (s, 3 H), 5.20 (q, 1 H, J = 8 Hz), 7.40 (d, 1 H, J = 11 Hz), 8.30–8.50 (br s, 1 H), 8.75 (d, 1 H, J = 8 Hz); ^{19}F NMR ϕ 61.5 (s, 3 F). Anal. Calcd for $C_{13}H_{13}F_4NO_3$: C, 50.81; H, 4.26; N, 4.56. Found: C, 50.55; H, 4.11; N, 4.37. Compound **8b**: yield 15%; mp 98–100 °C; MS, m/e 303 (M^+); ^1H NMR δ 1.35 (d, 6 H), 2.25 (s, 3 H), 5.20 (q, 1 H, J = 8 Hz), 7.30–8.30 (m, 2 H), 7.90–8.20 (br s, 1 H); ^{19}F NMR ϕ 59.0 (s, 3 F).

3,5-Bis(trifluoromethyl)-2-hydroxypyridine (9A). Method B: yield 40%; mp 145.5 °C; MS, m/e 231 (M^+); ^1H NMR δ 8.0 (br s); ^{19}F NMR ϕ 67.5 (s, 3 F), 63.5 (s, 3 F). Anal. Calcd for $C_7H_3F_6NO$: C, 36.38; H, 1.31; N, 6.06. Found: C, 36.09; H, 1.19; N, 6.05.

2-Hydroxy-5-(trifluoromethyl)-3-(pentafluoroethyl)pyridine (9B). Method B: yield 25%; mp 98.2 °C; MS, m/e 281 (M^+); ^1H NMR δ 8.0 (br s); ^{19}F NMR ϕ 116.5 (s, 2 F), 84.0 (s, 3 F), 63.5 (s, 3 F). Anal. Calcd for $C_8H_3F_8NO$: C, 34.18; H, 1.07; N, 4.98. Found: C, 33.99; H, 1.03; N, 4.95.

Methyl 5-(Heptafluoropropyl)-2-furancarboxylate (10). Method B: yield 33%; oil; MS, m/e 294; ^1H NMR δ 3.90 (3 H, t), 6.90 (1 H, m), 7.20 (1 H, m); ^{19}F NMR ϕ 128.0 (s, 2 F), 113.5 (m, 2 F), 81.5 (t, 3 F, J = 8.3).

3′,5′-Di-*O*-acetyl-5-(trifluoromethyl)-2′-deoxyuridine (11). 3′,5′-Di-*O*-acetyl-2′-deoxyuridine (3.00 g, 9.6 mmol) was treated with trifluoroacetic acid (3.43 g, 29 mmol) and xenon difluoride (3.25 g, 19 mmol) to give 11 (1.21 g, 33% yield) after purification with silica gel chromatography ($CHCl_3$/EtOH, 20:1): amorphous powder; MS [field desorption (FD) method], m/e 380 (M^+); ^1H NMR δ 2.05 (s, 3 H), 2.10 (s, 3 H), 2.30–2.60 (m, 2 H), 4.20–4.50 (m, 4 H), 5.10–5.35 (m, 1 H), 6.10–6.40 (dd, 1 H, J = 8 Hz), 8.00 (1 H, s), 9.30 (br s, 1 H); ^{19}F NMR ϕ 67.0 (s, 3 F).

3′,5′-Di-*O*-acetyl-5-(pentafluoroethyl)-2′-deoxyuridine (12): yield 31%; mp 117–119 °C; MS (FD method), m/e 430 (M^+); ^1H NMR δ 2.05 (s, 3 H), 2.10 (s, 3 H), 2.30–2.60 (m, 2 H), 4.20–4.50 (m, 4 H), 5.10–5.35 (m, 1 H), 6.10–6.40 (dd, 1 H, J = 8 Hz), 8.00 (1 H, s), 9.30 (br s, 1 H); ^{19}F NMR ϕ 112.5 (s, 2 F), 84.0 (s, 3 F). Anal. Calcd for $C_{15}H_{15}F_5N_2O_7$: C, 41.87; H, 3.51; N, 6.51. Found: C, 42.01; H, 3.52; N, 6.50.

5-(Trifluoromethyl)-2′-deoxyuridine (13). The diacetoxy compound 11 (0.380 g, 1 mmol) was treated with a saturated ammonia solution of methanol (2 mL) at room temperature for 10 h and evaporated in vacuo to give the residue. To the crude products was added hexane/ether (1:1) at 0 °C to give the crystals (0.243 g, 82% yield): mp 179–182 °C (lit.[9b] mp 182–183 °C); MS (FD method), m/e 296.

5-(Pentafluoroethyl)-2′-deoxyuridine (14): mp 172–175 °C; MS (FD method), m/e 346; ^1H NMR (CD_3OD) δ 2.30–2.40 (m, 2 H), 2.80 (br s, 2 H), 3.80 (d, 2 H, J = 8 Hz), 3.90–4.00 (m, 1 H), 4.15 (br s, 1 H), 4.40–4.50 (m, 2 H), 6.10–6.30 (m, 1 H), 8.70 (br s, 1 H); ^{19}F NMR (CD_3OD) ϕ 112.5 (s, 2 F), 84.0 (s, 3 F). Anal. Calcd for $C_{11}H_{11}F_5N_2O_5$: C, 38.16; H, 3.20; N, 8.09. Found: C, 38.10; H, 3.11; N, 8.01.

***N*-[2-(Trifluoromethyl)-4-(trimethylsilyl)phenyl]acetamide (15) and *N*-[3-(Trifluoromethyl)-4-(trimethylsilyl)phenyl]acetamide (16).** *N*-[4-(Trimethylsilyl)phenyl]acetamide (207 mg, 1 mmol) was treated with xenon difluoride (254 mg, 1.5 mmol) and trimethylsilyl trifluoroacetate (372 mg, 2 mmol) to give **15** (92 mg, 34%) and **16** (23 mg, 8%) after silica gel chromatography ($CHCl_3$/AcOEt, 20:1). Compound **15**: mp 133.5–134.5 °C; MS, m/e 275 (M^+); ^1H NMR δ 0.30 (s, 9 H), 7.30–7.60 (br s, 1 H), 7.60–7.80 (m, 2 H), 8.00–8.30 (m, 1 H); ^{19}F NMR ϕ 63.5 (s, 3 F). Anal. Calcd for $C_{12}H_{16}F_3NOSi$: C, 52.34; H, 5.86; N, 5.09. Found: C, 52.21; H, 5.58; N, 4.99. Compound **16**: mp 78–80 °C; MS, m/e 275 (M^+); ^1H NMR δ 0.30 (s, 9H), 7.42–7.90 (m, 3 H), 8.10–8.30 (br s, 2 H); ^{19}F NMR ϕ 60.5 (s, 3 F).

2-Chloro-5-(trimethylsilyl)benzotrifluoride (17) and 2-(Trimethylsilyl)-5-chlorobenzotrifluoride (18). Method A. After the reaction, the mixture was treated with a 10-fold excess of trifluoroacetic acid at room temperature to convert (4-chlorophenyl)trimethylsilane left to chlorobenzene (protodesilylation). By the procedure, trifluoromethylated compounds could be easily separated from the mixtures: bp 150 °C (oven temp) (14 mmHg); net yields are 30% (17) and 8% (18) checked by GLC analysis (OV-17, 2.0 × 3 mm, column temp 80 °C. Compound **17**: ^1H NMR δ 0.18 (s, 9 H), 7.30–7.70 (m, 3 H); ^{19}F NMR ϕ 62.0 (s, 3 F); HRMS calcd for $C_{10}H_{12}ClF_3Si$ 252.0350, found 252.0341. Compound **18**: ^1H NMR δ 0.18 (s, 9 H), 7.30–7.70 (m, 3 H); ^{19}F NMR ϕ 58.5 (s, 3 F); HRMS found 252.0333.

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Registry No. **1**, 98-08-8; **2A**, 320-50-3; **2B**, 115591-62-3; **2C**, 115591-63-4; **3a**, 115591-64-5; **3b**, 115591-65-6; **4a**, 115591-66-7; **4b**, 115591-67-8; **5a**, 348-90-3; **5b**, 344-53-6; **6a**, 114973-35-2; **6b**, 1994-23-6; **6c**, 115591-68-9; **7a**, 115603-77-5; **7b**, 115591-69-0; **8a**, 115591-71-4; **8b**, 115591-72-5; **9a**, 38609-76-6; **9b**, 115591-73-6; **10**, 104939-25-5; **11**, 65499-42-5; **12**, 84500-35-6; **13**, 70-00-8; **14**, 84500-36-7; **15**, 115591-74-7; **16**, 115591-75-8; **17**, 453-54-3; **18**, 115603-78-6; XeF_2, 13709-36-9; CF_3CO_2H, 76-05-1; $C_2F_5CO_2H$, 422-64-0; $C_3F_7CO_2H$, 375-22-4; benzene, 71-43-2; 1,4-dichlorobenzene, 106-46-7; methyl 4-chlorobenzoate, 1126-46-1; 3,4-dimethoxy-1-nitrobenzene, 709-09-1; *N*-[4-chlorophenyl]acetamide, 539-03-7; *N*-[2,5-difluorophenyl]acetamide, 398-90-3; *N*-[3,5-dichlorophenyl]acetamide, 31592-84-4; isopropyl 5-acetamido-4-fluorobenzoate, 115591-70-3; 1,2-dihydro-2-oxo-5-(trifluoromethyl)pyridine, 33252-63-0; methyl 2-furancarboxylate, 611-13-2; 3′,5′-di-*O*-acetyl-2′-deoxyuridine, 13030-62-1; *N*-[4-(trimethylsilyl)phenyl]acetamide, 17983-71-0; trimethylsilyl trifluoroacetate, 400-53-3; (4-chlorophenyl)trimethylsilane, 10557-71-8.

Facile Isomerization of 2-(Dicyanomethylene)-1,3-indandione to 2,3-Dicyano-1,4-naphthoquinone

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There is considerable interest in highly conjugated, planar, electron-acceptor molecules that form stable anion radical salts with appropriate cationic species, as many of these salts are organic semiconductors or organic metals.[1]

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