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1,ω-Perfluoroalkylation of Aromatics via Bis-Decarboxylation of Perfluorodicarboxylic Acids with XeF_2

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It has been shown that fluoro-substituted aliphatic acids reacts with xenon difluoride, XeF_2, to give unstable derivatives of the type $(RCOO)_2Xe$ or RCOOXeF[1] which, in turn, undergo a spontaneous decarboxylative decomposition leading to the formation of fluoroalkyl radicals.[2] This process has been suggested as a new preparative procedure to introduce a fluorinated alkyl framework into a variety of organic molecules.[3] The goal of the present work was to extend this method to the generation of 1,ω-diradicals, *via* the treatment of dicarboxylic fluorinated acids with XeF_2 and subsequently intercepting them either by aromatics or halogens as an entry to valuable synthetic products.

First of all, we have found that the model compound, namely hexafluoroglutaric acid (1) reacts with XeF_2 in the presence of different aromatic substrates to give the corresponding 1,3-diarylhexafluoropropanes 2–4 (yields 45–65%).[4]

$$\underset{1}{HOOC(CF_2)_3COOH} + XeF_2 + \underset{2\text{–}4}{ArH} \rightarrow Ar(CF_2)_3Ar + HF + CO_2 + Xe$$

$$Ar = C_6H_5\ (2),\ CH_3C_6H_4\ (3),\ FC_6H_4\ (4)$$

The reaction proceeds under moderately mild conditions and in the case of the substituted aromatic compounds 3 and 4 gave a mixture of ortho-, meta-, and para-isomers (determined by ^{19}F NMR).

Secondly, if the analogous reactions of hexafluoroglutaric acid with XeF_2 were performed in the presence of bromine or chlorine, the formation of 1,3-dibromo- (5) or 1,3-dichlorohexafluoropropanes (6) was observed as the result of trapping of the radical intermediates with halogen. Formally, this reaction may be considered as a synthetic equivalent of the Borodin–Hunsdiecker reaction.[5]

$$HOOC(CF_2)_3COOH + XeF_2 + X_2 \rightarrow X(CF_2)_3X + HF + CO_2 + Xe$$

$$X = Br\ (5),\ Cl\ (6)$$

The introduction of a perfluorinated residue into an organic compound imparts specific and often useful properties which cannot be achieved by other functional groups[6] and hence this simple procedure could prove to be synthetically attractive, especially if it turns out to be generally applicable.

Experimental Section

The ^1H and ^{19}F NMR spectra were recorded on a Bruker CXP-200 spectrometer (chemical shifts are relative to TMS and CF_3COOH, respectively). The IR spectra were taken on a Specord IR-75 spectrometer in CCl_4. The mass spectra were obtained on a Finnigan mass spectrometer at 70 eV (the temperature of the ionization chamber was 120 °C).

1,3-Diphenylhexafluoropropane (2). To a solution of acid 1 (1.52 g, 6.33 mmol) in benzene (2.0 g, 25.6 mmol) and methylene chloride (20 mL) was added XeF_2 (1.07 g, 6.33 mmol). The mixture was stirred for 3 h at 15–20 °C and then treated with aqueous bicarbonate. The usual workup with a purification by preparative chromatography on Silufol 100 × 250 (hexane/$CHCl_3$, 3:1) gave 0.9 of **2** (47% yield): ^1H NMR (200 MHz, $CDCl_3$) δ 7.49 (m, 10H, $2C_6H_5$); ^{19}F NMR (188 MHz, $CDCl_3$) δ −45.3 (s, 2F, CF_2), −32.3 (s, 4F, $2CF_2Ph$); MS *m/z* 304 (M^+), 158, 127, 77. Anal. Calcd for $C_{15}H_{10}F_6$: C, 59.22; F, 37.47. Found: C, 59.90; F, 37.59.

1,3-Ditolylhexafluoropropane (3). In a similar manner acid 1 (1.52 g, 6.33 mmol), methylene chloride (20 mL), tolune (2.5 g, 27.43 mmol), and XeF_2 (1.07 g, 6.33 mmol) gave 1.3 g of **3** (62% yield) as a mixture of isomers: ^1H NMR (200 MHz, $CDCl_3$) δ 2.22 s, 2.40 s (6H, $2CH_3$), 7.24 (m, 8H, $2C_6H_4$); ^{19}F NMR δ singlets at −45.3, −45.2, −45.0, −44.1, −43.9 (2F, CF_2), −32.8, −32.7, −32.3, −32.2, −32.1, −31.8, −31.6, −28.3, −27.8, (4F, $2CF_2Tol$); MS *m/z* 332 (M^+), 241, 141, 91. Anal. Calcd for $C_{17}H_{14}F_6$: C, 61.45; F, 34.30. Found: C, 61.90; F, 34.60.

(1,3-Difluorophenyl)hexafluoropropane (4). In a similar manner acid 1 (1.52 g, 6.33 mmol), methylene chloride (20 mL), fluorobenzene (2.4 g, 25 mmol), and XeF_2 (1.07 g, 6.33 mmol) gave 1.4 g of **4** (65% yield) as a mixture of isomers: ^1H NMR (200 MHz, $CDCl_3$) δ 7.15 (m, 8H, $2C_6H_4$); ^{19}F NMR (188 MHz, $CDCl_3$) δ singlets at −46.0, −46.3, −47.0 (2F, CF_2), −35.7, −35.2 (2F, $2C_6H_4F$), −34.3, −34.0, −33.5, −33.18, −32.8 (4F, $2CF_2Ar$); MS *m/z* 340 (M^+), 245, 145, 95. Anal. Calcd for $C_{13}H_8F_8$): C, 52.96; F, 44.67. Found: C, 52.10; F, 45.20.

1,3-Dibromohexafluoropropane (5). An amount of 1.2 g (4.99 mmol) of the acid 1 was dissolved in methylene chloride (20 mL), and bromine (1.0 g, 6.32 mmol) and XeF_2 (0.85, 5.05 mmol) were added. The reaction mixture was cooled to 0–5 °C, stirred intensively for an additional 3 h at 15–20 °C, and then treated with aqueous $Na_2S_2O_3$. The usual workup[3a,4] and distillation of the residue gave 1.1 g of **5** (71% yield); bp 76 °C, n_d^{20} 1.3529 (lit.

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[1] (a) Musher, J. I. *J. Am. Chem. Soc.* **1968**, *69*, 412. (b) Gregoric, A.; Zupan, M. *J. Org. Chem.* **1979**, *44*, 412.

[2] (a) Zupan, M. In *The Chemistry of Halides, Pseudo-Halides and Azides*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; p 665. (b) Patrick, T. B.; Johri, K. K.; White, D. H.; Bertrand, W. S.; Mokhtar, R.; Keibourn, M. R.; Welch, M. J. *Can. J. Chem.* **1986**, *64*, 138. (c) Patrick, T. B.; Khazaeli, S.; Nadji, S.; Hering-Smith, K.; Reif, K. *J. Org. Chem.* **1993**, *58*, 705.

[3] (a) Brel, V. K.; Koz'min, A. S.; Martynov, I. V.; Uvarov, V. I.; Zefirov, N. S.; Zhdankin, V. V.; Stang, P. J. *Tetrahedron Lett.* **1990**, *31*, 4799. (b) Tanabe, Y.; Matsuo, N.; Ohno, N. *J. Org. Chem.* **1988**, *53*, 688.

[4] Polyfluorinated aromatics have been made by the Wurtz–Fittig synthesis: (a) *Organic Fluorine Chemistry*; Hudlický, M., Ed.; Plenum Press: New York, 1971; p 129. (b) McLoughlin, V. C. R.; Thrower, J.; White, J. M. *Chem. Eng. News* **1967**, *45* (34), 40.

[5] *Org. React.* **1959**, *9*, 445.22.

[6] Yoshida, M.; Kamigata, N. *J. Fluorine Chem.* **1990**, *49*, 1. Bravo, P.; Pregnolato, M.; Resnati, G. *J. Org. Chem.* **1992**, *57*, 2726. Chen., Q.-Y.; Chen, M.-J. *Phosphorus, Sulfur Silicon* **1992**, *68*, 205. *Fluorine-containing Molecules: Structure, Reactivity, Synthesis, and Applications*; Leibman, J. F., Greenberg, A., Dolbier, W. R., Jr., Eds.; VCH Publishers: New York, 1988; p 292.

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data[7] bp 74.2 °C, n_d^{20} 1.3526); ^{19}F NMR δ −45.3 (s, 2F, CF_2), 15.1 (s, 4F, $2CF_2Br$). Anal. Calcd for $C_3Br_2F_6$: C, 11.63; F, 36.79. Found: C, 12.00; F, 38.10.

1,3-Dichlorohexafluoropropane (6). In a similar manner acid 1 (1.2 g, 4.99 mmol), methylene chloride (20 mL), chlorine (0.7 g, 9.85 mmol), and XeF_2 (0.85 g, 5.02 mmol) gave 0.6 g of 6 (54% yield): bp 36 °C, n_D^{20} 1.3065 (lit. data[8] bp 35.8 °C, n_D^{20} 1.3030); ^{19}F NMR (188 MHz, $CDCl_3$) δ −40.5 (s, 2F, CF_2), 12.2 (s, 4F, $2CF_2Cl$). Anal. Calcd for $C_3Cl_2F_6$: C, 16.31; F, 51.60. Found: C, 16.20; F, 52.00.

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(7) Hauptschein, H.; Stokes, C. S.; Grosse, A. V. *J. Am. Chem. Soc.* **1952**, *74*, 1974.

(8) Brandt, A.; Emellus, H. J.; Haszeldine, R. N. *J. Chem. Soc.* **1952**, 2252.