Maillard reaction and not to any amine-containing Maillard reaction products.[22]

We suggest that the mechanism of sulfite inhibition of the cross-linking and browning of the Maillard reaction also involves formation of AFGPs from early Maillard reaction products followed by irreversible reaction of sulfite ion with the electrophilic carbons of AFGP to form compounds **9** and **10** (Nu = SO_3H). These sites in the AFGP are then blocked from reaction with other nucleophiles that might be present such as an amino acid or a protein. Efforts are under way to isolate an AFGP/bisulfite adduct, to determine whether AFGPs are present in the noninhibited Maillard reaction, and to learn the fate of AFGPs in the presence of amino acids and proteins.[23]

Experimental Section

The sodium phosphate buffer was 0.5 M in phosphate and adjusted to pH 7.35 with NaOH and then filtered through a 0.2-μ membrane. The IR spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. The UV spectra were obtained on a Hewlett-Packard 8450A spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Nicolet/Oxford NT300 (300 MHz) instrument in D_2O with (trimethylsilyl)propionic acid or dioxane as a reference. Final purification of the AFGPs was performed with a Pharmacia FPLC and a Mono Q HR10/10 anion-exchange column. HPLC analysis was performed with a Hewlett-Packard 1084B liquid chromatograph with a HP 79850B LC terminal. A Supelcosil C18 reverse-phase column (25 cm × 4.6 mm, 5-μm packing) was used at a flow rate of 1 mL/min with detection at 300 nm and elution with 100 mM HOAc (A1), 100 mM HOAc in 5% MeOH (A2), or 100 mM HOAc in 50% MeOH (B).

Generation and Purification of G-AFGP (2a–2b). Glucose (5 g, 28 mmol) was dissolved in 10 mL of sodium phosphate buffer. Sodium sulfite (250 mg, 2.0 mmol) and 6-AHA (500 mg, 3.8 mmol) were added and the pH of the solution was adjusted to 7.35. The solution was placed in the dark at 37 °C in a tightly closed tube. After 26 days the incubation mixture was added to a column containing 50 g of Dowex AG 1X4 anion-exchange resin (acetate form, 100–200 mesh). Elution with H_2O (1 L) gave a fraction containing glucose and the Amadori product of 6-AHA. After an additional 400 mL of 100 mM HOAc, material strongly absorbing at 300 nm eluted. This fraction was neutralized with ammonium hydroxide and lyophilized to yield 380 mg (25%) of a viscous, brown oil. A portion (55 mg) of this material was purified by FPLC anion chromatography (30-min gradient from 0 to 50 mM ammonium acetate in 5% MeOH) to yield a hygroscopic, amorphous, dull yellow solid (21 mg, 38%). This material was sensitive to the chromatographic conditions: only 50% of the material purified by anion FPLC was recoverable when the spectroscopically pure compound was rechromatographed. IR (neat) 3400–3100, 2870, 1710, 1645, 1100, 1040 cm^{-1}; MS, see Table II; ^1H NMR, see Table I; ^{13}C NMR[24] 181.8 + 181.2, 178.8, 135.9 + 135.8, 131.1 + 130.7, 128.2 + 127.3, 121.6 + 120.5, 76.6 + 76.2, 75.4 + 75.1, 74.4 + 73.9, 72.2 + 71.6, 70.5, 66.9 + 66.8, 62.7 + 62.6, 48.9, 33.8, 30.0, 25.0, 23.7 ppm; HPLC; 30-min gradient from 10% Al to 90% B. The chromatogram consisted of four peaks (94.5%) at 17.9, 18.2, 19.2, and 19.8 min in a 1:1:4:8 ratio. The area of these peaks was seen to decrease when the sample was exposed for longer periods of time to the eluents.

Generation and Purification of X-AFGP (1a–1b, R = H). Xylose (1.14 g, 7.6 mmol) was dissolved in 10 mL of sodium phosphate buffer. Sodium sulfite (480 mg, 3.8 mmol) and 6-AHA (500 mg, 3.8 mmol) were added and the pH was adjusted to 7.35. The solution was placed in the dark at 37 °C in a tightly closed tube. After 8 days, the incubation mixture was added to 50 g of anion-exchange resin. The 100 mM HOAc eluate (1 L) was collected, neutralized with ammonium hydroxide, and lyophilized to yield 194 mg (14%) of a viscous, brown oil. FPLC purification (30-min gradient from 0 to 50 mM ammonium acetate in 5% MeOH) of 27 mg of this material gave 8.3 mg (31%) of a yellow, hygroscopic solid. IR (neat) 3400–3100, 2870, 1710, 1645, 1100, 1035 cm^{-1}; MS, see Table II; ^1H NMR, see Table I; ^{13}C NMR[24] 182.0 + 181.7, 179.2, 135.6 + 135.0, 131.7 + 131.4, 127.6 + 127.4, 123.0 + 122.6, 75.0, 74.5 + 74.4, 68.1 + 67.7, 66.2 + 66.0, 63.1 + 62.6, 48.9, 33.8, 30.0, 25.0, 23.8 ppm; HPLC, 30-min gradient from 10% A2 to 75% B. The chromatogram consisted of four peaks (85%) at 14.1, 14.3, 14.9, and 15.3 min in a 1:1.3:1.3:1.8 ratio. The area of these peaks was seen to decrease when the sample was exposed for longer periods of time to the eluents.

Registry No. **1a**, 113778-91-9; **1b**, 113792-87-3; **2a**, 113778-89-5; **2b**, 113778-90-8; 6-AHA, 60-32-2; D-glucose, 50-99-7; D-xylose, 58-86-6.

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(24) Only the major resonances are presented. For both X-AFGP and G-AFGP, there were additional, smaller resonances from the pyrrolyl and glycosyl carbons of the minor isomers.

Notes

A Remarkably Simple Perfluoroalkylation in the Presence of an Electron Mediator

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Perfluoroalkyl iodides are useful reagents for the perfluoroalkylation of organic molecules.[1-10] However, synthetic methods for the compounds with long perfluoroalkyl chains in the presence of a metal (Zn, Mn, Mg, Al, or Fe) usually require some type of activation, i.e. ultrasonic ir-

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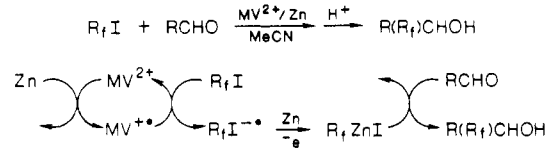
Table I. Preparation of α-Perfluoroalkyl Carbinols

R_fI	RCHO	product[a]	reactn time (h)	yield (%)
CF_3I	PhCHO	$Ph(CF_3)CHOH$[c]	15	52
CF_3I	$CH_3(CH_2)_4CHO$	$CH_3(CH_2)_4(CF_3)CHOH$[d]	15	48
CF_3CF_2I	PhCHO	$Ph(C_2F_5)CHOH$[c]	21	57
CF_3CF_2I	$PhCH_2CH_2CHO$	$PhCH_2CH_2(C_2F_5)CHOH$[b]	17	51
C_4F_9I	PhCHO	$Ph(C_4F_9)CHOH$[c]	14	42
C_4F_9I	$CH_3(CH_2)_4CHO$	$CH_3(CH_2)_4(C_4F_9)CHOH$[d]	25	64
$C_6F_{13}I$	PhCHO	$Ph(C_6F_{13})CHOH$[c]	13	65
$C_6F_{13}I$	$PhCH_2CH_2CHO$	$PhCH_2CH_2(C_6F_{13})CHOH$[b]	39	57
$C_6F_{13}I$	$CH_3(CH_2)_6CHO$	$CH_3(CH_2)_6(C_6F_{13})CHOH$[b]	48	68
$C_8F_{17}I$	PhCHO	$Ph(C_8F_{17})CHOH$[c]	14	52
$C_8F_{17}I$	CH_3CH_2CHO	$CH_3CH_2(C_8F_{17})CHOH$[d]	24	53

[a] Structures were determined by means of IR, NMR, and mass spectral data. [b] New compounds. The microanalysis was in satisfactory agreement with the calculated values (C, H, N; ±0.4%). [c] Kitazume, T.; Ishikawa, N. *J. Am. Chem. Soc.* **1985**, *107*, 5186. [d] Kitazume, T.; Ishikawa, N. *Nippon Kagaku Kaishi* **1984**, 1725.

Scheme I



radiation,[2,3] catalysis by metal complexes,[4] photolysis, electrolysis,[5] thermolysis of free radical initiators, and preferably, an inert atmosphere, and the formation of R_fR_f and/or R_fH have been sometimes observed. Therefore, in the field of fluorine chemistry, it would be useful to have a new moderate technical method to introduce perfluoroalkyl groups in the organic molecules.

This work describes the synthetic utilization of the zinc–methyl viologen system as an effective electron mediator[11–15] which should accelerate the conversion of perfluoroalkyl iodides to α-perfluoroalkyl carbinols in a Barbier-type reaction as shown in Scheme I.

We attempted the Barbier-type reaction in an electron-transfer system containing the reducing agent (Zn) and MV^{2+} as electron-transfer catalyst (ETC). The results shown in Table I support a new approach, which is capable of converting perfluoroalkyl iodides to α-perfluoroalkyl carbinols via Barbier-type reaction. Without methyl viologen, the reaction did not proceed at all. However, in the Zn–MV^{2+} system, the formation of (perfluoroalkyl)zinc reagents in situ were checked by ^{19}F NMR.

Experimental Section

1-(Perfluorohexyl)-1-phenylcarbinol. A suspension of zinc powder (0.35 g, 0.005 g-atom), perfluorohexyl iodide (2.3 g, 5 mmol), and benzaldehyde (1.06 g, 10 mmol) in acetonitrile (20 mL) was stirred at room temperature. Into the mixture, methyl viologen (MV^{2+},$2Cl^{1-}$) (50 mg, 0.16 mmol; 3.2 mol % of perfluorohexyl iodide) was added, and then the whole was stirred at room temperature. After 14 h of stirring, the solution was poured into a 2% HCl solution and an oily material extracted with diethyl ether. After the extereal solution was dried over magnesium sulfate, the solvent was removed. The product was purified by chromatography on silica gel.

1-(Trifluoromethyl)-1-phenylcarbinol. A flask containing commercially available zinc powder (1.30 g, 0.02 g-atom), trifluoromethyl iodide (3.0 g, 20 mmol), and benzaldehyde (3.18 g, 30 mmol) in acetonitrile (50 mL) and then equipped with a dry ice–acetone reflux condenser was stirred at room temperature. Into the mixture, methyl viologen (MV^{2+},$2Cl^{1-}$) (200 mg, 0.64 mmol; 3.2 mol % of trifluoromethyl iodide) was added, and then the whole was stirred for 15 h at room temperature and then worked up as usual. Distillation gave 1-(trifluoromethyl)-1-phenylethanol in a yield of 52%, bp 80–83 °C (3 mmHg): ^{19}F NMR (CCl_4) φ 78.5 (CF_3, d, J_{CF_3-CH} = 6.5 Hz); ^1H NMR ($CDCl_3$) δ 5.00 (CH, q), 4.0 (OH), 7.4 (Ar H).

Registry No. CF_3I, 2314-97-8; PhCHO, 100-52-7; $Ph(CF_3)CHOH$, 340-04-5; $H_3C(CH_2)_4CHO$, 66-25-1; $H_3C(CH_2)_4(CF_3)CHOH$, 80768-53-2; F_3CCF_2I, 354-64-3; $Ph(C_2F_5)CHOH$, 345-40-4; $Ph(CH_2)_2CHO$, 104-53-0; $Ph(CH_2)_2(C_2F_5)CHOH$, 90550-19-9; C_4F_9I, 423-39-2; $Ph(C_4F_9)CHOH$, 78960-83-5; $H_3C(CH_2)_4(C_4H_9)CHOH$, 95452-56-5; $C_6F_{13}I$, 355-43-1; $Ph(C_6F_{13})CHOH$, 57242-02-1; $Ph(CH_2)(C_6F_{13})CHOH$, 111822-76-5; $H_3C(CH_2)_6CHO$, 124-13-0; $H_3C(CH_2)_6(C_6F_{13}CHOH$, 111822-77-6; $C_8F_{17}I$, 507-63-1; $Ph(C_8F_{17})CHOH$, 111822-78-7; H_3CCH_2CHO, 123-38-6; $H_3CCH_2(C_8F_{17})CHOH$, 95452-57-6; Zn, 7440-66-6; methyl viologen, 1910-42-5.

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A Remarkably Simple Route to Perfluoroalkylated Olefins and Perfluoroalkanoic Acids

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Bioactive materials and industrial chemicals that contain a trifluoromethyl group and/or a perfluoroalkyl (R_f) group have been extensively studies.[1,2] In fact, a variety of perfluoroalkylations based on the synthetic applications of perfluoroalkylmetallic reagents[3–9] and/or perfluoroalkyl radicals[9–13] have been reported. However, these methods require ultrasound, photolysis, and thermolysis in excess

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