J. Org. Chem. **1982**, *47*, 2789–2790

(12), 132 (40), 131 (100), 130 (69); mol wt 216.1269 (calcd for $C_{13}H_{16}N_2O$ 216.1262).

Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.22; H, 7.40; N, 12.96. Found: C, 72.16; H, 7.36; N, 12.87.

Imidazolidinone 8: 72% yield (from $CHCl_3$); mp 160–162 °C; IR (KBr) 3200, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (s, 3 H), 1.59 (s, 3 H), 2.78–2.95 (m, 3 H), 3.97 (s, 6 H), 4.13 (d, J = 7 Hz, 1 H), 4.61 (s, 1 H), 4.75 (br s, 1 H), 6.64 (s, 1 H), 6.68 (s, 1 H); ^{13}C NMR ($CDCl_3$) 24.0, 28.5, 29.5, 37.0, 55.8, 56.1, 59.3, 64.1, 108.8, 112,2, 124.1, 127.9, 147.7, 148.1, 159.8 ppm; mass spectrum, *m/e* (relative intensity) 276 (19), 192 (19), 191 (100), 190 (20), 176 (30); mol wt 276.1468 (calcd for $C_{15}H_{20}N_2O_3$ 276.1474).

Imidazolidinone 10: 68% yield (from benzene–chloroform, 1:1); mp 216–219 °C; IR (KBr) 3250, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 3 H), 1.44 (s, 3 H), 2.00–3.44 (m, 6 H), 3.80 (s, 3 H), 4.38–4.94 (br s, 1 H), 4.61 (s, 1 H), 6.50–7.13 (m, 3 H); ^{13}C NMR ($CDCl_3$) 25.3, 26.4, 29.6, 31.1, 37.6, 55.2, 57.8, 73.4, 111.7, 116.7, 127.2, 129.3, 141.0, 159.1, 160.2 ppm; mass spectrum, *m/e* (relative intensity) 260 (23), 176 (18), 175 (100), 160 (15), 147 (29); mol wt 260.1529 (calcd for $C_{15}H_{20}N_2O_2$ 260.1525).

Anal. Calcd for $C_{15}H_{20}N_2O_2$: C, 69.20; H, 7.74; N, 10.76. Found: C, 69.23; H, 7.78; N, 10.78.

3-(3-Methoxybenzyl)-5,5-dimethyl-2-imidazolone (9): 27% yield (from EtOH); mp 186.5–189.5 °C; IR (KBr) 3200, 1700 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 1.79 (s, 3 H), 1.85 (s, 3 H), 3.71 (s, 3 H), 4.64 (s, 2 H), 6.56–7.50 (m, 4 H), 9.63 (br s, 1 H); ^{13}C NMR (Me_2SO-d_6) 8.1, 8.9, 41.6, 54.8, 111.0, 112.0, 112.3, 112.9, 118.6, 129.5, 140.4, 153.4, 159.3 ppm; mass spectrum, *m/e* (relative intensity) 232 (100), 121 (72), 111 (24), 91 (21), 78 (20), 77 (14).

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.15; H, 6.92; N, 11.91.

3-Phenethyl-5,5-dimethyl-2-imidazolone (7). A benzene (80 mL) solution of **5a** (1.43 g, 0.005 mol) and *p*-toluenesulfonic acid monohydrate (1.43 g, 0.0075 mol) was heated to reflux (24 h) during which time the H_2O was azeotropically removed. The benzene solution was then washed with H_2O (2 × 20 mL), dried (Na_2SO_4), and concentrated to dryness. The crude product was recrystallized from EtOH to give 1.00 g (93%) of **7**: mp 164–167 °C; IR (KBr) 3200, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.69 (s, 3 H), 1.94 (s, 3 H), 2.89 (t, J = 8 Hz, 2 H), 3.75 (t, J = 8 Hz, 2 H), 7.19 (s, 5 H), 10.25 (br s, 1 H); ^{13}C NMR ($CDCl_3$) 8.9, 9.4, 36.0, 42.6, 112.1, 113.7, 126.4, 128.5, 129.0, 138.9, 154.4 ppm; the signals at 128.5 and 129.0 ppm were approximately twice the intensity of neighboring peaks; mass spectrum, *m/e* (relative intensity) 216 (43), 125 (81), 112 (100), 111 (18), 105 (22), 97 (80), 91 (19).

Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.22; H, 7.40; N, 12.96. Found: C, 71.96; H, 7.44; N, 12.88.

Acknowledgment. We thank Mr. Sergio Cortes for many helpful discussions. Support of this work by the National Institutes of Health (Grant No. NS15604) is gratefully acknowledged.

Registry No. 4a, 81572-12-5; **4b**, 81572-13-6; **4c**, 81572-14-7; **4d**, 81572-15-8; **4e**, 77-71-4; **5a**, 81572-16-9; **5b**, 81572-17-0; **5c**, 81572-18-1; **5d**, 81572-19-2; **6**, 81572-20-5; **7**, 65383-36-0; **8**, 81583-49-5; **9**, 81572-21-6; **10**, 81572-22-7; phenethyl bromide, 103-63-9; 3,4-dimethoxyphenethyl bromide, 40173-90-8; *m*-methoxybenzyl chloride, 824-98-6; (*m*-methoxyphenyl)propyl bromide, 6943-97-1.

Synthesis of Tetrakis(perfluorocyclohexyl)methane and Bis(perfluorocyclohexyl)difluoromethane by Direct Fluorination

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Carefully controlled low-temperature direct fluorination has become perhaps the most facile chemical technique for rapid preparation of unknown fluorocarbon compounds and particularly structurally unknown[1] classes of compounds. The synthesis of tetrakis(perfluorocyclohexyl)methane and bis(perfluorocyclohexyl)difluoromethane was undertaken because they possess chemical and stereochemical properties thought to be advantageous for use in fluorocarbon emulsions for oxygen transport (see Figure 1). Such emulsions are currently used as artificial blood in humans[2] and were studied in earlier pioneering experiments[3] establishing the utility of this novel concept.

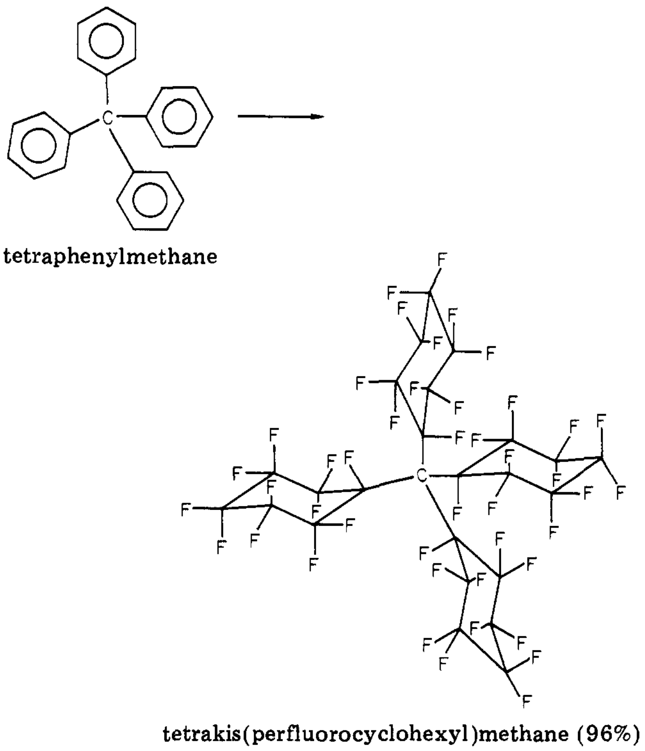

Figure 1.

We have previously shown that polynuclear aromatic systems could be exhaustively fluorinated to produce their saturated fluoroalkane analogues.[1] Thus, it appeared possible that both tetraphenylmethane and diphenylmethane could be converted to their perfluorocyclohexyl analogues.

Experimental Section

Fluorination of Tetraphenylmethane. Tetraphenylmethane (0.26 g) was ground to a fine powder (100 mesh) and placed in a nickel flow reactor described previously for the direct fluorination of solids.[1] After following the reaction conditions described below, 0.89 g of the white solid, tetrakis(perfluorocyclohexyl)methane (96% yield), was recovered from the reactor (mp 91–92 °C). ^{19}F NMR in perfluorobenzene consisted of a broad multiplet centered at +124 ppm from $CFCl_3$ and a second multiplet at +180 from $CFCl_3$ which integrated for 10 and 1, respectively. Infrared analysis of a KBr disk gave absorptions at 1190 (br), 1000 (m), 960 (m), 550 (w), 495 (w), and 470 (w) cm^{-1}. Mass spectral analysis gave a base peak of *m/e* 281 ($C_6F_{11}^+$) along with peaks at 855, 574, and 293 corresponding to the parent minus one, two, and three perfluorophenyls, respectively.

Anal. Calcd for $C(C_6F_{11})_4$: C, 26.4; F, 73.6. Found: C, 26.1; F, 73.4.

Fluorination of Diphenylmethane. Diphenylmethane (0.24 g) was placed in a fluorine reactor, and the reaction conditions below were followed. Bis(perfluorocyclohexyl)difluoromethane was obtained in 93% yield (0.72 g) by recrystallization in hexafluorobenzene. ^{19}F NMR of the product dissolved in C_6F_6 gave

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(2) T. Kawabata, *Jpn. Times*, 10 (1980).

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Table I. Reaction Conditions

temp, °C	He, cm^3/min	F_2, cm^3/min	time, days
−80	60	1.0	0.5
−80	30	1.0	0.5
−80	10	1.0	0.5
−80	0	1.0	1.0
RT[a]	0	1.0	1.0
RT	0	5.0	3.0
+50	0	2.0	3.0
RT	60	0.0	1.0

[a] Room temperature.

Table II. Reaction Conditions

temp, °C	He, cm^3/min	F_2, cm^3/min	time, days
−80	60	1.0	1.0
−80	30	1.0	0.5
−80	10	1.0	0.5
−80	0	1.0	1.0
RT[a]	0	1.0	1.0
RT	0	5.0	3.0
+50	0	2.0	3.0
RT	60	0.0	1.0

[a] Room temperature.

two broad multiplets centered around +120 and +180 ppm from $CFCl_3$ which integrated for 11 and 1, respectively. Infrared analysis utilizing a KBr disk gave absorptions at 1180 (br), 1000 (m), 960 (m), 500 (w), and 480 (w) cm^{-1}. The highest molecular weight fragment observed in the mass spectrum, *m/e* 331, corresponded to the parent minus one perfluorophenyl. Freezing-point depression of bis(perfluorocyclohexyl)difluoromethane in C_6F_6 gave a molecular weight of 550 g/mol (theoretical: 612 g/mol).

Anal. Calcd for $C(C_6F_{11})_2F_2$: C, 25.5; F, 74.5. Found: C, 25.7; F, 74.1.

Discussion

The liquid range of either new compound may occur at temperatures too high for use as a blood substitute. However, as part of a multicomponent emulsion or fluorocarbon solution these perfluorocyclohexyl compounds may have utility and are currently under study. The perfluoro ring systems appear to be a favorable structural feature in fluorocarbons that dissolve oxygen[4] and it is our hypothesis that maximum oxygen solubility is obtained in fluorocarbon systems with bulky side groups which by steric bulk produce intermolecular "hole" large enough to at least partially accommodate O_2. Interestingly, the somewhat lower melting point of the tetrakis(perfluorocyclohexyl)methane may indicate more random packing in the solid state and weaker lattice interaction than in the lower molecular weight, higher melting material.

The solubility of both compounds in C_6F_6 facilitated both their purification through recrystallization and allowed a check on their molecular weights by freezing-point depression. The molecular weight of a number of fluorocarbons including perfluorohexane, perfluoromethyl- and dimethylcyclohexane, and perfluoroadamantane were determined independently with values falling within 50–75 mass units of theoretical. The complex multiplet evidenced in the CF_2 region of the ^{19}F NMR is expected in analogy with the large number of overlapping A-B systems seen in the spectrum of perfluoromethylcyclohexane. Nonetheless, integral ratios obtained for the CF_2 and CF regions were obtained consistent with the expected structure. Similarly, the broad dominant band in the C–F stretching region of the infrared is typical of that found in fluoroalkanes.

The physical appearance of tetrakis(perfluorocyclohexyl)methane is very interesting. Its appearance is like that of a clear glistening glass with some sharp edges. This physical appearance and its unusual steric bulk have made it worthwhile to attempt to grow single crystals and determine the crystal structures.[5] The rather cautious reaction conditions were chosen to produce the high yields (97% and 93%, respectively) and optimum reaction times were not considered or explored.

Perhaps the greatest significance of this work, aside from the fact that the crowded $C(C_6F_{11})_4$ compound can be prepared at all, is the fact that $C(C_6F_{11})_4$ is the first four coordinate perfluorocyclohexyl compound. As such, this work forecasts the synthesis of an unknown class of compounds, perfluorocyclohexyl organometallics $[M(C_6F_{11})_n$ when M, *n*) = (Ge, 4), (Si, 4), (Sn, 4), (W, 6), etc.], and the very interesting class of bases and stabilizing ligands $[A(C_6F_{11})_n$ when (A, *n*) = (N, 3), (P, 3), and (B, 3)].

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Registry No. Tetraphenylmethane, 630-76-2; tetrakis(perflurocyclohexyl)methane, 81372-16-9; diphenylmethane, 101-81-5; bis(perfluorocyclohexyl)difluoromethane, 423-06-3.

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Heterogeneous Permanganate Oxidations. 2. Oxidation of Alcohols Using Solid Hydrated Copper Permanganate[1]

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The heterogeneous oxidation of secondary alcohols by permanganate ion is a convenient and efficient method for the preparation of ketones.[2,3] In most of the published procedures the alcohol, dissolved in an organic solvent, is added to potassium permanganate mixed with an inert solid, and, after a certain period of stirring and/or refluxing, the product is obtained by separating and concentrating the organic solution. This approach is an improvement over traditional procedures for permanganate oxidations because of the ease with which the product may be isolated and because it can be used to selectively oxidize unsaturated alcohols without damage to the carbon–carbon double or triple bonds.[3]

Menger and Lee[4] have noted that hydration of the inert solid is essential for an efficient reaction. For example,

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