Then a mixture of 2.9 mL of nitric acid and 2.9 mL of sulfuric acid was added dropwise to the sulfuric acid solution at –12 to ~–10 °C. After the reaction mixture was stirred at this temperature for 30 min, it was poured into ice–water. The precipitated crystals were collected and washed with water to give 3.7 g (93%) of 4,4'-diacetyl-2,2'-dinitrodiphenylmethane (18): colorless plates (EtOH); mp 152.5–155.0 °C; IR (KBr) 1680, 1530 cm^{-1}; NMR (CDCl$_3$) δ 2.65 (6 H, s), 4.74 (2 H, s), 7.24 (2 H, d, J = 8 Hz), 8.08 (2 H, dd, J = 8 Hz, J = 2 Hz), 8.55 (2 H, d, J = 2 Hz). Anal. Calcd for C$_{17}$H$_{14}$N$_2$O$_6$: C, 59.65; H, 4.12; N, 8.18. Found: C, 59.49; H, 4.10; N, 8.18.

Nitrations of 24 and 27. The nitrations of **24** and **27** were carried out and the mixtures treated and worked up as described above. The yields of the products are given in Scheme IV.

4-*tert*-Butyl-2,6-dimethylnitrobenzene (30): colorless prisms (EtOH); mp 84–86 °C (lit.[18] mp 85 °C); NMR (CDCl$_3$) δ 1.30 (9 H, s), 2.30 (6 H, s), 7.10 (2 H, s).

4,4'-Di-*tert*-butyl-2,2',6,6'-tetramethyl-3-nitrodiphenylmethane (31): colorless plates (EtOH); mp 136.9–137.1 °C; NMR (CDCl$_3$) δ 1.27 (9 H, s), 1.33 (9 H, s), 1.91 (3 H, s), 2.08 (6 H, s), 2.17 (3 H, s), 2.17 (3 H, s), 4.00 (2 H, s), 6.93 (2 H, s), 7.08 (1 H, s). Anal. Calcd for C$_{25}$H$_{35}$NO$_2$: C, 78.69; H, 9.25; N, 3.67. Found: C, 78.39; H, 9.23; N, 3.66.

4-*tert*-Butyl-2,6-dimethylnitrobenzene (30): colorless plates (EtOH); mp 136.9–137.1 °C; NMR (CDCl$_3$) δ 1.27 (9 H, s), 1.33 (9 H, s), 1.91 (3 H, s), 2.08 (6 H, s), 2.17 (3 H, s), 4.00 (2 H, s), 6.93 (2 H, s), 7.08 (1 H, s). Anal. Calcd for C$_{25}$H$_{35}$NO$_2$: C, 78.69; H, 9.25; N, 3.67. Found: C, 78.39; H, 9.23; N, 3.66.

4-*tert*-Butyl-2,2',6,6'-tetramethyl-3-nitro- (32a) or 4-*tert*-butyl-2,2',6,6'-tetramethyl-3'-nitrodiphenylmethane (32b): colorless plates (EtOH); mp 144.4–145.8 °C; NMR (CDCl$_3$) δ 1.32 (9 H, s), 2.15 (6 H, s), 2.42 (3 H, s), 2.48 (3 H, s), 3.82 (2 H, s), 7.05 (4 H, s). Anal. Calcd for C$_{21}$H$_{27}$NO$_2$: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.25; H, 8.47; N, 4.30.

4,4'-Di-*tert*-butyl-2,2',6,6'-tetramethyl-3,3'-dinitrodiphenylmethane (33): colorless needles (EtOH); mp 157–158 °C; NMR (CDCl$_3$) δ 1.35 (18 H, s), 1.96 (6 H, s), 2.17 (6 H, s), 4.10 (2 H, s), 7.20 (2 H, s). Anal. Calcd for C$_{25}$H$_{34}$N$_2$O$_4$: C, 70.39; H, 8.04; N, 6.54. Found: C, 70.32; H, 8.04; N, 6.44.

2,6-Dimethyl-4-nitrophenol (34): colorless prisms (EtOH); mp 176–177 °C (lit.[19] mp 170–171.5 °C). This compound was also prepared by nitration of 2,6-dimethylphenol with nitric acid. The melting point of compound **34** which was prepared by nitration of 2,6-dimethylphenol is also 176–177 °C.

2,6-Dimethyl-1,4-benzoquinone (35): yellow needles; mp 71–73 °C (lit.[19] mp 72–73 °C).

Registry No. 8, 4957-14-6; 9, 4956-99-4; 10, 19099-48-0; 11, 790-82-9; 12, 99-99-0; 13, 100-12-9; 14, 3282-56-2; 15, 76947-17-6; 16, 3344-27-2; 17, 76947-18-7; 18, 76947-19-8; 19, 67364-88-9; 20, 76947-20-1; 24, 65338-71-8; 27, 5384-21-4; 30, 6279-89-6; 31, 76947-21-2; 32, 76986-84-0; 33, 76947-22-3; 34, 2423-71-4; 35, 527-61-7.

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F-2-Methyl-2-pentanol. An Easily Prepared Perfluorinated Tertiary Alcohol[1]

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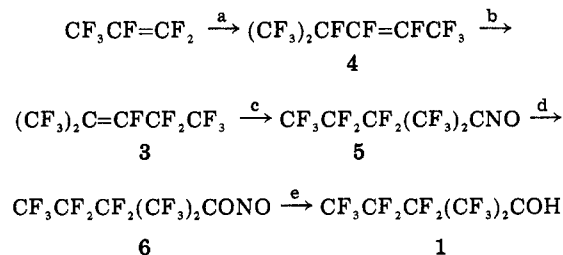
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We report here a synthesis of the title compound (**1**) which can be carried out in ordinary glassware from an

Scheme I^a

CF$_3$CF=CF$_2$ $\xrightarrow{a}$ (CF$_3$)$_2$CFCF=CFCF$_3$ $\xrightarrow{b}$

4

(CF$_3$)$_2$C=CFCF$_2$CF$_3$ $\xrightarrow{c}$ CF$_3$CF$_2$CF$_2$(CF$_3$)$_2$CNO $\xrightarrow{d}$

3   **5**

CF$_3$CF$_2$CF$_2$(CF$_3$)$_2$CONO $\xrightarrow{e}$ CF$_3$CF$_2$CF$_2$(CF$_3$)$_2$COH

6   **1**

^{a} (a) KF, 18-crown-6, acetonitrile, 10–15 °C. (b) KF, 18-crown-6, dimethylacetamide, reflux. (c) KF, NOCl or N$_2$O$_4$, dimethylacetamide, ca. 0 °C. (d) O$_2$ or N$_2$O$_4$ at room temperature. (e) H$_2$O.

inexpensive starting material and common reagents. Fluorinated alcohols, particularly 2,2,2-trifluoroethanol and 2*H*-*F*-2-propanol (hexafluoro-2-propanol), have attracted attention as specialty solvents, owing to their low nucleophilicity,[2] powerful H-bond donor ability,[3] and optical transparency. Perfluorinated tertiary alcohols as a class should possess those qualities as well as exceptional chemical unreactivity.

F-*tert*-Butanol (**2**), the only commercially available perfluorinated alcohol, has received little attention as a solvent because of its high price and modest liquid range (–15 to +45 °C); it has been prepared by disproportionation of *F*-acetone catalyzed by CsF–H$_2$O,[4] by halogen exchange from (CF$_3$)$_2$CCl$_3$COH,[5] and by several routes from the dangerously toxic *F*-isobutene.[6] Other perfluorinated tertiary alcohols have been prepared by reaction of perfluorinated ketones with perfluorinated organometallic reagents[7] and by SbF$_5$-catalyzed rearrangment of *F*-oxiranes.[8]

Our synthesis of **1** is similar to Knunyants and Dyatkin's original route to **2**,[6a,c] but we have simplified the procedure and reagents. In addition, we report convenient and reproducible conditions for the preparation of *F*-2-methyl-2-pentene (**3**), the stable dimer of *F*-propene, in kilogram quantities without the use of pressure equipment. Alcohol **1** is thus accessible in two to four steps and in over 50% overall yield from *F*-propene, a fluoropolymer intermediate[9] priced below $10/lb in bulk.

(1) This paper presents the results of one phase of research conducted in part at the Jet Propulsion Laboratory, California Institute of Technology, for the National Institutes of Health, by agreement with the National Aeronautics and Space Administration.

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The anionic dimerization of *F*-propene to give **3** was described first in the patent literature[10] and most recently by Dmowski, Flowers, and Haszeldine;[11] we find that reaction of *F*-propene with KF and 18-crown-6 in acetonitrile at atmospheric pressure gives largely the unstable dimer, *F*-3-methyl-2-pentene (**4**), and that **4** must be refluxed (ca. 50 °C) for several days with the same catalyst in dimethylacetamide (DMA) to effect isomerization to **3**. The difference between our conditions and Dmowski et al.'s are probably due to the much smaller ratio of catalyst to olefins in our work. We were unable to reproduce the preparation of **3** with the special amine catalyst of von Halasz et al.[12]

Addition of the elements of nitrosyl fluoride to **3** is effected by passing either N_2O_4 or NOCl into a cold, well-stirred suspension of KF and **3** in DMA. If excess N_2O_4 is used, the blue nitrosoalkane **5** is slowly oxidized in situ to the nitrite **6**; with NOCl, **5** is isolated and without purification oxidized to **6** with a slow stream of O_2 at room temperature. The two-step procedure gave a purer product and seems safer, since solutions of N_2O_4 in organic solvents have been reported to explode.[13] Neither **5** nor **6** was isolated in analytically pure form; their structures are assigned by analogy.[14] The oxidation of **5** by N_2O_4 or O_2 probably occurs through a radical-chain mechanism and takes place under milder conditions than those reported for the oxidation of $(CF_3)_3CNO$;[6c,f] models suggest that relief of steric repulsions as the $CF_3CF_2CF_3(CF_3)_2C\cdot$ radical becomes planer may account for its more ready formation vs. $(CF_3)_3C\cdot$.

Several alkyl ethers of **1** were prepared for evaluation as the oxygen-carrying phase of fluorochemical emulsion artificial blood;[15] a typical procedure for the preparation of one of these is described in the Experimental Section.

Experimental Section

Potassium fluoride was dried at 180 °C in a vacuum oven, ground in a ball mill, and manipulated thereafter in a glovebox; other chemicals and reagents were used as received. Fluorine NMR spectra were measured on precalibrated chart paper with a Varian T-60 spectrometer; the triplet of $CFCl_2CF_2Cl$ was used as an internal reference, and 72.0 ppm was added to the observed chemical shifts to obtain ϕ^*.

F-2-Methyl-2-propene (3). A 3-L, three-necked flask was surrounded by a cooling bath and equipped with a magnetic stirring bar, an immersion thermometer, a large cold finger charged with dry ice/2-propanol on the center neck, and a $CaCl_2$-filled exit trap. The flask was charged with 30 g of KF, 32 g of 18-crown-6/acetonitrile complex, and 524 mL of spectrograde CH_3CN. *F*-Propene was introduced through a side neck directly from a cylinder at a rate such that a thin stream of condensate fell from the condenser tip into the stirred KF suspension. The pot temperature rose initially to 50 °C, but for the rest of the reaction was kept between 10 and 15 °C by periodic additions of dry ice to the external 2-propanol bath. Refluxing of *F*-propene stopped almost immediately if the introduction was interrupted, and the mildly exothermic dimerization resumed when the gas flow was restarted. After about 3 h the working capacity of the

flask was reached, and the mixture was allowed to stir overnight and come to room temperature. Stirring was then stopped and the clear lower layer siphoned out. The yield of crude dimers was 2430 g; analysis by NMR indicated ca. 27% **3** and 73% **4**; trimers were not detected. In another run, three successive batches of mixed dimers totaling 8263 g were obtained by using the same sample of catalyst, without noticeable loss of activity.

Isomerization of 4 to 3. The 2430 g of dimer mixture was combined in another 3-L, round-bottomed flask with 20 g of 18-crown-6/acetonitrile complex, 30 g of KF, and 250 mL of DMA. The mixture was refluxed under an efficient condenser for 13 days, after which NMR analysis showed isomerization to **3** to be >95% complete. Direct distillation from the pot gave 2111 g of **3**, bp 51–60 °C, suitable for the preparation of **1**.

F-2-Methyl-2-pentanol (1). A mixture of 500 mL of DMA, 50 g of dry KF (0.86 mol), and 171.3 g of **3** (0.571 mol) in a 1-L, three-necked flask was stirred at 4–7 °C (external ice–salt bath) while 109 g of N_2O_4 (1.18 mol) was slowly distilled in in a slight flow of O_2. A −28 °C (boiling CF_2Cl_2) cold finger was used to minimize escape of NO_2. The addition was slightly exothermic and was interrupted whenever the pot temperature reached 7 °C. Immediately after the addition the reaction mixture was deep blue; NMR examination of the lower fluorochemical phase showed complete consumption of starting olefin and a single predominate product, presumably $CF_3CF_2CF_2(CF_3)_2CNO$ (**5**, *gem*-CF_3 quintet at ϕ^* 63.7). The reaction mixture was allowed to warm slowly to room temperature with stirring. After 18 h the blue color had disappeared, and the lower phase was light yellow, consistent with $CF_3CF_2CF_2(CF_3)_2CONO$ (**6**, *gem*-CF_3 quintet at ϕ^* 68.5). After approximately an additional 48 h, most of the fluorochemical phase had dissolved in the DMA, and much white solid was present. Water (ca. 400 mL) and 6.2 g of H_3BO_3 (0.1 mol) were added; the lower phase re-formed, and most of the solid dissolved. Sulfamic acid was added in small portions to destroy the nitrous acid present, and the reaction mixture was distilled at atmospheric pressure until the condensate was clear. The distillate consisted of a lower fluorochemical phase and an upper aqueous phase, both almost colorless. Potassium hydroxide (37.4 g, 0.66 mol) was added to the distillate, whereupon most of the lower phase dissolved in the aqueous layer. A small amount of neutral material was distilled under aspirator pressure into a −78 °C trap, and then the clear aqueous KOH solution was acidified with H_2SO_4. The lower phase which formed was separated, mixed with 25 mL of 96% H_2SO_4, and distilled at aspirator pressure into a dry ice cooled receiver: yield 108.9 g of **1** as a dense, water-white liquid (56.7%); bp 93 °C (728 mm); d^{24} 1.770 g cm⁻³; NMR ϕ^* 68.9 (6 F, t of t), 76.8 (3 F, t), 109.9 (2 F, m), 118.9 (2 F, m).

Anal. Calcd for $C_6F_{13}OH$: C, 21.45; H, 0.30; O, 4.76; F, 73.49. Found: C, 21.19; H, 0.49; F, 73.28.

The neutral fraction weighed 17.5 g (approximately 9% yield) and consisted of a mixture of two still-unidentified $CF_3CF_2CF_2(CF_3)_2CX$ products. The *gem*-$(CF_3)_2$ triplet of triplets of the major (~60%) component appears at ϕ^* 63.9; the *gem*-$(CF_3)_2$ triplet of triplets of the minor component at ϕ^* 67.6.

Alternate Procedure. Dried KF (58 g, 1.0 mol), 550 mL of DMA, and 201.3 g (0.671 mol) of **3** were combined and stirred magnetically in a 1-L, three-necked flask equipped with a cold-finger condenser, thermometer well, and drying tube. The mixture was cooled to −20 °C in a dry ice/2-propanol bath, and nitrosyl chloride was passed in, keeping the temperature below −5 °C, until a green color persisted (the reaction product forms a clear blue lower layer, and the presence of excess yellow-brown NOCl causes the mixture to appear green). An NMR spectrum of the blue lower layer showed complete consumption of starting material. The reaction mixture was poured into a 2-L separatory funnel containing 30 g of boric acid in ca. 1 L of ice–water. The blue lower layer was drawn off, placed, without further purification, in a 250-mL, three-necked flask equipped with a cold-finger condenser and oxidized with a slow stream of oxygen. The blue liquid turned green and then yellow within 30 min; the oxidation is exothermic. The crude yellow nitrite ester was poured into 800 mL of water, stirred until gas evolution (NO and NO_2) ceased, and then made strongly basic by addition of 60 g of KOH pellets. Insoluble material (40.8 g) was removed by direct-steam distillation; distillation was stopped when the distillate ran clear of insoluble material. The residual aqueous solution was cooled and acidified

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with sulfuric acid. The lower layer which formed was separated and mixed with 75 mL of 96% H_2SO_4, and the mixture was distilled at aspirator pressure into a dry ice cooled receiver. This gave a yield of 145.5 g (64.5%) of colorless 1, pure by NMR.

2-*n*-Butoxy-*F*-2-methylpentane. Dimethyl sulfoxide (125 g), alcohol 1 (25.0 g, 0.0744 mol), KOH pellets (9.9 g, 0.115 mol), and 1-iodobutane (18.4 g, 0.100 mol) were combined and stirred at room temperature for 3 days. (When 1 was mixed with Me_2SO, heat was evolved; on a larger scale, provision for cooling should be made.) At the end of the reaction period the mixture was poured into ca. 300 mL of water, and the crude lower layer was separated and dried over solid KOH. Distillation of the crude product at aspirator pressure into a dry ice cooled receiver gave 24.8 g of colorless liquid (84% yield). The analytical sample was obtained by preparative gas chromatography: bp 138 °C (732 mm); d^{21} 1.473 g cm^{-3}.

Anal. Calcd for $C_{10}H_9OF_{13}$: C, 30.63; H, 2.31; O, 4.08; F, 62.98. Found: C, 30.47; H, 2.25.

Note Added in Proof. After submission of this manuscript, preparation of 1 by the method of ref 8 was reported.[16]

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(-)-Methyl cis-3-Hydroxy-4,5-oxycyclohex-1-enecarboxylate: Stereospecific Formation from and Conversion to (-)-Methyl Shikimate; Complex Formation with Bis(carbomethoxy)hydrazine

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Our interest in the chemistry of shikimic acid derivatives prompted us to investigate the reaction of (-)-methyl shikimate (1) with triphenylphosphine/azodicarboxylates as a route to triphenylphosphorane derivative 2 that would
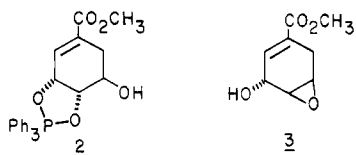
reasonably be expected to fragment to *anti*-hydroxy epoxide 3. In cyclic systems, *cis*-1,2-diols afford triphenylphosphoranes under the reaction conditions,[1-3] whereas epoxides are formed from the corresponding reaction of *trans*-1,2-diols.[2-5] Reaction of (-)-1 with triphenyl-

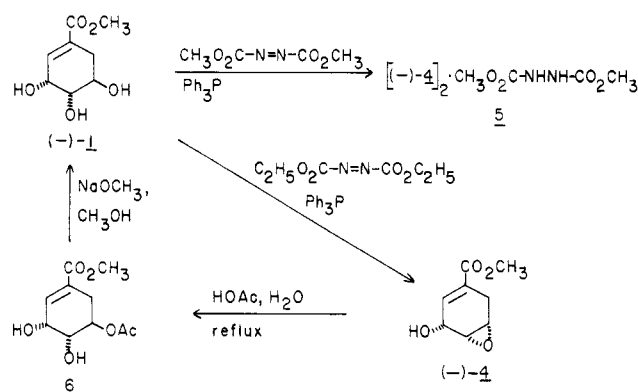(1) Kimura, J.; Fujisawa, Y.; Sawada, T.; Mitsonobu, O. *Chem. Lett.* 1974, 691-692.
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Scheme I

phosphine/dimethyl or diethyl azodicarboxylate did not follow the expected course but gave instead *syn*-hydroxy epoxide (-)-4 which, depending on the azodicarboxylate used, was obtained as such or as a complex with the hydrazine product of the reaction. Described herein are the details of the reaction and a procedure to regenerate (-)-1 from (-)-4 in high optical purity.

Reaction of (-)-1 with triphenylphosphine/dimethyl azodicarboxylate in tetrahydrofuran (THF) followed by removal of solvent gave a crude residue, the ^1H NMR spectrum of which indicated the absence of epoxy H. It was not possible to isolate a pure product on workup, but distillation of the residue and recrystallization afforded 5 (93% yield), a sharp-melting, 2:1 complex of (-)-4 and bis(carbomethoxy)hydrazine (Scheme I). Complex 5 survived sublimation (75 °C, 0.05 mm) and chromatography (silica gel), but pure (-)-4 could be obtained from complex 5 in 15-25% yield by two-phase distribution in $CHCl_3/H_2O$. The superior procedure for preparation of (-)-4 involved reaction of (-)-1 with triphenylphosphine/diethyl azodicarboxylate. The reaction followed a similar course, but in this case pure (-)-4 was obtained in 77% yield by preparative plate chromatography (silica gel) of the material obtained from distillation of the reaction mixture.

The formation and stability of complex 5 is unusual. That the product is indeed complex 5 and not a covalent adduct from bis(carbomethoxy)hydrazine and (-)-4 (or an intermediate derived from 1) was suggested from comparison of the ^1H NMR spectra of (-)-4 and 5. When the additional absorption for the hydrazine derivative of complex 5 is taken into account, with the exception of the chemical shift position of the hydroxyl proton, the chemical shift positions and line shapes in the spectra of (-)-4 and 5 are virtually identical. Furthermore, if (-)-4 and bis(carbomethoxy)hydrazine (2:1 molar ratio, respectively) are dissolved in diethyl ether with slight warming to effect solution, complex 5 crystallizes in near quantitative yield upon addition of petroleum ether. The melting point and IR and ^1H NMR spectra of 5 prepared by the two routes are identical.

The syn relationship of the hydroxyl and epoxide groups of (-)-4 was suggested from the ^1H NMR spectrum. The absorption for the hydroxyl proton of (-)-4 and of complex 5 in $CDCl_3$ appears as a sharp doublet with $J_{H_3-OH} = 10.7$ Hz in each case. Consequently, the conformation of the carbocyclic ring must be such that H_3 and the hydroxyl proton are antiperiplanar, and the hydroxyl proton is hydrogen-bonded to the *syn*-epoxide group.[6] In dimethyl-d_6 sulfoxide the intramolecular hydrogen bonding

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