

time was 4 h. The products were potassium 2-phenylbenzenesulfonate (62%), biphenylene sultine (2, 26%), and 2-phenylphenol (4%).

Reaction of 1 with KOH in the Absence of 18-Crown-6 in Mesitylene (20 h). The reaction was run exactly as it was in the presence of the crown ether. For efficient removal of unreacted 1 from the precipitated acid salts and KOH, after filtration of the precipitate, the mixture was washed with 50 mL of CHCl_3 . Unreacted 1 (0.494 g, 20%) was isolated from the combined CHCl_3 and mesitylene layers. The amount of 2-phenylbenzenesulfonate was determined by UV spectroscopy (72%). The ether layer from the acid hydrolysis contained only a trace of sultine 2 and 2-phenylphenol as determined by GC.

Ultraviolet Spectra of 2, 7, and 8. A stock solution of 2 (1.20×10^{-3} M) was prepared by dissolving 0.0130 g (0.060 mmol) of 2 in 90% CH_3CN -10% H_2O in a 50-mL volumetric flask. The stock solution was diluted 1/10, and the spectrum of 2 (curve a, Figure 1) was determined. To 1 mL of stock solution and 5 mL of 90% CH_3CN -10% H_2O in a 10-mL volumetric flask was added 0.2 mL of 2.5 M KOH. The mixture was diluted to 10 mL and the spectrum of 7 recorded (curve b, Figure 1). To 1 mL of stock solution and 5 mL of 90% CH_3CN -10% H_2O was added 0.2 mL of 2.5 M KOH. After several minutes (long enough for 7 to be formed from the 2 in the stock solution), 0.1 mL of concentrated HCl was added, the mixture diluted to 10 mL, and the spectrum of 8 recorded (curve c, Figure 1). If 2 mL of concentrated HCl, rather than 0.1 mL, was used, the spectrum of the solution changed over a period of a few hours, the final spectrum becoming identical with that of 2 (curve a, Figure 1).

Reaction of 2 with Methylmagnesium Iodide. Methylmagnesium iodide (1.0 mmol) in ether was added dropwise to a solution of 2 (0.210 g, 1.0 mmol) in 5 mL of ether. The solution was stirred for 30 min, the milky white suspension was poured into 20 mL of cold 5% aqueous NH_4Cl , and the solid was collected,

washed successively with water, acetone, and ether, and dried (MgSO_4). The solid (0.158 g, 0.68 mmol, 68%; 203-205.5 °C dec) was identified as 2-[2-(methylsulfinyl)phenyl]phenol based on spectral properties and elemental analysis: IR (KBr) 3150 (br, OH), 1590 (m), 1475 (m), 1450 (s), 1375 (m), 1010 (s), 1000 (s), 965 (m), 840 (m), 780 (m), 765 (s); $^1\text{H NMR}$ ($\text{CH}_3\text{CN}-\text{D}_2\text{O}$, 1/1) δ 2.58 (s, 3 H), 6.9-8.1 (m, 8 H). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$: C, 67.21; H, 5.20; S, 13.80. Found: C, 66.90; H, 5.22; S, 13.61.

Oxidation of 2 to Dibenz[*c,e*][1,2]oxathiin 6,6-Dioxide. To a stirred solution of 30% H_2O_2 (0.264 g, 2.3 mmol) in 3 mL of acetic acid was added 2 (0.069 g, 0.32 mmol). The solution was refluxed for 23 h, cooled, and poured onto ice. The solid was dissolved in CHCl_3 , and the CHCl_3 solution was washed successively with water, saturated NaHCO_3 , and water and dried (CaCl_2). Evaporation of the CHCl_3 gave solid dibenz[*c,e*][1,2]oxathiin 6,6-dioxide: mp 105-106.5 °C (lit.⁹ mp 108.5-109.5 °C); 0.069 g (0.30 mmol, 93%); IR (CDCl_3) 3065 (w), 1475 (m), 1430 (m), 1375 (s), 1205 (s), 1175 (s), 1140 (m), 1070 (m).

Flash Vacuum Pyrolysis of 2. Flash vacuum pyrolyses were carried out by vaporizing at 80 °C 100-150-mg samples of 2 into a 1.5×20 cm pyrolysis chamber at 10-20 μmHg . The pyrolysate was collected on a cold finger cooled to -196 °C with liquid N_2 . The temperature of the pyrolysis was monitored at the center of the pyrolysis chamber by using a Barber-Coleman thermocouple, the accuracy of which is estimated to be ± 10 °C. This FVP apparatus will be described in a forthcoming publication. The yields of reaction products (Table I) were determined by GLC using a 6 ft \times $1/8$ in. OV-17 on Anakorm Q 90/100-mesh column by comparison of peak areas with standard solutions of the reaction products via the internal standard method.

Registry No. 1, 1016-05-3; 2, 77123-91-2; 3, 132-64-9; 4, 132-65-0; 5, 4371-25-9; 6, 77123-92-3; 7, 77123-93-4; 8, 77136-31-3; 2-phenylphenol, 90-43-7; potassium 2-phenylbenzenesulfonate, 65426-43-9.

Notes

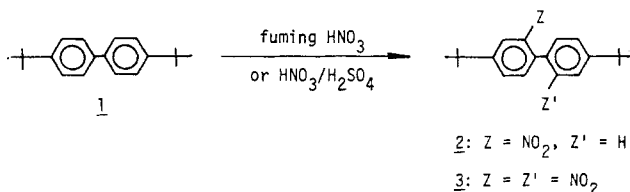
Friedel-Crafts Chemistry. 6. Substituent Effects on the Ipsio Nitration and the Novel Nitration of Some Diphenylmethanes^{1a}

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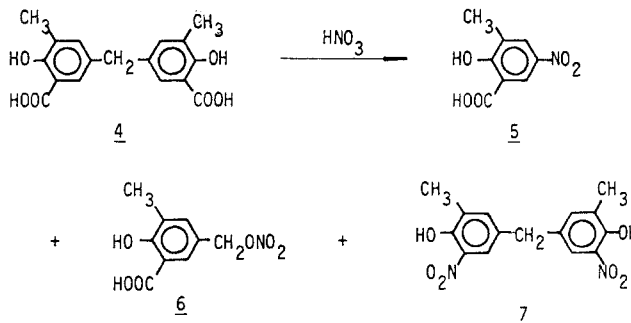
Received March 20, 1980

The nitration of 4,4'-di-*tert*-butylbiphenyl (1) with fuming nitric acid and with mixed nitric-sulfuric acids has afforded 2-nitro- (2) and 2,2'-dinitro-4,4'-*tert*-butylbiphenyl



(3).^{2,3} These compounds are useful intermediates for the

Scheme I



preparation of carbazoles. Products resulting from replacement of the *tert*-butyl group were not observed, although such an "ipso" attack, with replacement of a group other than hydrogen on an aromatic ring carbon, is well-known.⁴ For example, nitration of the diphenylmethane 4 produces the ipso nitration product 5 in addition to 6 and 7⁵ (Scheme I). There has been little systematic investigation of the nitration of diphenylmethanes, however. The present study was undertaken to determine the yields

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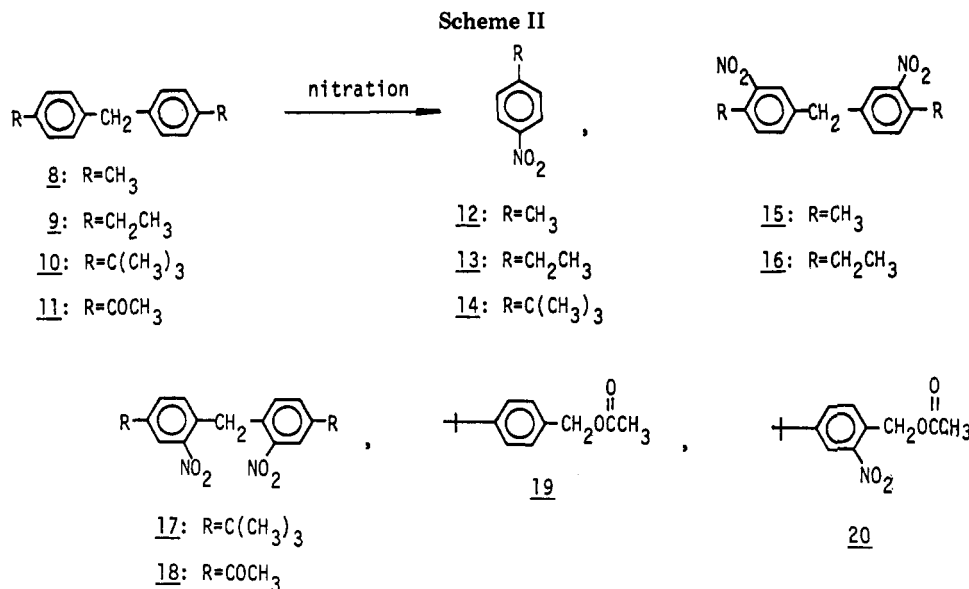


Table I. Nitration of 4,4'-Disubstituted Diphenylmethanes

run	substance	reagent	solvent	temp, °C	time, h	product (% yield)
1	8	HNO ₃ /H ₂ SO ₄	CH ₃ NO ₂	3	1	12 (18), 15 (43)
2	9	HNO ₃ /H ₂ SO ₄	CH ₃ NO ₂	3	2.5	13 (31), 16 (17)
3	10	HNO ₃ /H ₂ SO ₄	CH ₃ NO ₂	3	1	14 (60)
4	10	Cu(NO ₃) ₂	Ac ₂ O	60	1	14 (81), 17 (8), 20 (31)
5	10	HNO ₃	CH ₃ NO ₂	2	1	no reaction
6	10	HNO ₃ (fuming)	Ac ₂ O	5	1	14 (72), 17 (1)
7	10	HNO ₃ (fuming)	Ac ₂ O	-50	1	14 (47), 17 (3), 19 (38), 20 (13)
8	11	HNO ₃ /H ₂ SO ₄	H ₂ SO ₄	3	1	18 (90)

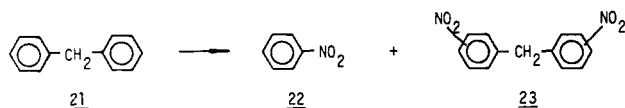
of normal and ipso nitration products from nitration of some diphenylmethanes.

Results and Discussion

Nitration of 4,4'-dimethyl- (8), 4,4'-diethyl- (9), 4,4'-di-*tert*-butyl- (10), and 4,4'-diacetyldiphenylmethane (11) was carried out under various conditions. The results are summarized in Table I and Scheme II.

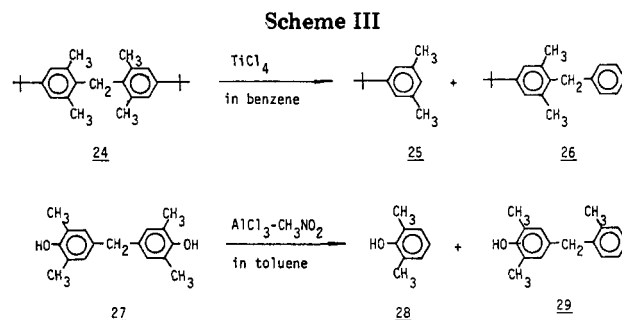
Nitration of 10, unlike that of its homologue 1, gave poor yields of the normal nitration product 17. 4-Nitro-*tert*-butylbenzene (14) was the major product under all conditions tested. When acetic anhydride was used as the solvent, the benzyl alcohol derivatives 19 and 20 were obtained in addition to 14 and 17. The formation of 20 may have resulted from nitration of the initial product 19.

Nitration of 8 and 9 also afforded the corresponding nitroalkylbenzenes: 4-nitrotoluene (12) and 4-nitroethylbenzene (13), respectively, together with the normal products 15 and 16. It was also found that nitration of diphenylmethane (21) gave a trace of nitrobenzene (22)



in addition to the mixture of dinitrodiphenylmethanes (23) that has been reported.⁶ The structures of products 15, 17, and 18 were confirmed by ¹H NMR data and elemental analyses.

It is noteworthy that nitrations of 8–10 produced only the para isomers 12–14, in contrast to the mixtures of ortho and para isomers formed by nitration of alkylbenzenes.⁷ Comparison of the yields of ipso nitration products from



21 and 8–10 indicates that the proportion of ipso nitration increases with increasing size of the *p*-alkyl substituents on these diphenylmethanes.

In contrast to the nitration of the electron-rich diphenylmethanes 8–10, nitration of electron-deficient 4,4'-diacetyldiphenylmethane (11) gave a 93% yield of the normal nitration product 18; no ipso product was isolated.

It is known that transalkylation of 4,4'-di-*tert*-butyl-2,2',6,6'-tetramethyldiphenylmethane (24) with TiCl₄ in benzene gives the benzyl derivative 26 rather than a compound derived by migration of a *tert*-butyl group⁸ (Scheme III). A similar result has been reported in the reaction of 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane (27) with toluene using AlCl₃-CH₃NO₂,⁹ a catalyst that is generally inactive for transbenzylation and isomerization of diphenylmethanes.^{10–13} These results suggest that ipso

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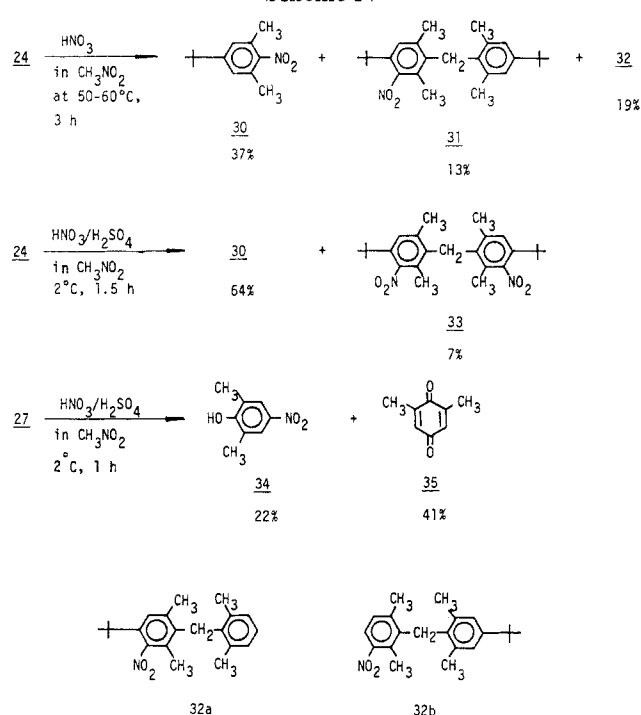
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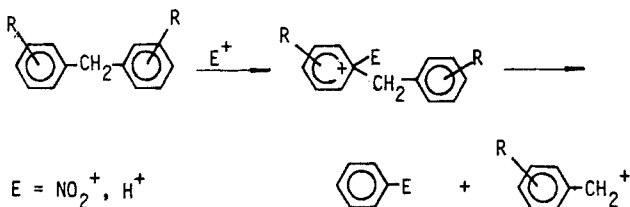
Scheme IV



protonation is occurring in such reactions; accordingly, we wished to determine whether the substituted diphenylmethanes **24** and **27** would undergo ipso nitration.

Nitration of **24** under mild conditions gave a 37% yield of the ipso nitration product **30**, as well as other nitration products **31** and **32a** or **32b** (Scheme IV). The yield of **30** increased to 64% under more drastic nitration conditions. In both cases, the yields of normal nitration products **31** and **33** were low. Although **32** appeared to be a single compound, the ^1H NMR data on it do not distinguish between structures **32a** and **32b**. Nitration of **27** in H_2SO_4 gave a 22% yield of the ipso nitration product **34** plus 41% of the oxidation product **35**.

These results show that electron-rich substituted diphenylmethanes undergo ipso attack in nitration reactions just as they do in protonation reactions.



Experimental Section

All melting and boiling points are uncorrected. Mass spectra were obtained on a JEOL Model JMS-01SG-2 spectrometer with a direct inlet (ionization energy 70 eV). IR spectra were measured on KBr pellets on a JASCO Model A-102 spectrophotometer. NMR spectra were determined at 100 MHz with a JEOL FX-100 spectrometer using Me_4Si as an internal reference.

Analytical Procedure. The analyses were carried out by gas chromatography using a Yanagimoto gas chromatograph: Model Yanaco G-180; 30% high-vacuum silicone grease; 75-cm column; rate of column temperature increase, 15 $^\circ\text{C}/\text{min}$; carrier gas, helium, 50 mL/min.

From the areas of individual peaks were calculated mole percent values for each product after the relative response data had been

determined by the internal method. Nitrobenzene was used as an internal standard.

Materials. The starting materials were prepared by reported methods. 4,4'-Dimethyldiphenylmethane (**8**): colorless prisms (EtOH); mp 28 $^\circ\text{C}$ (lit.¹⁴ mp 28.5 $^\circ\text{C}$). 4,4'-Diethyldiphenylmethane (**9**): pale yellow oil; bp 160–164 $^\circ\text{C}$ (6 mm) [lit.¹⁵ bp 142 $^\circ\text{C}$ (2 mm)]. 4,4'-Di-*tert*-butyldiphenylmethane (**10**): colorless needles (EtOH); mp 90–91 $^\circ\text{C}$ (lit.⁹ mp 90–91 $^\circ\text{C}$). 4,4'-Diacetyldiphenylmethane (**11**): pale yellow plates (EtOH); mp 94–96 $^\circ\text{C}$ (lit.¹⁶ mp 92.5–93 $^\circ\text{C}$).

Nitration of 8–10 with Mixed Nitric and Sulfuric Acids.

To a suspension of 1 g of a 4,4'-dialkyldiphenylmethane (**8**–**10**) in 30 mL of nitromethane was added dropwise at constant temperature (Table I) a mixture of 0.6 mL of concentrated nitric acid and 1.5 mL of concentrated sulfuric acid. After the reaction mixture was stirred for the specified time, it was poured into ice-water, and the organic layer was extracted with ether. The ether solution was washed with 5% sodium hydroxide solution and water, dried over sodium sulfate, and evaporated in vacuo. The residue was analyzed by gas chromatography, and the products were separated by liquid chromatography on silica gel by using a mixture of hexane and benzene as an eluent. The yields of products are shown in Table I.

4,4'-Dimethyl-3,3'-dinitrodiphenylmethane (15): colorless needles (EtOH); mp 173–175.5 $^\circ\text{C}$; NMR (CDCl_3) δ 2.56 (6 H, s), 4.04 (2 H, s), 7.25 (4 H, s), 7.55 (2 H, s). Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4$: C, 62.93; H, 4.93; N, 9.78. Found: C, 62.87; H, 4.94; N, 9.56.

4,4'-Diethyl-3,3'-dinitrodiphenylmethane (16): pale yellow needles (EtOH); mp 153–155 $^\circ\text{C}$ (lit.¹⁷ mp 148–150 $^\circ\text{C}$); NMR (CDCl_3) δ 1.26 (6 H, t, $J = 6$ Hz), 2.88 (4 H, q, $J = 6$ Hz), 4.05 (2 H, s), 7.32 (4 H, s), 7.70 (2 H, s). The amounts of known compounds **12**–**14** were determined by GC analysis as described above.

Nitration of 10 with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in Acetic Anhydride.

To a suspension of 0.5 g of **10** in 5 mL of acetic anhydride was slowly added at 5–10 $^\circ\text{C}$ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.3 g) with stirring. After the reaction mixture was stirred for 1 h, it was treated and worked up as described above to give **14**, **17**, and **20**. The yields of the products are shown in Table I.

The Nitration of 21. To a suspension of 1 g of diphenylmethane in 90 mL of nitromethane was added dropwise at 2 $^\circ\text{C}$ a mixture of 0.8 mL of fuming nitric acid and 2 mL of concentrated sulfuric acid. After the reaction mixture was stirred for 1 h, it was poured into ice-water, and the organic layer was extracted with ether. The ether solution was washed with 5% sodium hydroxide solution and water, dried over sodium sulfate, and evaporated in vacuo. The residue was analyzed by gas chromatography, and a trace amount of nitrobenzene was detected: the yield (ca 2%) of nitrobenzene was calculated by the gas chromatographic method using biphenyl as a standard substance.

4,4'-Di-*tert*-butyl-2,2'-dinitrodiphenylmethane (17): pale yellow needles (MeOH); mp 98–99 $^\circ\text{C}$; IR (KBr) 1520, 1340, 830 cm^{-1} ; NMR (CDCl_3) δ 1.34 (18 H, s), 4.59 (2 H, s), 7.08 (2 H, d, $J = 8.4$ Hz), 7.57 (2 H, dd, $J = 8.4$ Hz, $J = 2.4$ Hz), 8.05 (2 H, d, $J = 2.4$ Hz). Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_4$: C, 68.09; H, 7.07; N, 7.56. Found: C, 67.81; H, 7.22; N, 7.43.

4-*tert*-Butyl-2-nitrobenzyl acetate (20): yellow oil; IR (NaCl) 2960, 1750, 1525, 1220 cm^{-1} ; NMR (CDCl_3) δ 1.36 (9 H, s), 2.16 (3 H, s), 5.16 (2 H, s), 7.16 (1 H, d, $J = 8.4$ Hz), 7.75 (1 H, dd, $J = 8.4$ Hz), 8.15 (1 H, d, $J = 2$ Hz). Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.13; H, 6.84; N, 5.64.

Nitration of 10 with Fuming Nitric Acid. To a suspension of 1 g of **10** in 30 mL of acetic anhydride was slowly added 0.3 mL of fuming nitric acid at 5 or –50 $^\circ\text{C}$. After the reaction mixture was stirred for 1 h, it was treated and worked up as described above to give the products shown in Table I.

Nitration of 11. To 7.14 mL of concentrated sulfuric acid was slowly added 3 g of 4,4'-diacetyldiphenylmethane (**11**) at –50 $^\circ\text{C}$.

(14) T. Reichstein and R. Oppenaver, *Helv. Chim. Acta*, **16**, 1373 (1933).

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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 $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_6$: 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 $\text{C}_{25}\text{H}_{35}\text{NO}_2$: 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 $\text{C}_{25}\text{H}_{35}\text{NO}_2$: 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 $\text{C}_{21}\text{H}_{27}\text{NO}_2$: 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 $\text{C}_{25}\text{H}_{34}\text{N}_2\text{O}_4$: 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 Alcohol¹

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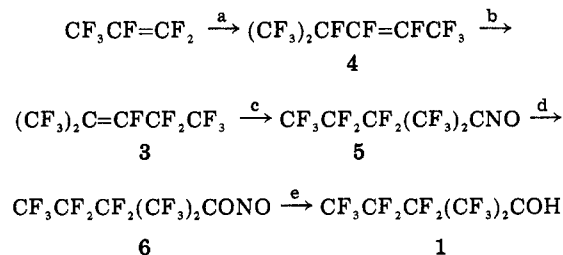
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We report here a synthesis of the title compound (1) which can be carried out in ordinary glassware from an

Scheme I^a



^a (a) KF, 18-crown-6, acetonitrile, 10-15 °C. (b) KF, 18-crown-6, dimethylacetamide, reflux. (c) KF, NOCl or N_2O_4 , dimethylacetamide, ca. 0 °C. (d) O_2 or N_2O_4 at room temperature. (e) H_2O .

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 $\text{CsF}\cdot\text{H}_2\text{O}$,⁴ by halogen exchange from $(\text{CF}_3)_2\text{CCl}_3\text{COH}$,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 reagents⁷ and by SbF_5 -catalyzed rearrangement 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 intermediate⁹ priced below \$10/lb in bulk.

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