leading to 4-substitution.

In order to obtain more mechanistic information we protonated 2,6-DMP, 4-benzyl-2,6-DMP, 2,6-DMA, and 4-benzyl-2,6-DMA in $FSO_3H + SbF_5$ (1:1)/SO_2ClF at low temperature. The ^{13}C NMR spectra clearly showed that whereas 2,6-DMP and 4-benzyl-2,6-DMP are C-protonated to form the corresponding benzenium ions, $\delta_{^{13}C\,(methylene)}$ 39.2 and 52, respectively, 2,6-DMA and 4-benzyl-2,6-DMA are O-protonated, $\Delta\delta_{^{13}C\,(OMe)}$ 13.5 and 12.35, respectively, and no arenium ion is formed. 2,6-DMA was previously shown by Brouwer et al.[9] to be O-protonated by ^1H NMR using $HF + BF_3$ at -100 °C.

Similarly, whereas low-temperature methylation of 2,6-DMA with $MeF/SbF_5/SO_2$ gave exclusively (^{13}C NMR) O-methylation, $\Delta\delta_{^{13}C\,(OMe)}$ 24.5, with 2,6-DMP the C-methylated species was observed as major species, $\delta_{^{13}C\,(methylene)}$ 58.2. The corresponding oxonium ion was also detected as a minor species, $\delta_{^{13}C\,(OMe)}$ 60.5.

For 2,6-DMA, the presence of a methyl group on oxygen is, therefore, sufficient to render the oxygen more accessible for protonation (methylation) than 2,6-DMP. Our control experiments suggest that competing O-benzylation, especially for 2,6-DMA for which a higher percentage of meta substitution is actually observed, is taking place, thus contributing to the overall percentage of meta substitution (see Scheme I).

Since the extent of intermolecular benzyl transfer was found to be only of minor significance in Miller's control experiments with 2,6-DMP, it has to be assumed that benzyl shift occurs preferentially through an intramolecular process involving a five-membered ring transition state.

Experimental Section

The aromatic substrates and benzyl chloride were commercially available samples of highest purity and used without further purification. Rigorously dried CCl_4 was used as solvent. Silver triflate was prepared from Ag_2CO_3 and triflic acid. Nitronium tetrafluoroborate was prepared and used as reported previously.[10]

Whereas 4-benzyl-2,6-DMP was synthesized according to the literature from 4-benzoyl-2,6-DMP by Clemenson reduction,[11] 4-benzyl-2,6-DMA was prepared by reduction of the 4-benzoyl-2,6-DMA using Et_3SiH/TFA reagent.[12]

GLC analyses were performed on a Varian Model 3700 gas chromatograph equipped with a 50-m capillary column (OV 101) and an online automatic integrator.

For 2,6-DMA and 2,6-DIP isomer distributions were also determined by NMR as previously described.[5]

^{13}C NMR spectra were recorded on a Varian FT-80 instrument equipped with a variable temperature probe.

General Procedure for Benzylation Reactions. To the aromatic compound (10 mmol) diluted in 15 mL of CCl_4 was added silver triflate (1.05 g, 4.08 mmol) and 2,4,6-TMP (1.02 g, 4.1 mmol) under dry nitrogen with good stirring at room temperature. Subsequently, benzyl chloride (0.515 g, 4.08 mmol) was dropwise added, whereupon AgCl was immediately precipitated. After continued stirring for 40 min at room temperature, the reaction mixture was filtered and was analyzed by GLC.

General Procedure for Nitration Reactions. To the aromatic compound (5 mmol) in 25 mL of solvent at 5-10 °C was added a slurry of 0.015 mol of $NO_2^+BF_4^-$ in 20 mL of the same solvent. After being vigorously stirred, the samples were quenched with water, separated, extracted with ether, washed with Na_2CO_3 solution, dried over $MgSO_4$, and analyzed by GLC.

Preparation of the Ions. For protonation studies, a cold slurry of the aromatic compound (50 mg) in SO_2ClF was added to Magic Acid (1 mL) in SO_2ClF (1 mL) at dry ice/acetone temperature with efficient vortex mixing.

For methylation reactions, methyl fluoride was slowly bubbled through a cold solution of SbF_5 in excess SO_2 until homogeneous. A proton-decoupled ^{13}C NMR spectrum of the resulting solution confirmed the formation of $MeSO_2^+SbF_6^-$ [$\delta_{^{13}C}$ 72.9 (s)], together with some uncomplexed MeF [$\delta_{^{13}C}$ 72.3 (d, J_{C-F} = 151 Hz)]. To this solution was added a cold solution of the aromatic compound (50-60 mg) in SO_2 with efficient vortex mixing.

Acknowledgment. I am indebted to Professor George A. Olah for his support and encouragement. I thank Professor Cerfontain for informing me of his sulfonation data prior to publication.

Registry No. $PhCH_2O_3CSF_3$, 17674-16-7; nitronium tetrafluoroborate, 13826-86-3; 2,6-DMA, 1004-66-6; 2,6-DMP, 576-26-1; 2,6-DIP, 2078-54-8; 3-benzyl-2,6-DMA, 69804-73-5; 4-benzyl-2,6-DMA, 61259-78-7; 3-benzyl-2,6-DMP, 31040-78-5; 4-benzyl-2,6-DMP, 41772-31-0; 3-benzyl-2,6-DIP, 97674-51-6; 4-benzyl-2,6-DIP, 61563-91-5; 3-nitro-2,6-DMA, 50536-74-8; 4-nitro-2,6-DMA, 14804-39-8; 3-nitro-2,6-DIP, 97674-52-7; 4-nitro-2,6-DIP, 1576-14-3; anisole, 100-66-3; *o*-benzylanisole, 883-90-9; *m*-benzylanisole, 23450-27-3; *p*-benzylanisole, 834-14-0.

(9) (a) Brouwer, D. M.; Mackor, E. L.; Maclean, C. *Rec. Trav. Chim. Pays-Bas* **1966**, *85*, 109. (b) For a review, see: Olah, G. A.; White, A. M.; O'Brien, D. H. *Chem. Rev.* **1970**, *70*, 561.
(10) Olah, G. A.; Kuhn, S.; Mlinko, A. *J. Chem. Soc.* **1956**, 4257.
(11) von Auwers, K.; Markovits, T. *Chem. Ber.* **1908**, *41*, 2332.
(12) West, C. T.; Donnelly, S. J.; Kooistra, D. A.; Doyle, M. P. *J. Org. Chem.* **1973**, *38*, 2675.

Synthesis of Novel Pyrazoles Containing Perfluoroalkyl Groups by Reactions of Perfluoro-2-methylpent-2-ene and Hydrazones

Isao Ikeda,* Yoshikazu Kogame, and Mitsuo Okahara

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka, Japan 565

Received March 8, 1985

In our studies of heterocyclic compounds from perfluoroolefins, we previously reported the synthesis of pyrazolium aminimine containing perfluoroalkyl groups from perfluoro-2-methylpent-2-ene (1) and 1,1-dimethylhydrazine.[1] In this note, we describe the synthesis of some novel pyrazoles containing perfluoroalkyl groups from 1 and hydrazones 2.

Perfluoro-2-methylpent-2-ene (1) reacted readily with hydrazone 2 (**a**; R = H; **b**; R = CH_3) in the presence of base such as sodium carbonate in THF at 0 °C to give the azines **3a,b** in 35% yield. Without base, this reaction proceeded to 3 in lower yield (Scheme I).

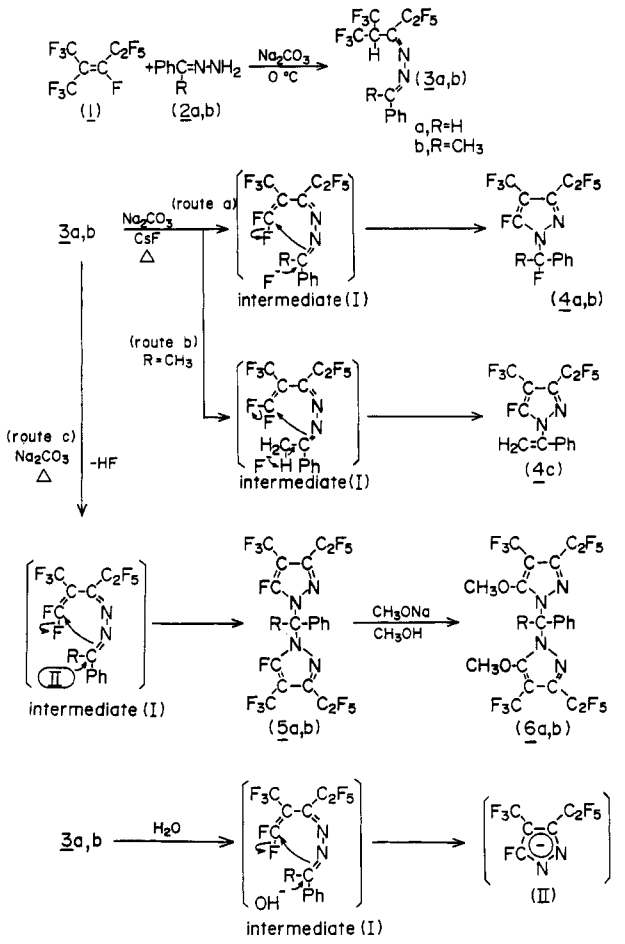
Spectral data of **3a,b** (Experimental Section) indicate the presence of both hexafluoroisopropyl and pentafluoroethyl groups. This reaction is assumed to proceed via nucleophilic attack of 2 on 1, followed by elimination of hydrogen fluoride and proton shift as suggested in the reaction of amine.[2]

Azine **3a** was readily and cleanly converted to pyrazole **4a** by heating with a mixture of sodium carbonate and cesium fluoride in dioxane at 100 °C. In the case of **3b** (R = CH_3), a mixture of **4b** and **4c** was obtained in 6:1 molar ratio (calculated from ^1H NMR). These cyclization to **4a,b** can be understood by fluoride attack on intermediate I followed by the steps shown in Scheme I (route a). From the fact that **4b** could not be dehydrofluorinated to **4c** in the corresponding reaction conditions, another cyclization mode leading to **4c** can be induced. The basicity

(1) Ikeda, I.; Tsukamoto, T.; Okahara, M. *Chem. Lett.* **1980**, 583.
(2) Maruta, M.; Kitazume, T.; Kubota, S.; Yoshimura, N.; Ishikawa, N. *Chem. Lett.* **1979**, 291.

0022-3263/85/1950-3640$01.50/0

Scheme I



of fluoride[3] may initiate this cyclization as shown in route b.

When azines **3a,b** were heated in the presence of sodium carbonate, without cesium fluoride, the reaction was slower and led to the bis(pyrazolyl)methanes **5a,b** (route c). The rate was much enhanced by addition of a small amount of water. The formation of benzaldehyde **2a** (R = H) or acetophenone **2b** (R = CH_3) in the reaction mixture was confirmed by GLC and IR. These results and mass spectral data support the structure of **5**. The ^1H and ^{19}F NMR spectra were complicated and did not clearly confirm **5**, but reaction of **5a,b** with sodium methoxide in methanol (Scheme I) gave the corresponding methoxy compounds, whose spectral data were fully consistent with these structures.

Concerning the mechanism for formation of **5a,b**, it is assumed that an anion II formed in the course of hydrolysis of **3a,b** plays a role as shown in Scheme I. Although the anion II may be generated from **4** by hydrolysis, this possibility seemes unlikely, since compounds **4** could not be hydrolyzed and were recovered quantitatively when treated in the corresponding reaction conditions in the presence of water. Without the addition of cesium fluoride, the function (as nucleophile or base toward **3a,b**) of the fluoride anion, which may be formed as the sodium salt from **3a,b**, is very weak, and this anion II can attack intermolecularly the intermediate I on its benzal carbon.

Experimental Section

^1H and ^{19}F NMR spectra were recorded with a Nihondenki JMN-PS-100 spectrometer, ^{19}F NMR spectra being obtained in the presence of benzotrifluoride as an internal or external standard and peak center positions being given in ppm upfield from trichlorofluoromethane. Mass spectra were determined with a Hitachi 260-10 spectrometer. GLC were carried out on a Shimadzu Model GC-4CPT instrument equipped with a thermal conductivity detector. The columns were Silicone OV-1 on a Uniport KS (60–80 mesh) (1 m × 3 mm) and Carbowax 20-M on a Celite 545 (60–80 mesh) (0.7 m × 3 mm). In distillation of **3–6**, a Kugelrohr apparatus was used.

Materials. Perfluoro-2-methylpent-2-ene (1) (donated from NEOS, Co., Kobe, Japan) was used after distillation (51 °C). Sodium carbonate (extra pure grade) was used after being ground to powder. Solvents were distilled before use. Hydrazones **2a,b** were prepared from the corresponding aldehyde or ketone and hydrazine hydrate in the presence of barium oxide.[4,5]

Preparation of 3a. Into a mixture of benzaldehyde hydrazone (**2a**) (0.29 g, 2.4 mmol), sodium carbonate (0.77 g, 7.2 mmol), and THF (10 mL) was added 1 (0.80 g, 2.7 mmol) in THF (10 mL) dropwise at 0 °C with stirring. After the addition of 1, stirring was continued for 1 h at room temperature. The solid material was filtered off. The filtrate was concentrated and distilled under reduced pressure [30 °C (0.02 torr)] to give a yellow liquid, **3a** (0.34 g, 35%): ^1H NMR ($CDCl_3$) δ 6.16 (1 H, sept, J_{HF} = 8.7 Hz), 7.32–7.62 (3 H, m), 7.78–7.96 (2 H, m), 8.16 (1 H, s); ^{19}F NMR ($CDCl_3$) 62.9 ppm (6 F, td, J_{FF} = 10.3 Hz, J_{HF} = 8.7 Hz), 81.7 (3 F, s), 112 .3 (2 F, sept, J_{FF} = 10.3 Hz); mass spectrum, *m/e* 400 (M^+), 381 (M^+ – F), 104 (Ph(H)C=N^+), 77 (Ph^+); IR 1630, 1560 cm^{-1}. Anal. Calcd for $C_{13}H_7N_2F_{11}$: C, 39.02; H, 1.76; N, 7.00. Found: C, 38.81; H, 1.88; N, 7.27.

Preparation of 3b. **3b** was prepared from acetophenone hydrazone (**2b**) (0.32 g, 2.4 mmol) and 1 (0.88 g, 7.2 mmol) by the same procedure as that for **3a**, yielding **3b** as a yellow liquid (0.3 g, 35%) [50 °C (0.08 torr)]: ^1H NMR ($CDCl_3$) δ 2.37 (3 H, m), 5.71 (1 H, br), 7.32–7.59 (3 H, m), 7.78–7.96 (2 H, m); ^{19}F NMR ($CDCl_3$) 63.0 ppm (6 F, td, J_{FF} = 9.8 Hz, J_{HF} = 8.6 Hz), 81.7 (3 F, s), 112.3 (2 F, sept, J_{FF} = 9.8 Hz); mass spectrum, *m/e* 414 (M^+), 395 (M^+ –F), 119 (Ph(CH_3)C=N^+), 104 (PhC≡N^+H), 77 (Ph^+). IR 1630, 1560 cm^{-1}. Anal. Calcd for $C_{14}H_9N_2F_{11}$: C, 40.60; H, 2.19; N, 6.76. Found: C, 40.60; H, 2.31; N, 6.86.

Preparation of 4a. **3a** (0.50 g, 1.3 mmol), sodium carbonate (0.66 g, 6.2 mmol), cesium fluoride (0.40 g, 2.6 mmol), and 1,4-dioxane (5 mL) were placed in a 50-mL flask and heated at 100 °C for 10 min with stirring. At this time, **3a** had been consumed and was not detected by GLC. The salts were filtered off, and the solvent was removed. The concentrate was distilled under reduced pressure [45 °C (0.2 torr)] to give a colorless liquid, **4a** (0.43 g, 91%): ^1H NMR ($CDCl_3$) δ 7.22 (1 H, d, J_{HF} = 45.5 Hz), 7.49 (5 H, s); ^{19}F NMR ($CDCl_3$) 57.3 ppm (3 F, dtq, J_{FF} = 13.3, 9.2, 2.4 Hz), 84.0 (3 F, q, J_{FF} = 2.4 Hz), 112.8 (2 F, q, J_{FF} = 9.2 Hz), 121.4 (1 F, q, J_{FF} = 13.3 Hz), 145.7 (1 F, d, J_{HF} = 45.5 Hz); mass spectrum, *m/e* 380 (M^+), 109 (Ph(H)C^+F), 77 (Ph^+); IR 1620, 1520 cm^{-1}. Anal. Calcd for $C_{13}H_6N_2F_{10}$: C, 41.07; H, 1.59; N, 7.37. Found: C, 40.98; H, 1.46; N, 7.64.

Preparation of 4b,c. The technique used in this preparation was the same as that for **4a**. **3b** (0.50 g, 1.2 mmol), sodium carbonate (0.63 g, 6.0 mmol), and cesium fluoride (0.40 g, 2.6 mmol) gave a colorless liquid [a mixture of **4b** and **4c**, 55 °C (0.15 torr)] (0.43 g, 90%). GLC analysis showed the mixture of two components, which were separated from each other by preparative GLC. Furthermore, each fraction was quantitatively analyzed by ^1H NMR. **4b**: ^1H NMR ($CDCl_3$) δ 2.25 (3 H, d, J_{HF} = 20.1 Hz), 7.28–7.50 (5 H, m); ^{19}F NMR ($CDCl_3$) 57.3 ppm(3 F, dtq, J_{FF} = 14.1, 9.2, 2.3 Hz), 83.9 (3 F, qt , J_{FF} = 2.3, 2.1 Hz), 112.4 (2 F, qq, J_{FF} = 9.2, 2.1 Hz), 116.6 (1 F, qd, J_{FF} = 14.1, 7.1 Hz), 119.1 (1 F, qd, J_{HF} = 20.1 Hz, J_{FF} = 7.1 Hz); mass spectrum, *m/e* 394 (M^+), 123 (PhC$^+$FCH_3), 103 (PhC$^+$=CH_2), 77 (Ph^+); IR 1620, 1520 cm^{-1}. Anal. Calcd for $C_{14}H_8N_2F_{10}$: C, 42.66; H, 2.05; N, 7.11. Found: C, 42.65; H, 2.22; N, 7.22. **4c**: ^1H NMR ($CDCl_3$) δ 5.65 (1 H, s), 5.85 (1 H, s), 7.26–7.48 (5 H, m); ^{19}F NMR ($CDCl_3$) 57.0 ppm (3 F, dtq, J_{FF} = 13.5, 9.4, 2.4 Hz), 84.0 (3 F, qq, J_{FF} = 2.4, 2.1 Hz), 112.8 (2 F, qq, J_{FF} = 9.4, 2.1 Hz), 119.9 (1 F, q, J_{FF} = 13.5 Hz); mass spectrum, *m/e* 374 (M^+), 355 (M^+ – F), 103 (PhC$^+$=CH_2), 77 (Ph^+); IR 1640, 1610, 1520 cm^{-1}. Anal. Calcd

(3) Clark, J. H. *Chem. Rev.* **1980**, *80*, 429.

(4) Curtius, T.; Pflug, L. *J. Prakt. Chem.* **1891**, *44*, 537.
(5) Curtius, T.; Frazen, H. *Chem. Ber.* **1902**, *35*, 3234.

for $C_{14}H_7N_2F_9$: C, 44.94; H, 1.89; N, 7.49. Found: C, 45.66; H, 1.70; N, 7.68.

Preparation of 5a. **3a** (0.65 g, 1.6 mmol), sodium carbonate (0.50 g, 4.7 mmol), and 1,4-dioxane (5 mL) were placed in a 50-mL flask and heated at 100 °C with stirring until **3a** could not be detected by GLC (it required one day). The salts were filtered off, and the solvent was removed. The concentrate was distilled under reduced pressure to give white granules, which were purified by silica gel chromatography (hexane) and recrystallization from hexane (0.22 g, 43%): mp 74.6–77.7 °C; ^{1}H NMR ($CDCl_3$) δ 7.28–7.67 (5 + 1 H, m); ^{19}F NMR ($CDCl_3$) 57.4 ppm (6 F, dtq, J_{FF} = 13.3, 9.6, 2.4 Hz), 84.0 (6 F, q, J_{FF} = 2.4 Hz), 112.6 (4 F, qd, J_{FF} = 9.6 Hz, J_{HF} = 7.5 Hz), 120.2 (2 F, q, J_{FF} = 13.3 Hz); mass spectrum, m/e 632 (M^+), 361 ($C_{13}H_6N_2F_9^+$); IR 1620, 1510 cm^{-1}. Anal. Calcd for $C_{19}H_6N_4F_{18}$: C, 36.09; H, 0.96; N, 8.86. Found: C, 36.06; H, 0.77; N, 8.97.

Preparation of 5b. The technique used in this preparation and purification was the same as that for **5a**. Treatment of **3b** (1.00 g, 2.4 mmol) with sodium carbonate (1.28 g, 12.1 mmol) gave white granules (0.17 g, 22%): mp 63.6–66.6 °C; ^{1}H NMR ($CDCl_3$) δ 6.87–7.00 (2 H, m), 7.44–7.60 (3 H, m); ^{19}F NMR ($CDCl_3$) 57.5 ppm (6 F, dt, J_{FF} = 14.1, 9.2 Hz), 84.0 (6 F, s), 112.2 (4 F, q, J_{FF} = 9.2 Hz), 113.4 (2 F, q, J_{FF} = 14.1 Hz); mass spectrum, m/e 646 (M^+), 631 ($M^+ - CH_3$), 375 ($C_{14}H_8N_2F_9^+$); IR 1620, 1510 cm^{-1}. Anal. Calcd for $C_{20}H_8N_4F_{18}$: C, 37.17; H, 1.25; N, 8.67. Found: C, 37.15; H, 1.02; N, 8.81.

Preparation of 6a. Methanol (3 mL) was placed in a 30-mL flask, and sodium metal (11 mg, 0.48 mmol) was dissolved in it with stirring. A solution of **5a** (100 mg, 0.16 mmol) in methanol (2 mL) was added dropwise at room temperature until **5a** was consumed and not detected by GLC (about 3 h). The solution was neutralized with 10% aqueous HCl. The product was extracted with benzene and purified by silica gel chromatography (hexane) and recrystallized from hexane to give white granules (82 mg, 79%): mp 68.2–73.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.91 (6 H, s), 7.25–7.54 (5 H, m), 7.70 (1 H, s); ^{19}F NMR ($CDCl_3$) 55.5 ppm (6 F, t, J_{FF} = 10.8 Hz), 83.9 (6 F, s), 112.0 (4 F, q, J_{FF} = 10.8 Hz); mass spectrum, m/e 656 (M^+), 373 ($C_{14}H_9N_2OF_8^+$); IR 1590, 1520 cm^{-1}. Anal. Calcd for $C_{21}H_{12}N_4O_2F_{16}$: C, 38.43; H, 1.84; N, 8.54. Found: C, 38.48; H, 1.53; N, 8.66.

Preparation of 6b. Treatment of **5b** (100 mg, 0.15 mmol) with sodium methoxide (sodium metal 11 mg, 0.48 mmol) by the same procedure as that for **6a** gave white granules (86 mg, 83%): mp 102.4–104.3 °C; ^{1}H NMR ($CDCl_3$) δ 2.63 (3 H, s), 3.55 (6 H, s), 6.88–7.08 (2 H, m), 7.35–7.52 (3 H, m); ^{19}F NMR ($CDCl_3$) 55.6 ppm (6 F, t, J_{FF} = 10.9 Hz), 83.8 (6 F, s), 111.6 (4 F, q, J_{FF} = 10.9 Hz); mass spectrum, m/e 670 (M^+), 655 ($M^+ - CH_3$), 387 ($C_{15}H_{11}N_2OF_8^+$); IR 1590, 1570, 1520 cm^{-1}. Anal. Calcd for $C_{22}H_{14}N_4O_2F_{16}$: C, 39.42; H, 2.11; N, 8.36. Found: C, 39.53; H, 1.84; N, 8.33.

Registry No. 1, 1584-03-8; **2a**, 5281-18-5; **2b**, 13466-30-3; **3a**, 97674-42-5; **3b**, 97674-43-6; **4a**, 97674-44-7; **4b**, 97674-45-8; **4c**, 97674-46-9; **5a**, 97674-47-0; **5b**, 97674-48-1; **6a**, 97674-49-2; **6b**, 97674-50-5.

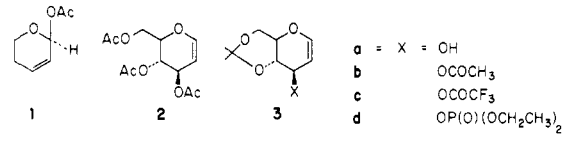
Pd(0)-Catalyzed C-Glycosylation: A Facile Alkylation of Trifluoroacetylglucal[1]

T. V. RajanBabu

Central Research & Development Department, E328/208, Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Delaware 19898

Received December 27, 1984

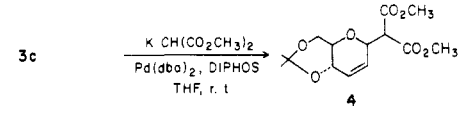
C-Glycosides are an important class of compounds receiving increasing attention from synthetic organic chemists recently.[2] The high stereochemical control accompanying transition-metal-mediated transformations[3] has prompted several groups[4-6] to employ such methods for C-glycosylations. Coupling of organomercury compounds with carbohydrate-derived enol ethers in the presence of stoichiometric amount of $Pd(OAc)_2$ has been reported.[4] Also a few β-dicarbonyl compounds in the presence of $Pd(CH_3CN)_2Cl_2$ and $BF_3{\cdot}Et_2O$ are known to add to various acylated glycals.[5] However, various other carbanions derived from, for example, dimethyl malonate and cyclohexane-1,3-dione fail to undergo this reaction. A Pd(0)-catalyzed reaction of acetoxydihydropyran **1** with tertiary carbanions like diethyl sodioformamidomalonate has been reported to proceed under more drastic (70 °C, 18 h, DMF) conditions.[6]



1 2 3

Conspicuously absent in these studies is the Pd(0)-catalyzed addition of the more useful malonate type carbon nucleophiles to glycals like **2** or **3**. The apparent lack of reactivity of electron-rich allylic acetates having oxygen conjugation has been observed before, and it is not surprising that further activation with Lewis acids[5] (for example $BF_3{\cdot}Et_2O$), and/or higher temperatures[6,7] are needed for the alkylation of these substrates. *Here we report a general solution to the problem by appropriately choosing the leaving group and the catalyst.* This is illustrated in a new C-glycosylation reaction via Pd(0)-catalyzed addition of stabilized carbon nucleophiles to a trifluoroacetylglucal.

We find that 4,6-isopropylidene-3-(trifluoroacetyl)-D-glucal **3c** reacts with potassium dimethyl malonate in the presence of 2–5 mol % bis(dibenzylideneacetone)–Pd(0) and bis(diphenylphosphino)ethane[8] to give **4** in 56% yield.



4

Reaction of the corresponding acetate **3b** or the phosphate[9] **3d** failed to yield any addition products even under conditions recommended[7] for relatively unreactive substrates. Triacetylglucal **2** was similarly recovered unchanged after heating for 7 h in toluene at 100 °C in the presence of $(Ph_3P)_4Pd$, DBU, and dimethyl malonate.

In the formation of **4** the reaction proceeds with remarkable stereospecificity as expected by the double inversion mechanism usually associated with these types of reactions.[3] The high-field (360 MHz) ^{1}H NMR spectra of the adducts are completely consistent with the assigned

(1) Contribution 3668 from Central Research & Development Department.

(2) See, for example: Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976. Reed, L. A.; Ito, Y.; Masamune, S.; Sharpless, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 6468 and references cited therein. Giese, B.; Dupuis, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 622.

(3) For examples in the Pd-catalyzed reactions, see: Tsuji, J. "Organic Synthesis with Pd Compounds"; Springer-Verlag: West Berlin, 1980. Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. Heck, R. *Acc. Chem. Res.* **1979**, *12*, 146.

(4) (a) Hacksell, U.; Daves, G. D., Jr. *J. Org. Chem.* **1983**, *48*, 2870 and references cited therein. (b) Czernecki, S.; Gruy, F. *Tetrahedron Lett.* **1981**, *22*, 437. (c) See also ref 6 for a related reaction.

(5) Yougai, S.; Miwa, T. *J. Chem. Soc., Chem. Commun.* **1983**, 68.

(6) Dunkerton, L. V.; Serino, A. J. *J. Org. Chem.* **1982**, *47*, 2812.

(7) Trost, B. M.; Gowland, F. W. *J. Org. Chem.* **1979**, *44*, 3448 and ref 3.

(8) Fiaud, J. C.; Malleron, J. L. Tetrahedron Lett. **1980**, *21*, 4437.

(9) Tanigawa, Y.; Nishimura, K.; Kawasaki, A.; Murahashi, S. I. *Tetrahedron Lett.* **1982**, *23*, 5549.

0022-3263/85/1950-3642$01.50/0