1189, 1107, 1066, 966, 942, 869, 777 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.44–1.57 (m, 6 H), 1.67 (dd, J = 6.6, 1.6 Hz, 3 H), 1.91 (t, J = 5.8 Hz, 2 H), 2.17 (t, J = 5.8 Hz, 2 H), 2.84 (s, 6 H), 4.80 (dq, J = 13.8, 6.8 Hz, 1 H), 5.58 (s, 1 H), 6.57 (dq, J = 13.8, 1.6 Hz, 1 H); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 15.0 (CH_3), 26.3, 26.4, 27.6, 28.1, 32.9 (CH_2), 38.3 ($N(CH_3)_2$), 103.9, 118.6, 130.5, 138.0 (C═C), 160.1 (C═O); CI-MS (*m*/*e*) 223 (M^+ + 1), 150; HRMS calcd for $C_{13}H_{22}N_2O$ 222.173 10, found 222.174 22.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 03233210 from the Ministery of Education, Science, and Culture, Japan.

Supplementary Material Available: Preparative methods, IR, MS, ^{1}H NMR, ^{13}C NMR, and HRMS spectral data, and actual ^{1}H NMR spectra of **1e**–**1h**, **2g**–**2k**, **4e**–**k** **5a**–**5c**, **6a**–**6c** (36 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Trityl Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate: A New Hydride Abstraction Reagent

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Received May 4, 1992

Introduction

Trityl tetraphenylborate, $Ph_3C^+BPh_4^-$, was recently shown to be a useful hydride or methyl anion abstraction reagent for organic and organometallic compounds.[1] Although the tetraphenylborate anion is less reactive toward some electrophilic cationic compounds than other widely used trityl cation counterions (i.e. ClO_4^-, BF_4^-, PF_6^-),[2] it still suffers from facile degradation and a tendency to π-coordinate through one of its phenyl groups.[3]

It is well-known that fluoro-substituted tetraarylborate derivatives have increased stability in acidic media relative to BPh_4^-.[4] This is possibly attributed to lower electron density in the vicinity of the boron–carbon bonds which reduces the susceptibility toward electrophilic attack. Indeed, the tetraarylborate derivatives $[B(C_6F_5)_4]^-$ and $[B(4\text{-}FC_6H_4)_4]^-$ have been used to stabilize highly reactive base-free cationic group 4 metallocene complexes.[5] $B[3,5\text{-}(CF_3)C_6H_3]_4^-$ was also found to be a highly stable counterion in combination with electrophilic cobalt complexes.[6] We have long had an interest in using hydride abstractions to generate highly electrophilic, cationic compounds through use of trityl salts which contain potentially less reactive anions than the derivatives so far reported. Here we report the synthesis of trityl tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (trityl TFPB)[7] and its utility in hydride and methyl anion abstractions on organic or organometallic compounds.

Experimental Section

Materials and General Procedures. Trityl triflate,[1] Cp_2ZrMe_2,[8] and $CpFe(CO)_2Pr$[9] were synthesized according to literature procedures. Ph_3CCl was synthesized from Ph_3COH and acetyl chloride.[10] Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone ketyl just prior to use. CH_2Cl_2 was distilled from P_2O_5 immediately before use. Hexane was stirred over H_2SO_4 and distilled. Benzene was shaken with H_2SO_4, dried by azeotropic removal of water, and distilled into a storage bottle with 4A molecular sieves. All experiments were performed under a dry-nitrogen atmosphere, and air-sensitive compounds were transferred in an argon-filled glovebox. The ^{1}H (270.17 or 399.78 MHz) and ^{13}C (67.94 or 100.53 MHz) NMR spectra were obtained on a JEOL GSX270 or a JEOL GSX400 spectrometer. ^{11}B (128.3 MHz) and ^{19}F (376.1 MHz) NMR spectra were obtained on a JEOL GSX400 spectrometer with chemical shifts reported relative to $BF_3{\cdot}OEt_2$ in $CDCl_3$ (0 ppm) and $CFCl_3$ in $CDCl_3$ (0 ppm), respectively. Elemental analyses were performed by Desert Analytics in Tucson, AZ. Mass spectra were obtained on a Hewlett-Packard 5988A mass spectrometer at 70 eV. Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Sodium Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (Sodium TFPB). Sodium TFPB was synthesized using a similar procedure to one previously described.[11] Mg turnings (0.92 g, 38 mmol) and 10 mL of ether were placed in a 250-mL 3-necked flask fitted with a condenser/N_2 inlet and 50-mL addition funnel. 3,5-Bis(trifluoromethyl)-1-bromobenzene (6.2 mL, 36 mmol) and 40 mL of ether were placed in the addition funnel and added dropwise to the flask over a period of 1 h so as to maintain a moderate reflux. The mixture was stirred for 4 h, giving a dark brown solution. $NaBF_4$ (0.93 g, 8.5 mmol), dried at 110 °C for 1 h under vacuum, was quickly added and the mixture stirred for another 12 h, producing a light tan suspension. This was slowly poured into 50 mL of water and saturated with NaCl, and the brown ether layer separated. After extraction of the water layer with an additional 50-mL portion of ether, the two portions were combined and the ether was removed by vacuum giving a thick, dark brown oil. The oil was shaken with 20 mL of benzene followed by decanting off the benzene and drying leaving a light brown solid. The solid was rinsed with 5 mL of CH_2Cl_2 and dried at 110 °C for 6 h, yielding 4.6 g of sodium TFPB. An additional 0.16 g was isolated from the CH_2Cl_2 rinse and dried giving a total yield of 4.76 g (60% yield) of sodium TFPB: ^{1}H NMR (400 MHz, CD_3CN) δ 7.69 (s, 4 H, H_p), 7.72 (s, 8 H, H_o); ^{13}C NMR (100.5 MHz, CD_3CN) δ 118.7 (C_p), 125.5 (q, J_{CF} = 273 Hz, CF_3), 129.9 (m, C_m), 135.7 (C_o), 162.6 (q, J_{BC} = 50.3 Hz, C_{ipso}); ^{11}B NMR (CD_3CN) δ −6.06; ^{19}F NMR (CD_3CN) δ −62.68.

Triphenylmethylium Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (Trityl TFPB). In a dry box, a 50-mL Schlenk tube equipped with a filter frit and a 50-mL round-bottomed flask was charged with trityl triflate (235 mg, 0.60 mmol) and sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (530 mg, 0.60 mmol). After the apparatus was removed from the dry box, 15

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mL of CH_2Cl_2 was quickly added by syringe through the neck of the Schlenk tube, and the contents were stirred for 6 h. The mixture was then transferred to the filter frit, and the round-bottomed flask was cooled at −78 °C to speed the filtering process. The volume of CH_2Cl_2 was reduced to 3 mL by vacuum, and 10 mL of hexane was added while swirling the solution to cause precipitation of a yellow solid. The liquid was decanted off, and the remaining solid was dried by vacuum giving 610 mg (92% yield) of trityl TFPB. Recrystallization once from CH_2Cl_2/hexane gave analytically pure sample: mp 191–193 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.6 Hz, 6 H, trityl C_o), 7.77 (t, J = 7.5 Hz, 6 H, trityl C_m), 8.14 (t, J = 7.5 Hz, 3 H, trityl C_p), 7.49 (s, 4 H, borate H_p), 7.70 (s, 8 H, borate H_o); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 130.5, 139.6, 142.1, 143.5 (trityl Ph), 210.6 (Ph_3C^+), 117.3 (borate C_p), 124.3 (q, J_{CF} = 273 Hz, CF_3), 128.7 (m borate C_m), 134.6 (borate C_o), 161.4 (q, J_{BC} = 50.4 Hz, borate C_{ipso}); ^{11}B NMR ($CDCl_3$) δ −6.84; ^{19}F NMR ($CDCl_3$) δ −62.5. Anal. Calcd for $C_{51}H_{27}BF_{24}$: C, 55.36; H, 2.46. Found: C, 55.51; H, 2.31.

Reaction of Trityl TFBP with Cycloheptatriene. Trityl TFPB (100 mg, 0.090 mmol) was dissolved in 1 mL of CH_2Cl_2 in a 5-mL flask fitted with a rubber septum. A syringe needle attached to a N_2 gas source was inserted through the septum. Cycloheptatriene (8.4 mg, 0.090 mmol) was added dropwise via syringe while stirring followed by addition of 3 mL of hexane to cause formation of a light yellow precipitate. The solution was syringed off and the remaining solid vacuum dried giving 75 mg of tropylium TFPB (86% yield): mp >190 °C dec; ^1H NMR (270 MHz, CD_3CN) δ 7.67 (s, 4 H, borate H_p), 7.71 (s, 8 H, borate H_o), 9.21 (s, 7 H, $C_7H_7^+$); ^{13}C NMR (67.94 MHz, CD_3CN) δ 156.3 ($C_7H_7^+$), all borate resonances were identical to those of the sodium salt; ^{19}F NMR (CD_3CN) δ −62.85. Anal. Calcd for $C_{39}H_{19}BF_{24}$: C, 49.08; H, 2.01. Found: C, 49.19; H, 1.87.

Reaction of Trityl TFPB with Cp_2ZrMe_2 in CD_3CN. Trityl TFPB (50 mg, 0.045 mmol), Cp_2ZrMe_2 (11 mg, 0.045 mmol), and 0.6 mL of CD_3CN were shaken together in a 5-mm NMR tube, resulting in a clear, light yellow solution within a few seconds. Based on comparison of ^1H NMR data with the literature values for the compound $Cp_2Zr(Me)(NCCD_3)^+BPh_4^-$ (lit.[2c] δ 0.079 (s, 3 H, $ZrCH_3$), 6.07 (s, 10 H, Cp)), the compound was deduced to be $Cp_2Zr(Me)(NCCD_3)^+B[3,5-(CF_3)_2C_6H_3]_4^-$: ^1H NMR (270 MHz, CD_3CN) δ 0.075 (s, 3 H, $ZrCH_3$), 2.16 (s, 3 H, Ph_3CMe), 6.07 (s, 10 H, Cp), 7.1–7.3 (m, 15 H, Ph_3CMe), 7.67 (s, 4 H, borate H_p), 7.71 (s, 8 H, borate H_o).

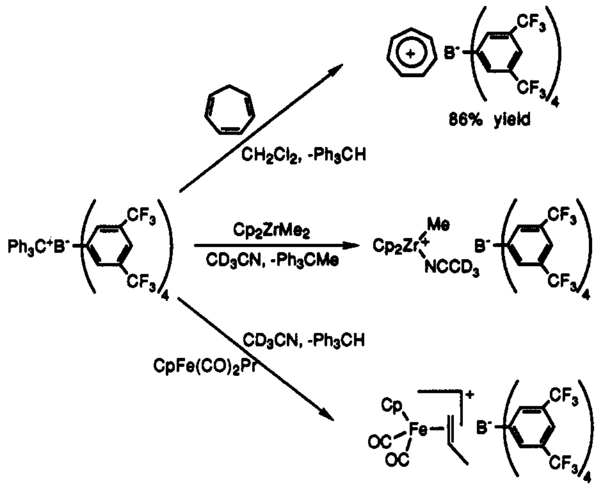
Reaction of Trityl TFPB with Cp_2ZrMe_2 in $CDCl_3$. When the same reaction as described above was performed in $CDCl_3$, a dark brown solution resulted. The ^1H NMR spectrum showed the formation of Ph_3CMe. However, there were several resonances in the $ZrCH_3$ region between 0.09 and 0.18 ppm, in the Cp region between 6.36 and 6.60 ppm, and extra peaks in the aryl region between 7.4 and 8.1 ppm, indicating decomposition of the zirconium species to several products.

Reaction of Trityl TFPB with $CpFe(CO)_2Pr$. Trityl TFPB (75 mg, 0.068 mmol) and 0.5 mL of CD_3CN were mixed in a NMR tube, and $CpFe(CO)_2Pr$ (15 mg, 0.068 mmol) was added by syringe. The contents were shaken for a few minutes, producing a light yellow solution. Comparison of its ^1H NMR data with the previously reported values[12] for $CpFe(CO)_2(\eta^2\text{-}H_2CCHCH_3)^+ClO_4^-$ indicated nearly quantitative formation of $CpFe(CO)_2(\eta^2\text{-}H_2CCHCH_3)^+TFPB^-$: ^1H NMR (270 MHz, CD_3CN) δ 1.76 (d, J = 6.6 Hz, 3 H, $\eta^2\text{-}H_2CCHCH_3$), 3.39 (d, J = 14.6 Hz, 1 H, $\eta^2\text{-}H_2CCHCH_3$), 3.75 (d, J = 8.1 Hz, 1 H, $\eta^2\text{-}H_2CCHCH_3$), 5.01 (m, 1 H, $\eta^2\text{-}H_2CCHCH_3$), 5.48 (s, 5 H, Cp), 5.59 (s, 1 H, Ph_3CH), 7.1–7.35 (m, 15 H, Ph_3CH), 7.67 (s, 4 H, borate H_p), 7.71 (s, 8 H, borate H_o).

Results and Discussion

Trityl tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (trityl TFPB) can be easily synthesized via a method similar to that described by Tilley[1] by combining trityl triflate and sodium TFPB in CH_2Cl_2 at room temperature. The sodium triflate byproduct is removed by filtration, giving high yields (>90%) of air-sensitive, bright yellow microcrystalline $Ph_3C^+TFPB^-$ (mp 191–193 °C) which can be stored for weeks under an inert atmosphere with no apparent decomposition. There are a number of favorable properties of trityl TFPB over the previously synthesized trityl tetraphenylborate.[1] Where $Ph_3C^+BPh_4^-$ is unstable in solution (i.e. acetonitrile or dichloromethane) and light-sensitive, trityl TFPB is not significantly light sensitive, and solutions of it in acetonitrile or CH_2Cl_2 are stable for several days without noticeable decomposition under an inert atmosphere at room temperature. In a similar fashion to $Ph_3C^+BPh_4^-$, trityl TFPB is unstable in THF or diethyl ether, producing dark brown or green solutions within a few minutes. The ^1H NMR resonances for the trityl cation in $Ph_3C^+BPh_4^-$ are obscured due to a small concentration of trityl radicals. Trityl TFPB differs in that all of the ^1H and ^{13}C NMR resonances for trityl TFPB are easily interpretable, indicating that trityl radicals are nonexistent or present in very small concentrations. Also, the impurity of trityl dimer present in samples of $Ph_3C^+BPh_4^-$ is not seen in the synthesis of trityl TFPB.

Scheme I



Examples of the utility of the $Ph_3C^+TFPB^-$ reagent in hydride or methyl anion abstractions are summarized in Scheme I. Hydride abstraction from cycloheptatriene with trityl TFPB in CH_2Cl_2 produces Ph_3CH and tropylium TFPB (>95% yield as determined by ^1H NMR) in an analogous way to $Ph_3C^+ClO_4^-$.[13] Tropylium TFPB was easily isolated by filtration as an air-sensitive, light yellow solid in 86% yield. Treatment of $CpFe(CO)_2CH_2CH_2CH_3$ (Cp = η^5-cyclopentadienyl) with trityl TFPB in acetonitrile-d_3 gave Ph_3CH and the ethylenic cation, $CpFe(CO)_2(\eta^2\text{-}H_2CCHCH_3)^+TFPB^-$, in nearly quantitative yield in solution as determined by ^1H NMR spectroscopy. The NMR spectrum of the cation is identical to that obtained from hydride abstraction using trityl perchlorate.[12] Methyl anion abstraction of Cp_2ZrMe_2 with trityl TFPB in acetonitrile-d_3 produced Ph_3CMe and the acetonitrile-coordinated cationic zirconium species, $Cp_2Zr(Me)(NCCD_3)^+$-$TFPB^-$. The presence of this compound in solution was determined through comparison of the ^1H NMR resonances for the zirconium cation with the previously reported values for $Cp_2Zr(Me)(NCCD_3)^+BPh_4^-$.[1,2c] However, reaction of Cp_2ZrMe_2 and trityl TFPB in the noncoordinating solvent chloroform-d gave several decomposition products as shown by the appearance of several methyl and

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η^5-cyclopentadienyl ^{1}H NMR resonances.

Acknowledgment. Financial support from the Air Force Office of Scientific Research through grant no. 91-0197 and Dow Corning Corp. is gratefully acknowledged.

Reductive Aromatization of Quinols. New Convenient Methods for the Regiospecific Synthesis of *p*-Hydroxy *C*-Aryl Glycals

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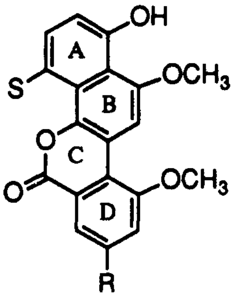
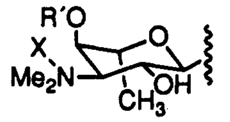
Received May 12, 1992

Among the naturally occurring *C*-aryl glycosides, the gilvocarcin antitumor antibiotics 1[2] are unique in that the carbohydrate substituent is positioned para to a phenolic hydroxyl group. Implicit in previous approaches to the establishment of this connection is the feasibility of liberating the phenolic hydroxyl group from a *p*-alkoxy *C*-aryl glycoside.[3-7] For simple alkyl phenyl ethers, this dealkylation has not been demonstrated, and successful prepartions of *p*-hydroxy *C*-aryl glycosides have required the use of protecting groups which are more easily removed.[3,6]



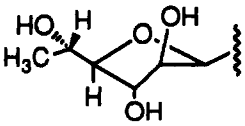
1, The Gilvocarcin *C*-Aryl Glycosides

Ravidomycins R=CH=CH$_2$ S=



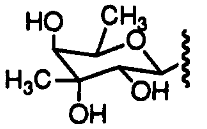
a Ravidomycin R′=Ac, X=electron pair
b Deacetylravidomycin R′=H, X=electron pair
c Deacetylravidomycin N-oxide R′=H, X=O

Gilvocarcins S=



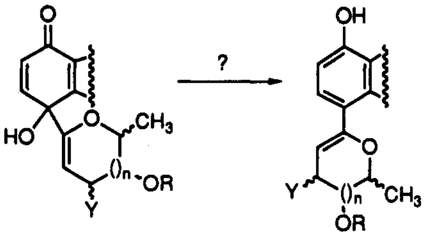
d M R=CH$_3$
e V R=CH=CH$_2$
f E R=CH$_2$CH$_3$

Chrysomycins S=



g A R=CH=CH$_2$
h B R=CH$_3$

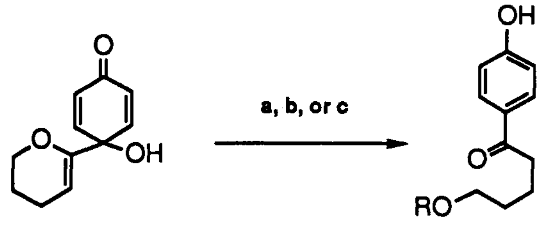
Scheme I



We have been exploring a "reverse polarity" approach in which the reductive aromatization of a quinol glycal would serve as a key step (Scheme I). In this approach, the free phenolic hydroxyl group would be generated directly by the method of synthesis.

In this paper, we are pleased to report the reductive aromatization of benzo- and naphthoquinol glycals. When coupled with the preparation of quinol glycals from quinones and lithio glycal reagents, this transformation provides a regiospecific synthesis of *p*-hydroxyaryl glycals in two simple steps.

Initial efforts to effect this type of transformation had been abandoned following the observation of hydrolytic ring opening in a model system (**2a** → **3** or **4**).[4]



2a

3 R = Ac
4 R = H

a) Zn/HOAc/H$_2$O b) Al(Hg)/THF/H$_2$O
c) 1. NaBH$_4$/EtOH, 2. NaOH/Δ

However, more recent experiments have revealed that the desired conversions (Scheme I) may be easily achieved. We have now shown that, under controlled conditions, dithionite solution reduces *p*-benzoquinol glycals to *p*-

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[1] Recipient of the 1991-92 Division of Organic Chemistry (American Chemical Society) Graduate Fellowship sponsored by The Rohm and Haas Co.

[2] (a) Gilvocarcins: Takahashi, K.; Yoshida, M.; Tomita, F.; Shirahata, K. *J. Antibiot.* **1981**, *34*, 271. (b) Ravidomycins: Findlay, J.; Liu, J.-S.; Radics, L.; Rakhit, S. *Can. J. Chem.* **1981**, *59*, 3018. Rakhit, S.; Eng, C.; Baker, H.; Singh, K. *J. Antibiot.* **1983**, *36*, 1490. Narita, T.; Matsumoto, M.; Mogi, K.; Kukita, K.-I.; Kawahara, R.; Nakashima, T. *J. Antibiot.* **1989**, *42*, 347. (c) Chrysomycins: Weiss, U.; Yoshihira, K.; Highet, R.; White, R.; Wei, T. *J. Antibiot.* **1982**, *35*, 1194.

[3] Suzuki recently reported the first total synthesis of Gilvocarcin M and revised the absolute configuration of the natural product: Matsumoto, T.; Hosoya, T.; Suzuki, K. *J. Am. Chem. Soc.* **1992**, *114*, 3568.

[4] Numerous *p*-alkoxy *C*-aryl glycosides have been prepared by coupling aryl ethers with carbohydrate derivatives and recently a novel preparation of a *p*-methoxy *C*-phenyl glycoside was reported by us. See: Parker, K. A.; Coburn, C. A. *J. Am. Chem. Soc.* **1991**, *113*, 8516 and references cited therein.

[5] Hart has prepared *p*-methoxy *C*-phenyl glycosides by electrophile-initiated cyclizations of substituted styrenes (D. J. Hart, personal communication).

[6] Only recently have *p*-hydroxy *C*-aryl glycosides been prepared. The methods which proved successful required temporary protection of the hydroxyl group. See: Farr, R. N.; Kwok, D.-I.; Daves, G. D., Jr. *J. Org. Chem.* **1992**, *57*, 2093.

[7] For other recent work on *C*-aryl glycoside construction, see: Martin, O. R.; Rao, P.; Kurz, K. G.; El-Shenawy, H. A. *J. Am. Chem. Soc.* **1988**, *110*, 8698 and references cited therein.

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