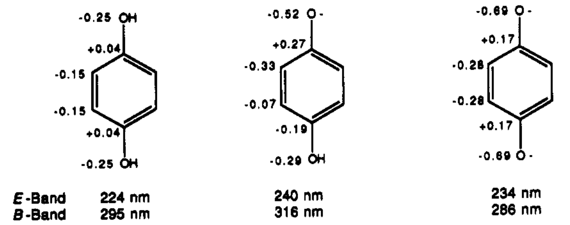

Figure 1. AM1 calculated net atomic charges for all non-hydrogen atoms and UV absorption data for hydroquinone, hydroquinone anion, and hydroquinone dianion.

corresponding anion by addition of 1 equiv of *tert*-butyllithium results in a bathochromic shift of both the *B*-band (316 nm) and the *E*-band (240 nm). This is attributed to interactions between nonbonding electrons of the anion and the benzenoid π-system.[11] However, addition of a 2-fold excess of *tert*-butyllithium, which forms the dianion of hydroquinone, results in hypsochromic shifts of the *B* band (286 nm) and a bathochromic shift of the *E*-band (234 nm) relative to the hydroquinone model. This observation can be interpreted as lack of interactions between nonbonding electrons of the vinylogous 1,4-dioxyanion and the benzenoid π-system. This unfavorable electronic interaction can be circumvented by an intramolecular nucleophilic attack of O-4 on the ester carbonyl resulting in the formation of 8.

Semiempirical molecular orbital calculations of the hydroquinone model using the AM1[12] Hamiltonian also support these observations. Calculations of net atomic charge for all non-hydrogen atoms are summarized in Figure 1. For the hydroquinone anion, charge delocalization is observed at the ortho and para positions relative to the oxyanion. However in the hydroquinone dianion system, charge delocalization is restricted to only the respective ortho positions with a positive charge residing on the ipso positions. This is consistent with the hypsochromic shift of the *B*-band for the hydroquinone dianion.

In conclusion, the ester cleavage reaction between bromojuglone acetates and Gilman reagents proceeds through the conjugate base of a hemi ortho ester intermediate derived from the hydroquinone dianion. Breakdown of this tetrahedral intermediate results in a peri transacylation reaction which upon atmospheric oxidation results in the formation of the respective bromojuglone as the major product.

Experimental Section

Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer 1600 FT-IR spectrometer. Ultraviolet spectra of tetrahydrofuran solutions were recorded on a Varian 2300 UV–vis spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Bruker AC 250 (250 MHz) instrument. Chemical shifts are reported in δ (ppm) downfield from internal tetramethylsilane. Tetrahydrofuran was distilled under nitrogen from CaH_2. Bromojuglone acetates 3 and 4 were synthesized according to the literature.[5]

General Procedure for Addition of Lithium Dialkylcuprates to Quinones. In a 250-mL round-bottom flask were placed CuI (4.0 g, 21 mmol) and THF (90 mL) under nitrogen. The solution was cooled to −78 °C and maintained at that temperature throughout the reaction. Added to the solution was 42 mmol of alkyllithium solution (*tert*-butyl or methyl[13]). The reaction mixture was allowed to stir for 20 min. To this solution was added 4 mmol of quinone dissolved in THF (50 mL). The reaction mixture was allowed to stir for 4 h followed by addition of saturated NH_4Cl (50 mL) at −78 °C. The resulting solution was stirred for 1 h, allowing the solution to warm to room temperature. The solvent was removed under reduced pressure and the residue diluted with dichloromethane (125 mL). The solution was washed with aqueous NH_4Cl (2 × 30 mL) and water (2 × 40 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure. Flash chromatography was performed on the crude product.

2-Bromo-5-hydroxy-1,4-naphthoquinone (1). Following the general procedure, quinone 3 afforded 1 (0.93 g, 92%): mp 134–135 °C (lit.[4] mp 136 °C). The spectra of the obtained product 1 were identical to those previously reported.[5]

3-Bromo-5-hydroxy-1,4-naphthoquinone (2). Following the general procedure, quinone 4 afforded 2 (0.88 g, 87%): mp 169–171 °C (lit.[4] mp 172 °C). The spectra of the obtained product 2 were identical to those previously reported.[5]

Procedure for Trapping the Hemi Ortho Ester Derived from 3. In a 250-mL round-bottom flask were placed CuI (2.0 g, 10.5 mmol) and THF (40 mL) under nitrogen. The solution was cooled to −78 °C and maintained at that temperature throughout the reaction. Added to the solution was 12.5 mL of 1.7 M *tert*-butyllithium (21 mmol). The reaction mixture was allowed to stir for 20 min. To this solution was added quinone 3 (1.2 g, 4 mmol) dissolved in THF (15 mL). The reaction mixture was allowed to stir for 30 min. Chlorotrimethylsilane (10 mL, 79 mmol) was added to the resulting solution, which was allowed to stir for 2 h. The reaction mixture was allowed to warm to room temperature and the solvent was removed under reduced pressure. The residue was diluted with pentane (250 mL) and filtered to remove the resulting salts. The filter cake was washed with CH_2Cl_2 (25 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford 9 (650 mg, 38%): mp 29–31 °C dec; IR ($CHCl_3$ solution) 3020, 2958, 1211, 742 cm^{-1}; ^1H ($CDCl_3$) δ 0.24 (s, 9 H), 0.28 (s, 9 H), 1.39 (s, 3 H), 7.09 (s, 1 H), 7.25 (dd, J = 1.1, 7.7, 1 H), 7.48 (t, J = 7.7, 1 H), 7.62 (dd, J = 1.1, 7.7, 1 H); ^{13}C δ 1.1, 1.7, 29.1, 106.3, 115.4, 116.8, 117.1, 121.9, 122.0, 123.3, 124.4, 125.3, 126.5, 134.6.

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Registry No. 1, 69008-03-3; 2, 52431-65-9; 3, 77189-69-6; 4, 77197-58-1; 9, 141612-10-4; 10, 141612-11-5; 11, 141612-12-6.

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A Simple High-Yield Preparation of Alkynylphosphonium Triflates

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Unsaturated phosphonium salts represent a useful class of reagents in organic synthesis.[1] They serve as valuable dienophiles in Diels–Alder cycloadditions, as precursors to certain ylides, and undergo numerous other desirable transformations.[1,2]

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In this paper, we wish to report the high-yield single-step formation of alkynylphosphonium triflates 2 via the reaction of readily available[3,4] alkynyl(phenyl)iodonium triflates 1 with Ph_3P.

$$\mathrm{RC{\equiv}CIPh(OTf)} + \mathrm{Ph_3P} \xrightarrow[\text{30 min, } -\mathrm{PhI}]{\mathrm{CH_2Cl_2},\ -78 \text{ to } 25\ ^\circ\mathrm{C}} \mathrm{RC{\equiv}CPPh_3(OTf)}$$

1a: R = CH_3
b: R = *t*-Bu
c: R = Me_3Si
d: R = *n*-Bu
e: R = Ph

2a: R = CH_3
b: R = *t*-Bu
c: R = Me_3Si
d: R = *n*-Bu
e: R = Ph

Reaction of 1 with a 5% excess of Ph_3P in CH_2Cl_2 at −78 to 25 °C for 30 min affords the appropriate crude alkynyl phosphonium triflates 2 in essentially quantitative yield. Recrystallization from CH_2Cl_2 and ether affords the pure final product in 88–98% isolated yield as colorless microcrystalline solids for **2a–d** and slight yellow for **2e**.

The product phosphonium salts are characterized by multinuclear NMR and IR spectroscopy and by elemental analysis. Specifically, the singlet between 5.2 and 7 ppm in the ^{31}P NMR spectrum is typical for the phosphorus signal in alkynylphosphonium salts.[5] The presence of the $^-OSO_2CF_3$ counter ion is indicated by the characteristic ^{19}F signal at −78 ppm as well as the typical absorptions[6] for ionic triflates in the IR spectrum. The IR spectrum shows signals for the C≡C bond between 2134 and 2212 cm^{-1}. Most characteristic are the C≡C signals in the ^{13}C NMR spectrum, where the C_α resonates between 60 and 79 ppm with a $^1J_{CP}$ = 162–192 Hz and the C_β is at much lower field between 118 and 133 ppm with a $^2J_{PC}$ = 12–33 Hz. The remainder of the ^{13}C spectra as well as the ^1H spectra are completely consistent with the proposed structures.

Finally, unlike the reaction of the analogous alkynyl(phenyl)iodonium tetrafluoroborate species,[7] the reaction of 1 with Ph_3P does not require light.[8] These reactions occur readily in the dark. Moreover, the reaction of 1 with Ph_3P is not inhibited by radical traps such as O_2 or 2,6-di-*tert*-butyl-4-methylphenol (BHT). Hence, we believe that, unlike the proposed radical cation-like reactions[7] of the $^-BF_4$ salts, the triflate salts 1 react by the standard[3] nucleophilic acetylenic substitution (S_N-A) process involving iodonium ylides and alkylidenecarbenes as intermediates.

Experimental Section

Melting points were obtained in capillary tubes and are uncorrected. Infrared (IR) spectra were recorded as CCl_4 thin films. NMR spectra were recorded on a Varian XL 300 spectrometer using $CDCl_3$ as solvent. Chemical shifts for ^{31}P are reported in parts per million downfield from 85% H_3PO_4, and ^{19}F NMR shifts are relative to $CFCl_3$. Commercially available Ph_3P was recrystallized from hexanes prior to use. CH_2Cl_2 was distilled from CaH_2. Alkynyl(phenyl)iodonium triflates 1 were prepared by standard methods.[3,4]

General Procedure for the Preparation of Alkynylphosphonium Triflates (2). Alkynyl(phenyl)iodonium triflate 1 (1.00 mmol) was dissolved in 30 mL of CH_2Cl_2 and then cooled to −78 °C. A solution of Ph_3P (1.05 mmol) in 10 mL of CH_2Cl_2 was added slowly over 2 min. The reaction mixture was then allowed to warm to room temperature over 30 min. Solvent was then removed by rotary evaporation, and the residue was washed several times with diethyl ether. The product was then recrystallized by dissolving the crude material in a small amount of CH_2Cl_2 followed by the addition of diethyl ether; the resulting crystals were washed again, filtered, and dried in vacuo.

Propynyl(triphenyl)phosphonium Triflate (2a). Yield: 446 mg (97%) as white crystals with mp 128–129 °C dec. IR: 2212 (C≡C), 1265, 1223, 1033 cm^{-1}. ^1H NMR: δ 7.76–7.74 (m, 3 H's), 7.74–7.60 (m, 12 H's), 5.20 ($^3J_{P,H}$ = 5 Hz). ^{13}C NMR: δ 135.65 ($^4J_{P,C}$ = 3 Hz), 132.97 ($^2J_{P,C}$ = 12 Hz), 130.52 ($^3J_{P,C}$ = 14 Hz), 121.41 (βC≡C, $^2J_{P,C}$ = 33 Hz), 120.83 ($^1J_{F,C}$ = 321 Hz), 118.16 ($^1J_{P,C}$ = 100 Hz), 60.14 (αC≡C, $^1J_{P,C}$ = 192 Hz), 6.32 ($^3J_{P,C}$ = 4 Hz). ^{31}P NMR: δ 5.99. ^{19}F NMR: δ −78.26. Anal. Calcd for $C_{22}H_{18}PSO_3F_3$: C, 58.67; H, 4.03. Found: C, 58.62; H, 3.99.

(3,3-Dimethylbutynyl)(triphenyl)phosphonium Triflate (2b). Yield: 484 mg (98%) as white crystals with mp 158–159 °C. IR: 2174 (C≡C), 1271, 1224, 1033 cm^{-1}. ^1H NMR: δ 7.85–7.81 (m, 3 H's), 7.76–7.61 (m, 12 H's), 1.45. ^{13}C NMR: δ 136.13 ($^4J_{P,C}$ = 3 Hz), 133.15 ($^2J_{P,C}$ = 12 Hz), 131.12 (βC≡C, $^2J_{P,C}$ = 28 Hz), 130.96 ($^3J_{P,C}$ = 14 Hz), 121.12 ($^1J_{F,C}$ = 321 Hz), 118.37 ($^1J_{P,C}$ = 100 Hz), 63.39 (αC≡C, $^1J_{P,C}$ = 187 Hz), 30.01 ($^3J_{P,C}$ = 3 Hz), 29.64. ^{31}P NMR: δ 6.02. ^{19}F NMR: δ −78.22. Anal. Calcd for $C_{25}H_{24}PSO_3F_3$: C, 60.97; H, 4.91. Found: C, 60.83; H, 4.95.

[(Trimethylsilyl)ethynyl](triphenyl)phosphonium Triflate (2c). Yield: 500 mg (98%) as white crystals with mp 134–136 °C dec. IR: 2212 (C≡C), 1272, 1225, 1033 cm^{-1}. ^1H NMR: δ 7.90–7.83 (m, 3 H's), 7.78–7.64 (m, 12 H's), 0.39. ^{13}C NMR: δ 136.07 ($^4J_{P,C}$ = 3 Hz), 133.06 ($^2J_{P,C}$ = 12 Hz), 132.94 (βC≡C, $^2J_{P,C}$ = 18 Hz), 130.80 ($^3J_{P,C}$ = 14 Hz), 120.87 ($^1J_{F,C}$ = 321 Hz), 117.45 ($^1J_{P,C}$ = 100 Hz), 83.97 (αC≡C, $^1J_{P,C}$ = 162 Hz), −1.22. ^{31}P NMR: δ 5.28. ^{19}F NMR: δ −78.22. Anal. Calcd for $C_{24}H_{24}PSiSO_3F_3$: C, 56.67; H, 4.76. Found: C, 56.45; H, 4.74.

Hexynyl(triphenyl)phosphonium Triflate (2d). Recrystallization from CH_2Cl_2 and hexanes gave 434 mg (88%) of white crystals with mp 97–98 °C dec. IR: 2208 (C≡C), 1262, 1224, 1029 cm^{-1}. ^1H NMR: δ 7.82–7.52 (m, 15 H's), 2.79–2.72, 1.76–1.65, 1.49–1.36, 0.93–0.85. ^{13}C NMR: δ 135.75 ($^4J_{P,C}$ = 3 Hz), 132.98 ($^2J_{P,C}$ = 12 Hz), 130.62 ($^3J_{P,C}$ = 14 Hz), 125.06 (βC≡C, $^2J_{P,C}$ = 31 Hz), 120.88 ($^1J_{F,C}$ = 321 Hz), 118.21 ($^1J_{P,C}$ = 108 Hz), 60.98 (αC≡C, $^1J_{P,C}$ = 190 Hz), 28.89, 22.01, 20.28 ($^3J_{P,C}$ = 3 Hz), 13.25. ^{31}P NMR: δ 5.97. ^{19}F NMR: δ −78.34. Anal. Calcd for $C_{25}H_{24}PSO_3F_3$: C, 60.97; H, 4.91. Found: C, 60.86; H, 4.90.

(Phenylethynyl)(triphenyl)phosphonium Triflate (2e). Recrystallization from THF and diethyl ether gave 441 mg (85%) of yellow crystals with mp 138–139 °C. IR: 2178 (C≡C), 1265, 1224, 1031 cm^{-1}. ^1H NMR: δ 7.89–7.72 (m, 17 H's), 7.64–7.57 (t, 1 H), 7.54–7.46 (t, 2 H's). ^{13}C NMR: δ 136.15 ($^4J_{P,C}$ = 3 Hz), 133.73 ($^4J_{P,C}$ = 2 Hz), 133.43, 133.26 ($^2J_{P,C}$ = 12 Hz), 130.98 ($^3J_{P,C}$ = 14 Hz), 129.34, 121.12 ($^1J_{F,C}$ = 321 Hz), 118.79 (βC≡C, $^2J_{P,C}$ = 31 Hz), 118.11 ($^1J_{P,C}$ = 100 Hz), 116.85 ($^3J_{P,C}$ = 5 Hz), 78.93 (αC≡C, $^1J_{P,C}$ = 187 Hz). ^{31}P NMR: δ 7.04. ^{19}F NMR: δ −78.16. Anal. Calcd for $C_{27}H_{20}PSO_3F_3$: C, 63.28; H, 3.93. Found: C, 63.12; H, 3.94.

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Electronic Substituent Effect of Nitrogen Ligands in Catalytic Asymmetric Hydrosilylation of Ketones: Chiral 4-Substituted Bis(oxazolinyl)pyridines

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Recent interest in transition-metal-catalyzed asymmetric reactions have focused attention on the development of chiral cyclic nitrogen ligands.[1] We have reported the chiral

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