A Donor-Type Cyclophane with a Strongly Bent Tetrathiafulvalene Unit

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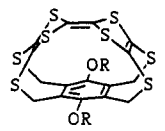
Two independent methods for synthesizing the phane-like tetrathiafulvalene derivative 1 are presented. The crystal-structure analysis of 1 reveals a strongly bent tetrathiafulvalene unit. Cyclic voltammetric investigations clearly show divergences from the redox properties of planar tetrathiafulvalenes. The reactivity toward electrophilic reagents has been studied in order to define consequences of the cyclic structure on the chemical behavior of 1. We found that the tetrathiafulvalene unit of 1 can be protonated reversibly with hydrogen chloride. The NMR spectroscopic analysis of the stable protonation product **20** is described.

Introduction

Radical cation salts of tetrathiafulvalene (TTF) as well as its derivatives belong to the most prominent examples of electrically conducting low-molecular-weight organic compounds.[1] A promising approach leading to new conducting materials comprises the synthesis of extended donor systems based on TTF subunits.[2-6] As an alternative to the previously described concept of conjugatively linked TTF units,[7,8] we have searched for a route to σ-bridged oligo-TTF systems, whereby the type of connection might permit linear or phane-like structures. As we have already reported, the trialkyl phosphite-induced condensation of dithione 4 leads in a suprisingly high yield to the cage-type molecule 1.[9] Due to the high ring strain, the TTF unit of 1 clearly deviates from planarity. A comparison with the noncyclic analogue 2 shows striking differences in the spectroscopic and, in particular, redox chemical characteristics. Such differences can be readily interpreted in terms of the unusual phane-like structure of 1.



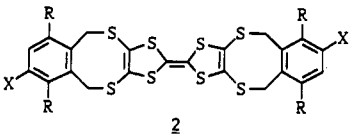
1

a: R = Propyl
b: R = Butyl
c: R = Hexyl
d: R = Hexoyl

Results and Discussion

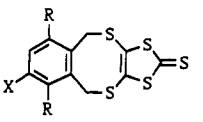
The synthesis of the bis(*o*-xylylenedithio)tetrathiafulvalene (**2a**) is achieved through a trialkyl phosphite-induced condensation of the 4,5-(*o*-xylylenedithio)-2-thioxo-1,3-dithiole (**3a**).[10]

The method lends itself to the preparation of 1, whereby 5*H*,13*H*-bis[1,3]dithiolo[4,5-*b*:4′,5′-*b*′]benzo[1,2-*f*:4,5-*f*′]-bis[1,4]dithiocin-2,10-dithione derivatives **4** are used in the coupling reaction. Dithiones of type **4** are available by reaction of tetrabromodurene with bis(tetraethylammonium)bis(2-thioxo-1,3-dithiole-4,5-dithiolate)zincate (**5**).[11] In order to obtain characterizable products, it is necessary to synthesize derivatives of the dithione **4** with solubility-improving substituents. The preparation of these species starts with a Williamson etherification of durohydroquinone (**6**)[12] leading to the *n*-alkyl hydroquinone ethers **7a–c**. The acylated derivative **7d** is easily generated by esterification of **6** with hexoyl chloride in pyridine. The photochemically initiated NBS bromination of **7a–d** provides the tetrabromodurene derivatives **8a–d**. Reaction of **8a–d** with the zincate **5** in THF/acetone gives the dithiones **4a–d**.



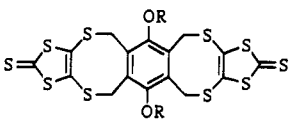
2

a: R = H, X = H
b: R = O-Hexyl, X = H
c: R = O-Butyl, X = Br



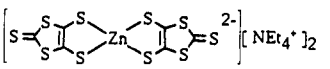
3

a: R = H, X = H
b: R = O-Hexyl, X = H
c: R = O-Butyl, X = Br



4

a: R = Propyl
b: R = Butyl
c: R = Hexyl
d: R = Hexoyl



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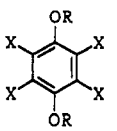

6, 7, 8

6: R = H, X = CH_3
7a: R = Propyl, X = CH_3 8a: R = Propyl, X = CH_2Br
7b: R = Butyl, X = CH_3 8b: R = Butyl, X = CH_2Br
7c: R = Hexyl, X = CH_3 8c: R = Hexyl, X = CH_2Br
7d: R = Hexoyl, X = CH_3 8d: R = Hexoyl, X = CH_2Br

When **4a–d** are subjected to a triethyl phosphite-induced coupling reaction, intramolecular fulvalene formation gives rise to the macrocycles **1a–d** (yield: **1a**, 38%; **1b**, 34%; **1c**, 37%; **1d**, 59%). Linear oligomers **9** are found generally in amounts between 10 and 15%.

As an alternative to the trialkyl phosphite-induced condensation of dithione **4**, the title compound can also be generated from bisdithiolium salts of type **10** by

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(12) Bothner-By, A. A. *J. Am. Chem. Soc.* **1953**, *75*, 728.

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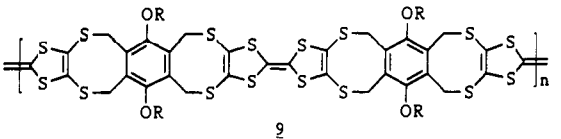

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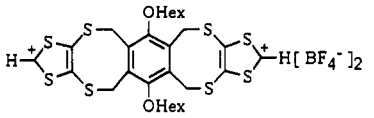

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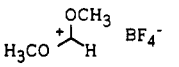

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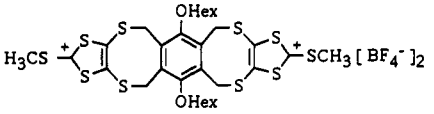

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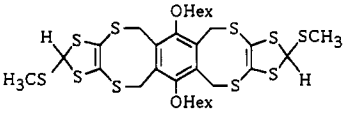


13

treatment with amines. The synthesis of **10** can be achieved in a three-step reaction sequence starting from the dithione precursor. In the first step a thiophilic methylation of **4c** with dimethoxycarbonium tetrafluoroborate (**11**)[13] leads to **12**.[14] Reaction of **12** with sodium borohydride in acetonitrile produces the bistrithioorthoformate **13**. Although two isomers of **13** are possible, only one isomer is formed, but it is unknown whether the cis or trans product is present. By treating **13** with tetrafluoroboric acid in acetic anhydride at 0 °C, the bisdithiolium salt **10** is generated as a beige-colored solid.

The addition of an excess of diisopropylethylamine to a solution of **10** in acetonitrile leads to the target compound **1c**. Unlike the triethyl phosphite-induced condensation of **4**, a significant concentration dependence of the intramolecular reaction is evident in the amine-induced carbene coupling. In the case of a 6.4×10^{-3} M solution of **10**, the yield of **1c** amounts to 61%, whereas oligomers of type **9** are only formed in 20%. By raising the concentration, the amount of **1c** is reduced and finally suppressed so that only oligomers **9** are isolated.

The crystal structure of **1a** is shown in Figure 1. As the view onto the plane of the benzene ring indicates, the basic skeleton of the compound possesses approximately ideal *mm*2 (C_{2v}) symmetry, i.e. the fulvalene double bond is located centrally above the benzene ring at a transannular distance of 3.91 Å. In spite of the ring strain in **1**, the benzene ring is, within the accuracy of the structure analysis, still planar.

Due to the high ring strain the TTF unit deviates considerably from planarity. The bending of the TTF skeleton is most clearly seen in the positions of the four sulfur atoms which surround the central double bond (S1, S2, S3, S4). The angles of the planes S1–S2–C2–C3 and S3–S4–C5–C6 (planes A, A′) with respect to plane S1–S2–S3–S4 (plane B) equal 50° and 48°, respectively. In the cyclophanes **14**[15] and **15**,[16] the TTF unit shows this bending at

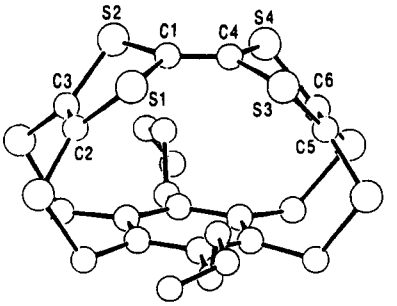
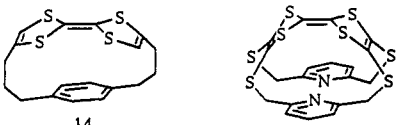


Figure 1. ORTEP diagram of the crystal structure analysis of **1a**.

positions S1, S2, S3, and S4.[17] In the case of **14**, the angle between the planes A, A′ and plane B is considerably smaller (28° and 33°, respectively), while the corresponding angle of **15** equals 45°, and the compound reveals a similar bending as in **1**. The ring strain squeezes the central fulvalene double bond of **1** out of plane B. The angle between the central double bond and the planes C1–S1–S2 and C4–S3–S4 equals 11°. The deviation of the central olefinic unit from planarity proves to be only 4° in **14**, whereas in the case of the cyclophanes **16** (27°)[18] and **17** (20°)[19] the deviation is much larger. The effect is unambigous, because the kink between planes A and B in **1** and **14** reduces the steric strain on the central olefinic unit. As a result, the strain must be less than in molecules such as **16** or **17**.



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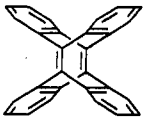

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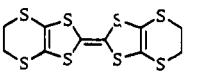

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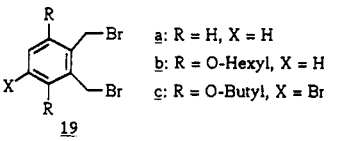

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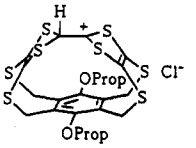

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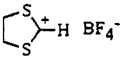

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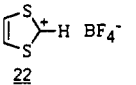

22

A comparison of the bond lengths of **1** and BEDT-TTF (**18**)[20] shows no apparent irregularities for the bonds C1–S1

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(1, 1.75 Å; 18, 1.76 Å) and C2–C3 (1, 1.34 Å; 18, 1.33 Å). In contrast, the central fulvalenic double bond (C1–C4) of 1 (1.35 Å) is longer by 0.04 Å than in 18 (1.31 Å). The bond length lies in a range that is typical for radical cation salts of BEDT-TTF (for example, β-(BEDT-TTF)$_2$I$_3$: C1–C4 = 1.35 Å[21]), which implies a weakening of the double-bond character of this bond. The length of S1–C2 in 1 (1.78 Å) lies between the corresponding bond length in 18 (1.75 Å) and the length of the C–S single bond in thioethers (1.81 Å). The lengthening of this bond and the buckling between plane A and plane B indicates that the π-configuration in 1 is disturbed and that the central and the peripheral double bonds are electronically less strongly coupled than in planar tetrathiafulvalenes.

Pecularities in physical and chemical characteristics of the donor cage 1 should clearly manifest themselves in a comparison with the linear tetrathiafulvalene **2**. Model compound **2a** must be disregarded because, due to insufficient solubility, spectroscopic and cyclic voltammetric investigations are greatly impaired. Analogous to the preparation of **3a** and **4a–d**, the thioketones **3b** and **3c** can be generated by reacting 1,4-bis(hexyloxy)-2,3-bis(bromomethyl)benzene (**19b**) or 1,4-bis(butyloxy)-2,3-bis(bromomethyl)-5-bromobenzene (**19c**) with zincate **5**. Coupling of **3b** and **3c** in triethyl phosphite produces the readily soluble tetrathiafulvalenes **2b** and **2c**. The spectroscopic analysis reveals several notable characteristics.

1. The resonances of the eight-membered-ring methylene protons in **1a–c** appear as an AB spin system (**1a**, J = 11.6 Hz; $\Delta_{\nu AB}/J$ = 2.1; **1b**, J = 11.0 Hz; $\Delta_{\nu AB}/J$ = 2.2; **1c**, J = 10.8 Hz; $\Delta_{\nu AB}/J$ = 2.4). In the case of the ester-substituted derivative **1d** a shift of the A branch to higher field is due to the magnetic influence of the ester-carbonyl group, which then results in an AX character of the spin system (J = 13.4 Hz; $\Delta_{\nu AB}/J$ = 9.4).

2. The ^{13}C-NMR chemical shift of the central fulvalenic double bond of the planar TTF systems **2b** and **2c** is δ_C = 111.9 and 112.0 ppm.[22] In contrast, the corresponding signal of the strained analogues **1a–d** lies between δ_C = 134 and 134.5 ppm.

3. Concerning the values of the optical absorption maxima, the UV/vis spectrum indicates no difference between **2** and **1** (**2b**, λ = 228, 314, and 333 nm; **1c**, λ = 227, 312, und 333 nm). The extinction coefficients ϵ of the TTF absorptions in **1** (**1c**: ϵ(312) = 4297, ϵ(333) = 3473) experience, however, a drastic reduction by approximately a factor of 4 compared to the planar systems **2** (**2b**: ϵ(314) = 16143, ϵ(333) = 15813).

Cyclic voltammetric investigations of **2b** (**2c**) prove two ideally reversible oxidations at 0.33 V (0.39 V) and 0.82 V (0.84 V).[23] On the other hand, the oxidation of **1a** at 0.93 V is irreversible under identical conditions. One observes the formation of a follow-up product which shows two reversible oxidation steps ($E_{1/2}^1$ = 0.36 V, $E_{1/2}^2$ = 1.03 V). Thus, compared to planar TTF's, **1** reveals a completely different redox behavior.

The question arises whether the strained, cyclic structure also has an effect on other chemical properties. The crystal structure demonstrates that the TTF moiety of **1** can be considered as being divided into three relatively independent tetrathioethylene units. Although tetrathioethylenes, in contrast to tetraoxy- or tetraamino-substituted ethylenes, show no reactivity toward electrophilic reagents,[24] the central fulvalene double bond of **1** might show increased reactivity as a result of steric strain.[25]

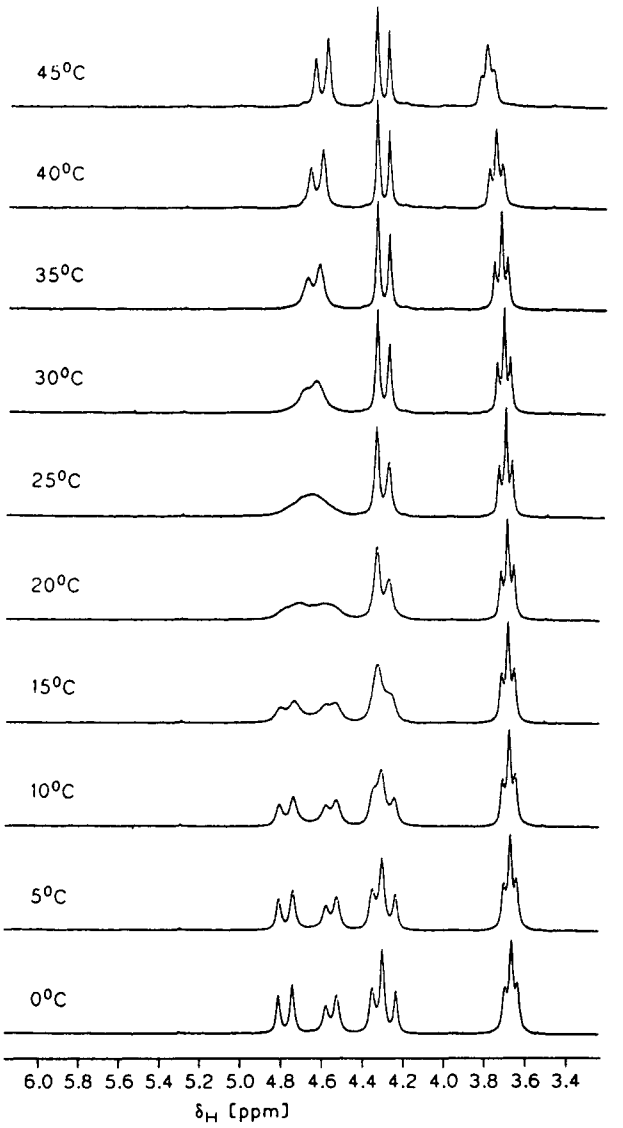

Figure 2. Temperature-dependence of the ^{1}H NMR spectrum (200 MHz) of **20** at δ 3.3–6.1.

We first studied the reaction of **1** with hydrogen halides. Solutions of **1a** in chloroform or dichloromethane were treated with gaseous hydrogen chloride at room temperature. Under these conditions, **1** was quantitatively protonated forming the red product **20**. According to spectroscopic investigations (described below), neither side reactions nor decomposition was observed, and a nucleophilic attack of the chloride ion on **20** can be ruled out. **20** is stable in solution for at least 2 weeks, and even after this period of time the protonation is completely reversible. Treatment of a 14-day-old solution of **20** with gaseous ammonia quantitatively gave back the intact neutral compound **1**.

So far a protonation of the central double bond of tetrathiafulvalenes could only be proven indirectly.[26,27] In

(21) Emge, T. J.; Leung, P. C. W.; Beno, M. A.; Wang, H. H.; Firestone, M. A.; Webb, K. S.; Carlson, K. D.; Williams, J. M.; Venturini, E. L.; Azevedo, L. J.; Schirber, J. E. *Mol. Cryst. Liq. Cryst.* **1986**, *132*, 363.

(22) The planarity of **2** is supported by the X-ray structure of a related system with fused eight-membered rings: Kumar, S. K.; Singh, H. B.; Das, K.; Sinha, U. C.; Mishnev, A. *J. Chem. Soc., Chem. Commun.* **1991**, 952.

(23) Potentials vs SCE with ferrocene calibration ($E_{1/2}$ = 0.31 V), dichloromethane, tetrabutylammonium hexafluorophosphate, 100 mV/s.

(24) Coffen, D. L.; Chambers, J. Q.; Williams, D. R.; Garrett, P. E.; Canfield, N. D. *J. Am. Chem. Soc.* **1971**, *93*, 2258.

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contrast, a direct spectroscopic detection of **20** was possible. The ^{1}H-NMR spectrum of **20** shows the slightly broadened signal of the added proton at δ_H = 6.22 ppm (CD_2Cl_2, −10 °C). The methylene protons of the eight-membered rings appear as two separate AB systems (AB1, δ_H = 4.32, 4.38, 4.50, 4.56 ppm; AB2, δ_H = 4.25, 4.32, 4.75, 4.82 ppm). Within the ^{1}H-NMR time scale, the added proton is fixed at temperatures up to 0 °C at one side of the central fulvalene double bond. Above 0 °C a migration of the proton between the two carbons of the central double bond can be observed. This exchanges the magnetic sites of the eight-membered-ring protons H_{A1}/H_{B1} and H_{A2}/H_{B2} (Figure 2). As a result of the different $\Delta\nu$ values of A1/A2 ($\Delta\nu$ = 12 Hz) and B1/B2 ($\Delta\nu$ = 45 Hz) in the slow exchange domain, the A branch possesses a coalescense temperature of 12.5 °C, whereas B1/B2 coalesces at 25 °C. The activation energy of the proton migration was estimated as $\Delta G^{\ddagger}$ (20 °C) = 61 ± 2 KJ mol^{-1}.

The ^{13}C-NMR chemical shift of the carbocationic center of **20** (δ_C = 221.0 ppm) corresponds to that of the 4,5-dihydro-1,3-dithiolium tetrafluoroborate **21** (δ_C = 221.2 ppm), but not to that of the 1,3-dithiolium tetrafluoroborate **22** (δ_C = 179.5 ppm).[28] This points toward a much lower delocalization of the positive charge in the bent system **20** compared to the planar 1,3-dithiolium salt **22**.

The UV/vis spectrum of **20** shows absorptions at λ = 242 (ε = 34657), 313 (23543), 363 (21711), and 527 nm (1072). Compared to **1**, the intensity of the absorptions is clearly enhanced and one observes a bathochromic shift of the benzene and of the longer wavelength TTF absorption (**1a**: λ = 227 (13009) and 332 (3032) nm). The band at 527 nm can be explained by a CT transition from the electron-rich benzene system to the carbocationic dithiolium system.

Apart from the protonation, no further reactions of **1** could be observed. Addition of Br_2 and I_2 did not occur, and also no radical cation salts were formed. **1** does not show any tendency toward Diels–Alder reactions. Neither the reaction with the electron-rich diene 2,3-dimethylbutadiene nor with electron-poor dienes such as 2,2-dimethoxy-1,3,4,5-tetrachlorocyclopentadiene or 1,2,4,5-tetrazene-3,6-dicarboxylic acid methyl ester succeeded (in the case of tetramethoxyethylene, the Diels–Alder reaction with the latter diene proceeds readily[29]). The results show that the steric strain in **1** causes no enhancement of the reactivity of the central olefinic structure.

Conclusion

Under the respective coupling conditions, dithiones of type **4** and bisdithiolium salts **10** show a distinct tendency toward self-condensation with formation of the cage-type molecule **1**. The ring strain causes a strong bending of the TTF unit of **1** as well as a bond lengthening of both the central fulvalene double bond and the bonds between the sulfur atoms and the peripheral carbon centers of the TTF unit. As a result, **1** possesses a completely different redox behavior than planar TTF. On the other hand, the steric strain leads to no increase in the reactivity of the central tetrathioethylene unit toward electrophilic reagents. The focus of present research is the determination of the irreversible oxidation mechanism of **1**. This includes the characterization of the observed follow-up product.

Experimental Section

Etherification of 6. Durohydroquinone (**6**)[30] (24 g, 0.144 mol) was added to a solution of sodium ethoxide (25 g, 0.368 mol) in ethanol (500 mL) under argon. The dark solution was heated under stirring, and the alkyl bromide (0.37 mol) was added dropwise over a period of 10 min. Then, the reaction mixture was refluxed for 5 h. Subsequently, the ethanol was evaporated and the remaining oil was treated with aqueous sodium hydroxide solution (5%) and extracted with ether. The solution was washed with water and dried over Na_2SO_4. After evaporation of the solvent, the ethers **7a–c** were obtained as white solids, which were recrystallized from ethanol. **7a** (21 g, 58%): mp 59 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.16 (t, 6 H), 1.92 (m, 4 H), 2.24 (s, 12 H), 3.68 (t, 4 H). **7b** (22.4 g, 56%): mp 55 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.98 (t, 6 H), 1.46–1.85 (m, 8 H), 2.14 (s, 12 H), 3.64 (t, 4 H). **7c** (28 g, 59%): mp 65 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.90 (t, 6 H), 1.20–1.50 (m, 12 H), 1.74 (m, 4 H), 2.14 (s, 12 H), 3.63 (t, 4 H).

Esterification of 6. Durohydroquinone (**6**) (10 g, 0.06 mol) was dissolved in pyridine (120 mL) under argon. Hexanoyl chloride (19 g, 0.138 mol) was added to the stirred solution over a 30-min period (the mixture was cooled, so that the temperature inside the flask did not exceed 35 °C). The mixture was stirred for 1 h. Then, 350 mL of a mixture of hydrochloric acid and ice (30 g of ice per 100 mL of 3 N hydrochloric acid) was added. The precipitate was filtered and washed with 0.1 N hydrochloric acid and water. Recrystallization of the crude product from 2-propanol afforded the ester **7d** as white needles (16.8 g, 77%): mp 128 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.05 (t, 6 H), 1.34–1.68 (m, 8 H), 1.90 (m, 4 H), 2.16 (s, 12 H), 2.72 (t, 4 H).

Bromination of 7. A solution of 0.1 mol of the durene derivative (**7a–d**) in CCl_4 (600 mL) was placed in a 1-L three-necked round-bottomed flask equipped with a reflux condensor under argon. After addition of *N*-bromosuccinimide (NBS) (75 g, 0.42 mol), the solution was refluxed while stirring vigorously and irradiating with a 200-W lamp. The end of the reaction was reached when the NBS was completely transformed into succinimide, which swam on the reaction mixture (about 1 h). After the mixture was cooled to room temperature, the succinimide was filtered off and the CCl_4 was evaporated. The residue was recrystallized from 2-propanol, giving **8a–d** as small white needles. **8a** (43 g, 76%): mp 84 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.19 (t, 6 H), 1.98 (t, 4 H), 4.17 (t, 4 H), 4.76 (s, 8 H). **8b** (44 g, 74%): mp 79 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.01 (t, 6 H), 1.52–1.91 (m, 8 H), 4.12 (t, 4 H), 4.72 (s, 8 H). **8c**: 53 g (78%); mp 91 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.92 (t, 6 H), 1.20–1.65 (m, 12 H), 1.87 (m, 4 H), 4.14 (t, 4 H), 4.75 (s, 8 H). **8d** (49 g, 72%): mp 163 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.94 (t, 6 H), 1.44 (m, 8 H), 1.85 (m, 4 H), 2.74 (t, 4 H), 4.45 (s, 8 H).

Preparation of 5*H*,13*H*-Bis[1,3]dithiolo[4,5-*b*:4′,5′-*b*′]-benzo[1,2-*f*:4,5-*f*′]bis[1,4]dithiocin-2,10-dithione Derivatives (4). A solution of the zincate **5** (13 g, 0.018 mol) in 200 mL of THF/acetone (7:3) was added dropwise to a solution of 0.015 mol of the tetrabromodurene derivative (**8a–d**) in THF (200 mL) with vigorous stirring over a 2-h period. Stirring at room temperature was continued for a further 12 h. The precipitate was filtered off and washed by stirring in methanol/water (4:1) and acetone, giving the dithiones **4a–d** as yellow powders. The compounds were pure enough for all further reactions. **4b** and **4c** were recrystallized from xylene. **4a** (5.93 g, 63%): mp 230 °C dec; IR (KBr) 2950–2856 (m), 1062 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{22}S_{10}O_2$: C, 41.4; H, 3.5; S, 50.2. Found: C, 41.5; H, 3.7; S, 49.8. **4b** (5.50 g, 55%): mp 233 °C dec; IR (KBr) 2948–2855 (m), 1064 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{26}S_{10}O_2$: C, 43.2; H, 3.9; S, 48.1. Found: C, 43.3; H, 4.0; S, 47.8. **4c** (7.10 g, 65%): 238 °C dec; ^{1}H NMR (200 MHz, $C_2D_2Cl_4$, 333 K) δ 0.85 (t, 6 H), 1.15–1.54 (m, 12 H), 1.78 (m, 4 H), 3.75 (t, 4 H), 4.29 (s, 8 H); IR (KBr) 2948–2857 (m), 1064 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{34}S_{10}O_2$: C, 46.5; H, 4.7, S, 44.3. Found: C, 46.7; H, 4.8; S, 44.2. **4d** (5.42 g, 48%): mp 237

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(30) Durohydroquinone (**6**) was prepared by reduction of duroquinone (30 g, 0.183 mol) with sodium borohydride (30 g, 0.792 mol) in ethanol at 0 °C under argon analogous to the procedure described in ref 12.

°C dec; IR (KBr) 2960–2854 (m), 1754 (s), 1062 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{30}S_{10}O_4$: C, 44.8; H, 4.0; S, 42.7. Found: C, 45.1; H, 4.1; S, 42.5.

Preparation of 10,17-Epithio-9,2-(epithiometheno)-5*H*,12*H*-1,3-dithiolo[4,5-*b*]benzo[1,2-*f*:4,5-*f*']bis[1,4]dithiocin Derivatives (1). A 0.002-mol sample of the 5*H*,13*H*-bis[1,3]-dithiolo[4,5-*b*:4',5'-*b*']benzo[1,2-*f*:4,5-*f*']bis[1,4]dithiocin-2,10-dithione derivative (**4a–d**) was suspended under argon in a mixture of 40 mL of triethyl phosphite (dried over sodium and freshly distilled) and 100 mL of xylene. The suspension was refluxed for 3 h. After this time, the hot reaction mixture was filtered to remove undissolved components. The solution was concentrated in a rotary evaporator with a vacuum of 10^{-2} bar, and the remaining oil was treated with 100 mL of methanol. A yellow precipitate of **1** formed, which was filtered off, washed with methanol, and chromatographed on silica gel with methylene chloride. **1a** (444 mg, 38%): mp 227 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.15 (t, 6 H), 1.93 (m, 4 H), 4.25 und 4.37 (AB, 8 H), 4.51 (t, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) 14.3, 19.51, 31.7, 75.2, 130.9, 134.5, 136.7, 152.8 ppm; mass spectrum (FD), *m/z* 574 (M^+, 100). Anal. Calcd for $C_{22}H_{22}S_8O_2$: C, 46.0; H, 3.9; S, 44.6. Found: C, 46.0; H, 3.7; S, 44.7. **1b** (432 mg, 34%): mp 236 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.05 (t, 6 H), 1.58 (m, 4 H), 1.90 (m, 4 H), 4.24 and 4.36 (AB, 8 H), 4.55 (t, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) 14.0, 19.2, 31.7, 32.6, 75.1, 130.9, 134.5, 136.6, 152.9 ppm; mass spectrum (FD), *m/z* 602 (M^+, 100). Anal. Calcd for $C_{24}H_{26}S_8O_2$: C, 47.8; H, 4.4; S, 42.5. Found: C, 47.9; H, 4.4; S, 42.3. **1c** (530 mg, 37%): mp 205 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (t, 6 H), 1.30–1.62 (m, 12 H), 1.90 (m, 4 H), 4.23 and 4.36 (AB, 8 H), 4.53 (t, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) 14.1, 22.7, 25.6, 30.5, 31.7, 31.8, 75.3, 130.8, 134.5, 136.6, 152.8 ppm; mass spectrum (FAB), *m/z* 658 (M^+, 100). Anal. Calcd for $C_{28}H_{34}S_8O_2$: C, 51.0; H, 5.2; S, 39.0. Found: C, 51.1; H, 5.1; S, 38.8. **1d** (804 mg, 59%): mp 186 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, 6 H), 1.42 (m, 8 H), 1.81 (m, 4 H), 2.72 (t, 4 H), 3.76 and 4.39 (AB, 8 H); ^{13}C NMR (50 MHz, $CDCl_3$) 13.8, 22.3, 24.5, 31.4, 32.0, 34.0, 129.8, 134.2, 135.5, 146.7, 171.6 ppm; mass spectrum (FD), *m/z* 686 (M^+, 100). Anal. Calcd for $C_{28}H_{30}S_8O_4$: C, 49.0; H, 4.4; S, 37.3. Found: C, 49.1; H, 4.5; S, 37.1.

7,15-Dihydro-6,14-bis(hexyloxy)-2,10-bis(methylthio)-5*H*,13*H*-bis[1,3]dithiolo[4,5-*b*:4',5'-*b*']benzo[1,2-*f*:4,5-*f*']bis-[1,4]dithiocinium Bistetrafluoroborate. Dimethoxycarbonium tetrafluoroborate (**11**)[31] (3.4 g, 0.021 mol) was suspended in dry methylene chloride (100 mL) under argon. A suspension of dithione **4c** (3 g, 0.004 155 mol) in methylene chloride (100 mL) was added. The reaction mixture was stirred at room temperature for 24 h. During this time a homogeneous solution formed. After evaporation of the methylene chloride, the remaining dark brown oil was dissolved in 20 mL of acetonitrile. The solution was filtered and poured into 1 L of diethyl ether while stirring vigorously. The resulting precipitate was filtered off in a cooled Büchner funnel and dried under reduced pressure, giving 3 g (79%) of **12** as a brown solid: mp 103 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.94 (t, 6 H), 1.29–1.58 (m, 12 H), 1.80 (m, 4 H), 3.05 (s, 6 H), 3.70 (t, 4 H), 4.56 (s, 8 H); ^{13}C NMR (50 MHz, $CDCl_3$) 14.0, 22.5, 23.0, 25.6, 30.1, 31.6, 34.7, 76.6, 131.5, 151.5, 151.9, 206.0 ppm.

7,15-Dihydro-6,14-bis(hexyloxy)-2,10-bis(methylthio)-5*H*,13*H*-bis[1,3]dithiolo[4,5-*b*:4',5'-*b*']benzo[1,2-*f*:4,5-*f*']bis-[1,4]dithiocin (13). To a solution of 2.9 g (0.003 13 mol) of **12** in 120 mL of acetonitrile was added 0.616 g (0.0163 mol) of sodium borohydride in small portions at room temperature. The mixture was stirred for 1 h. After addition of water (200 mL), the precipitate of **13** was collected by filtration. The crude product was chromatographed on silica gel with methylene chloride. Recrystallization from a small amount of methylene chloride afforded **13** (1.6 g, 68%) as a white powder: mp 196 °C dec; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.95 (t, 6 H), 1.39 (m, 8 H), 1.52 (m, 4 H), 1.86 (m, 4 H), 2.15 (s, 6 H), 3.89 (m, 4 H), 4.09 and 4.39 (AB, 8 H), 5.58 (s, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2) 12.9, 14.2, 23.0, 26.0, 30.6, 32.1, 33.6, 58.0, 77.0, 128.0, 131.3, 152.2 ppm; mass spectrum (EI), *m/z* 754 (M^+, 3.1), 707 ($M^+ - SCH_3$, 100), 660 ($M^+ - 2\,SCH_3$, 59).

(31) Dimethoxycarbonium tetrafluoroborate (**11**) was prepared from $BF_3{\cdot}OEt_2$ (2.7 mL of a 10 M solution, 0.027 mol) and trimethyl orthoformate (2.7 mL, 0.0245 mol) according to the procedure given in ref 13a.

7,15-Dihydro-6,14-bis(hexyloxy)-5*H*,13*H*-bis[1,3]dithiolo-[4,5-*b*:4',5'-*b*']benzo[1,2-*f*:4,5-*f*']bis[1,4]dithiocinium Bistetrafluoroborate (10). A cooled (0 °C) suspension of 254 mg (0.000 337 mol) of **13** in acetic anhydride (10 mL) under argon was treated with tetrafluoroboric acid (0.003 285 mol, 0.45 mL of a 54% solution in diethyl ether). The mixture was stirred at 0 °C for 90 min. During this time a homogeneous solution formed. The product was precipitated by addition of 100 mL of diethyl ether/hexane (1:1) at −15 °C. The precipitate was filtered, giving, after washing with diethyl ether and methylene chloride, 222 mg (79%) of **10** as a beige-colored powder: mp 191 °C dec; ^{1}H NMR (400 MHz, acetonitrile-d_3; the ^{1}H NMR shows two ion-pair isomers I and II) δ 0.96 (m, 6 H), 1.41 (m, 8 H), 1.54 (m, 4 H), 1.87 (m, 4 H), 3.78 (t of I) and 3.90 (m of II) (together 4 H), 4.51 (s of I) and 4.09, 4.12, 4.37, 4.40 (AB of II) and 4.58, 4.61, 4.73, 4.76 (AB of II) (together 8 H), 10.80 (s of I) and 5.95 (s of II) and 10.78 (s of II) (together 2 H); ^{13}C NMR (75 MHz, acetonitrile-d_3) 14.4, 23.4, 26.3, 30.8, 32.4, 35.1, 77.1, 132.6, 152.4, 160.7, 180.2 ppm.

Preparation of 1c via Amine-Induced Coupling of 10. To a solution of 160 mg (1.92×10^{-4} mol) of **10** in 30 mL of acetonitrile under argon was added 5 mL of diisopropylethylamine via a syringe. The solution was then stirred at room temperature for 1 h. After this period, the solvent was evaporated and the remaining solid was washed with methanol. Chromatography on silica gel with methylene chloride afforded 77 mg (61%) of **1c**.

Preparation of the 2,3-Bis(bromomethyl)benzene Derivatives 19b and 19c. 1,4-Bis(hexyloxy)-2,3-dimethylbenzene, as well as 1,4-bis(butyloxy)-2,3-dimethylbenzene were prepared from 2,3-dimethyl-*p*-hydroquinone according to the procedure used for the synthesis of **7a–c**. Photochemically induced bromination of 5.4 g (0.0216 mol) of 1,2-bis(butyloxy)-2,3-dimethylbenzene, analogous to the preparation of **8a–d**, afforded the 1,4-bis(butyloxy)-2,3-bis(bromomethyl)-5-bromobenzene (**19c**) as a colorless oil (5.15 g, 49%): bp 205 °C (6×10^{-2} bar); ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.99 (t, 3 H), 1.01 (t, 3 H), 1.30–2.01 (m, 8 H), 3.98 (t, 2 H), 4.04 (t, 2 H), 4.70 (s, 2 H), 4.71 (s, 2 H), 7.04 (s, 1 H).

The synthesis of **19b** succeeded in the following manner: To a refluxing solution of 10 g (0.033 mol) of 1,4-bis(hexyloxy)-2,3-dimethylbenzene in 100 mL of carbon tetrachloride was added 12 g (0.0674 mol) of NBS in 400-mg portions. A small amount of α,α'-azoisobutyronitrile (AIBN) was added before each NBS addition (the solution should be nearly colorless before each new AIBN and NBS addition). After all of the NBS was added (about 2 h), the succinimide was filtered off and the solvent was evaporated. Recrystallization of the solid residue from ethanol gave 13.6 g (89%) of **19b** as small white needles: mp 39 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 6 H), 1.21–1.62 (m, 12 H), 1.80 (m, 4 H), 3.98 (t, 4 H), 4.74 (s, 4 H), 6.78 (s, 2 H).

Preparation of the 4,5-(*o*-Xylylenedithio)-2-thioxo-1,3-dithiole Derivatives 3b and 3c. A solution of the zincate **5** (3.7 g, 0.005 13 mol) in 100 mL of THF/acetone (7:3) was added dropwise to a solution of 0.01 mol of **19b** or **19c**, respectively, in THF (100 mL) with vigorous stirring over a 2-h period. Stirring was continued for 12 h at room temperature. The solvent was then evaporated, and the solid residue was stirred in methanol/water (4:1) to remove inorganic components. The crude product was chromatographed on silica gel with methylene chloride, giving **3b/c** as yellow powders. **3b** (3.38 g, 67%): mp 99 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (t, 6 H), 1.22–1.60 (m, 12 H), 1.69 (m, 4 H), 3.91 (t, 4 H), 4.40 (s, 4 H), 6.75 (s, 2 H). **3c** (2.20 g, 40%): mp 116 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.98 (t, 3 H), 1.00 (t, 3 H), 1.26–1.94 (m, 8 H), 3.92 (t, 2 H), 3.94 (t, 2 H), 4.38 (s, 2 H), 4.39 (s, 2 H), 7.01 (s, 1 H).

Preparation of 2b and 2c. The tetrathiafulvalenes **2b** and **2c** were prepared according to the procedure described for the synthesis of **1a–d**. After coupling of 1 g (0.002 mol) of **3b** and 1.05 g (0.002 mol) of **3c**, **2b** and **2c** were isolated as yellow powders. **2b** (0.31 g, 33%): mp 184 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (t, 12 H), 1.20–1.60 (m, 24 H), 1.78 (m, 8 H), 3.91 (t, 8 H), 4.30 (s, 8 H), 6.75 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$, + 3 mg $Cr(acac)_2$) 14.2, 23.0, 26.4, 29.8, 31.9, 32.1, 69.8, 111.9, 113.0, 125.4, 131.0, 150.8 ppm; mass spectrum (FD), *m/z* 936 (M^+, 100). **2c** (0.37 g, 38%): mp 206 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, 6 H), 1.00 (t, 6 H), 1.40–1.66 (m, 8 H), 1.66–1.94 (m, 8 H), 3.93 (t, 4 H), 3.95 (t, 4 H), 4.26 (s, 4 H), 4.29 (s, 4 H), 6.99 (s, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.8, 14.0, 19.2, 19.3, 31.3, 31.7, 31.8,

32.4, 68.9, 74.9, 112.0, 116.4, 117.0, 124.5, 128.1, 131.1, 133.2, 147.9, 153.0 ppm; mass spectrum (FAB), m/z 980, 982, 984 (M^+, 26, 89, 46), 213 (1,4-dioxo-2,3-dimethylene-5-bromobenzene, 100).

Protonation of 1a with Gaseous Hydrogen Chloride. Gaseous hydrogen chloride was bubbled through a 0.02 M solution of **1a** in chloroform or methylene chloride, whereat the color of the yellow solution turned red. The experiment can be carried out in deuterated solvents in a NMR tube for direct NMR spectroscopic monitoring of the formation of **20**: ^{1}H NMR (200 MHz, CD_2Cl_2, 263 K) δ 1.10 (t, 6 H), 1.85 (m, 4 H), 3.64 (m, 4 H), 4.35 and 4.53 (AB, 4 H), 4.29 and 4.79 (AB, 4 H), 6.22 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$, 293 K) 10.9, 23.7, 32.8, 60.2, 78.3, 129.8, 132.0, 151.9, 158.0, 221.0 ppm.

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Registry No. **1a**, 117408-79-4; **1b**, 138572-23-3; **1c**, 117408-80-7; **1d**, 139200-57-0; **2b**, 138572-22-2; **2c**, 139200-58-1; **3b**, 139200-59-2; **3c**, 117408-82-9; **4a**, 117408-77-2; **4b**, 139200-60-5; **4c**, 117408-78-3; **4d**, 139200-61-6; **5**, 72022-68-5; **6**, 527-18-4; **7a**, 139200-62-7; **7b**, 139200-63-8; **7c**, 117408-74-9; **7d**, 139200-64-9; **8a**, 117408-75-0; **8b**, 139200-65-0; **8c**, 117408-76-1; **8d**, 139200-66-1; **10**, 139200-68-3; **11**, 139200-70-7; **12**, 139200-72-9; **13**, 139200-73-0; **19b**, 139200-74-1; **19c**, 117408-81-8; **20**, 139200-75-2; 1,4-bis(hexyloxy)-2,3-dimethylbenzene, 139200-76-3; 1,4-bis(butyloxy)-2,3-dimethylbenzene, 139200-77-4; 2,3-dimethyl-*p*-hydroquinone, 608-43-5; hexanoyl chloride, 142-61-0; 1-bromopropane, 106-94-5; 1-bromobutane, 109-65-9; 1-bromohexane, 111-25-1.

Supplementary Material Available: Positional parameters and their estimated standard deviations (Table 1), bond distances (Table 2), bond angles (Table 3), dihedral angles between planes (Table 4) of **1a**, and ^{1}H NMR spectra of selected compounds (28 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.

Chiral Synthesis via Organoboranes. 34. Selective Reductions. 47. Asymmetric Reduction of Hindered α,β-Acetylenic Ketones with *B*-Chlorodiisopinocampheylborane to Propargylic Alcohols of Very High Enantiomeric Excess. Improved Workup Procedure for the Isolation of Product Alcohols

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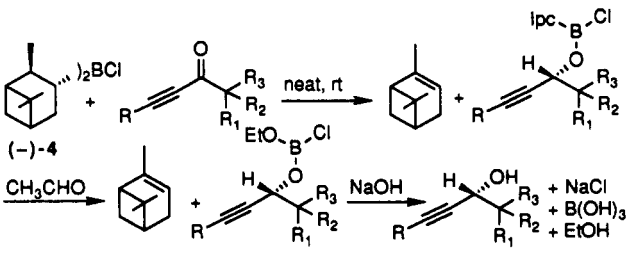
The Midland reagent, Alpine-Borane (**2a**), is excellent for the asymmetric reduction of many acetylenic ketones, but it fails with hindered derivatives. On the other hand, *B*-chlorodiisopinocampheylborane (DIP-Chloride, **4**) reacts with hindered α,β-acetylenic ketones to provide the corresponding propargylic alcohols in 96 to ≥99% ee. The reaction is in accordance with the tentative mechanism proposed earlier. While 4-phenyl-3-butyn-2-one is reduced in only 21% ee, **4** reduces 4-methyl-1-phenyl-1-pentyn-3-one in 53% ee and 4,4-dimethyl-1-phenyl-1-pentyn-3-one in ≥99% ee. The generality of this observation is demonstrated by reducing a series of hindered acetylenic ketones with increasing steric requirements and differing electronic environments. Thus, 2,2-dimethyl-4-tridecyn-3-one, 1-cyclopentyl-4,4-dimethyl-1-pentyn-3-one, and 3,3-dimethyl-5-tetradecyn-4-one are all reduced to the corresponding alcohols in ≥99% ee. 4,4-Dimethyl-1-pentadecen-6-yn-5-one and 2-methyl-2-phenyl-4-tridecyn-3-one are reduced in 96% ee and 97% ee, respectively. A modified and operationally simpler workup procedure for obtaining the alcohols in high isolated yields is described. Comparison of reagent **4** with **2a** is also made, making clear the range of applicability of each reagent. This development makes it possible to reduce asymmetrically any acetylenic ketone by a judicious choice of either **2a** or **4**.

Asymmetric reduction of prochiral ketones, one of the best methods for the preparation of optically active *secondary* alcohols,[2] became more practical when Brinkmeyer and Kapoor reported[3] the successful reduction of alkynyl ketones to the corresponding propargylic alcohols in 62–84% ee with Mosher's (2*S*,3*R*)-(+)-4-(dimethylamino)-1,2-diphenyl-3-methyl-2-butanol (Aldrich, Chirald)–$LiAlH_4$ (LAH) complex (**1**).[4] Until this discovery in 1977 aralkyl ketones had been the only class of ketones that had provided satisfactory asymmetric reduction. Since then asymmetric reduction of ketones has developed into a major area of asymmetric synthesis.[5] Of the many classes of ketones that can be reduced asymmetrically, the class of α,β-acetylenic ketones has achieved special importance because the product alcohol retains the acetylenic moiety which can be transformed into many other functional groups[6] and many research groups have sought to

Scheme I



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(2) (a) Brown, H. C.; Ramachandran, P. V. *Acc. Chem. Rev.* **1992**, *25*, 16. (b) Midland, M. M. *Chem. Rev.* **1989**, *89*, 1553. (c) Morrison, J. D., Ed. *Asymmetric Synthesis*; Academic: New York, 1983; Vol. 2, Chapters 2, 3, and 4.

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(5) For a review of various chiral reducing agents, see: Brown, H. C.; Park, W. S.; Cho, B. T.; Ramachandran, P. V. *J. Org. Chem.* **1987**, *52*, 5406.

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