Asymmetric Reduction. A Convenient Method for the Reduction of Alkynyl Ketones

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Received September 19, 1995 (Revised Manuscript Received February 22, 1996)

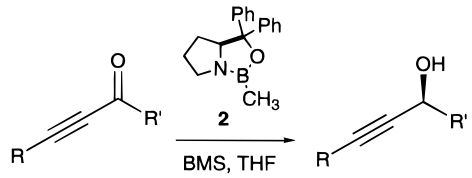
In order to prepare a cyclic enediynediol for attachment to biopolymers, we required a method for the asymmetric reduction of alkyl alkynyl ketones. In the system of interest, both Alpineborane[1] and Binal-H[2] gave unsatisfactory results. We postulated that the long reaction times required for reduction by these reagents allowed for the competitive degradation of our substrate. We therefore sought an alternative reagent which would effect the desired chiral reduction rapidly at low temperature.[3]

Since the initial reports by Itsuno[4] on the chiral reduction of ketones by borane in the presence of an amino acid, numerous papers have described similar reductions by borane in the presence of chiral oxazaborolidine catalysts.[5] Although these reagents have been applied to produce a wide variety of chiral alcohol structures, to date this methodology has not been applied to the reduction of alkynyl ketones.

We have found that the reduction of conjugated alkynyl ketones **1** with borane methyl sulfide complex (BMS) in the presence of chiral oxazaborolidine **2** (derived from α,α-diphenyl-L-prolinol) affords propargyl alcohols **3** in a reaction which is both enantioselective and relatively fast at low temperature (Scheme 1). We have now assigned the configuration of these alcohols (see below) as *S*.

Preparation of Substrates and Reagents. The oxazaborolidine **2** could be prepared just prior to reaction and used without purification. Alternatively, if a larger quantity of reagent was desired for use at a later date, the reagent could be purified by vacuum distillation and stored according to the procedure described by Mathre, Jones, Blacklock, *et al.*[6]

Scheme 1

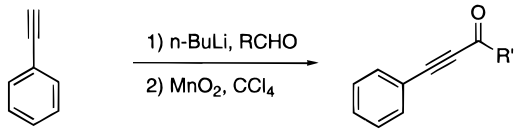


1a-g **3a-g**

1a R = Ph, R' = -CH_3
1b R = Ph, R' = -CH_2CH_3
1c R = Ph, R' = -$(CH_2)_5CH_3$
1d R = Ph, R' = -$CH(CH_3)_2$
1e R = Ph, R' = -cyclohexyl
1f R = H, R' = -$(CH_2)_6CH_3$
1g R = H, R' = -cyclohexyl

3a R = Ph, R' = -CH_3
3b R = Ph, R' = -CH_2CH_3
3c R = Ph, R' = -$(CH_2)_5CH_3$
3d R = Ph, R' = -$CH(CH_3)_2$
3e R = Ph, R' = -cyclohexyl
3f R = H, R' = -$(CH_2)_6CH_3$
3g R = H, R' = -cyclohexyl

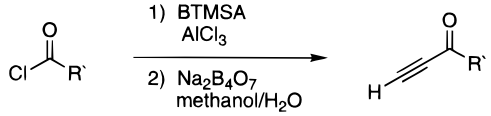
Scheme 2



1b-e

1b R' = -CH_2CH_3
1c R' = -$(CH_2)_5CH_3$
1d R' = -$CH(CH_3)_2$
1e R' = -cyclohexyl

Scheme 3



4 **1f,g**

Of the ketones chosen for study only 5-phenyl-4-butyn-3-one (**1a**) was commercially available.[7] Phenyl alkynyl ketones **1b**−**e** were conveniently obtained by the two-step sequence shown in Scheme 2. Thus, addition of an aldehyde to lithiated phenylacetylene yielded the racemic propargyl alcohol. Subsequent oxidation of the crude material with manganese dioxide generated the desired ketones in moderate-to-good yields.

Model systems for the study of the reduction of terminal alkynyl ketones were obtained most efficiently according to literature procedures (Scheme 3).[8] Thus, ynones **1f** and **1g** were prepared by treating the commercially available acid chlorides with bis(trimethylsilyl)-acetylene (BTMSA) in the presence of aluminum chloride followed by desilylation of the Friedel−Craft product.

Asymmetric Reduction Studies. Reactions were performed on approximately 50 mg of ketone in THF. The mole equivalents of oxazaborolidine **2** and BMS and the temperature were varied. The asymmetric reductions of phenyl alkynyl ketones **1a**−**e** were complete in less than 1 h at −30 °C.

The reduction, performed with either stoichiometric or catalytic amounts of oxazaborolidine **2**, provided excellent yields of the propargyl alcohols. Enantiomeric excesses were determined by calculation of the integrals of the

† Government Assistance in Areas of National Need Fellow, 1993−95; Corinna Borden Keen Fellow, 1995−96.

(1) For a review of Alpineborane reductions, see: Midland, M. M.; Tramontano, A.; Kazubski, A. Graham, R. S.; Tsai, D. J. S.; Cardin, D. B. *Tetrahedron* **1984**, *40*, 1371.

(2) (a) Nishizawa, M.; Yamada, M.; Noyori, R. *Tetrahedron Lett.* **1981**, *22*, 247. (b) Noyori, R.; Tomino, I.; Tanimoto, Y.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6709.

(3) The complementary approach, enantioselective addition of an acetylide to an aldehyde, was not necessarily compatible with our overall scheme. For the enantioselective alkynylation of aldehydes, see: Corey, E. J.; Cimprich, K. A. *J. Am. Chem. Soc.* **1994**, *116*, 3151.

(4) (a) Itsuno, S.; Ito, K.; Hirao, A.; Nakahama, S. *J. Chem. Soc., Chem. Commun.* **1983**, 469. (b) Itsuno, S.; Ito, K.; Hirao, A.; Nakahama, S. *J. Org. Chem.* **1984**, *49*, 555. (c) Itsuno, S.; Nakano, M.; Miyazaki, K.; Masuda, H.; Ito, K.; Hirao, A.; Nakahama, S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2039.

(5) (a) Corey E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551. (b) For an extensive review with 74 references see: Wallbaum, S.; Martens, J. *Tetrahedron Asymmetry* **1992**, *3*, 1475. (c) Corey, E. J.; Azimioara, M.; Sarshar, S. *Tetrahedron Lett.* **1992**, *33*, 3429. (d) Jones, D. K.; Liotta, D. C.; Shinkai, I.; Mathre, D. J. *J. Org. Chem.* **1993**, *58*, 799.

(6) Mathre, D. J.; Jones, T. K.; Xavier, L. C.; Blacklock, T. J.; Reamer, R. A.; Mohan, J. J.; Turner Jones, E. T.; Hoogsteen, K.; Baum, M. W.; Grabowski, E. J. J. *J. Org. Chem.* **1991**, *56*, 751.

(7) Ketone **1a** was purchased from the Aldrich Chemical Co. Ketones **1b**,**d**−**g** and alcohols **3a**−**d**,**f**,**g** are known compounds (see Table 1 for references).

(8) (a) Schwab, J. M.; Lin, D. C. T. *J. Am. Chem. Soc.* **1985**, *107*, 6046. (b) Walton, D. R. M.; Waugh, F. *J. Organomet. Chem.* **1972**, *37*, 45.

S0022-3263(95)01712-9 CCC: $12.00

NMR spectra of the corresponding Mosher esters.[9] In all cases, the results (yield and enantiomeric excesses) obtained with reagent prepared immediately prior to reduction were comparable to those obtained with reagent which had been stored.

The enantiomeric excess of the product alcohol was significantly larger when an excess of the oxazaborolidine **2** was used. For example, the reduction of ketone **1e** at −30 °C with 5 mol equiv of BMS in the presence of 0.5 mol equiv of oxazaborolidine **2** provided alcohol **3e** in 86% enantiomeric excess (entry 11, Table 1). However, the same reaction with 2 mol equiv of the reagent, under otherwise identical conditions, gave a 96% enantiomeric excess (entry 13, Table 1).

Table 1. Reduction of Alkynyl Ketones

entry	ketone	**2** (equiv)	BMS (equiv)	*T* (°C)	alcohol **3**	yield (%)	ee (%)
1	**1a**	2.0	5.0	−20	**3a**[1]	80	64
2	**1a**	2.0	5.0	−30	**3a**	80	71
3	**1a**	2.0	5.0	−40	**3a**	73	66
4	**1b**[10]	2.0	5.0	−30	**3b**[11]	84	88
5	**1c**	1.0	5.0	−30	**3c**[12]	84	82
6	**1c**	2.0	5.0	−30	**3c**	73	88
7	**1d**[13]	2.0	5.0	−30	**3d**[14]	85	94
8	**1e**[15]	1.0	5.0	0	**3e**	30	74
9	**1e**	1.0	5.0	−30	**3e**	100	92
10	**1e**	1.0	5.0	−50	**3e**	89	86
11	**1e**	0.5	5.0	−30	**3e**	83	86
12	**1e**	0.5	1.1	−30	**3e**	90	84
13	**1e**	2.0	5.0	−30	**3e**	92	96
14	**1f**[16]	2.0	5.0	0	**3f**[17]	26	86
15	**1f**	2.0	5.0	−10	**3f**	48	86
16	**1f**	2.0	5.0	−30	**3f**	54	95
17	**1g**[18]	2.0	5.0	0	**3g**[18]	35	86
18	**1g**	2.0	5.0	−30	**3g**	81	98

The data also show that the selectivity of the reduction improved when the size of the alkyl group increased. For example, the reduction of alkynyl ketone **1a** (R′ = methyl) at −30 °C with 2 mol of oxazaborolidine **2** and 5 mol of BMS per mole of substrate gave **3a** with 71% ee (entry 2, Table 1). Under the same conditions, the sterically more hindered ketone **1b** (R′ = ethyl) provided the corresponding alcohol **3b** with an 88% ee and ketone **1e** (R′ = cyclohexyl) provided alcohol **3e** with a 96% ee (entries 4 and 13, respectively, Table 1).

The terminal alkynyl ketones **1f** and **1g** were reduced more rapidly (<20 min) than the phenylalkynyl ketones **1a**−**e**, giving equally satisfactory results (Scheme 1, Table 1). Again, the size of the alkyl group appears to influence the selectivity of the reaction. For example, reduction of ketone **1f** at −30 °C provided alcohol **3f** in 54% yield with 95% ee (entry 16, Table 1); under the same conditions the sterically more hindered ketone **1g** afforded propargyl alcohol **3g** in 81% yield with 98% ee (entry 18, Table 1).

Assignment of Configuration of Chiral Propargyl Alcohols. Comparison of the ^{1}H NMR spectra of the (*R*)-Mosher esters[19] of alcohols **3a**−**g** suggested that the predominant component of each belonged to a single diastereomeric series. For each sample, the major diastereomer exhibited the higher field methoxyl signal (3.55 *vs* 3.60 ppm).[20]

Additional correlations could be made for the Mosher esters of the terminal propargyl alcohols. The (*S*)-Mosher ester of alcohol **3f** shows the signals for both methoxyl and acetylenic peaks of the major diastereomer (3.60 and 2.53 ppm) downfield of the corresponding signals for the minor diastereomer (3.55 and 2.50 ppm). The same chemical shift relationships were observed for the (*S*)-Mosher esters of the major and minor enantiomers of **3g**.[21]

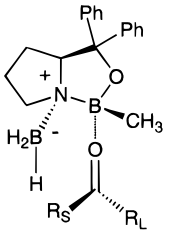


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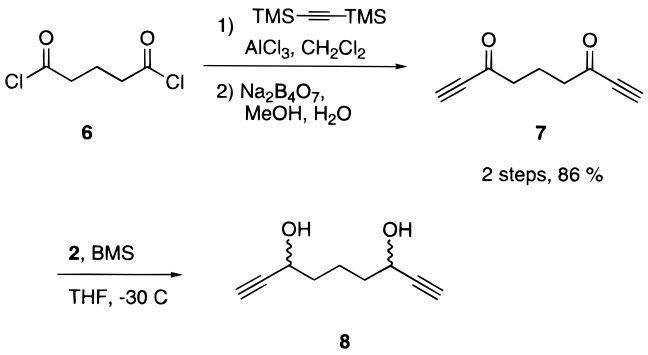
Figure 1.

Scheme 4



The major enantiomer of alcohol **3f** was assigned the *S*-configuration by comparison of the optical rotation of our sample with the literature value, $[\alpha]^{20}_D = -3.9°$ ($CHCl_3$).[17b] The optical rotation of alcohol **3f** (prepared under the conditions indicated in entry 16, Table 1) was $[\alpha]^{25}_D = -3.4°$ ($CHCl_3$). The enantiomeric excess for this sample as determined from the ^{1}H NMR of the Mosher ester was 90%. *We therefore assign the absolute configuration of all chiral alcohols* (**3a**−**g**) *obtained in this study as S and we conclude that reduction of alkynyl ketones with BMS in the presence of oxazaborolidine* **2** *provides the corresponding propargyl alcohols with the S-configuration.*

The observed enantiomeric assignments are consistent with the general mechanistic picture originally proposed by Corey.[5a] It appears that the alkynyl substituent adopts the position of the sterically smaller R_S and the bulkier group occupies the R_L position (Figure 1) for the proposed transition state assembly (**5**).

Synthesis of a Model Chiral Diynediol. Because we are particularly interested in the synthesis of chiral diynediols, we examined the reduction of diynedione **7**. This substrate was readily obtained by addition of 2.2 mol equiv of bis(trimethylsilyl)acetylene to glutaroyl dichloride (**6**) in the presence of aluminum chloride and desilylation of the crude double acylation product (86%, Scheme 4).

Reduction of diynedione **7** at −30 °C with 5 mol of BMS and 1 mol of oxazaborolidine **2** per mole of dione provided a mixture of diastereomeric diols **8** in 84% yield. The ratio of diasteriomers was determined by analysis of the

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(12) Daeuble, J. F.; McGettigan, C.; Stryker, J. M. *Tetrahedron Lett.* **1990**, *31*, 2397.

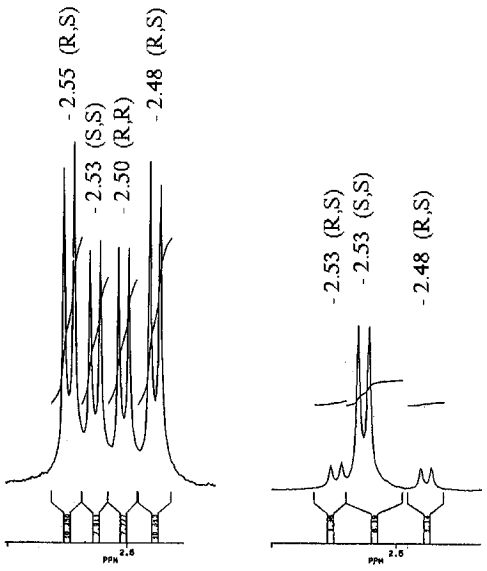

Figure 2.

^{1}H NMR spectra of the Mosher diesters of the product mixture. The (*S*)-Mosher diesters exhibited three doublets in the region corresponding to signals for acetylenic protons: a small signal at 2.55 ppm, a large signal at 2.53 ppm, and a second small signal (equal in intensity to the first signal) at 2.48 ppm (Figure 2).

This pattern was consistent with a mixture of Mosher esters in which the major product is derived from the (*S*,*S*)-diol and the minor product from the (*R*,*S*)-diol if and only if the Mosher ester of the (*R*,*S*)-diol gives two signals, neither of which coincides with that of the (S)-Mosher ester of the (*S*,*S*)-diol. In order to verify this premise, we prepared the (*S*)-Mosher diester of a sample of diols **8** which had been prepared by a nonstereoselective process.[22] This sample showed four doublets of approximately equal intensity in the acetylenic proton region: at 2.55, 2.53, 2.50, and 2.48 ppm. We conclude then that, in the (*S*)-Mosher esters of diols **8**, the signals at 2.53 represent the ester of the (*S*,*S*)-diol, that at 2.50 ppm the ester of the (*R*,*R*)-diol, and those at 2.55 and 2.48 the two diastereomeric centers in the (*R*,*S*)-diol.

Our chiral reduction then afforded a major diol with *S*,*S*-configuration in 54% de (77% ee per carbonyl reduced). The minor product diol was assigned the *R*,*S*-configuration. No (*S*)-Mosher ester product derived from (*R*,*R*)-diol **8** was detected.

As expected, the selectivity of the reduction improved when an excess of oxazaborolidine **2** was used. When diynedione **7** was reduced with 3 mol of oxazaborolidine **2** per mole of doine, diols **8** were obtained in 67% yield with a 66% de (83% ee per carbonyl reduced) of the *S*,*S*-product.

Conclusion

In this study we have shown the general applicability of chiral oxazaborolidine **2** to the reduction of alkynyl ketones. The short reaction times and low temperatures required for reduction make this procedure an attractive alternative to existing methodology, especially when longer reaction times are problematic. Therefore, the methodology described above represents a useful addition to the tools of asymmetric synthesis.

Experimental Section

General. Melting points are uncorrected. High-resolution mass spectra were obtained under electron impact (EI), chemical ionization (CI), or fast atom bombardment (FAB) conditions. Thin layer chromatography (TLC) was carried out on precoated silica gel 60F 250 plates. Preparative thin layer chromatography was performed on precoated silica gel plates (1000 mm). Flash column chromatography was performed with silica gel 60 (230−400 mesh). THF was distilled from sodium benzophenone ketyl. Methylene chloride was distilled from CaH_2. Toluene was dried over 4 Å molecular sieves.

General Procedure for the Preparation of Alkynyl Ketones. The procedure described for **1e** was also applied for the syntheses of **1b**−**d**.

1-Cyclohexyl-3-phenyl-2-propyn-1-one (1e). To a solution of 476 mg (4.66 mmol) of phenylacetylene in 5 mL of dry THF at 0 °C was added 2.91 mL (4.66 mmol) of n-BuLi (1.6 M in hexane). After 15 min, 0.57 mL (52 mg, 4.7 mmol) of cyclohexanecarboxaldehyde was added dropwise over 2 min. After being stirred for 30 min, the reaction was quenched with 1 mL of methanol and diluted with 20 mL of ether. The solution was washed with 1 M HCl (2 × 20 mL) followed by water, 5% $NaHCO_3$ (2 × 20 mL), and brine (2 × 20 mL). The organic layer was dried over Na_2SO_4 and filtered through a thin bed of silica gel. Evaporation of the solvent gave an orange oil. This crude material was dissolved in 15 mL of CCl_4. After addition of two scoops of powdered 4 Å molecular sieves, the reaction mixture was aged for 30 min. Then, 7.31 g (84.1 mmol) of MnO_2 was added. After 20 min the black slurry was filtered through a glass fritt and washed through with two 10 mL portions of CCl_4. Evaporation of the solvent followed by bulb-to-bulb vacuum distillation afforded 762 mg (77% overall) of ketone **1e** as a pale yellow oil. In some cases, a portion of the ketone was further purified just prior to reduction by preparative thin layer chromatography (1:4 ethyl ether:hexanes).

1-Phenyl-1-pentyn-3-one (1b). Phenylacetylene (527 mg, 5.16 mmol), BuLi (3.23 mL, 5.2 mmol), propionaldehyde (0.37 mL, 5.2 mmol), and MnO_2 (8.2 g, 94 mmol) afforded 446 mg (55%).

1-Phenyl-1-nonyn-3-one (1c). Phenylacetylene (899 mg, 8.80 mmol), BuLi (5.50 mL, 8.8 mmol), heptanal (1.23 mL, 8.80 mmol), and MnO_2 (11.5 g, 132 mmol) afforded 1.08 g (58%): IR (neat) 3061, 2929, 2201, 1672 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.57 (m, 2 H), 7.42 (m, 3 H), 2.65 (t, J = 7.4 Hz, 2 H), 1.75 (m, 2 H), 1.34 (m, 6 H), 0.90 (t, J = 6.2 Hz, 3 H); ^{13}C NMR ($CHCl_3$) δ 188.3, 133.0, 130.6, 120.1, 90.5, 87.8, 45.5, 31.5, 28.6, 24.1, 22.4, 14.0; HRMS (MH^+) calcd 215.1436, found 215.1432.

4-Methyl-1-phenyl-1-pentyn-3-one (1d). Phenylacetylene (542 mg, 5.32 mmol), BuLi (3.33 mL, 5.3 mmol), isobutyraldehyde (0.38 mL, 5.3 mmol), and MnO_2 (8.4 g, 96 mmol) afforded 367 mg (39%).

General Procedure for the Preparation of Terminal Alkynyl Ketones. The procedure described for **6** was also applied for the syntheses of **1f** and **1g**.

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(18) Kluge, A. F.; Kertesz, D. J.; O-Yang, C.; Wu, H. Y. *J. Org. Chem.* **1987**, *52*, 2860.
(19) "(*R*)-Mosher ester" refers to esters prepared from the (*S*)-Mosher acid chloride; likewise, "(*S*)-Mosher ester" refers to esters prepared from the (*R*)-Mosher acid chloride.
(20) Conversely, in the ^{1}H NMR spectra of the (*S*)-Mosher esters, the methoxyl peak for the major diastereomer appears downfield of the methoxyl peak for the minor diastereomer.
(21) As expected, the ^{1}H NMR spectrum of the (*R*)-Mosher ester of alcohol **3g** shows both the methoxyl and acetylenic hydrogen peaks for the major diastereomer to be upfield of those for the minor diastereomer.
(22) The *stereo-random* sample of diols **8** was obtained in 99% yield (983 mg, 6.47 mmol) by treatment of glutaric dialdehyde (653 mg) with an excess of ethynylmagnesium bromide (52 mL, 0.5 M in THF) in THF at ambient temperature.

1,8-Nonadiyne-3,7-dione (6). To a stirred solution of 1.81 g (10.7 mmol) of glutaroyl dichloride and 5.3 mL (4.0 g, 24 mmol) of bis(trimethylsilyl)acetylene in 50 mL of dry CH_2Cl_2 at 0 °C was added 3.3 g (25 mmol) of $AlCl_3$. After 2.5 h, the mixture was poured into 100 mL of ice−water. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic layer was washed with 5% $NaHCO_3$ (4 × 25 mL) and dried over $MgSO_4$. Filtration through silica gel followed by evaporation of the solvent and bulb to bulb vacuum distillation provided 2.97 g of a crude yellow oil (95% yield). This material (504 mg) was dissolved in 15 mL of methanol, and 2 mL of water and a catalytic amount of borax were added to the stirred solution. After 0.5 h the reaction was complete (TLC). The mixture was diluted with 40 mL of 1% citric acid and extracted with ethyl acetate (3 × 25 mL). The organic layer was washed with 40 mL of brine, dried over Na_2SO_4, and filtered. Evaporation of the solvent provided 237 mg of an orange oil. Flash chromatography (10% ethyl acetate in hexanes) afforded 214 mg (1.56 mmol, 89% yield overall) of dione **6** as a colorless oil: IR (neat) 3261, 2941, 2899, 2093, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.24 (s, 2 H) 2.68 (t, J = 3.1 Hz, 4 H), 2.03 (m, 2 H); ^{13}C NMR ($CHCl_3$) δ 186.0, 81.1, 78.9, 43.8, 17.3; HRMS calcd 148.0524, found 148.0520.

1-Decyn-3-one (1f). Octanoyl chloride (624 mg, 3.83 mmol), bis(trimethylsilyl)acetylene (0.95 mL, 4.2 mmol), $AlCl_3$ (560 mg, 4.21 mmol), and borax (93 mg, 0.38 mmol) afforded 458 mg (79%).

1-Cyclohexyl-2-propyn-1-one (1g). Cyclohexylcarboxylic acid chloride (708 mg, 4.83 mmol), bis(trimethylsilyl)acetylene (1.20 mL, 5.31 mmol), $AlCl_3$ (706 mg, 5.31 mmol), and borax (110 mg, 0.45 mmol) afforded 450 mg (73%).

General Procedure for the Synthesis of Propargyl Alcohols. The procedure described for the preparation of **3g** was applied, as modified in Table 1, for the syntheses of alcohols **3a**−**f** and diols **8**. For yield and enantiomeric excesses, refer to Table 1.

(*S*)-1-Cyclohexyl-2-propyn-1-ol (3g). A solution of 44 mg (0.32 mmol) of ketone **1g** in 1.5 mL of THF was dried over 4 Å molecular sieves for 2 h and subsequently added by syringe to a dry flask charged with 0.65 mmol of reagent **2** and 1.5 mL of THF. The solution was cooled to −30 °C. Then, 0.16 mL (1.6 mmol, ~10 M) of boron methyl sulfide complex was added over 5−10 min. Reaction progress was monitored by TLC (small aliquots were diluted with ether and quenched with 1 M HCl). After the reaction appeared to be complete, it was quenched by slow dropwise addition of 1.0 mL of methanol. The solution was diluted with 20 mL of ether and washed with saturated $NH_4^+Cl^-$ (2 × 10 mL), 5% $NaHCO_3$ (2 × 10 mL), and brine (2 × 10 mL). The organic layer was dried over $MgSO_4$, filtered through silica gel, and concentrated. Column chromatography (10% ethyl acetate in hexanes) afforded 36 mg (0.26 mmol, 81%) of a colorless crystalline solid: mp 49−50 °C.

(*S*)-1-Cyclohexyl-3-phenyl-2-propyn-1-ol (3e): IR (neat) 3340 (b), 2925, 2852, 2230, 1598, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (m, 2 H), 7.32 (m, 3 H), 4.39 (d, J = 5.9 Hz, 1 H), 2.05 (m, 1 H), 1.93 (m, 2 H), 1.78 (m, 2); ^{13}C NMR ($CDCl_3$) δ 131.7, 128.3, 128.2, 122.7, 89.2, 85.6, 67.7, 44.3, 28.6, 28.2, 26.4, 25.9, 25.88; HRMS calcd 214.1357, found 214.1355.

1,8-Nonadiyne-3,7-diol (8): IR (neat) 3290, 2949, 2868, 2114 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.41 (m, 2 H), 2.48 (d, J = 2.1 Hz, 2H), 1.79 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 84.63, 73.14, 62.09, 37.03, 20.62, 20.59; HRMS calcd (MH^+) 159.0916, found 159.0913.

Acknowledgment. Financial support from the Petroleum Research Fund (Grant No. 24010-AC, administered by the American Chemical Society) and from the National Science Foundation (Grant No. CHE-95-21055) is gratefully acknowledged.

Supporting Information Available: ^1H and ^{13}C NMR and IR spectra for 1-phenyl-1-nonyn-3-one (**1c**), 1-cyclohexyl-3-phenyl-2-propyn-1-ol (**3e**), 1,8-nonadiyne-3,7-dione (**6**), and 1,8-nonadiyne-3,7-diols (**8**) are provided. ^1H NMR spectra of the Mosher esters derived from alcohols **3f**,**g** and **8** are also provided (21 pages). This material is contained in 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.

JO951712O