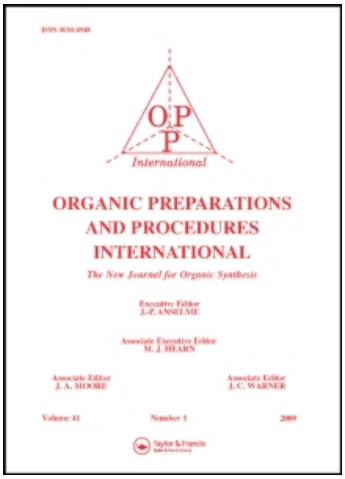

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PREPARATION OF LOW MOLECULAR WEIGHT, OPTICALLY ACTIVE ALLYLIC ALCOHOLS FROM (S)-(-)-ETHYL LACTATE

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6. For the synthesis of **2i** the aqueous layer was acidified with HCl (1:1) and then the neutral compounds were extracted with ether. The desired product was obtained by ether extraction of the basified aqueous layer.

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PREPARATION OF LOW MOLECULAR WEIGHT, OPTICALLY ACTIVE ALLYLIC ALCOHOLS FROM (*S*)-(-)-ETHYL LACTATE

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(07/27/92)

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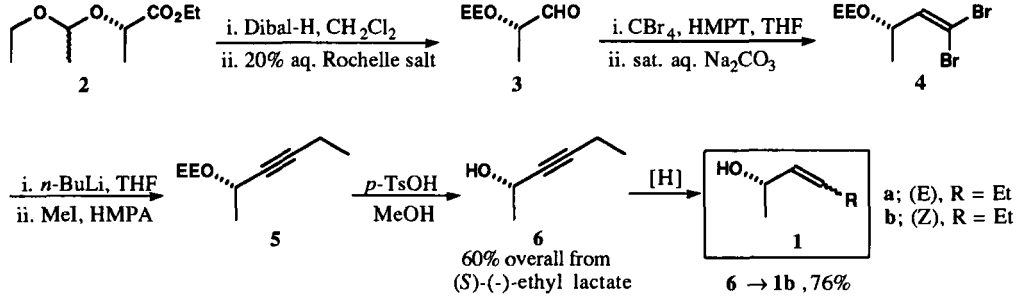
In conjunction with various [2,3]sigmatropic,[1] enolate Claisen,[2] and aza-Claisen[3] rearrangement studies ongoing in our laboratories, we required ready access to a variety of enantiomerically pure secondary allylic alcohols of general structure **1**. Optically enriched crotyl alcohols (i.e., **1** where



R = Me) are available by Sharpless kinetic resolution,[4] but optical purities are only modest (≈ 91% ee) and α,β-ynone reduction protocols[5] are problematic in purifying the volatile product from the chiral

auxiliary. In this study, we have developed a facile, multigram procedure to prepare (*S*)-propargyl (i.e., **6**) and (*S*)-(*E* or *Z*)-allyl (i.e., **1**) alcohols with ≥98% enantiomeric excess from (*S*)-(-)-ethyl lactate.

Diisobutylaluminum hydride reduction of ethyl [S-(R*,S*)]-2-(1-ethoxyethoxy)-propanoate (**2**)[6] followed by work-up with aqueous Rochelle salt (NaK tartrate) gave propanal derivative **3** in essentially quantitative yield. Treating this crude aldehyde with the carbon tetrabromide/[tris(dimethylamino)]phosphine (HMPT) reagent[7] in THF delivered dibromoalkene **4** in 84% yield. One-pot bis-dehydrobromination/alkylation cleanly produced alkyne **5** as long as hexamethylphosphoramide (HMPA) is added to the lithio alkyne intermediate ***after*** ethyl iodide has been added. If HMPA is added before the alkyl iodide, *n*-butyl bromide (from the reaction of **4** with *n*-BuLi) leads to significant amounts of butylated alkyne; butylation is completely avoided by first adding excess alkyl iodide. Alcohol deprotection with *p*-toluenesulfonic acid in methanol followed by simple distillation produced propargylic alcohol **6** in 60% overall yield from (*S*)-ethyl lactate. Subsequent lithium aluminum hydride reduction produced (*S*)-(*E*)-allylic alcohol **1a** while Lindlar catalyzed hydrogenation produced (*S*)-(*Z*)-allylic alcohol **1b** with yields of 78% and 76%, respectively. Finally, it is noteworthy that this chemistry provides access to a wide spectrum of (*S*)-allylic alcohols; limited only by the need for a primary alkyl iodide in the alkylation step.

EXPERIMENTAL SECTION

Elemental analyses were performed at the MidWest Microla, Indianapolis. Mass spectra were obtained with VG TRIO2 (high resolution; VG-11-250 data system) and VG ZAB-HS-2F (FAB) anaalytical instruments Dr. Dan Jones at the Facility for Advanced Instrumentation, University of California, Davis. Magnetic resonance spectra were obtained on a General electric QE-300 (330 MHz) spectrometer using the solvent as internal standard. Multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; bs, broad singlet; m, multiplet. Infrared spectra were recorded with an IBM FTIR-32 with IBM 9000 data system. Capillary GC analysis was performed on a Hewlett Packard 5890A gas chromatrograph equipped with flame ionization detector.

[*S*-(*R,*S**)]-2-(1-Ethoxyethoxy)propanal (3).**- Diisobutylaluminum hydride (580 mL of 1.0 M solution in hexanes) was added over 45 min to a -78° solution of ethyl [*S*,-(*R**,*S**)]-2-(1-ethoxyethoxy)propanoate (**2**[6]; 100.3 g, 0.53 mol) in dry CH_2Cl_2 (650 mL; 5 L/3-neck flask equipped with a mechanical stirrer) under argon. After stirring at -78° for an additional 1.25 hr, 20% aq. sodium potassium tartrate (3.5 L) was added to the vigorously stirred reaction mixture. The cooling bath was removed and, after 45 min of stirring, the two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (4 x 600 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated by rotary evaporation at room temperature yielding **3** (77.5 g, 100%) as a 1:1 mixture of diastereomers. Distillation leads to significant decomposition, so this pale yellow oil was used in the next step without further purification. FT-IR (neat): 2981, 2714, 1734 (C=O), 1133, 1100, 1077 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.99-1.45 (m, 9 H), 3.4-3.7 (m, 2 H), 3.87 (dq, *J* = 1.0, 7.0 Hz, 0.5 H, (*S*,*R**)-isomer, C<u>H</u>C(=O)H), 4.08 (dq, *J* = 1.0, 7.0 Hz, 0.5 H, (*S*,*S**)-isomer,

C<u>H</u>C(=O)H), 4.67 (q, J = 5.2 Hz, 0.5 H, (*S*,*R**)-isomer, $CH_3C\underline{H}(OR)(OR')$), 4.77 (q, J = 5.4 Hz, 0.5 H, (*S*,*S**)-isomer, $CH_3C\underline{H}(OR)(OR')$), 9.53 (d, J = 2.0 Hz, 0.5 H, (*S*,*R**)-isomer, C(=O)H), 9.56 (d, J = 1.0 Hz, 0.5 H, (*S*,*S**)-isomer, C(=O)H); ^{13}C NMR ($CDCl_3$): δ 14.9, 15.0, 15.5, 15.6, 20.0, 61.0, 61.3, 75.0, 99.4, 100.3, 203.4 (C=0). An analytical sample was prepared by preparative gas chromatography (SE-30).

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.56; H, 9.81

[*S*-(*R, *S**)]-2-(1-ethoxyethoxy)-3-hexyne (6).**- A solution of carbon tetrabromide (154.9 g, 0.47 mol) in dry THF (1.2 L; 3 L/3-neck flask equipped with a mechanical stirrer) under nitrogen was cooled to -30° and (tris(dimethylamino))phosphine (HMPT, 175 mL, 1.03 mol) was added over 45 min. The solution became cloudy from the first drop of HMPT and went through a yellow to green to brownish-pink color progression. The resulting slurry was stirred for an additional 10 min at -30° at which time aldehyde **3** (68.3 g, 0.467 mol; in 50 mL dry THF) was added, *via* cannula, over 15 min. After stirring for 1 hr at -30°, the cooling bath was replaced with an ice water bath for 30 min and the reaction was quenched by the addition of a saturated aqueous sodium carbonate solution (350 mL). THF was removed by rotary evaporation and the residue was taken up in water (1 L) and extracted with 1:1::ether:petroleum ether (4 x 500 mL). The combined organic phase was washed with water (0°, 2 x 200 mL) and brine, dried ($MgSO_4$), and concentrated by rotary evaporation to yield **4** (117.8 g, 84%) as a light orange-colored oil [*note: this reaction produces 2 equivalents of hexamethylphosphor-amide (HMPA) and all neccesary precautions for handling this compound must be exercised*]. FT-IR (neat): 2978, 1615 (C=CBr_2), 1443, 1131 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18-1.34 (m, 9 H), 3.40-3.68 (m, 2 H), 4.30-4.38 (m, 0.5 H, (*S*,*R**)-isomer, C<u>H</u>CH=CBr_2), 4.45-4.51 (m, 0.5 H, (*S*,*S**)-isomer, C<u>H</u>CH=CBr_2), 4.64-4.72 (m, 1 H, $CH_3\underline{H}C(OR)(OR')$), 6.38 (d, J = 8.3 Hz, 0.5 H, (*S*,*R**)-isomer, C<u>H</u>=CBr_2), 6.47 (d, J = 8.1 Hz, 0.5 H, (*S*,*S**)-isomer, C<u>H</u>=CBr_2); ^{13}C NMR ($CDCl_3$): δ 15.1, 15.3, 19.9, 20.0, 20.1, 20.2, 60.5, 61.2, 89.6, 98.1, 99.0, 140.7, 141.5.

Purification of [*S*-(*R**,*S**)]-1,1-bibromo-3-(1-ethoxyethoxy)but-1-ene (**4**) proved fruitless due to the lability of the 1-ethoxyethoxy protecting group. Thus, **4** was used in the next step without purification. *n*-BuLi (625 mL of a 1.6 M solution in hexanes) was added to a solution of **4** (125.5 g, 0.42 mol) in dry THF (1 L, under nitrogen) at -78° over 50 min. The flask was stirred for 1 hr at -78°, then warmed to room temperature for 1 hr, and finally cooled to 0°. Iodoethane (648 g, 4.2 mol) was added over 40 min followed by the addition of dry hexamethylphosphoramide (200 mL). The reaction was stirred 30 min at 0° and then the ice bath was removed and stirring was continued overnight at which time THF was removed *in vacuo* and the residue was taken up in 1.2 L of water. This aqueous phase was extracted with 1:1::ether:petroleum ether (4 x 500 mL) and the combined organic layers were washed with water (0°; 2 x 150 mL) and brine, dried ($MgSO_4$), and carefully concentrated by rotary evaporation to yield **5** (70.0 g, 100%, 1:1 mixture of diastereomers) as a light orange oil. FT-IR (neat) 2981, 2242 (CC), 1100, 1073 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (t, J = 7.5 Hz, 0.5 x 3H, (*S*,*R**)-isomer, $CCCH_2C\underline{H}_3$), 1.12 (t, J = 7.5 Hz, 0.5 x 3H, (*S*,*S**)-isomer, $CCCH_2C\underline{H}_3$), 1.19 (t, J = 7.1 Hz, 0.5 x 3H, (*S*,*R**)-isomer, $OCH_2C\underline{H}_3$), 1.19 (t, J = 7.1 Hz, 0.5 x 3H, (S,S*)-isomer,

$OCH_2C\underline{H}_3$), 1.32 (d, J = 5.3 Hz, 3H, (S,R*)- and (S,S*)-isomer, $C\underline{H}_3HC(OR)(OR')$), 1.38 (d, J = 6.6 Hz, 0.5 x 3H, (*S*,*R**)-isomer, $C\underline{H}_3HCCC$), 1.39 (d, J = 6.7 Hz, 0.5 x 3H, (*S*,*S**)-isomer, $C\underline{H}_3HCCC$), 2.19 (dq, J = 7.5, 1.8 Hz, 2H, $CCC\underline{H}_2CH_3$), 3.42-3.78 (m, 2H, $OC\underline{H}_2CH_3$), 4.30 (tq, J = 6.7, 1.9 Hz, 0.5 x 1H, (*S*,*R**)-isomer, $CH_3\underline{H}CCC$), 4.45 (tq, J = 6.7, 1.9 Hz, 0.5 x 1H, (*S*,*S**)-isomer, $CH_3\underline{H}CCC$), 4.83 (q, J = 5.3 Hz, 0.5 x 1H, (*S*,*R**)-isomer, $CH_3\underline{H}C(OR)(OR')$), 4.95 (q, J = 5.3 Hz, 1H, (*S*,*S**)-isomer, $CH_3\underline{H}C(OR)(OR')$); ^{13}C NMR ($CDCl_3$) δ 12.2, 13.7, 13.7, 15.0, 15.2, 20.1, 20.3, 22.5, 22.7, 60.0, 60.9, 61.1, 61.3, 79.3, 80.2, 85.7, 86.2, 97.5, 98.3.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.91; H, 10.53

(*S*)-3-Hexyn-2-ol (6).- To a 250 mL round-bottom flask equipped with a stir bar containing [*S*-(*R**, *S**)]-2(1-ethoxyethoxy)-3-hexyne (**5**; 70.6 g, 0.41 mol) and dry methanol (100 mL) was added p-toulenesulfonic acid (0.60 g, 3.68 mmol, monohydrate). The reaction vessel was fitted with a condenser, flushed with argon, and brought to reflux for 3 hrs at which time TLC analysis indicated the starting material had been consumed. The vessel was cooled to room temperature, potassium carbonate (7 g) was added, and stirring was continued an additional 30 min after which time the methanol was removed by atmospheric distillation through a Vigreux columnn (12 cm). The residue was diluted with ether (250 mL), filtered through a sintered glass funnel containing celite, and the filtrate concentrated at atmospheric pressure. The residue was distilled (90-95°/85 mm Hg) yielding **6** (29.1 g, 71.2 %) as a pale yellow oil. The overall yield from (*S*)-(-)-ethyl lactate was 60%, $[\alpha]_D^{20}$ -42.4° (*c* 3.75, $CHCl_3$). FT-IR (neat): 3381-3341 (OH), 2980, 2246 (CC), 1320, 1059 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.11 (t, J = 7.5 Hz, 3 H, $C\underline{H}_3CH_2CC$), 1.40 (d, J = 6.6 Hz, 3 H, CH_3CC), 2.04 (br. s, 1 H, $HCO\underline{H}$), 2.18 (dq, J = 7.5, 1.8 Hz, 2 H, $CH_3C\underline{H}_2CC$), 4.49 (q, J = 6.4 Hz, 1 H, $\underline{H}COH$); ^{13}C NMR ($CDCl_3$): δ 12.2, 13.7, 24.6, 58.3, 81.7, 85.7. HRMS (FAB): calcd for [$C_6H_{10}O$ + H] 99.0810; found, 99.0817.

(*S*)-(*E*)-3-Hexen-2-ol (1a).- Lithium aluminum hydride (5.8 g, 0.15 mol) was added to a 1 L round bottom flask that was then fitted with a condenser and blanketed under argon. Dry THF (250 mL) was added and the slurry was brought to a reflux. To this refluxing slurry was added propargylic alcohol **6** (10.0 g, 0.10 mol), as a solution in dry THF (10 mL), over 30 min. The reaction was refluxed for 10 hrs at which time it was cooled to 0° and quenched by the careful addition of water (6 mL), 10% sodium hydroxide solution (6 mL), and water (12 mL). After stirring at room temperature for 2 hrs, this mixture was filtered and the aluminum salts were well triturated with ether. The combined organic rinses were dried ($MgSO_4$) and concentrated by distillation through a 12 cm vigeroux column at atmospheric pressure. The resulting crude product was distilled (87-90°/92 mm Hg) to yield **1a** as a colorless oil (7.85 g, 78%) [$[\alpha]_D^{20}$ -15.9° (*c* 3.20, $CHCl_3$); FT-IR (neat) 3370-3342 (OH), 2967, 1671 (C=C), 1061, 1019 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, J = 7.5 Hz, 3 H, $C\underline{H}_3CH_2C{=}C$), 1.25 (d, J = 6.3 Hz, 3 H, $C\underline{H}_3HCOH$), 1.46 (d, J = 4.0 Hz, 1 H, COH), 2.03 (quintet, J = 6.7 Hz, 2 H, $CH_3C\underline{H}_2C{=}C$), 4.2-4.35 (m, 1 H, $CH_3C\underline{H}OH$), 5.50 (dd, J = 15.5, 6.6 Hz, 1 H, $HOCHC\underline{H}{=}C$), 5.68 (dt, J = 15.5, 6.1 Hz, 1 H, $CH_3CH_2C\underline{H}{=}C$); ^{13}C NMR ($CDCl_3$) δ 13.3, 23.3, 25.5, 68.6, 132.2, 133.3]. Mosher derivatization [1,3-dicyclohexylcarbodiimide, 4-(*N*,*N*-dimethylamino)pyridine, and (*R*)-(+)-

α-methoxy-α-(trifluoromethyl)phenyl acetic acid in dichloromethane] followed by capillary GC analysis [β-cyclodextran, 30m x 0.25mm, H_2 carrier gas, head pressure 6 psi, 220° injection port, oven 120°, isothermal, retention time: (*R*,*S*)-isomer 80.57 min (99.3%) and (*R*,*R*)-isomer 79.43 min (0.7%)] established that **1a** was obtained in 98.6% ee.

Anal. Calcd. for $C_6H_{12}O$: C, 71.95; H, 12.08. Found: C, 71.76; H, 11.74

(*S*)-(*Z*)-3-Hexen-2-ol (1b).- A 25 mL round-bottom flask was charged with Lindlar's catalyst [palladium (5%) on calcium carbonate, poisoned with lead; 0.50 g] and sealed with a septum. Dry hexane (8 mL) and freshly distilled quinoline (0.4 mL) were added and the flask was evacuated and flushed with hydrogen gas three times before being fitted with a balloon containing approximately 2.8 liters of hydrogen gas. (*S*)-3-Hexyn-2-ol (**5**; 3.0 g, 31 mmol) was added, via syringe, and the reaction was stirred at room temperature. The reaction was monitored by capillary GC (DB210, 30m x 0.25mm, H_2 carrier gas, linear velocity 44.2 cm/sec, 125° injection port, oven 30°, isothermal, alkyne 2.41 min, alkene 2.05 min). After 5 hrs, the reaction was stopped and the catalyst was removed by filtration through Celite®. The hexane was removed by atmospheric distillation and the resulting oil was distilled (96-100°/95 mm Hg) to yield **1b** (2.34 g, 76%) as a colorless oil [$[\alpha]_D^{20}$ -13.14°(*c* 4.02, $CHCl_3$); FT-IR (neat) 3361-3337 (OH), 3009, 2968, 1656 (C=C), 1066 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.5 Hz, 3 H, $C\underline{H}_3CH_2C$=C), 1.23 (d, *J* = 6.3 Hz, 3 H, $C\underline{H}_3HCOH$), 1.48 (d, *J* = 3.5 Hz, 1 H, COH), 2.03-2.14 (m, 2 H, $CH_3C\underline{H}_2C$=C), 4.64 (d of quintets, *J* = 6.74, 3.4 Hz, 1 H, $CH_3C\underline{H}OH$), 5.33-5.45 (m, 2 H, $C\underline{H}$=$C\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 14.3, 20.8, 23.6, 63.5, 132.2, 133.4]. Mosher derivatization [dicyclohexylcarbodiimide, 4-(*N*,*N*-dimethylamino)pyridine, and (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenyl acetic acid in dichloromethane] followed by capillary GC analysis [β-cyclodextran, 30m x 0.25mm, H_2 carrier gas, head pressure 6 psi, 220° injection port, oven 150°, isothermal, retention time: (*R*,*S*)-isomer 20.23 min (98.8%) and (*R*,*R*)-isomer 19.54 min (1.2%)] established that **1b** was obtained in 97.6% ee.

Anal. Calcd. for $C_6H_{12}O$: C, 71.95; H, 12.08. Found: C, 72.05; H, 12.07

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AN IMPROVED PREPARATION OF 2,4-DINITROPHENYL THIOETHERS FROM THIOLCARBONIC ESTERS

Submitted by (07/30/92)

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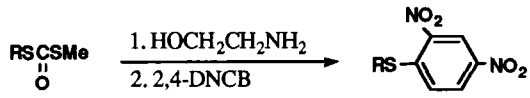
Thiolcarbonic esters are useful precursors of thiols. However, not only are these compounds often oils and have an unpleasant odor but they are also susceptible to nucleophiles. Therefore, milder conditions than refluxing with hydroxide ion are preferred for liberation of thiols. For this purpose, aminolysis reactions have been successfully used to give good yields of thiols. 2-Aminoethanol and ethylenediamine are mild reagents requiring only brief reaction times at low temperatures under neutral and non-aqueous conditions.[1] On the other hand, the most useful derivatives of alkyl- and arylthiols are the 2,4-dinitrophenyl sulfides and the corresponding sulfones.[2] The 2,4-dinitrophenyl sulfones are particularly valuable because they exhibit a wide range of melting points. However, in the method usually employed when only a small amount of thiol or its precursor is available, difficulty is sometimes encountered in the isolation of the sulfide. In the case of allylic thiols, excess of alkali causes a red coloration and a side reaction. We now report a one-pot synthetic method of the 2,4-dinitrophenyl sulfides from xanthates, dithiolcarbonates and trithiocarbonates without isolation of thiols.



The process can be carried out in a one vessel. A solution of thiolcarbonic ester and a large excess (3-5 eq.) of ethanolamine in a minimum volume of ethanol is heated at 70-80° for 10 min. After cooling, 2,4-dinitrochlorobenzene (2,4-DNCB) is added to the solution to give the 2,4-dinitrophenyl sulfide. In the case of S-alkyl S-methyl esters, alkanethiols were trapped exclusively and