ment. Purchase of the NT-360 was made possible by an instrumentation grant from the National Science Foundation (CHE-79-04832). We are grateful for financial support from the National Institutes of Health (Grant PHS GM26294) and from both the Committee on Research and the Cancer Research Coordinating Committee of the University of California.

Registry No. **2**, 40458-77-3; **4**, 87615-78-9; **5**, 87615-79-0; *endo*-**6**, 87615-80-3; *exo*-**6**, 87679-02-5; *endo*-**7**, 87615-81-4; *exo*-**7**, 87679-03-6; *endo*-**8**, 87615-82-5; *exo*-**8**, 87615-83-6; *endo*-**9**, 87615-84-7; *exo*-**9**, 87615-85-8; **10**, 87615-86-9; *m*-hydroxybenzaldehyde, 100-83-4.

Chiral Acetylenes as Synthetic Intermediates. 4.[1] Synthesis and Chiroptical Properties of Optically Active α,β-Acetylenic Ketones

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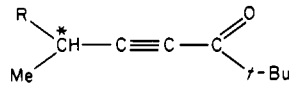
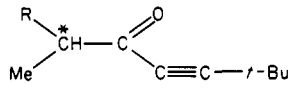
The preparation of some optically active α,β-acetylenic ketones from chiral 1-alkynes or acid chlorides is reported along with the evaluation of the stereospecificity of the synthetic methods adopted. For the compounds prepared, the CD spectra are presented and discussed; Cotton effects are observed in correspondence with the n → π* and π → π* transitions. In agreement with previous hypotheses, another electronic transition at ~250 nm is also measured in the CD spectra of the title compounds.

1-Alkynyl ketones are extremely versatile substrates for several organic syntheses as the acetylenic unit provides a convenient handle which may be converted into a variety of functionalities. Specifically, they are precursors of the corresponding 1-alkynyl carbinols, which are useful intermediate building blocks of various natural products.[2] Thus, numerous methods for carrying out the preparation of α,β-acetylenic ketones have been reported.[3-6] Our interest in this class of compounds derives from the possibility of preparing optically active α,β-acetylenic ketones. The availability of such compounds should permit their use in the synthesis of optically active heterocycles[7] and should offer some information about their chiroptical properties, which to date have received no attention.

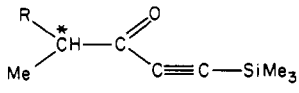
We report here the synthesis and the chiroptical properties of a series of optically active α,β-acetylenic ketones **1–3**.



1a,b



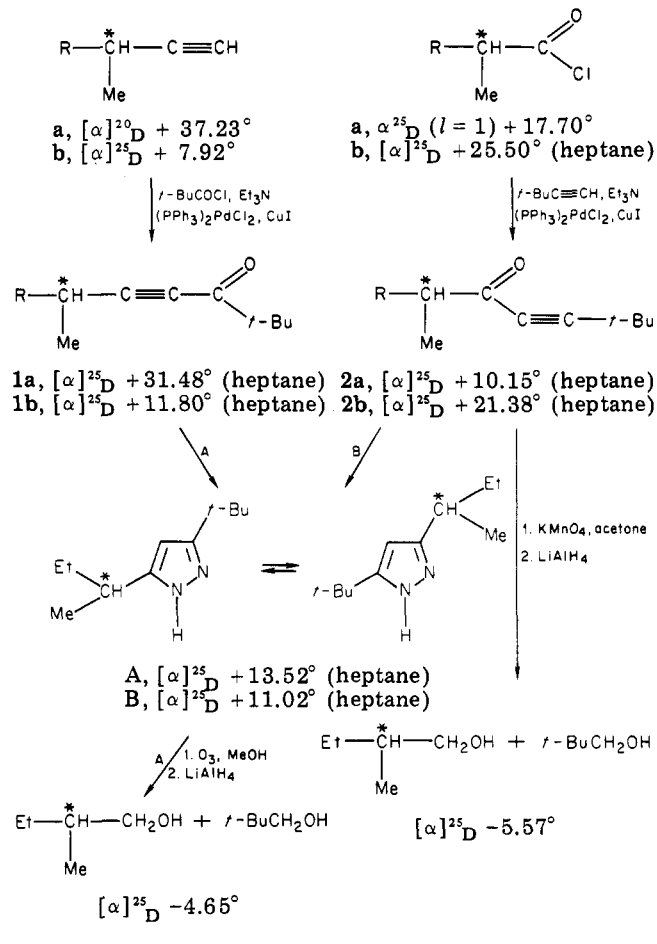
2a,b



3a,b

a, R = Et; b, R = *t*-Bu

Scheme I



Results and Discussion

Synthesis of the Optically Active α,β-Acetylenic Ketones 1–3. Since optically active acyl chlorides and 1-alkynes were readily available,[7,8] we looked for a route

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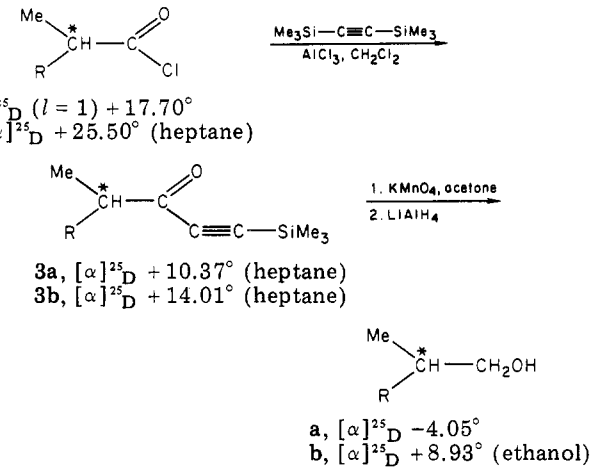
to 1-alkynyl ketones that would be based on acylation of 1-alkynes. Thus, compounds **1** and **2** were prepared through the copper(I)iodide–dichlorobis(triphenylphosphine)palladium(II)-catalyzed reaction of acyl chlorides with 1-alkynes[5] (Scheme I).

Therefore, (*S*)-2,2,6-trimethyl-4-octyn-3-one (**1a**) was prepared from (*S*)-3-methyl-1-pentyne [optical purity (o.p.) 80.1%],[8] which was obtained from (*S*)-2-methylbutanal[9] via a known procedure.[10] The 1-alkyne was treated with pivaloyl chloride according to a literature procedure,[5] to yield (87%) **1a**, $[\alpha]^{25}_D$ +31.48° (heptane). (*S*)-2,2,6,7,7-Pentamethyl-4-octyn-3-one (**1b**) was obtained by reaction of pivaloyl chloride with (*S*)-3,4,4-trimethyl-1-pentyne (o.p. 62.9%),[10,11] which was prepared from the corresponding 1-alkene via a bromination–dehydrobromination procedure.[11] Compound **1b**, $[\alpha]^{25}_D$ +11.80° (heptane), was obtained in 82% yield.

The preparation of (*S*)-2,6,6-trimethyl-3-octyn-5-one (**2a**) was carried out starting from (*S*)-2-methylbutanoyl chloride (o.p. 96.5%).[12] Reaction of the acyl chloride with 3,3-dimethyl-1-butyne[5] yielded (47%)[13] **2a**, $[\alpha]^{25}_D$ +10.15° (heptane). Analogously, (*S*)-2,3,3-trimethylbutanoyl chloride (o.p. 52.6%), from (*S*)-2,3,3-trimethylbutanoic acid,[11] was treated as above with 3,3-dimethyl-1-butyne to yield (68%)[13] (*S*)-2,2,6,7,7-pentamethyl-3-octyn-5-one (**2b**), $[\alpha]^{25}_D$ +21.38° (heptane).

Since reductive ozonolysis to the corresponding optically active carbinols[14,15] failed, the optical purity of the 1-alkynyl ketones **1a** and **2a** was estimated by cyclization into the corresponding dialkylpyrazole,[16] followed by reductive ozonolysis of the heterocyclic intermediate.[17] Thus, compound **1a** was treated with hydrazine sulfate to give (72%) **4**, $[\alpha]^{25}_D$ + 13.52° (heptane), and the subsequent exposure of **4** with a stream of ozonized oxygen, followed by reduction with $LiAlH_4$, afforded, after preparative GLC purification, (*S*)-2-methyl-1-butanol, $[\alpha]^{25}_D$ −4.65°.[14] The optical purity was unchanged. Analogously, compound **2a** was converted into compound **4**, $[\alpha]^{25}_D$ + 11.02° (heptane). By the comparison of its rotatory power with that of the sample obtained from **1a**, it could be assigned an optical purity of 65.1%, which is lower than that of the starting (*S*)-2-methylbutanoyl chloride. In order to check if the observed racemization occurred during the synthesis of **2a** or in the subsequent cyclization to **4**, a sample of **2a** was oxidized with $KMnO_4$, according to the reported[18] oxidation of diarylacetylenes.[19] The reduction with $LiAlH_4$ of the mixtures of acids recovered gave (*S*)-2-methyl-1-butanol, $[\alpha]^{25}_D$ −5.57°, o.p. 95.7%[14] (Scheme I). The data obtained indicate therefore that the sequences adopted for the synthesis of the 1-alkynyl ketones **1** and **2** occurred

Scheme II



with high stereospecificity and did not involve the carbon atom in the α-position with respect to the triple bond and to the carbonyl group.

On this basis, samples of **1b** and **2b** prepared were attributed the same optical purity as the starting (*S*)-3,4,4-trimethyl-1-pentyne and (*S*)-2,3,3-trimethylbutanoyl chloride, respectively.

The trimethylsilyl ketones **3** were prepared through the $AlCl_3$-catalyzed reaction[4] of (*S*)-2-methylbutanoyl and (*S*)-2,3,3-trimethylbutanoyl chlorides with bis(trimethylsilyl)acetylene (Scheme II). (*S*)-2,2,6-Trimethyl-2-sila-3-octyn-5-one (**3a**), $[\alpha]^{25}_D$ +10.37° (heptane), and (*S*)-2,2,6,7,7-pentamethyl-2-sila-3-octyn-5-one (**3b**), $[\alpha]^{25}_D$ + 14.01° (heptane), were so obtained with 84% and 94% yields, respectively. The minimum optical purity of **3a** and **3b** was also determined by oxidation with $KMnO_4$ in acetone,[18] followed by reduction of the mixture of acids with $LiAlH_4$. Thus, **3a** gave (*S*)-2-methyl-1-butanol, $[\alpha]^{25}_D$ −4.05° (heptane),[20] while **3b** yielded (*S*)-2,3,3-trimethyl-1-butanol, $[\alpha]^{25}_D$ +8.93° (ethanol),[15] having optical purities (61.2% and 21.6%, respectively) much lower than those of the starting materials. The high value of racemization encountered is certainly due to the strongly Lewis acidic conditions adopted, and even though we have reduced the reaction time to 15 min,[21] the reaction occurred with low optical yields.[22]

In this respect, it is noteworthy that any further attempt to obtain **3a** in a satisfactory chemical and optical yield failed. In fact, the copper(I) iodide–dichlorobis(triphenylphosphine)palladium(II)-catalyzed reaction[5] of (*S*)-2-methylbutanoyl chloride with (trimethylsilyl)-acetylene gave the ketone **3a** only in traces, while condensation of cuprous (trimethylsilyl)acetylide[3] with (*S*)-2-methylbutanoyl chloride yielded (35%) **3a**, having $[\alpha]^{25}_D$ +9.42° (heptane) and o.p.55.6% and therefore noticeably racemized.[23]

In conclusion, the procedures we have adopted represent satisfactory routes for preparing optically active α,β-

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(13) These low yields may be attributed to the high volatility of the 1-alkyne used and to the possible reaction of the acyl chlorides with triethylamine, which is a necessary component of the reaction.
(14) Rossi, R.; Diversi, P.; Ingrosso, G. *Gazz. Chim. Ital.* **1968**, *98*, 1391.
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(19) To evaluate the stereospecificity of the method, a sample of **1a**, o.p. 80.1%, was oxidized to a mixture of (*S*)-2-methylbutanoic and pivalic acids. After reduction with $LiAlH_4$, a sample of (*S*)-2-methyl-1-butanol, o.p. 80.7%, was recovered by preparative GLC.
(20) Giacomelli, G.; Caporusso, A. M.; Lardicci, L. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1933.
(21) In these conditions **3a**, $[\alpha]^{25}_D$ +21.45° (heptane), o.p. 33%, was obtained.
(22) The racemization does not depend on the particular structure of the ketones **3**; in fact, treatment of (*S*)-2,3,3-trimethylbutanoyl chloride with 2,2,5,5-tetramethyl-2-sila-3-hexyne with $AlCl_3$ yielded (92%) **2b**, $[\alpha]^{25}_D$ +12.21° (heptane), o.p. 30%.
(23) In this case, purification of the ketone, which is to be achieved by chromatography on silica gel, might have caused racemization of **3a**. However, successive elutions on silica gel did not change the optical activity of **3a**. Such a racemization seems therefore to be due to the reaction conditions adopted.

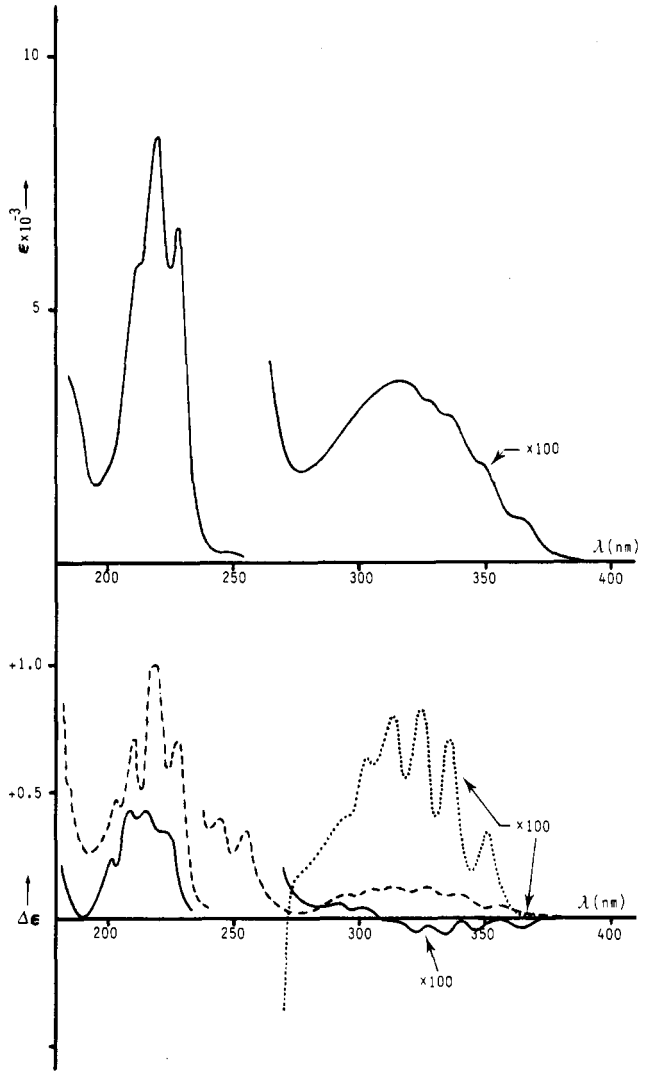

Figure 1. CD Spectra of **1a** (–) and **1b** (- -), at room temperature and at –180 °C (**1b**, ··), in 3-methylpentane solution; CD data are corrected for 100% optical purity of the samples. In the upper part the UV spectrum of **1a** is also reported.

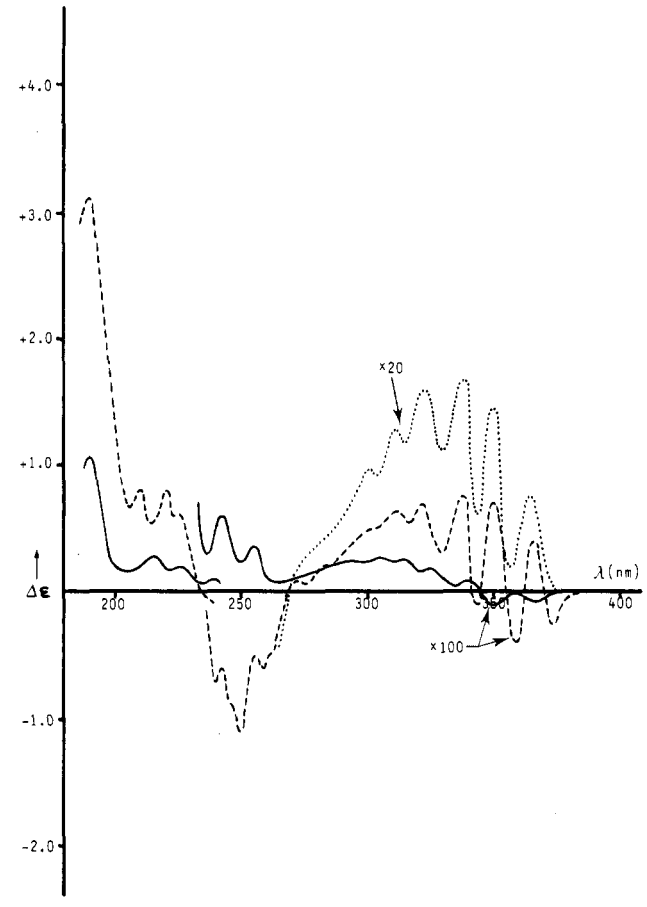

Figure 2. CD Spectra of **2a** (–) and **2b** (- -), at room temperature and at –180 °C (**2b**, ··), in 3-methylpentane solution; CD data are corrected for 100% optical purity of the samples.

acetylenic ketones in good yields, even if, at least in some cases, a certain degree of racemization may be encountered.

Circular Dichroism of the α,β-Acetylenic Ketones 1–3. Only a few studies of the spectroscopical properties of 1-alkynyl carbonyl compounds have been reported.[24-26] In the UV spectra of propynal and 2-butynal[24] at least two absorptions can be observed in the range of 400–190 nm, the first one being weak and lying in the 400–300 nm region, while the second transition, some hundred times more intense, is located at around 210 nm. In addition, another weak transition is also predicted at around 250 nm on theoretical grounds.[24]

In Figure 1 is reported the UV spectrum of **1a**, which is nearly identical with those of the other ketones **1** and **2**. In all the cases the UV spectra of the 1-alkynyl ketones **1** and **2** in heptane solution at room temperature are characterized, in the 420–180 nm region, by two main regions of absorption. The long-wavelength band, centered at around 320 nm, is weak ($\epsilon \simeq 40$), while the second absorption, at around 220 nm, is relatively intense ($\epsilon \simeq 8000$).

The CD spectra of compounds **1** and **2**, as given in Figures 1 and 2, exhibit several Cotton effects in the same spectral range and in particular two bands with well-resolved fine structure, in correspondence with the aforementioned UV maxima: a weak band at around 320 nm ($\Delta\epsilon \leq +0.07$) and a relatively strong positive band at 220–210 nm ($\Delta\epsilon = +0.2/1.0$). Moreover, the CD spectra of **1** and **2** exhibit a relatively weak optically active absorption band at around 250 nm, which has the same positive sign in **1** and **2a** and the opposite sign in **2b** (Figures 1 and 2).

Indeed, the relatively high g ($g = \Delta\epsilon/\epsilon$)[27] factor ($g \geq 0.01$) indicates the n → π* nature of the first absorption band,[24] while the noticeably lower g factor value ($g \simeq 10^{-4}$) supports the hypothesis that the electronically allowed π → π* transition is responsible for the absorption at around 220 nm.[24]

By examining more closely the CD spectra of Figures 1 and 2, it appears that, with the exception of compound **1b**, the n→π* band of the carbonyl group shows a clear fine structure with opposite sign patterns. However, by lowering the temperature, both in compound **1b** and **2b** this Cotton effect becomes more positive and increases significantly and the small negative humps in **2b** practically disappear (Figures 1 and 2). This fact could be related to the presence at room temperature of equilibria involving at least two conformational isomers having rotational strength of opposite sign.[28]

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(27) Mason, S. F. *Quart. Rev.* **1963**, *17*, 20.

Regarding the strong Cotton effect at shorter wavelengths than 200 nm (Figures 1 and 2), it may be suggested that this results from the C=O n → σ* transition.[29] In fact, the position of this band agrees very well with that of similar Cotton effects, already observed in saturated[30] and α,β-unsaturated ketones.[29]

The presence of a relatively weak CD band at around 250 nm is noteworthy; such an absorption is particularly evident in the CD spectrum of **2b** ($\Delta\epsilon = -0.1$) (Figure 2). In the analysis of the near UV absorption spectrum of 2-butynal,[24] the feature present at around 250 nm was attributed to a transition from the in-plane π MO to the out-of-plane π* MO of the acetylenic linkage. Such a transition, involving a rotation of charge (around the axis of the acetylene chromophore) should be magnetically allowed,[28] giving rise to a strong *g* factor in the CD spectrum. Unfortunately, from the present CD data, it is impossible to determine the *g* factor value with accuracy, as the UV absorption in this region strongly overlaps with the more intense 220 nm band and this makes it difficult to evaluate the molar extinction coefficient of the 250 nm transition and therefore to confirm the above assignment on this ground.

The room temperature UV and CD curves of compounds **3** (Figure 3) are qualitatively similar to those of the ketones **1** and **2**. The presence of a trimethylsilyl group linked to the triple bond causes a general red shift of the maxima of the UV bands; the n → π* transition is in fact located at around 335 nm, while the π → π* transition, which shows a diffuse quartet appearance, is centered at around 225 nm. In this case, there is also evident a shoulder at 250 nm. Similar considerations can be made for the CD spectra of compounds **3**; moreover, at least for **3b**, there is a particularly noticeable negative band of relatively intense rotatory strenght ($\Delta\epsilon \simeq -0.2$), lying at around 260 nm, which confirms the presence of another electronic transition in this spectral region.[24]

Experimental Section

IR Spectra were recorded on a Perkin-Elmer 180 spectrometer for liquid films and UV spectra on a Jasco UVIDEC-710 spectrophotometer for heptane solutions. ^{1}H NMR spectra (60 MHz) and ^{13}C NMR Fourier-transform spectra (25.2 MHz) were obtained with a Varian T-60 and a Varian XL-100 spectrometer in $CDCl_3$ solutions with Me_4Si as an internal standard. The theoretical chemical shifts of the carbon atoms, evaluated in all cases by means of the additivity rule,[31] were in good agreement with the experimental ones. Optical rotations were measured on a Perkin-Elmer 142 automatic polarimeter in an 1-dm tube; unless otherwise specified, rotations refer to those of the pure liquid. CD Spectra were recorded on a Jasco J-500 C spectropolarimeter equipped with a DP-500 N data processor. Mass spectra were taken at 70 eV on a Varian Mat CH-7 GC-MS spectrometer. GLC analyses (Perkin-Elmer 3920 B) and preparative GLC (Perkin-Elmer F-21) were performed with SE-30 and Carbowax 20M (Cw 20M) as stationary phases and nitrogen as carrier gas. All new compounds gave satisfactory microanalyses for C and H (within ±0.3%). All solvents were reagent grade materials, purified by standard methods and redistilled before use. 3,3-Dimethyl-1-butyne, trimethylsilylacetylene, bis(trimethylsilyl)acetylene, and pivaloyl chloride were commercial products (Fluka), which were carefully distilled before use. (*S*)-3-Methyl-1-pentyne ($[\alpha]^{20}_D$ + 37.23°),[8] (*S*)-3,4,4-trimethyl-1-pentyne ($[\alpha]^{25}_D$ + 7.92°),[11] (*S*)-2-methylbutanoic acid ($[\alpha]^{25}_D$ +19.10°),[32] and (*S*)-2,3,3-trimethylbutanoic acid ($[\alpha]^{25}_D$ + 27.99°, ethanol)[11] were synthesized by published methods. Dichlorobis(triphenylphosphine)palladium was prepared as described in the literature.[33] All reactions involving air-sensitive materials were conducted under a nitrogen atmosphere.

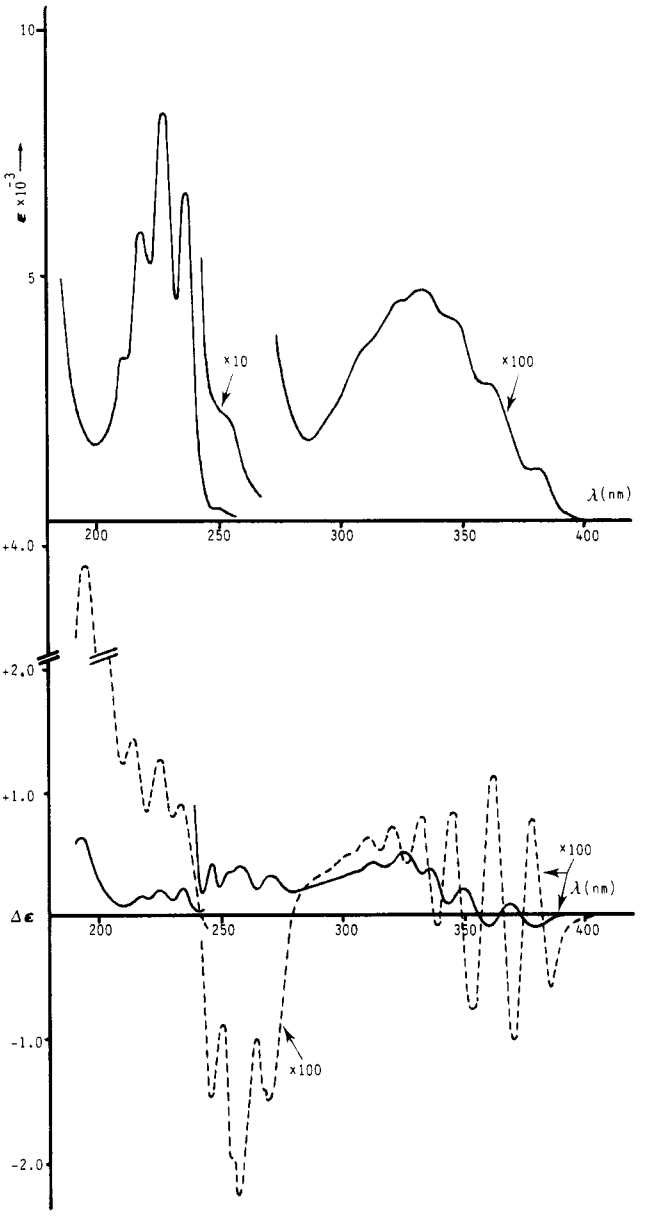

Figure 3. CD spectra of **3a** (–) and **3b** (- -) at room temperature; CD data are corrected for 100% optical purity of the samples. In the upper part the UV spectrum of **3a** is also reported.

Optically Active Acid Chlorides. (*S*)-2-Methylbutanoyl chloride, bp 72 °C (160 mm), $[\alpha]^{25}_D$ +17.70° (*l* 1),[12] and (*S*)-2,3,3-trimethylbutanoyl chloride, bp 78 °C (105 mm), $[\alpha]^{25}_D$ +25.50° (*c* 4.2, heptane), were obtained from the corresponding acids via a known procedure.[12] In order to determine the optical purity of (*S*)-2,3,3-trimethylbutanoyl chloride, a sample was hydrolyzed at room temperature with 10% Na_2CO_3 to give (*S*)-2,3,3-trimethylbutanoic acid, $[\alpha]^{25}_D$ +21.58° (*c* 3.1, ethanol).[11]

(*S*)-2,2,6-Trimethyl-4-octyn-3-one (1a). A solution containing 9.0 g (110 mmol) of (*S*)-3-methyl-1-pentyne, pivaloyl chloride (13.3 g, 110 mmol), cuprous iodide (110 mg, 0.58 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (110 mg, 0.16 mmol) in 200 mL of dry triethylamine was stirred for 6 h at room temperature and was then allowed

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(33) King, A. O.; Negishi, E.; Villani, F. J.; Silveira, A. *J. Org. Chem.* **1978**, *43*, 358.

to stand for 3 days. Methanol (55 mL) was added to the reaction mixture and the solvent removed under reduced pressure; the residue was then treated with water and extracted with pentane. The organic extracts were dried over Na_2SO_4 and concentrated. Distillation gave pure **1a** (15.9 g, 87%): bp 89 °C (15 mm); $[\alpha]^{25}_D$ +31.48° (*c* 2.9, heptane); IR 2200, 1667 cm^{-1}; ^1H NMR δ 1.12 (9 H, s), 1.17 (3 H, t), 1.22 (3 H, d), 1.53 (2 H, m), 2.52 (1 H, m); ^{13}C NMR δ 11.7, 19.7, 26.1, 27.9, 29.2, 44.5, 78.9, 99.0, 193.6; mass spectrum, *m/e* 166 (M^+), 57 (100%).

(*S*)-2,2,6,7,7-Pentamethyl-4-octyn-3-one (1b). In the manner described above for the preparation of **1a**, (*S*)-3,4,4-trimethyl-1-pentyne (2.20 g, 20 mmol) and pivaloyl chloride (2.42 g, 20 mmol) gave pure **1b** (3.2 g, 82%): bp 110 °C (17 mm); $[\alpha]^{25}_D$ +11.80° (*c* 3.9, heptane); IR 2200, 1670 cm^{-1}; ^1H NMR δ 1.00 (9 H, s), 1.12 (9 H, s), 1.18 (3 H, d), 2.40 (1 H, q); ^{13}C NMR δ 14.2, 25.1, 26.2, 32.4, 36.6, 43.5, 79.1, 97.0, 192.2; mass spectrum, *m/e* 194 (M^+), 57 (100%).

(*S*)-2,2,6-Trimethyl-3-octyn-5-one (2a). In the manner described for the preparation of **1a**, 3,3-dimethyl-1-butyne (10.0 g, 122 mmol) and (*S*)-2-methylbutanoyl chloride (13.3 g, 110 mmol) gave **2a** (8.6 g, 47%): bp 85 °C (14 mm); $[\alpha]^{25}_D$ +10.15° (*c* 3.6, heptane); IR 2200, 1665 cm^{-1}; ^1H NMR δ 1.03 (3 H, t), 1.18 (9 H, s), 1.20 (3 H, d), 1.53 (2 H, m), 2.34 (1 H, m); ^{13}C NMR δ 10.1, 14.3, 24.5, 26.8, 28.8, 48.6, 77.0, 99.7, 189.5; mass spectrum, *m/e* 166 (M^+), 109 (100%).

(*S*)-2,2,6,7,7-Pentamethyl-3-octyn-5-one (2b). In the manner described for the preparation of **1a**, 3,3-dimethyl-1-butyne (5.4 g, 66 mmol) and (*S*)-2,3,3-trimethylbutanoyl chloride (7.4 g, 50 mmol) gave **2b** (6.6 g, 68%): bp 98 °C (12 mm); $[\alpha]^{25}_D$ +21.38° (*c* 2.5, heptane); IR 2205, 1660 cm^{-1}; ^1H NMR δ 0.93 (9 H, s), 1.07 (3 H, d), 1.26 (9 H, s), 2.32 (1 H, q); ^{13}C NMR δ 10.5, 26.2, 28.4, 31.5, 56.2, 78.8, 99.8, 189.6; mass spectrum, *m/e* 194 (M^+), 137 (100%).

(*S*)-2,2,6-Trimethyl-2-sila-3-octyn-5-one (3a). Method A. A solution containing (*S*)-2-methylbutanoyl chloride (16.9 g, 140 mmol) and bis(trimethylsilyl)acetylene (23.9 g, 140 mmol) in 500 mL of anhydrous dichloromethane was cooled to 0 °C, and anhydrous $AlCl_3$ (20.8 g, 160 mmol) was added within a few minutes. After the mixture had stirred at room temperature for 30 min, dilute HCl was added, and the mixture was extracted with diethyl ether. By distillative workup, the dried extracts (Na_2SO_4) gave **3a** (21.4 g, 84%): bp 88 °C (20 mm); $[\alpha]^{25}_D$ +10.37° (*c* 6.5, heptane); IR 2150, 1675 cm^{-1}; ^1H NMR δ 0.23 (9 H, s), 0.90 (3 H, t), 1.11 (3 H, d), 1.59 (2 H, m), 2.37 (1 H, m); ^{13}C NMR δ −0.7, 11.4, 15.4, 25.6, 49.7, 98.9, 104.9, 192.3; mass spectrum, *m/e* 182 (M^+), 125 (100%).

Method B. According to the Logue and Moore procedure,[3] (*S*)-2-methylbutanoyl chloride (4.34 g, 36 mmol) was treated, at 0 °C in THF, with cuprous (trimethylsilyl)acetylide (32 mmol). The reaction mixture was stirred for 20 h at room temperature and the solvent was then removed in vacuo. After the described workup and purification by chromatography on a short column of silica gel (hexane), distillation gave **3a** (2.3 g, 35%): bp 88 °C (20 mm); $[\alpha]^{25}_D$ +9.42° (*c* 6.3, heptane).

(*S*)-2,2,6,7,7-Pentamethyl-2-sila-3-octyn-5-one (3b). A solution of (*S*)-2,3,3-trimethylbutanoyl chloride (4.4 g, 30 mmol) and bis(trimethylsilyl)acetylene (5.1g, 30 mmol) in dichloromethane (100 mL) was treated at 0 °C with $AlCl_3$ (4.4 g, 33 mmol), as described above. The mixture was stirred at room temperature for 30 min, then hydrolyzed with dilute HCl and extracted with ether. By distillative workup, the dried extracts (Na_2SO_4) gave **3b** (5.9 g, 94%): bp 99 °C (28 mm); $[\alpha]^{25}_D$ +14.01° (*c* 1.1, heptane); IR 2150, 1670 cm^{-1}; ^1H NMR δ 0.23 (9 H, s), 0.97 (9 H, s), 1.10 (3 H, d), 2.41 (1 H, q); ^{13}C NMR δ −0.7, 12.1, 27.9, 33.4, 57.6, 97.9, 103.3, 191.1; mass spectrum, *m/e* 43 (100%).

3(5)-[1,1-Dimethylethyl]-5(3)-[(*S*)-1-methylpropyl]-pyrazole (4). From 1a. A concentrated solution of Na_2CO_3 (9.9 mmol) was added slowly (1 h) to a boiling mixture of **1a** (1.62 g, 9.8 mmol) and hydrazine sulfate (1.32 g, 10.2 mmol) in ethanol (16 mL). The reaction mixture was refluxed for an additional 20 h, then extracted with pentane. Evaporation of the dried extracts (Na_2SO_4) gave **4** (1.27 g, 72%), which was purified by sublimation (80 °C at 0.1 mm): mp 89 °C; $[\alpha]^{25}_D$ +13.52° (*c* 1.5, heptane); ^1H NMR δ 1.35 (9 H, s), 0.7–1.9 (8 H, m), 2.5–3.0 (1 H, m), 5.85 (1 H, s), 11.0 (1 H, s).

From 2a. According to the procedure described above, compound **2a** (1.0 g, 6 mmol) afforded the pyrazole **4** (0.96 g, 89%): mp 89 °C; $[\alpha]^{25}_D$ +11.02° (*c* 2.1, heptane).

Ozonolysis of 3(5)-[1,1-Dimethylethyl]-5(3)-[(*S*)-1-methylpropyl]pyrazole (4). Ozonized oxygen was passed through a solution of **4** (1.17 g, 6.5 mmol), $[\alpha]^{25}_D$ +13.52° (heptane), in ethanol (50 mL) at room temperature for 9 h. The solvent was carefully removed in vacuo and the crude ozonide was decomposed in ethereal solution (100 mL) with $LiAlH_4$ (2.5 g). After hydrolysis, preparative GLC (Cw 20M) gave a pure sample of (*S*)-2-methyl-1-butanol: $[\alpha]^{25}_D$ −4.65° (lit.[14] $[\alpha]^{25}_D$ −5.80°, for the optically pure compound).

$KMnO_4$ Oxidation of the α,β-Acetylenic Ketones. Typical Procedure. An aqueous solution of $KMnO_4$ (6.0 g, 1 L) was added dropwise at room temperature to a solution of (*S*)-2,2,6-trimethyl-4-octyn-3-one (**1a**) (2.0 g, 12 mmol), $[\alpha]^{25}_D$ +31.48° (heptane), in acetone (1.5 L). The resulting mixture was stirred overnight, then the solvent was removed under reduced pressure, and the residue was treated with concentrated NaOH (40 mL). Manganese dioxide was removed by filtration and washed with water. The combined filtrates were acidified with dilute H_2SO_4 and extracted with ether. The residue obtained after evaporation of the dried extracts (Na_2SO_4), was added to a suspension of $LiAlH_4$ (2.12 g, 56 mmol) in diethyl ether (50 mL) and the mixture was refluxed for 5 h. After hydrolysis, preparative GLC (Cw 20M) gave a pure sample of (*S*)-2-methyl-1-butanol: $[\alpha]^{25}_D$ −5.33° (*c* 2.5, heptane) (lit.[20] $[\alpha]^{25}_D$ −6.59° (heptane), for the optically pure compound).

In the similar manner, **2a**, $[\alpha]^{25}_D$ +10.15° (heptane), gave a sample of (*S*)-2-methyl-1-butanol having $[\alpha]^{25}_D$ −5.57°.

Analogously, **3a**, $[\alpha]^{25}_D$ +10.37°, gave (*S*)-2-methyl-1-butanol having $[\alpha]^{25}_D$ −4.05° (*c* 7.5, heptane) and **3b**, $[\alpha]^{25}_D$ +14.01° (heptane), afforded (*S*)-2,3,3-trimethyl-1-butanol having $[\alpha]^{25}_D$ +8.93° (*c* 5.3, ethanol) (lit.[15] $[\alpha]^{25}_D$ +41.4° (ethanol), for the optically pure compound).

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Registry No. **1a**, 87569-06-0; **1b**, 87569-07-1; **2a**, 87569-08-2; **2b**, 87569-09-3; **3a**, 87569-10-6; **3b**, 87569-11-7; **4**, 87585-89-5; (*S*)-2-methylbutanoyl chloride, 27763-54-8; (*S*)-2,3,3-trimethylbutanoyl chloride, 87569-05-9; pivaloyl chloride, 3282-30-2; (*S*)-3,4,4-trimethyl-1-pentyne, 40824-46-2; (*S*)-2-methyl-1-butanol, 1565-80-6; (*S*)-2,3,3-trimethyl-1-butanol, 54712-26-4; (*S*)-3-methyl-1-pentyne, 2868-07-7; 3,3-dimethyl-1-butyne, 917-92-0; bis(trimethylsilyl)acetylene, 14630-40-1; cuprous (trimethylsilyl)acetylide, 53210-13-2.