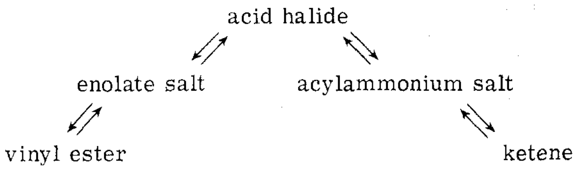
also take place either by nucleophilic attack on the ester carbonyl, or by formation of the vinyl ester enolate and loss of carboxylate. In either case an equal mixture of the two cycloadducts would be expected.

These results clearly demonstrate to us that the enolate forming step in the triethylamine reaction with α-halo acid halides is reversible and furthermore suggests the precursor to halogenated ketenes is the acylammonium salt.

Consequently, it has become clear that a complex series of equilibria are involved in the dehydrohalogenation of α-halo acid halides. The data are consistent with a single pathway to ketene through the acylammonium salt as illustrated.



Experimental Section

Proton nmr spectra were recorded on a Jeolco Minimar 60-Mhz and a Jeolco PS-100 nmr spectrometers employing tetramethylsilane as an internal standard and CCl$_4$ as a solvent. Solvents and triethylamine were distilled from sodium and stored over Linde type 4-A molecular sieve. Vpc was performed on an F & M Scientific Model 700 gas chromatograph with a 10 ft × 0.25 in. column packed with 10% SE-30 on acid washed chromosorb W (80/100).

***tert*-Butylbromo- and *tert*-Butylchloroketenes.** To a stirred solution of 0.1 mol of triethylamine in 90 ml of chloroform was added dropwise 0.1 mol of 2-bromo-3,3-dimethylbutanoyl chloride or 2-chloro-3,3-dimethylbutanoyl chloride in 10 ml of chloroform at room temperature. The ketene was observed by ir: *tert*-butylbromoketene, 2121 cm^{-1}, and *tert*-butylchloroketene, 2110 cm^{-1}. *tert*-Butylbromoketene persisted in the reaction mixture for 3 days while *tert*-butylchloroketene was observable for only 4 hr. Numerous attempts to isolate the *tert*-butylbromoketene were unsuccessful.

Attempts to trap an enolate from 2-halo-3,3-dimethylbutanoyl chloride with the starting acid halide as previously described were unsuccessful.[8] Efforts to trap an enolate with the more effective acylating agent, trichloroacetyl chloride, are described.

To a stirred solution of 0.05 mol of triethylamine in 40 ml of chloroform was added dropwise 0.05 mol of 2-chloro-3,3-dimethylbutanoyl chloride in 10 ml of chloroform at room temperature. After the addition was complete, 0.05 mol of trichloroacetyl chloride was added and the reaction mixture stirred overnight. No evidence of the mixed vinyl ester, 1,2-dichloro-3,3-dimethyl-1-butenyl trichloroethanoate, was found, only nonvolatile polymeric products.

Vinyl Ester from α-Chlorobutyryl Chloride and the Enolate of α-Chloropropionyl Chloride, I, II, III, and IV. A solution 0.05 mol of α-chloropropionyl chloride in 10 ml of chloroform was added dropwise to a stirred solution of 0.05 mol of triethylamine in 75 ml of chloroform at −78°. Stirring was continued for 0.5 hr after the addition was complete and then 0.05 mol of α-chlorobutyryl chloride in 10 ml of chloroform was added dropwise. The reaction mixture was then allowed to warm to room temperature and stirred overnight. A 100-ml portion of hexane was then added to precipitate the amine salt. Filtration, concentration on a rotatory evaporator, and distillation afforded 6 ml, 49–73° at 0.25 mm, of the four vinyl esters in a ratio of 1:1:0.7:0.6 for I, II, III and IV, respectively, as evidenced by vpc and nmr. Geometrical isomers of the four vinyl esters were not separated under these vpc conditions. The simple vinyl esters, I and IV, have been previously described.[8] The two mixed vinyl esters, II and III, could not be separated by distillation nmr, δ (for the mixture), 1.0 (m, 3 H), 1.65 (d, 1.4 H), 2.0 (s, 0.9 H), 2.15 (s, 0.7 H), 2.10 (m, 2 H), and 4.25 (m, 1 H).

Anal. Calcd for $C_7H_9Cl_3O_2$: C, 36.28; H, 3.98. Found: C, 36.52; H, 3.91.

Generation of Methylchloro- and Ethylchloroketenes from α-Chlorobutyryl Chloride and the Enolate of α-Chloropropionyl Chloride. The enolate salt of α-chloropropionyl chloride was prepared at −78° as described above. To this solution were added with stirring 0.05 mol of α-chlorobutyryl chloride and 0.05 mol of freshly cracked cyclopentadiene. The reaction solution was allowed to warm to room temperature and stirring continued overnight. The amine salt was precipitated by the addition of 100 ml of hexane and removed by filtration. Concentration on a rotatory evaporator and vacuum distillation afforded 3.2 g (40%) of an equal mixture of 7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one and 7-chloro-7-ethylbicyclo[3.2.0]hept-2-en-6-one as determined by vpc and comparison with known samples of the two cycloadducts.

Generation of Methylchloro- and Ethylchloroketenes from 1,2-Dichloro-1-butenyl 2-Chloropropanoate and 1,2-Dichloropropenyl 2-Chlorobutanoate. The mixed vinyl esters, II and III, were collected in a 2:1 ratio respectively by preparative vpc. A 50-μl portion of this mixture was added to 0.5 ml of chloroform and 150 μl of freshly cracked cyclopentadiene and 100 μmol of triethylamine. The mixture was stirred at room temperature overnight. Both 7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one and 7-chloro-7-ethylbicyclo[3.2.0]hept-2-en-6-one were formed in equal amounts as determined by vpc and comparison with known samples of the cycloadduct.

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Registry No.—I, 52920-13-5; II, 52920-14-6; III, 52920-15-7; IV, 23649-91-4; V, 33471-78-2; VI, 52920-16-8; *tert*-butylbromoketene, 29264-48-0; *tert*-butylchloroketene, 52920-17-9; 2-bromo-3,3-dimethylbutanoyl chloride, 29336-30-9; 2-chloro-3,3-dimethylbutanoyl chloride, 52920-18-0; α-chloropropionyl chloride, 7623-09-8; triethylamine, 121-44-8; α-chlorobutyryl chloride, 7623-11-2; α-chloropropionyl chloride enolate salt with triethylamine, 50635-68-2.

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Synthesis of 5-Ethynyl-2,2′-bithienyl and Related Compounds[1]

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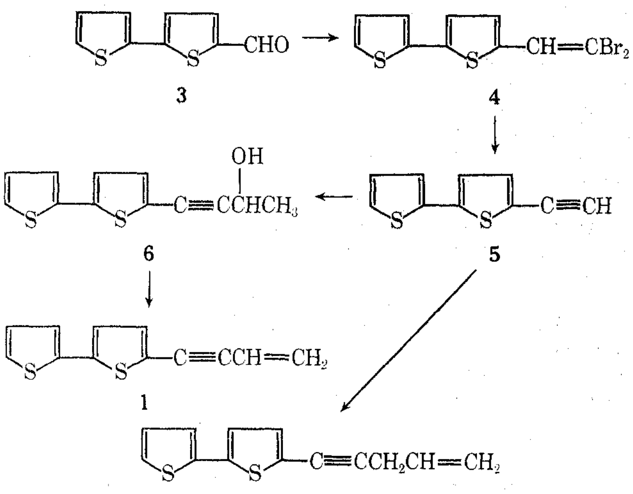
Because of the potential importance of certain 5-substituted-2,2′-bithienyls in the study of nematode control,[3] we were prompted to synthesize 5-(3-buten-1-ynyl)-2,2′-bithienyl (**1**), a highly potent naturally occurring nematicide. Even though **1** has been previously synthesized,[4] we desired an economical synthesis which would provide a better supply of **1** and related compounds for physiological testing. Also, we required a synthesis of 5-(3-penten-1-ynyl)-2,2′-bithienyl (**2**) for comparison of its ultraviolet spectrum with that of **1**.

The synthesis of **1** was accomplished as shown in Scheme I. A key step in this synthesis is the high yield preparation of 5-ethynyl-2,2′-bithienyl (**5**) using the Corey and Fuchs method.[5] Vapor phase dehydration of 5-(3-hydroxy-1-butynl)-2,2′-bithienyl (**6**) over alumina at 540° (0.18 mm) produced a mixture containing **5**, **6**, and **1**. The low yield of **1** (30%) in this step may partially be due to the competitive retro aldol reaction which produces **5**. Attempted dehydra-

Scheme I



tion of **6** in acidic aqueous medium is reportedly unsuccessful.[4a] Pyrolysis of 5-(3-acetoxy-1-butynyl)-2,2′-bithienyl furnished impure **1** in very low yield. Compound **1** was not produced when coupling of **5** with vinyl bromide was attempted.[6] The improved preparation of **5** provides facile entry into the synthesis of potential nematicides. For example, coupling of the acetylenic Grignard reagent from **5** with 3-bromopropene in the presence of cuprous chloride[7] afforded **2** in 99% yield (77% overall from **3**).

Ultraviolet spectroscopy is used extensively for the identification of naturally occurring acetylenes. The ultraviolet absorption is shifted 15–30 nm higher on conjugation with an olefin.[7] The ultraviolet spectrum of the naturally occurring nematicide showed λ_{max} 340 nm (isooctane).[3b] This absorption when compared with the λ_{max} of 335 nm (hexane) for 5-(1-butynyl)-2,2′-bithienyl led to the suggestion of structure **2** for the natural product.[9] Synthesis later proved the correct structure **1**.[4a] We have found λ_{max} (*n*-hexane) for **1** at 344 and 256 nm and λ_{max} (*n*-hexane) for **2** at 336, 255, and 240 (sh) nm. The anticipated wavelength increase is absent in the enyne **1**. Thus, in the 2,2′-bithienyl series, ultraviolet spectroscopy is not always a reliable method for providing correct structural assignments.

Experimental Section

5-Formyl-2,2′-bithienyl (3). A. Formylation of 2,2′-bithienyl[10] according to Uhlenbroek and Bijloo furnished **3** in 85% yield, mp 54.5–55.5° (lit.[3a] mp 56°). B. Metalation of 2,2′-bithienyl followed by formylation with *N,N*-dimethylformamide after the method of Wynberg and Bontjes[11] afforded **3** in 68% yield, mp 57–57.5°, and 5,5′-diformyl-2,2′-bithienyl (13%), mp 210–212° (lit.[12] mp 217°). Method A proved to be the better procedure for preparing **3**.

5-(2,2′-Dibromoethenyl)-2,2′-bithienyl (4). Triphenylphosphine, (20.98 g, 0.08 mol), 5.23 g (0.08 mol) of zinc dust, and 26.54 g (0.08 mol) of carbon tetrabromide were placed in a flame-dried, 500-ml, three-necked, round-bottom flask equipped with magnetic stirrer and gas inlet valve. Anhydrous dichloromethane (100 ml) was added under nitrogen pressure, and the system was closed to the atmosphere after spontaneous refluxing ceased. More dichloromethane was added as required to compensate for loss by evaporation. The mixture was stirred at room temperature for 28 hr and then 6.13 g (0.032 mol) of 5-formyl-2,2′-bithiophene was added under a nitrogen atmosphere and stirring was continued for 2 hr. The reaction mixture was extracted with five 100-ml portions of petroleum ether. Dichloromethane was added when the reaction mixture became too viscous for further extraction. The extracts were filtered and evaporated under reduced pressure, leaving a green residue. Crystallization from hexane produced 9.09 g (82%) of **4**; mp 112–112.5°; ir (KBr) 3070, 3000 (aromatic), 1600 (C=C), 840, 795, 700 (5-monosubstituted-2,2′-bithienyl[12]), 821 (trisubstituted alkene), 535 cm^{-1} (C–Br); nmr (CDCl$_3$) δ 7.5 (s, 1 H, HC=C), 6.8–7.3 (m, 5 H, aromatic).

Anal. Calcd for $C_{10}H_6S_2Br_2$: C, 34.3; H, 1.7; S, 18.3; Br, 45.6. Found: C, 34.1; H, 1.8; S, 18.4; Br, 45.5.

5-Ethynyl-2,2′-bithienyl (5). A solution of 3.50 g (0.01 mol) of **4** in 100 ml of dry ether was cooled to −78° under dry nitrogen. *n*-Butyllithium (15.5 ml, 2.01 *M*, 0.03 mol) was diluted with 15 ml of dry ether and added dropwise to the cold solution. After stirring 1 hr at −78°, the mixture was allowed to warm to room temperature and stirring was continued 1 additional hr. The mixture was poured into water and extracted with ether. Drying (MgSO$_4$) followed by concentration on a rotary evaporator produced 1.9 g (100%) of pure **5**[4a] (nmr determination) as an oil: ir (neat) 3290 (C≡CH), 2100 cm^{-1} (C≡C); nmr (CDCl$_3$) δ 6.8–7.2 (m, 5 H, aromatic) and 3.35 (s, 1 H, C≡C*H*). Compound **5** was too unstable to attempt elemental analyses. *Anal.* Calcd: mol wt, 194. Found (mass spectrum): mol wt 194.

5-(3-Hydroxyl-1-butynyl)-2,2′-bithienyl (6). To a solution of 9.8 ml (0.52 *M*, 5.1 mequiv) of ethylmagnesium bromide in 10 ml of dry ether was added 0.95 g (5.0 mequiv) of **5** in 20 ml of dry ether. The mixture was heated at reflux for 0.5 hr. After cooling to 5°, 0.44 g (0.01 mol) of acetaldehyde in 20 ml of cold dry ether was added during 10 min. The mixture was heated at reflux for 0.5 hr, cooled, and poured into 100 ml of 1 *N* ammonium chloride solution. The organic layer and two 150-ml ether extracts of the aqueous layer were combined, dried (MgSO$_4$), and concentrated on a rotary evaporator. The remaining yellow oil (1.08 g, 92%) was shown pure by nmr spectroscopy. Chromatography of a small sample on Florisil using hexane–ether eluent furnished **6** as yellow crystals, mp 58–58.5° (lit.[4a] mp 59°), with little loss of material: ir (KBr) 3340 cm^{-1} (OH), 2200 (C≡C); nmr (CDCl$_3$) δ 6.9–7.3 (m, 5 H, aromatic), 4.75 (q, 1 H, J = 6 Hz, CHOH), 2.1 (broad, 1 H, OH), 1.5 (d, 3 H, J = 6 Hz, CH$_3$).

5-(3-Buten-1-ynyl)-2,2′-bithienyl (1). A 4 in. by 0.5 in. Pyrex tube was loosely packed with 0.31 g of neutral alumina and 0.24 g of Pyrex wool. The tube was placed in a Sargent-Welch horizontal oven and phenol (2 g) was vaporized at 540° (0.18 mm) through the tube. A mixture of 0.21 g (0.9 mmol) of **6** and 0.1 g of anhydrous sodium carbonate was placed in a 25-ml round-bottomed flask. The flask was connected to the pyrolysis tube and heated to 230° (0.18 mm). The vapors were passed through the pyrolysis tube at 540° (0.18 mm) and collected in an exit flask at −70°. The product (140 mg) consisted of a mixture of 52 mg of **6** (0.22 mmol), 49 mg of **1** (33% based on 0.68 mmol of **1** consumed), and 39 mg of **5** (30% based on 0.68 mmol of **1** consumed) as determined by nmr spectroscopy.

Chromatography on alumina (hexane-ether) furnished 44 mg (30%) of pure **1** as a yellow oil. The ir and nmr spectra of **1** were identical with published spectra.[3b,4a] Compound **1** is converted to a gum on long exposure to light or air.

5-(4-Penten-1-ynyl)-2,2′-bithienyl (2). To 24 ml of 0.38 *M* (8.3 mmol) of ethylmagnesium bromide under a dry nitrogen atmosphere was added 1.57 g (8.3 mmol) of **5** in 25 ml of dry ether during 10 min. Addition of **5** caused a gentle reflux. After complete addition, the mixture was heated at reflux for 1 hr. Dry freshly prepared cuprous chloride (0.41 g, 4.1 mmol) was added and the contents were cooled to 25°. Freshly distilled 3-bromopropene (1.08 g, 9 mmol) in 10 ml of ether was added dropwise during 5 min. The reaction mixture was stirred for 12 hr and then poured into 100 ml of 1 *M* ammonium chloride solution. The organic layer was separated and combined with three 100-ml ether extracts of the aqueous layer. The organic solution was dried (MgSO$_4$) and concentrated on a rotary evaporator to give 1.56 g of a brown oil which nmr analysis showed to contain 0.78 g (99% based on consumed **5**) of **2** and 0.79 g of **5**. Pure **1** was obtained by preparative gas chromatography using a 5 ft by 0.25 in. 20% SE-30 column at 210°: ir (neat) 3110, 3080 (aromatic), 2240 (C≡C), 990, 917 cm^{-1} (vinyl); nmr (CDCl$_3$) δ 6.8–7.2 (m, 5 H, aromatic), 5.0–6.2 (m, 3 H, vinyl), 3.2 (d, 2 H, J = 5 Hz, CH$_2$).

Anal. Calcd for $C_{13}H_{10}S_2$: C, 67.8; H, 4.4; S. 27.8. Found: C, 68.0; H, 4.4; S, 27.6

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Registry No.—**1**, 1134-61-8; **2**, 52906-76-0; **3**, 3779-27-9; **4**, 52906-77-1; **5**, 4743-21-9; **6**, 6522-33-4.

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A Practical Synthesis of the Sex Pheromone of the Pink Bollworm

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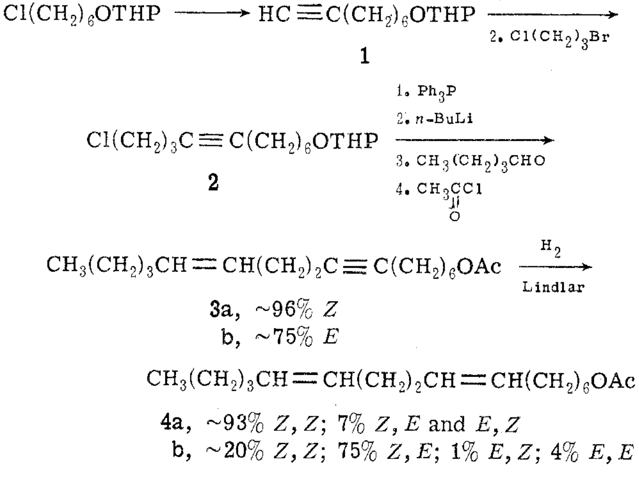
The sex pheromone of the pink bollworm moth, *Pectinophora gossypiella*, is a 1:1 mixture of (*Z,Z*)- and (*Z,E*)-7,11-hexadecadien-1-ol acetates.[1] The presence of the other two isomers of this diene, or a distinctly different ratio of the two natural isomers, causes a loss in potency of the mixture.[2] We sought to develop a route to the two desired isomers, or mixtures thereof, that would be sufficiently free of the other isomers, and that could be used to prepare the quantities of material required for testing and for subsequent control efforts. Preferably such a route would require no more than simple or fractional distillations for purification of intermediates and would avoid column chromatography. Our earlier efforts to synthesize the dienes involved the coupling of allylic Grignard reagents[2,3] and the elaboration of 1,5-hexadiyne[2] and were only partially successful. Another synthesis has been recently reported, but overall yields are low and isomer composition was determined only by infrared data.[4] We report here a useful route that starts with hexamethylene chlorohydrin (see Scheme I).

Scheme I



$$Cl(CH_2)_6OTHP \xrightarrow{LiC\equiv CH} \underset{\mathbf{1}}{HC\equiv C(CH_2)_6OTHP} \xrightarrow[2.\ Cl(CH_2)_3Br]{1.\ n\text{-BuLi}}$$

$$\underset{\mathbf{2}}{Cl(CH_2)_3C\equiv C(CH_2)_6OTHP} \xrightarrow[3.\ CH_3(CH_2)_3CHO;\ 4.\ CH_3\underset{O}{\underset{\|}{C}}Cl]{1.\ Ph_3P;\ 2.\ n\text{-BuLi}}$$

$$CH_3(CH_2)_3CH{=}CH(CH_2)_2C\equiv C(CH_2)_6OAc \xrightarrow[Lindlar]{H_2}$$

3a, ~96% *Z*
b, ~75% *E*

$$CH_3(CH_2)_3CH{=}CH(CH_2)_2CH{=}CH(CH_2)_6OAc$$

4a, ~93% *Z*, *Z*; 7% *Z*, *E* and *E*, *Z*
b, ~20% *Z*, *Z*; 75% *Z*, *E*; 1% *E*, *Z*; 4% *E*, *E*

The tetrahydropyranyl ether (THP) of the chlorohydrin was treated with lithium acetylide ethylenediamine complex to give the THP of 7-octyn-1-ol (**1**)[5] in 84% yield. The lithium salt of this acetylene was added to a solution of 1-bromo-3-chloropropane in HMPA–THF to obtain the γ-chloropropylated acetylene, **2** (53% yield); unreacted **1** could be recovered (36%). The triphenylphosphonium salt of **2** was converted to an ylide with *n*-butyllithium in HMPA–THF and allowed to react with valeraldehyde. The use of HMPA as a cosolvent in Wittig condensations has been shown to produce olefins that are $\simeq$96% cis.[6] The resulting THP of (predominantly) (*Z*)-11-hexadecen-7-yn-1-ol was transformed directly to the acetate, **3a** (58% yield from the phosphonium salt). Although **3a** was not resolved by capillary gas chromatography, the diene acetate, **4a**, obtained by hydrogenation of **3a** over Lindlar catalyst was separated into two peaks (7:93). The major peak was identical with a previously prepared sample of the *Z,Z* isomer.[2] The *Z,E* and *E,Z* pair were not distinguishable. Since catalytic hydrogenation of the acetylene was expected to produce about 3–4% (*E*)-7 double bond and the directed Wittig reaction was expected to produce about 4% (*E*)-11 double bond, the minor peak was assumed to be a composite of the *Z,E* and *E,Z* isomers in roughly equal proportions.

Attempts to produce (*E*)-11-hexadecen-7-yn-1-ol THP from **2** by Schlosser's modification to the Wittig reaction[7] failed. Also, the use of a less polar solvent (toluene) increased the proportion of trans, but the cis linkage still predominated. Isomerization of **3a** with aqueous nitrous acid at 70–75°[8] isomerized the 11 double bond to a mixture in which trans predominated, **3b**. This treatment does not shift the double bond;[9] also the gas chromatograms of the diene acetate, **4b**, resulting from hydrogenation of **3b** gave no indication of position isomerization. The *Z,Z* glc peak constituted 20% of the mixture; hence the *E,Z* content could only be ~1%, and the major peak, 75%, must be almost entirely *Z,E*. The *E,E* isomer, ~4%, was due to that proportion of the hydrogenation of **3b** that produced the 7 trans double bond.

Although the synthesis does not produce either desired isomer absolutely pure (to date no reported synthesis does), it is clear that **4a** and **4b** may be relatively easily prepared and that a combination of the two preparations will give the desired isomer ratio with only a few per cent of the unwanted *E,Z* and *E,E* isomers. Preliminary tests revealed that a blend of these preparations is as attractive to male pink bollworm moths as those preparations currently available.[10]

Experimental Section

Boiling points are uncorrected. Ir spectra were determined in CCl_4 using a Perkin-Elmer Model 457A grating spectrophotometer.[11] Nmr spectra were taken in CCl_4 on a Varian Associates T-60 spectrometer and chemical shifts are reported in parts per million (δ) downfield relative to TMS as internal standard. Glc analyses were performed with an Aerograph 1520 instrument employing an SE-30 column (0.92 m × 0.63 cm 5% on Anakrom ABS), and the analyses of the diene acetates were performed with a Hewlett-Packard 5720A instrument employing an EGGS-X SCOT column (15 m × 0.05 cm). Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, Tenn.

7-Octyn-1-ol Tetrahydropyranyl Ether (1). This compound was prepared as described:[5] yield from hexamethylene chlorohydrin THP, 84%: bp 83–90° (0.25 mm); $n^{25}D$ 1.4580 [lit.[4] $n^{25}D$ 1.4590].

11-Chloro-7-undecyn-1-ol Tetrahydropyranyl Ether (2). Compound 1 (80 g, 0.38 mol) was converted to a lithium salt by adding *n*-butyllithium (206 ml of 2.04 *M* in hexane) to a solution of 1 in THF (200 ml) that was kept under nitrogen and at 0–5° with an ice bath. The resulting solution was transferred to a dropping funnel and then added dropwise to a solution of 1-bromo-3-