ination reaction.[1,2] However, they also indicate that the frequently reported statement that syn elimination reactions are favored by base association should be more appropriately replaced by the statement that base association disfavors syn eliminations much less than anti eliminations.

A point of interest is that in the syn elimination practically identical values of deuterium kinetic isotope effects are found for the reactions promoted by solvated $C_6H_5O^-$ ($k_i^H/k_i^D = 2.5$) and by $C_6H_5O^-Li^+$ pairs ($k_{ip}^H/k_{ip}^D = 2.4$). This finding is also confirmed by the observation that the values of k_i/k_{obsd} for **2** and **3** fit exactly the same plot, k_i/k_{obsd} vs. [LiBr] (Figure 1), thus indicating that the two reactions are similarly affected by the increase in LiBr concentration. Similar k^H/k^D values for syn eliminations promoted by associated and nonassociated base are not entirely expected, owing to the possible nonlinearity of the proton transfer in the former case. However, this factor might play a minor role when the proton transfer to the base has progressed to a large degree in the transition state,[11] which should be the case for the reactions of **2**, exhibiting quite small values of deuterium kinetic isotope effect.

In the substitution reactions of **5** an approximate k_{ip} value of 1.5×10^{-3} M^{-1} s^{-1} can be calculated, ca. 170-fold smaller than k_i for the same reaction. Even though the error in this case is certainly very large since the intercept of the plot is not far from zero, it seems possible to conclude that the difference in reactivity between solvated $C_6H_5O^-$ ions and $C_6H_5O^-Li^+$ pairs is less in the substitution reaction that in the anti elimination. This conclusion is also supported by the fact that the plots of k_i/k_{obsd} vs. [LiBr] for the reactions of **4** and **5** fit different lines (Figure 1).

Thus, on the basis of the above results, it would seem that the reactivity ratio k_{ip}/k_i for the reactions of phenoxides in Me_2SO decreases in the order syn elimination > substitution > anti elimination.

Even though extention of this study to other substrates[12] is necessary in order to establish if this conclusion can be generalized and to which extent, it is interesting to note that the above order is that which, according to a recent suggestion,[13] should be expected on the basis of the probable geometrical arrangement of the transition states of these three processes when an associated base is the reacting species. An additional role could be also played by the degree of C-leaving group bond breaking in the transition state which determines the fraction of negative charge on the leaving group and consequently the strength of the interaction with the cation in the transition state. However, this factor is certainly less important than the geometrical one when syn and anti eliminations are compared. Accordingly, there is no doubt that the transition state of the syn eliminations from **2** is more carbanionic (and therefore with less C–Cl bond breaking) than the transition state of the anti eliminations from **4**.

Experimental Section

Materials. *trans*-2,3-Dichloro-2,3-dihydrobenzofuran (**2**) and *trans*-2,3-dichloro-2,3-dihydro-3-deuteriobenzofuran (**3**) were prepared by chlorine addition in Et_2O at −5–0 °C on the corresponding benzofuran;[14] the NMR spectrum (CCl_4) of **3** exhibited peaks at δ 6.40 (1 H, s, 2-H) and 6.88–7.55 (4 H, m, ArH). 2-Phenethyl chloride (**4**) (Fluka) was purified by distillation [bp 84–85 °C (15 mm)]. *n*-Butyl bromide (**5**) (Erba RPE) was distilled in the presence of anhydrous K_2CO_3 at atmospheric pressure (bp 101 °C). Phenol (Erba RPE) was used without further purification. Lithium bromide (Hoescht), a commercial sample, was dried at 120 °C before use. Tetraethylammonium bromide (Erba RS) was used without further purification.

Solvent and Base. Me_2SO (99%, v/v) was prepared by placing exactly 10 mL of water into a 1-L volumetric flask that was then made up to the mark with Me_2SO (Erba RPE) previously degassed with dry N_2. Tetraethylammonium phenoxide was prepared by adding, under nitrogen, a 0.0116 M solution of tetraethylammonium hydroxide in 99% Me_2SO to a solution of phenol in the same solvent. The former solution was obtained by placing 250 μL of tetraethylammonium hydroxide (Fluka, 20% in water) into a 25-mL volumetric flask, which was then made up to the mark with 99% Me_2SO.

Kinetic Study. Kinetic experiments were carried out by following spectrophotometrically the disappearance of the phenoxide ion in the range 310–330 nm depending on the concentration of the lithium bromide. At this wavelength no appreciable absorbance is exhibited by the reaction products. The reactions were brought about in a stoppered two-limb silica cell. In one limb was placed the substrate solution (1 mL) and in the other at first the phenol–LiBr solution (1 mL) and successively, under nitrogen, an amount of 0.0116 M tetraethylammonium hydroxide solution calculated on the basis of previous spectrophotometric titration of the phenol solution as described in the literature[15] (100–200 μL). The cell was placed in the thermostated compartment of a Beckmann DB-GT spectrophotometer. After 20 min the solutions were mixed throughly and the cell was rapidly placed again in the cell compartment of the spectrophotometer. The final product of the reaction from **2** and **3** with phenoxide ion was the expected 3-chlorobenzofuran, as shown by comparison (GPC analysis[14] at 120 °C) with an authentic specimen.[14]

Acknowledgment. This work was carried out with the financial support of the Italian National Research Council (C.N.R.).

Registry No. **2**, 63361-57-9; **3**, 70749-80-3; **4**, 622-24-2; **5**, 109-65-9; tetraethylammonium phenoxide, 32580-85-1; $C_6H_5O^-Li^+$, 555-24-8.

(11) Saunders, W. H., Jr. *Chem. Scr.* **1975**, *8*, 27.

(12) Since k_i/k_{ip} values depend on the nature of the leaving group, only systems with the same leaving group should be compared. This requirement is substantially fulfilled by our substrates since chlorine and bromine have very similar electronegativity (for instance σ^* is 1.05 for $-CH_2Cl$ and 1.00 for $-CH_2Br$).

(13) Závada, J.; Pánková, M. *Collect. Czech. Chem. Commun.* **1978**, *43*, 1080.

(14) Baciocchi, E.; Ruzziconi, R.; Sebastiani, G. V. *J. Org. Chem.* **1979**, *44*, 28.

(15) Mandolini, L.; Masci, B.; Roelens, S. *J. Org. Chem.* **1977**, *42*, 3733.

Rearrangement of 6-Substituted 2,7-Dioxabicyclo[3.2.0]hept-3-enes to Furans

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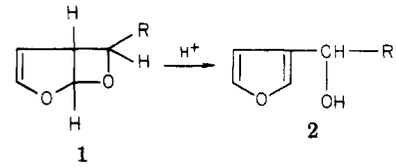
Received February 21, 1979

Photochemical cycloaddition of aldehydes to furan leads to 6-substituted 2,7-dioxabicyclo[3.2.0]hept-3-enes (**1**) in good yields.[1,2] It has been shown that protic acids induce the conversion of **1** to the furan system; this opens a simple and practical route to 3-furylmethanols[2,3] (**2**).



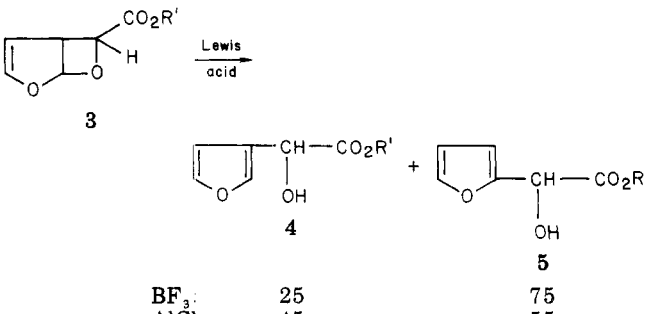
1 **2**

(1) S. Toki, K. Shima, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **38**, 760 (1965); K. Shima and H. Sakurai, *ibid.*, **39**, 1806 (1966).

(2) A. Zamojski and T. Kožluk, *J. Org. Chem.*, **42**, 1089 (1977).

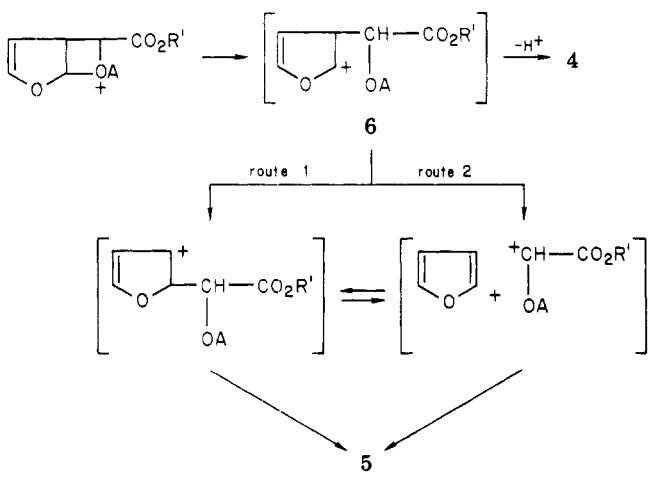
0022-3263/79/1944-3720$01.00/0

Scheme I[a]



[a] The proportion of both isomeric furylglycolates was estimated for R' = (−)-menthyl.

Scheme II



Replacement of protic acids by Lewis acids (boron trifluoride, aluminum trichloride, stannic tetrachloride) in the rearrangement of alkyl 2,7-dioxabicyclo[3.2.0]-hept-3-ene-6-carboxylate (**3**) brought about a more complex transformation: a mixture of two products was isolated from the reaction. One of the products was the expected ester **4**. The other was identified as the ester of (2-furyl)glycolate (**5**) (Scheme I).

The possibility that **5** was formed from **4** through a 1,2-rearrangement could be excluded as follows: samples of **4a** (R' = *n*-Bu) in ether solution were kept with Lewis acids for several hours. They remained unchanged even after 48 h.

It was obvious, therefore, that isomerization of **3** to **4** and **5** must occur at the stage of reorganization of the bicyclic compound. The mechanism in Scheme II comprising two routes leading to **5** can be proposed for this reaction. This mechanism postulates the formation of a carbocation (**6**) which can be stabilized by splitting off a proton to form **4**. On the other hand, **6** can undergo a 1,2-rearrangment to a more stable carbocation which splits off a proton to form **5** (route 1), or **6** can dissociate into furan and a complex composed of alkylglyoxylate and Lewis acid. This complex, being a reactive species, can attack the furan molecule at C-2, furnishing **5** (route 2).

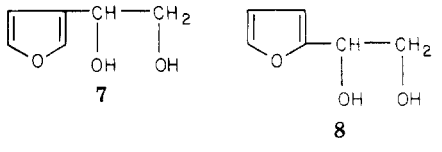
The results of boron trifluoride catalyzed rearrangement of butyl 2,7-dioxabicyclo[3.2.0]hept-3-ene-6-carboxylate (**3a**, R' = *n*-Bu) in different solvents demonstrate that the proportion between isomeric furylglycolates **4** and **5** (R' = *n*-Bu) is dependent on the polarity of the reaction medium: in more polar solvents the yield of doubly rearranged product **5** is higher (Table I). This can be regarded as an indication that carbocation **6** is, in fact, an intermediate in the rearrangement. It is well-known that polar solvents promote the formation of charged species.

Table I. Rearrangement of Butyl 2,7-Dioxabicyclo[3.2.0]hept-3-ene-6-carboxylate (3a) with $BF_3 \cdot Et_2O$

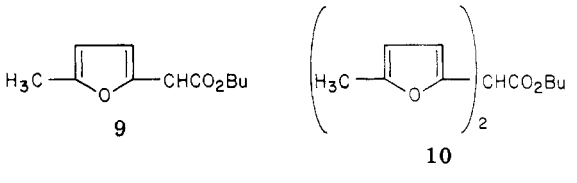
solvent	ϵ	total yield,[a] %	ratio of products 4	5
carbon tetrachloride	2.24	50	67	33
diethyl ether	4.34	70	30	70
chloroform	4.81	50	27	73
tetrahydrofuran	7.58	75	100	
acetonitrile	37.5	50	11	89

[a] Yield of **4** + **5** isolated by distillation. The residue was tar (cf. Experimental Section).

The decision in favor of routes 1 or 2 leading to **5** could be made after rearranging optically active methyl 2,7-dioxabicyclo[3.2.0]hept-3-ene-6-carboxylate (**3b**, R' = Me). Treatment with boron trifluoride etherate in ether solution gave the expected esters **4b** and **5b** (R' = CH_3) which were reduced with $LiAlH_4$ to diols **7** and **8**. The diols could be



isolated in pure states, and their optical activity could be measured. Whereas **7** retained its original optical activity, diol **8** was completely racemized. This result showed that "migration" of the $CHOHCO_2Me$ grouping was connected with the loss of its configuration. It has been shown earlier[4] that in 1,2-rearrangement of carbocations the migrating chiral group completely retains its configuration. We think, therefore, that route 1 (Scheme II) in our rearrangement should be abandoned in favor of route 2. This conclusion was further supported by the results of BF_3-catalyzed rearrangement of **3a** conducted in 2-methylfuran–ether (1:1) solution. In the postreaction mixture three products were identified by means of TLC, GLC, and ^1H NMR spectra: butyl (3-furyl)glycolate (**4a**), butyl [2-(5-methylfuryl)]glycolate (**9**), and butyl bis[2-(5-methylfuryl)]acetate (**10**) obtained in a proportion of



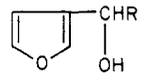
1.4:2.6:1.0. Compounds **9** and **10** could be formed only as a result of the attack of the boron trifluoride–butyl glyoxylate complex, liberated during the rearrangement, on 2-methylfuran molecules present in large excess. In fact, it was observed earlier that aldehydes can be formed from the retrocleavage of **1** when more concentrated (ca. 2–5%) acids were used for the rearrangement reaction.[2,3]

The results of Lewis acid catalyzed rearrangement of **3** raised the question of homogeneity of 3-furylmethanols obtained earlier.[2] By application of GLC and high-pressure LC methods we could show that butyl (3-furyl)glycolate (**4a**) obtained from **3a** did not contain more than 0.4% of the 2-substituted isomer **5a**. The contents of 2-substituted furans in 3-furylmethanols **11** and **12** obtained by *p*-

(3) T. Kitamura, Y. Kawakami, T. Imagawa, and M. Kawanishi, *Synth. Commun.*, 521 (1977).

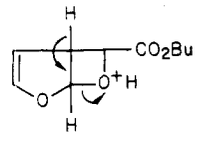
(4) J. J. Beggs and M. B. Meyers, *J. Chem. Soc. B*, 930 (1970).

toluenesulfonic acid catalyzed isomerization of 1 (R = CH_3 and C_6H_5, respectively) was below 0.1%.



11, R = CH_3
12, R = C_6H_5

Obviously, another mechanism of isomerization must be operative when the reaction is conducted in the presence of protic acids. We measured the rates of isomerization of **3a** with *p*-toluenesulfonic acid at different temperatures. The following parameters of activation were obtained: $\Delta H^{\ddagger}$ = 48.6 kJ/mol and $\Delta S^{\ddagger}_{20^\circ}$ = −141.6 J/K (−33.8 eu). High negative entropy of activation can be regarded as an indication of the highly organized transition state of the isomerization, as in **13**.



13

We conclude therefore that isomerization of **3** can proceed according to two different mechanisms: (i) with protic acids in a concerted way (at least in diethyl ether or tetrahydrofuran solution) and (ii) with Lewis acids with the intermediation of a carbocation which gives rise to secondary reactions.

Experimental Section

n-Butyl and (−)-menthyl 2,7-dioxabicyclo[3.2.0]hept-3-ene-6-carboxylates (**3a** and **3c**) were obtained by irradiation of the solution of the appropriate glyoxylate ester in furan according to ref 1 and 2. Partially optically active methyl 2,7-dioxabicyclo[3.2.0]hept-3-ene-6-carboxylate (**3b**) ([α]^{22}D 13.5°, $CHCl_3$) was obtained by methanolysis of (−)-menthyl ester **3c** in absolute methanol in the presence of sodium hydrogen carbonate.[7]

Alkyl (2-furyl)glycolates **5a** and **5c**,[5] butyl [2-(5-methylfuryl)]glycolate (**9**),[6] butyl bis[2-(5-methylfuryl)]acetate (**10**),[6] and 3- and 2-(1,2-dihydroxyethyl)furans (**7**[2] and **8**[5]) were prepared according to procedures described in literature.

Esters **4a** and **5a** display very close-lying peaks on high-pressure LC (30-cm column packed with Lichrosorb 60 SI, elution 7:3 with hexane–ethyl acetate) with the latter having shorter retention volume. A 300-mg sample of **4a** obtained from isomerization of **3a** with *p*-toluenesulfonic acid[2] was run on high-pressure LC, and the "front part" of the appearing peak (containing potentially all contamination with **5a**) was collected. This represented $^1/_{79}$th of the sample. This material was, in turn, converted into trimethylsilyl ether and analyzed by GLC (2-m column packed with 3% OV-17 on Chromosorb WT). The presence of **5a** could be detected at levels that corresponded to ca. 0.4% in the original sample.

1-(2-Furyl)ethanol (**14**) and (2-furyl)phenylmethanol (**15**) were obtained by the Grignard method from 2-furylaldehyde and methylmagnesium iodide or phenylmagnesium bromide, respectively.[8] 3-Furylmethanols **11** and **12** were obtained from the corresponding bicyclic compounds (**1**, R = CH_3 and C_6H_5) according to ref 2. Both pairs of isomeric compounds, i.e., **11**–**14** and **12**–**15**, give well-separated peaks on high-pressure LC (the same column and eluent as above). No presence of 2-furylmethanols **14** and **15** could be detected in the samples of **11** and **12**. The detection limit was estimated at ca. 0.1%.

Isomerization of (−)-Menthyl 2,7-Dioxabicyclo[3.2.0]-hept-3-ene-6-carboxylate (3c) with Lewis Acids. A solution of the ester **3c** (100 mg) in ether (1 mL) was treated with 1 drop of boron trifluoride etherate (or stannic chloride or ca. 20 mg of aluminum chloride) and left at room temperature for 6 h. After neutralization with 2 drops of triethylamine the solution was filtered through a short column of alumina and evaporated to dryness. The residue was distilled from a glass bulb at 120 °C (10^{-4} torr) (air-bath temperature), affording a mixture (ca. 60–65 mg) of esters **4c** and **5c**. The mixture was not separable on TLC. The composition of the mixture was determined by integration of ^{1}H NMR (C_6D_6 solution) signals of the furan moiety. Ester **4c** displayed signals of H-2, H-4, and H-5 at δ 7.45, 6.44, and 7.14. Ester **5c** showed signals of H-3, H-4, and H-5 at δ 6.10, 6.27, and 7.13. Signals of the $CH(OH)CO_2C_{10}H_{19}$ proton appeared at δ 5.11 for **4c** and at δ 5.19 for **5c**.

The proportions of esters **4c** and **5c** are shown in Scheme I.

Rearrangement of Butyl 2,7-Dioxabicyclo[3.2.0]hept-3-ene-6-carboxylate (3a) in Different Solvents. A solution of **3a** (200 mg) in 2 mL of the solvent (carbon tetrachloride, ethyl ether, chloroform, tetrahydrofuran, and acetonitrile) was treated with 2 drops of boron trifluoride etherate. The initially colorless solution darkened gradually. After 1 h at room temperature 3 drops of triethylamine were added and the solution was filtered through a short column of neutral alumina and evaporated to dryness. The residue was distilled at 105 °C (0.4 torr) (air-bath temperature). The yields of esters **4a** and **5a** and their proportions are given in Table I.

3- and 2-(1,2-Dihydroxyethyl)furans (7 and 8). A mixture of methyl esters **4b** and **5b** (obtained from rearrangement of 450 mg of **3b**) was reduced with lithium aluminum hydride in tetrahydrofuran solution under typical conditions. After workup, liquid diols **7** and **8** (together 170 mg) were separated by high-pressure LC on a column packed with Lichrosorb SI-60 10μ with hexane–ethyl acetate (2:3) as eluent. Diol **8** obtained as the first fraction did not show any optical activity. Diol **7** had [α]^{20}D −1.08° in ethanol.[7]

Rearrangement of 3a with Boron Trifluoride Etherate in 2-Methylfuran–Ether Solution. A sample of **3a** (80 mg) was dissolved in 2-methylfuran–ether (1:1) solution (1 mL) and treated with 1 drop of diluted (1:5) boron trifluoride etherate solution in ether. The reaction was interrupted after 5 min by addition of 2 drops of triethylamine. After filtration through a layer of neutral alumina, the dark solution was checked by TLC; the presence of **10** could be detected by comparison with an authentic sample.

After evaporation of the solvent, the residue was distilled under diminished pressure, and for the material obtained (ca. 40 mg) a ^{1}H NMR spectrum was recorded. Signals of **4a**, **9**, and **10** could be easily recognized. This material was also checked by gas chromatography (1-m column packed with 4% of Rheoplex 400 on Chromosorb WT). From the ^{1}H NMR spectrum and GLC the ratio of products **4a**, **9**, and **10** was estimated as 1.4:2.6:1.0.

Kinetics of Isomerization of 3a. For kinetic measurement a solution of **3a** (C_0 = 0.478 mol/L) in purified tetrahydrofuran was used. *p*-Toluenesulfonic acid hydrate (C_{cat} = 0.0115 mol/L) served as the catalyst. The aliquots of the reaction mixture were taken every 10 min until completion. The samples were immediately neutralized with triethylamine solution in tetrahydrofuran and evaporated to dryness. The residue was dissolved in a standard volume of hexane–ethyl acetate (7:3) solution. This solution was run on high-pressure LC (a 30-cm column filled with Lichrosorb SI-60 10μ, eluent 7:3 hexane–ethyl acetate). From the surface of peaks of compounds **3a** and **4a** the concentration of the substrate was calculated by using correction factors obtained earlier for solutions of **3a** and **4a** of known concentrations (Table II). The enthalpy and entropy of activation were calculated for 293.2 K. For a lower concentration of the catalyst (C_{cat} = 0.004 mol/L) similar activation parameters were obtained: ΔH = 44.8 kJ/mol, $\Delta S_{293.2}$ = −162.6 J/K.

Table II

T, K	10^4k, mol^{-1} s^{-1}	r
282.9	3.24	0.996
293.4	7.06	0.992
308.5	19.72	0.988

(5) O. Achmatowicz, Jr., and A. Zamojski, *Rocz. Chem.*, **42**, 453 (1968).
(6) O. Achmatowicz, Jr., and B. Szechner, *Rocz. Chem.*, **46**, 513 (1972).
(7) S. Jarosz and A. Zamojski, unpublished results.
(8) F. N. Peters, Jr., and R. Fischer, *J. Am. Chem. Soc.*, **52**, 2079 (1930).

Registry No. 3a, 61063-39-6; **3b**, 71031-61-3; **3c**, 71031-62-4; **4a**, 61063-43-2; **4b**, 71031-63-5; **4c**, 71031-64-6; **5a**, 19377-74-3; **5b**, 19377-70-9; **5c**, 71031-65-7; **7**, 71031-66-8; **8**, 19377-75-4; **9**, 36626-07-0; **10**, 36626-08-1.

A Convenient Stereoselective Route to the Sex Pheromone of the Red Bollworm Moth via an Allylic Sulfenate to Sulfoxide Rearrangement

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Received April 17, 1979

Among the insect pests for which a sex pheromone has been identified is the red bollworm moth, *Diparopsis castanea* Hmps., which does substantial damage to the cotton crop in southeastern Africa. The most potent of the sex pheromones produced by the virgin female of this species has been shown by Nesbitt and co-workers[1] to be (*E*)-9,11-dodecadien-1-ol acetate (**7**). Five synthetic routes to this pheromone have been reported.[2] Unfortunately, all of these methods are nonstereoselective and generally require a lengthy sequence of reactions. We wish to report a different synthetic approach which is both stereoselective and convenient for small-scale preparation of this pheromone (**7**).

In planning the route to **7**, allylic alcohol **4** (Scheme I) seemed to be the most attractive intermediate. Once synthesized, it can be treated with 2,4-dinitrobenzenesulfenyl chloride[3] in the presence of triethylamine, using a method recently developed by Reich and co-workers[4] for the 1,4-dehydration of allylic alcohols. The sulfenate ester initially formed from allylic alcohol **4** under such reaction conditions should rapidly rearrange to the corresponding allylic sulfoxide, which can subsequently undergo a syn elimination to afford conjugated diene **5**.

Allylic alcohol **4** was obtained in 55% yield by addition of crotonaldehyde (**3**)[5] to the Grignard reagent prepared from the tetrahydropyranyl ether derivative **2** of 8-bromo-1-octanol.[6] The latter compound (**1**) was in turn readily obtained in 90% yield by continuous extraction with cyclohexane of a solution of 1,8-octanediol[3] in aqueous hydrobromic acid at 75 °C. As we had anticipated, treatment of allylic alcohol **4** with an excess of 2,4-dinitrobenzenesulfenyl chloride and triethylamine at 80 °C afforded the desired conjugated diene **5** in 37% yield, after purification via column chromatography. The total synthesis was formally completed by removal of the tetrahydropyranyl blocking group to give (*E*)-9,11-dodecadien-1-ol (**6**) in approximately 18% overall yield from 1,8-octanediol. The physical and spectral properties of the latter alcohol **6** were consistent with those previously reported[7] for this same compound.

Since the *E* and *Z* stereoisomers of dienol **6** have been reported[8] to be difficult to resolve by chromatographic methods, the stereoisomeric purity of our final product was determined by subjecting dienol **6** to a previously utilized[9] procedure. The latter involved selective epoxidation of the internal double bond in **7** followed by VPC analysis of the corresponding monoepoxide. The failure to detect any of the *Z* stereoisomer indicated that the [2,3]-sigmatropic rearrangement of the sulfenate ester derived from allylic alcohol **4** proceeded stereospecifically. In view of the stereoselectivity of this process and the few steps required overall, the method reported in this note is a convenient one for synthesis of small quantities of the sex pheromone of the red bollworm moth.

Experimental Section

General. Reactions were carried out under a nitrogen atmosphere. The isolation of reaction products was accomplished by extracting them with the specified solvent. The combined extracts were washed thoroughly with 1 M aqueous sodium hydroxide solution followed by water and saturated brine and then dried over anhydrous magnesium sulfate. The solvent was removed from the dried extracts by using a rotary evaporator under reduced pressure. Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. Tetrahydrofuran was purified prior to use by distillation from lithium aluminum hydride. The NMR spectra were recorded with a Varian EM-360 spectrometer, and infrared spectra were obtained, using a Beckman Acculab 1 spectrophotometer. Vapor-phase chromatography (VPC) was performed on a Hewlett-Packard 5750 chromatograph, using a 6 ft × 0.125 in. SE-30 column. Where indicated, percentages refer to peak areas without correction for response factors relative to an internal standard. The microanalysis was performed by Micro-Tech Laboratories, Skokie, Ill.

8-Bromo-1-octanol (1). The procedure[6] utilized by Chapman and co-workers to prepare bromide **1** was modified as follows: A mixture of 1,8-octanediol[3] (4.23 g, 28.9 mmol), 130 mL of 48% aqueous hydrobromic acid, and 40 mL of H_2O was heated at 75 °C for 72 h while being continuously extracted with cyclohexane. The product was isolated from the cyclohexane extract in the usual manner, affording 5.44 g (90%) of monobromide **1**, the physical and spectral properties of which were identical with those previously reported[6] for this same compound. VPC analysis (oven temperature 182 °C, flow 15 mL/min) indicated the product (retention time, 5.4 min) to be >98% pure.

8-Bromo-1-(tetrahydropyran-2-yloxy)octane (2). The procedure[6] utilized by Chapman and co-workers to prepare tetrahydropyranyl ether **2** was modified as follows: A solution of 1.40 g (6.69 mmol) of alcohol **1** and 1.0 mL (11.0 mmol) of 2,3-dihydropyran in 8.0 mL of anhydrous ether containing 13 mg of *p*-toluenesulfonic acid monohydrate was stirred at room temperature for 16 h. The product was recovered by dilution of this mixture with 25 mL of ether followed by the general experimental isolation procedure. Removal of the solvent followed by evaporative distillation gave 1.93 g (98%) of tetrahydropyranyl ether **2**: bp 90–100 °C (bath temperature) (0.07 mm) [lit.[6] bp 99 °C (0.02 mm)]; the NMR spectrum was identical with that previously reported[6] for this same compound.

(*E*)-12-(Tetrahydropyran-2-yloxy)-2-dodecen-4-ol (4). A 50-mL, three-necked flask was charged with Mg turnings (411 mg, 16.9 mg-atoms) and a magnetic stirring bar and dried for 2 h in an oven at 125 °C. After the mixture was cooled under nitrogen, a small crystal of iodine and approximately 10% of a solution of bromide **2** (1.30 g, 4.44 mmol) in anhydrous tetrahydrofuran (8.0 mL) were added. After initiation of the reaction, as signified by the discharge of the dark iodine color, the rest of the bromide–THF solution was added dropwise over 30 min. After this mixture was stirred at room temperature for an additional 60 min, the solution was transferred via pipet to another 50-mL,

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(5) NMR analysis of crotonaldehyde (purified by distillation prior to its addition to the reaction mixture) indicated the presence of only the *E* stereoisomer.
(6) 8-Bromo-1-octanol (**1**) and the corresponding tetrahydropyranyl ether (**2**) have previously been synthesized, using a similar approach. See Chapman, O. L.; Mattes, K. C.; Sheridan, R. S.; Klun, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 4878.
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