structure **16** can be assigned to this substance. Apparently, nucleophile-induced decarboxylation is faster than episulfone formation in the 12-membered ring series. Further chlorination and eventual Ramberg–Backlund reaction must then take place to account for the appearance of **16**.

The one-pot Ramberg–Backlund process does not work with simple, unactivated sulfones. Di-*n*-butyl sulfone and the ten-membered ring sulfone **17**[3] are recovered unchanged from treatment with sodium hydride and hexachloroethane.[6]

Experimental Section

Sulfones were prepared from the known sulfides by typical *m*-chloroperbenzoic acid oxidation: sulfone **1**, bp 113–125 °C (0.1 mm, Kugelrohr); **3**, bp 125–130 °C (0.1 mm, Kugelrohr); **10**, mp 54–55 °C (from ether–hexane); **12**, bp 140–150 °C (0.1 mm, Kugelrohr). *E,E* sulfone ester **15** crystallized as the major component from MCPBA oxidation of an *E,E* and *E,Z* mixture of sulfides:[1b] mp 79–80 °C (from ether–hexane); 270 MHz NMR ($CDCl_3$; *J* values based on decoupling experiments) δ 5.7 (1 H, dt, J = 15.6, 7 Hz), 5.45 (1 H, m, J_{vinyl} = 15.1 Hz), 5.34 (1 H, m, J_{vinyl} = 15.6 Hz), 5.22 (1 H, dt, J = 15.6, 7 Hz), 4.15 (2 H, q, J = 7 Hz), 3.82 (1 H, dd, J = 7.3, 3.9 Hz), 3.25 (2 H, m), 2.65–2.8 (4 H, m), 2.16 (2 H, m), 1.85 (2 H, m), 1.57 (2 H, br s), 1.32 (3 H, t, J = 7 Hz); *m/e* 286.12310 (calcd for $C_{14}H_{22}O_4S$, 286.12388). Chloro sulfone ester **4** was obtained from **3** using the standard Ramberg–Backlund procedure (see below): mp 68–70 °C (from hexane); NMR ($CDCl_3$) δ 5.1 (singlet, $HC(Cl)CO_2C_2H_5$); *m/e* 242.03785 (calcd for $C_8H_{15}ClO_4S$, 242.03795).

General Procedure for One-Pot Ramberg–Backlund Sulfur Extrusion. The sulfone (1 mmol) was added to a magnetically stirred suspension of NaH (57% dispersion in oil, washed with hexane; 3.5 mmol) in 10 mL of dimethoxyethane (distilled from $LiAlH_4$) under nitrogen flow. The mixture was cooled in an ice bath and recrystallized. Hexachloroethane (1.2 mmol) was added. After the initial mild exothermic reaction had subsided, the ice bath was removed and the mixture was stirred at 20 °C for 3–24 h. The yellow mixture was then cooled, and water was cautiously added. Extraction with ether (2 × 20 mL), drying ($MgSO_4$), and concentration (aspirator) gave an oily residue. The sulfur extrusion product was then isolated by distillation (Kugelrohr). Unreacted α-chloro sulfone ester remained in the pot residue and was isolated by chromatography (PLC, silica gel). Characterization of carbocyclic sulfur extrusion products follows.

***(E,E)*-2-Carboethoxycycloocta-1,4-diene 11:** foul-smelling liquid; bp 80–90 °C (0.2 mm, Kugelrohr); 100 MHz NMR ($CDCl_3$) δ 6.72 (1 H, br t, J = 8 Hz), 5.8 (1 H, ddd, J = 16, 9, 6 Hz), 5.36 (1 H, ddd, J = 16, 10, 5 Hz), 4.1 (2 H, q, J = 7 Hz), 3.0 (2 H, ABX, J_{AB} = 16 Hz, J_{AX} = 9 Hz, J_{BX} = 5 Hz), 1.3–2.5 (6 H, m), 1.28 (3 H, t); IR (neat) 1705, 985 cm^{-1}; *m/e* 180.11566 (calcd, 180.11503).

***(E,E)*-2-Carboethoxycyclonona-1,4-diene 14:** liquid; bp 115–125 °C (0.2 mm, Kugelrohr); 100 MHz NMR ($CDCl_3$) δ 6.96 (1 H, br t, J = 8 Hz), 5.3–5.8 (2 H, m), 4.2 (2 H, q, J = 7 Hz), 3.5 (1 H, br d, J = 16 Hz), 3.0 (1 H, dd, J = 16, 8 Hz), 1.5–2.6 (7 H, m), 1.3 (3 H, t, J = 7 Hz), 1.1 (1 H, m); IR (neat) 1710, 988 cm^{-1}; *m/e* 194.13050 (calcd for $C_{12}H_{18}O_2$, 194.13068). At 270 MHz, the olefinic region of δ 5.3–5.8 is resolved and a trans vinyl coupling of 15.4 Hz is present.

2-Chlorocycloundeca-1,4,7-triene (16). Sulfone ester **15** (30 mg, 0.11 mmol) was dissolved in dry DME (1 mL) and stirred under nitrogen. Potassium *tert*-butoxide (26 mg, 0.23 mmol) and C_2Cl_6 (55 mg, 0.23 mmol) were added. After 16 h at 20 °C, the product was recovered by the usual ether–aqueous workup. Separation by PLC (silica gel, 3% ethyl acetate–hexane) gave a major zone at R_f 0.6 of 7 mg (35%) of **16**. The oily product slowly solidified: mp 66–70 °C; 270 MHz NMR ($CDCl_3$) δ 4.95–5.25 (5 H, m), 2.97 (2 H, m), 2.6–2.75 (2 H, m), 2.33 (1 H, m), 2.11 (3 H, m), 1.6–1.9 (2 H, m); IR (neat) 980, 960 cm^{-1}; *m/e* 182.08607 (calcd for $C_{11}H_{15}Cl$, 182.08623).

Acknowledgment. This work was supported by PHS Grant CA17918-02.

Registry No.—**1**, 66102-12-3; (*E*)-**2**, 22210-20-4; (*Z*)-**2**, 66102-13-4; **3**, 66102-14-5; **4**, 66102-15-6; (*E*)-**7**, 66102-16-7; (*Z*)-**7**, 66102-17-8; **10**, 66102-18-9; **11**, 66102-19-0; **12**, 66102-20-3; **13**, 66102-21-4; **14**, 66102-22-5; **15**, 66102-23-6; **16**, 66102-24-7; hexachloroethane, 67-72-1.

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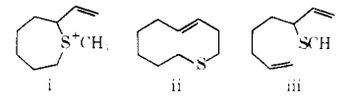

i ii iii

(4) Identical with authentic iii, prepared by methylation of the corresponding mercaptan.[5]
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Stereoselective Synthesis of (*E*)- and (*Z*)-1-(Phenylseleno)-1-alkenes[1]

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Recently we described a procedure for the preparation of 1-(phenylseleno)-1-alkenes[2] via the addition of phenylselenenyl bromide to monosubstituted alkenes **1** under thermodynamically controlled conditions, followed by dehydrobromination of the resulting Markownikoff adducts **2**. Although this transformation was regioselective, it was not stereoselective; initial experiments involving the dehydrobromination of **2** with potassium *tert*-butoxide in THF led to the formation of both (*E*)-1-(phenylseleno)-1-alkenes **3** and (*Z*)-1-(phenylseleno)-1-alkenes **4** (Table I).

We now wish to report procedures for the stereoselective preparation of both (*E*)- and (*Z*)-1-(phenylseleno)-1-alkenes.

A number of base–solvent systems were examined for the dehydrobromination of **2** in an effort to improve the ratio of *E–Z* isomers. The highest *E–Z* ratios were obtained utilizing lithium diisopropylamide (LDA) in Et_2O at 0 °C (Table I). The presence of even small amounts of THF (10% by vol) in the LDA–Et_2O procedure resulted in *E–Z* ratios similar to

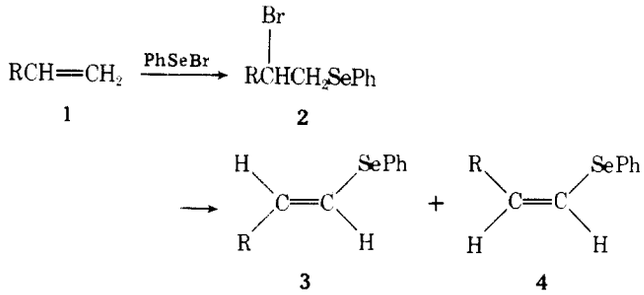
Table I. Percentage of 3/4 Formed by Dehydrobromination of β-Bromoalkyl Phenyl Selenides 2[a]

			reaction conditions[b]		
	β-bromoalkyl phenyl selenide **2**		*t*-BuOK–THF	LDA–Et_2O	registry no. of **3**/registry no. of **4**
entry	R	registry no.	**3**/**4**	**3**/**4**	
a	Me	68001-59-2	55/45	77/23	68001-61-6/ 68001-62-7
b	*n*-Bu	63831-75-4	60/40	91/9	67649-77-8/ 67649-78-9
c	*i*-Pr	66221-89-4	73/27	96/4	67649-79-0/ 68001-63-8
d	*t*-Bu	66221-91-8	100/0		63831-89-0
e	Ph	68001-60-5	100/0		60466-40-2

[a] Percentages determined by VPC analysis on a 24 ft × ⅛ in. 1.5% DEGS on 100/120 Chromosorb G column. Preparations of mixtures of the following *E* and *Z* isomers have been reported: **3a/4a** (ref 8a,2); **3b/4b** (ref 3,2); **3c/4c** (ref 2); **3e/4e** (ref 3). For preparation of **3d**, see ref 2. The preparation of stereoisomerically pure **3e** and **4e** has been reported (ref 3), although the assignment of stereochemistry is clearly incorrect.[10] [b] In all instances, isolated yields of the (phenylseleno)alkenes were >90%.

0022-3263/78/1943-4885$01.00/0

Scheme I



those obtained with *t*-BuOK in THF. The rate of dehydrobromination of **2** by LDA in hexane was extremely slow, and extensive decomposition occurred. No significant improvement in the *E*–*Z* ratio was obtained when the dehydrobromination with *t*-BuOK in THF was carried out at −78 °C, rather than 0 °C.

Since only the *E* isomer was available stereoselectively by the dehydrobromination of **2**, an alternate method for the stereoselective formation of (*Z*)-1-(phenylseleno)-1-alkenes **4** was investigated. Reaction of 1-(phenylseleno)-1-alkynes **5**, readily prepared from the corresponding lithium acetylides and PhSeBr,[3] with dicyclohexylborane followed by protonolysis with HOAc[4] gave **4** in good yields; VPC analysis indicated >95% isomeric purity (Scheme II).

Finally, additional approaches for the preparation of (*E*)-1-(phenylseleno)-1-alkenes **3** utilizing organoboranes were examined. In an approach patterned after the procedure of Brown for the stereoselective synthesis of alkenyl iodides,[5] alkynes were converted to (*E*)-alkenylboronic acids **6**; treatment of **6** with NaOH (1 equiv) followed by PhSeBr stereoselectively gave (*E*)-1-(phenylseleno)-1-alkenes **3** in good yields with isomeric purity >95%. Likewise, reaction of the (*E*)-alkenylmercuric chloride[6] **7e** with PhSeCl[7] gave **3e** with isomeric purity >95% (Scheme III).

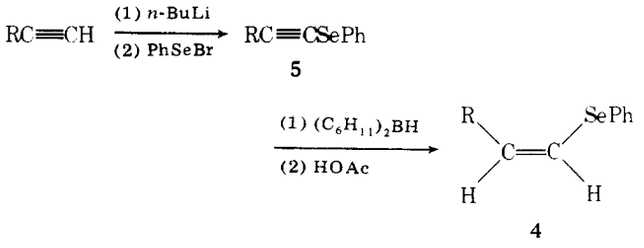
Thus, it is now possible to stereoselectively prepare both (*E*)- and (*Z*)-1-(phenylseleno)-1-alkenes.[8] We have utilized these substances as synthons for the formation of new carbon to carbon bonds;[9] further investigations concerning their utility are in progress.

Experimental Section

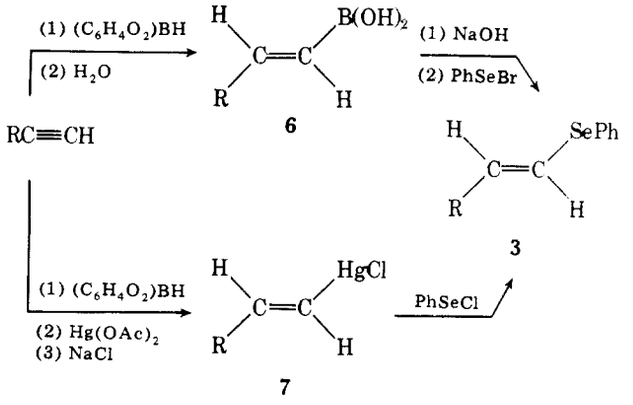
^{1}H-NMR spectra were recorded for CCl_4 solutions with tetramethylsilane as an internal standard on either a Varian EM 360L or HA 100. IR spectra were recorded on a Beckman Acculab 4. Vapor phase chromatography (VPC) analyses were performed on a Hewlett Packard 5830A gas chromatograph using a 24 ft by $\frac{1}{8}$ in. 1.5% DEGS on 100/120 Chromosorb G column. Diethyl ether and tetrahydrofuran were freshly distilled from sodium benzophenone under an atmosphere of N_2, diisopropylamine was distilled from CaH_2, and *t*-BuOK was freshly sublimed.

General Procedure for Dehydrobromination with *t*-BuOK in THF. To a solution of the β-bromoalkyl phenyl selenide **2**[2] (1.00 mmol) in THF (10 mL) cooled to 0 °C under an atmosphere of Ar was added a solution of *t*-BuOK (1.20 mmol) in THF (10 mL). The reaction mixture was stirred at 0 °C for 1 h, the THF was removed in vacuo, and the residue was dissolved in Et_2O (50 mL), washed with H_2O (2 × 10 mL) and brine (10 mL), and dried ($MgSO_4$). Evaporation

Scheme II



Scheme III



of the Et_2O in vacuo and purification of the residue by evaporative distillation gave the 1-(phenylseleno)-1-alkene mixtures; in all instances, the yields were >90%. Table I indicates the percentage of **3**/**4** formed under these conditions.

General Procedure for Dehydrobromination with LDA in Et_2O. To a solution of *i*-Pr_2NH (2.2 mmol) in Et_2O (2.0 mL) at 0 °C under an atmosphere of Ar was added a solution of *n*-BuLi in hexane (2.4 M, 0.80 mL, 2.0 mmol) and the reaction mixture was stirred for 10 min. A solution of the β-bromoalkyl phenyl selenide **2**[2] (1.00 mmol) in Et_2O (2.0 mL) was added, and stirring at 0 °C was continued for 6 h. The reaction mixture was treated with Et_2O (50 mL), washed with saturated aqueous NH_4Cl (2 × 10 mL) and brine (10 mL), and dried ($MgSO_4$). Evaporation of the Et_2O in vacuo and purification of the residue by evaporative distillation gave the 1-(phenylseleno)-1-alkene mixtures; in all instances, the yields were >90%. Table I indicates the percentage of **3**/**4** formed under these conditions.

Preparation of 1-(Phenylseleno)-1-hexyne (5b). To a solution of 1-hexyne (25.0 mmol) in THF (10 mL) cooled to 0 °C under an atmosphere of Ar was added a solution of *n*-BuLi in hexane (2.40 *M*, 10.4 mL, 25.0 mmol). The reaction mixture was stirred at 0 °C for 5 min, and a solution of PhSeBr (20.0 mmol) in THF (10 mL) was added dropwise over 5 min with stirring. The reddish-brown color of PhSeBr disappeared immediately. The THF was removed in vacuo and the residue was treated with Et_2O (100 mL), washed with H_2O (2 × 20 mL) and brine (10 mL), and dried ($MgSO_4$). Evaporation of the Et_2O in vacuo and purification by evaporative distillation (170 °C, 2 mm) gave 1-(phenylseleno)-1-hexyne as a colorless liquid (97%): ^{1}H NMR (CCl_4) δ 0.75–1.72 (m, 7 H), 2.28–2.60 (m, 2 H), 7.12–7.70 (m, 5 H); IR (neat) 2200 (w), 1600, 1495, 1460, 750, 700 cm^{-1}.

Preparation of (Phenylseleno)-1-phenylacetylene (5e). Prepared according to the literature procedure (ref 3).

Synthesis of (*Z*)-1-(Phenylseleno)-1-hexene (4b) by Dicyclohexylborane Reduction of 5b. To dicyclohexylborane (1.00 mmol) in THF (10 mL) cooled to −20 °C under an atmosphere of Ar was added a solution of 1-(phenylseleno)-1-hexyne (1.00 mmol) in

Table II. ^{1}H NMR Data[a]

3a:	δ 1.78 (d, *J* = 6 Hz, 3 H), 5.99 (dq, *J* = 15 Hz, 6 Hz), and 6.39 (d, *J* = 15 Hz) [total 2 H], and 7.00–7.71 (m, 5 H)
3b:	δ 0.65–1.62 (m, 6 H), 1.85–2.32 (m, 2 H), 6.02 (dt, *J* = 15 Hz, 6 Hz), and 6.42 (d, *J* = 15 Hz) [total 2 H], and 7.10–7.61 (m, 5 H)
3c:	δ 0.93 (d, *J* = 6 Hz, 6 H), 2.25 (m, 1 H), 5.92 (dd, *J* = 15 Hz, 6 Hz), and 6.32 (d, *J* = 15 Hz) [total 2 H], and 7.01–7.65 (m, 5 H)
3d:	δ 1.06 (s, 9 H), 6.04 (d, *J* = 16 Hz), and 6.41 (d, *J* = 16 Hz) [total 2 H], and 7.10–7.50 (m, 5 H)
3e:	δ 6.70 (d, *J* = 16 Hz) and 7.10–7.50 (m), includes partially obscured d at 7.20
4b:	δ 0.70–1.55 (m, 7 H), 1.90–2.41 (m, 2 H), 5.91 (dt, *J* = 10 Hz, 6.5 Hz), and 6.35 (dt, *J* = 10 Hz, 1 Hz) [total 2 H], and 6.96–7.52 (m, 5 H)
4e:	δ 6.71 (d, *J* = 10 Hz) and 6.97 (d, J = 10 Hz) [total 2 H], and 7.15–7.70 (m, 10 H)

[a] CCl_4 solution with tetramethylsilane as an internal standard.

THF (10 mL). The reaction mixture was allowed to warm to 20 °C and stirred for 2 h. Acetic acid (10 mmol) was added and stirring was continued for 30 min. The THF was removed in vacuo. The residue was dissolved in hexane (50 mL), washed with H_2O (2 × 50 mL), and dried ($MgSO_4$) and the hexane was evaporated. The residue was purified by filtration through a short column of silica gel (10 g) with hexane, followed by evaporative distillation (110 °C, 0.05 mm) to give (*Z*)-1-(phenylseleno)-1-hexene (85%): VPC analysis (24 ft × ⅛ in., 1.5% DEGS on 100/120 Chromosorb G, 180 °C, 30 mL He/min) indicated >95% isomeric purity; ^1H NMR, see Table II; IR (neat) 1595, 1490, 1455, 1035, 745, 700 cm^{-1}.

Synthesis of (*Z*)-1-(Phenylseleno)-2-phenylethene (4e)[10] by Dicyclohexylborane Reduction of 5e. The experimental procedure described above was utilized on **5e** to give (*Z*)-1-(phenylseleno)-2-phenylethene (90%): bp 100 °C, 0.05 mm; ^1H NMR, see Table II; IR (neat) 1610, 1585, 1485, 1450, 1080, 1030, 955, 740, 700 cm^{-1}.

Synthesis of (*E*)-1-(Phenylseleno)-1-hexene (3b) from (*E*)-1-Hexenylboronic Acid (6b). A mixture of 1-hexyne (1.10 mmol) and catecholborane (1.00 mmol) was refluxed in an atmosphere of Ar for 2 h. The mixture was cooled to 25 °C, H_2O (3 mL) was added, and the reaction was stirred for 1 h. A solution of 0.50 M NaOH (2.0 mL) was added, the reaction mixture was stirred for 1 min, and a solution of PhSeBr (1.00 mmol) in THF (5 mL) was added. The dark green reaction mixture was stirred for 5 min, the THF was removed in vacuo, and the residue was extracted with ether (2 × 25 mL). The ether extracts were dried ($MgSO_4$), the ether was evaporated, and the residue was purified by evaporative distillation (85 °C, 0.01 mm) to give (*E*)-1-(phenylseleno)-1-hexene (70%). VPC analysis indicated >95% isomeric purity. ^1H NMR was identical to sample prepared by dehydrohalogenation of **2b.**

Synthesis of (*E*)-1-(Phenylseleno)-2-phenylethene (3e)[10] from (*E*)-2-Phenyl-1-ethenylboronic Acid (6e). The experimental procedure described above was utilized on **6e** to give (*E*)-1-(phenylseleno)-2-phenylethene (90%): bp 100 °C, 0.05 mm; ^1H NMR identical to sample prepared by dehydrohalogenation of **2e;** IR (neat) 1685, 1480, 1445, 1070, 1025, 1005, 950, 735, 690 cm^{-1}.

Synthesis of (*E*)-1-(Phenylseleno)-2-phenylethene (3e)[10] from (*E*)-2-Phenyl-1-ethenylmercuric Chloride (7e). A mixture of phenylacetylene (1.00 mmol) and catecholborane (1.00 mmol) under an atmosphere of Ar was heated at 140 °C for 10 min. The reaction was cooled to 0 °C and treated with THF (5 mL), $Hg(OAc)_2$ (1.0 mmol) was added, and the mixture was stirred vigorously for 10 min and then poured into ice water (10 mL) containing NaCl (10 mmol). The THF was removed in vacuo, and the resulting alkenylmercuric chloride **7e** was dried in vacuo. A suspension of the alkenylmercuric chloride in CH_2Cl_2 (5 mL) was treated with a solution of PhSeCl (1.00 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The mixture was stirred for 10 min, treated with Et_2O (50 mL), washed with H_2O (2 × 10 mL) and brine (10 mL), and dried ($MgSO_4$). Evaporation of the solvents in vacuo and purification by filtration through a column of silica gel (10 g) with hexane, followed by evaporative distillation (100 °C, 0.05 mm), gave (*E*)-1-(phenylseleno)-2-phenylethene (80%). ^1H NMR was identical to samples prepared above.

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Registry No.—**4e,** 60466-30-0; **5b,** 68001-64-9; **5e,** 30665-96-4; **6b,** 42599-18-8; **6e,** 6783-05-7; **7e,** 36525-03-8; 1-hexyne, 693-02-7; phenylselenenyl bromide, 34837-55-3; phenylacetylene, 536-74-3.

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(10) The assignment of the stereochemistry of the PhCH=CHSePh isomers made by Petragnani, Rodrigues, and Comasseto (ref 3) is clearly incorrect. These workers assigned the compound with $J_{CH=CH}$ = 10 Hz as the trans isomer and the compound with $J_{CH=CH}$ = 16 Hz as the cis isomer. We have also carried out the addition of PhSeH to PhC≡CH as described[3] and obtained (*E*)-1-(phenylselno)-2-phenylethene (**3e**): $J_{CH=CH}$ = 16 Hz.

Stereochemistry of Woodhousin[1]

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The results of our recent X-ray analysis of tirotundin ethyl ether (**1b**)[2] raised doubts, for reasons that have been discussed,[2] about the C-8 stereochemistry previously assigned to the heliangolides woodhousin,[3] tifruticin, and deoxytifruticin.[4] Because of this and the close relationship of woodhousin to several other hemiacetalic heliangolides,[5] we have examined single crystals of woodhousin by X-ray crystallography. The results led to structure **2a,** thus confirming our earlier conclusions about the structure and stereochemistry of woodhousin, with the exception of the configuration at C-8. Our results also establish the full stereochemistry of tagitinin B, which has been identified[5b] as desacetylwoodhousin, and tagitinin C, which has been correlated with tagitinin B, as **2b** and **3,** respectively.

Crystal data of **2a** are listed in Table I. Figure 1 is a stereoscopic drawing of the molecule which represents the absolute configuration as well since then the sign of the C=C—C=O torsion angle (ω_2 of Table II), which has been related[6] to the Cotton effect associated with the n → π^* transition of an α,β-unsaturated lactone, corresponds to the observed[3] positive sign of the Cotton effect. As usual, the sign of ω_2 is paired with the sign of the C(α)–C(β)–C(γ)–O torsion angle (ω_3). It is noteworthy that in comparison with tirotundin, introduction of the C-4, C-5 double bond has had the effect of changing the chirality of the lactone chromophore, although the overall shape of the molecule has not changed significantly.

The crystal structure (Figure 1) supports our original attribution[3] of the abnormally low shift of H-7 in heliangolides of the woodhousin type to the configuration of the hemiacetal linkage (3*S*, 10*R* in woodhousin) which places H-7 in proximity to the ether oxygen. In our earlier discussion of wood-

Table I. Crystal Data for Woodhousin

formula	$C_{21}H_{28}O_8$, orthorhombic
space group	$P2_12_12_1$ (Z = 4)
a, Å	10.013 (3)
b, Å	12.974 (2)
c, Å	16.877 (4)
d_{calcd}, g cm^{-3}	1.237

Table II. Lactone Ring Torsion Angles of Woodhousin

C(6)–O(3)–C(12)–C(11)	ω_1	−7.3°
C(13)–C(11)–C(12)–O(4)	ω_2	10.0°
C(11)–C(7)–C(6)–O(3)	ω_3	11.1°
C(5)–C(6)–C(7)–C(8)	ω_4	131.4°

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