150 °C (10 min), 10 °C/min, 200 °C (5 min); 4/13: 180 °C (5 min), 10 °C/min, 240 °C (10 min); 7/16: 180 °C (5 min), 20 °C/min, 250 °C (5 min); 2/11: 130 °C (5 min), 10 °C/min, 200 °C (5 min); 5/14: 180 °C (5 min), 10 °C/min, 250 °C (5 min).

General Procedures for Cyclopropanation of 3 and 6 (Analytical GC Runs). A magnetically stirred solution of Et_2Zn (51 μL, 0.50 mmol, 2.00 equiv) in dry DCE (0.75 mL) was cooled to 0 °C, and the dihalomethane (1.00 mmol, 4.00 equiv) was added via syringe. The reaction mixture was stirred for 5 min at 0 °C, and a solution of the olefin (0.25 mmol) in DCE (0.50 mL) was added slowly via syringe. The reaction mixture was quenched by the addition of saturated NH_4Cl (2 mL), was allowed to warm to room temperature, and was stirred vigorously for 10 min. A 1.00 M stock solution of cyclododecane in DCE (250 μL) was then added. An aliquot of the reaction mixture was filtered through a pipette of silica gel with EtOAc as the eluent and partially concentrated. Determination of the product ratios was accomplished by GC analysis using the programs indicated as follows: 3/12, 160 °C isothermal; 6/15, 80 °C (3 min), 10 °C/min, 240 °C (3 min). Final ratios and yields were calculated on the basis of independently obtained response factors as described above.

Acknowledgment. We are grateful to the National Institutes of Health (GM-30938) and the National Science Foundation (Presidential Young Investigator Award CHE 8451321) for support of this project. Matching funds were provided by the Upjohn Company and Stuart Pharmaceuticals.

Registry No. 1, 935-31-9; 2, 873-66-5; 3, 4407-36-7; 4, 101306-31-4; 5, 83977-12-2; 6, 62860-38-2; 7, 102922-57-6; 8, 128820-14-4; 9, 99267-72-8; 10, 286-92-0; 11, 57637-49-7; 12, 79981-48-9; 13, 136616-39-2; 14, 136616-40-5; 15, 136616-41-6; 16, 136616-42-7; 17, 136658-31-6; 18 (isomer 1), 99267-80-8; 18 (isomer 2), 136658-32-7; DCE, 107-06-2; Et_2Zn, 557-20-0; $ClCH_2I$, 593-71-5; CH_2I_2, 75-11-6; *trans*-cinnamaldehyde, 14371-10-9.

One-Flask, Regiospecific Conversions of Allylic Alcohols into Two-Carbon-Extended, Conjugated Dienoate Esters. Use of a New Sulfinyl Orthoester

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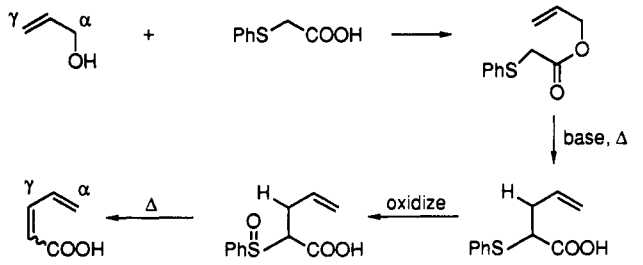
Sixteen differently substituted primary and secondary allylic alcohols are shown to react with sulfinyl orthoacetate 1 at 100 °C sequentially via a [3,3] sigmatropic rearrangement and then a β-elimination of benzenesulfenic acid to form conjugated dienoate esters 5–13 in 45–95% yields. This one-flask, intramolecular carbon–carbon bond-forming process represents a simple and convenient method for regiospecific γ-attachment of a two-carbon (ethoxycarbonyl)methylene unit via the synthetic equivalent of an S_N2' process. Two examples are given in which rationally designed dienoates 20 and 24, prepared via this one-flask process and carrying a pendant alkene unit, undergo intramolecular 2 + 4 cycloaddition producing bicyclic cyclohexenes 21 and 25.

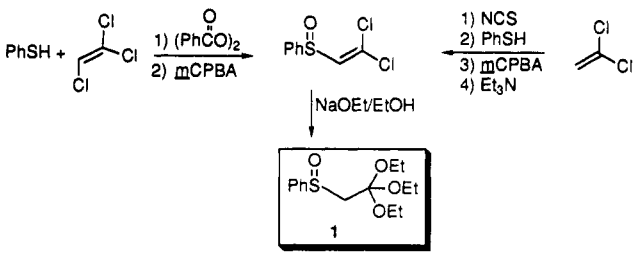
Introduction

In connection with a project on asymmetric total synthesis of hormonally active vitamin D_3 analogues, we required a simple and high-yield synthetic method for conversion of a cyclohexenyl allylic alcohol into the corresponding two-carbon-extended, conjugated dienoate ester.[1] Although the standard protocol of orthoester Claisen rearrangement to form a γ,δ-unsaturated ester[2] proceeded well, subsequent introduction of the requisite α,β-unsaturation under various conditions proceeded poorly.[1a] Likewise, Ireland ester enolate Claisen rearrangement[2g] of a cyclohexenyl allylic α-(phenylthio)acetate, although successful, was not high yielding, and it involved a linear sequence of steps including isolation of three intermediates on the path toward the 2,4-pentadienoic acid product (Scheme I). Based on our interest in sulfoxide chemistry,[3]

Scheme I



Scheme II



we have overcome this difficulty and have developed a streamlined process using an orthoester carrying a sulfinyl group designed to undergo spontaneous thermal β-elimination[4] under the same reaction conditions used for the

(1) (a) Posner, G. H.; Kinter, C. M. *J. Org. Chem.* **1990**, *55*, 3967. (b) Posner, G. H.; Nelson, T. D. *Ibid.* **1991**, *56*, 4339.

(2) For reviews, see: (a) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1. (b) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. (c) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 1. (d) Ziegler, F. E. *Chem. Rev.* **1988**, *88*, 1423. (e) Blechert, S. *Synthesis* **1989**, 71. See also: (f) Johnson, W. S.; Werthermann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970**, *82*, 741. (g) Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 5897.

(3) (a) Posner, G. H. *Pure Appl. Chem.* **1990**, *62*, 1949. (b) Posner, G. H. *Acc. Chem. Res.* **1987**, *20*, 72.

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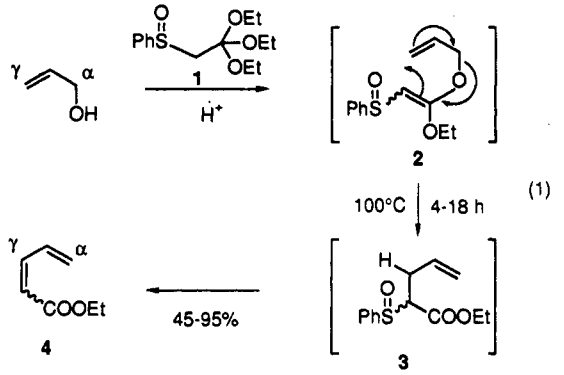
initial [3,3] sigmatropic rearrangement (eq 1).[5-7] This



one-flask convergent sequence involving presumably intermediate allylic vinylic ethers 2[8] and α-sulfinyl esters 3 proceeds conveniently on a gram scale without isolation of any intermediate and allows intramolecular attachment of a two-carbon unit regiospecifically to the γ-carbon atom of an allylic alcohol. Herein is reported a full account of the scope of this synthetic method as well as some examples of intramolecular Diels–Alder reactions of dienoate esters 4 prepared easily via eq 1 carrying a suitably positioned dienophilic alkene unit.

Results and Discussion

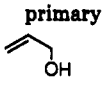
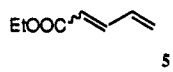
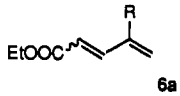
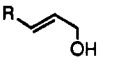
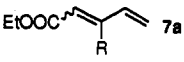
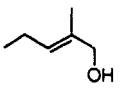
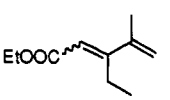
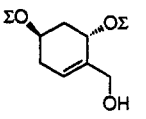
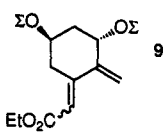
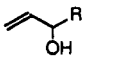
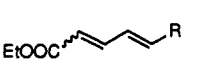
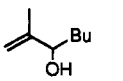
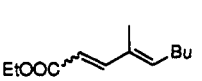
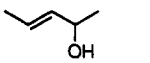
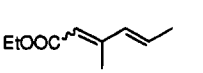
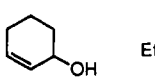
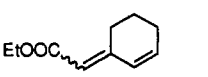
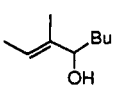
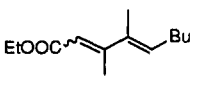
We have prepared sulfinyl orthoester 1 in two ways (Scheme II). Ionic addition of benzenesulfenyl chloride to 1,1-dichloroethylene gave a 1,1,1-trichloro thioether that underwent sulfide oxidation and then dehydrochlorination to form phenyl 2,2-dichlorovinyl sulfoxide.[9] More conveniently and rapidly, radical addition of benzenethiol to trichloroethylene followed by sulfide oxidation gave the same phenyl 2,2-dichlorovinyl sulfoxide.[10] Refluxing this dichlorovinyl sulfoxide with ethanolic sodium ethoxide gave the desired, new sulfinyl orthoester 1 as an oil in good overall yield. Storage of this orthoester neat at 0 °C for 2 months produced no deterioration in purity.

A series of differently substituted primary, secondary, and tertiary allylic alcohols was studied to establish the scope of the one-flask, tandem rearrangement–elimination sequence illustrated in eq 1.

Unsubstituted allyl alcohol reacted with 2 equiv of sulfinyl orthoester 1 and a catalytic amount of 2,4,6-trimethylbenzoic acid in methylene chloride in a sealed tube at 100 °C for 6 h to produce ethyl pentadienoate (5) isolated after chromatography as a 1:4 mixture of *Z* and *E* geometric isomers in 75% yield (Table I). The mainly *E* stereochemistry of the α,β-double bond in this conjugated dienoate 5 is fixed during the in situ pyrolytic elimination of benzenesulfenic acid via two diastereomeric transition states.[4] No evidence was obtained via an NMR time study for any *E* ⇄ *Z* isomerization during the course of the reaction.

β-Substituted, γ-substituted, and β,γ-disubstituted *primary* allylic alcohols reacted similarly to form 2-carbon extended conjugated dienoates 6–9 in 51–90% yields (Table I). It is particularly noteworthy from a practical

Table I. Two-Carbon Chain Extension According to eq 1

allylic alcohol	product dienoate		% yield of purified product
primary			
		5	75
		6a R = Me	51
		6b R = Et	74
		7a R = Me	71
		7b R = Et	68
		7c R = n-Pent	60
		7d R = MeCH=CH	90
		8	74
 Σ = SiMe$_2$Bu-t		9	86
secondary			
		10a R = Me	79
		10b R = n-Pent	67
		10c R = allyl	74
		11	73
		12	45
		13	95
		14	60

(4) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.

(5) For related [3,3] sigmatropic rearrangements of sulfide-containing allylic vinylic ether systems, see: (a) Lythgoe, B.; Millner, J. R.; Tideswell, J. *Tetrahedron Lett.* **1975**, 2593. (b) Lythgoe, B.; Manwaring, R.; Milner, J. R.; Moran, T. A.; Nambudiry, M. E. N.; Tideswell, J. *J. Chem. Soc., Perkin Trans. 1* **1978**, 387. (c) Ager, D. J.; Cookson, R. C. *Tetrahedron Lett.* **1982**, *23*, 3419. See also: (d) Raucher, S.; Hwang, K.-J.; MacDonald, J. E. *Tetrahedron Lett.* **1979**, 3057.

(6) For an analogous two-pot procedure see: Nakai, T.; Tanaka, K.; Ogasawara, K.; Ishikawa, W. *Chem. Lett.* **1981**, 1289. Nakai, T.; Setoi, H.; Kageyama, Y. *Tetrahedron Lett.* **1981**, *29*, 4097.

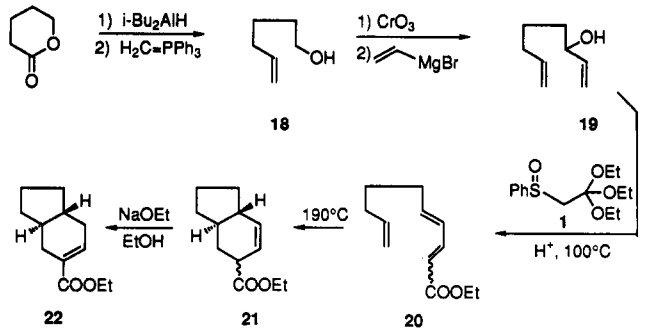
(7) For an analogous procedure leading to α-methylene-γ,δ-unsaturated esters, see: Vatele, J. M. *Tetrahedron Lett.* **1983**, *24*, 1239 and references cited therein. See also: Vatele, J. M. *Tetrahedron* **1986**, *42*, 4443.

(8) For structurally related Claisen rearrangements of silyl ketene acetals, see: Ireland, R. E.; Wipf, P.; Armstrong, J. D., III. *J. Org. Chem.* **1991**, *56*, 650 and references cited therein.

(9) Nagashima, E.; Suzuki, K.; Sekiya, M. *Chem. Pharm. Bull.* **1981**, *29*, 1274.

(10) Cristol, S. J.; Jarvis, B. B. *J. Am. Chem. Soc.* **1966**, *88*, 3095.

Scheme III



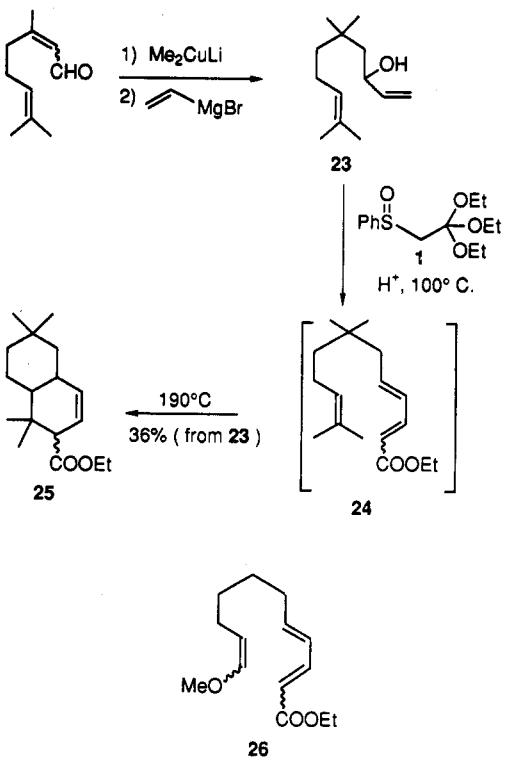
viewpoint that preparation of complex, highly functionalized dienoate **9** proceeded on gram scale, and even multigram scale reactions also should be possible. It is particularly noteworthy also from a synthetic viewpoint that γ-substituted allylic alcohols enter successfully into this regiospecific two-carbon γ-attachment process. Formation of cross-conjugated dienoate **7d** in 90% yield is a particularly good example of this γ-regiocontrol. In contrast, conversion of such γ-substituted allylic alcohols into better electrophiles (e.g., allylic sulfonates or halides) followed by nucleophilic displacement with, for example, α-sulfenyl or α-sulfinyl ester enolate ions has been reported to involve poor α- vs γ-regiocontrol and to produce hard to separate mixtures of structural isomers.[11,12] Our only poor results obtained with this class of γ-substituted allylic alcohol reactants were with cinnamyl alcohol and myrtenol, possibly due to instability in these two cases of reactants and/or products toward the acidic conditions used.

Unsubstituted *secondary* allylic alcohols reacted smoothly with sulfinyl orthoester **1** to form linear alkadienoates **10a–c** in 67–79% yields. Even under these reaction conditions, nonconjugated trienoate **10c** was formed to the exclusion of its fully conjugated isomer. As expected from the established stereochemical outcome of the Claisen orthoester [3,3] sigmatropic rearrangement process, the γ,δ-double bond geometry is almost completely *E*.[2,8] Similarly, β-substituted, γ-substituted, and β,γ-disubstituted secondary alcohols were converted into dienoates **11–14** in 45–95% overall yields. Of special note is the γ-regiocontrol in this *intra*molecular formation of dienoate **14**; activation of the reactant hydroxyl group followed by *inter*molecular nucleophilic displacement is expected to involve poor α- vs γ-regiocontrol because the S_N2 vs S_N2' pathways would be similar in energy.[11,12]

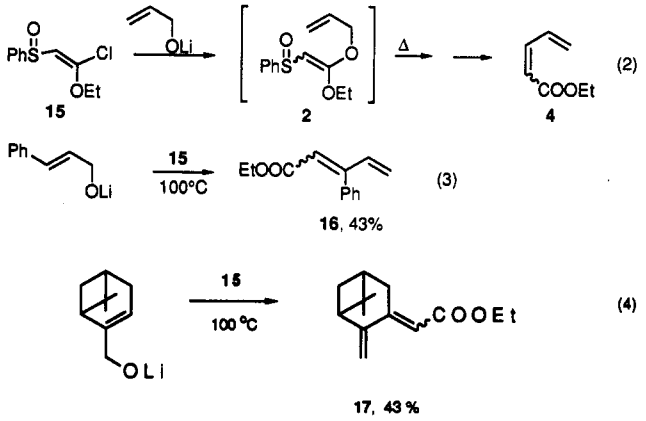
Neither tertiary allylic alcohol 3-methyl-3-butenol nor linalool entered successfully into this two-carbon extension process. TLC monitoring of the progress of these attempted reactions showed no evidence for the first exchange step between sulfinyl orthoester **1** and these tertiary allylic alcohols.

The possibility of using basic instead of acidic conditions for this two-carbon chain extension was also examined because of its potential usefulness with acid-sensitive allylic alcohols. 1-Chloro-1-ethoxy-2-(phenylsulfinyl)ethylene (**15**),[13] prepared by treating the corresponding *geminal* dichloride with 1 equiv of lithium ethoxide, reacted with allyloxy anions presumably via an elimination–addition

Scheme IV



mechanism[14] to form intermediate allylic vinylic ethers **2** and ultimately to produce dienoates **4** (eq 2). Although



these basic conditions[13] worked better than the acidic conditions used with sulfinyl orthoester **1** in a couple of instances (e.g., with cinnamyl alcohol, eq 3, and with myrtenol, eq 4), use of sulfinyl orthoester **1** under acidic conditions was generally much more reliable and convenient. Tertiary alcoholates did not react effectively with sulfinylethylene **15**.

The effectiveness and efficiency of the protocol in eq 1 for tandem, one-flask [3,3] sigmatropic rearrangements of allylic alcohols followed by spontaneous thermal β-elimination of benzenesulfenic acid prompted us to design some allylic alcohols in which a pendant alkene unit would be carried untouched through this sequence of reactions and would finally intercept the newly formed dienoate functionality via an intramolecular 2 + 4 cycloaddition reaction. Toward this goal, olefinic alcohol **18** was prepared easily from the corresponding commercially available lactone

(11) For a review, see: Magid, R. M. *Tetrahedron* **1980**, *36*, 1901.
(12) For organometallic direct alkylation of allylic alcohols, see: (a) Tanigawa, Y.; Ohta, H.; Sonoda, A.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1978**, *100*, 4610. (b) Goering, H. L.; Tseng, C. C. *J. Org. Chem.* **1985**, *50*, 1597.
(13) For details on preparation and use of this hetero-substituted olefin, see the following article: Posner, G. H.; Carry, J.-C.; Crouch, R. D.; Johnson, N. *J. Org. Chem.*, in press.
(14) For a review of the chemistry of chloro(sulfenyl)alkynes, see: Mirskova, A. N.; Seredkina, S. G.; Voronkov, M. G. *Sulfur Reports* **1989**, *9*, 75. See also: Radchenko, S. I.; Petrov, A. A. *Russ. Chem. Rev.* **1989**, *58*, 1671.

(Scheme III). Allylic alcohol **19** reacted with sulfinyl orthoester **1** as expected to form alkenyl dienoate **20** that at 190 °C underwent intramolecular Diels–Alder cycloaddition[15] giving trans bicyclic cyclohexene **22** in good yield as a single stereoisomer after base-promoted double-bond isomerization. This one-flask conversion of acyclic unsaturated allylic alcohol **19** into structurally more complex bicyclic cyclohexene **21** represents a series of five consecutive in situ transformations: allylic alcohol exchange with orthoester **1**, loss of ethanol to form an allylic vinylic ether, [3,3] sigmatropic rearrangement, β-elimination, and finally intramolecular 2 + 4 cycloaddition. In a similar fashion, unsaturated allylic alcohol **23** was converted into alkenyl dienoate **24** and then in situ into bicyclic cyclohexene **25** in 36% overall yield (Scheme IV). Lewis acids[16] such as $TiCl_4$, $SnCl_4$, BF_3–etherate, Et_2AlCl, and $ZnBr_2$ did not promote cyclization of alkenyl dienoate **24** between −78 °C and room temperature. Clearly other unsaturated alcohols can be envisioned to enter successfully into this protocol and to produce interesting and useful cyclic products rapidly, efficiently, and conveniently.

Unexpectedly, all attempts to coax methoxyvinyl dienoate **26** into an intramolecular inverse-electron-demand cycloaddition[17] under thermal conditions or with Lewis acid catalysts failed.

Conclusion

The two-carbon regiospecific chain extension described in this paper for preparation of diverse conjugated dienoate esters represents a simple, useful, and convenient *one-flask procedure without isolation of intermediates*. Other applications of this protocol are envisioned.[18]

Experimental Section

Melting points are uncorrected. NMR spectra were recorded on an instrument operating at 400 MHz. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

All reagents were used as received except where noted. *n*-BuLi was titrated with 2,5-dimethoxybenzyl alcohol.[19] MeLi was used as received. THF was freshly distilled from sodium benzophenone, and CH_2Cl_2 was distilled from CaH_2. Triethylamine was distilled from CaH_2.

2-Octen-1-ol[20] and 2-methyl-2-penten-1-ol[21] were prepared by DIBALH reduction of the corresponding aldehyde and ethyl ester, respectively. 3-Methyl-2-octen-4-ol was prepared by BuLi addition to 2-methyl-2-butenal. 2-Methyl-1-hepten-3-ol[22] was prepared by addition of BuLi to methacrolein. In each case, the allylic alcohol had spectroscopic properties identical to those reported.

2,2,2-Trichloroethyl Phenyl Sulfoxide. To a solution of 2.98 g of 2,2,2-trichloroethyl phenyl sulfide[9] (11.64 mmol, 1 equiv) in 10 mL of CH_2Cl_2 under nitrogen at −20 °C was added, via cannula, 2.51 g of 80% *m*-CPBA (11.71 mmol, 1.01 eq) in 25 mL of CH_2Cl_2. The mixture was stirred at −15 °C for 30 min and was poured into 50 mL of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with Et_2O (3 × 25 mL). The combined organic extract was dried over $MgSO_4$, filtered, and concd to give 3.48 g of a pale yellow solid which, after column chromatography (eluting solvent: 20% Et_2O/20% CH_2Cl_2/hexanes), yielded 2.32 g (78%) of 2,2,2-trichloroethyl phenyl sulfoxide as a white solid which was spectroscopically identical with literature data:[9] mp 103–105 °C (lit.[9] mp 100–101 °C).

1,1-Dichloro-2-(phenylsulfinyl)ethylene. A. From 2,2-Dichlorovinyl Phenyl Sulfide. The above procedure using 6.00 g (29.4 mmol) of 2,2-dichlorovinyl phenyl sulfide[10] in 100 mL of CH_2Cl_2 and 9.69 g (30.9 mmol) of 50–60% *m*-CPBA yielded after column chromatography (eluting solvent: 20% Et_2O/hexanes) 1,1-dichloro-2-(phenylsulfinyl)ethylene (2.99 g, 43%) as a colorless oil.

B. From 2,2,2-Trichloroethyl Phenyl Sulfoxide. Following the procedure described in the literature,[9] 2,2,2-trichloroethyl phenyl sulfoxide (2.03 g, 7.93 mmol) yielded 1,1-dichloro-2-(phenylsulfinyl)ethylene (1.55 g, 89%) as a yellow oil which slowly solidified to a waxy solid. The product was spectroscopically identical with literature data.[9]

2-(Phenylsulfinyl)-1,1,1-triethoxyethane (1). To 3.00 g (13.6 mmol) of 1,1-dichloro-2-(phenylsulfinyl)ethylene in 15 mL of absolute ethanol was added 10.2 mL (27.2 mmol) of 21% NaOEt/EtOH solution. A precipitate formed immediately. The reaction mixture was heated at reflux overnight. After the mixture was cooled to rt, the precipitate was separated by centrifugation, the resultant supernatant was removed, and the precipitate was washed with absolute ethanol. The combined supernatant was concd to yield 4.84 g of crude product. Short-path column chromatography using silica gel which had been pretreated with 25% Et_2O/5% Et_3N/hexanes and elution with this same solvent system afforded **1** (2.66 g, 90%) as a light brown oil: IR ($CHCl_3$, cm^{-1}) 2990, 1443, 1249, 1225, 1196, 1055; ^1H NMR ($CDCl_3$) δ 1.17 (t, J = 7.0 Hz, 9 H), 3.33 (dd, J = 47.5, 14.0 Hz, 2 H), 3.57 (ddq, J = 50.0, 9.2, 7.0 Hz, 6 H), 7.48 (m, 3 H), 7.70 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.9 (3C), 58.2 (3C), 63.2, 111.9, 124.4, 129.0 (2C), 130.9 (2C), 145.2. HRMS calcd for $C_{12}H_{17}SO_3$ (M − OEt) 241.0898, found 241.0901.

General Procedure for Conversion of Allylic Alcohols into Conjugated Dienoates. A mixture of 1 equiv of a substrate allylic alcohol, 2 equiv of sulfinyl orthoester **1**, and a catalytic quantity (~20 mg per mmol of alcohol) of 2,4,6-trimethylbenzoic acid in CH_2Cl_2 (~1.7 mL per mmol of alcohol) was prepared in a hydrolysis tube (ChemGlass CG-4506 or Kontes 896860). The system was purged with N_2, sealed, and heated to 100–120 °C for 2–18 h. The reaction progress was followed by TLC of aliquots taken after cooling the reaction vessel to rt. When the reaction was complete, the mixture was concd in vacuo. (More volatile products were concd at 0 °C). Column chromatography (typical eluting solvent: 0–2% Et_2O/pentane) yielded the desired dienyl esters.

Ethyl 2,4-Pentadienoate (5). Allyl alcohol (10.2 mg, 0.175 mmol) was reacted as described to yield 16.4 mg (75%) of dienyl ester which was spectroscopically identical with data reported in the literature.[23]

Ethyl 4-Methyl-2,4-pentadienoate (6a). Methallyl alcohol (24 mg, 0.283 mmol) yielded 20.3 mg (51%) of dienyl ester which was spectroscopically identical with data reported in the literature.[24] (NMR with mesitylene as an internal standard indicated 56% yield.)

Ethyl 4-Ethyl-2,4-pentadienoate (6b). 2-Ethyl-2-propen-1-ol (15 mg, 0.175 mmol) yielded 18.6 mg (69%) of dienyl ester as a mixture of geometric isomers which was spectroscopically identical with data reported in the literature.[24]

Ethyl 3-Methyl-2,4-pentadienoate (7a). Crotyl alcohol (13.6 mg, 0.189 mmol) yielded 18.4 mg (71%, E/Z (1:1)) of dienyl ester which was spectroscopically identical with data reported in the literature.[25]

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Ethyl 3-Ethyl-2,4-pentadienoate (7b). *trans*-2-Penten-1-ol (33.6 mg, 0.390 mmol) yielded 41.0 mg (69%, E/Z (~1:1)) of desired product as a colorless liquid. The geometric isomers were separable by short-path column chromatography.

E isomer: IR ($CHCl_3$, cm^{-1}) 1706; ^1H NMR ($CDCl_3$) δ 1.10 (t, J = 7.6 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 2.79 (q, J = 7.6 Hz, 2 H), 4.17 (q, J = 7.2 Hz, 2 H), 5.40 (dd, J = 19.9, 10.9 Hz, 1 H), 5.60 (dd, J = 17.6, 9.6 Hz, 1 H), 5.73 (s, 1 H), 6.30 (dd, J = 17.5, 10.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.2, 14.3, 26.2, 59.8, 116.5, 119.6, 133.1, 156.1, 166.5; HRMS calcd for $C_9H_{14}O_2$ 155.0994, found 155.0996.

Z isomer: IR ($CHCl_3$, cm^{-1}) 1706; ^1H NMR ($CDCl_3$) δ 1.13 (t, J = 7.4 Hz, 3 H), 1.29 (t, J = 7.2 Hz, 3 H), 2.39 (dq, J = 7.6, 1.2 Hz, 2 H), 4.17 (q, J = 7.2 Hz, 2 H), 5.40 (dd, J = 19.9, 10.8 Hz, 1 H), 5.60 (dd, J = 17.6, 9.6 Hz, 1 H), 5.70 (s, 1 H), 7.72 (dd, J = 17.8, 11.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.3, 20.4, 59.8, 116.5, 119.0, 138.7, 158.3, 166.5; HRMS calcd for $C_9H_{14}O_2$ 155.0994, found 155.0996.

Ethyl 3-Ethenyl-2-octenoate (7c). 2-Octen-1-ol (54 mg, 0.422 mmol) yielded 49.2 mg (60%, E/Z (~1:1)) of dienyl ester as a colorless liquid. The geometric isomers were not totally separable.

Z isomer: IR ($CHCl_3$, cm^{-1}) 1705; ^1H NMR ($CDCl_3$) δ 0.89 (m, 4 H), 1.20–1.40 (m, 6 H), 1.50 (m, 2 H), 2.35 (m, 1 H), 4.17 (q, J = 7.2 Hz, 2 H), 5.45 (d, J = 11.2 Hz, 1 H), 5.60 (d, J = 18.0 Hz, 1 H), 5.69 (s, 1 H), 7.72 (dd, J = 18.0, 11.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 22.5, 27.2, 28.7, 31.7, 33.5, 59.8, 117.2, 119.9, 133.2, 155.1, 166.4; HRMS calcd for $C_{12}H_{20}O_2$ 196.1463, found 196.1465.

E isomer: IR ($CHCl_3$, cm^{-1}) 1705; ^1H NMR ($CDCl_3$) δ 0.89 (m, 4 H), 1.20–1.40 (m, 6 H), 1.50 (m, 2 H), 2.76 (m, 1 H), 4.17 (q, J = 7.2 Hz, 2 H), 5.36 (d, J = 10.8 Hz, 1 H), 5.61 (d, J = 17.2 Hz, 1 H), 5.74 (s, 1 H), 6.30 (dd, J = 17.2, 10.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 27.2, 29.3, 32.2, 33.7, 59.8, 119.0, 119.3, 139.1, 157.1, 166.6; HRMS calculated for $C_{12}H_{20}O_2$ 196.1463, found 196.1465.

Ethyl 3-Ethenyl-2,4-hexadienoate (7d). 2,4-Hexadien-1-ol (17.2 mg, 0.175 mmol) yielded 26.1 mg of triene (90%), a colorless oil, as a mixture of geometric isomers: IR ($CHCl_3$, cm^{-1}) 1705; ^1H NMR ($CDCl_3$) δ 1.28 (m, 3 H), 1.84 (d, J = 5.2 Hz, 3 H), 1.88 (d, J = 4.4 Hz, 3 H), 4.17 (m, 2 H), 5.45–5.60 (m, 2 H), 5.75 (d, J = 9.6 Hz, 1 H), 6.18 (m, 1 H), 5.29 (d, J = 12.4 Hz, 1 H), 7.35 (d, J = 12.4 Hz, 1 H), 6.51 (dd, J = 16.8, 10.4 Hz, 1 H), 7.47 (dd, J = 16.8, 11.2 Hz, 1 H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43. Found: C, 72.72; H, 8.19.

Ethyl 3-Ethyl-4-methyl-2,4-pentadienoate (8). 2-Methyl-2-penten-1-ol (18.2 mg, 0.182 mmol) yielded 2 geometric isomers, separable by short-path column chromatography, of dienyl ester in 74% yield. NMR yield of the reaction indicated 83% yield.

E isomer: 12.3 mg (39% yield): IR ($CHCl_3$, cm^{-1}) 1716; ^1H NMR ($CDCl_3$) δ 1.09 (t, J = 7.6 Hz, 3 H), 1.30 (t, J = 7.2 Hz, 3 H), 1.93 (s, 3 H), 2.84 (q, J = 7.6 Hz, 2 H), 4.18 (q, J = 7.2 Hz, 2 H), 5.23 (s, 1 H), 5.40 (s, 1 H), 5.83 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 14.3, 21.0, 21.7, 59.7, 115.3, 117.7, 142.7, 160.6, 166.9. HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1152.

Z isomer: 10.9 mg (35% yield); IR ($CHCl_3$, cm^{-1}) 1716; ^1H NMR ($CDCl_3$) δ 1.06 (t, J = 7.2 Hz, 3 H), 1.26 (t, J = 7.2 Hz, 3 H), 1.93 (s, 3 H), 2.24 (m, 2 H), 4.12 (q, J = 7.2 Hz, 2 H), 4.67 (s, 1 H), 4.94 (s, 1 H), 5.58 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 14.1, 22.2, 31.3, 59.7, 111.6, 114.5, 145.4, 163.7, 166.2; HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1152.

Conjugated Dienyl Ester 9. 4,6-Bis(*tert*-butyldimethylsiloxy)-1-cyclohexenemethanol (1.127 g, 3.03 mmol) yielded 1.148 g (86%, E/Z = 3/1) of conjugated dienyl ester **9**, having spectroscopic properties identical to those reported in the literature.[26]

Ethyl 2,4-Hexadienoate (10a). 3-Buten-2-ol (12.6 mg, 0.175 mmol) yielded 19.4 mg of ethyl sorbate (79%, E/Z = ~5/1) as a colorless liquid with spectral characteristics identical with an authentic sample from Aldrich Chemical Co.

Ethyl 2,4-Decadienoate (10b). 1-Octen-3-ol (22 mg, 0.175 mmol) yielded 23.0 mg (67%) of dienyl ester as a colorless liquid with spectral characteristics identical with those reported in the literature.[27]

Ethyl 2,4,7-Octatrienoate (10c). 1,5-Hexadien-2-ol (17.2 mg, 0.175 mmol) yielded 21.6 mg (74%) of triene as a colorless oil: IR ($CHCl_3$, cm^{-1}) 1704; ^1H NMR ($CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3 H), 2.93 (t, J = 6.4 Hz, 2 H), 4.20 (q, J = 7.2 Hz, 2 H), 5.05–5.10 (m, 2 H), 5.75–5.90 (m, 2 H), 6.10–6.25 (m, 2 H), 7.27 (dd, J = 16.0, 10.0 Hz, 1 H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.28; H, 8.43. Found: C, 71.8; H, 8.41.

Ethyl 4-Methyl-2,4-nonadienoate (11). 2-Methyl-1-hepten-3-ol (22 mg, 0.175 mmol) yielded ester **11** (25.1 mg, 73%) as a colorless oil: IR ($CHCl_3$, cm^{-1}) 1700; ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3 H), 1.20–1.40 (m, 7 H), 1.77 (s, 3 H), 2.18 (q, J = 7.2 Hz, 2 H), 4.21 (q, J = 7.2 Hz, 2 H), 5.78 (d, J = 15.6 Hz, 1 H), 5.90 (m, 1 H), 7.32 (d, J = 15.6 Hz, 1 H). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.47; H, 10.20. Found: C, 73.20, H, 10.22.

Ethyl 3-Methyl-2,4-hexadienoate (12). 3-Penten-2-ol (17.1 mg, 0.199 mmol) yielded 13.7 mg of dienyl ester (45%) as a colorless liquid. The product was an inseparable mixture of isomers.

Major isomer: IR (CHCl3, cm^{-1}) 1702; ^1H NMR ($CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3 H), 1.85 (d, J = 5.2 Hz, 3 H), 2.26 (d, J = 1.2 Hz, 3 H), 4.16 (q, J = 7.2 Hz, 2 H), 5.67 (s, 1 H), 6.13 (m, 2 H), 7.60 (d, J = 16.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 18.6, 21.1, 59.6, 117.5, 132.1, 135.0, 152.6, 167.3; HRMS calcd for $C_9H_{14}O_2$ 154.0994, found 154.0996.

Minor isomer: IR ($CHCl_3$, cm^{-1}) 1702; ^1H NMR ($CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3 H), 1.89 (dd, J = 6.8, 1.2 Hz, 3 H), 1.98 (d, J = 1.2 Hz, 3 H), 4.16 (q, J = 7.2 Hz, 2 H), 5.59 (s, 1 H), 6.13 (m, 2 H), 7.50 (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 18.9, 21.1, 59.6, 115.6, 129.1, 133.9, 151.2, 166.5; HRMS calcd for $C_9H_{14}O_2$ 154.0994, found 154.0996.

Cyclohexene 13. 2-Cyclohexen-1-ol (17.2 mg, 0.175 mmol) yielded 27.7 mg (95%) of dienyl ester as a colorless liquid: IR ($CHCl_3$, cm^{-1}) 1700; ^1H NMR ($CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 1 H), 1.70–1.85 (m, 2 H), 2.20 (m, 2 H), 2.96 (m, 1 H), 4.15 (q, J = 7.2 Hz, 2 H), 5.48, 5.57 (s, 1 H), 6.21 (m, 1 H), 6.12, 7.46 (d, J = 11.2 Hz, 1 H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43. Found: C, 72.11; H, 8.38.

Ethyl 3,4-Dimethyl-2,4-nonadienoate (14). 3-Methyl-2-octen-4-ol (57 mg, 0.401 mmol) yielded dienyl ester (45.7 mg, 54%) as two diastereomers which were not completely separable.

Major isomer: IR ($CHCl_3$, cm^{-1}) 1703; ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3 H), 1.20–1.40 (m, 7 H), 1.80 (s, 3 H), 2.17 (q, J = 7.2 Hz, 2 H), 2.31 (s, 3 H), 4.16 (q, J = 7.2 Hz, 2 H), 5.83 (s, 1 H), 5.93 (t, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 14.2, 14.4, 15.4, 20.4, 22.4, 59.7, 63.0, 114.8, 116.0, 127.0, 127.5, 134.0, 136.2, 158.5, 168.0; HRMS calcd for $C_{13}H_{22}O_2$ 210.1620, found 210.1621.

Minor isomer: ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3 H), 1.20–1.40 (m, 7 H), 1.77 (s, 3 H), 1.92 (s, 3 H), 2.05 (q, J = 7.2 Hz, 2 H), 4.09 (q, J = 7.2 Hz, 2 H), 5.20 (t, J = 7.2 Hz, 1 H), 5.58 (s, 1 H).

Ethyl 3-Phenyl-2,4-pentadienoate (16). Cinnamyl alcohol (53 mg, 0.397 mmol) was treated with reagent **15**[13] to yield dienyl ester as two geometric isomers.

Major isomer (colorless oil, 23.1 mg, 29%): IR ($CHCl_3$, cm^{-1}) 1708; ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 7.2 Hz, 3 H), 4.23 (q, J = 7.2 Hz, 2 H), 5.32 (dm, J = 17.4 Hz, 1 H), 5.60 (dm, J = 11.6 Hz, 1 H), 5.81 (s, 1 H), 7.35 (m, 5 H), 7.95 (dd, J = 17.4, 11.6 Hz, 1 H); HRMS calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0996.

Minor isomer (colorless oil, 11.2 mg, 14%): IR ($CHCl_3$, cm^{-1}) 1719; ^1H NMR ($CDCl_3$) δ 1.05 (t, J = 7.2 Hz, 3 H), 4.00 (q, J = 7.2 Hz, 2 H), 5.10 (d, J = 16.0 Hz, 1 H), 5.45 (d, J = 10.4 Hz, 1 H), 5.98 (s, 1 H), 6.65 (dd, J = 16.0, 10.4 Hz, 1 H), 7.10–7.50 (m, 5 H); HRMS calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0998.

Bicyclic Dienoate 17. Myrtenol (38.4 mg, 0.252 mmol) was treated with reagent **15**[13] to yield 24.4 mg (43%) of dienyl ester **17** as a colorless oil: IR ($CHCl_3$, cm^{-1}) 1696; ^1H NMR ($CDCl_3$) δ 0.74 (s, 3 H), 1.13 (d, J = 10.0 Hz, 1 H), 1.30 (m, 6 H), 2.10 (m, 1 H), 2.45 (m, 1 H), 2.54 (t, J = 5.6 Hz, 1 H), 2.98 (dm, J = 19.2 Hz, 1 H), 3.20 (dm, J = 19.6 Hz, 1 H), 4.18 (q, J = 7.2 Hz, 2 H), 4.76 (s, 1 H), 5.51 (s, 1 H), 6.33 (s, 1 H).

General Procedure for Preparation of Allylic Alcohols with Pendant Dienophile. The appropriate lactone was treated with 1 equiv of DIBAL-H[28] to afford, after column chromatog-

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raphy, the corresponding lactol. Treatment of the lactol with 2.5 equiv of the appropriate Wittig reagent (generated by the addition of *n*-BuLi or KHMDS to the alkyl triphenylphosphonium halide) in THF at −78 °C followed by warming to rt yielded the olefinic alcohol. The latter was subjected to Collins oxidation, and the crude aldehyde was treated with 1.2 equiv of vinylmagnesium bromide in THF at 0 °C to give the desired alcohol.

Allylic Alcohol 19. δ-Valerolactone (1.70 mL, 1.83 g, 18.3 mmol) gave after purification via column chromatography (eluting solvent: 20% Et_2O/hexanes) alcohol **19** (392 mg, 17% overall) as a yellow oil: IR ($CHCl_3$, cm^{-1}) 3359; ^1H NMR ($CDCl_3$) δ 1.50–1.60 (m, 5 H), 2.08 (q, J = 6.8 Hz, 2 H), 4.10 (m, 1 H), 5.01 (dd, J = 16.8, 2.0 Hz, 1 H), 4.95 (dd, J = 10.0, 2.0 Hz, 1 H), 5.11 (dd, J = 10.4, 1.6 Hz, 1 H), 5.22 (d, J = 17.2 Hz, 1 H), 5.85 (m, 2 H).

1-Methoxy-1,8-nonadien-7-ol. ε-Caprolactone (1.67 mL, 1.72 g, 15.0 mmol) gave after purification via column chromatography (eluting solvent: 25% Et_2O/hexanes) 1-methoxy-1,8-nonadien-7-ol (665 mg, 26% overall) as a mixture of geometric isomers, yellowish oil.

Major isomer (499 mg, 19.5%): IR ($CHCl_3$, cm^{-1}) 3607, 3473; ^1H NMR ($CDCl_3$) δ 1.30–1.60 (m, 7 H), 1.93 (q, J = 6.8 Hz, 2 H), 3.50 (s, 3 H), 4.09 (q, J = 6.4 Hz, 1 H), 4.72 (m, 1 H), 5.22 (dd, J = 17.2, 1.2 Hz, 1 H), 5.87 (m, 1 H), 6.28 (d, J = 12.8 Hz, 1 H).

Minor isomer (166 mg, 6.5%): IR ($CHCl_3$, cm^{-1}) 3607, 3473; ^1H NMR ($CDCl_3$) δ 1.30–1.60 (m, 7 H), 2.08 (q, J = 6.8 Hz, 2 H), 3.57 (s, 3 H), 4.09 (q, J = 6.4 Hz, 1 H), 4.32 (q, J = 6.4 Hz, 1 H), 5.11 (dd, J = 10.4, 1.6 Hz, 1 H), 5.80 (m, 1 H), 5.87 (m, 1 H).

Alkenyl Dienoate 20. Allylic alcohol **19** (46 mg, 0.365 mmol) was treated with sulfinyl orthoester **1** as previously described to yield 45 mg (60%) of dienoate **20** as a colorless oil: IR ($CHCl_3$, cm^{-1}) 1703; ^1H NMR ($CDCl_3$) δ 1.29 (t, J = 7.2 Hz, 3 H), 1.53 (t, J = 7.2 Hz, 2 H), 2.07 (q, J = 7.6 Hz, 2 H), 2.18 (q, J = 7.2 Hz, 2 H), 4.19 (q, J = 7.2 Hz, 2 H), 4.98 (m, 2 H), 5.80 (m, 2 H), 6.14 (m, 2 H), 7.26 (dd, J = 15.6, 10.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 27.9, 32.5, 33.1, 60.2, 114.9, 119.3, 120.6, 138.2, 144.1, 145.0, 167.5; HRMS calcd for $C_{12}H_{28}O_2$ 194.1307, found 194.1310.

Bicyclic Cyclohexenyl Ester 22. Dienyl ester **20** (20 mg, 0.103 mmol) and CH_2Cl_2 (500 μL) were heated in a sealed tube to 190 °C overnight. After being cooled, the resultant mixture was concd and, then, mixed with 1 mL of absolute EtOH and 3 drops of 21% NaOEt/EtOH and stirred overnight at rt. Ether was added, and 2 drops of saturated aqueous NH_4Cl was added. The mixture was filtered through $MgSO_4$ and concd to give, after column chromatography (eluting solvent: 2% Et_2O/hexanes), 9.7 mg (49%) of liquid conjugated ester **22** as a single diastereomer assigned trans stereochemistry in analogy with literature reports on intramolecular Diels–Alder reactions leading to *trans*-hydroindenes:[15d,g] IR ($CHCl_3$, cm^{-1}) 1702; ^1H NMR ($CDCl_3$) δ 1.29 (t, J = 7.2 Hz, 3 H), 1.35 (m, 3 H), 1.70 (m, 3 H), 1.85–2.10 (m, 4 H), 2.25–2.70 (m, 2 H), 4.18 (q, J = 7.2 Hz, 2 H), 6.97 (m, 1 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.22; H, 9.28. Found: C, 73.92; H, 9.38.

5,5,9-Trimethyl-1,8-decadien-3-ol (23). To a solution of 3,3,7-trimethyl-6-octenal[29] (1.85 g, 11.0 mmol) in 20 mL of THF at 0 °C was added 13.2 mL of 1.0 M vinylmagnesium bromide (13.2 mmol, 1.2 equiv). The solution warmed to rt over 2 h and was quenched with aqueous NH_4Cl. After extraction of the aqueous layer with Et_2O, the combined organic phase was dried over $MgSO_4$, filtered, and concd. Column chromatography yielded 1.75 g (80%) of alcohol **23** as a colorless oil: IR ($CHCl_3$, cm^{-1}) 3370, 1643; ^1H NMR ($CDCl_3$) δ 0.959 (s, 3 H), 0.963 (s, 3 H), 1.26–1.31 (m, 3 H), 1.47 (m, 2 H), 1.60 (s, 3 H), 1.68 (s, 3 H), 1.92 (m, 2 H), 4.26 (m, 1 H), 5.05 (dt, J = 10.4, 1.6 Hz, 1 H), 5.10 (tt, J = 7.2, 1.6 Hz, 1 H), 5.21 (dt, J = 17.2, 1.6 Hz, 1 H), 5.90 (m, 1 H).

Ethyl 7,7,11-Trimethyl-2,4,10-dodecatrienoate (24). 5,5,9-Trimethyl-1,8-decadien-3-ol (143 mg, 0.722 mmol) yielded 113.8 mg (60%) of the *E,E* dienyl ester as a colorless liquid: IR ($CHCl_3$, cm^{-1}) 1716; ^1H NMR ($CDCl_3$) δ 0.89 (s, 6 H), 1.20 (m, 2 H), 1.29 (t, J = 7.2 Hz, 3 H), 1.60 (s, 3 H), 1.69 (s, 3 H), 1.93 (m, 2 H), 2.07 (d, J = 6.4 Hz, 2 H), 4.20 (q, J = 7.2 Hz, 2 H), 5.08 (m, 1 H), 5.79 (d, J = 15.2 Hz, 1 H), 6.16 (m, 2 H), 7.27 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 17.6, 22.7, 27.0, 34.0, 42.0, 45.5, 60.2, 119.3, 124.9, 130.5, 141.8, 144.9, 167.4; HRMS calcd for $C_{17}H_{28}O_2$ 264.2089, found 264.2092.

Bicyclic Cyclohexenyl Ester 25. A. From Purified Triene 24. Triene **24** (19.9 mg, 0.075 mmol) in 500 μL of CH_2Cl_2 was heated in a sealed tube to 150 °C overnight. TLC analysis showed mostly triene remained. The mixture was heated for a second night at 170 °C, and TLC, again, showed starting material remaining. Heating to 190 °C for a third night yielded (18.9 mg of crude Diels–Alder product. After column chromatography (eluting solvent: 0.5% ether/pentane), 12.6 mg (63%) of desired product **25** was obtained.

B. From Crude Triene 24. A mixture of 5,5,9-trimethyl-1,8-decadien-3-ol (70 mg, 0.350 mmol), sulfinyl orthoester **1** (200 mg, 0.700 mmol), and catalytic 2,4,6-trimethylbenzoic acid in 500 μL of CH_2Cl_2 was heated in a sealed tube to 150 °C overnight. TLC analysis of a cooled aliquot of the reaction mixture indicated the presence of triene **24**. The reaction vessel was resealed and heated to 190 °C overnight. The mixture was cooled and concd to give 200 mg of crude product. Column chromatography (eluting solvent: 0–1.5% Et_2O/hexanes) yielded 32.4 mg (36%) of desired product **25**. An additional fraction contained 11.9 mg (13%) of reactant triene **24**. Although both the ^1H and ^{13}C NMR spectra are consistent with one diastereomer being formed, its relative stereochemistry is unclear and no definite stereochemical assignment can be made based on literature precedent:[15d,h] IR ($CHCl_3$, cm^{-1}) 1706; ^1H NMR ($CDCl_3$) δ 0.88 (s, 3 H), 0.91 (s, 3 H), 0.92 (s, 3 H), 0.94 (s, 3 H), 1.00–1.20 (m, 4 H), 1.26 (t, J = 7.2 Hz, 3 H), 1.35–1.70 (m, 3 H), 1.90 (m, 1 H), 2.70 (m, 1 H), 4.11 (q, J = 7.2 Hz, 2 H), 5.50 (m, 1 H), 5.60 (d, J = 10.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 21.4, 22.2, 25.0, 25.2, 30.8, 33.0, 33.8, 34.1, 39.8, 43.6, 45.7, 54.6, 60.2, 122.4, 135.5, 173.8; HRMS calcd for $C_{17}H_{28}O_2$ 264.2089, found 264.2093.

Ethyl 11-Methoxy-2,4,10-undecatrienoate (26). 1-Methoxy-1,8-nonadien-7-ol (210 mg, 1.24 mmol) was treated with sulfinyl orthoester **1** as previously described to yield 177.1 mg (60%) of ester **26**, a colorless oil, as a mixture of geometric isomers (3:1 ratio).

Major isomer: IR ($CHCl_3$, cm^{-1}) 1717; ^1H NMR ($CDCl_3$) δ 1.25 (t, J = 7.2 Hz, 3 H), 1.30–1.45 (m, 4 H), 1.87 (q, J = 7.2 Hz, 2 H), 2.10 (q, J = 7.2 Hz, 2 H), 3.45 (s, 3 H), 4.15 (q, J = 7.2 Hz, 2 H), 4.65 (m, 1 H), 5.73 (d, J = 16.0 Hz, 1 H), 6.08 (m, 2 H), 6.25 (d, J = 12.0 Hz, 1 H), 7.20 (dd, J = 16.0, 12.0 Hz, 1 H).

Minor isomer: IR ($CHCl_3$, cm^{-1}) 1717; ^1H NMR ($CDCl_3$) δ 1.25 (t, J = 7.2 Hz, 3 H), 1.30–1.45 (m, 4 H), 2.00 (q, J = 7.2 Hz, 2 H), 2.10 (q, J = 7.2 Hz, 2 H), 3.53 (s, 3 H), 4.15 (q, J = 7.2 Hz, 2 H), 4.25 (m, 1 H), 5.73 (d, J = 16.0 Hz, 1 H), 5.82 (m, 1 H), 6.08 (m, 2 H), 7.20 (m, 1 H).

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Registry No. 1, 127492-03-9; (*E*)-**5**, 13369-23-8; (*E*)-**6a**, 13369-24-9; (*E*)-**6b**, 13369-25-0; (*Z*)-**6b**, 136707-73-8; (*E*)-**7a**, 37850-26-3; (*Z*)-**7a**, 37850-27-4; (*E*)-**7b**, 136707-74-9; (*Z*)-**7b**, 136707-75-0; (*E*)-**7c**, 136707-76-1; (*Z*)-**7c**, 136707-77-2; (*E,E*)-**7d**, 136707-78-3; (*Z,E*)-**7d**, 136707-79-4; (*E*)-**8**, 136707-80-7; (*Z*)-**8**, 136707-81-8; (*E*)-**9**, 81506-23-2; (*Z*)-**9**, 81570-20-9; (*E*)-**10a**, 2396-84-1; (*Z*)-**10a**, 53282-25-0; **10b**, 136707-82-9; **10c**, 136736-31-7; **11**, 136707-83-0; (*E*)-**12**, 86459-90-7; (*Z*)-**12**, 130484-18-3; **13**, 136707-84-1; (*E*)-**14**, 136707-85-2; (*Z*)-**14**, 136707-86-3; (*E*)-**15**, 136707-87-4; (*E*)-**16**, 34260-86-1; (*Z*)-**16**, 63909-19-3; **17**, 136707-88-5; **18**, 821-41-0; **19**, 30385-19-4; **20**, 136707-89-6; **22**, 136707-90-9; **23**, 136707-91-0; (*E*)-**24**, 136707-92-1; **25**, 136707-93-2; **26**, 136707-94-3; 2,2,2-trichloroethyl phenyl sulfoxide, 79894-51-2; 2,2,2-trichloroethyl phenyl sulfide, 56354-48-4; 1,1-dichloro-2-(phenylsulfinyl)ethylene, 40976-97-4; 2,2-dichlorovinyl phenyl sulfide, 3559-72-6; allyl alcohol, 107-18-6; methallyl alcohol, 513-42-8; 2-ethyl-2-propen-1-ol, 4435-54-5; (*E*)-crotyl alcohol, 504-61-0; (*E*)-2-penten-1-ol, 1576-96-1; (*E*)-2-octen-1-ol, 18409-17-1; (*E,E*)-2,4-hexadien-1-ol, 17102-64-6; (*E*)-2-methyl-2-penten-1-ol, 16958-19-3; (4*R*-*trans*)-4,6-bis(*tert*-butyldimethylsiloxy)-1-cyclo-

(29) Funakoshi, K.; Togo, N.; Koga, I.; Sakai, K. *Chem. Pharm. Bull.* **1989**, *37*, 1990.

hexene-1-methanol, 127492-02-8; 3-buten-2-ol, 598-32-3; 1-octen-3-ol, 3391-86-4; 1,5-hexadien-3-ol, 924-41-4; 2-methyl-1-hepten-3-ol, 13019-19-7; (*E*)-3-penten-2-ol, 3899-34-1; 2-cyclohexen-1-ol, 822-67-3; (*E*)-3-methyl-2-octen-4-ol, 136707-95-4; (*E*)-cinnamyl alcohol, 4407-36-7; (*R*)-(−)-myrtenol, 19894-97-4; δ-valerolactone, 542-28-9; methylenetriphenylphosphorane, 3487-44-3; vinylmagnesium bromide, 1826-67-1; ξ-caprolactone, 502-44-3; (*E*)-1-methoxy-1,8-nonadien-7-ol, 136707-96-5; (*Z*)-1-methoxy-1,8-nonadien-7-ol, 136707-97-6; 3,3,7-trimethyl-6-octenal, 17920-90-0; 2,4,6-trimethylbenzoic acid, 480-63-7.

Supplementary Material Available: Characterization of new compounds by NMR (20 pages). Ordering information is given on any current masthead page.

One-Flask, Consecutive [3,3] and [2,3] Sigmatropic Rearrangements for Conversions of Propargylic Alcohols into Two-Carbon-Extended 4-Oxo-2-alkenoate Esters. Use of a New 1-Chloro-1-ethoxy-2-sulfinylethylene

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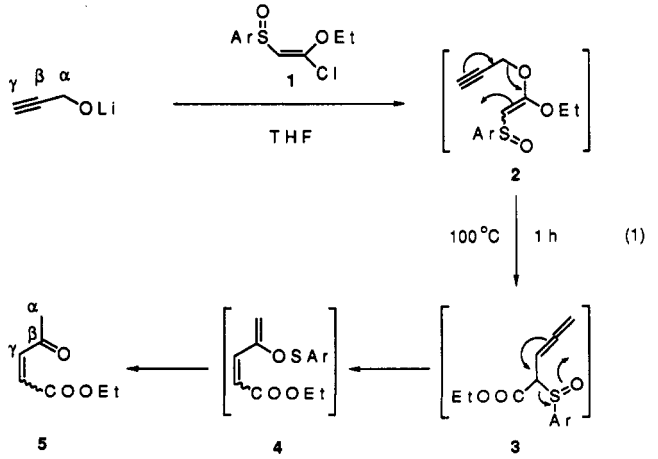
Seven differently substituted primary and secondary propargylic alcohols are shown to react with (arylsulfinyl)vinylic chloride **1a** at 100 °C for 1 h sequentially via a [3,3] sigmatropic rearrangement and then a [2,3] sigmatropic rearrangement to form 4-oxo-2-alkenoates **8a–8e** and **9a** and **9b** in 52–80% yields. This one-flask, intramolecular carbon–carbon bond-forming process represents a simple and convenient method not only for regiospecific γ-attachment onto a propargylic alcohol of a two-carbon (ethoxycarbonyl)methylene unit but also for α → β transposition of oxygen. The synthetic utility of this procedure is illustrated further by eqs 2 and 3 for preparation of regiospecifically functionalized carbocycles and heterocycles. Also, two different primary allenic allylic alcohols are shown to produce directly two-carbon extended 3-(hydroxyalkyl)-2,4-pentadienoates (*E*)-**18** and the corresponding unsaturated lactones (*Z*)-**18** in 37–41% yields.

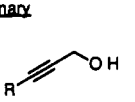
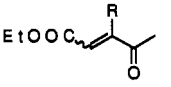
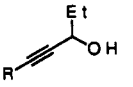
Introduction

In connection with our design, synthesis, and use of a new sulfinyl orthoester for one-flask conversions of allylic alcohols into 2-carbon-extended dienoate esters,[1] we have discovered (1) that 1-chloro-1-ethoxy-2-(arylsulfinyl)-ethylenes **1** are easily prepared[2] and (2) that the sulfinylethylene **1** with Ar = 4-ClPh is a relatively stable compound that, among the aryl derivatives studied, reacts most efficiently with propargylic alcoholates to form 2-carbon-extended 4-oxo-2-alkenoate esters **5** (eq 1). This one-flask



sequence proceeds most likely via [3,3]-sigmatropic rearrangement of intermediate allylic propargylic ethers **2** and subsequent [2,3]-sigmatropic rearrangement of intermediate β-allenic aryl sulfoxides **3**. Herein is reported a full account of this new synthetic method, including some applications and limitations, as well as some similar transformations of allenic allylic alcohols.

Table I. Two-Carbon Chain Extension According to eq 1 with Ar = 4-ClPh

propargylic alcohol	product 4-oxo-2-alkenoate	% yield of purified product
Primary		
		
	8a, R = Me	55
	8b, R = Ph	57
	8c, R = Me_3Si	52
	8d, R = t-$BuMe_2SiOCH_2$	80
	8e, R = $ClCH_2$	77
Secondary		
		
	9a, R = Me	66
	9b, R = Et	77

Results and Discussion

Although primary and secondary propargylic alcohols did react with sulfinyl orthoacetate $PhS(O)CH_2C(OEt)_3$ under acidic conditions[1] to produce 4-oxo-2-alkenoates, consistently and considerably better results were obtained under basic conditions using 1-chloro-1-ethoxy-2-(aryl-

(1) Posner, G. H.; Crouch, R. D.; Kinter, C. M.; Carry, J.-C. *J. Org. Chem.*, in press.
(2) For a review of related (organothio)chloroacetylenes, see: Mirskova, A. N.; Seredkina, S. G.; Voronkov, M. G. *Sulfur Reports* **1984**, *9*, 75.

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