α,β-Unsaturated Acetals as Precursors of α-Substituted Ethoxy Dienes. Useful Reagents for Nucleophilic Acylation

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The reaction of (*E*)-1,1-diethoxybut-2-ene (**1a**) and 1,1-diethoxy-3-methylbut-2-ene (**1b**) with 2 equiv of *sec*-butyllithium complexed with potassium *tert*-butoxide (Schlosser's base) in THF at −95 °C gives 1-metalated 1-ethoxy 1,3-dienes that are synthetically equivalent to acyl anions. Subsequent reaction with suitable electrophiles, such as alkyl halides, aldehydes, ketones, carbon dioxide, and carboxylic acid derivatives, affords (*E*)-1-substituted 1-ethoxy 1,3-dienes **2a**–**i**. Experimental procedures are given for the reaction of the carbanionic intermediates with the electrophiles. Some typical examples for the conversion of the produced α-substituted alkoxy dienes into the corresponding α,β-unsaturated carbonyl compounds are also reported. In particular, in the case in which crotonaldehyde is used as an electrophile, the addition product **2c** undergoes acid-catalyzed conversion to compounds **4c**, **5c**, and **6c** as a function of the experimental conditions.

Introduction

One of the objectives of organic synthesis is the development of techniques for assembling carbon atoms and functional groups. For this purpose it is desirable to have reagents of opposite polarity for the introduction of suitable synthons.[1] The design of new intermediates that are the equivalents of inaccessible nucleophiles or electrophiles is a suitable strategy for general methods in organic synthesis.[2] Among the most commonly encountered reactive sites are carbonyl groups which, in their normal reactivity, provide acyl cation and enolate anion equivalents. General methods for supplying complementary acyl anions and enolate cations have been investigated and are now available. Many authors have shown that sulfur-stabilized anions act as nucleophilic acylating equivalents.[3] In particular, 2-substituted 1,3-dithianes can be metalated by butyllithium in THF to give the corresponding 2-lithium derivatives that react with various electrophiles to form products. The dithianylidene anion,[4] an ambident unsymmetric allylic anion with dithio substituents, can function as an equivalent of an α,β-unsaturated acyl anion when the reaction takes place at the α-terminus, while the anion can act as an equivalent of the β-anion of a carboxylic acid when the reaction occurs at the γ-site. The regioselective behavior of such unsymmetric allylic anions has been extensively investigated:[5] the studied factors include the effect of substituents,[6] solvent,[4] counter cation,[7] and the nature of the electrophile.[8] However, no unequivocal rule has been established to interpret the observed regioselectivity. In particular, dithio-substituted crotyllithium, generated from 2-(1-propen-1-yl)-1,3-dithiane and butyllithium, reacts with aldehydes to give γ-products, with ketones at either the α- and γ-terminus, depending on the nature of ketone, and with alkyl halides and heavy water at the α-site.[9]

We have recently reported[10] that α-substituted alkoxy dienes can be readily obtained from α,β-unsaturated acetals by reaction with electrophiles in the presence of 2 equiv of a strong non-nucleophilic organic base (Schlosser's base; LICKOR). The reaction is initiated by a 1,4-elimination, which is immediately followed by the α-metalation of the produced alkoxy diene and gives the final product by reaction with the electrophile.[10] In contrast, it should be pointed out that when acetals of acrolein and crotonaldehyde react with butyllithium, *sec*-butyllithium, or *tert*-butyllithium mainly addition products result.[11] Moreover, as the LICKOR-mediated reaction yields an intermediate localized vinylic carbanion, regioselective addition of electrophiles to that carbanion is observed regardless of their nature. Even in the case of **1b**, a β-methyl-α,β-unsaturated acetal, where 1,4-elimination yields an intermediate alkoxy diene with both α- and δ-sites that can undergo deprotonation (Scheme 1a), reaction with electrophiles affords α-substituted alkoxy dienes selectively.[10b]

In this paper we provide the details of our work on the reaction of α-metalated alkoxy dienes with various electrophiles and on the acidic hydrolysis of α-substituted alkoxy dienes. The reaction was carried out under aqueous conditions or in the presence of Amberlyst-15 in chloroform solution, affording different hydrolysis products, according to the reaction conditions.

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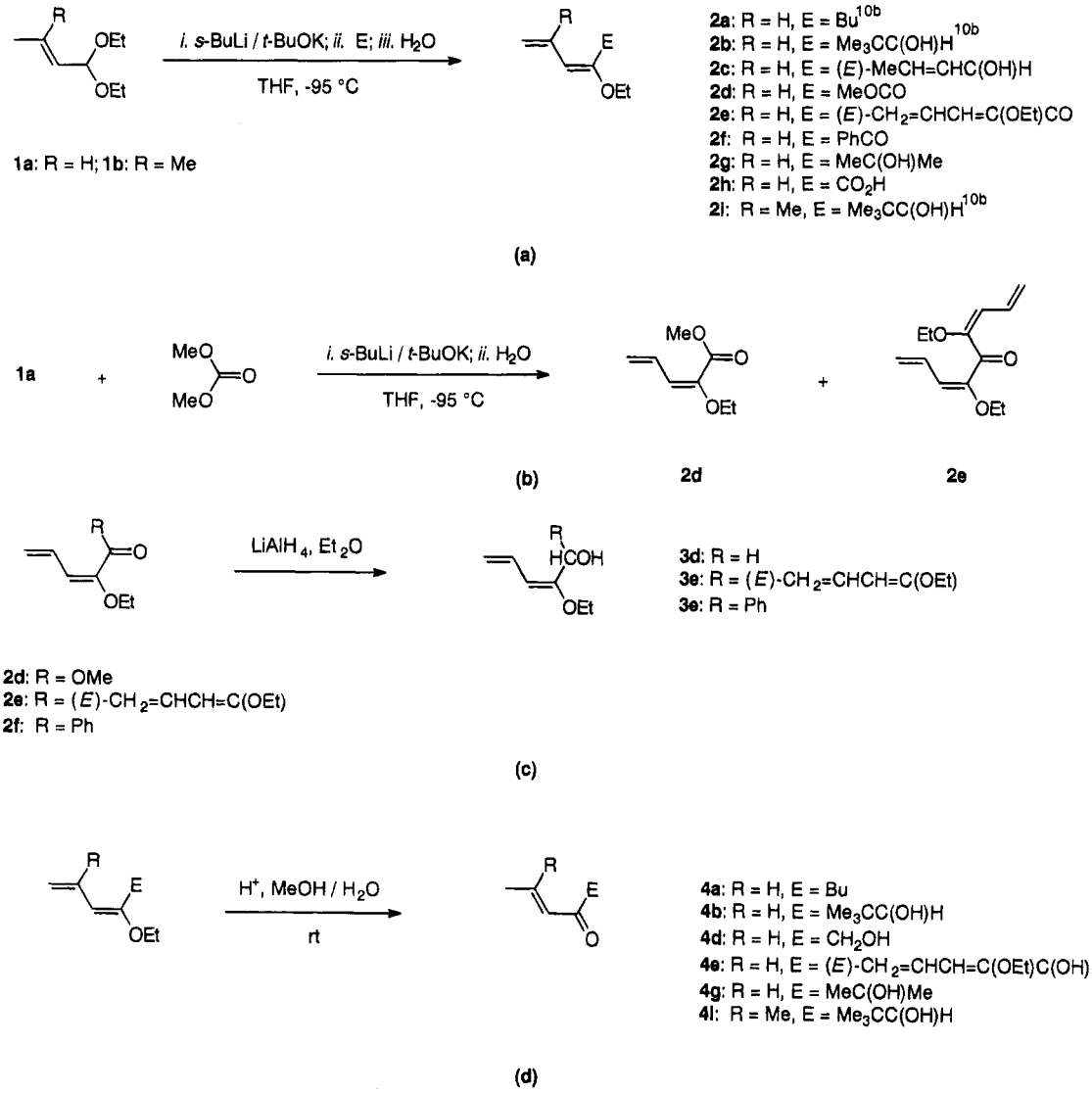
Scheme 1



Results and Discussion

α-Substituted alkoxy dienes **2a–i** can be readily generated from α,β-unsaturated acetals **1a,b** by reaction with 2 equiv of *sec*-butyllithium complexed with potassium *tert*-butoxide.[12] Compounds **2a,b** and **2i** have been previously described: reaction yields of purified products were 60%, 70%, and 80%, respectively.[10b] Here we report in addition the synthesis of alkoxy dienes **2c–h**, obtained using crotonaldehyde, dimethyl carbonate, ethyl benzoate, acetone, and carbon dioxide as electrophiles (Table 1). The products are reported in Scheme 1a. With dimethyl carbonate, two products (**2d** and **2e**), both coming from an acyl nucleophilic substitution, can be obtained (Scheme 1b). In particular, when the molar ratio between the metalated alkoxy diene and the carbonate is 1:5, the main product results from the monoacyl substitution (**2d**, 70%), while the bis-substitution product **2e** (10%) is only formed as a minor component. On the other hand, working with a molar ratio 1:0.5, **2e** is obtained as the only isolated product (90%).

Table 1. 1-Substituted 1-Ethoxy 1,3-Dienes 2c-h Obtained from Acetal 1a and Electrophiles[a]

electrophile	product	yield[b] (%)
MeCH=CHCHO	**2c**	90
$MeOCO_2Me$	**2d**[c]	70
$MeOCO_2Me$	**2e**[d]	90
$PhCO_2Et$	**2f**	65
MeCOMe	**2g**	91
CO_2	**2h**	48

[a] **1a** (2.5 mmol); *s*-BuLi (5.0 mmol); *t*-BuOK (5.0 mmol); electrophile (2.7 mmol); THF (5.0 mL); $T = -95$ °C. [b] Isolated yield of purified product. [c] $MeOCO_2Me$:**1a** molar ratio = 5:1. [d] $MeOCO_2Me$:**1a** molar ratio = 0.5:1.

Products **2a**, **2b**, **2g**, and **2i**, like all enol ethers, undergo acidic hydrolysis[13] to afford the enones **4a**, **4b**, **4g**, and **4i** (Table 2 and Scheme 1d). Moreover, the hydrolysis of compound **2c** yields three products, depending on the reaction conditions. In particular, if the hydrolysis is carried out according to method A (aqueous

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Table 2. Acid-Catalyzed Conversion of 1-Substituted 1-Ethoxy Dienes 2a–c, 3d–f, and 2g–i into α,β-Unsaturated Carbonyl Compounds[a]

substrate	reaction condns[b]	product	yield[c] (%)
2a	A	**4a**	90
2b	A	**4b**	85
2c	A	**4c**	90
2c	B	**5c**	85
2c	C	**6c**	70
3d	A	**4d**	70
3e	A	**4e**	78[d]
3f	A	**4f**	trace[e]
2g	A	**4g**	90
2i	A	**4i**	40

[a] Substrate (2.5 mmol); T = rt. [b] A: catalyst, 0.02 N HCl; solvent, MeOH:H_2O (4:1), 25 mL. B: catalyst, Amberlyst-15 (0.15 g, 0.7 mequiv); solvent, $CHCl_3$, 25 mL. C: catalysts, 0.02 N HCl; solvent, THF:H_2O (1:10). [c] Isolated yield of products. [d] All attempts to hydrolyze compound **3e** to the corresponding 1,3-dione were unsuccessful: the reaction does not proceed beyond the hydrolysis of only one vinyl ether moiety. [e] By GC–MS; **3f** does not undergo hydrolysis with good yields using method A, B, or C (see Experimental Section).

methanolic HCl; see Experimental Section) the ketone **4c** (90%) is obtained. The acidic reaction promotes both the hydrolysis of the vinyl ether moiety and the dehydration of the allylic alcohol. Subsequent transposition of the intermediate carbocation and nucleophilic attack of the methanol results in **4c**. Under the conditions of method B (chloroform suspension of Amberlyst-15; see Experimental Section) the ketone **5c** (85%) is isolated. This ketone results from the same mechanistic pathway proposed for compound **4c**, but in this case, the ethyl alcohol obtained from the hydrolysis of the vinyl ether acts as the nucleophile attacking the intermediate carbocation. Working otherwise in an aqueous THF solution of 0.02 N HCl (method C; see Experimental Section) the main product isolated is the ketone **6c** (70%), while **5c** is only formed as a minor component (15%). The structure of compounds **4c**, **5c**, and **6c** were confirmed by the presence in the ^{1}H NMR spectra of two signals: the first (3H), centered at *ca.* δ 1.25, which appears as a doublet (J = 7 Hz), is assignable to H(8), and the second (1H), centered at *ca.* δ 3.95, which appears as a doublet of quintuplets (J = 1.5 and 7 Hz), is assignable to H(7). Moreover, the spectra show a doublet of doublets (3H) (J = 7 and 1.5 Hz), centered at *ca.* δ 1.90, assigned to allylic H(1). The results are reported in Table 2, and the products **4c**, **5c**, and **6c** are shown in Scheme 2.

On the other hand, the dimethyl carbonate and ethyl benzoate derivatives **2d–f** do not hydrolyze under the experimental conditions of methods A, B, or C. This increase is probably due to the presence of the geminal carbonyl function that destabilizes the positive charge that forms during the hydrolysis. If these intermediates first are reduced to alcohol derivatives **3d–f** (Scheme 1c) with lithium aluminum hydride in diethyl ether at room temperature, subsequent hydrolysis yields the α-hydroxy ketones **4d–f** (Table 2). Alcohols **3d–f** were isolated in 75%, 85%, and 65% crude yields, respectively, and were used without further purification (see Experimental Section).

As discussed in the preceding paper[10b] the 1,4-elimination reaction of the α,β-unsaturated acetals affords the intermediate alkoxy dienes to give exclusively the *E* products. Moreover, in the case of crotonaldehyde the reaction produces the 1,2-addition product. The structure of the 1,2-addition product was characterized by the appearance of a doublet at δ 4.70, assignable to the C(OH)*H* group. The absence of the product from the conjugate 1,4-addition was deduced from the absence of a triplet attributable to the CHO group in the ^{1}H NMR spectrum of the crude reaction product.

Experimental Section

Flasks and all the equipment used for the generation and reactions of metalated alkoxy dienes were flame dried under argon. Anhydrous THF was obtained by distillation from benzophenone ketyl. *s*-BuLi (1.4 M solution in cyclohexane) was purchased from Aldrich. *t*-BuOK, obtained from Merck, was sublimated *in vacuo* (0.1 Torr) prior to the reaction. All commercially available chemicals were reagent grade and were used without further purification. The syntheses of α,β-unsaturated acetals **1a,b** and of 1-substituted 1-alkoxy 1,3-dienes **2a,b** and **2i** have been previously reported.[10b] ^{1}H-NMR spectra were recorded in $CDCl_3$ solution, using TMS as internal standard. J values are given in Hz. ^{13}C-NMR were recorded in $CDCl_3$ solution. A cross-linked methyl silicone capillary column (25-m × 0.2-mm × 0.33-μm film thickness) was used for GC–MS spectra. Preparative column chromatography was carried out on Merck silica gel 60 with diethyl ether–light petroleum ether (bp 30–60 °C) as an eluant. Products that were not purified by column chromatography were bulb-to-bulb (Kugelrohr) distilled.

General Procedure for the Synthesis of 1-Substituted 1-Ethoxy 1,3-Dienes. Under an atmosphere of argon, *t*-BuOK (0.56 g, 5.0 mmol) was added to 5.0 mL of anhydrous THF at rt. The suspension was cooled to −95 °C, and *s*-BuLi (1.4 M solution in cyclohexane, 3.57 mL, 5.0 mmol) was added dropwise with stirring. After 15 min, acetal **1a** (0.36 g, 2.5 mmol) was added to the resulting pale yellow solution. After a few seconds the solution turned purple and was stirred at −95 °C for 2 h. After the addition of a suitable electrophile (2.7 mmol) the color was discharged. The mixture was allowed to react for 2 h at −95 °C and was then quenched with a THF solution of H_2O (0.5 mL). The mixture was poured into water, the organic phase was separated, and the aqueous phase was extracted twice with diethyl ether (50 mL). The combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated to give crude products. In the case of product **2h**, CO_2 was bubbled into the flask until color was discharged; afterwards the reaction mixture was poured into water, acidified to pH 2 with HCl, and then extracted with diethyl ether, according to the usual workup. Further purification of the products was carried out by means of chromatography on a SiO_2 column.

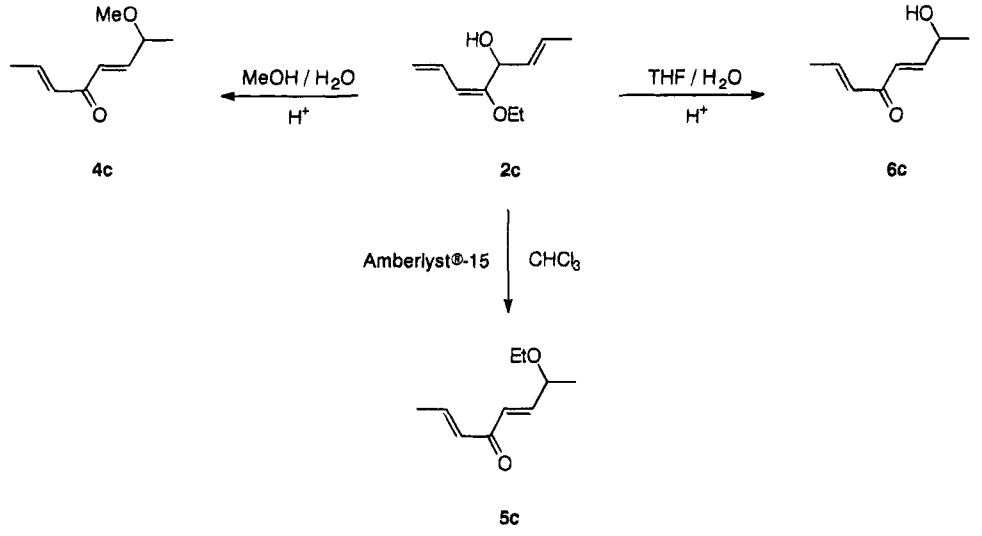
(2*E*,5*E*)-5-Ethoxyocta-2,5,7-trien-4-ol (2c): colorless oil, 0.37 g (90% yield); ^{1}H NMR δ (60 MHz) 1.25 (3 H, t, J = 7), 1.65 (3 H, d, J = 6), 2.70 (1 H, br s), 3.70 (2 H, q, J = 7), 4.50–5.40 (5 H, m), 4.70 (1 H, d, J = 6), 6.05–6.70 (1 H, m, J = 16, 10, 10); MS *m/z* (relative intensity) 168 ($M^{\bullet+}$, 2) 123 (4), 79 (100), 41 (95). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.6; H, 9.7.

Methyl (*E*)-2-ethoxypenta-2,4-dienoate (2d): diethyl ether:light petroleum ether, 10:90; colorless oil, 0.27 g (70% yield); ^{1}H NMR δ (60 MHz) 1.25 (3 H, t, J = 7), 3.65 (3 H, s), 3.70 (2 H, q, J = 7), 4.80 (1 H, dd, J = 10, 2), 5.10 (1 H, dd, J = 16, 2), 5.60 (1 H, d, J = 10), 6.05–6.70 (1 H, m, J = 16, 10, 10); MS *m/z* (relative intensity) 156 ($M^{\bullet+}$, 8), 68 (100), 39 (25). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.4; H, 7.8.

(1*E*,3*E*)-4,6-Diethoxynona-1,3,6,8-tetraen-5-one (2e): colorless oil, 0.25 g (90% yield); ^{1}H NMR δ (60 MHz) 1.25 (3 H, t, J = 7), 3.70 (2 H, q, J = 7), 4.70 (1 H, dd, J = 10, 2), 4.90 (1 H, dd, J = 16, 2), 5.40 (1 H, d, J = 10), 6.20–6.85 (1 H, m, J = 16, 10, 10); MS *m/z* (relative intensity) 222 ($M^{\bullet+}$, 2), 69 (65), 68 (44), 41 (100), 39 (97). Anal. Calcd for $C_{13}H_8O_3$: C, 70.24; H, 8.16. Found: C, 69.9; H, 8.2.

(*E*)-2-Ethoxy-1-phenylpenta-2,4-dien-1-one (2f): diethyl ether:light petroleum ether, 5:95; colorless oil 0.33 g (65% yield); ^{1}H NMR δ (60 MHz) 1.25 (3 H, t, J = 7), 3.70 (2 H, q, J = 7), 4.80 (1 H, dd, J = 10, 2), 5.05 (1 H, dd, J = 16, 2), 5.55 (1 H, d, J = 10), 6.05–6.70 (1 H, m, J = 16, 10, 10), 7.05–7.80

Scheme 2



(5 H, m); MS *m/z* (relative intensity) 202 ($M^{\bullet+}$, 9), 105 (98), 77 (100), 51 (43), 39 (30). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.4; H, 7.0.

(*E*)-3-Ethoxy-2-methylhexa-3,5-dien-2-ol (2g): colorless oil, 0.35 g (91% yield); ^{1}H NMR δ (60 MHz) 1.10 (6 H, s), 1.20 (3 H, t *J* = 7), 2.50 (1 H, br s), 3.40 (2 H, q, *J* = 7), 4.80 (1 H, dd, *J* = 10, 2), 5.05 (1 H, dd, *J* = 16, 2), 5.55 (1 H, d, *J* = 10), 6.05–6.70 (1 H, m, *J* = 16, 10, 10); MS *m/z* (relative intensity) 156 ($M^{\bullet+}$, 18), 59 (27), 43 (100), 41 (42). Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.3; H, 10.4.

(*E*)-2-Ethoxypenta-2,4-dienoic acid (2h): colorless oil, 0.17 g (48% yield); ^{1}H NMR δ (60 MHz) 1.30 (3 H, t, *J* = 7), 3.40 (2 H, q, *J* = 7), 4.80 (1 H, dd, *J* = 10, 2), 5.05 (1 H, dd, *J* = 16, 2), 5.55 (1 H, d, *J* = 10), 6.05–6.70 (1 H, m, *J* = 16, 10, 10), 7.60 (1 H, br s); MS *m/z* (relative intensity) 142 ($M^{\bullet+}$, 11), 68 (100), 41 (17), 39 (42). Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.4; H, 7.2.

General Procedure for the Reduction of Ketones 2d–f to Alcohols 3d–f with $LiAlH_4$. To a solution of ketones **2d–f** (2.0 mmol; **2d**, 0.31 g; **2e**, 0.44 g; **2f**, 0.40) in anhydrous Et_2O (30 mL) at rt was added $LiAlH_4$ (0.04 g, 1.0 mmol) with stirring. The reaction was followed by TLC (Et_2O:light petroleum ether, 40:60). After the disappearance of the spot corresponding to the carbonyl intermediate the reaction mixture was quenched with H_2O (1 mL) and aqueous NaOH (15%, 1 mL). The reaction mixture was then poured into water, the organic phase was separated, and the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated to give crude products.

(*E*)-2-Ethoxypenta-2,4-dien-1-ol (3d): colorless oil, 0.19 g (75% yield); ^{1}H NMR δ (60 MHz) 1.10 (3 H, t, *J* = 7), 2.30 (1 H, br s), 3.35 (2 H, q, *J* = 7), 3.75 (2 H, s), 4.35 (1 H, dd, *J* = 10, 2), 4.55 (1 H, dd, *J* = 16, 2), 4.90 (1 H, d, *J* = 10), 5.70–6.55 (1 H, m, *J* = 16, 10, 10); MS *m/z* (relative intensity) 128 ($M^{\bullet+}$, 28), 69 (60), 41 (49), 39 (100); IR (cm^{-1}) 3400–3320, 1640.

(1*E*,3*E*)-4,6-Diethoxynona-1,3,6,8-tetraen-5-ol (3e): colorless oil, 0.38 g (85% yield); ^{1}H NMR δ (60 MHz) 1.25 (6 H, t, *J* = 7), 2.60 (1 H, br s), 3.70 (4 H, q, *J* = 7), 4.65 (2 H, dd, *J* = 10, 2), 4.80 (2 H, dd, *J* = 16, 2), 4.90 (1 H, s), 5.0 (2 H, d, *J* = 10), 6.05–6.70 (2 H, m, *J* = 16, 10, 10); MS *m/z* (relative intensity) 224 ($M^{\bullet+}$, 2), 207 (1), 69 (65), 53 (100), 41 (65); IR (cm^{-1}) 3500–3420, 1630.

(*E*)-1-Phenyl-2-ethoxypenta-2,4-dien-1-ol (3f): colorless oil, 0.26 g (65% yield); ^{1}H NMR δ (60 MHz) 1.25 (3 H, t, *J* = 7), 3.70 (2 H, q, *J* = 7), 4.50 (1 H, s), 4.65 (1 H, dd, *J* = 10, 2), 4.80 (1 H, dd, *J* = 16, 2), 5.20 (1 H, d, *J* = 10), 6.05–6.70 (1 H, m, *J* = 16, 10, 10), 7.15–7.60 (5 H, br s); MS *m/z* (relative intensity) 204 ($M^{\bullet+}$, 32), 105 (38), 79 (61), 77 (100), 39 (49); IR (cm^{-1}) 3490–3300, 1630.

General Procedure for the Acid-Catalyzed Conversion of Substituted Alkoxy Dienes into α,β-Unsaturated Carbonyl Compounds Method A. Alkoxy diene **2a–c**, **2g–i**, or **3d–f** (2.5 mmol) was stirred in 25 mL of aqueous methanolic (1:4) 0.02 N HCl at rt for 2–6 h. After this time the solution was neutralized was 5% aqueous $NaHCO_3$ and concentrated *in vacuo*. The reaction mixture was then extracted twice with Et_2O (50 mL), and the organic phase was washed with brine, dried (Na_2SO_4), filtered, and concentrated to give crude product.

Method B. Alkoxy diene **2c** (2.5 mmol) was stirred in 25 mL of $CHCl_3$, in the presence of Amberlyst-15 (0.15 g, 0.7 mequiv), at room temperature for 2 h. After this time the resin was filtered off and the reaction mixture was then washed with 5% aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated to give crude product **5c**.

Method C. Alkoxy diene **2c** (2.5 mmol) was stirred in 15 mL of aqueous THF (1:10) and 0.02 N HCl at room temperature for 3 h. After this time the reaction was worked up as reported for method A to give crude product **6c**.

(*E*)-Oct-2-en-4-one (4a): diethyl ether:light petroleum ether, 50:50; colorless oil, 0.28 g (90% yield); ^{1}H NMR δ (60 MHz) 1.05 (3 H, t, *J* = 6), 1.15–1.70 (4 H, m), 2.05 (3 H, d, *J* = 6), 2.60 (2 H, t, *J* = 6), 6.0 (1 H, d, *J* = 16), 6.50–7.05 (1 H, dq, *J* = 16, 6); MS *m/z* (relative intensity) 111 ($M^{\bullet+}$ – Me, 6), 84 (21), 69 (100), 41 (43); IR (cm^{-1}), 1680, 1630. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.1; H, 11.3.

(*E*)-2,2-Dimethyl-3-hydroxyhept-5-en-4-one (4b): diethyl ether:light petroleum ether, 50:50; colorless oil, 0.33 g (85% yield); ^{1}H NMR δ (60 MHz) 0.70 (9 H, s), 1.70 (3 H, d, *J* = 6), 2.70 (1 H, br s), 3.70 (1 H, s), 6.0 (1 H, d, *J* = 16), 6.35–7.0 (1 H, dq, *J* = 16, 6); MS *m/z* (relative intensity) 100 ($M^{\bullet+}$ – Bu, 50), 69 (99), 57 (48), 41 (100); IR (cm^{-1}) 3470–3350, 1680, 1620. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.3; H, 9.9.

(2*E*,5*E*)-7-Methoxyocta-2,5-dien-4-one (4c): colorless oil, 0.35 g (90% yield); ^{1}H NMR δ (300 MHz) 1.30 (3 H, d, *J* = 6), 1.95 (3 H, dd, *J* = 7, 2), 3.35 (3 H, s), 3.95 (1 H, dquint., *J* = 6, 1), 6.37 (1 H, dq, *J* = 15, 2), 6.47 (1 H, dd, *J* = 15, 1), 6.75 (1 H, dd, *J* = 15, 6), 6.97 (1 H, dq, *J* = 15, 7); ^{13}C NMR δ 18.36, 20.34, 56.59, 85.75, 127.38, 130.24, 143.77, 147.12, 189.19; MS *m/z* (relative intensity) 154 ($M^{\bullet+}$, 6), 139 (22), 85 (24), 69 (40), 43 (100), 41 (66); IR (cm^{-1}) 1665, 1640, 1615. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.8; H, 9.2.

(2*E*,5*E*)-7-Ethoxyocta-2,5-dien-4-one (5c): colorless oil, 0.35 g (83% yield); ^{1}H NMR δ (300 MHz) 1.15 (3 H, t, *J* = 7) 1.23 (3 H, d, *J* = 6), 1.87 (3 H, dd, *J* = 7, 2), 3.35 (1 H, qd, *J* = 7, 2), 3.45 (1 H, qd, *J* = 7, 2), 3.97 (1 H, dquint, *J* = 6, 1), 6.30 (1 H, dq, *J* = 15, 2), 6.47 (1 H, dd, *J* = 15, 1), 6.70 (1 H, dd, *J* = 15, 6), 6.87 (1 H, dq, *J* = 15, 7); ^{13}C NMR δ 15.17, 18.21, 20.59, 64.15, 74.57, 127.07, 130.07, 143.44, 147.88, 189.06; MS *m/z* (relative intensity) 168 ($M^{\bullet+}$, 2), 139 (23), 69 (45), 43 (100), 41 (73); IR (cm^{-1}) 1670, 1640, 1620. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.5; H, 9.7.

(2*E*,5*E*)-7-Hydroxyocta-2,5-dien-4-one (6c): diethyl ether: light petroleum ether, 30:70; colorless oil, 0.24 g (70% yield); ^{1}H NMR δ (300 MHz) 1.25 (3 H, J = 7), 1.85 (3 H, d, J = 6, 2), 2.70 (1 H, br s), 4.42 (1 H, dquint, J = 1.5, 7), 6.25 (1 H, dq, J = 15, 1.5), 6.45 (1 H, dd, J = 15, 1.5), 6.80 (1 H, dd, J = 15, 7), 6.85 (1 H, dq, J = 15, 7); ^{13}C NMR δ 18.28, 22.48, 66.92, 125.38, 130.35, 144.02, 148.70, 188.80; MS *m/z* (relative intensity) 125 ($M^{\bullet+}$ − Me, 2), 97 (68), 69 (51), 43 (100), 41 (68); IR (cm^{-1}) 3470−3320, 1685, 1630, 1610. Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.7; H, 8.8.

(*E*)-1-Hydroxypent-3-en-2-one (4d): colorless oil, 0.18 g (70% yield); ^{1}H NMR δ (60 MHz) 1.70 (3 H, d, J = 6), 2.80 (1 H, br s), 4.05 (2 H, s), 5.25 (1 H, d, J = 16), 5.65 (1 H, dq, J = 16, 6); MS *m/z* (relative intensity) 100 ($M^{\bullet+}$, 30); IR (cm^{-1}) 1680. Anal. Calcd for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 60.1; H, 7.9.

(2*E*,6*E*)-6-Ethoxy-5-hydroxynona-2,6,8-trien-4-one (4e): colorless oil, 0.38 g (78% yield); ^{1}H NMR δ (60 MHz) 1.20 (3 H, 7, J = 6), 1.70 (3 H, d, J = 6), 2.60 (1 H, br s), 3.35 (2 H, q, J = 6), 4.75−5.20 (4 H, m), 5.75−6.90 (3 H, m); MS *m/z* (relative intensity) 196 ($M^{\bullet+}$, 5), 69 (100), 97 (2), 53 (64), 41 (93); IR (cm^{-1}) 3490−3320, 1690, 1630. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.1; H, 8.1.

1-Hydroxy-1-phenylpent-3-en-2-one (4f): MS *m/z* (relative intensity) 176 ($M^{\bullet+}$, 1), 107 (98), 77 (66), 69 (63), 41 (37).

(*E*)-5-Hydroxy-5-methylhex-2-en-4-one (4g): colorless oil, 0.28 g (90% yield); ^{1}H NMR δ (60 MHz) 1.10 (6 H, s), 1.90 (3 H, d, J = 7), 2.50 (1 H, br s), 6.05 (1 H, d, J = 16), 6.50−7.05 (1 H, dq, J = 16, 7); MS *m/z* (relative intensity) 113 ($M^{\bullet+}$ − Me, 1), 69 (12), 59 (100), 43 (27), 41 (24); IR (cm^{-1}) 3500−3320, 1690, 1630. Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: 65.7; H, 9.4.

(*E*)-3-Hydroxy-2,2,6-trimethylhept-5-en-4-one (4i): colorless oil, 0.17 g (40% yield); ^{1}H NMR δ (60 MHz) 0.90 (9 H, s), 1.85 (3 H, d, J = 1.2), 2.10 (3 H, d, J = 1.2), 2.5 (1 H, br s), 5.95 (1 H, br s); MS *m/z* (relative intensity) 114 ($M^{\bullet+}$ − Bu, 18), 87 (12), 83 (100), 57 (18), 55 (28); IR (cm^{-1}) 3460−3350, 1680, 1630. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.6; H, 10.6.

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Supplementary Material Available: ^{1}H- and ^{13}C-NMR (300 MHz) of **4c**, **5c**, and **6c** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.