Stereoselective Syntheses of β,γ-Unsaturated Esters and γ-Lactones: 1-(Benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-1-propene, a Protected $=CCH_2CO_2Et$ Synthon Equivalent

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1-(Benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-1-propene (**3**), prepared from *N*-(α-ethoxyallyl)benzotriazole (**1**), underwent selective Horner reactions with aldehydes to give substituted dienes. Subsequent hydrolysis of these intermediates readily produced β,γ-unsaturated esters **2a**−**c** in good yields. Similar reactions with ketones followed by hydrolysis of **10** produced, depending on the conditions, either the corresponding γ,γ-disubstituted β,γ-unsaturated esters **11a**−**d** or γ-lactones **9a**−**c** and **13**. A double lithiation process provided β,γ,γ-trisubstituted β,γ-unsaturated esters **15, 18**, and β,γ,γ-trisubstituted γ-lactone **14**.

Introduction

The Wittig−Horner reaction has frequently been utilized for the preparation of α,β-unsaturated acids and their esters: it enables easy control of the geometry of the double bond by an appropriate choice of reagents and solvent, and the phosphorus reagents are readily available.[1−4] However, examples of the preparation of β,γ-unsaturated acids by the Wittig−Horner reaction are rare.[5,6] Janecki and Bodalski[7] prepared β,γ-unsaturated amides *via* the aminolysis of β-(diethoxyphosphoryl)γ-lactones, themselves formed by reaction of deprotonated β-(diethoxyphosphoryl)propionic acid with a carbonyl compound followed by cyclization. However, direct reaction of β-(diethoxyphosphoryl)-substituted esters with carbonyl compounds normally occurs at the α-position to the ester group to give the α-[(diethoxyphosphoryl)-methyl]-substituted acrylate derivatives[8,9] instead of β,γ-unsaturated esters because the α-proton in the β-(diethoxyphosphoryl)-substituted esters is more acidic than the β-proton.

We have recently reported the advantageous use of readily available *N*-(α-ethoxyallyl)benzotriazole **1** for the syntheses of functionalized vinyl ketones,[10] cyclopropanes,[11] γ-lactones,[11] β,γ-unsaturated carboxylic acids,[11] ketones,[12] 1,4-diketones,[12] 2-cyclopentenones[12] and α-keto enamines.[12] Reactions of deprotonated **1** with diverse electrophiles (alkyl halides, aldehydes, ketones, and α,β-unsaturated esters) usually give exclusively α-products, although highly sterically hindered electrophiles (bulky ketones) gave exclusively γ-alkylated products. In the present work, we demonstrate that reaction of deprotonated **1** with chlorodiphenylphosphine gives exclusively the γ-product, which is subsequently smoothly oxidized *in situ* to generate 1-(benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-(*E*)-prop-1-ene (**3**). Phosphine oxide **3** undergoes stereoselective Horner reactions to yield substituted dienes, the hydrolysis of which, depending on the conditions, affords convenient routes to both β,γ-unsaturated esters and γ-lactones.

Results and Discussion

3-(Benzotriazol-1-yl)-3-ethoxy-1-propene (**1**) was previously prepared in almost quantitative yield by reacting benzotriazole with acrolein diethyl acetal in "performance fluid (PF5070)" in an inverse Dean−Stark apparatus;[10] we now find that directly heating benzotriazole and acrolein diethyl acetal in hexane for 6 h affords **1** in 87% yield.

Stereoselective Reactions of 1-(Benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-1-propene (3) with Aldehydes Leading to β,γ-Unsaturated Esters. Treatment of **1** with 1 equiv of BuLi followed by reaction with chlorodiphenylphosphine and subsequently with H_2O_2 gave 1-(benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-(*E*)-prop-1-ene (**3**) in 60% yield, regio- and stereo-specifically (Scheme 1). No α-product and no *Z*-isomer were observed in the NMR spectra of the crude mixture. This γ-regiospecificity is analogous to the reaction of the allylic anion from **1** with sterically hindered diketones.[12]

Treatment of **3** with 1 equiv of BuLi at −78 °C in THF, followed by reaction with benzaldehyde at −78 to +20 °C for 4 h, gave diene **4a** in 80% yield together with a small amount of **5a** (*E,E*-:*Z,E*- = *ca.* 8:1, as determined from the NMR spectra of the crude mixture), which was removed by column chromatography. Compounds **4b**,**c** were similarly prepared in 55−71% yields, and again small amounts of **5b**,**c** (*E,E*-:*Z,Z*-, *ca.* 10:1) were removed during column chromatography.

The Horner reaction has been extensively investigated.[2,3] Addition of a nonstabilized carbanion of a

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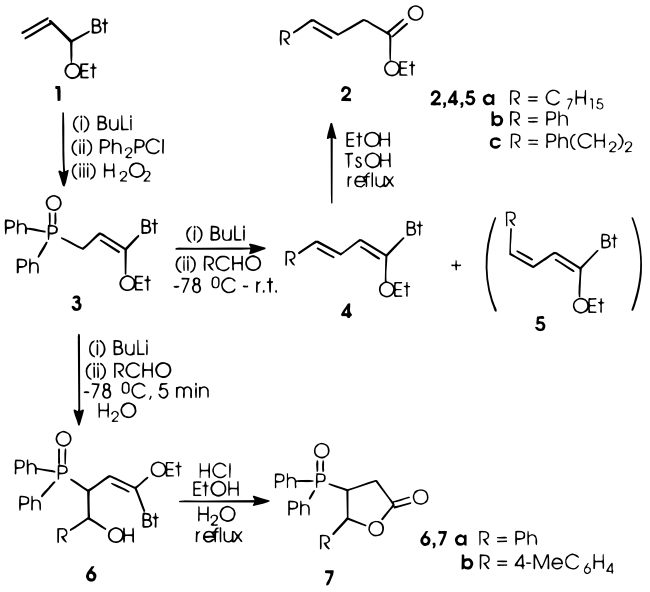
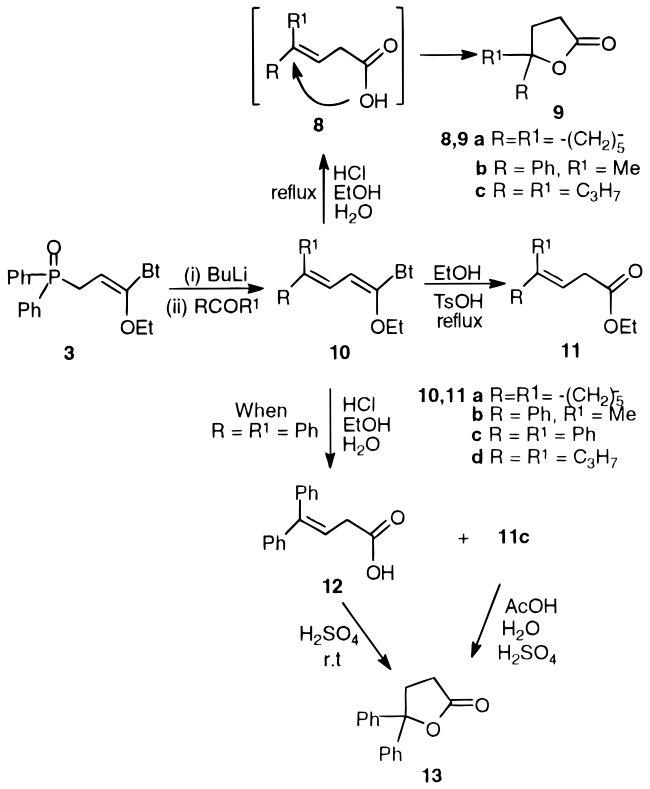
Scheme 1



Scheme 2



phosphine oxide ($Ph_2P(O)CH_2R$) to an aldehyde gives predominantly an *erythro* intermediate, which can be separated by flash column chromatography and crystallization. Stereospecific elimination produces pure (*Z*)-alkenes.[13−15] However, stabilized ylides produce (*E*)-alkenes,[2,3] and in the present cases the anions are stabilized by the *β*-benzotriazolylvinyl group.

Treatment of **4a**−**c** with $TsOH·H_2O$−EtOH readily afforded the *β*,*γ*-unsaturated esters **2a**−**c** in 88−95% yields. *β*,*γ*-Unsaturated esters have previously been prepared by (i) reaction of organoboranes with either α,*β*-unsaturated *γ*-bromo esters[16] or ethyl (dimethylsulfuranylidene)acetate,[17] (ii) electrocatalyzed carboxylation of allyl chlorides,[18] (iii) carbonylation of (η^3-allyl)$Fe(CO)_3$(NO),[19] (iv) palladium-catalyzed carbonylation of allyl phosphates, acetates,[20] or halides,[21] (v) palladium- and nickel-catalyzed coupling of vinyl bromides with Reformasky reagents,[22] (vi) isomerization of α,*β*-unsaturated esters,[23−26] and (vii) treatment of α,*β*-unsaturated α-bromo esters with dialkyl phosphonates.[27] No previous report has been found for the preparation of *β*,*γ*-unsaturated esters *via* formation of the C=C double bond.

Alternatively, reaction of **3** with benzaldehyde for 5 min at −78 °C, and subsequent quenching with water, gives hydroxyphosphine **6a** in 66% yield as a mixture of *threo* and *erythro* diastereomers (5:1), which were separated by column chromatography. Compound **6b** was similarly prepared in 68% yield as a mixture of diastereomers (*threo*:*erythro*, 5.5:1 from crude NMR spectra). Further treatment of **6a**,**b** with HCl−EtOH−H_2O gave the *β*-(diphenylphosphoryl)-substituted lactones **7a**,**b** in 79−80% yields. Analogous *γ*-substituted *β*-(diethoxyphosphoryl) *γ*-lactones were previously prepared by LDA-promoted reactions of *β*-(diethoxyphosphoryl)propanecarboxylic acids with carbonyl compounds.[7] The *E*-:*Z*-ratios in Wittig−Horner products are determined by the *threo*:*erythro* ratios in the intermediates.[3]

Reaction of 3 with Ketones for the Syntheses of *β*,*γ*-Unsaturated Esters 11a−d and *γ*-Lactones 9a−c and 13. Reactions of the deprotonated 1-(benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-(*E*)-prop-1-ene (**3**) with ketones gave the Horner products **10** even at low temperatures (−78 °C), although a higher reaction temperature (at 20 °C) can substantially reduce the reaction time (Scheme 2). The contrast to the aldehyde cases is probably due to the relatively high thermodynamic stability of the C=C double bond with three substituents and the steric kinetic substituents' effect. Thus, treatment of **3** with 1 equiv of BuLi at −78 °C in THF, followed by reaction with cyclohexanone at −78 °C for 10 h, gave 1,3-diene **10a** in 93% yield. The reaction was also complete at 20 °C after only 1 h as monitored by TLC. Compounds **10c**,**d** were obtained in 60−70% yields when benzophenone and 4-heptanone were employed as the electrophiles. The structures of **10a**,**c**,**d** were fully supported by NMR spectra and by elemental analyses. When unsymmetrical acetophenone was used as the electrophile, the *E*,*E*-isomer **10b** was produced in 73% yield along with a small amount of *Z*,*E*-isomer (*E*,*E*-:*Z*,*E*-, 8:1 by ^{1}H NMR spectra). The *E*,*E*-structure was supported by the NOE technique.

Hydrolyses of **10**, as carried out in the cases of **4**, generated the expected *β*,*γ*-unsaturated esters **11a**−**d** in

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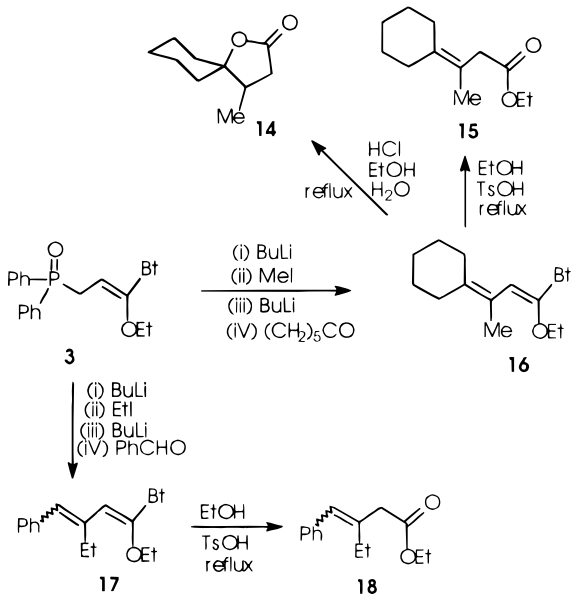
Scheme 3



71−99% yields. By contrast, aqueous hydrolysis (H_2SO_4−EtOH−H_2O) of **10a**,**b**,**d** gave γ-substituted γ-lactones **9a**−**c** in 82−90% yields, probably *via* the β,γ-unsaturated acids **8**. Conversions of γ,γ-disubstituted β,γ-unsaturated acids and esters to the corresponding lactones under acidic conditions have been reported previously.[28−31]

Under acidic conditions, similar to those used for the conversion of **10a,b,d** into **9a**−**c**, no lactone **13** was formed. Compound **10c** formed acid **12** (32%) and the corresponding ester **11c** (50%). Further treatment of **12** in concentrated sulfuric acid at 20 °C converted it into lactone **13** in 95% yield. Acidic hydrolysis and cyclization of **11c** with AcOH−H_2−H_2SO_4 also easily produced the lactone **13** in 92% yield. The structures of esters **11a**−**d** and lactones **9a**−**c** and **13** were confirmed by NMR spectroscopy and CHN analyses.

Double Lithiation of 1-(Benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-(*E*)-prop-1-ene (3) for the Preparation of β,γ,γ-Trisubstituted Esters 15 and 18 and β,γ,γ-Trisubstituted Lactone 14. Strong activation of the α-methylene protons by the benzotriazo-1-ylvinyl group in **3** allows the phosphine oxides **3** to undergo two lithiations. Thus, as shown in Scheme 3, an alkyl group can be introduced before the Horner reaction is carried out. Treatment of **3** with 1 equiv of BuLi, followed by quenching with methyl iodide and then with another equiv of BuLi, and finally with cyclohexanone, gives diene **16** in 65% yield. Hydrolyses under conditions similar to those used for the preparations of **11** and **9** convert **16** into the β,γ,γ-trisubstituted ester **15** (98%) and the β,γ,γ-trisubstituted lactone **14** (80%), respectively. However, reaction of **3** with benzaldehyde in a similar sequence (see Scheme 3) gives compound **17** as a mixture of two stereoisomers (*E*,*E*-:*Z*,*E*-, *ca.* 2:1): evidently, the tertiary anion, formed after the second deprotonation of **3**, reacts with benzaldehyde with poor stereoselectivity. Hydrolyses of **17**, carried out as in the case of **4**, generated the expected β,γ-unsaturated ester **18** in 96% yield.

In conclusion, 1-(benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxyprop-1-ene has been shown to be an efficient $=CCH_2CO_2Et$ synthon equivalent for the convenient stereoselective synthesis of β,γ-unsaturated esters and γ-lactones.

Experimental Section

General Comments. Melting points were determined on a hot stage apparatus without correction. ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ with TMS or $CDCl_3$, respectively, as the internal reference. Elemental analyses and high-resolution mass spectra were performed within the department. Column chromatography was carried out on MCB silica gel (230−400 mesh). Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone. Lithiation reactions were carried out under the protection of dry nitrogen.

Modified Procedure for the Preparation of 3-(Benzotriazol-1-yl)-3-ethoxy-1-propene (1). A mixture of acrolein diethyl acetal (3.91 g, 30 mmol) and benzotriazole (5.36 g, 45 mmol) in hexane (30 mL) was heated under reflux for 6 h. After cooling, diethyl ether (300 mL) was added, and the solution was washed with saturated aqueous Na_2CO_3 solution (2 × 150 mL) and water (150 mL). Evaporation of the solvent and separation by column chromatography (hexane/ethyl acetate, 14:1) gave 5.27 g of pure product (87%). The spectral data are the same as reported in the literature.[10]

Preparation of 1-(Benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-(*E*)-prop-1-ene (3). To a solution of 3-(benzotriazol-1-yl)-3-ethoxy-1-propene (**1**) (4.06 g, 20 mmol) in THF (100 mL) at −78 °C was added BuLi (1.6 M, 13.8 mL). After 5 min, chlorodiphenylphosphine (4.41 g, 20 mmol) was added, and the reaction was kept at −78 °C for 3 h and at 20 °C for 1 h. Water (80 mL) and H_2O_2 (2 mL) were added, and the mixture was stirred at 20 °C for another 10 h. The solution was then diluted with water (300 mL) and extracted with diethyl ether (2 × 150 mL). The organic phase was separated and dried ($MgSO_4$). Evaporation of the solvent and separation by column chromatography (hexane/ethyl acetate, 1:4) gave 4.81 g of product: yield 60%; mp 108−110 °C; ^1H NMR δ 1.18 (t, 3 H, J = 7.1 Hz), 3.41−3.56 (m, 4 H), 5.41 (dt, 1 H, J_{PH} = 6.0 Hz, J_{HH} = 8.0 Hz), 7.31−7.60 (m, 9 H), 7.82−7.95 (m, 4 H), 8.03 (d, 1 H, J = 8.3 Hz); ^{13}C NMR δ 14.4, 28.0 (d, J_{PC} = 69.6 Hz), 66.4, 98.0 (d, J_{PC} = 8.6 Hz), 110.4, 119.5, 124.2, 128.2, 128.4 (d, J_{PC} = 11.9 Hz), 130.7 (d, J_{PC} = 9.3 Hz), 131.4, 131.7, 132.1, 132.7, 144.9 (d, J_{PC} =12.8 Hz), 145.1. Anal. Calcd for $C_{23}H_{22}N_3O_2P$: C, 68.48; H, 5.50; N, 10.42. Found: C, 68.35; H, 5.63; N, 10.31.

General Procedure for the Preparation of Dienes 4a−c and 10a−d. To a solution of 1-(benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-(*E*)-prop-1-ene **(3)** (2.82 g, 7 mmol) in dry THF (70 mL) at −78 °C was added BuLi (1.6 M, 4.8 mL). The solution was stirred at this temperature for 5 min, and the appropriate electrophile (benzaldehyde, octanal, 3-phenylpropionaldehyde, cyclohexanone, acetophenone, benzophenone, 4-heptanone dipropyl ketone, 7 mmol) was added. After being stirred at −78 °C for 3 h, the solution was allowed to warm to room temperature and kept for an additional hour. Water (50 mL) was added and the mixture extracted with diethyl ether (2 × 100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue, which was chromatographed on silica gel (hexane/ethyl acetate, 10:1).

1-(Benzotriazol-1-yl)-1-ethoxy-(*E*,*E*)-undeca-1,3-diene (4a) was obtained as a colorless oil: yield 80%; ^1H NMR δ 0.91 (t, 3 H, J = 6.8 Hz), 1.21−1.55 (m, 13 H), 2.20 (q, 2 H, J = 6.9 Hz), 3.78 (q, 2 H, J = 7.1 Hz), 5.84−5.97 (m, 1 H), 6.09 (d, 1 H, J = 10.9 Hz), 6.49 (dd, 1 H, J = 15.4 and 10.9 Hz), 7.40 (t, 1 H, J = 7.4 Hz), 7.53 (t, 1 H, J = 7.4 Hz), 7.75 (d, 1 H, J = 8.5 Hz), 8.08 (d, 1 H, J = 8.3 Hz); ^{13}C NMR δ 13.9, 14.6, 22.5, 29.0, 29.1, 31.7, 33.0, 67.3, 109.8, 111.1, 119.9, 122.2, 124.3, 128.2, 132.1, 136.8, 141.7, 145.7. Anal. Calcd for $C_{19}H_{27}N_3O$: C, 72.81; H, 8.68; N, 13.41. Found: C, 73.06; H, 9.14; N, 13.72.

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1-(Benzotriazol-1-yl)-1-ethoxy-4-phenyl-(*E,E*)-buta-1,3-diene (4b) was obtained as a colorless oil: yield 55%; ^{1}H NMR δ 1.36 (t, 3 H, J = 7.1 Hz), 3.83 (q, 2 H, J = 7.1 Hz), 6.28 (d, 1 H, J = 11.0 Hz), 6.69 (d, 1 H, J = 15.9 Hz), 7.18−7.62 (m, 8 H), 7.77 (d, 1 H, J = 8.3 Hz), 8.09 (d, 1 H, J = 8.3 Hz); ^{13}C NMR δ 14.5, 67.6, 109.1, 111.0, 119.8, 120.9, 124.3, 126.1, 127.5, 128.2, 128.3, 131.7, 133.0, 136.9, 143.4, 145.5. Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 73.71; H, 6.26; N, 14.28.

1-(Benzotriazol-1-yl)-1-ethoxy-6-phenyl-(*E,E*)-hexa-1,3-diene (4c) was obtained as a colorless oil: yield 71%; ^{1}H NMR δ 1.31 (t, 3 H, J = 7.1 Hz), 2.48−2.62 (m, 2 H), 2.79 (t, 2 H, J = 7.2 Hz), 3.76 (q, 2 H, J = 7.1 Hz), 5.87−5.99 (m, 1 H), 6.10 (d, 1 H, J = 10.8 Hz), 6.52 (dd, 1 H, J = 15.4, 10.8 Hz), 7.17−7.37 (m, 5 H), 7.41 (t, 1 H, J = 7.3 Hz), 7.53 (t, 1 H, J = 7.7 Hz), 7.75 (d, 1 H, J = 8.3 Hz), 8.09 (d, 1 H, J = 8.3 Hz); ^{13}C NMR δ 14.6, 34.7, 35.5, 67.4, 109.5, 111.2, 120.0, 123.0, 124.4, 125.8, 128.2, 128.3, 132.5, 135.3, 141.4, 142.1, 145.7. Anal. Calcd for $C_{20}H_{21}N_3O$: C, 75.21; H, 6.63; N, 13.16. Found: C, 75.16; H, 6.68; N, 13.08.

1-(Benzotriazol-1-yl)-1-ethoxy-4,4-cyclohexylbuta-1,3-diene (10a) was obtained as a colorless oil: yield 93%; ^{1}H NMR δ 1.33 (t, 3 H, J = 7.1 Hz), 1.24−1.34 (m, 6 H), 2.09−2.19 (m, 4 H), 3.77 (q, 2 H, J = 6.9 Hz), 6.23 (d, 1 H, J = 11.4 Hz), 6.34 (d, 1 H, J = 11.4 Hz), 7.39 (t, 1 H, J = 7.2 Hz), 7.52 (t, 1 H, J = 7.2 Hz), 7.75 (d, 1 H, J = 8.4 Hz), 8.06 (d, 1 H, J = 8.4 Hz); ^{13}C NMR δ 14.5, 26.4, 27.4, 28.3, 29.3, 37.3, 67.0, 105.5, 111.0, 113.6, 119.6, 124.1, 128.0, 131.8, 142.0, 145.4, 145.8. Anal. Calcd for $C_{17}H_{21}N_3O$: C, 72.06; H, 7.47; N, 14.83. Found: C, 71.80; H, 7.64; N, 14.61.

1-(Benzotriazol-1-yl)-1-ethoxy-4-phenylpenta-1,3-diene (10b) was obtained as a colorless oil: yield 73%; ^{1}H NMR δ 1.33 (t, 3 H, J = 7.2 Hz), 2.20 (s, 3 H), 3.80 (q, 2 H, J = 7.2 Hz), 6.50 (d, 1 H, J = 11.4 Hz), 6.93 (d, 1 H, J = 11.4 Hz), 7.28−7.48 (m, 4 H), 7.52−7.60 (m, 3 H), 7.80 (d, 1 H, J = 8.3 Hz), 8.11 (d, 1 H, J = 8.4 Hz); ^{13}C NMR δ 14.7, 16.3, 67.7, 106.4, 111.2, 119.0, 120.0, 124.5, 125.6, 127.3, 128.3, 128.4, 132.0, 138.1, 142.8, 143.8, 145.8. Anal. Calcd for $C_{19}H_{19}N_3O$: C, 74.73; H, 6.27; N, 13.76. Found: C, 74.28; H, 6.51; N, 13.43.

1-(Benzotriazol-1-yl)-1-ethoxy-4,4-diphenylbuta-1,3-diene (10c): yield 70%; mp 72−74 °C; ^{1}H NMR δ 1.37 (t, 3 H, J = 7.2 Hz), 3.84 (q, 2 H, J = 7.2 Hz), 6.23 (d, 1 H, J = 11.4 Hz), 7.20 (d, 1 H, J = 11.4 Hz), 7.22−7.40 (m, 11 H), 7.47 (t, 1 H, J = 7.2 Hz), 7.68 (d, 1 H, J = 8.4 Hz), 8.01 (d, 1 H, J = 8.4 Hz); ^{13}C NMR δ 14.7, 67.6, 107.3, 111.0, 119.7, 119.9, 124.4, 127.5, 128.1, 128.2, 128.3, 130.1, 131.8, 139.1, 141.9, 144.0, 144.2, 145.5. Anal. Calcd for $C_{24}H_{21}N_3O$: C, 78.45; H, 5.76; N, 11.44. Found: C, 78.82; H, 5.86; N, 11.44.

1-(Benzotriazol-1-yl)-1-ethoxy-4-propylhepta-1,3-diene (10d) was obtained as a colorless oil: yield 60%; ^{1}H NMR δ 0.93 (t, 3 H, J = 7.4 Hz), 0.97 (t, 3 H, J = 7.4 Hz), 1.34 (t, 3 H, J = 7.1 Hz), 1.42−1.6 (m, 4 H), 2.12−2.25 (m, 4 H), 3.79 (q, 2 H, J = 7.0 Hz), 6.28−6.38 (m, 2 H), 7.41 (t, 1 H, J = 7.2 Hz), 7.54 (t, 1 H, J = 7.2 Hz), 7.77 (d, 1 H, J = 8.4 Hz), 8.09 (d, 1 H, J = 8.3 Hz); ^{13}C NMR δ 13.8, 14.0, 14.7, 21.3, 33.0, 39.7, 67.3, 106.4, 111.2, 116.8, 119.9, 124.3, 128.1, 132.2, 142.0, 145.7, 146.2. Anal. Calcd for $C_{18}H_{25}N_3O$: C, 72.21; H, 8.42; N, 14.03. Found: C, 71.92; H, 8.80; N, 14.25.

General Procedure for the Preparation of β,γ-Unsaturated Esters 2a-c, 11a-d, 15 and 18. A mixture of diene **4a** (or **4b,c**, **10a**−**d**, **16**, **17**) (2 mmol) and *p*-toluenesulfonic acid monohydrate (10 mg) in anhydrous ethanol (20 mL) was heated under reflux for 40 h. After cooling, diethyl ether (150 mL) was added, and the solution was washed with saturated Na_2CO_3 solution (2 × 100 mL). Evaporation of the solvent gave a residue, which was chromatographed on silica gel (hexane/ethyl acetate, 50:1).

Ethyl 3-undecenoate (2a) was obtained as a colorless oil: yield 95%; ^{1}H NMR δ 0.89 (t, 3 H, J = 6.9 Hz), 1.20−1.45 (m, 13 H), 2.03 (q, 2 H, J = 7.0 Hz), 3.02 (d, 2 H, J = 5.3 Hz), 4.14 (q, 2 H, J = 7.1 Hz), 5.47−5.65 (m, 1 H); ^{13}C NMR δ 14.0, 14.1, 22.6, 29.1, 29.3, 31.8, 32.4, 38.1, 60.3, 121.5, 134.7, 172.0. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.28; H, 11.56.

Ethyl 4-phenyl-3-butenoate (2b) was obtained as a colorless oil: yield 88%; ^{1}H NMR δ 1.29 (t, 3 H, J = 7.1 Hz), 3.24 (d, 2 H, J = 7.0 Hz), 4.18 (q, 2 H, J = 7.1 Hz), 6.25−6.40 (m, 1 H), 6.50 (d, 1 H, J = 15.9 Hz), 7.20−7.45 (m, 5 H); ^{13}C NMR δ 14.1, 38.3, 60.6, 121.7, 126.1, 127.4, 128.4, 133.2, 136.8, 171.3. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.78; H, 7.81.

Ethyl 6-phenyl-3-hexenoate (2c) was obtained as a colorless oil: yield 94%; ^{1}H NMR δ 1.24 (t, 3 H, J = 7.1 Hz), 2.30−2.40 (m, 2 H), 2.69 (t, 2 H, J = 7.4 Hz), 3.00 (d, 2 H, J = 4.8 Hz), 4.12 (q, 2 H, J = 7.1 Hz), 5.50−5.65 (m, 2 H), 7.12−7.21 (m, 3 H), 7.22−7.32 (m, 2 H); ^{13}C NMR δ 14.1, 34.1, 35.5, 38.0, 60.3, 122.3, 125.7, 128.1, 128.3, 133.5, 141.6, 171.8. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.47; H, 8.24.

Ethyl 3-cyclohexylidenepropanoate (11a) was obtained as a colorless oil:[32] yield 90%; ^{1}H NMR δ 1.27 (t, 3 H, J = 7.2 Hz), 1.45−1.65 (m, 6 H), 2.07−2.18 (m, 4 H), 3.04 (d, 2 H, J = 7.2 Hz), 4.14 (q, 2 H, J = 7.2 Hz), 5.26 (t, 1 H, J = 7.2 Hz); ^{13}C NMR δ 14.1, 26.6, 27.4, 28.3, 28.8, 32.9, 36.9, 60.3, 112.4, 143.2, 172.4.

Ethyl 4-phenyl-(*E*)-3-pentenoate (11b) was obtained as a colorless oil: yield 88%; ^{1}H NMR δ 1.25 (t, 3 H, J = 7.1 Hz), 2.06 (s, 3 H), 3.22 (d, 2 H, J = 7.0 Hz), 4.14 (q, 2 H, J = 7.1 Hz), 5.95 (t, 1 H, J = 7.1 Hz), 7.15−7.42 (m, 5 H); ^{13}C NMR δ 14.1, 16.0, 34.4, 60.5, 119.2, 125.6, 126.9, 128.0, 137.8, 143.0, 171.6. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.31; H, 7.86.

Ethyl 4,4-diphenyl-3-butenoate (11c) was obtained as a colorless oil: yield 71%; ^{1}H NMR δ 1.23 (t, 3 H, J = 7.1 Hz), 3.14 (d, 2 H, J = 7.4 Hz), 4.14 (q, 2 H, J = 7.1 Hz), 6.27 (t, 1 H, J = 7.4 Hz), 7.08−7.46 (m, 10 H); ^{13}C NMR δ 14.1, 35.4, 60.5, 120.4, 127.2, 127.3, 128.2, 129.6, 139.1, 141.8, 144.5, 171.6. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.16; H, 6.81. Found: C, 80.75; H, 6.85.

Ethyl 4-propyl-3-heptenoate (11d) was obtained as a colorless oil: yield 99%; ^{1}H NMR δ 0.85−0.95 (m, 6 H), 1.26 (t, 3 H, J = 7.1 Hz), 1.31−1.51 (m, 4 H), 2.00 (t, 4 H, J = 7.1 Hz), 3.05 (d, 2 H, J = 7.1 Hz), 4.13 (q, 2 H, J = 7.1 Hz), 5.34 (t, 1 H, J = 7.1 Hz); ^{13}C NMR δ 13.7, 14.0, 14.1, 21.1, 21.3, 32.3, 33.6, 38.9, 60.3, 116.0, 143.0, 172.4. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.94; H, 11.06.

Ethyl 3-methyl-4,4-penteno-3-butenoate (15) was obtained as a colorless oil: yield 98%; ^{1}H NMR δ 1.26 (t, 3 H, J = 7.1 Hz), 1.46−1.62 (m, 6 H), 1.76 (s, 3 H), 2.13−2.23 (m, 4 H), 3.08 (s, 2 H), 4.13 (q, 2 H, J = 7.2 Hz); ^{13}C NMR δ 14.1, 18.6, 26.7, 27.8, 27.9, 30.6, 30.8, 39.4, 60.2, 117.4, 136.8, 172.1. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.20; H, 10.43.

Ethyl 3-ethyl-4-phenyl-3-butenoate (18) was obtained as a colorless oil: yield 96% (a mixture of *E*- and *Z*- isomers, ratio *ca.* 2.3:1 from ^{1}H NMR): ^{1}H NMR (peaks for the minor isomer are given in square brackets) δ 1.13 (t, 3 H, J = 7.6 Hz) [1.05 (t, 3 H, J = 7.6 Hz)], 1.26 (t, 3 H, J = 7.1 Hz), 2.27 (q, 2 H, J = 7.4 Hz) [2.34 (q, 2 H, J = 7.4 Hz)], 3.21 (s, 3 H) [3.16 (s 3 H)], 4.16 (q, 2 H, J = 7.1 Hz), 6.49 (s, 1 H) [6.38 (s, 1 H)], 7.13−7.38 (m, 5 H); ^{13}C NMR (it is difficult to assign all of the carbon peaks to two isomers, so all peaks are listed) δ 12.3, 12.6, 14.1, 24.0, 30.4, 37.0, 42.4, 60.5, 60.6, 126.4, 126.5, 127.4, 128.0, 128.1, 128.4, 128.5, 128.7, 136.9, 137.4, 137.6, 171.6, 171.7. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.39; H, 8.40.

General Procedure for the Preparation of 6a,b. To a solution of 1-(benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-(*E*)-prop-1-ene (**3**) (2.02 g, 5 mmol) in THF (50 mL) at −78 °C was added BuLi (1.6 M, 3.8 mL). The solution was stirred at this temperature for 5 min, and the appropriate electrophile (benzaldehyde or *p*-tolualdehyde, 5 mmol) was added. After being stirred at −78 °C for an additional 5 min, water (50 mL) was added, and the mixture was extracted with diethyl ether (2 × 100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue, which was chromatographed on silica gel (hexane/ethyl acetate, 3:2). In the case of **6a**, two diastereomers have been isolated and charac-

(32) Piva, O. *Tetrahedron* **1994**, *50*, 13687.

terized; in the case of **6b**, only the major isomer was isolated and characterized.

1-(Benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-4-hydroxy-4-phenyl-1-butene (6a) was obtained as two diastereomers. Isomer I: yield 11%; mp 148−151 °C; ^{1}H NMR δ 0.80 (t, 3 H, J = 7.2 Hz), 2.48−2.60 (m, 1 H), 3.08−3.20 (m, 1 H), 4.00 (dd, 1 H, J = 11.5, 7.2 Hz), 5.31 (s, 1 H), 5.53 (d, 1 H, J = 8.5 Hz), 5.77 (dd, 1 H, J = 11.3, 5.6 Hz), 7.10−7.22 (m, 2 H), 7.27−7.50 (m, 9 H), 7.58−7.65 (m, 3 H), 7.88−8.00 (m, 3 H), 8.03−8.15 (m, 2 H); ^{13}C NMR δ 14.1, 45.1 (d, J_{PC} = 67.7 Hz), 66.1, 71.3, 98.7, 110.2, 119.4, 124.1, 125.6, 127.1, 127.8, 128.0, 128.1, 128.2, 128.8 (d, J_{PC} = 11.6 Hz), 130.7 (d, J_{PC} = 8.9 Hz), 131.8, 131.9, 132.1 (d, J_{PC} = 2.5 Hz), 141.9, 144.9, 145.1 (d, J_{PC} = 12.4 Hz). Anal. Calcd for $C_{30}H_{28}N_3O_3P$: C, 70.72; H, 5.54; N, 8.25. Found: C, 70.96; H, 5.39; N, 8.28. Isomer II: yield 55%; mp 159−165 °C; ^{1}H NMR δ 1.01 (t, 3 H, J = 7.2 Hz), 2.72−2.82 (m, 1 H), 3.02−3.17 (m, 1 H), 4.27 (q, 1 H, J = 10.0 Hz), 4.80 (dd, 1 H, J = 11.5 and 5.8 Hz), 5.12 (t, 1 H, J = 9.0 Hz), 6.76 (d, 1 H, J = 7.8 Hz), 7.18−8.17 (m, 19 H); ^{13}C NMR δ 14.5, 45.3 (d, J_{PC} = 68.3 Hz), 66.0, 74.4, 101.6, 110.0, 119.6, 124.3, 127.0, 127.7, 127.9, 128.2, 128.3, 130.0 (d, J_{PC} = 9.1 Hz), 131.4, 131.9, 132.0, 141.8 (d, J_{PC} = 11.4 Hz), 144.4 (d, J_{PC} = 12.5 Hz), 145.0. Anal. Calcd for $C_{30}H_{28}N_3O_3P$: C, 70.72; H, 5.54; N, 8.25. Found: C, 70.95; H, 5.69; N, 7.98.

1-(Benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-4-hydroxy-4-(4-methylphenyl)-1-butene (6b) was obtained as two diastereomers. The major isomer was isolated and characterized: yield 68%; mp 174−179 °C; ^{1}H NMR δ 0.82 (t, 3 H, J = 7.2 Hz), 2.26 (s, 3 H), 2.47−2.61 (m, 1 H), 3.08−3.12 (m, 1 H), 3.92 (dd, 1 H, J = 11.4, 6.9 Hz), 5.06 (s, 1 H), 5.43 (d, 1 H, J = 8.4 Hz), 5.70 (dd, 1 H, J = 11.4, 5.7 Hz), 7.07−7.17 (m, 3 H), 7.25−7.53 (m, 7 H), 7.55−7.68 (m, 3 H), 7.85−7.92 (m, 2 H), 7.98 (d, 1 H, J = 8.1 Hz), 8.05−8.12 (m, 2 H); ^{13}C NMR δ 14.3, 20.9, 45.2 (d, J_{PC} = 67.1 Hz), 66.3, 71.5, 98.9, 110.5, 119.8, 124.3, 125.7, 128.1, 128.3, 128.6 (d, J_{PC} = 11.4 Hz), 129.0 (d, J_{PC} = 11.4 Hz), 130.7, 130.9, 131.0, 132.2 (d, J_{PC} = 15.0 Hz), 136.9, 138.8 (d, J_{PC} = 12.5 Hz), 145.2. Anal. Calcd for $C_{31}H_{30}N_3O_3P$: C, 71.12; H, 5.78; N, 8.03. Found: C, 70.89; H, 5.86; N, 7.94.

General Procedure for the Preparation of Lactones 7a,b. A mixture of hydroxyphosphine oxide **6a (**Isomer II**)** or **6b** (2 mmol), hydrochloric acid (5 mL), ethanol (25 mL), and water (25 mL) was heated under reflux for 24 h. After cooling, diethyl ether (150 mL) was added, and the solution was washed with saturated Na_2CO_3 solution (2 × 100 mL). Evaporation of the solvent gave a residue, which was chromatographed on silica gel (hexane/ethyl acetate, 15:1).

β-(Diphenylphosphoryl)-γ-phenyl-γ-butyrolactone (7a): yield 80%; mp 170−174 °C; ^{1}H NMR δ 2.67−2.84 (m, 1 H), 3.07−3.26 (m, 1 H), 3.44−3.52 (m 1 H), 5.71 (dd, 1 H, J = 11.3, 8.5 Hz), 6.88−6.99 (m, 2 H), 7.02−7.32 (m, 5 H), 7.33−7.58 (m, 6 H), 7.70−7.82 (m, 2 H); ^{13}C NMR δ 29.9, 43.2 (d, J_{PC} = 73.0 Hz), 80.3 (d, J_{PC} = 2.3 Hz), 126.2, 128.3, 128.4, 128.5, 128.6, 128.9, 129.0, 130.4 (d, J_{PC} = 9.1 Hz), 130.8 (d, J_{PC} = 9.4 Hz), 132.0 (d, J_{PC} = 2.7 Hz), 132.3 (d, J_{PC} = 3.1 Hz), 137.8, 173.8 (d, J_{PC} = 11.7 Hz). Anal. Calcd for $C_{22}H_{19}O_3P$: C, 72.92; H, 5.28. Found: C, 73.11; H, 5.42.

β-(Diphenylphosphoryl)-γ-(4-methylphenyl)-γ-butyrolactone (7b): yield 79%; mp 178−183 °C; ^{1}H NMR δ 2.24 (s, 3 H), 2.68−2.73 (m, 1 H), 3.05−3.21 (m, 1 H), 3.41−3.57 (m, 1 H), 5.68 (dd, 1 H, J = 11.5, 8.3 Hz), 6.83 (d, 2 H, J = 8.4 Hz), 6.89 (d, 2 H, J = 8.2 Hz), 7.19−7.29 (m, 2 H), 7.32−7.58 (m, 6 H), 7.70−7.85 (m, 2 H); ^{13}C NMR δ 20.7, 29.6, 42.7 (d, J_{PC} = 72.8 Hz), 80.1, 125.9, 128.1, 128.2, 128.4, 128.6, 128.8, 130.1 (d, J_{PC} = 9.1 Hz), 130.6 (d, J_{PC} = 9.1 Hz), 131.7, 132.0, 134.6, 138.3, 173.8 (d, J_{PC} = 11.4 Hz). Anal. Calcd for $C_{23}H_{21}O_3P$: C, 73.40; H, 5.62. Found: C, 73.18; H, 5.67.

General Procedure for the Preparation of Lactones 9a−c and 14. A mixture of diene **10a (**or **10b,d**, **16**) (3 mmol), hydrochloric acid (1 mL), ethanol (15 mL), and water (15 mL) was heated under reflux for 24 h. After cooling, diethyl ether (150 mL) was added, and the solution was washed with saturated Na_2CO_3 solution (2 × 100 mL). Evaporation of the solvent gave a residue, which was chromatographed on silica gel (hexane/ethyl acetate, 10:1).

γ,γ-Spiro[cyclohexane-γ-butyrolactone] (9a) was obtained as a colorless oil (lit.[33] 80−110 °C/mmHg): yield 82%;^{1}H NMR δ 1.37−1.87 (m, 10 H), 2.03 (t, 2 H, J = 8.7 Hz), 2.58 (t, 2 H, J = 8.4 Hz); ^{13}C NMR δ 22.3, 24.7, 28.3, 32.5, 36.6, 86.1, 176.5.

γ-Methyl-γ-phenyl-γ-butyrolactone (9b) was obtained as a colorless oil (lit.[30] 140−145 °C/mmHg): yield 89%; ^{1}H NMR δ 1.72 (s, 3 H), 2.36−2.72 (m, 4 H), 7.27−7.50 (m, 5 H); ^{13}C NMR δ 28.7, 29.1, 35.9, 86.7, 123.9, 127.4, 128.4, 144.2, 176.2.

γ,γ-Dimethyl-γ-butyrolactone (9c) was obtained as a colorless oil: yield 79%; ^{1}H NMR δ 0.95 (t, 6 H, J = 7.4 Hz), 1.26−1.46 (m, 4 H), 1.56−1.70 (m, 4 H), 2.04 (t, 2 H, J = 8.5 Hz), 2.58 (t, 2 H, J = 8.5 Hz); ^{13}C NMR δ 14.0, 16.5, 28.8, 30.5, 40.7, 88.7, 176.7. Anal. Calcd for $C_{10}H_{18}O_2P$: C, 70.55; H, 10.66. Found: C, 70.26; H, 10.97.

β-Methyl-γ,γ-cyclohexyl-γ-butyrolactone (14) was obtained as a colorless oil: yield 80%; ^{1}H NMR δ 1.06 (d, 3 H, J = 6.6 Hz), 1.20−1.80 (m, 10 H), 2.20−2.35 (m, 2 H), 2.58−2.78 (m, 1 H); ^{13}C NMR δ 14.0, 21.4, 22.2, 25.0, 30.4, 35.7, 36.3, 39.0, 87.7, 175.7. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.36; H, 10.05.

Hydrolysis of Diene 10c for the Preparation of 12 and 11c. A mixture of diene **10c** (1.22 g, 3.32 mmol), hydrochloric acid (1 mL), ethanol (15 mL), and water (15 mL) was heated under reflux for 24 h. After cooling, diethyl ether (150 mL) was added, and the solution was washed with saturated Na_2CO_3 solution (2 × 100 mL). Evaporation of the solvent gave a residue, which was chromatographed on silica gel (hexane/ethyl acetate, 33:1) to give 4,4-diphenyl-3-butenoic acid **(12)** (0.25 g, 32%) and the ester **11c (**0.44 g, 50%). Compound **11c** showed identical spectroscopic features as that previously obtained.

4,4-Diphenyl-3-butenoic acid (12): yield 32%; mp 116−117 °C (lit.[30] mp 115−116 °C); ^{1}H NMR δ 3.20 (d, 2 H, J = 7.4 Hz), 6.25 (t, 1 H, J = 7.4 Hz), 7.15−7.42 (m, 11 H); ^{13}C NMR δ 35.1, 119.4, 127.3, 127.4, 128.1, 128.3, 129.6, 139.0, 141.7, 145.2, 178.3.

Conversion of 4,4-Diphenyl-3-butenoic Acid 12 to γ,γ-Diphenyl-γ-butyrolactone 13. 4,4-Diphenyl-3-butenoic acid (**12**) (0.13 g, 0.5 mmol) was dissolved in concd sulfuric acid (5 mL) at room temperature, and the solution was kept for 0.5 h. The mixture was then poured into ice−water (*ca.* 50 mL), extracted with ether (50 mL), and washed with saturated Na_2CO_3 solution (50 mL). Evaporation of the solvent gave the pure product **13** (0.12 g): yield 92%; mp 88−89 °C (lit.[30] mp 87−90 °C); ^{1}H NMR δ 2.54 (t, 2 H, J = 7.7 Hz), 2.88 (t, 2 H, J = 7.7 Hz), 7.21−7.51 (m, 10 H); ^{13}C NMR δ 28.9, 35.5, 89.6, 125.3, 127.8, 128.5, 142.9, 175.9.

Conversion of Ethyl 4,4-Diphenyl-3-butenoate 11c to γ,γ-Diphenyl-γ-butyrolactone (13). Ester **11c** (0.27 g, 1 mmol) was heated under reflux in a mixture of water (10 mL) and acetic acid (10 mL) for 10 h. After cooling, concd sulfuric acid (10 mL) was added and the solution stirred for 24 h. Water (50 mL) was then added, and the whole mixture was extracted with diethyl ether (2 × 100 mL) and washed with saturated Na_2CO_3 solution (2 × 100 mL). Evaporation of the solvent gave the expected γ,γ-diphenyl-γ-butyrolactone **(13)** **(**0.22 g, 92%). Compound **13** showed spectroscopic features identical to those previously obtained.

General Procedure for the Preparation of Dienes 16 and 17. To a solution of 1-(benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxy-(*E*)-prop-1-ene (**3**) (2.02 g, 5 mmol) in THF (50 mL) at −78 °C was added BuLi (1.6 M, 3.2 mL). After the mixture was stirred at this temperature for 5 min, the appropriate electrophile (MeI or EtI, 5 mmol) was added and the solution warmed to room temperature and kept for 1 h. The solution was cooled to −78 °C, BuLi (1.6 M, 3.2 mL) was added, and after 5 min the appropriate electrophile (cyclohexanone or benzaldehyde, 5 mmol) was added and the solution gradually warmed to room temperature and kept for 1 h. Water (50 mL) was then added, and the mixture was extracted with diethyl ether (2 × 100 mL) and dried over anhydrous

(33) Jacobson, R. M.; Lahm, G. P.; Clader, J. W. *J. Org. Chem.* **1980**, *45*, 395.

$MgSO_4$. Evaporation of the solvent gave a residue that was chromatographed on silica gel (hexane/ethyl acetate, 10:1).

1-(Benzotriazol-1-yl)-1-ethoxy-4,4-cyclohexyl-3-methylbuta-1,3-diene (16) was obtained as a colorless oil: yield 65%; ^{1}H NMR δ 1.31 (t, 3 H, J = 7.2 Hz), 1.47−1.67 (m, 6 H), 2.07 (s, 3 H), 2.20−2.38 (m, 4 H), 3.75 (q, 2 H, J = 7.2 Hz), 6.20 (s, 1 H), 7.39 (t, 1 H, J = 7.7 Hz), 7.52 (t, 1 H, J = 8.0 Hz), 7.75 (d, 1 H, J = 8.2 Hz), 8.07 (d, 1 H, J = 8.2 Hz); ^{13}C NMR δ 14.7, 26.5, 27.7, 30.5, 31.5, 66.8, 109.1, 111.0, 119.8, 124.1, 128.0, 132.2, 141.0, 141.9, 145.5. Anal. Calcd for $C_{18}H_{23}N_3O$: C, 72.70; H, 7.80; N, 14.13. Found: C, 72.35; H, 8.02; N, 13.99.

1-(Benzotriazol-1-yl)-1-ethoxy-3-ethyl-4-phenylbut-1,3-diene (17) was obtained as a colorless oil: yield 51% (a mixture of *E,E*- and *Z,E*-isomers, ratio *ca.* 2:1 from ^{1}H NMR); ^{1}H NMR (peaks for the minor isomer are given in square brackets) δ 1.25−1.38 (m, 6 H), 2.62−2.78 (m, 2 H), 3.68−3.82 (m, 2 H), 6.20 (s, 1 H) [5.92 (s, 1 H)], 6.55 (s, 1 H) [6.85 (s, 1 H)], 7.13−7.48 (m, 6 H), 7.69 (d, 1 H, J = 8.3 Hz) [7.78 (d, 1 H, J = 8.2 Hz)], 8.09 (t, 1 H, J = 9.4 Hz); ^{13}C NMR (all peaks are listed, due to the difficulty of the assignment) δ 13.9, 14.1, 14.6, 23.2, 29.3, 66.8, 106.6, 110.8, 110.9, 111.0, 111.6, 119.9, 124.3, 124.4, 126.6, 128.0, 128.1, 128.2, 128.3, 128.6, 129.0, 129.8, 131.3, 132.3, 136.7, 137.4, 137.5, 137.8, 142.2, 143.4, 145.5, 145.6. Anal. Calcd for $C_{20}H_{21}N_3O$: C, 75.21; H, 6.63; N, 13.16. Found: C, 75.56; H, 6.98; N, 13.46.

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