A Novel Heterocycle-Stabilized Allylic Anion Route to Cyclopropanes, 1-Ethoxy-1-vinylethylene Oxides, 1-Hydroxyalkyl 2-Methoxyethyl Ketones, 1-Hydroxyalkyl Vinyl Ketones, β-Ethoxy-β-vinylalkyl Alcohols, γ-Lactones, and β,γ-Unsaturated Carboxylic Acids

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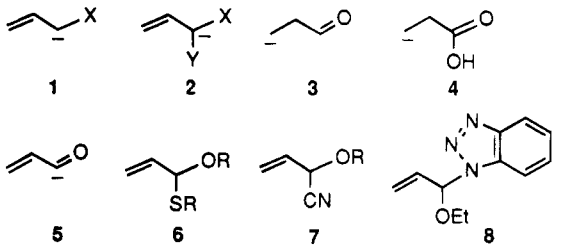
Treatment of *N*-(α-ethoxyallyl)benzotriazole (**8**) with butyllithium followed by α,β-unsaturated esters at −78 °C formed the 1,4-adducts **11** which underwent internal displacement of the benzotriazolyl group at 20 °C to give cyclopropanecarboxylic esters **14** and **15**. In the presence of $ZnBr_2$, addition of anion **13** to cyclic and methyl ketones gave 1-ethoxy-1-vinylethylene oxides **25** in good yields. Epoxides **25** were subsequently converted to 1-hydroxyalkyl 2-methoxyethyl ketones **24**, 1-hydroxyalkyl vinyl ketones **26**, and β-ethoxy-β-vinylalkyl alcohols **27**. Treatment of anion **13** with aromatic ketones or sterically hindered aliphatic ketones produced γ-alkylated adducts **31** which were hydrolyzed to β,γ-unsaturated carboxylic acids **32** (R^1, R^2 = aromatic) or γ-lactones **33** (R^1, R^2 = aliphatic).

Functionalized allyl anions are of particular importance in synthetic organic chemistry as they are frequently used (i) to generate multifunctional compounds by further elaboration of the C=C bond and (ii) to achieve stereocontrol. The synthetic utility and mechanistic features of many allylic systems have been investigated.[1a-e] The most common heteroatom-stabilized allyl anion systems **1** and **2**, available by deprotonation of the corresponding allyl derivatives, have shown synthetic versatility in reactions with electrophiles at either the α- or γ-position. Following removal of the heteroatoms by hydrolysis, anions **1** and **2** represent the homoenolate anion synthon equivalents **3** and **4** and the reversed polarity equivalent **5**. As discussed in the preceding paper,[2] the synthetic utility of allyl anions **1** and **2** usually depends on (i) the degree of regioselectivity in their reactions with electrophiles, (ii) the availability of their precursors, and (iii) the ease of removal of the heteroatoms at the end of the reaction sequence. Frequently, this removal is achieved only with considerable difficulty from their alkylation adducts; for example, the conversion of γ-alkylation adducts of α-alkylthioallyl sulfides (**2**, X = Y = SR)[3a,b] and α-alkylation adducts of α-alkoxyallyl sulfides **6**[4a,b] to the corresponding carbonyl compounds requires complexation with a metal cation (usually a mercury salt) or oxidation of one sulfur atom to render it more electrophilic. Removal of the cyano group from the α-alkylated protected cyanohydrins **7** by hydrolysis evolves HCN.[5] Direct displacement of the cyano and alkylthio groups from α-alkylated intermediates of **6** and **7** by a carbanion has not been achieved. We now extend our investigations[2] to cases where one heteroatom of **2** is in the form of a benzotriazolyl group and report further examples of either α-alkylation or γ-alkylation of allyl anion **13** (readily generated from **8** with butyllithium or LDA) with high regioselectivity depending on the electrophile. The α-alkylation adducts of allyl anion **13** can undergo either (i) hydrolysis under mild conditions to form carbonyl compounds or (ii) intramolecular nucleophilic substitution to form cyclic compounds; the latter represents new reactions of heterocycle-stabilized allyl anions.



1 2 3 4 5 6 7 8

In the preceding paper,[2] we described the use of *N*-(α-ethoxyallyl)benzotriazole (**8**) in novel syntheses of vinyl ketones and functionalized vinyl ketones based on the lithiation of **8** to form allyl anion **13**, followed by α-alkylation of **13** and facile hydrolysis of the resulting α-alkylated adducts. Our preliminary communication[6] disclosed the γ-alkylation of **13** with 2,4-dimethylpentanone and internal substitution reactions of the α-alkylation adducts derived from α,β-unsaturated esters and cyclohexanone. We now provide details of the previously communicated work for the syntheses of cyclopropanecarboxylic esters **14** and **15**, 1-hydroxyalkyl 2-methoxyethyl ketones **24**, 1-ethoxy-1-vinylethylene oxides **25**, 1-hydroxyalkyl vinyl ketones **26**, and γ-lactones **33** and describe new reactions of **13** with ketones for the synthesis of β-ethoxy-β-

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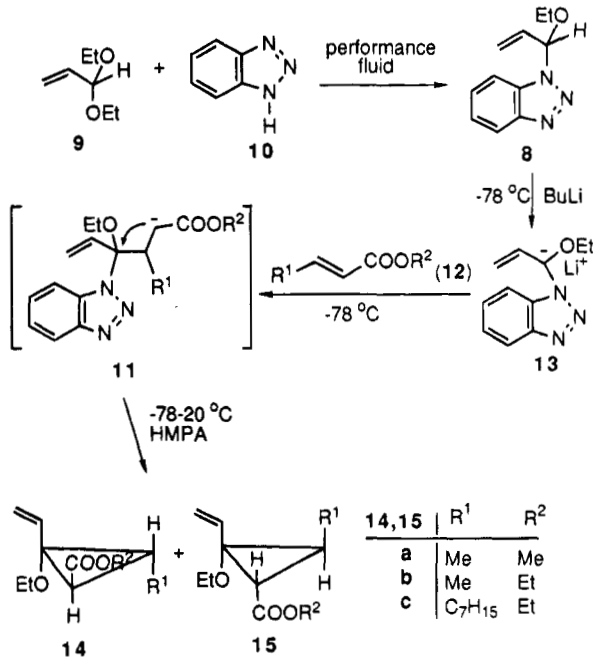
Scheme 1

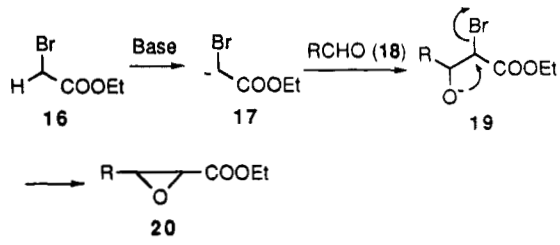


vinylalkyl alcohols **27** and β,γ-unsaturated carboxylic acids **32**.

Results and Discussion

Reactions of Allyl Anion 13 with α,β-Unsaturated Esters: Preparation of Cyclopropanecarboxylic Esters. We reported in the preceding paper[2] that treatment of anion **13** with α,β-unsaturated esters at −78 °C followed by immediate quenching with water at the same temperature gave Michael addition intermediates which were hydrolyzed with $H_2C_2O_4$−SiO_2−H_2O to give β-propenoylcarboxylic esters in 60−70% yield. We now show that when the same reactions of **13** with α,β-unsaturated esters are carried out at −78 °C, but the reaction mixtures are allowed to warm to 20 °C before quenching, cyclopropanes are obtained (Scheme 1). Thus, treatment of **8** with butyllithium at −78 °C in an oxygen free atmosphere gave a deep green solution, which was then reacted *in situ* with an α,β-unsaturated ester at −78 °C for 4 h. Subsequent treatment with HMPA (still at −78 °C) for 2 h was followed by allowing the reaction mixture to warm to 20 °C over a 24 h period. The solution was finally quenched with H_2O at 20 °C to give mixtures of **14** and **15** in *ca.* equal amounts in 51−58% total yield. In the absence of HMPA, cyclopropanecarboxylic esters **14** and **15** were still obtained, but in lower yields. Compounds **14** and **15** were readily isolated as mixtures by distillation under vacuum. Cyclopropane isomer pairs **14** and **15** are separated on TLC, with **15** having the higher polarity. Each of the three mixtures was separated into the two individual isomers (**14a/15a**; **14b/15b**; **14c/15c**) by column chromatography on silica gel (hexane/ether, 10:1). The structures of the individual compounds were supported by NMR spectral data and elemental analyses. Individual isomers were identified by NOE and 2D NMR spectral data. For example, in the case of **15a**, selective irradiation of (i) the methyl protons at 1.05 ppm (doublet) on the three-membered ring or (ii) the cyclopropane proton at 1.70 ppm (doublet) each resulted in significant enhancement of the vinyl proton signal (doublet of doublets) at 5.68 ppm. The coupling

Scheme 2



constant between the two cyclopropane protons of 6.8 Hz supports a *trans* relationship. The cyclopropane proton signals of **14a−c** are overlapped at around 1.8 ppm, while the corresponding quintet or multiplet signals of **15a−c** are shifted to a lower field (*ca.* 2.15 ppm) and the doublet signals to a higher field (*ca.* 1.70 ppm). Although the ester group is more electron withdrawing than the methyl group, the quintet or multiplet signal of the cyclopropane proton geminal to the methyl group occurs at almost the same field in **14a,b** and at a lower field (*ca.* 2.15 ppm) in **15a,b** than the doublet signal (*ca.* 1.7 ppm) of the proton geminal to the ester group. Presumably, this is attributable to the field effects of the ester and vinyl groups.

The reaction mechanism involves addition of carbanion **13** to the double bond of the α,β-unsaturated esters to give intermediates **11** which undergo an internal (probably S_N1 type) displacement to generate the three-membered ring. The isolation of propenoyl carboxylic esters, generated by hydrolysis of **11** with $H_2C_2O_4$−SiO_2−H_2O as described in the preceding paper,[2] indicates that the Michael addition of **13** to **12** giving **11** is accomplished at −78 °C, while the internal displacement **11** → **14**, **15** proceeds at a higher temperature. An alternative mechanism *via* an α-ethoxyalkyl carbene intermediate, which might be formed by elimination of the benzotriazolyl group from **13**, is considered less likely because attempted cyclopropanation with cyclohexene was unsuccessful, although reaction of the putative singlet carbene with the C=C bond of an α,β-unsaturated ester should also give the two isomers **14** and **15**.

The present addition−substitution to form cyclopropanes is closely related to the Darzens glycidic ester condensation (Scheme 2) which involves generation of a carbanion from an activated halide (**17**) and subsequent addition to an aldehyde or ketone to generate the diastereomeric aldolates **19**. An internal S_N2 displacement affords α,β-epoxy ester **20**.[7] This condensation requires the reactants (typically α-halo esters) to possess both a carbanion-stabilizing group (often an ester) and a leaving group (usually a halide). Substituents incapable of stabilizing carbanions, such as alkoxy groups, cannot be incorporated into the resulting epoxides or cyclopropanes. The present method for cyclopropanation is based on a single substituent, benzotriazolyl, serving both as the activating group and as the leaving group.

The OR group of **11** should significantly assist scission of the C−benzotriazolyl bond in the intramolecular substitution. This is consistent with the many known intermolecular transformations of this type which all require preliminary ionization assisted by one or more electron donor substituents α to the benzotriazolyl group (S_N1 type mechanism).[8] *N*-(α-Alkoxyalkyl)benzotriazoles

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Table 1. Preparation of Compounds 14, 15, 23–27, and 31–33

compd	R^1	R^2	R	yield (%)	formula	CHN analysis, found (required) C	H	N
14a, 15a	Me	Me		58	$C_{10}H_{16}O_3$	64.90 (64.99)	8.90 (8.75)	
14b, 15b	Me	Et		51	$C_{11}H_{18}O_3$	66.44 (66.61)	9.27 (9.15)	
14c, 15c	C_7H_{15}	Et		54	$C_{17}H_{30}O_3$	71.93 (72.30)	10.84 (10.71)	
23a	$-(CH_2)_5-$			75	$C_{17}H_{23}N_3O_2$	67.82 (67.75)	7.77 (7.69)	14.00 (13.94)
23b	Ph	Me		55	$C_{19}H_{20}N_3O_2$	70.63 (70.57)	6.63 (6.55)	13.08 (12.99)
24a	$-(CH_2)_5-$			62	$C_{10}H_{18}O_3$	64.72 (64.47)	9.91 (9.75)	
24b	*n*-Bu	Me		60	$C_{10}H_{20}O_3$	63.54 (63.80)	10.78 (10.71)	
24c	$PhCH_2CH_2$	Me		52	$C_{14}H_{20}O_3$	71.03 (71.16)	8.49 (8.53)	
24d	Ph	Me		48	$C_{12}H_{16}O_3$	68.87 (69.19)	7.68 (7.75)	
25a	$-(CH_2)_5-$			72	$C_{11}H_{18}O_2$	72.16 (72.48)	10.29 (10.66)	
25b	*n*-Bu	Me		65	$C_{11}H_{20}O_2$	71.32 (71.68)	11.13 (10.95)	
26a	$-(CH_2)_5-$			68	$C_9H_{14}O_2$	69.91 (70.10)	9.24 (9.15)	
26b	Ph	Me		48	$C_{11}H_{12}O_2$	74.83 (74.98)	7.01 (6.86)	
27a	$-(CH_2)_4-$		Me	71	$C_{11}H_{20}O_2$	71.38 (71.70)	11.13 (10.94)	
27b	$-(CH_2)_5-$		Ph	50	$C_{17}H_{24}O_2$	78.20 (78.42)	9.37 (9.29)	
27c	$-(CH_2)_5-$		*p*-MeC_6H_4	53	$C_{18}H_{26}O_2$	78.55 (78.79)	9.74 (9.55)	
27d	*n*-Bu	Me	Me	65	$C_{12}H_{24}O_2$	71.72 (71.75)	12.21 (12.08)	
31a	*c*-C_6H_{11}	*c*-C_6H_{11}		81	$C_{24}H_{35}N_3O_2$	72.85 (72.51)	8.95 (8.87)	10.27 (10.57)
31b	Ph	Ph		78	$C_{24}H_{23}N_3O_2$	74.87 (74.78)	6.06 (6.01)	10.94 (10.90)
31c	biphenyl-2,2′-diyl			76	$C_{24}H_{21}N_3O_2$	75.33 (75.18)	5.56 (5.52)	11.01 (10.96)
32a	Ph	Ph		67	$C_{16}H_{14}O_2$	80.57 (80.65)	5.92 (5.92)	
32b	biphenyl-2,2′-diyl			74	$C_{16}H_{12}O_2$	81.06 (81.34)	5.08 (5.12)	
33a	*c*-C_6H_{11}	*c*-C_6H_{11}		75	$C_{16}H_{26}O_2$	76.72 (76.75)	10.64 (10.47)	
33b	*i*-Pr	*i*-Pr		76	$C_{10}H_{18}O_2$	70.20 (70.53)	10.91 (10.66)	

require heating in toluene to achieve ionization for successful intermolecular Grignard reactions.[9] The unexpectedly facile intramolecular nucleophilic displacement of the benzotriazolyl group from **11** (at *ca.* 20 °C) in the present case may be explained by the steric relief achieved as a result of cyclopropanation. This explanation suggests that the size of the R^1 group of **11** should affect the likelihood of the internal S_N1 reaction occurring, as was indeed supported by our unsuccessful attempts to generate the three-membered ring from ethyl acrylate (R^1 = H).

The mechanism shown in Scheme 1 indicates that four cyclopropane isomers are possible. However, only the two (**14** and **15**) that were subsequently isolated were observed by NMR in the condensation mixture; in both cases, the two substituents originating from the *trans* α,β-unsaturated esters are *trans* to each other. This result can be rationalized by two considerations: (i) rotations of the newly formed σ-bond in **11** and of the single bond originating from the C=C fragment of the α,β-unsaturated ester are restricted at low temperatures because Li^+ is chelated to both the newly formed carbanion and the ethoxy and/or benzotriazolyl group in the highly crowded structure, and (ii) cyclopropane esters in which the bulky R^1 and ester groups are as far from each other as possible are more stable. We believe that the first consideration is the major reason why the other two possible isomers originating from *trans* esters, which would contain three substituents on the same side of the three-membered ring, are not formed. When $ZnBr_2$ was stirred with **11** at −78 °C for 1 h then at 20 °C for 24 h, the resulting mixtures showed complex NMR spectra probably due to the presence of all four isomers. Coordination of **11** with $ZnBr_2$ may destroy the chelated structure with Li^+ or alternatively, $ZnBr_2$ may help convert the S_N2-like internal displacement of the benzotriazolyl group (*via* an intimate ion pair intermediate) to an S_N1 reaction (*via* a solvent separated ion pair) with free rotation of the related σ-bonds.[10]

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Synthetic approaches to cyclopropane derivatives have received much attention due to their importance in theoretical, practical, and bioorganic chemistry, as evidenced by the extensive literature on this subject.[11a,b] The most common route to this class of compounds involves addition of a carbene synthon to a double bond, e.g., diazo compounds to olefins.[12] Although the efficiency of this method has been improved by the addition of transition metal catalysts,[13a,b] the procedure suffers from the explosive nature of diazo compounds.[12] Numerous electrophilic transition metal carbene complexes have recently been developed for the transfer of carbene ligands to alkenes to form cyclopropanes.[14] However, successful transfers are limited to nucleophilic alkenes, and transfer yields are often reduced by rapid intramolecular rearrangements or other modes of decomposition. The synthesis of vinyl-substituted cyclopropane esters by the carbene method is further complicated by problems of regioselectivity if dienes are used as starting materials. The present method for the preparation of cyclopropanecarboxylic esters combines readily available starting materials, mild conditions, and simple procedures.

Reactions of α-Position of Allyl Anion 13 with Ketones: Preparation of 1-Hydroxyalkyl 2-Methoxyethyl Ketones 24, 1-Ethoxy-1-vinylethylene Oxides 25, 1-Hydroxyalkyl Vinyl Ketones 26, and β-Ethoxy-β-vinylalkyl Alcohols 27. As already briefly described in our preliminary paper,[6] reaction of anion **13** with cyclic ketones or alkyl methyl ketones under the conditions of Scheme 1 gives adducts **23** in 55–75% yield; full details of characterization by NMR and elemental analyses are now provided (see Table 1). We now show that adducts **23** can be converted into 1-hydroxyalkyl vinyl ketones **26** in quantitative yield by treatment with $H_2C_2O_4-SiO_2-H_2O$ under the same experimental conditions as previously given for similar hydrolyses (Scheme

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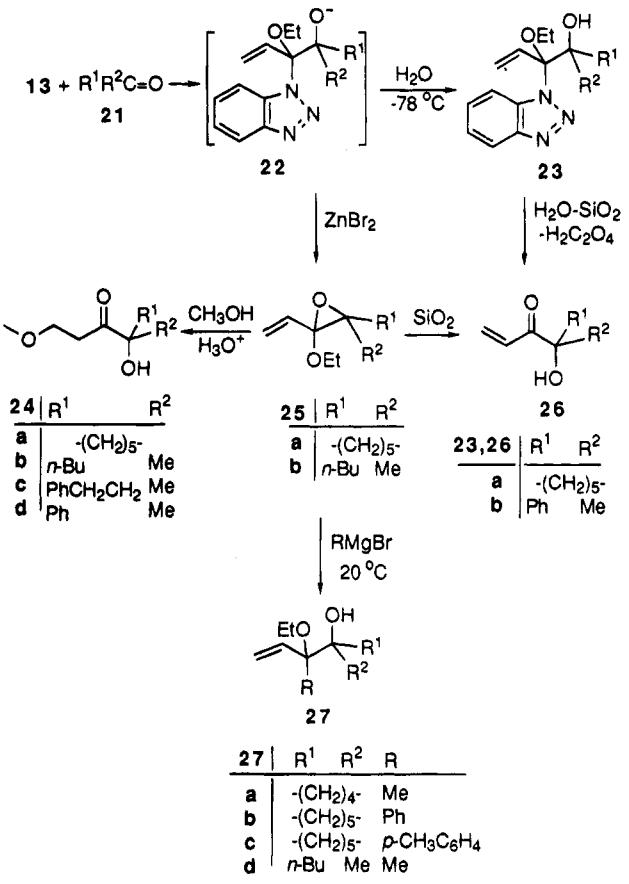
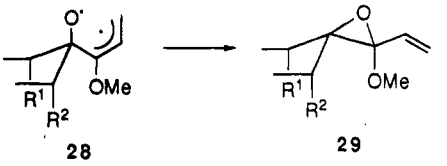
Scheme 3



3). No Darzens-type reaction to form epoxides **25** was observed under these conditions. Apparently, the newly generated oxygen anion **22** is not as nucleophilic as carbanion **11** and is unable to displace the benzotriazolyl group. Alternatively, the reason may be that the benzotriazolyl group is intrinsically not as good a leaving group as a halide, although the leaving ability of the benzotriazolyl group in **22** is enhanced by the steric relief gained from the conversion of crowded **22** to epoxides **25**. We have previously reported that ionization of *N*-(α-alkoxyalkyl)benzotriazoles by C-benzotriazolyl scission could be achieved by heating to temperatures above 100 °C.[9,15] However, in the present case, when **22** was refluxed in THF, reversion to the starting materials occurred.

Fortunately, we now find that cyclization of adducts **22** to epoxides **25** can be accomplished with the assistance of $ZnBr_2$. Thus, treatment of anion **13** with cyclic ketones or methyl ketones at −78 °C for 3 h and then for an additional 12 h at 20 °C followed by stirring with $ZnBr_2$ in THF for 5 h gave epoxides **25** which could be isolated (see below) in yields of 65−72%. The transformation **22** → **25** is related to the previously reported lithium tetrafluoroborate-assisted ionization of *N*-(α-aminoalkyl)-benzotriazoles[16] in which lithium tetrafluoroborate acts both as a salt, increasing the ionizing power of the solvent, and as a Lewis acid source. In the present intramolecular substitution at 20 °C by an oxygen anion, which is less nucleophilic than a carbanion, we believe that the leaving ability of the benzotriazolyl group in **22** is enhanced by the presence of $ZnBr_2$ mainly due to coordination of Zn^{2+} at the 3-position of the benzotriazolyl ring.

Scheme 4



The first alkoxy-substituted vinyl epoxides to be reported were of type **29** and were prepared by Magnus *et al.* by reaction of allene oxides with dicyclic ketones *via* a single electron transfer mechanism (Scheme 4).[17] The formation of vinyl epoxides **29** from **28** requires R^1 and R^2 to be conformationally rigid in the axial position; other ketones gave only dihydrofuran derivatives. The present method appears to be much more general and converts simple cyclic and methyl ketones to 1-ethoxy-1-vinylethylene oxides **25** probably *via* an ionic mechanism. In contrast to the work of Magnus, we have not found that intermediates **22** generate detectable quantities of dihydrofurans which would be formed by internal S_N2' attack of the oxygen anion at the vinyl group with simultaneous rearrangement of the C=C bond. This result can be rationalized by Baldwin's rules: formation of the five-membered dihydrofuran ring from **22** would require an unfavorable *endo-trig* process.[18a,b]

Vinyl epoxides **25** are reasonably stable under neutral and basic conditions, although they are partially hydrolyzed during workup and completely hydrolyzed on column chromatography, to give the same 1-hydroxyalkyl vinyl ketones **26** as were obtained from **23** following the $H_2C_2O_4$−H_2O−SiO_2 procedure described above. Epoxides **25a,b** were isolated for characterization purposes by distillation and were fully characterized by NMR and elemental analyses. The two characteristic ^{13}C signals of the epoxide ring appeared at *ca.* 68 and 89 ppm. Epoxide **25b** showed two sets of resonances in both the ^1H and ^{13}C NMR spectra, indicating a mixture of two stereoisomers. However, derivatives **25** were advantageously used without purification for the preparation of **24a−d** and **26a,b**; for the preparation of **27a−d**, derivatives **25** were used *in situ*.

No reactions of 1-ethoxy-1-vinylethylene oxides **25** have previously been reported. We have found that the synthetic utility of **25** can be realized by elaboration of either the epoxide ring, the C=C bond, or both functionalities. Epoxides **25** were converted to 1-hydroxyalkyl 2-methoxyethyl ketones **24** at 70 °C by acidic hydrolysis in CH_3OH−H_2O−HCl *via* an S_N2' mechanism. In the absence of acid, vinyl epoxides **25** were, as mentioned above, converted by wet silica gel into 1-hydroxyalkyl vinyl ketones **26** in good yield. This could involve attack of a water molecule at either of the epoxide carbons; however, we believe that such attack leading to cleavage of the epoxide ring occurs at the epoxide carbon originating from anion **13**. This is supported by the fact that treatment of **25** *in situ* with Grignard reagents at 20 °C gave β-ethoxy β-vinyl alcohols **27** in 50−71% overall yields. In these transformations of **22** to **24** and **27**, the

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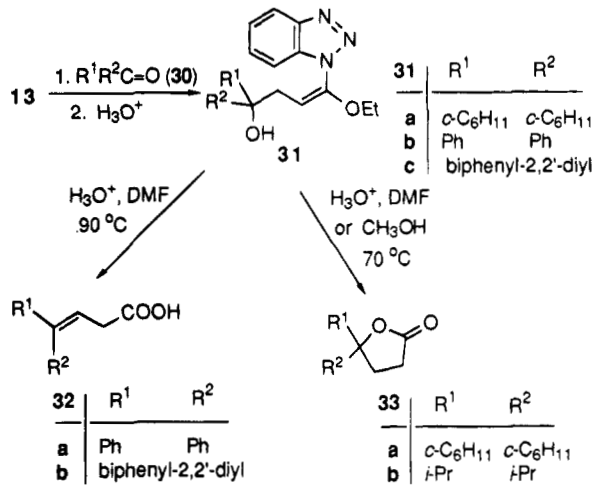
presence of $ZnBr_2$ is essential and compounds **25** are the key intermediates as demonstrated by the fact that the benzotriazolyl group of **22** cannot be directly replaced by Grignard reagents at 20 °C. Moreover, under forcing conditions (refluxing THF), attempts to carry out Grignard reactions of **22** in the absence of $ZnBr_2$ led to reversion of **22** back to the starting ketones.

From a synthetic point of view, allyl anion **13** thus also provides convenient approaches to highly functionalized compounds of types **24**, **26**, and **27**. The overall yields and analysis data for these compounds are listed in Table 1: all structures were consistent with the NMR spectra. Derivatives of these classes are important precursors or building blocks for natural product syntheses.[19a-d] Apparently, allyl anion **13** is well suited to the preparation of hydroxy ketones with the additional β'-methoxy (**24**) and vinyl (**26**) functionalities. γ-Unsaturated α,β-diol derivatives were previously synthesized by the addition of γ-alkoxy allylic organometallics to carbonyl compounds.[19b,c,20a-c] The present method affords what appears to be the first preparation of vinyl 1,2-diol derivatives in which both carbons adjacent to oxygen are tertiary.

Reactions of γ-Position of Allyl Anion 13 with Ketones: Preparation of β,γ-Unsaturated Carboxylic Acids 32 and γ-Lactones 33. Treatment of anion **13** with 3-heptanone under the same conditions resulted in recovery of the starting ketone and *N*-(α-ethoxyallyl)-benzotriazole (**8**), presumably because intermediate **22** was destabilized by the two bulky R^1 and R^2 groups. As a result, 3-heptanone was deprotonated by anion **13** to form an unreactive enolate. We believe that competition between enolization of the ketone and alkylation of anion **13** occurs as long as the ketone contains an acidic α-proton; successful alkylation requires either an uncrowded enolizable ketone (such as a cyclic or methyl ketone) or a nonenolizable ketone. On the basis of this consideration, aromatic ketones were reacted with anion **13** to give the γ-adducts **31b,c** exclusively in good yield, by γ-attack of anion **13** at the ketonic carbonyl. The sterically hindered α-terminus of anion **13** evidently cannot attack crowded ketones to form stable α-alkylation adducts similar to **22**. A most surprising result was observed in the reaction of anion **13** with dicyclohexyl ketone, which is both crowded and enolizable. Adduct **31a** was formed exclusively in good yield; no starting ketone or α-alkylation product was observed by NMR. We assume that the enolate form of dicyclohexyl ketone is less favorable (less acidic) because of the increased crowding caused by the two bulky groups. Therefore, the ketone form exists as a very dominant species and is susceptible to nucleophilic attack by anion **13**. This rationalization is supported by the work of Stalick *et al.*[21] which shows that addition product yields of lithium alkynides to 2,4-dimethyl-3-pentanone are significantly higher than those to acetone and 3-pentanone.

Adducts **31** are readily identified in the ^1H NMR spectra by the signals of the CH and CH_2 groups originating from the vinyl fragment of **8**, which occur as triplets at *ca.* 5.6 ppm and doublets at fields of 2.60 to 3.40 ppm. The absence of vinyl signals in the ^1H spectrum demonstrates the high regioselectivity in the formation of the γ-alkylation adducts. Compound **31a** was isolated as an oil, but was found to crystallize after absorption of a water molecule from air. The presence of the H_2O incorporated into this crystal was confirmed by elemental analysis. Adducts **31** can be visualized as protected carboxylic acids. Thus, treatment of the unpurified adducts **31** obtained from dicyclohexyl ketone and 2,4-dimethylpentanone with DMF–HCl–H_2O or CH_3OH–HCl–H_2O gave γ-lactones **33a,b** in good yield. Treatment of **31b,c** derived from aromatic ketones in DMF–HCl–H_2O at *ca.* 90 °C gave β,γ-unsaturated carboxylic acids **32a,b** in quantitative yield (Scheme 5). Both γ-lactones and β,γ-unsaturated carboxylic acids have displayed diverse and significant biological activity, and not unexpectedly, many methods have been reported for their preparation.[22a-j] Our method for the preparation of γ,γ-diaryl-substituted β,γ-unsaturated carboxylic acids and γ-lactones with bulky γ-substituents are based on readily available starting materials and mild conditions. The structures of compounds **31**, **32**, and **33** were elucidated by NMR and the structures of all new compounds confirmed by elemental analyses. Table 1 lists the overall yields and analytical data of these products.

Scheme 5



Conclusion

In summary, further examples of the versatile synthetic utility of our new heterocycle-stabilized propenoyl or homoenolate anion **13** are illustrated by its behavior as a synthon equivalent of **34** for the preparation of cyclopropanecarboxylic esters, 1-ethoxy-1-vinylethylene oxides, and β-ethoxy-β-vinylalkyl alcohols, of **35** for the preparation of 1-hydroxyalkyl vinyl ketones, of **36** for the preparation of 1-hydroxyalkyl 2-methoxyethyl ketones,

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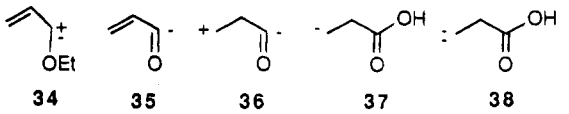
of **37** for the preparation of lactones, and of **38** for the preparation of β,γ-unsaturated carboxylic acids.



34 **35** **36** **37** **38**

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$. THF was freshly distilled from sodium–benzophenone ketyl immediately before use. Lithiations were carried out in an argon atmosphere created by purging air with a vacuum pump followed by filling with argon several times. Compound **8** was prepared as previously described.[2]

Preparation of Cyclopropanecarboxylic Esters 14 and 15. Representative Procedure for Methyl 2-*trans*-Ethoxy-3-*trans*-methyl-2-*cis*-vinylcyclopropane-1-carboxylate (14a) and Methyl 2-*cis*-Ethoxy-3-*trans*-methyl-2-*trans*-vinylcyclopropane-1-carboxylate (15a). *N*-(α-Ethoxyallyl)-benzotriazole (**8**, 2.5 g, 12.0 mmol) was stirred with butyllithium (6.5 mL, 2 M, 13.0 mmol) in THF (60 mL) at −78 °C for 2 h to give a deep green solution to which was added an α,β-unsaturated ester (methyl crotonate for **14a** and **15a**, 1.20 g, 12.3 mmol). The mixture was stirred for 4 h at −78 °C, followed by stirring with HMPA (4.5 g, 25 mmol) at the same temperature for 2 h. The mixture was then allowed to warm to 20 °C, and stirring was continued for 24 h. The mixture was quenched with water (30 mL) and extracted with ether (2 × 40 mL). The extracts were washed with NaOH (2 N, 2 × 30 mL) and dried ($MgSO_4$), and the solvent was removed to give an oily residue which was distilled under reduced pressure to give a 1:1 mixture of **14a** and **15a** (1.35 g, 58% total yield, bp 55–59 °C/0.3 mmHg). Cyclopropanes **14a** and **15a** were separated by column chromatography (silica gel, hexane/ether, 10:1). NMR data of **14a**: ^1H NMR δ 1.21–1.32 (m, 6 H, the overlapped signals of two CH_3), 1.73–1.84 (m, 2 H, the overlapped signals of two cyclopropane protons), 3.48–3.54 (m, 1 H), 3.67 (s, 3 H), 3.67–3.78 (m, 1 H), 5.21 (dd, J = 11.0, 1.6 Hz, 1 H), 5.35 (dd, J = 17.5, 1.6 Hz, 1 H), 6.82 (dd, J = 17.5, 11.0 Hz, 1 H); ^{13}C NMR δ 11.2, 15.2, 28.9, 35.0, 51.7, 64.1, 71.1, 114.3, 133.6, 171.4. NMR data of **15a**: ^1H NMR δ 1.05 (d, J = 6.8 Hz, 3 H), 1.16 (t, J = 6.8 Hz, 3 H), 1.70 (d, J = 6.8 Hz, 1 H), 2.13 (quintet, J = 6.8 Hz, 1 H), 3.17–3.28 (m, 1 H), 3.59–3.68 (m, 1 H), 3.71 (s, 3 H), 5.32 (dd, J = 10.5, 1.6 Hz, 1 H), 5.38 (dd, J = 17.0, 1.6 Hz, 1 H), 5.68 (dd, J = 17.0, 10.5 Hz, 1 H); ^{13}C NMR δ 12.7, 15.1, 27.3, 33.6, 51.7, 63.6, 71.8, 116.8, 133.9, 170.2.

Ethyl 2-*trans*-ethoxy-3-*trans*-methyl-2-*cis*-vinylcyclopropane-1-carboxylate (14b) and ethyl 2-*cis*-ethoxy-3-*trans*-methyl-2-*trans*-vinylcyclopropane-1-carboxylate (15b) were prepared as a 1:1 mixture from ethyl crotonate in 51% yield (bp 61–67 °C/0.5 mmHg) and were separated by column chromatography (silica gel, hexane/ether, 10:1). NMR data of **14b**: ^1H NMR δ 1.13–1.23 (m, 9 H, the overlapped signals of three CH_3), 1.62–1.73 (m, 2 H, the overlapped signals of two cyclopropane protons), 3.37–3.56 (m, 1 H), 3.57–3.68 (m, 1 H), 3.98–4.12 (m, 2 H), 5.12 (dd, J = 10.5, 1.5 Hz, 1 H), 5.25 (dd, J = 17.0, 1.5 Hz, 1 H), 5.75 (dd, J = 17.0, 10.5 Hz, 1 H); ^{13}C NMR δ 11.1, 14.2, 15.2, 28.7, 35.2, 60.4, 64.1, 71.0, 114.2, 133.7, 170.9. NMR data of **15b**: ^1H NMR δ 1.05 (d, J = 6.5 Hz, 3 H), 1.15 (t, J = 7.0 Hz, 3 H), 1.28 (t, J = 7.0 Hz, 3 H), 1.69 (d, J = 6.5 Hz, 1 H), 2.12 (quintet, J = 6.5 Hz, 1 H), 3.16–3.28 (m, 1 H), 3.57–3.68 (m, 1 H), 4.16 (q, J = 7.0 Hz, 2 H), 5.33 (d, J = 10.0 Hz, 1 H), 5.38 (d, J = 17.0 Hz, 1 H), 5.68 (dd, J = 17.0, 10.0 Hz, 1 H); ^{13}C NMR δ 12.9, 14.4, 15.4, 27.5, 34.1, 60.7, 63.8, 72.0, 116.9, 134.3, 169.9.

Ethyl 2-*trans*-ethoxy-3-*trans*-heptyl-2-*cis*-vinylcyclopropane-1-carboxylate (14c) and ethyl 2-*cis*-ethoxy-3-*trans*-heptyl-2-*trans*-vinylcyclopropane-1-carboxylate (15c) were prepared as a 1:1 mixture from ethyl *trans*-2-decenoate in 54% yield (bp 87–91 °C/1 mmHg) and were separated by column chromatography (silica gel, hexane/ether, 10:1). NMR data of **14c**: ^1H NMR δ 0.85 (t, J = 6.7 Hz, 3 H), 1.13–1.35 (m, 16 H including two CH_3), 1.35–1.55 (m, 2 H), 1.60–1.75 (m, 1 H), 1.78 (d, J = 6.7 Hz, 1 H), 3.42–3.51 (m, 1 H), 3.68–3.78 (m, 1 H), 4.08–4.20 (m, 2 H), 5.20 (dd, J = 10.7, 1.6 Hz, 1 H), 5.32 (dd, J = 17.4, 1.6 Hz, 1 H), 5.86 (dd, J = 17.4, 10.7 Hz, 1 H); ^{13}C NMR δ 14.0, 14.2, 15.2, 22.6, 26.2, 29.0, 29.1, 29.2, 31.8, 34.3, 34.6, 60.4, 64.0, 71.1, 113.9, 133.9, 171.0. NMR data of **15c**: ^1H NMR δ 0.85 (t, J = 7.0 Hz, 3 H), 1.17 (t, J = 7.0 Hz, 3 H), 1.22–1.50 (m, 15 H including one CH_3), 1.72 (d, J = 6.7 Hz, 1 H), 2.05–2.13 (m, 1 H), 3.18–3.30 (m, 1 H), 3.57–3.68 (m, 1 H), 4.05–4.22 (m, 2 H), 5.32 (dd, J = 10.5, 1.5 Hz, 1 H), 5.37 (dd, J = 17.0, 1.5 Hz, 1 H), 5.68 (dd, J = 17.0, 10.5 Hz, 1 H); ^{13}C NMR δ 14.0, 14.2, 15.2, 22.6, 27.9, 28.7, 29.0, 29.1, 31.7, 33.1, 33.3, 60.5, 63.6, 71.6, 116.4, 134.2, 169.7.

Preparation of α-(Benzotriazol-1-yl)-α-ethoxyallyl Alcohols 23. Representative Procedure for 1-[1-(Benzotriazol-1-yl)-1-ethoxyprop-2-enyl]cyclohexanol (23a). *N*-(α-Ethoxyallyl)benzotriazole (**8**, 2.5 g, 12.5 mmol) in THF (80 mL) was stirred at −78 °C under argon with butyllithium (6.5 mL, 2 M, 13.0 mmol) for 10 min followed by stirring with a ketone (cyclohexanone for **23a**, 1.10 g, 11.0 mmol) at −78 °C for 3 h and then at 20 °C for 10 h. The brown solution was quenched with water (40 mL) and extracted with ether (2 × 40 mL). The organic layer was washed with H_2O (30 mL) and dried ($MgSO_4$) and the solvent removed to give a solid which was washed with hexane–ether, yield 75%: mp 135.5–136.5 °C; ^1H NMR δ 0.95–1.12 (m, 1 H), 1.27 (t, J = 7.0 Hz, 3 H), 1.30–1.85 (m, 9 H), 2.54 (s, 1 H, OH), 3.20–3.35 (m, 1 H), 3.57–3.70 (m, 1 H), 5.52 (d, J = 17.5 Hz, 1 H), 5.73 (d, J = 11.5 Hz, 1 H), 6.94 (dd, J = 17.5, 11.5 Hz, 1 H), 7.35–7.42 (m, 1 H), 7.45–7.52 (m, 1 H), 7.90 (d, J = 8.5 Hz, 1 H), 8.07 (d, J = 8.5 Hz, 1 H); ^{13}C NMR δ 14.8, 21.2, 25.5, 31.5, 31.9, 60.5, 78.5, 100.8, 114.5, 119.6, 120.3, 123.8, 127.3, 132.4, 134.0, 145.9.

3-(Benzotriazol-1-yl)-3-ethoxy-2-phenylpent-4-en-2-ol (23b) was prepared in 55% yield from acetophenone as a solid: mp 167.5–168.5 °C; ^1H NMR δ 1.30 (t, J = 7.0 Hz, 3 H), 1.68 (s, 3 H), 3.15–3.25 (m, 1 H), 3.48 (s, 1 H, OH), 3.62–3.72 (m, 1 H), 5.49 (d, J = 17.8 Hz, 1 H), 5.73 (d, J = 11.6 Hz, 1 H), 6.78 (dd, J = 17.8, 11.6 Hz, 1 H), 7.00–7.20 (m, 5 H), 7.25–7.35 (m, 2 H), 7.50 (d, J = 8.5 Hz, 1 H), 8.02 (d, J = 8.5 Hz, 1 H); ^{13}C NMR δ 14.7, 24.9, 60.9, 80.3, 100.1, 113.9, 119.5, 120.9, 123.5, 126.7, 127.2, 127.3, 127.4, 132.1, 134.2, 141.6, 145.6.

Preparation of 1-Hydroxyalkyl 2-Methoxyethyl Ketones 24. Representative Procedure for 1-Hydroxycyclohexyl 2-Methoxyethyl Ketone (24a). *N*-(α-Ethoxyallyl)-benzotriazole (**8**, 2.5 g, 12.5 mmol) in THF (80 mL) was stirred at −78 °C under argon with butyllithium (6.5 mL, 2 M, 13.0 mmol) for 10 min. The green solution was stirred with a ketone (cyclohexanone for **24a**, 1.10 g, 11.0 mmol) for 3 h at −78 °C and then for 12 h at 20 °C. Into this solution was injected $ZnBr_2$ (2.8 g, 12.5 mmol) in THF (40 mL) and the mixture stirred at 20 °C for 5 h to give a suspension which was quenched with H_2O (30 mL) and extracted with ether (2 × 40 mL). The combined organic layer was washed with NaOH (3 N, 2 × 30 mL) and dried ($MgSO_4$) and the solvent removed to give a liquid which was heated in methanol (20 mL) and HCl (2 N, 20 mL) at 70 °C for 3 h. After most of the methanol and some of the water were removed under vacuum, the residue was extracted with CH_2Cl_2 (3 × 25 mL). The extract was washed with water (10 mL) and dried over $MgSO_4$ and the solvent removed to give a liquid which was distilled, yield 62%: bp 89–93 °C/2 mmHg; ^1H NMR δ 1.25–1.35 (m, 1 H), 1.45–1.58 (m, 2 H), 1.62–1.78 (m, 7 H), 2.88 (t, J = 6.5 Hz, 2 H), 3.35 (s, 3 H), 3.64 (s, 1 H, OH), 3.69 (t, J = 6.5 Hz, 2 H); ^{13}C NMR δ 20.9, 25.2, 33.5, 36.4, 58.9, 67.9, 78.1, 213.7.

4-Hydroxy-1-methoxy-4-methyl-3-octanone (24b) was prepared from 2-hexanone in 60% overall yield and purified by distillation: bp 101–103 °C/2 mmHg; ^1H NMR δ 0.90 (t, J = 7.0 Hz, 3 H), 1.00–1.10 (m, 1 H), 1.25–1.43 (m, 3 H), 1.37 (s, 3 H), 1.65–1.76 (m, 2 H), 2.80 (t, J = 7.0 Hz, 2 H), 3.38 (s, 3 H), 3.61 (t, J = 7.0 Hz, 2 H), 3.88 (s, 1 H, OH); ^{13}C NMR δ 13.8, 22.8, 25.0, 25.1, 25.3, 36.3, 39.0, 58.7, 67.5, 78.8, 213.0.

4-Hydroxy-1-methoxy-4-methyl-6-phenyl-3-hexanone (24c) was prepared from 4-phenylbutan-2-one as an oil and

purified by column chromatography (silica gel, hexane/Et_2O, 3:1), yield 52%: ^1H NMR δ 1.40 (s, 3 H), 1.97–2.10 (m, 2 H), 2.35–2.37 (m, 1 H), 2.70–2.82 (m, 1 H), 2.77 (t, J = 6.1 Hz, 2 H), 3.34 (s, 3 H), 3.68 (t, J = 6.1 Hz, 2 H), 4.02 (s, 1 H, OH), 7.13–7.22 (m, 3 H), 7.23–7.31 (m, 2 H); ^{13}C NMR δ 25.1, 29.6, 36.4, 41.2, 58.8, 67.5, 78.6, 125.8, 128.2, 128.3, 141.6, 212.8.

4-Hydroxy-1-methoxy-4-phenyl-3-pentanone (24d) was prepared from acetophenone as an oil and purified by column chromatography (silica gel, hexane/Et_2O, 3:1), yield 48%: ^1H NMR δ 1.72 (s, 3 H), 2.65 (t, J = 6.2 Hz, 2 H), 3.22 (s, 3 H), 3.47–3.61 (m, 2 H), 4.61 (s, 1 H, OH), 7.27–7.40 (m, 3 H), 7.42–7.48 (m, 2 H); ^{13}C NMR δ 24.5, 36.3, 58.6, 67.6, 79.9, 125.8, 127.9, 128.5, 141.4, 210.2.

Preparation of 1-Ethoxy-1-vinylethylene Oxides 25. Representative Procedure for 2-Ethoxy-2-vinyl-1-oxaspiro[2.5]octane (25a). *N*-(α-Ethoxyallyl)benzotriazole (**8**, 2.5 g, 12.5 mmol) in THF (80 mL) was stirred at −78 °C under argon with butyllithium (6.5 mL, 2 M, 13.0 mmol) for 10 min. The green solution was stirred with a ketone (cyclohexanone for **25a**, 1.10 g, 11.0 mmol) for 3 h at −78 °C and then for 12 h at 20 °C. To this solution was injected $ZnBr_2$ (2.8 g, 12.5 mmol) in THF (40 mL), and the mixture was stirred for 5 h to give a suspension which was quenched with H_2O (30 mL) and extracted with ether (2 × 40 mL). The combined organic layer was washed with 3 N NaOH (2 × 30 mL) and dried ($MgSO_4$) and the solvent removed to give a liquid. Pure product (1.45 g, 72%) was obtained by distillation: bp 60–61 °C/4.5 mmHg; ^1H NMR δ 1.17 (t, J = 7.0 Hz, 3 H), 1.30–1.85 (m, 10 H), 3.55–3.75 (m, 2 H), 5.43 (d, J = 10.5 Hz, 1 H), 5.48 (d, J = 17.0 Hz, 1 H), 5.90 (dd, J = 17.0, 10.5 Hz, 1 H); ^{13}C NMR δ 15.3, 24.6, 24.8, 25.7, 29.7, 29.9, 60.9, 70.2, 89.7, 120.6, 131.7.

3,4-Epoxy-3-ethoxy-4-methyloct-1-enes (25b) were prepared as a mixture (*ca.* 1:1) of two isomers from 2-hexanone in 65% yield and purified by distillation: bp 75–78 °C/4.5 mmHg; ^1H NMR δ 0.81–0.95 (m, 3 H), 1.12–1.22 (m, 4 H), 1.25–1.45 (m, 5 H), 1.42 (s, 3 H), 3.54–3.70 (m, 2 H), 5.39–5.51 (m, 2 H), 5.70–5.93 (m, 1 H); ^{13}C NMR δ 13.9, 14.0, 15.3, 16.8, 17.1, 22.7, 22.8, 23.3, 26.1, 27.2, 32.7, 33.0, 41.6, 60.9, 68.6, 68.9, 89.3, 89.4, 120.4, 120.6, 131.9, 132.2.

Preparation of 1-Hydroxyalkyl Vinyl Ketones 26. Representative Procedure for 1-Propenoylcyclohexan-1-ol (26a). *N*-(α-Ethoxyallyl)benzotriazole (**8**, 2.5 g, 12.5 mmol) in THF (80 mL) was stirred at −78 °C under argon with butyllithium (6.5 mL, 2 M, 13.0 mmol) for 10 min followed by stirring with a ketone (cyclohexanone for **26a**, 1.10 g, 11.0 mmol) at −78 °C for 3 h and then at 20 °C for 10 h. The brown solution was quenched with water (40 mL) and extracted with ether (2 × 40 mL). The organic layer was washed with H_2O (30 mL) and dried ($MgSO_4$) and the solvent removed to give a solid which was washed with hexane–ether. The solid was stirred for 5 min with silica gel (30 g) in CH_2Cl_2 (60 mL) containing $H_2C_2O_4$ (0.4 g) and H_2O (0.5 mL). After the silica gel and $H_2C_2O_4$ were filtered off, the filtrate was washed with NaOH (2 N, 2 × 15 mL) and dried ($MgSO_4$) and the solvent removed to give pure **26a** in a total yield of 68%. The same compound was also prepared *via* intermediate **25a**. 2-Ethoxy-2-vinyl-1-oxaspiro[2.5]octane (**25a**, 0.5 g, 2.7 mmol) was passed through a short chromatographic column (silica gel, hexane/ether, 1:1). A liquid product was collected in 81% yield by removal of the solvent and was purified by distillation: bp 55–58 °C/0.5 mmHg; ^1H NMR δ 1.20–1.35 (m, 1 H), 1.45–1.55 (m, 2 H), 1.60–1.80 (m, 7 H), 3.75 (s, 1 H, OH), 5.83 (d, J = 10.5 Hz, 1 H), 6.50 (d, J = 17.0 Hz, 1 H), 6.87 (dd, J = 17.0, 10.5 Hz, 1 H); ^{13}C NMR δ 20.9, 25.2, 33.3, 77.0, 129.2, 130.3, 202.6.

4-Hydroxy-4-phenylpent-1-en-3-one (26b) was prepared from acetophenone *via* **23b** in 48% overall yield as an oil: ^1H NMR δ 1.76 (s, 3 H), 4.67 (s, 1 H, OH), 5.66 (dd, J = 9.9, 2.1 Hz, 1 H), 6.42 (dd, J = 17.1, 2.1 Hz, 1 H), 6.53 (dd, J = 17.1, 9.9 Hz, 1 H), 7.25–7.40 (m, 3 H), 7.42–7.47 (m, 2 H); ^{13}C NMR δ 23.9, 78.8, 126.1, 127.9, 128.5, 129.3, 130.6, 140.9, 199.5.

Preparation of β-Ethoxy-β-vinylalkyl Alcohols 27. Representative Procedure for 1-(1-Ethoxy-1-methylallyl)-cyclopentan-1-ol (27a). *N*-(α-Ethoxyallyl)benzotriazole (**8**, 2.5 g, 12.5 mmol) in THF (80 mL) was stirred at −78 °C under argon with butyllithium (6.5 mL, 2 M, 13 mmol) for 10 min. A ketone (cyclopentanone for **27a**, 0.9 g, 11.0 mmol) was added and the mixture stirred at −78 °C for 3 h and then at 20 °C for 12 h. Into this solution was injected $ZnBr_2$ (2.8 g, 12.5 mmol) in THF (40 mL), and the mixture was stirred for 5 h to give a suspension which was reacted with a Grignard reagent (methylmagnesium iodide in Et_2O for **27a**, 3 M, 8 mL, 24 mmol) at 20 °C for 10 h. The mixture was quenched with H_2O (10 mL) and extracted with ether (3 × 40 mL). The extracts were washed with NaOH (3 N, 2 × 30 mL) and dried ($MgSO_4$), and the solvent was removed to give an oil which was purified by column chromatography (silica gel, hexane/Et_2O, 6:1), yield 71%: ^1H NMR δ 1.14 (t, J = 7.0 Hz, 3 H), 1.29 (s, 3 H), 1.45–1.58 (m, 4 H), 1.67–1.85 (m, 4 H), 2.39 (s, 1 H, OH), 3.28–3.42 (m, 2 H), 5.18 (dd, J = 17.7, 1.4 Hz, 1 H), 5.27 (dd, J = 11.0, 1.4 Hz, 1 H), 5.90 (dd, J = 17.7, 11.0 Hz, 1 H); ^{13}C NMR δ 16.0, 16.3, 24.3, 35.1, 35.3, 57.9, 81.7, 86.4, 117.0, 140.7.

1-(1-Ethoxy-1-phenylallyl)cyclohexan-1-ol (27b) was prepared from cyclohexanone and phenylmagnesium bromide in 50% overall yield as an oil and purified by column chromatography (silica gel, hexane/Et_2O, 6:1): ^1H NMR δ 0.75–0.95 (m, 2 H), 1.23 (t, J = 6.9 Hz, 3 H), 1.30–1.80 (m, 8 H), 2.57 (s, 1 H, OH), 3.16–3.27 (m, 1 H), 3.28–3.40 (m, 1 H), 5.21 (d, J = 18.0 Hz, 1 H), 5.56 (d, J = 11.3 Hz, 1 H), 6.35 (dd, J = 18.0, 11.3 Hz, 1 H), 7.25–7.43 (m, 5 H); ^{13}C NMR δ 15.3, 21.5, 21.6, 25.8, 31.1, 31.7, 59.0, 75.8, 88.0, 120.5, 126.9, 127.1, 129.5, 135.1, 137.6.

1-[1-Ethoxy-1-(4-methylphenyl)allyl]cyclohexan-1-ol (27c) was prepared from cyclohexanone and *p*-methylphenylmagnesium bromide in 53% yield as an oil, and purified by column chromatography (silica gel, hexane/Et_2O, 6:1): ^1H NMR δ 0.72–0.98 (m, 2 H), 1.20 (t, J = 7.0 Hz, 3 H), 1.24–1.76 (m, 8 H), 2.36 (s, 3 H), 2.54 (s, 1 H, OH), 3.12–3.23 (m, 1 H), 3.25–3.37 (m, 1 H), 5.20 (dd, J = 17.0, 1.6 Hz, 1 H), 5.53 (dd, J = 11.2, 1.6 Hz, 1 H), 6.34 (dd, J = 17.0, 11.2 Hz, 1 H), 7.13 (d, J = 8.4 Hz, 2 H), 7.25 (d, J = 8.4 Hz, 2 H); ^{13}C NMR δ 15.3, 20.9, 21.6, 25.8, 31.1, 31.7, 59.0, 75.8, 87.9, 120.3, 127.8, 129.5, 134.5, 135.2, 136.4.

3-Ethoxy-3,4-dimethyloct-1-en-4-ol (27d) was prepared as a mixture (79:21) of two diastereoisomers from 2-hexanone and methylmagnesium iodide in 65% yield as an oil and purified by column chromatography (silica gel, hexane/Et_2O, 6:1): ^1H NMR δ 0.88–0.97 (m, 3 H), 1.10 (s, 2.27 H), 1.11 (s, 0.63 H), 1.14 (t, J = 7.0 Hz, 3 H), 1.23 (s, 3 H), 1.25–1.40 (m, 4 H), 1.40–1.70 (m, 2 H), 2.62 (s, 0.79 H), 2.66 (s, 0.21 H), 3.27–3.42 (m, 2 H), 5.15 (dd, J = 17.8, 1.4 Hz, 1 H), 5.27 (dd, J = 11.0, 1.4 Hz, 1 H), 5.91 (dd, J = 17.8, 11.0 Hz, 1 H); ^{13}C NMR δ 14.1, 15.1, 15.8, 20.7, 23.5, 25.8, 35.9, 57.6, 76.1, 82.5, 116.6, 140.3.

Preparation of Ethyl 1-(Benzotriazol-1-yl)-4-hydroxybuten-1-yl Ethers 31. Representative Procedure for 4-(Benzotriazol-1-yl)-1,1-dicyclohexyl-4-ethoxybut-3-en-1-ol (31a). *N*-(α-Ethoxyallyl)benzotriazole (**8**, 2.5 g, 12.5 mmol) in THF (80 mL) was stirred at −78 °C under argon with butyllithium (6.5 mL, 2 M, 13 mmol) for 10 min. A ketone (dicyclohexyl ketone for **31a**, 11.0 mmol) in THF (10mL) was added and the mixture stirred at −78 °C for 3 h and then at 20 °C for 12 h. The solution was quenched with water (30 mL) and extracted with ether (2 × 40 mL). The extracts were washed with H_2O (30 mL) and dried ($MgSO_4$), and the solvent was removed to give an oil which was purified by column chromatography (silica gel, hexane/Et_2O, 6:1). The eluent was dried over $MgSO_4$ and the solvent removed to give an oil, yield 81%. The oily product crystallized (plates, mp 71–73 °C) on exposure to air after a few days. The molecular formula of the crystal was identified by elemental analysis as $C_{24}H_{37}N_3O_3$ (Required: C, 69.36; H, 8.97; N, 10.11. Found: C, 69.29; H, 9.03; N, 10.09); i.e., the crystalline product contains one more water molecule than the oily product **31a**: ^1H NMR δ 1.13–1.30 (m, 8 H), 1.30 (t, J = 7.0 Hz, 3 H), 1.55–1.75 (m, 4 H), 1.75–1.93 (m, 10 H), 2.63 (d, J = 7.7 Hz, 2 H), 3.64 (q, J = 7.0 Hz, 2 H), 4.78 (s, 1 H, OH), 5.45 (t, J = 7.7 Hz, 1 H), 7.42 (t, J = 8.2 Hz, 1 H), 7.55 (t, J = 8.2 Hz, 1 H), 7.72 (d, J = 8.3 Hz, 1 H), 8.09 (d, J = 8.3 Hz, 1 H); ^{13}C NMR δ 14.8, 26.7, 27.0, 27.5, 30.1, 44.7, 66.4, 77.4, 106.8, 110.8, 120.0, 124.8, 128.3, 132.4, 143.4, 145,6.

4-(Benzotriazol-1-yl)-4-ethoxy-1,1-diphenylbut-3-en-1-ol (31b) was prepared from benzophenone in 78% yield and recrystallized from hexane/EtOAc: mp 121–122 °C; ^{1}H NMR δ 1.20 (t, J = 7.0 Hz, 3 H), 2.96 (s, 1 H, OH), 3.39 (d, J = 7.4 Hz, 2 H), 3.50 (q, J = 7.0 Hz, 2 H), 5.33 (t, J = 7.4 Hz, 1 H), 7.20–7.40 (m, 9 H), 7.46–7.55 (m, 4 H), 7.95 (d, J = 8.1 Hz, 1 H); ^{13}C NMR δ 14.8, 38.2, 66.6, 78.0, 104.9, 110.9, 119.2, 119.9, 124.4, 126.2, 127.1, 128.3, 131.3, 144.6, 145.4, 146.5.

9-[3-(Benzotriazol-1-yl)-3-ethoxyallyl]-9-hydroxyfluorene (31c) was prepared from 9-fluorenone in 76% yield and recrystallized from hexane/EtOAc: mp 177–178 °C; ^{1}H NMR δ 1.12 (t, J = 7.0 Hz, 3 H), 2.65 (s, 1 H, OH), 3.19 (d, J = 7.6 Hz, 2 H), 3.34 (q, J = 7.0 Hz, 2 H), 4.96 (t, J = 7.6 Hz, 1 H), 7.02 (d, J = 7.8 Hz, 1 H), 7.27–7.41 (m, 6 H), 7.63 (t, J = 8.7 Hz, 4 H), 7.95 (d, J = 7.8 Hz, 1 H); ^{13}C NMR δ 14.7, 35.5, 66.4, 81.8, 104.2, 110.7, 119.7, 119.9, 123.9, 124.2, 128.0, 129.1, 132.4, 139.4, 144.3, 145.3, 148.1.

Preparation of β,γ-Unsaturated Carboxylic Acids 32. Representative Procedure for 4,4-Diphenyl-3-butenoic Acid (32a). Crude compound **31b** prepared as above from *N*-(α-ethoxyallyl)benzotriazole (12.5 mmol) and benzophenone (11.0 mmol) was heated at 90 °C in a mixture of DMF (40 mL) and HCl (3 N, 10 mL) for 6 h. After removal of most of the methanol with a rotovapor, the residue was extracted with $CHCl_3$ (2 × 40 mL). The extracts were washed with H_2O (10 mL) and dried ($MgSO_4$), and the solvent was removed to give a solid which was dissolved in saturated aqueous $NaHCO_3$ solution (100 mL) and washed with CH_2Cl_2 (2 × 30 mL). The aqueous solution was acidified (pH < *ca.* 3.0) with 6 N HCl and was extracted with CH_2Cl_2 (3 × 30 mL). The extracts were washed with H_2O (30 mL) and dried ($MgSO_4$), and the solvent was removed to give a solid product, yield 67%: mp 114.5–115.5 °C; ^{1}H NMR δ 3.21 (d, J = 7.4 Hz, 2 H), 6.25 (t, J = 7.4 Hz, 1 H), 7.17–7.45 (m, 10 H), 11.0 (bs, 1 H); ^{13}C NMR δ 35.2, 119.4, 127.4, 127.5, 128.1, 128.4, 129.7, 139.0, 141.7, 145.2, 178.4.

3-(9-Fluorenylene)propionic acid (32b) was prepared from 9-fluorenone in 74% yield: mp 205.5–206.5 °C; ^{1}H NMR δ 3.82 (d, J = 7.1 Hz, 2 H), 6.96 (t, J = 7.1 Hz, 2 H), 7.25–7.45 (m, 4 H), 7.65–7.75 (m, 5 H including COOH); ^{13}C NMR δ 33.6, 118.4, 118.8, 119.0, 120.8, 123.7, 126.0, 126.1, 126.8, 127.2, 135.6, 135.7, 137.5, 137.8, 139.7, 171.7.

Preparation of γ-Lactones 33. Representative Procedure for 5,5-Dicyclohexyl-4,5-dihydro-2(3*H*)-furanone (33a). *N*-(α-Ethoxyallyl)benzotriazole (**8**, 2.5 g, 12.5 mmol) in THF (80 mL) was stirred at −78 °C under argon with butyllithium (6.5 mL, 2 M, 13 mmol) for 10 min. A ketone (dicyclohexyl ketone for **33a**, 11.0 mmol) was added and the mixture stirred at −78 °C for 3 h and then at 20 °C for 12 h. The solution was quenched with water (30 mL) and extracted with ether (2 × 40 mL). The extracts were washed with H_2O (30 mL) and dried ($MgSO_4$), and the solvent was removed to give an oil which, without further purification, was heated at 70 °C in a mixture of DMF or MeOH (40 mL) and 1 N HCl (10 mL) for 6 h. The mixture was made basic by the addition of 3 N NaOH and extracted with ether (2 × 40 mL). The extracts were dried ($MgSO_4$), and the solvent was removed to give a liquid which was purified by chromatography (silica gel, hexane/ether, 4:1), yield 75%: mp 89.0–89.5 °C; ^{1}H NMR δ 0.97–1.37 (m, 10 H), 1.58–1.88 (m, 12 H), 2.03 (t, J = 9.5 Hz, 2 H), 2.51 (t, J = 9.5 Hz, 2 H); ^{13}C NMR δ 24.3, 26.0, 26.2, 26.3, 29.6, 43.2, 92.7, 177.6.

5,5-Diisopropyl-4,5-dihydro-2(3*H*)-furanone (33b) was prepared as an oil from 2,4-dimethyl-3-pentanone and was purified by distillation, yield 76%: bp 86–87 °C/0.4 mmHg; ^{1}H NMR δ 0.93 (d, J = 7.0 Hz, 6 H), 0.96 (d, J = 7.0 Hz, 6 H), 1.95 (t, J = 9.0 Hz, 2 H), 2.10 (heptet, J = 7.0 Hz, 2 H), 2.55 (t, J = 9.0 Hz, 2 H); ^{13}C NMR δ 16.4, 16.5, 23.4, 29.7, 33.6, 93.2, 177.6.

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