Novel Routes to Enol Ethers, Unsymmetrical Ketones, α-Bromoalkyl Ketones, 1,4-Diketones, 2-Ethoxy-2-cyclopentenones, and α-Keto Enamines

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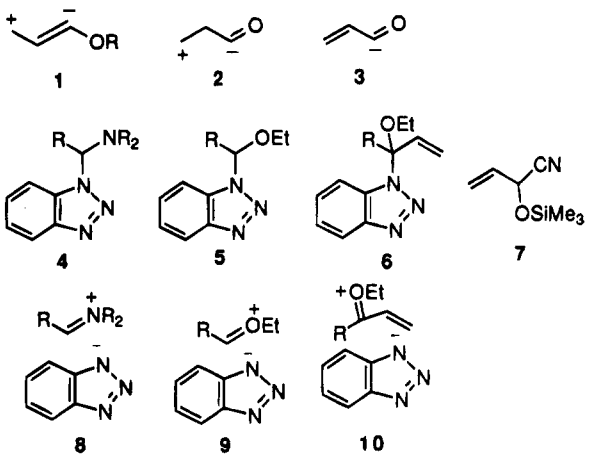
Highly regioselective S_N2' reactions of adducts **6** (readily prepared by reactions of halides with the allyl anion **12** of **11**) with Grignard reagents gave enol ethers **13**, which were converted (in one-pot reactions from **11**) into ketones **14** and α-bromoalkyl ketones **15** in good yields. The monoprotected 1,4-diketone derivative **16** (prepared by Michael addition of the allyl anion **12** with methyl vinyl ketone) was converted both into 1,4-diketones **18** and into protected γ-hydroxyalkyl ketone **20** by selective Grignard reactions, which could be directed either to the carbonyl, or the protected propenoyl, or to both functionalities. The allyl anion **12** with α-substituted acetic esters gave α-acylated adducts **24**, which underwent *in situ* unfavored *endo-trig* cyclization upon treatment with NaH and secondary amines, to give 2-ethoxy-2-cyclopentenones **27** and **28** and α-keto enamines **25** in good yield. The mechanism for the cyclization is discussed.

Synthetic applications of S_N2' reactions[1] of organocopper reagents[2] with allyl carboxylates, sulfonates, and phosphonates, including regioselective and diastereoselective asymmetric syntheses,[3] have recently received attention. S_N2' reactions of α,β-unsaturated acetals or ketals with organocoppers or with organonickel reagents provide enol ethers with high regioselectivity, while Grignard reactions with these allylic derivatives usually gave a mixture of γ-alkylated and α-alkylated products.[5a,b] We found no literature S_N2' reactions with a heterocycle as leaving group.



1 2 3 4 5 6 7 8 9 10

Synthon equivalents of **1** and **2** are of potential importance because they introduce both a nucleophile and an electrophile constructing two new C–C bonds: the few previous examples include alkoxyallenes.[6a,b] Vinylacyl anion equivalent **3** is not a practical synthon equivalent of **2**, because α-thioalkyl allyl ethers and *O*-protected cyanohydrins **7**[7] did not react directly with carbanions to produce ketones. Poor regioselectivity of the Michael addition[8] of Grignard reagents to vinyl ketones restricts the utility of **3** as the synthon equivalent of **2**.

The benzotriazole group in benzotriazole derivatives **4** and **5** (available in excellent yields[9]) is readily displaced either by a hydride anion donor or by the carbanion of organolithiums, Grignard reagents, or zinc reagents (RLi, RMgBr, or R_2Zn) leading to amines,[9] or to ethers,[10] in high yields. The exocyclic lone ion pair on the nitrogen in **4**, or on the oxygen in **5**, assists the departure of the benzotriazole anion *via* ion-pair intermediates **8** and **9**, respectively. Compounds of type **6** should also dissociate into ion pairs **10** to which a nucleophile could add to the γ-position with departure of the benzotriazolyl group and with the rearrangement of the C=C bond to give enol ethers in novel heterocycle-mediated S_N2' reactions.

The two preceding papers[11a,b] apply the novel heterocycle-stabilized homoenolate anion **12** to the synthesis of vinylcyclopropanecarboxylic esters, vinyloxiranes, and vinylketones. The facile lithiation of **11**, and subsequent regioselective α-reactions with electrophiles, forms intermediates **6** still containing the labile benzotriazolyl leaving group, which[11a] can be hydrolyzed to vinyl ketones; similar intermediates derived from α,β-unsaturated esters and from methyl and cyclic ketones undergo internal nucleophilic substitution to form vinyl-substituted three-membered rings.[11b] We now report that the same intermediates **6** undergo S_N2' (γ-alkylation) reac-

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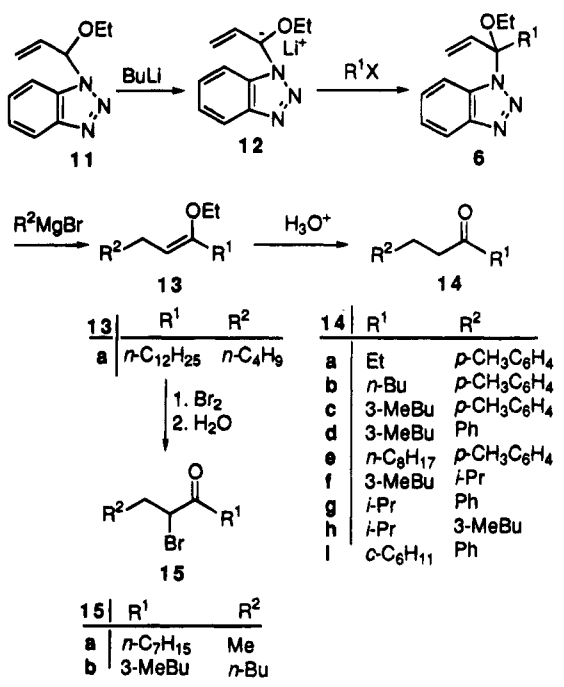
Scheme 1



tions with Grignard reagents to give enol ethers **13**, which can either be isolated or be converted *in situ* into unsymmetrical ketones **14** or α-bromoalkyl ketones **15**. Previously reported compounds of type **16**[11a] are now shown to undergo Grignard reactions to give 1,4-diketones **18** or protected γ-hydroxyalkyl ketones **20** depending on the conditions. Allyl anion **12** reacts with esters to give the acylated adducts **24** which, with NaH or a secondary amine, undergo *anti*-Baldwin's rule-type intramolecular S_N2' cyclizations to give 2-ethoxy-2-cyclopentenones **27** and **28** and α-keto enamines **25**.

Results and Discussion

Intermolecular S_N2' Reactions of α-(Benzotriazolyl)allylic Ethers 6, Preparation of Enol Ethers, Unsymmetrical Ketones, α-Bromoalkyl Ketones, 1,4-Diketones, γ-Hydroxyalkyl Ketones, and α-Hydroxyalkyl Ketones. As previously discussed,[11a,b] compounds **6** were prepared by treatment of *N*-(α-ethoxyallyl)-benzotriazole (**11**) with butyllithium, followed by reaction with halides (Scheme 1). Although **6** can be isolated, they were advantageously prepared in THF and reacted *in situ* with Grignard reagents to give enol ethers **13** with rearrangement of the C=C bond (S_N2' reaction). Disappearance of the terminal vinyl group ^{1}H NMR signals, formation of a new triplet around 4.5 ppm, and C-13 signals at *ca.* 158 ppm in the crude products all demonstrated the high regioselectivity of these reactions; no allylic ethers (from an S_N reaction of **6** at the carbon α to benzotriazolyl) were detected. Previous uncatalyzed Grignard reactions with α,β-unsaturated ketals and acetals had given mixtures of α- and γ-products[5a,b] or mainly γ-products using Cu or Ni complex catalysis.[4b-d] The present exclusive formation of γ-alkylated products in the absence of any catalyst is rationalized by the bulky benzotriazolyl together with the α-alkyl substituent hindering nucleophile attack at the α-position.

Displacement of the benzotriazole group from adducts **6** by Grignard reagents under milder conditions (in refluxing THF) than those previously reported for the Grignard reactions of ether benzotriazole derivatives[10] (refluxing at 110 °C) can be accounted for by the S_N2' mechanism: steric crowding around the α-center from the benzotriazolyl group and the α-alkyl substituent facilitates scission of the C-benzotriazole bond, while attack at the γ-position is not blocked by the α-substituents. Although formation of the C–C bond between the γ-position and the R^2 group must occur rapidly after scission of the benzotriazolyl group at the α-position, we believe that displacement of benzotriazole involves ion pair intermediates **10**, as supported by unsuccessful attempts at displacement of the benzotriazolyl group by a carbanion from *N*-(α-alkylallyl)benzotriazole. Intermediate **10** is apparently a compact ion pair, in which no migration of the benzotriazolyl group occurs: such migration occurs quantitatively under other conditions.[11a,12]

The present procedure provides an efficient method for the preparation of enol ethers, which have considerable synthetic utility.[13,14] It is usually difficult to prepare enol ethers of ketones regioselectively by the thermolysis of ketals,[15a,b] and direct alkylidenation of an ester carbonyl group requires metal carbene complex intermediates[16a,b] or Tebbe complexes.[17] Ketone enol ethers are now obtained regiospecifically. The crude enol ethers showed clean spectra, but column chromatography on silica gel converts them partially into ketones. One enol ether **13a** was isolated for characterization purposes. Nine other enol ethers **13** were each directly hydrolyzed by 2 *N* HCl into the corresponding ketones **14a-i** prior to purification and characterization. Neither adducts **6** nor enol ethers **13** needed to be isolated, and reactions **11** → **14** (four steps) are all conveniently carried out in one pot. Table 1 lists unsymmetrical ketones **14a-i** prepared from various halides. Both R^1 and R^2 are originally derived from halides which are added to the equivalent **2** as either the electrophile (α-alkylation) or as the nucleophile (Grignard reaction). Primary halides usually gave ketones in good yields, while when R^1 = secondary alkyl the yields are moderate or low, presumably because the alkylation step of **12** was accompanied by elimination of the halides, as mentioned in a preceding paper.[11a] In all cases, an excess of the Grignard reagent was used without unwanted side reactions.

Two enol ethers **13** were similarly converted *in situ* into α-bromoalkyl ketones **15a,b** in high yield, following a literature procedure.[18] Enol ether **13a**, ketones **14a-i**, and α-bromoalkyl ketones **15a,b** were all characterized by NMR spectroscopy and elemental analyses. The characteristic carbon signals of enol ether **13a** appeared at around 156 ppm, while the carbonyl signals of ketones **14** appeared at *ca.* 210 ppm.

The present preparation of ketones has two particular advantages: it provides (i) a high yielding, one-pot synthesis of ketones with the construction of two new C–C bonds and (ii) more options for the synthesis of unsymmetrical ketones; for example, ketones **14f** and

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Table 1. Preparation of Compounds 13a, 14–18, 20, 23–25, and 27–29

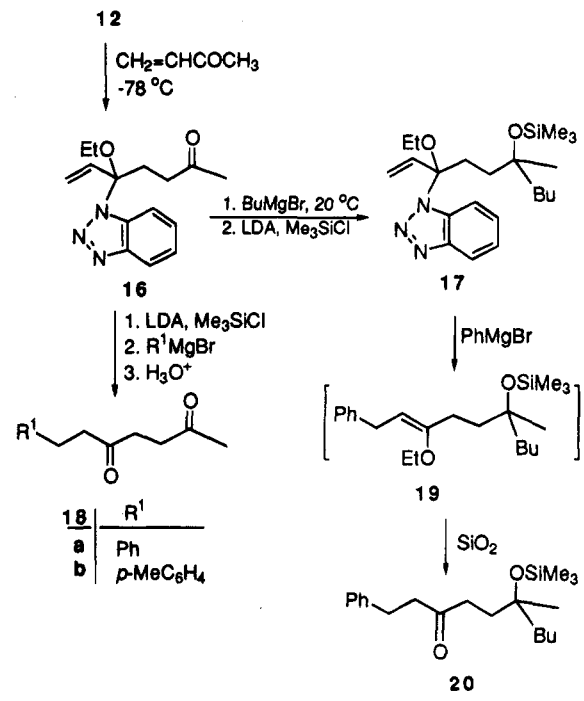
compd	R^1(Ar)	R^2	yield (%)	CHN analysis or HRMS, found (required) molec formula	C	H	N
13a	*n*-$C_{12}H_{25}$	*n*-C_4H_9	43	$C_{21}H_{42}O$	80.92 (81.21)	13.80 (13.64)	
14a	Et	*p*-MeC_6H_4	81	$C_{12}H_{16}O$	81.43 (81.77)	9.14 (9.15)	
14b	*n*-Bu	*p*-MeC_6H_4	76	$C_{14}H_{20}O$	82.05 (82.30)	9.93 (9.87)	
14c	3-MeBu	*p*-MeC_6H_4	79	$C_{15}H_{22}O$	82.35 (82.52)	10.26 (10.16)	
14d	3-MeBu	Ph	55	$C_{14}H_{20}O$	81.92 (82.30)	10.14 (9.87)	
14e	*n*-C_8H_{17}	*p*-MeC_6H_4	67	$C_{18}H_{28}O$	83.27 (83.02)	10.94 (10.84)	
14f	3-MeBu	*i*-Pr	49	$C_{11}H_{22}O$	77.80 (77.58)	12.94 (13.02)	
14g	*i*-Pr	Ph	40	$C_{12}H_{16}O$	81.48 (81.77)	9.11 (9.15)	
14h	*i*-Pr	3-MeBu	33	$C_{11}H_{22}O$	77.78 (77.58)	13.02 (13.02)	
14i	*c*-C_6H_{11}	Ph	31	$C_{15}H_{20}O$	83.08 (83.29)	9.48 (9.32)	
15a	*n*-C_7H_{15}	Me	85[a]	$C_{11}H_{21}OBr$	52.97 (53.02)	8.22 (8.49)	
15b	3-MeBu	*n*-Bu	90[a]	$C_{12}H_{23}OBr$	54.62 (54.76)	8.55 (8.81)	
16			84	$C_{15}H_{19}N_3O_2$		274.1606 (274.1556)	
17			48	$C_{22}H_{37}N_3O_2Si$	65.73 (65.46)	9.46 (9.24)	10.22 (10.41)
18a	Ph		51	$C_{13}H_{16}O_2$		[b]	
18b	*p*-MeC_6H_4		56	$C_{14}H_{18}O_2$	76.87 (77.03)	8.45 (8.31)	
20			24	$C_{20}H_{34}O_2Si$	71.73 (71.88)	10.26 (10.24)	
23a[c]	*p*-MeC_6H_4	Ph	47	$C_{17}H_{18}O_2$	80.01 (80.28)	7.32 (7.13)	
23b[c]	*p*-MeC_6H_4	Me	25	$C_{12}H_{16}O_2$	74.77 (74.96)	8.30 (8.39)	
23c[c]	Ph	Me	20	$C_{12}H_{16}O_2$	74.61 (74.97)	8.51 (8.39)	
24a	Ph		90	$C_{19}H_{19}N_3O_2$	71.35 (71.01)	6.21 (5.96)	13.06 (13.07)
24b	*n*-C_7H_{15}		72	$C_{20}H_{29}N_3O_2$	70.15 (69.94)	8.70 (8.51)	12.20 (12.23)
25			54	$C_{18}H_{17}NO$	81.76 (82.10)	6.61 (6.51)	5.53 (5.32)
27a	Ph		62	$C_{13}H_{14}O_2$	77.40 (77.20)	7.05 (6.98)	
27b	1-naphthyl		67	$C_{17}H_{16}O_2$	80.66 (80.93)	6.37 (6.39)	
27c	*p*-$MeOC_6H_4$		57	$C_{14}H_{16}O_3$	72.19 (72.39)	6.77 (6.94)	
27d	*p*-ClC_6H_4		55	$C_{13}H_{13}O_2Cl$		237.0691 (237.0682)	
28a	Me		28	$C_8H_{12}O_2$	68.32 (68.55)	8.69 (8.63)	
28b	*n*-Bu		36	$C_{11}H_{18}O_2$	72.19 (72.49)	9.96 (9.95)	
29			23	$C_{11}H_{13}N_3O$	65.27 (65.01)	6.54 (6.45)	20.40 (20.67)

[a] Yield of the crude products which are >95% pure based on the NMR spectra. [b] Identical NMR data to those reported in the reference.[30] [c] R^3 = H (**23a**), H (**23b**), Me (**23c**).

14h were each prepared from isopropyl bromide and 3-methylbutyl bromide by using different reaction sequences. Conversely, ketone **14d** was prepared both from 2-phenylethyl bromide and isopropyl bromide and from 3-methylbutyl bromide and bromobenzene. Our method seems suitable for the preparation of libraries of ketones. Moreover, the present route to α-bromoalkyl ketones is regiospecific.

Compounds of type **16**, readily available by 1,4-addition of the allyl anion **12** to α,β-unsaturated ketones, comprise protected propenoyl ketones.[11a] They were previously hydrolyzed by $H_2C_2O_4$–SiO_2–H_2O to β-propenoylalkyl ketones in good yield.[11a] We now find that if the carbonyl group of **16** is protected as its silyl enol ether, treatment with Grignard reagents in refluxing THF followed by hydrolysis gives unsymmetrical 1,4-diketones **18** (Scheme 2). By contrast, direct treatment of **16** with a Grignard reagent at 20 °C followed by reaction with trimethylsilyl chloride gave selective reaction at the unprotected carbonyl group to give **17**: this is consistent with the results in Scheme 1: displacement of the benzotriazolyl group by Grignard reagents *via* S_N2' reaction requires moderately forcing conditions of refluxing in THF. As expected, further treatment of **17** with another Grignard reagent in refluxing THF followed by hydrolysis during column chromatography gave γ-((trimethylsilyl)oxy)alkyl ketone **20**. These reactions leading to **18** and **20** are of synthetic interest: 1,4-diketones are valuable synthetic precursors,[19] and most previous preparations[20a–f] are either quite lengthy and/or require special reagents. We now prepare 1,4-diketones by a simple procedure from easily accessible starting materials with the construction of two new C–C bonds.

Scheme 2



Compounds **21**, generated from the allyl anion **12** with aldehydes or ketones, reverted back to their starting materials when they were refluxed in THF with Grignard reagents. However, protection of the hydroxy group of **21** with trimethylsilyl chloride and subsequent treatment with Grignard reagents gave α-hydroxyalkyl ketones **23a-c** in moderate overall yield after hydrolysis (Scheme 3). The low yields are probably due to incomplete

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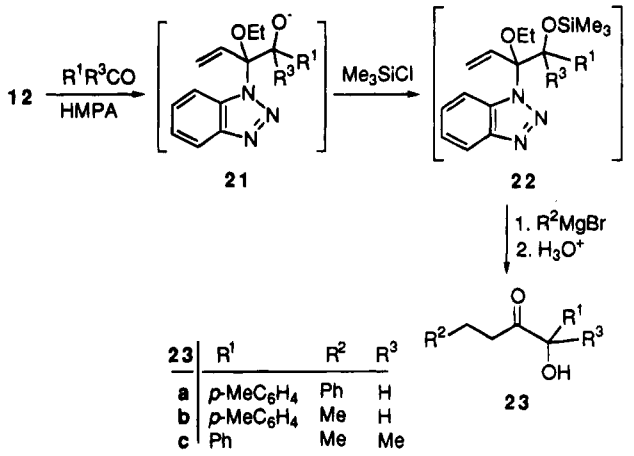
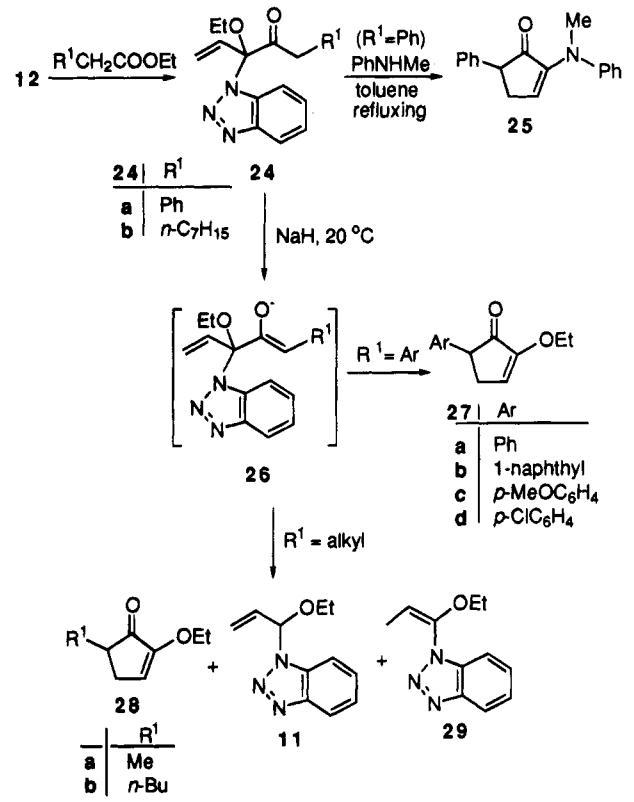
Scheme 3



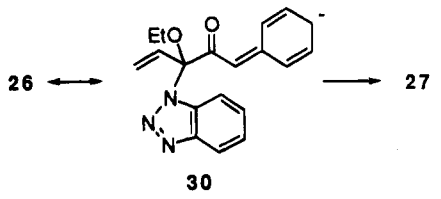
Scheme 4



protection of the hydroxy group, and this reaction needs further study.

Intramolecular S_N2' Reactions of α-Acylated Benzotriazole Derivatives 24, Preparation of 2-Ethoxy-2-cyclopentenones, and α-Keto Enamines. Reactions of allyl anion **12** with acyl chlorides gave mixtures but esters formed the expected acylated adducts **24** in good yield, even readily enolizable ethyl α-arylacetates (Scheme 4). Compounds **24a,b** were isolated and characterized, and the analogs were used directly in subsequent reactions. By contrast, **12** did not react with 3-pentanone;[11b] although the ketonic carbonyl is more electrophilic than that of an ester, the products are more sterically crowded than compounds of type **24**. As previously discussed,[11a] adducts **6** derived from halides are hydrolyzed by $H_2C_2O_4$–SiO_2–H_2O to vinyl ketones; however, compounds of type **24** are more resistant. Hydrolysis of **24** with HCl–H_2O gave ketones with a β-benzotriazolyl substituent. We now find that compounds **24** possessing a proton at the carbon α to the carbonyl group are converted by NaH at 20 °C into 2-ethoxy-2-cyclopentenones **27** and **28**. Compounds **24** derived from ethyl 2-arylacetates gave 5-aryl-2-ethoxy-2-cyclopentenones **27a-d** in good yield, while those derived from esters with R^1 = alkyl gave the expected **28a,b** in moderate or low yield, with **11** and **29** obtained as major byproducts.

Scheme 5



The mechanism for the formation of compounds **27** and **28** probably involves an enolate intermediate **26,** which undergoes internal S_N2' displacement of benzotriazole to give the cyclized products **27** and **28**. Formation of **11** involves a retro-aldol condensation of **26** *via* the allyl anion **12**, and compound **29** was formed by rearrangement of anion **12**. We believe that the retro-aldol condensation of **26** is in competition with the cyclization. When R^1 = alkyl or H, difficulty in the formation of a five-membered ring from **26** by an unfavored *endo-trig* process[21] leads to the retro-aldol condensation becoming a significant process. When R = aryl, the conjugated aromatic system facilitates cyclization of **26**, probably by converting the *endo-trig* process to a favored *exo-trig* process *via* the resonance form **30** (Scheme 5). This rationalization is supported by the fact that, when R^1 = H, treatment of **24** with NaH gave no compound of type **28**.

From a synthetic point of view, the present reaction provides an unprecedented cyclization route to 2-alkoxy-2-cyclopentenones. 2-Alkoxy-α,β-unsaturated ketones (diosphenol ethers) are important as physiologically-active substances[22] and in carbonyl transformations,[23a-c] photochemical transformations,[24a-d] and carbocation rearrangements.[25] Previous syntheses of diosphenol ethers invariably involved diosphenols or 1,2-diketones.[22,26a,b] α-Alkylation of 1,2-cyclopentanedione, followed by elaboration of the resulting 1,2-diketones, could afford **28** but not 5-aryl derivatives **27**. The present method produces regiospecifically 5-aryl-2-ethoxy-2-cyclopentenones **27** with

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the C=C bond not conjugated with the aryl (**27**) or alkyl (**28**) substituent. One compound of type **24** was also converted in good yield by *N*-methylaniline into the α-keto enamine **25**, a member of a class of synthetic importance,[27a-c] previous preparations of which started from the corresponding 1,2-diketones.[28]

Compounds **25, 27a-d,** and **28a,b** are new, and their structures were characterized by NMR spectroscopy and elemental analysis. In the ^{1}H NMR, the geminal CH_2 group protons of the cyclopentenone ring of both **25** and **27** appear at different field as double double doublets near 2.9−3.1 and 2.4−2.65 ppm, respectively, with a large geminal splitting. The double doublet signal at *ca.* 3.5−3.6 ppm of **25** and **27** belongs to the proton on the CH group adjacent to the aryl group. The sp^2 carbons connected with the ethoxy group of **27a-d** resonate at *ca.* 155 ppm and that connected to the amino group of **25** at *ca.* 147 ppm.

Conclusions. In summary, we have developed new synthetic methodology which combines α-alkylation of the allyl anion **12** with subsequent intermolecular or intramolecular S_N2' reactions. Advantages compared with the possible use of cyanohydrin **7** or acrolein diethyl acetal include: (i) S_N2' displacement of the CN^- group by a Grignard reagent from the α-alkylated adducts of **7** could be complicated by the addition of the Grignard reagent to the CN group, and (ii) lithiation of acrolein diethyl acetal is extremely difficult,[29a,b] although α-alkylated α,β-unsaturated ketals were reported[7] to undergo copper- or nickel-complex-catalyzed S_N2' reactions. The synthetic utility of the present methodology is illustrated by the convenient synthesis of enol ethers, α-bromoalkyl ketones, ketones, 1,4-diketones, α-diosphenol ethers, and α-keto enamines *via* synthons **1** and **2** with the construction of two carbon−carbon bonds.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300 MHz spectrometer in $CDCl_3$. THF was freshly distilled from sodium−benzophenone ketyl immediately before use. Lithiation was carried out in an argon atmosphere created by evacuating the flask using a vacuum pump followed by filling it with argon several times. All Grignard reagents were prepared as required from the corresponding halide with magnesium.

Preparation of Ethyl Nonadec-6-en-7-yl Ether (13a). *N*-(α-Ethoxyallyl)benzotriazole (3.03 g, 15 mmol) was stirred with butyllithium (8 mL, 2 *M*, 16 mmol) in THF (100 mL) at −78 °C for 5 min to give a green solution to which was added 1-bromododecane (3.7 g, 15 mmol), the mixture being stirred at −78 °C for 4 h. *n*-Butylmagnesium bromide (30 mmol in 40 mL diethyl ether) was added at −78 °C, and the mixture was warmed to 20 °C before heating under reflux for 10 h. The reaction was quenched with water (10 mL) and extracted with diethyl ether (3 × 40 mL). The extract was washed with NaOH (2 N, 25 mL) and dried ($MgSO_4$) and the solvent removed to give **13a** which was distilled under vacuum to give a mixture of two isomers as a yellow oil (7.8:1), yield 43%: ^{1}H NMR δ 0.80−0.86 (m, 6 H), 1.15−1.29 (m, 27 H), 1.34−1.45 (m, 2 H), 1.85−1.95 (m, 2 H), 2.03 (t, J = 7.4 Hz, 2 H), 3.56 (q, J = 6.9 Hz, 2 H), 4.25 (t, J = 7.4 Hz, 1 H); ^{13}C NMR δ 14.1, 14.7, 22.7, 26.8, 27.3, 27.9, 29.3, 29.4, 29.6, 29.7, 29.8, 30.2, 30.3, 30.9, 31.5, 31.7, 32.0, 61.7, 97.2, 156.2.

Preparation of Unsymmetrical Ketones 14. Representative Procedure for 1-(*p*-Methylphenyl)pentan-3-one (14a). *N*-(α-Ethoxyallyl)benzotriazole (3.03 g, 15 mmol) was stirred with butyllithium (8 mL, 2 M, 16 mmol) in THF (100 mL) at −78 °C for 5 min followed by stirring with a halide (iodoethane for **14a**, 2.3 g, 15 mmol) at −78 °C for 4 h. A Grignard reagent ((*p*-methylphenyl)magnesium bromide for **14a**, 30 mmol in 30 mL diethyl ether) was added at −78 °C, and the mixture was warmed to 20 °C before being heated under reflux for 10 h. The reaction was quenched with HCl (2 N, 25 mL) at 0 °C, and the reaction mixture was stirred for 10 h at 20 °C and extracted with diethyl ether. The extract was washed with NaOH (2 N, 25 mL) and dried ($MgSO_4$) and the solvent removed to give **14a** which was purified by column chromatography to give a yellow oil (silica gel, hexane/Et_2O, 10:1), yield 81%: ^{1}H NMR δ 1.02 (t, J = 7.3 Hz, 3 H), 2.29 (s, 3 H), 2.37 (q, J = 7.3 Hz, 2 H), 2.68 (t, J = 7.2 Hz, 2 H), 2.84 (t, J = 7.3 Hz, 2 H), 7.06 (s, 4 H); ^{13}C NMR δ 7.6, 20.8, 29.4, 36.0, 43.9, 128.1, 129.0, 135.4, 138.0, 210.4.

1-(*p*-Methylphenyl)heptan-3-one (14b) was prepared from 1-bromobutane and (*p*-methylphenyl)magnesium bromide as a yellow oil and purified by column chromatography (silica gel, hexane/Et_2O, 10:1), yield 76%: ^{1}H NMR δ 0.90 (t, J = 7.3 Hz, 3 H), 1.24−1.36 (m, 2 H), 1.50−1.60 (m, 2 H), 2.32 (s, 3 H), 2.38 (t, J = 7.4 Hz, 2 H), 2.70 (t, J = 7.8 Hz, 2 H), 2.86 (t, J = 7.7 Hz, 2 H), 7.08 (s, 4 H); ^{13}C NMR δ 13.8, 20.9, 22.2, 25.8, 29.3, 42.6, 44.3, 128.1, 129.0, 135.4, 138.0, 210.3.

6-Methyl-1-(*p*-methylphenyl)heptan-3-one (14c) was prepared from 1-bromo-3-methylbutane and (*p*-methylphenyl)-magnesium bromide as a yellow oil and purified by column chromatography (silica gel, hexane/Et_2O, 10:1), yield 79%: ^{1}H NMR δ 0.87 (d, J = 6.4 Hz, 6 H), 1.40−1.56 (m, 3 H), 2.30 (s, 3 H), 2.37 (t, J = 7.6 Hz, 2 H), 2.70 (t, J = 7.4 Hz, 2 H), 2.83 (t, J = 7.3 Hz, 2 H), 7.07 (s, 4 H); ^{13}C NMR δ 20.9, 22.2, 27.6, 29.4, 32.5, 41.0, 44.3, 128.1, 129.1, 135.4, 138.0, 210.3.

6-Methyl-1-phenylheptan-3-one (14d) was prepared from 1-bromo-3-methylbutane and phenylmagnesium bromide as a yellow oil and purified by column chromatography (silica gel, hexane/Et_2O, 10:1), yield 55%. This compound was also prepared from 1-bromo-2-phenylethane and isopropylmagnesium bromide in a similar yield: ^{1}H NMR δ 0.88 (d, J = 6.2 Hz, 6 H), 1.40−1.57 (m, 3 H), 2.37 (t, J = 7.7 Hz, 2 H), 2.73 (t, J = 7.4 Hz, 2 H), 2.89 (t, J = 7.3 Hz, 2 H), 7.15−7.21 (m, 3 H), 7.23−7.32 (m, 2 H); ^{13}C NMR δ 22.3, 27.6, 29.8, 32.5, 41.0, 44.2, 126.0, 128.2, 128.4, 141.1, 210.3.

1-(*p*-Methylphenyl)undecan-3-one (14e) was prepared from 1-bromooctane and (*p*-methylphenyl)magnesium bromide as a yellow oil and purified by column chromatography (silica gel, hexane/Et_2O, 10:1), yield 67%: ^{1}H NMR δ 0.89 (t, J = 7.0, 3 H), 1.18−1.34 (m, 9 H), 1.47−1.60 (m, 2 H), 2.31 (s, 3 H), 2.37 (t, J = 7.5 Hz, 3 H), 2.70 (t, J = 7.8 Hz, 2 H), 2.86 (t, J = 7.8 Hz, 2 H), 7.08 (s, 4 H); ^{13}C NMR δ 13.8, 14.0, 20.9, 22.3, 22.6, 23.8, 25.8, 29.2, 29.3, 31.8, 42.7, 43.0, 44.3, 128.1, 129.1, 135.4, 138.0, 210.3.

2,8-Dimethylnonan-5-one (14f) was prepared from 1-bromo-3-methylbutane and isopropylmagnesium bromide as a yellow oil and purified by column chromatography (silica gel, hexane/Et_2O, 10:1), yield 49%: ^{1}H NMR δ 0.88 (d, J = 6.2 Hz, 12 H), 1.43−1.61 (m, 6 H), 2.40 (t, J = 7.5 Hz, 4 H); ^{13}C NMR δ 22.3, 27.7, 32.7, 40.8, 211.7.

4-Methyl-1-phenylpentan-3-one (14g) was prepared from 2-bromopropane and phenylmagnesium bromide as a yellow oil and purified by column chromatography (silica gel, hexane/Et_2O, 10:1), yield 40%: ^{1}H NMR δ 1.07 (d, J = 7.0 Hz, 6 H), 2.50−2.62 (m, 1 H), 2.76 (t, J = 7.0 Hz, 2 H), 2.89 (t, J = 7.0 Hz, 2 H), 7.14−7.23 (m, 3 H), 7.24−7.31 (m, 2 H); ^{13}C NMR δ 18.0, 29.7, 40.8, 41.8, 125.9, 128.2, 128.3, 141.2, 213.5.

2,8-Dimethylnonan-3-one (14h) was prepared from 2-bromopropane and (3-methylbutyl)magnesium bromide as a yellow oil and purified by column chromatography (silica gel, hexane/Et_2O, 10:1), yield 33%: ^{1}H NMR δ 0.87 (d, J = 6.6 Hz, 6 H), 1.10 (d, J = 7.0 Hz, 6 H), 1.12−1.24 (m, 2 H), 1.25−1.34 (m, 2 H), 1.49−1.60 (m, 3 H), 2.45 (t, J = 7.4 Hz, 2 H), 2.61

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(heptet, J = 7.0 Hz, 1 H); ^{13}C NMR δ 18.2, 22.5, 24.0, 27.1, 27.8, 38.7, 40.3, 40.7, 214.8.

Cyclohexyl 2-phenylethyl ketone (14i) was prepared from bromocyclohexane and phenylmagnesium bromide as a yellow oil and purified by column chromatography (silica gel, hexane/Et_2O, 10:1), yield 31%: ^{1}H NMR δ 1.15–1.40 (m, 5 H), 1.62–1.70 (m, 1 H), 1.70–1.87 (m, 4 H), 2.25–2.35 (m, 1 H), 2.76 (t, J = 7.0 Hz, 2 H), 2.87 (t, J = 7.0 Hz, 2 H), 7.15–7.21 (m, 3 H), 7.22–7.30 (m, 2 H); ^{13}C NMR δ 25.6, 25.8, 28.3, 29.6, 42.1, 50.8, 125.9, 128.2, 128.3, 141.3, 212.9.

Preparation of α-Bromoalkyl Ketones 15. Representative Procedure for 3-Bromoundecan-4-one (15a). *N*-(α-Ethoxyallyl)benzotriazole (3.03 g, 15 mmol) was stirred with butyllithium (8.5 mL, 2 M, 17 mmol) in THF (100 mL) at −78 °C for 5 min followed by stirring with a halide (1-bromoheptane for **15a**, 2.7 g, 15 mmol) at −78 °C for 4 h. A Grignard reagent in diethyl ether (methylmagnesium bromide for **15a**, 30 mmol in 30 mL diethyl ether) was added at −78 °C, and the mixture was warmed to 20 °C before being heated under reflux for 10 h. The reaction was quenched with water (10 mL) and extracted with diethyl ether. The extract was washed with NaOH (2 N, 25 mL) and dried ($MgSO_4$) and the solvent removed to give an oil which was dissolved in CCl_4 (50 mL). To the solution was added Br_2 (2.6 g, 16.5 mmol) in CCl_4 (20 mL) dropwise at 0 °C, and the reaction mixture was stirred at 0 °C for 2 h and then at 20 °C for 1 h. The reaction was quenched with water and extracted with diethyl ether (3 × 40 mL). The extract was washed with NaOH (2 N, 3 × 15 mL) and dried ($MgSO_4$) and the solvent removed to give a brown oil with >95% purity of **15a** based on the NMR spectra, yield 85%. The analysis sample was purified by column chromatography (silica gel, hexane/Et_2O, 5:1): ^{1}H NMR δ 0.75–0.87 (m, 3 H), 0.98 (t, J = 7.3 Hz, 3 H), 1.19–1.38 (m, 8 H), 1.85–1.99 (m, 2 H), 2.02–2.14 (m, 2 H), 4.60 (t, J = 7.3 Hz, 0.5 H), 4.66 (t, J = 7.3 Hz, 0.5 H); ^{13}C NMR δ 11.9, 14.1, 22.5, 26.1, 27.2, 28.7, 31.5, 32.5, 50.1, 51.8, 194.4.

6-Bromo-2-methylundecan-5-one (15b) was prepared from 1-bromo-3-methybutane and butylmagnesium bromide as an brown oil in 90% yield (crude product with >95% purity based on the NMR spectra). The analysis sample was purified by column chromatography (silica gel, hexane/Et_2O, 5:1): ^{1}H NMR δ 0.85–1.03 (m, 9 H, overlapped signals of three methyl groups), 1.25–1.53 (m, 8 H), 1.70–1.82 (m, 1 H), 1.85–2.05 (m, 3 H), 2.07–2.20 (m, 1 H), 4.75 (t, J = 7.3 Hz, 0.5 H), 4.81 (t, J = 7.3 Hz, 0.5 H); ^{13}C NMR δ 13.9, 22.0, 22.7, 26.2, 26.8, 31.1, 32.5, 41.2, 49.3, 50.2, 194.2.

Preparation of 5-(Benzotriazol-1-yl)-5-ethoxyhept-6-en-2-one (16). The deep green solution of anion **12** as prepared for **13a** from **11** (2.0 g, 10.0 mmol) was stirred with methyl vinyl ketone (0.7 g, 10 mmol) for 3 h at −78 °C. The mixture was quenched with water (30 mL) at −78 °C and extracted with diethyl ether (3 × 40 mL) at ambient temperature. The extract was washed with NaOH (2 N, 2 × 30 mL) and dried ($MgSO_4$) and the solvent removed to give **16** which was purified by column chromatography (silica gel, hexane/Et_2O, 5:1) to give a yellow oil, yield 84%: ^{1}H NMR δ 1.10 (t, J = 7.0 Hz, 3 H), 2.18 (s, 3 H), 2.56–2.62 (m, 2 H), 2.81–2.98 (m, 2 H), 2.99–3.08 (m, 1 H), 3.27–3.38 (m, 1 H), 5.49 (d, J = 10.9 Hz, 1 H), 5.57 (d, J = 17.3 Hz, 1 H), 6.25 (dd, J = 17.3, 10.9 Hz, 1 H), 7.35–7.48 (m, 2 H), 7.80 (d, J = 8.2 Hz, 1 H), 8.06 (d, J = 8.2 Hz, 1 H); ^{13}C NMR δ 14.7, 30.0, 37.5, 58.2, 93.8, 112.8, 118.2, 119.7, 124.0, 127.2, 132.0, 135.9, 146.6, 206.8.

Preparation of Trimethylsilyl 3-(Benzotriazol-1-yl)-3-ethoxy-6-methyldec-1-en-6-yl Ether (17). A crude mixture of 5-(benzotriazol-1-yl)-5-ethoxyhept-6-en-2-one (**16**) prepared from **11** (2.0 g, 10.0 mmol) was dissolved in diethyl ether and stirred with butylmagnesium bromide (12 mmol in 12 mL of diethyl ether) for 2 h at 0 °C. The reaction mixture was quenched with saturated NH_4Cl aqueous solution (40 mL) and extracted with diethyl ether (3 × 30 mL). The extract was washed with NaOH (2 N, 15 mL) and dried ($MgSO_4$) and the solvent removed to give an oil. This was dissolved in THF (100 mL) and stirred with LDA (11.0 mmol) at −78 °C for 10 min, followed by stirring with trimethylsilyl chloride (14.5 mmol) at −78 °C for 2 h and then at 20 °C for 10 h. The reaction was quenched with water (20 mL) and extracted with diethyl ether (2 × 30 mL) and then washed with saturated $NaHCO_3$ (2 × 20 mL) and dried ($MgSO_4$). Removal of the solvent gave **16** which was purified by column chromatography (silica gel, AcOEt/hexane, 1:5) to give a yellow oil, in 48% yield: ^{1}H NMR δ 0.12 (s, 4.5 H), 0.14 (s, 4.5 H), 0.92 (t, J = 7.2 Hz, 3 H), 1.15 (t, J = 7.1 Hz, 3 H), 1.27 (s, 3 H), 1.28–1.70 (m, 8 H), 2.57–2.87 (m, 2 H), 3.05–3.15 (m, 1 H), 3.37–3.48 (m, 1 H), 5.50 (ddd, J = 10.7, 3.4, 1.0 Hz, 1 H), 5.53 (dd, J = 17.5, 4.4 Hz, 1 H), 6.27–6.40 (m, 1 H), 7.38–7.52 (m, 2 H), 7.89 (d, J = 8.2 Hz, 1 H), 8.11 (d, J = 8.2 Hz, 1 H); ^{13}C NMR δ 2.5, 2.6, 14.1, 14.8, 23.2, 26.3, 26.6, 27.3, 27.7, 31.0, 34.9, 41.7, 42.2, 57.9, 75.5, 94.8, 113.0, 117.4, 119.7, 123.9, 126.9, 132.2, 136.7, 146.7.

Preparation of 1,4-Diketones 18. Representative Procedure for 7-Phenylheptane-2,5-dione (18a). The crude mixture of **16** prepared from **11** (2.7 g, 13.5 mmol) in THF (100 mL) was stirred with LDA (9.3 mL, 1.5 M, 14 mmol) at −78 °C for 15 min, followed by addition Me_3SiCl (1.6 g, 15 mmol) and stirring for a further 12 h at 20 °C. The mixture was heated under reflux with phenylmagnesium bromide (27 mmol in 27 mL of diethyl ether) for 12 h. The reaction was quenched with water (10 mL) at 0 °C and extracted with diethyl ether (4 × 50 mL). The solvent was removed and the residue stirred with hydrochloric acid (2 N, 10 mL) in methanol (20 mL) for 5 h. After removal of most of the methanol and water, the residue was extracted with CH_2Cl_2 (3 × 30 mL). The extract was washed with NaOH (2 N, 2 × 20 mL) and dried ($MgSO_4$) and the solvent removed to give **18a** which was purified by column chromatography (silica gel, diethyl ether) to give a brown oil, yield 51%: ^{1}H NMR δ 2.15 (s, 3 H), 2.62–2.73 (m, 4 H), 2.75–2.84 (m, 2 H), 2.87–2.95 (m, 2 H), 6.53-6.71 (m, 3 H), 7.12–7.31 (m, 2 H); ^{13}C NMR δ 29.4, 29.5, 35.9, 36.6, 43.8, 125.8, 128.0, 128.2, 140.7, 206.8, 208.1.

7-(*p*-Methylphenyl)heptane-2,5-dione (18b) was prepared from (*p*-methylphenyl)magnesium bromide as a yellow oil and purified by column chromatography (silica gel, diethyl ether), yield 54%: ^{1}H NMR δ 2.18, (s, 3 H), 2.31 (s, 3 H), 2.63–2.73 (m, 4 H), 2.75–2.83 (m, 2 H), 2.84–2.92 (m, 2 H), 7.08 (s, 4 H); ^{13}C NMR δ 21.1, 29.4, 30.0, 36.3, 37.0, 44.5, 128.2, 129.2, 135.6, 138.0, 207.3, 208.6.

Preparation of 6-Methyl-6-((trimethylsilyl)oxy)-1-phenyldecan-3-one (20). Crude **17** prepared from **11** (2.7 g, 13.5 mmol) *via* **16** was heated in THF (100 mL) with phenylmagnesium bromide (17 mmol in 100 mL of THF) under reflux for 10 h. The reaction was quenched with water (10 mL) and extracted with diethyl ether (3 × 40 mL). The extract was washed with NaOH (2 N, 25 mL) and dried ($MgSO_4$) and the solvent removed to give an oil which was hydrolyzed to **20** during column chromatography purification (silica gel, Et_2O) to give a yellow oil, overall yield 24%: ^{1}H NMR δ 0.01 (s, 9 H), 0.82 (t, J = 6.8 Hz, 3 H), 1.07 (s, 3 H), 1.12–1.22 (m, 4 H), 1.30–1.37 (m, 2 H), 1.54–1.70 (m, 2 H), 2.34 (t, J = 7.8 Hz, 2 H), 2.67 (t, J = 7.6 Hz, 2 H), 2.82 (t, J = 7.6 Hz, 2 H), 7.09–7.11 (m, 3 H), 7.16–7.21 (m, 2 H); ^{13}C NMR δ 2.6, 14.1, 23.2, 26.5, 27.3, 29.9, 35.4, 38.0, 42.4, 44.2, 75.3, 126.0, 128.3, 128.4, 141.2, 210.3.

Preparation of α-Hydroxyalkyl Ketones 23. Representative Procedure for 1-Hydroxy-1-(*p*-methylphenyl)-4-phenylbutan-2-one (23a). *N*-(α-Ethoxyallyl)benzotriazole (**2**, 2.03 g, 10 mmol) was stirred with butyllithium (5.5 mL, 2 M, 11 mmol) in THF (100 mL) at −78 °C for 5 min followed by stirring with the aldehyde (*p*-tolualdehyde for **23a**, 1.2 g, 10 mmol), and the resulting mixture was stirred at −78 °C for 4 h. Me_3SiCl (1.3 g, 12 mmol) was added, and the reaction mixture was stirred for 12 h at 20 °C and then heated under reflux with the Grignard reagent (phenylmagnesium bromide for **23a**, 20 mmol in 30 mL diethyl ether) for 12 h. The reaction was stirred with HCl (2 N, 10 mL) at 20 °C for 10 h and extracted with diethyl ether. The extract was dried ($MgSO_4$) and the solvent removed to give **23a** which was purified by column chromatography (silica gel, Et_2O/petroleum ether, 1:6) to give a yellow oil, yield 47%: ^{1}H NMR δ 2.31 (s, 3 H), 2.58–2.64 (m, 2 H), 2.70–2.90 (m, 2 H), 4.32 (d, J = 4.3 Hz, 1 H), 4.96 (d, J = 4.3 Hz, 1 H), 7.02 (d, J = 6.5 Hz, 2 H), 7.11–7.22 (m, 6 H), 7.30–7.33 (m, 1 H); ^{13}C NMR δ 21.0, 29.5, 39.3, 79.5,

125.3, 126.1, 127.2, 128.1, 128.3, 128.3, 129.5, 134.8, 138.4, 140.2, 208.7.

1-Hydroxy-1-(*p*-methylphenyl)pentan-2-one (23b) was prepared from *p*-tolualdehyde and methylmagnesium bromide as a yellow oil and purified by column chromatography (silica gel, Et_2O/petroleum ether, 1:6), yield 25%: ^1H NMR δ 0.79 (t, J = 7.5 Hz, 3 H), 1.44–1.61 (m, 2 H), 2.29 (t, J = 6.7 Hz, 2 H), 2.33 (s, 3 H), 4.36 (d, J = 4.4 Hz, 1 H), 5.02 (d, J = 4.4 Hz, 1 H), 7.15–7.21 (m, 4 H); ^{13}C NMR δ 13.4, 17.0, 21.0, 39.5, 79.4, 127.2, 129.5, 135.1, 138.3, 209.6.

1-Hydroxy-1-methyl-1-phenylpentan-2-one (23c) was prepared from acetophenone and methylmagnesium bromide as a yellow oil and purified by column chromatography (silica gel, Et_2O/petroleum ether, 1:6), yield 20%: ^1H NMR δ 0.75 (t, J = 7.5 Hz, 3 H), 1.40–1.60 (m, 2 H), 1.76 (s, 3 H), 2.20–2.45 (m, 2 H), 4.65 (s, 1 H), 7.25–7.45 (m, 5 H); ^{13}C NMR δ 13.4, 17.3, 24.0, 37.4, 79.7, 126.0, 127.9, 128.5, 141.6, 211.8.

Preparation of Benzotriazole Derivatives 24. Representative Procedure for 3-(Benzotriazol-1-yl)-3-ethoxy-1-phenylpent-4-en-2-one (24a). *N*-(α-Ethoxyallyl)benzotriazole (**2**, 2.03 g, 10.0 mmol) was stirred with butyllithium (5.5 mL, 2 M, 11 mmol) in THF (100 mL) at −78 °C for 10 min, followed by stirring with the ester (ethyl 2-phenylacetate for **24a**, 1.65 g, 10.0 mmol), and the mixture was stirred at −78 °C for 4 h. The reaction was quenched with water (30 mL) and extracted with diethyl ether (3 × 40 mL). The extract was dried ($MgSO_4$) and the solvent removed to give an oil which was purified by column chromatography (silica gel, EtOAc/hexane, 1:5) to give a white solid, yield 90%: mp 65–66 °C; ^1H NMR δ 1.11 (t, J = 7.1 Hz, 3 H), 2.80–2.92 (m, 1 H), 3.50–3.61 (m, 1 H), 3.94 (d, J = 15.9 Hz, 1 H), 4.13 (d, J = 15.9 Hz, 1 H), 5.82 (d, J = 10.8 Hz, 1 H), 5.89 (d, J = 17.5 Hz, 1 H), 6.88 (dd, J = 17.5, 10.8 Hz, 1 H), 7.18–7.29 (m, 6 H), 7.32–7.37 (m, 2 H), 8.08–8.10 (m, 1 H); ^{13}C NMR δ 14.8, 43.1, 59.8, 96.3, 111.2, 120.0, 121.5, 124.3, 126.9, 127.8, 128.3, 129.6, 130.3, 132.0, 133.0, 146.1, 198.4.

3-(Benzotriazol-1-yl)-3-ethoxydodec-1-en-4-one (24b) was prepared from ethyl octanoate as a yellow oil and purified by column chromatography (silica gel, Et_2O/petroleum ether, 1:6), yield 72%: ^1H NMR δ 0.88 (t, J = 6.6 Hz, 3 H) 1.10 (t, J = 7.0 Hz, 3 H), 1.21–1.37 (m, 10 H), 1.54–1.70 (m, 2 H), 2.66–2.89 (m, 3 H), 3.52-3.57 (m, 1 H), 5.80 (d, J = 10.8 Hz, 1 H), 5.86 (d, J = 17.5 Hz, 1 H), 6.88 (dd, J = 17.5, 10.8 Hz, 1 H), 7.39–7.49 (m, 3 H), 8.11 (d, J = 8.2 Hz, 1 H); ^{13}C NMR δ 14.0, 14.8, 22.5, 23.5, 28.9, 29.0, 29.1, 31.6, 36.4, 59.8, 96.3, 111.3, 120.1, 121.0, 124.3, 127.8, 130.6, 132.1, 146.2, 201.4.

Preparation of 2-(*N*-Methyl-*N*-phenylamino)-5-phenylcyclopent-2-enone (25). *N*-(α-Ethoxyallyl)benzotriazole (**2**, 2.03 g, 10 mmol) was stirred with butyllithium (5.5 mL, 2 M, 11 mmol) in THF (100 mL) at −78 °C for 10 min, followed by stirring with ethyl 2-phenylacetate (1.65 g, 10.0 mmol). The mixture was stirred at −78 °C for 4 h, quenched with water (30 mL) at −78 °C, and extracted with diethyl ether (2 × 40 mL). The extract was washed with NaOH (2 N, 2 × 30 mL) and dried ($MgSO_4$) and the solvent removed to give an oil which was heated under reflux with *N*-methylaniline (1.2 g, 11 mmol) in toluene (50 mL) for 12 h. The reaction was quenched with water (20 mL) at 20 °C and extracted with diethyl ether (2 × 30 mL). The extract was dried ($MgSO_4$) and the solvent removed to give **25** which was purified by column chromatography (silica gel, AcOEt/hexane, 1:5) to give a yellow oil, yield 54%: ^1H NMR δ 2.58–2.67 (m, 1 H), 3.08 (ddd, J = 18.7, 7.0, 3.2 Hz, 1 H), 3.17 (s, 3 H), 3.60 (dd, J = 7.0, 2.4 Hz, 1 H), 6.83 (t, J = 3.2 Hz, 1 H), 6.89–6.94 (m, 3 H), 7.16–7.31 (m, 7 H); ^{13}C NMR δ 33.3, 39.3, 51.2, 120.1, 121.9, 126.6, 126.7, 127.4, 128.5, 128.6, 137.6, 139.2, 147.3, 147.6, 203.1.

Preparation of Diosphenols 27 and 28 and Benzotriazole Derivative 29. Representative Procedure for 2-Ethoxy-5-phenylcyclopent-2-enone (27a). *N*-(α-Ethoxyallyl)benzotriazole (**2**, 2.03 g, 10 mmol) was stirred with butyllithium (5.5 mL, 2 M, 11 mmol) in THF (100 mL) at −78 °C for 10 min, followed by stirring with the ester (ethyl 2-phenylacetate for **24a**, 1.65 g, 10.0 mmol) at −78 °C for 4 h. To the mixture was added NaH (0.36 g, 15 mmol) at −78 °C, and the resulting mixture was stirred at 20 °C for 12 h. The reaction was quenched with water (30 mL) and extracted with diethyl ether (2 × 40 mL). The extract was washed with NaOH (2 N, 2 × 30 mL) and dried ($MgSO_4$) and the solvent removed to give **27a**, which was purified by column chromatography to give a yellow oil (silica gel, AcOEt/hexane, 1:5), yield 62%: ^1H NMR δ 1.36 (t, J = 7.0 Hz, 3 H), 2.50 (ddd, J = 17.8, 2.8, 2.6 Hz, 1 H), 2.98 (ddd, J = 17.8, 6.9, 3.1 Hz, 1 H), 3.52 (dd, J = 6.9, 2.6 Hz, 1 H), 3.92 (q, J = 7.0 Hz, 2 H), 6.44 (t, J = 3.1 Hz, 1 H), 7.10–7.29 (m, 5 H); ^{13}C NMR δ 14.0, 31.9, 49.5, 65.2, 126.5, 127.3, 128.2, 128.3, 139.1, 155.2, 201.5.

2-Ethoxy-5-(1-naphthyl)cyclopent-2-enone (27b) was prepared from ethyl 1-naphthoate and purified by column chromatography (silica gel, AcOEt/hexane, 1:5) to give a yellow solid, yield 67%: mp 118–119 °C; ^1H NMR δ 1.41 (t, J = 7.0 Hz, 3 H), 2.53 (ddd, J = 17.9, 2.8, 2.6 Hz, 1 H), 3.11 (ddd, J = 17.9, 6.9, 2.4 Hz, 1 H), 3.95 (q, J = 7.0 Hz, 2 H), 4.15 (dd, J = 6.9, 2.4 Hz, 1 H), 6.38 (t, J = 3.1 Hz, 1 H), 7.20 (d, J = 7.2 Hz, 1 H), 7.36 (t, J = 7.3 Hz, 1 H), 7.40–7.48 (m, 2 H), 7.68–7.75 (m, 2 H), 7.77–7.85 (m, 1 H); ^{13}C NMR δ 14.2, 32.2, 47.7, 65.5, 123.1, 125.3, 125.5, 125.8, 126.1, 127.6, 128.8, 131.5, 133.9, 135.8, 155.9, 202.3.

2-Ethoxy-5-(*p*-methoxyphenyl)cyclopent-2-enone (27c) was prepared from ethyl *p*-methoxybenzoate and purified by column chromatography (silica gel, AcOEt/hexane, 1:5) to give a yellow solid, mp 94–95 °C, yield 57%: ^1H NMR δ 1.39 (t, J = 7.0 Hz, 3 H), 2.51 (ddd, J = 17.8, 2.6, 2.6 Hz, 1 H), 3.03 (ddd, J = 17.8, 6.8, 3.2 Hz, 1 H), 3.52 (dd, J = 6.8, 2.2 Hz, 1 H), 3.75 (s, 3 H), 3.96 (q, J = 7.0 Hz, 2 H), 6.44 (t, J = 3.1 Hz, 1 H), 6.84 (d, J = 8.6 Hz, 2 H), 7.07 (d, J = 8.6 Hz, 2 H); ^{13}C NMR δ 14.2, 32.2, 49.0, 55.1, 65.4, 114.0, 126.3, 128.5, 131.3, 155.5, 158.4, 202.1.

5-(*p*-Chlorophenyl)-2-ethoxycyclopent-2-enone (27d) was prepared from ethyl *p*-chlorobenzoate and purified by column chromatography (silica gel, AcOEt/hexane, 1:5) to give a yellow solid, yield 55%: mp 138–140 °C; ^1H NMR δ 1.40 (t, J = 7.0 Hz, 3 H), 2.52 (ddd, J = 18.1, 2.6, 2.7 Hz, 1 H), 3.03 (ddd, J = 18.1, 6.8, 3.2 Hz, 1 H), 3.55 (dd, J = 6.8, 2.3 Hz, 1 H), 3.94 (q, J = 7.0 Hz, 2 H), 6.47 (t, J = 3.1 Hz, 1 H), 7.10 (d, J = 8.4 Hz, 2 H), 7.25 (d, J = 8.4 Hz, 2 H); ^{13}C NMR δ 14.1, 31.9, 49.0, 65.5, 126.5, 128.6, 128.9, 132.5, 137.7, 155.4, 201.2.

2-Ethoxy-5-methylcyclopent-2-enone (28a) was prepared from ethyl propionate as a yellow oil and purified by column chromatography (silica gel, AcOEt/hexane, 1:5), yield 28%: ^1H NMR δ 1.21, (d, J = 7.5 Hz, 3 H), 1.40 (t, J = 7.1 Hz, 3 H), 2.11 (ddd, J = 17.6, 2.8, 2.6 Hz, 1 H), 2.40–2.45 (m, 1 H), 2.79 (ddd, J = 17.6, 6.4, 3.2 Hz, 1 H), 3.94 (q, J = 7.1 Hz, 2 H), 6.33 (t, J = 3.1 Hz, 1 H); ^{13}C NMR δ 14.2 16.2, 16.3, 31.0, 38.4, 65.2, 125.6, 155.4, 205.2.

5-Butyl-2-ethoxycyclopent-2-enone (28b) was prepared from ethyl pentanonate as a yellow oil and purified by column chromatography (silica gel, AcOEt/hexane, 1:5), yield 36%: ^1H NMR δ 0.88–0.93 (m, 3 H), 1.27–1.35 (m, 5 H), 1.40 (t, J = 7.1 Hz, 3 H), 1.82–1.85 (m, 1 H), 2.20 (ddd, J = 16.7, 3.0, 3.0 Hz, 1 H), 2.32–2.38 (m, 1 H), 2.70 (ddd, J = 16.7, 6.3, 3.2 Hz, 1 H), 3.93 (q, J = 7.0 Hz, 2 H), 6.34 (t, J = 3.1 Hz, 1 H); ^{13}C NMR δ 13.8, 14.2, 22.5, 28.9, 29.0, 31.1, 43.8, 65.2, 125.9, 155.9, 204.8.

Ethyl 1-(benzotriazol-1-yl)-1-propenyl ether (29) was isolated as a 5:1 mixture of two isomers in the preparation of **28a** by column chromatography (silica gel, AcOEt/hexane, 1:5), yellow oil, yield 23%: ^1H NMR δ 1.28 (t, J = 7.0 Hz, 3 H), [1.35 (t, J = 7.1 Hz, 3 H, minor isomer), [1.54 (d, J = 7.0 Hz, 3 H, minor isomer)], 1.91 (d, J = 7.0 Hz, 3 H), 3.67 (q, J = 7.0 Hz, 2 H), [3.93 (q, J = 7.1 Hz, 2 H, minor isomer)], [5.12 (q, J = 7.0 Hz, 2 H, minor isomer)], 5.45 (q, J = 7.0 Hz, 1 H), 7.38 (t, J = 7.2 Hz, 1 H), 7.51 (t, J = 7.2 Hz, 1 H), 7.71 (d, J = 8.3 Hz, 1 H), 8.06 (d, J = 8.3 Hz, 1 H); ^{13}C NMR δ 10.2, 14.5, 66.3, 104.8, 110.9, 119.7, 124.1, 128.0, 132.0, 143.5, 145.4.

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