JOC Article

β-Acylvinyl Anion and Dianion Equivalents: Lithiation of 1-[(2*EZ*)-3-Chloroprop-2-enyl]-1*H*-1,2,3-benzotriazole: Preparation and Elaboration of 1-(2-Oxiranylvinyl)-1*H*-benzotriazoles

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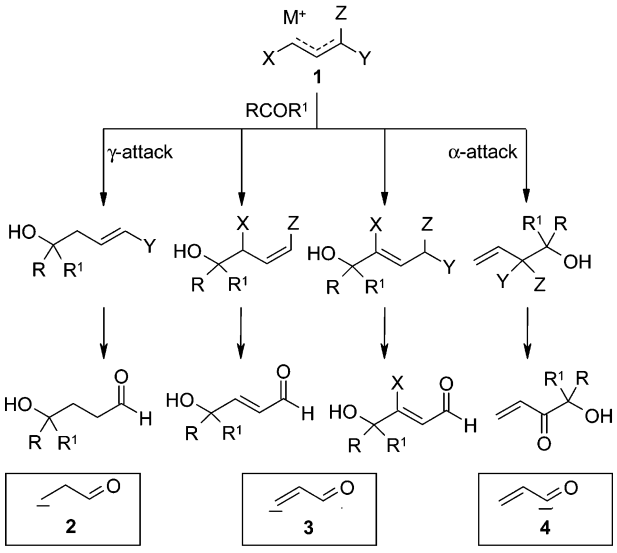
The allyllithium generated from 1-[(2*EZ*)-3-chloroprop-2-enyl]-1*H*-1,2,3-benzotriazole (**5**) and LDA, in the presence of HMPA, reacts with enolizable and nonenolizable carbonyls solely at the CCl terminus to give 1-(2-oxiranylvinyl)benzotriazoles **6a**−**g** in 61−82% yields. Allyllithiums generated from **6a**,**c** reacted exclusively at the CBt terminus to give **10a**−**d** in 68−88% yields. Acidic hydrolysis of (oxiranylvinyl)benzotriazoles **6a**−**g** and **10a**−**d** provided 4-hydroxyalk-2-en-1-one derivatives **12a**,**b**,**c**,**e**,**g**, **13a**−**d**, and furan **14** in 54−86% yields.

Introduction

Regiocontrol in the deprotonation-substitution of unsymmetrically substituted allylic systems is challenging. Heteroatom-stabilized allylic anions of type **1** are synthetically important as 3-carbon homologating agents.[1] Species **1** can act as diverse reversed-polarity equivalents: homoenolate anions **2**,[2] β-acylvinyl anions **3**,[3] or α,β-unsaturated acyl anions **4**[4a−c] (Scheme 1). The α/γ-regiochemistry of ambident allylic anions is controlled in a complex manner by several factors, such as the nature of the heteroatom(s), charge delocalization, steric effects, countercation, type of electrophile, solvation, and additives.[5] Allylic anions stabilized by a wide variety of heteroatoms including oxygen, sulfur, selenium, nitrogen, phosphorus, boron, silicon, and halogens have been examined.[6]

Prior to the advent of the in situ quench procedure (Barbier technique),[7] 1-chloroallyllithiums were underutilized because of facile self-coupling. 1-Chloroallyllithiums preferentially react at the CH_2 terminus with carbonyl compounds and at the CCl terminus with aliphatic halides.[8a−c] However, replacement of the lithium counterion with zinc results in a regioselective reaction at the CCl terminus with aldehydes as electrophiles.[9] Chloroallyllithiums generated from *trans*-cinnamyl chloride and 2-[(1*E*)-3-chloroprop-1-enyl]-1,3-benzothiazole react with

SCHEME 1



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nonenolizable ketones and aromatic aldehydes at the CCl terminus exclusively.[10]

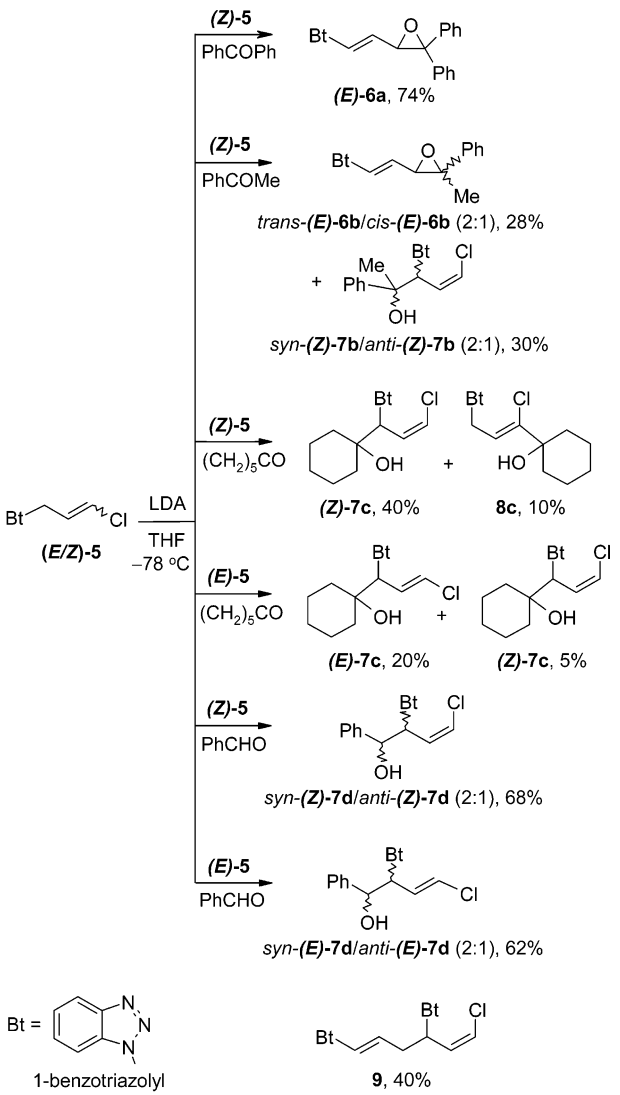
The regioselectivity of additions of 1,1-dichloroallyllithium to carbonyl compounds has been suggested to depend on electronic factors. Carbonyl compounds with electron-withdrawing substituents usually favor bond formation at the CH_2 terminus, and those with electron-releasing groups favor bond formation at the CCl_2 terminus.[11] The attack could be directed to the CCl_2 terminus exclusively by the presence of additives such as ^{t}BuOK[12] or cryptand[2.2.1].[13]

1-Chloro-(1-trimethylsilyl)allyllithium is less selective as compared to 1,1-dichloroallyllithium, and both α- and γ-adducts result from reactions with carbonyl compounds.[14] The anion derived from (*E*)-3-chloro-1-phenylsulfonylprop-1-ene reacts with aldehydes exclusively at the CCl terminus.[15] Both (*E*)- and (*Z*)-γ-chloroallylphosphonamides react exclusively at the CCl terminus with α,β-unsaturated ketones to give the corresponding cyclopropanes.[16]

The synthetic utility of allyllithiums generated from 1-allylbenzotriazole,[17a,b] 1-(1-ethoxyprop-2-enyl)-1*H*-1,2,3-benzotriazole,[18] 3-(benzotriazol-1-yl)-1-ethoxyprop-1-ene,[19] and 1-(3-morpholinoprop-2-enyl)benzotriazole[20] is well established. Anions generated from these *N*-allylbenzotriazoles react exclusively at the CBt terminus with aldehydes and nonhindered ketones. However, the regiochemistry is reversed to give γ-adducts when the intermediate 1-(benzotriazol-1-yl)-3-(diphenylphosphoryl)-1-ethoxyprop-1-ene is first generated in situ from 1-(1-ethoxyprop-2-enyl)-1*H*-1,2,3-benzotriazole; deprotonation of the phosphoryl intermediate and subsequent reaction with carbonyl compounds now result in hydroxyalkylation exclusively at the CP terminus.[21]

We now report regiospecific lithiation-substitutions of 1-[(2*EZ*)-3-chloroprop-2-enyl]-1*H*-1,2,3-benzotriazole and its utilization as β-acylvinyl anion ($^-$CH=CHCHO) or β-acylvinyl dianion ($^-$COCH=CH$^-$) equivalents.

SCHEME 2



Results and Discussion

Regioselectivity of Reactions of Lithiated (*E*)-5 and (*Z*)-5 with Carbonyl Compounds. 1-[(2*EZ*)-3-Chloroprop-2-enyl]-1*H*-1,2,3-benzotriazole (**5**) was prepared by the reaction of BtNa and (1*EZ*)-1,3-dichloroprop-1-ene. **(*Z*)-5** (47%) and **(*E*)-5** (21%) were separated by silica gel column chromatography. Unlike (1*E*)-3-chloro-1-phenylsulfonylprop-1-ene,[15] no *E*/*Z*-isomerization was observed when a 1:1 mixture of **(*E*)-5** and **(*Z*)-5** was stirred with Et_3N in $CHCl_3$ at 20 °C for 3 h. Under Barbier conditions,[7] lithiated **(*E*)-5** or **(*Z*)-5** reacted with various carbonyl compounds at the CBt terminus to give the corresponding homoallylic alcohols **7b**−**d** or at the CCl terminus to give either the corresponding (oxiranylvinyl)benzotriazoles **6a**,**b** or allylic alcohol **8c** (Scheme 2).

Lithiation of **(*Z*)-5** with LDA at −78 °C and trapping with benzophenone gave vinyloxirane **(*E*)-6a** in 74% yield as the sole product (Scheme 2). However, reaction of benzophenone with lithiated **(*E*)-5** provided a complex mixture of products having both (*Z*)- and (*E*)-configured double bonds as shown by the ^{1}H NMR spectrum.

Deprotonation of **(*Z*)-5** and reaction with acetophenone at −78 °C gave products from attack at both the CBt and

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(17) (a) Katritzky, A. R.; Wang, X.; Denisenko, A. *J. Org. Chem.* **2001**, *66*, 2850. (b) 1- or 2-Allylbenzotriazoles are known to isomerize in the presence of ^{t}BuOK in ^{t}BuOH but undergo lithiation-substitution without isomerization. For details see: Katritzky, A. R.; Li, J.; Malhotra, N. *Liebigs Ann. Chem.* **1992**, 843. (c) Absence of the isomerization of the double bond suggests the irreversible nature of lithiation-substitution. Also, no isomerization of the unreacted starting material **(*Z*)-5** was detected after reaction with benzaldehyde, benzophenone, or acetophenone as indicated by the ^{1}H NMR spectra of the crude products.
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the CCl termini in a 1:1 ratio to give (i) vinyloxiranes *trans*-**(*E*)-6b** and *cis*-**(*E*)-6b** in a combined yield of 28% in a 2:1 ratio and (ii) homoallylic alcohols **(*Z*)-7b** as mixed diastereomers in 30% yield in a 2:1 ratio. No formation of the corresponding isomerized alcohol **(*E*)-7b** was detected in the ^{1}H NMR spectrum of the crude product mixture.[17b,c] Furthermore, no change in the reaction yield or the 1:1 product ratio arising from the reaction of acetophenone at the CBt and the CCl termini was observed when the reaction was carried out at −30 °C.

Cyclohexanone reacted with the anion generated from **(*Z*)-5** preferentially at the CBt terminus to give **(*Z*)-7c** in 40% yield; the attack at the CCl terminus now resulted in allylic alcohol **8c** in 10% yield instead of a vinyloxirane. However, the reaction of cyclohexanone with the anion from **(*E*)-5** gave the products from the reaction at the CBt terminus exclusively, with isomerization of the double bond to give alcohols **(*E*)-7c** and **(*Z*)-7c** in 20% and 5% yields, respectively.

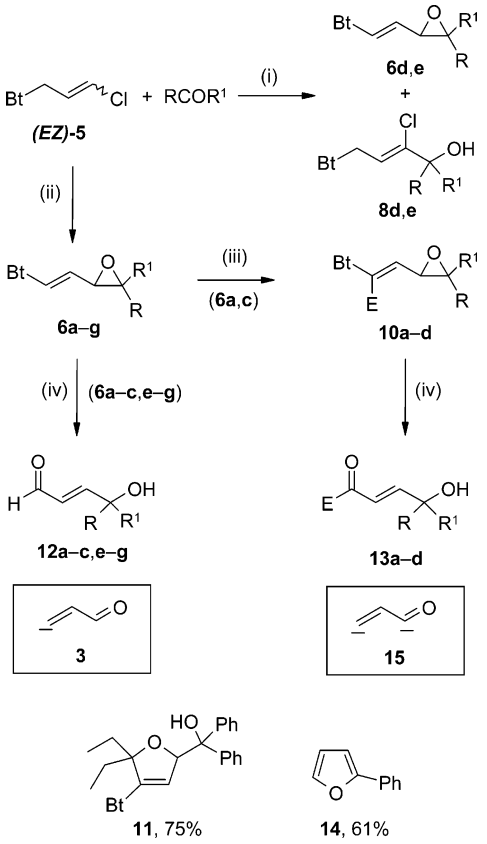
Lithiated **(*Z*)-5** and **(*E*)-5** each reacted with benzaldehyde only at the CBt terminus to provide the corresponding homoallylic alcohols **(*Z*)-7d** and **(*E*)-7d** in 68% and 62% yields, respectively. Compounds **(*Z*)-7d** and **(*E*)-7d** were each formed as a mixture of *syn*- and *anti*-diastereomers in the ratio 2:1. No *Z* → *E* isomerization was detected in the ^{1}H NMR spectrum of the crude material when **(*Z*)-5** was used as a reactant with benzaldehyde, but *E* → *Z* isomerization was evident (ca. 10% from the ^{1}H NMR spectrum of the crude product mixture). The *syn*-stereochemistry of the major isomers of **(*Z*)-7d** and **(*E*)-7d** were each unambiguously determined by X-ray crystallography.

The reaction of lithiated **(*Z*)-5** with hydrocinnamaldehyde did not give any of the expected products; only the corresponding self-coupling product (**9**) was obtained in 40% yield (Scheme 2).

Regiospecific Reactions of Lithiated (*EZ*)-5 with Carbonyl Compounds in the Presence of HMPA: Preparation of (Oxiranylvinyl)benzotriazoles. Use of coordinating solvents often results in improved regioselectivity.[22a] Indeed, only the products arising from substitution at the CCl terminus were obtained when the lithiation-substitution was performed in the presence of HMPA. Initial experiments with benzaldehyde and *p*-chlorobenzophenone conducted in THF/HMPA (ratio 10:1) resulted in substitution at the CCl terminus only. However, with benzaldehyde, the oxirane (**6d**) and the alcohol (**8d**) were obtained in 32% and 30% yields, respectively (Scheme 3). Similarly, the reaction with *p*-chlorobenzophenone provided **6e** and **8e** in 40% and 39% yields, respectively. The structure of alcohol **8d** was confirmed by X-ray crystallography. An increase in the amount of HMPA (THF/HMPA 5:1) resulted in the formation of oxiranes **(*E*)-6a**−**g** in 61−82% yields (Scheme 3, Table 1). Apparently, HMPA directs the attack of the electrophile to the CCl terminus and also facilitates ring closure to give the oxirane.[22b]

The reaction with acetophenone gave an isomeric mixture of vinyloxirane **6b** in the ratio 2:1, with *trans*- and *cis*-configuration at the oxirane ring and (*E*)-configuration ($J_{trans} \sim 14$ Hz) at the double bond in 73% yield. The major and minor isomers were separated by column chromatography, and the major isomer was assigned as *trans*-**(*E*)-6b** by single-crystal X-ray analysis. Similarly, reaction with benzaldehyde gave a mixture of *cis*-**(*E*)-6d** ($J_{vic} = 4.1$ Hz) and *trans*-**(*E*)-6d** ($J_{vic} = 1.6$ Hz) in a 2:1 ratio in 69% yield. Again, the isomers could be separated by column chromatography. With *p*-chlorobenzophenone, *p*-methoxybenzophenone, and *p*-methylbenzophenone, the respective products **(*E*)-6e**, **(*E*)-6f**, and **(*E*)-6g** were each formed as mixtures of isomers in the ratio 1:1 in 61−82% yield.

SCHEME 3[a]



[a] (i) LDA, THF/HMPA (10:1), −78 °C; (ii) LDA, THF/HMPA (5:1). −78 °C; (iii) *n*-BuLi, THF, −78 °C, E^+; (iv) *p*-TsOH, THF, reflux, 30 min. For descriptions of R, R^1, and E in **6**, **10**, **12**, and **13**, see Tables 1 and 2.

TABLE 1. Preparation of γ-Hydroxy-α,β-enals 12a,b,c,e,g via (Oxiranylvinyl)benzotriazoles 6a−g

entry	R	R^1	oxirane, yield[a] (%)	aldehyde, yield[a] (%)
1	Ph	Ph	**6a** (78)	**12a** (73)
2	Ph	Me	**6b** (73)[b]	**12b** (74)
3		$(CH_2)_5$	**6c** (72)	**12c** (62)
4	Ph	H	**6d** (69)[c]	
5	Ph	*p*-ClPh	**6e** (76)[d]	**12e** (86)
6	Ph	*p*-MeOPh	**6f** (82)[d]	
7	Ph	*p*-MePh	**6g** (61)[d]	**12g** (54)

[a] Isolated yields. [b] Isolated yield of *trans*- and *cis*-isomers is 50% and 23%, respectively. [c] Isolated yield of *trans*- and *cis*-isomers is 47% and 22%, respectively. [d] Product is a mixture of isomers in the ratio 1:1.

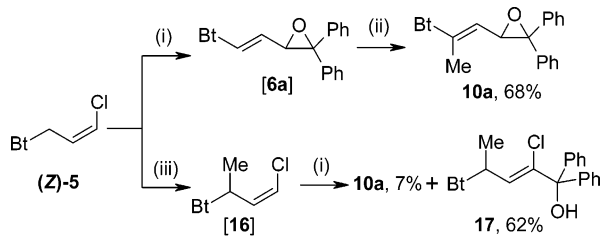
(22) (a) Still, W. C.; Macdonald, T. L. *J. Org. Chem.* **1976**, *41*, 3620. (b) Apparently, in the presence of HMPA, lithiation-substitution proceeds in a reversible manner, and formation of the oxirane ring drives the equilibrium in the forward direction.

TABLE 2. Preparation of γ-Hydroxy-α,β-enones 13a−d via (Oxiranylvinyl)benzotriazoles 10a−d

entry	R	R^1	E	oxirane, yield[a] (%)	ketone, yield[a] (%)
1	Ph	Ph	Me	**10a** (88)	**13a** (76)
2	Ph	Ph	Et	**10b** (72)	**13b** (78)
3	Ph	Ph	Bu	**10c** (68)	**13c** (82)
4	$(CH_2)_5$		Me	**10d** (85)	**13d** (56)

[a] Isolated yields.

SCHEME 4[a]



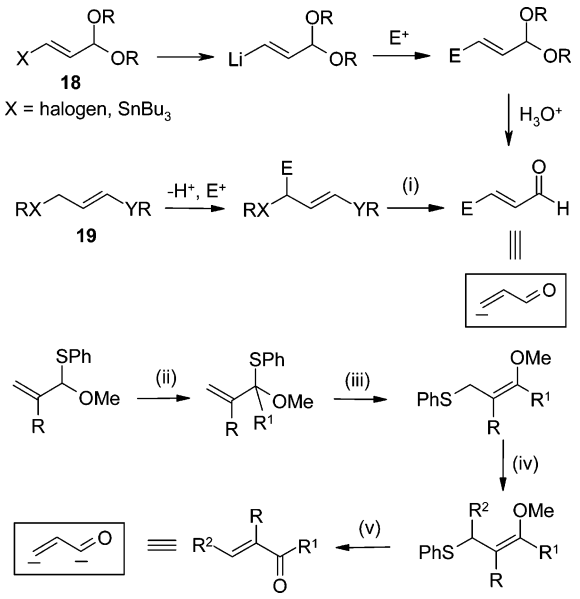
[a] (i) LDA, THF, PhCOPh, −78 °C; (ii) BuLi, MeI, −78 °C; (iii) LDA, THF, MeI, −78 °C

Regiospecific Lithiation-Substitutions of (Oxiranylvinyl)benzotriazoles. Vinyloxiranes **6a**,**c** were further lithiated and reacted with alkyl halides to provide alkylation exclusively at the CBt terminus. Lithiation of **6a** with BuLi and trapping with various alkyl iodides at −78 °C gave the alkylated products **10a**−**c** in 68−88% yields (Scheme 3, Table 2). Interestingly, the *E*-stereochemistry of the double bond is retained, which is evident from the X-ray structure of **10a** and also by $J_{allylic} = 1$ Hz between the methyl group and the allylic proton attached to the oxirane ring. Similarly, lithiation and subsequent methylation of **6c** provided vinyloxirane **10d** in 85% yield. However, the procedure was limited to the use of alkyl iodides as electrophiles; the use of 3-pentanone to trap lithiated **6a** resulted in the oxirane ring opening to give **11** in 75% yield. The structure for compound **11** was unambiguously determined by X-ray crystallography. Thus, both alkyl iodides and carbonyl compounds react at the CBt terminus of (oxiranylvinyl)-benzotriazole.

Starting from **(*Z*)-5**, a one-pot, two-step procedure using the sequence **(*Z*)-5** → [**6a**] → **10a** gave **10a** in 68% yield (Scheme 4). However, changing the sequence to **(*Z*)-5** → [**16**] → **10a** resulted in a low yield of **10a** (7%) along with **17** in 62% yield. The regiochemistry of the addition of MeI to the lithiated **(*Z*)-5** has been assigned by analogy to the ^{1}H NMR spectra of 1-(1-methylprop-2-enyl)-1*H*-1,2,3-benzotriazole[17b] and 3-chlorobut-1-ene.[23] The methine proton in 1-(1-methylprop-2-enyl)-1*H*-1,2,3-benzotriazole [CH_2═CH−C*H*(Me)Bt] and in 3-chlorobut-1-ene [CH_2═CH−C*H*(Me)Cl] appears at 5.57 and 4.34 ppm, respectively; the ^{1}H NMR spectrum of **16** showed the signal for the allylic methine proton at 5.95 ppm. Furthermore, no *Z* → *E* isomerization was observed.

Acid-Catalyzed Hydrolysis of (Oxiranylvinyl)-benzotriazoles: Preparation of α,β-Unsaturated Carbonyl Compounds. The synthetic utility of heteroatom-stabilized allylic systems as β-acylvinyl anion equivalents is well established.[3a] A direct approach toward the generation of β-acylvinyl anion equivalents involves the use of protected carbonyl systems **18**, which can undergo halogen[3b−d] or tin[3e,f]−lithium exchange (Scheme 5). An alternative route involves the use of heteroallylic systems of type **19**, which carry the carbonyl group in the heterovinyl mask.[5,6] Deprotonation-electrophilic substitution followed by unmasking provides an easy introduction of the β-acylvinyl moiety to the electrophilic reagent. The thio (X = Y = SR and X = SR, Y = OR)[3g,h,24] and seleno (X = Y = Se)[3i] analogues of **19** have been used extensively; however, these systems require oxidative unmasking in the presence of reagents such as $HgCl_2$, H_2O_2, $NaIO_4$, or MoO_5. In the case of allylic sulfones,[3j,k] often DBU is required for the final elimination of the sulfonyl group, and 4*H*-1,3-dioxin (RX, YR = $^-OCH_2O^-$ in **19**) requires prolonged thermolysis at 150 °C for 72 h for deprotection.[3l]

SCHEME 5[a]



[a] X = Y = S, (i) $HgCl_2$; X = Y = Se, (i) H_2O_2; X = S, Y = O, (i) $NaIO_4$ or MoO_5; X = SO_2, Y = O, (i) DBU or SiO_2; X = Y = O, (i) 150 °C, 72 h; (ii) LDA, R^1X, THF, −78 °C; (iii) SiO_2, hexane, reflux, 4 h; (iv) BuLi, TMEDA, THF, 0 °C, R^2X; (v) $NaIO_4$, dioxane/H_2O.

Although systems of type **19** have been widely utilized as β-acylvinyl anion equivalents, reports on their use as β-acylvinyl dianion equivalents are rare. Mandai et al. introduced α-methoxyallyl sulfides as β-acylvinyl dianion equivalents; electrophilic substitution (α- to SPh) followed by silica-gel-promoted thioallylic rearrangement facilitated the second electrophilic substitution at the other end of the allylic system. Furthermore, oxidative removal of the heteroatoms provided α,β-unsaturated carbonyl compounds (Scheme 5).[24]

Starting from **(*EZ*)-5**, we have successfully carried out two successive lithiation-electrophilic substitutions to get (oxiranylvinyl)benzotriazoles **6a**−**g** and **10a**−**d**. Furthermore, hydrolysis of (oxiranylvinyl)benzotriazoles under mild conditions provided the corresponding α,β-unsaturated carbonyl derivatives. Thus, the treatment of

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6a,**b**,**c**,**e**,**g** with *p*-TsOH (10 mol %) in THF at reflux for 30 min resulted in the formation of γ-hydroxy-α,β-enals **12a**,**b**,**c**,**e**,**g** in 54−86% yields (Scheme 3, Table 1). Under identical conditions, the hydrolysis of **6d** resulted in the formation of 2-phenylfuran (**14**) in 61% yield. However, the hydrolysis of **6f** resulted in the formation of **12f** in low yield (ca. 10%) along with other benzotriazole-containing byproducts as shown by the ^{1}H NMR spectrum of the crude material. Similarly, acidic hydrolysis of alkylated (oxiranylvinyl)benzotriazoles **10a**−**d** provided γ-hydroxy-α,β-enones **13a**−**d** in 56−82% yields (Scheme 3, Table 2). Thus, **5** functions as a synthetic equivalent for both β-formylvinyl anion **3** and β-acylvinyl dianion **15**.

Conclusions

In summary, we have shown that 3-chloroallylbenzotriazole (**5**), in the presence of HMPA, undergoes a regiospecific lithiation-substitution at the CCl terminus to give (oxiranylvinyl)benzotriazoles **6a**−**g**. Furthermore, lithiation-alkylation of **6a**,**c** takes place exclusively at the CBt terminus to give **10a**−**d** in good yields. Acidic hydrolysis of **6a**−**g** and **10a**−**d** provided the corresponding 4-hydroxyalk-2-en-1-one derivatives **12a**,**b**,**c**,**e**,**g**, and **13a**−**d**, respectively, establishing the utility of **5** as a β-acylvinyl anion and dianion equivalent. Furthermore, our procedure requires only a catalytic amount of acid for unmasking, which is milder than the oxidative unmasking procedures used for other β-acylvinyl anion equivalents.

Experimental Section

1-[(*E*)-2-(3,3-Diphenyloxiran-2-yl)vinyl]-1*H*-1,2,3-benzotriazole (6a). White needles (from CH_2Cl_2/hexanes); yield, 78%; mp 122−125 °C. ^{1}H NMR δ: 8.04 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 14.5 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.47−7.31 (m, 10H), 7.29−7.24 (m, 1H), 5.99 (dd, *J* = 14.5, 8.0 Hz, 1H), 4.06 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR δ: 146.4, 140.1, 136.5, 131.4, 128.7, 128.6, 128.4, 128.3, 127.4, 126.8, 124.9, 120.6, 116.3, 110.1, 68.3, 64.9. Anal. Calcd for $C_{22}H_{17}N_3O$: C, 77.86; H, 5.05; N, 12.38. Found: C, 77.46; H, 4.95; N, 12.49.

(4*Z*)-3-(1*H*-1,2,3-Benzotriazol-1-yl)-5-chloro-2-phenylpent-4-en-2-ol (7b). White needles (from EtOAc/hexanes); yield, 30%; major diastereomer: mp 132−133 °C. ^{1}H NMR δ: 7.89 (d, *J* = 8.4 Hz, 1H), 7.46−7.28 (m, 5H), 7.11−7.06 (m, 2H), 7.00−6.97 (m, 1H), 6.70 (dd, *J* = 9.6, 7.3 Hz, 1H), 6.47 (d, *J* = 7.3 Hz, 1H), 6.15 (d, *J* = 9.6 Hz, 1H), 4.81 (s, 1H), 1.73 (s, 3H). ^{13}C NMR δ: 144.5, 144.3, 133.0, 128.2, 127.7, 127.1, 126.6, 124.1, 123.8, 119.8, 109.3, 77.4, 63.0, 27.0. Anal. Calcd for $C_{17}H_{16}ClN_3O$: C, 65.07; H, 5.14; N, 13.39. Found: C, 65.32; H, 5.10; N, 13.32.

1-[3-(1*H*-1,2,3-Benzotriazol-1-yl)-1-chloroprop-1-enyl]-cyclohexanol (8c). White needles (from EtOAc/hexanes); yield, 10%; mp 113−114 °C. ^{1}H NMR δ: 8.03 (d, *J* = 8.2 Hz, 1H), 7.54−7.44 (m, 2H), 7.38−7.33 (m, 1H), 6.21 (t, *J* = 6.5 Hz, 1H), 5.46 (d, *J* = 6.5 Hz, 2H), 2.42 (s, 1H), 1.87−1.56 (m, 9H), 1.25−1.18 (m, 1H). ^{13}C NMR δ: 146.3, 146.2, 132.9, 127.7, 124.3, 120.2, 117.8, 109.7, 74.8, 47.0, 35.6, 25.4, 21.7. Anal. Calcd for $C_{15}H_{18}ClN_3O$: C, 61.75; H, 6.22; N, 14.40. Found: C, 62.05; H 6.27; N, 14.46.

1-[4-(1*H*-1,2,3-Benzotriazol-1-yl)-6-chloro-1,5-hexadienyl]-1*H*-1,2,3-benzotriazole (9). White needles (from EtOAc/hexanes); yield, 40%; mp 156−157 °C. ^{1}H NMR δ: 8.09−8.02 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.53−7.35 (m, 6H), 6.48−6.37 (m, 3H), 6.04−5.97 (m, 1H), 3.51−3.41 (m, 1H), 3.29−3.19 (m, 1H). ^{13}C NMR δ: 146.1, 145.9, 132.9, 131.3, 128.9, 128.3, 127.8, 126.4, 124.5, 124.3, 122.6, 120.3, 120.2, 115.5, 109.9, 109.4, 55.8, 34.9. Anal. Calcd for $C_{18}H_{15}ClN_6$: C, 61.63; H, 4.31; N, 23.96. Found: C, 61.91; H, 4.23; N, 24.38.

1-[(*E*)-2-(3,3-Diphenyloxiran-2-yl)-1-methylvinyl]-1*H*-1,2,3-benzotriazole (10a). Colorless cubes (from CH_2Cl_2/hexanes); yield, 88%; mp 102−104 °C. ^{1}H NMR δ: 8.02−8.00 (m, 1H), 7.54−7.51 (m, 2H), 7.46−7.34 (m, 8H), 7.31−7.25 (m, 2H), 6.84−6.82 (m, 1H), 5.35 (dd, *J* = 8.4, 1 Hz, 1H), 4.28 (d, *J* = 8.4 Hz, 1H), 2.67 (d, *J* = 1 Hz, 3H). ^{13}C NMR δ: 146.4, 139.9, 138.1, 137.1, 131.8, 128.7, 128.5, 128.3, 128.0, 127.1, 124.5, 120.3, 117.8, 111.2, 67.9, 62.5, 16.9. Crystal data: triclinic, space group $P\bar{1}$, *a* = 7.628(1) Å, *b* = 9.693(1) Å, *c* = 13.398(1) Å, α = 76.206(1)°, β = 76.886(1)°, γ = 72.791(1)°, *V* = 905.8(1) Å^3, *F*(000) = 372, *Z* = 2, *T* = −110 °C, μ (Mo Kα) = 0.081 mm^{-1}, D_{calcd} = 1.296 g cm^{-3}, crystal size 0.39 × 0.26 × 0.18 mm^3, $2\theta_{max}$ = 45° (CCD area detector, Mo Kα radiation), 245 parameters, GOF = 1.17, wR(F^2) = 0.1076 (all 2370 data), R = 0.0485 (2145 data with $I > 2\sigma I$). Anal. Calcd for $C_{23}H_{19}N_3O$: C, 78.16; H, 5.42; N, 11.89. Found: C, 78.27; H, 5.51; N, 11.99.

2-[3-(1*H*-1,2,3-Benzotriazol-1-yl)-5,5-diethyl-2,5-dihydrofuran-2-yl](diphenyl)methanol (11). White pellets (from CH_2Cl_2/hexanes); yield, 75%; mp 122−124 °C. ^{1}H NMR δ: 8.08 (d, *J* = 8.2 Hz, 1H), 7.64−7.61 (m, 2H), 7.57−7.50 (m, 4H), 7.44−7.35 (m, 5H), 7.30−7.25 (m, 2H), 5.99 (d, *J* = 1.4 Hz, 1H), 5.77 (d, *J* = 1.4 Hz, 1H), 3.19 (s, 1H), 2.26−2.07 (m, 2H), 2.01−1.81 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR δ: 145.8, 145.5, 144.2, 139.7, 133.0, 128.7, 128.5, 128.3, 127.8, 127.5, 127.5, 126.2, 124.9, 120.5, 116.3, 111.1, 94.4, 88.5, 79.3, 31.4, 31.3, 8.8, 8.5. Crystal data: monoclinic, space group $P2_1/c$, *a* = 14.113(4) Å, *b* = 9.571(3) Å, *c* = 17.403(5) Å, β = 106.192(6)°, *V* = 2257(1) Å^3, *F*(000) = 904, *Z* = 4, *T* = −105 °C, μ (Mo Kα) = 0.080 mm^{-1}, D_{calcd} = 1.252 g cm^{-3}, crystal size 0.54 × 0.42 × 0.21 mm^3, $2\theta_{max}$ = 50° (CCD area detector, Mo Kα radiation), 292 parameters, GOF = 0.90, wR(F^2) = 0.0827 (all 3935 data), R = 0.0366 (2459 data with $I > 2\sigma I$). Anal. Calcd for $C_{27}H_{27}N_3O_2$: C, 76.21; H, 6.40; N, 9.87. Found: C, 75.97; H 6.44; N, 9.86.

(2*E*)-4-Hydroxy-4,4-diphenylbut-2-enal (12a). Yellow needles (from Et_2O/hexanes); yield, 73%; mp 119−120 °C. ^{1}H NMR δ: 9.69 (d, *J* = 7.8 Hz, 1H), 7.38−7.32 (m, 10H), 7.28 (d, *J* = 15.6 Hz, 1H), 6.51 (dd, *J* = 15.6, 7.9 Hz, 1H), 2.48 (s, 1H). ^{13}C NMR δ: 193.6, 160.3, 144.0, 130.1, 128.9, 128.4, 127.1, 79.5. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.57; H, 5.89.

(3*E*)-5-Hydroxy-5,5-diphenylpent-3-en-2-one (13a). Colorless needles (from CH_2Cl_2/hexanes); yield, 76%; mp 152−154 °C. ^{1}H NMR δ: 7.35−7.25 (m, 11H), 6.48 (d, *J* = 15.6 Hz, 1H), 2.52 (s, 1H), 2.29 (s, 3H). ^{13}C NMR δ: 198.6, 150.6, 144.6, 128.7, 128.1, 127.1, 79.2, 28.4. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.50; H, 6.18.

2-Phenylfuran (14).[25] Yellow oil; yield, 61%. ^{1}H NMR δ: 7.69−7.66 (m, 2H), 7.46−7.35 (m, 3H), 7.28−7.22 (m, 1H), 6.64 (d, *J* = 3.3 Hz, 1H), 6.46 (dd, *J* = 3.3, 1.8 Hz, 1H). ^{13}C NMR δ: 154.2, 142.3, 131.1, 128.9, 127.5, 124.0, 111.8, 105.1.

1-(1-Methylprop-2-enyl)-1*H*-1,2,3-benzotriazole (16). Yellow oil; not isolated. ^{1}H NMR δ: 8.06 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.51−7.46 (m, 1H), 7.39−7.34 (m, 1H), 6.28−6.22 (m, 2H), 5.95 (dq, *J* = 6.9, 5.9 Hz, 1H), 1.92 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR δ: 146.2, 132.5, 130.9, 127.4, 124.1, 121.0, 120.1, 109.7, 52.1, 19.9.

4-(1*H*-1,2,3-Benzotriazol-1-yl)-2-chloro-1,1-diphenylpent-2-en-1-ol (17). White needles (from Et_2O/hexanes); yield, 62%; mp 102−104 °C. ^{1}H NMR δ: 8.05 (d, *J* = 8.4 Hz, 1H), 7.54−7.45 (m, 2H), 7.41−7.36 (m, 1H), 7.32−7.26 (m, 10H), 5.98−5.89 (m, 2H), 3.26 (s, 1H), 1.87 (d, *J* = 6.3 Hz). ^{13}C NMR δ: 146.2, 142.5, 132.6, 129.7, 128.5, 128.4, 128.4, 127.9, 127.7, 127.4, 124.3, 120.3, 109.8, 82.9, 54.2, 20.1. Anal. Calcd for

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$C_{23}H_{20}ClN_3O$: C, 70.85; H, 5.17; N, 10.78. Found: C, 71.27; H, 5.24; N, 10.73.

Supporting Information Available: General experimental methods and procedures, characterization data for compounds **6b**−**g**, **7c**,**d**, **8d**,**e**, **10b**−**d**, **12b**,**c**,**e**,**g**, **13b**−**d**, ^{1}H and ^{13}C NMR spectra for the compounds with HRMS (**12e**,**g**), and X-ray structures for ***trans*-6b**, ***syn*-(*Z*)-7d**, ***syn*-(*E*)-7d**, **8d**, **10a**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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