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Lithiation of 1-Chloromethylbenzotriazole: Generation and Elaboration of Benzotriazolyloxiranes

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1-Benzotriazolylchloromethyllithium generated from 1-chloromethylbenzotriazole (**1**) and LDA reacts with enolizable and nonenolizable ketones to give benzotriazolyloxiranes **2a**−**g** in good yields. The oxiranyllithiums **4a**−**d** generated from **2a**−**d** and *n*-BuLi at −78 °C were trapped by a variety of electrophiles to give oxiranyl derivatives **5a**−**j** in good to excellent yields. Lewis-acid-promoted nucleophilic ring opening of benzotriazolyloxiranes **2a**,**f**,**g** with allyltrimethylsilane gave the corresponding 1,7-octadien-4-ols **6a**−**c** in 68−75% yield. Hydrolysis of α-acylbenzotriazolyloxiranes **5g**,**h** provided 3-hydroxy-1,2-diones **7a** and **7b** in 73 and 86% yield, respectively.

Introduction

The synthetic potential of carbenoids, in particular α-haloalkyllithiums, is well documented.[1] α-Haloorganometals and metalloids derived from alkyl[2] and allyl halides,[3] α-halo-esters, -amides, and -nitriles,[4] 2-halomethylbenzothiazoles,[5] 2-halomethyloxazoles,[6] and 2- and 3-halomethylpyridines[7] can be trapped effectively with carbonyl compounds to give oxiranes.

Oxiranes are versatile synthetic intermediates.[8] Oxiranes can be deprotonated by a strong base to give highly reactive oxiranyl anions, which frequently spontaneously ring open to diverse products.[9] Rare examples of the trapping of nonstabilized oxiranyl anions have been reported.[10] However, many oxiranes with anion stabilizing aromatic,[11] heteroaromatic,[12] unsaturated,[13] silicon-linked,[14] or electron-withdrawing substituents[15−17] are lithiated and trapped efficiently to give substituted oxiranes.

Benzotriazolyloxiranes have earlier been prepared by the epoxidation of 1-(1-alkenyl)benzotriazoles using *m*-CPBA[18a] and dimethyldioxirane.[18b] The hydrolysis of α-alkyl- and α-(α-hydroxyalkyl)-benzotriazolyloxiranes gives the corresponding α-hydroxy ketones.[18a] We now report another convenient and general method for the preparation of benzotriazolyloxiranes and their further transformations to octa-1,7-dien-4-ols and 3-hydroxy-1,2-diones. Such dienes are useful substrates for ring-closing

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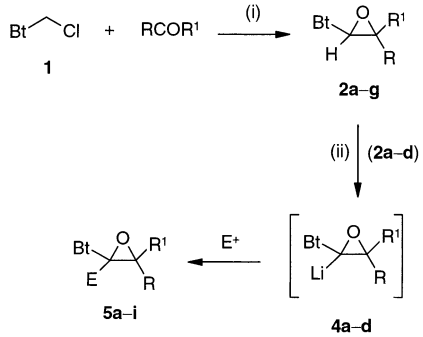
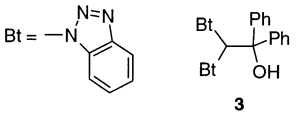
SCHEME 1



(i) Base, THF, -78 °C; (ii) *n*-BuLi, THF, -78 °C



2	R	R¹	Y(%)
a	Ph	Ph	68
b	Et	Et	72
c	-(CH$_2$)$_5$-		70
d	Ph	Et	68
e	Ph	Me	62
f	Ph	*p*-ClPh	75
g	Ph	*p*-MePh	69

(For description of R, R¹ and E in **5a**–**i** see Table 1)

diene metathesis,[19] and vicinal carbonyl systems play a vital role in the therapeutic activity of a number of immunosuppressants.[20]

Results and Discussion

Preparation of Benzotriazolyloxiranes. Lithiation of 1-chloromethylbenzotriazole (**1**) with LiHMDS at −40 °C and trapping with benzophenone under Barbier conditions gave the desired oxirane **2a** in 18% yield along with the alcohol **3** in 62% yield (Scheme 1).[21] The structure of alcohol **3** is supported by ^{1}H NMR and ^{13}C NMR spectroscopy and also by X-ray crystallography. Compound **3** arises from a base-promoted reaction involving two molecules of 1-chloromethylbenzotriazole,[22] and its formation was reduced to a large extent by using LDA as a base at −78 °C, when **2a** was obtained in an improved yield of 40%.

Formation of the side product **3** indicated a competition between 1-chloromethylbenzotriazole and benzophenone as electrophiles. An obvious solution to this problem would be to use a slight excess of benzophenone, which should increase the yield of the desired product **2a** due to an increase in the concentration of this electrophile. Indeed, when 1.5 equiv of benzophenone was used, **2a** could be obtained in 68% yield without the formation of **3**. This procedure worked well with a variety of aromatic and aliphatic ketones but remained unsuccessful in the case of aldehydes (Scheme 1). Reactions with propiophenone and *p*-methylbenzophenone gave the benzotriazolyloxiranes **2d** and **2g** as a mixture of diastereomers in the ratios 3.3/1 and 1.3/1, respectively. The major isomers were separated and studied by X-ray crystallography. Crystals of the major isomer of **2d** were all severely twinned. Nevertheless, a partial structure solution could be extracted from a twinned data set, and this showed that it is the trans isomer. The X-ray crystal structure of the major isomer of **2g** showed that it is the cis isomer. With acetophenone and *p*-chlorobenzophenone, the respective products **2e** and **2f** were each formed as single diastereomers as indicated by the ^{1}H NMR spectra.

TABLE 1. Reaction of Benzotriazolyloxiranyllithiums with Electrophiles

entry	oxiranyl lithium	E$^+$	R	R^1	E	product Y (%)[a]
1	**4a**	MeI	Ph	Ph	Me	**5a** (82)
2	**4a**	BuBr	Ph	Ph	Bu	**5b** (76)
3	**4b**	Me$_3$SiCl	Et	Et	SiMe$_3$	**5c** (69)
4	**4c**	PhCH=NPh	−(CH$_2$)$_5$−		PhCH(NHPh)	**5d** (78)[b]
5	**4a**	PhCHO	Ph	Ph	PhCHOH	**5e** (92)[c]
6	**4a**	Et$_2$CO	Ph	Ph	Et$_2$CHOH	**5f** (83)
7	**4a**	PhCO$_2$Et	Ph	Ph	COPh	**5g** (72)
8	**4c**	PhCO$_2$Et	−(CH$_2$)$_5$−		COPh	**5h** (76)
9	**4d**	PhCO$_2$Et	Ph	Et	COPh	**5i** (68)

[a] Isolated yields. [b] Product is a mixture of isomers in a 2:1:1 ratio. [c] Product is a mixture of syn/anti isomers in a 1:1 ratio.

Generation and Trapping of Oxiranyl Anions. While other oxiranyl anions are generated and trapped from −90 to −110 °C,[9a,c] addition of *n*-BuLi to 3,3-diphenylbenzotriazolyloxirane (**2a**) at −78 °C followed by addition of methyl iodide or *n*-butyl bromide gave the alkylated products **5a** and **5b** in 82 and 76% yield, respectively. Similarly, coupling of 3,3-diethylbenzotriazolyloxiranyllithium (**4b**) with trimethylsilyl chloride gave **5c** in 69% yield. The procedure worked well with a variety of electrophiles to give the corresponding α-substituted products in 68−92% yield (Scheme 1, Table 1).

To the best of our knowledge, use of Schiff's bases to trap oxiranyl anions has not previously been reported. However, reaction of *N*-(phenylmethylidene)aniline with oxiranyllithium **4c** gave **5d** in 78% yield as a mixture of three isomers in a 2:1:1 ratio. The major isomer of **5d** was separated by silica gel column chromatography, and its structure was determined as anti by single-crystal X-ray crystallography. Compound *anti*-**5d** crystallizes with two independent molecules in the asymmetric unit, which differ in the orientation of the phenyl substituents and the conformation of the cyclohexane ring.

Reaction of oxiranyllithium **4a** with benzaldehyde gave the desired epoxy alcohol **5e** as a mixture of syn and anti isomers in a 1:1 ratio. One of the isomers was separated by recrystallization and was assigned as *anti*-**5e** by X-ray analysis; again, *anti*-**5e** crystallizes with two molecules in the asymmetric unit, but these have almost identical

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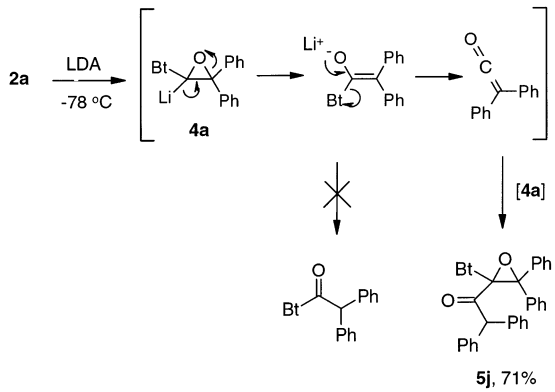
SCHEME 2



structures and conformations. The ^{1}H NMR spectrum of *anti*-**5e** displayed signals for C*H*(O) and O*H* protons at 4.85 and 4.35 ppm, respectively, whereas the corresponding signals for the *syn*-**5e** isomer appeared at 5.16 and 2.59 ppm, respectively.

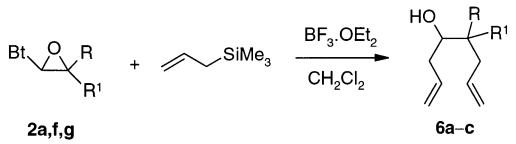
α-Acyloxiranes are versatile building blocks capable of functionalization at both the ketone and the oxirane moieties.[23] Reaction of oxiranyllithiums **4a** or **4c** with ethyl benzoate gave the α-acylated products **5g** and **5h** in 72 and 76% yield, respectively. Lithiation of the trans isomer of benzotriazolyloxirane **2d** provided configurationally stable oxiranyllithium **4d**, which was trapped with ethyl benzoate to give exclusively the trans product **5i** in 68% yield. The trans stereochemistry for **5i** was unambiguously determined by X-ray analysis; once again, there are two independent molecules in the asymmetric unit.

Acylbenzotriazoles are good acylating agents,[24] and an attempt was made to prepare acylbenzotriazoles via base-promoted rearrangement of benzotriazolyloxiranyllithium **4a**. However, this resulted in the formation of **5j**. A possible explanation is that the base and **2a** generate the corresponding enolate and the ketene by the loss of the benzotriazolyl group. The oxiranyllithium **4a** is apparently stable enough to be trapped by the ketene thus generated in situ giving α-acylated benzotriazolyloxirane **5j** in 71% yield (Scheme 2).

Preparation of 5,5-Diaryl-1,7-octadien-4-ols. Nucleophilic ring opening of 3,3-diarylbenzotriazolyloxiranes **2a**,**f**,**g** on treatment with allyltrimethylsilane and BF_3·OEt_2 gave the corresponding 5,5-diarylocta-1,7-dien-4-ols **6a**−**c** in 68−75% yield (Scheme 3). Similar ring openings tried with 1-(3-ethyl-3-phenyl-2-oxiranyl)-1*H*-1,2,3-benzotriazole (**2d**) or 1-(2-methyl-3,3-diphenyl-2-oxiranyl)-1*H*-1,2,3-benzotriazole (**5a**) yielded a mixture of rearranged products along with the desired 1,7-octadiene-4-ols in low yields.

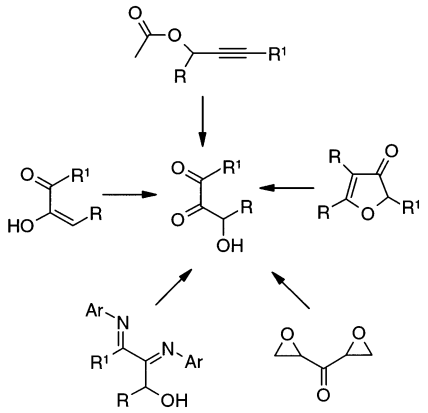
Preparation of 3-Hydroxy-1,2-diones. 3-Hydroxy-1,2-diones have earlier been prepared by either the oxidation of 2-hydroxy-2-ene-1-ones,[25a] the hydrolysis of the corresponding imines[25b] or ring opening of diepoxy ketones,[25c] the oxidation and subsequent hydrolysis of α-acetoxyacetylenes,[25d] or the oxidation of 3(2*H*)-furanone[25e] (Scheme 4). α-Alkyl and α-(α-hydroxyalkyl)-benzotriazolyloxiranes of the type **5a**,**b**,**e**,**f** have already been utilized for the synthesis of corresponding α-hydroxy ketones.[18a] Similarly, treatment of α-acylbenzotriazolyloxiranes **5g**,**h** with perchloric acid readily gave 3-hydroxy-1,2-diones **7a** and **7b** in 73 and 86% yield, respectively (Scheme 5). Thus, a general and efficient route is now available for the preparation of 3,3-dialkyl or -aryl substituted acylbenzotriazolyloxiranes and the corresponding 3-hydroxy-1,2-diones.

SCHEME 3

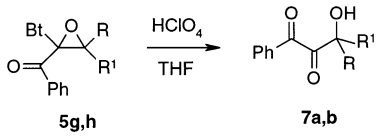


6	R	R^1	Y(%)
a	Ph	Ph	75
b	Ph	*p*-ClPh	73
c	Ph	*p*-MePh	68

SCHEME 4



SCHEME 5



7	R	R^1	Y(%)
a	Ph	Ph	73
b	-(CH$_2$)$_5$-		86

Conclusions

In summary, we have shown that α-anion stabilization by the benzotriazolyl group can also be utilized for the preparation of 3,3-disubstituted benzotriazolyloxiranes and 2,3,3-trisubstituted benzotriazolyloxiranes. Further, nucleophilic ring opening of benzotriazolyloxiranes pro-

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vides easy access to 1,7-octadien-4-ols and 3-hydroxy-1,2-diones.

Experimental Section

All of the reactions were carried out under N_2. THF was distilled from sodium/benzophenone prior to use. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ (with TMS for ^{1}H and chloroform-*d* for ^{13}C as the internal reference). Column chromatography was performed on silica gel 200−425 mesh.

General Procedure for the Preparation of Benzotriazolyloxiranes 2. To a solution of 1-chloromethylbenzotriazole (**1**)[26] (0.50 g, 3 mmol) and ketone (4.5 mmol) in THF (10 mL) at −78 °C was added LDA [freshly prepared from *n*-BuLi (1.5 M in hexanes, 3 mL, 4.5 mmol) and diisopropylamine (0.7 mL, 5 mmol) at 0 °C in THF (20 mL)]. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm to 20 °C. After the mixture was stirred for 3 h, aqueous NH_4Cl was added, and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography using hexanes/EtOAc (95:5) as eluent to give **2a**−**g**.

1-(3,3-Diphenyl-2-oxiranyl)-1-*H*-1,2,3-benzotriazole (2a). Colorless cubes (from EtOAc/hexanes); yield, 68%; mp 135−137 °C; ^{1}H NMR δ 7.89−7.86 (m, 1H), 7.37 (s, 6H), 7.20−7.14 (m, 4H), 7.06−7.05 (m, 3H), 6.14 (s, 1H); ^{13}C NMR δ 145.3, 137.1, 133.3, 132.3, 128.7, 128.6, 128.5, 128.2, 128.1, 127.3, 126.5, 123.8, 119.2, 111.6, 73.7, 67.8. Anal. Calcd for $C_{20}H_{15}N_3O$: C, 76.66; H, 4.82; N, 13.41. Found: C, 76.62; H, 4.61; N, 13.38.

1-(3,3-Diethyl-2-oxiranyl)-1*H*-1,2,3-benzotriazole (2b). Yellow oil; yield, 72%; ^{1}H NMR δ 8.06 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.52−7.47 (m, 1H), 7.41−7.36 (m, 1H), 5.52 (s, 1H), 1.93−1.85 (m, 2H), 1.49−1.41 (m, 2H), 1.12 (t, J = 7.5 Hz, 3H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 145.7, 133.7, 128.1, 124.5, 120.0, 111.5, 70.8, 68.4, 25.5, 22.7, 9.0, 8.7. Anal. Calcd for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.46; H, 7.13; N, 19.28.

1-(1-Oxaspiro[2.5]oct-2-yl)-1*H*-1,2,3-benzotriazole (2c). White cubes (from CH_2Cl_2/hexanes); yield, 70%; mp 103−105 °C; ^{1}H NMR δ 8.06 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.51−7.46 (m, 1H), 7.40−7.35 (m, 1H), 5.45 (s, 1H), 1.87−1.75 (m, 4H), 1.66−1.57 (m, 4H), 1.48−1.47 (m, 2H); ^{13}C NMR δ 145.7, 133.7, 128.1, 124.5, 120.0, 111.4, 71.2, 66.4, 33.2, 29.1, 25.3, 24.7, 24.4. Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 68.35; H, 6.71; N, 18.29.

1-(3-Ethyl-3-phenyl-2-oxiranyl)-1*H*-1,2,3-benzotriazole (2d). White cubes (from CH_2Cl_2/hexanes); yield, 68% (cis and trans); mp 74−76 °C; trans isomer: ^{1}H NMR δ 8.10 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.56−7.53 (m, 3H), 7.48−7.37 (m, 4H), 5.56 (s, 1H), 2.25−2.12 (m, 1H), 1.56−1.44 (m, 1H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 145.8, 136.7, 133.6, 128.9, 128.7, 128.4, 126.5, 124.7, 120.2, 111.3, 72.6, 68.4, 24.2, 9.1. Anal. Calcd for $C_{16}H_{15}N_3O$: C, 72.43; H, 5.70; N, 15.84. Found: C, 72.72; H, 5.58; N, 15.87.

1-(3-Methyl-3-phenyl-2-oxiranyl)-1*H*-1,2,3-benzotriazole (2e). Yellow oil; yield, 62%; ^{1}H NMR δ 8.10 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.57−7.52 (m, 3H), 7.48−7.40 (m, 4H), 5.54 (s, 1H), 1.66 (s, 3H); ^{13}C NMR δ 145.8, 138.4, 133.4, 128.9, 128.8, 128.4, 125.6, 124.7, 120.2, 111.3, 72.0, 64.0, 17.7. Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.99; H, 4.94; N, 16.72.

1-[3-(4-Chlorophenyl)-3-phenyl-2-oxiranyl]-1*H*-1,2,3-benzotriazole (2f). White cubes (from EtOAc/hexanes); yield, 75%; mp 114−116 °C; ^{1}H NMR δ 7.94−7.91 (m, 1H), 7.48−7.36 (m, 6H), 7.32−7.22 (m, 2H), 7.17−7.14 (m, 2H), 7.10−7.06 (m, 2H), 6.13 (s, 1H); ^{13}C NMR δ 145.6, 136.9, 135.0, 132.7, 132.3, 129.7, 129.3, 129.0, 128.8, 128.0, 126.8, 124.4, 119.8, 111.6, 73.6, 67.7. Anal. Calcd for $C_{20}H_{14}ClN_3O$: C, 69.07; H, 4.06; N, 12.08. Found: C, 69.27; H, 3.91; N, 11.86.

1-[3-(4-Methylphenyl)-3-phenyl-2-oxiranyl]-1*H*-1,2,3-benzotriazole (2g). White needles (from CH_2Cl_2/hexanes); yield, 69%; mp 122−124 °C; cis isomer: ^{1}H NMR δ 7.92−7.89 (m, 1H), 7.43−7.39 (m, 6H), 7.22−7.19 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 7.8 Hz, 2H), 6.12 (s, 1H), 2.16 (s, 3H); ^{13}C NMR δ 145.7, 138.8, 137.8, 132.7, 130.7, 129.2, 129.0, 128.8, 128.3, 127.6, 126.8, 124.2, 119.6, 112.0, 74.1, 68.1, 21.3. Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.83. Found: C, 77.07; H, 5.28; N, 12.84.

2,2-Di(1*H*-1,2,3-benzotriazol-1-yl)-1,1-diphenyl-1-ethanol (3). White cubes (from EtOAc); yield, 62%; mp 235−237 °C; ^{1}H NMR δ 8.53 (s, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.48−7.42 (m, 2H), 7.38−7.31 (m, 6H), 7.18−7.16 (m, 6H), 6.21 (s, 1H); ^{13}C NMR δ 145.9, 142.3, 132.7, 129.1, 128.7, 128.2, 125.6, 125.1, 120.4, 111.1, 82.6, 76.4; HRMS Calcd for $C_{26}H_{20}N_6O$ ($M^+ + 1$) 433.1771, found 433.1746.

General Procedure for the Preparation of Benzotriazolyloxiranes 5. To a stirred solution of **2** (0.15 g, 0.5 mmol) in THF (5 mL) at −78 °C was added *n*-BuLi (1.5 M in THF, 0.4 mL, 0.6 mmol). After 5 min, electrophile (0.6 mmol) was added, and the reaction mixture was stirred for 30 min at −78 °C and then allowed to warm to 20 °C. After the mixture was stirred for 2 h, aqueous NH_4Cl was added. The aqueous layer was extracted with diethyl ether, and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography using EtOAc/hexanes (5:95) to give **5a**−**j**.

1-(2-Methyl-3,3-diphenyl-2-oxiranyl)-1*H*-1,2,3-benzotriazole (5a). Colorless oil; yield, 82%; ^{1}H NMR δ 7.85 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 7.3 Hz, 2H), 7.44−7.39 (m, 2H), 7.36−7.25 (m, 2H), 7.20−7.15 (m, 3H), 6.95−6.90 (m, 3H), 1.98 (s, 3H); ^{13}C NMR δ 145.2, 137.1, 135.9, 132.9, 128.8, 128.4, 128.0, 127.9, 127.4, 127.2, 126.9, 123.9, 119.5, 112.0, 78.6, 72.6, 20.5. Anal. Calcd for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.23; N, 12.83. Found: C, 77.35; H, 5.29; N, 12.81.

1-(2-Butyl-3,3-diphenyl-2-oxiranyl)-1*H*-1,2,3-benzotriazole (5b). White needles (from Et_2O/pentane); yield, 76%; mp 65−67 °C; ^{1}H NMR δ 7.85−7.81 (m, 2H), 7.62 (d, J = 7.3 Hz, 2H), 7.43−7.38 (m, 2H), 7.35−7.30 (m, 2H), 7.23−7.14 (m, 3H), 6.90−6.88 (m, 3H), 2.76−2.67 (m, 1H), 1.80−1.72 (m, 1H), 1.48−1.42 (m, 1H), 1.17−1.16 (m, 3H), 0.70 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ 145.0, 137.2, 136.1, 133.8, 128.7, 128.4, 127.9, 127.8, 127.5, 127.1, 126.8, 123.8, 119.4, 112.0, 81.3, 72.8, 32.9, 25.9, 22.3, 13.8. Anal. Calcd for $C_{24}H_{23}N_3O$: C, 78.02; H, 6.27; N, 11.37. Found: C, 77.82; H, 6.60; N, 11.50.

1-[3,3-Diethyl-2-(trimethylsilyl)-2-oxiranyl]-1*H*-1,2,3-benzotriazole (5c). Yellow oil; yield, 69%; ^{1}H NMR δ 8.02 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.45−7.40 (m, 1H), 7.35−7.30 (m, 1H), 1.87−1.70 (m, 2H), 1.26−1.01 (m, 5H), 0.86 (t, J = 7.4 Hz, 3H), 0.08 (s, 9H); ^{13}C NMR δ 145.3, 134.0, 127.4, 124.1, 119.7, 112.3, 75.7, 70.8, 24.6, 23.1, 9.4, 8.9, −1.9. Anal. Calcd for $C_{15}H_{23}N_3OSi$: C, 62.24; H, 8.01; N, 14.52. Found: C, 62.50; H, 8.51; N, 14.53.

***N*-[[2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-oxaspiro[2.5]oct-2-yl](phenyl)methyl]aniline (5d).** Colorless cubes (from EtOAc/hexanes); yield, 78%; mp 147−149 °C; anti isomer: ^{1}H NMR δ 7.88 (d, J = 8.2 Hz, 1H), 7.16−7.05 (m, 4H), 7.02−6.92 (m, 5H), 6.85 (d, J = 8.4 Hz, 1H), 6.64 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 8.0 Hz, 2H), 5.72 (d, J = 7.5 Hz, 1H), 4.95 (d, J = 7.5 Hz, 1H), 2.13−1.96 (m, 2H), 1.84−1.82 (m, 2H), 1.69−1.65 (m, 1H), 1.53 (s, 3H), 1.20−1.12 (m, 1H), 1.03−0.95 (m, 1H); ^{13}C NMR δ 145.9, 144.4, 137.0, 134.4, 129.3, 128.5, 128.1, 127.6, 127.0, 124.0, 119.2, 117.9, 113.5, 111.4, 81.2, 72.0, 59.6, 31.1, 30.3, 25.4, 25.1, 24.4. Anal. Calcd for $C_{26}H_{26}N_4O$: C, 76.07; H, 6.38; N, 13.65. Found: C, 75.68; H, 6.54; N, 13.67.

[2-(1*H*-1,2,3-Benzotriazol-1-yl)-3,3-diphenyl-2-oxiranyl]-(phenyl)methanol (5e). White needles (from CH_2Cl_2/hexanes); yield (syn and anti), 92%; anti isomer; mp 185−187 °C; ^{1}H NMR δ 7.92 (d, J = 7.0 Hz, 2H), 7.75 (d, J = 4.9 Hz, 1H),

(26) Burckhalter, J. H.; Stephens, V. C.; Hall, L. A. R. *J. Am. Chem. Soc.* **1952**, *74*, 3868.

7.53−7.48 (m, 2H), 7.43 (d, J = 6.9 Hz, 1H), 7.24−7.05 (m, 10H), 6.93 (s, 3H), 4.84 (d, J = 8.4 Hz, 1H), 4.32 (d, J = 8.1 Hz, 1H); ^{13}C NMR δ 144.3, 138.2, 136.2, 135.6, 134.6, 129.1, 129.0, 128.3, 128.1, 127.8, 127.6, 126.6, 125.9, 124.0, 119.4, 111.5, 81.5, 75.0, 73.8. Anal. Calcd for $C_{27}H_{21}N_3O_2$: C, 77.31; H, 5.05; N, 10.02. Found: C, 77.03; H, 4.89; N, 10.08.

3-[2-(1*H*-1,2,3-Benzotriazol-1-yl)-3,3-diphenyl-2-oxiranyl]-3-pentanol (5f). White needles (from CH_2Cl_2/hexanes); yield, 83%; mp 62−64 °C; ^{1}H NMR δ 7.95 (d, J = 8.5 Hz, 1H), 7.78−7.73 (m, 3H), 7.40−7.34 (m, 3H), 7.28−7.24 (m, 3H), 7.18 (t, J = 7.8 Hz, 1H), 6.87−6.76 (m, 3H), 1.96 (s, 1H), 1.91−1.82 (m, 2H), 1.56−1.47 (m, 1H), 1.43−1.36 (m, 1H), 1.09 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 144.5, 137.6, 137.4, 134.2, 128.6, 128.1, 127.7, 127.6, 127.6, 126.7, 125.9, 123.8, 119.4, 112.6, 84.3, 77.8, 73.1, 29.2, 28.8, 8.6, 7.7. Anal. Calcd for $C_{25}H_{25}N_3O_2$: C, 75.16; H, 6.31; N, 10.52. Found: C, 74.90; H, 6.46; N, 10.37.

[2-(1*H*-1,2,3-Benzotriazol-1-yl)-3,3-diphenyl-2-oxiranyl]-(phenyl)methanone (5g). White needles (from CH_2Cl_2/hexanes); yield, 72%; mp 142−144 °C; ^{1}H NMR δ 8.15 (d, J = 7.7 Hz, 2H), 7.90 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.57−7.47 (m, 3H), 7.43−7.23 (m, 9H), 7.10−7.08 (m, 3H); ^{13}C NMR δ 189.1, 145.4, 134.6, 134.4, 133.8, 133.2, 130.0, 129.0, 128.6, 128.6, 128.4, 128.3, 128.2, 127.5, 124.5, 120.0, 111.3, 78.7, 72.5. Anal. Calcd for $C_{27}H_{19}N_3O_2$: C, 77.68; H, 4.59; N, 10.07. Found: C, 77.62; H, 4.70; N, 10.17.

[2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-oxaspiro[2.5]oct-2-yl]-(phenyl)methanone (5h). White needles (from Et_2O); yield, 76%; mp 148−150 °C; ^{1}H NMR δ 8.30 (d, J = 7.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.59−7.53 (m, 2H), 7.51−7.44 (m, 2H), 7.39−7.34 (m, 1H), 2.07−1.99 (m, 1H), 1.90−1.84 (m, 2H), 1.79−1.68 (m, 4H), 1.59−1.48 (m, 3H); ^{13}C NMR δ 189.1, 145.7, 134.9, 133.5, 133.1, 130.2, 129.1, 128.9, 124.9, 120.1, 111.4, 71.2, 31.7, 31.2, 25.3, 24.5, 24.3. Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 72.08; H, 5.99; N, 12.68.

[2-(1*H*-1,2,3-Benzotriazol-1-yl)-3-ethyl-3-phenyloxiran-2-yl](phenyl)methanone (5i). White cubes (from CH_2Cl_2/hexanes); yield, 68%; mp 114−116 °C; trans isomer: ^{1}H NMR δ 8.05 (d, J = 8.1 Hz, 3H), 7.94 (d, J = 8.4 Hz, 1H), 7.60−7.55 (m, 1H), 7.49−7.38 (m, 4H), 7.33−7.17 (m, 5H), 2.78−2.66 (m, 1H), 1.68−1.56 (m, 1H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 188.2, 145.7, 134.4, 133.8, 133.5, 133.0, 129.9, 129.0, 128.8, 128.6, 127.1, 125.0, 120.3, 111.3, 78.2, 73.5, 26.9, 9.0. Anal. Calcd for $C_{23}H_{19}N_3O_2$: C, 74.78; H, 5.18; N, 11.37. Found: C, 74.77; H, 5.24; N, 11.44.

1-[2-(1*H*-1,2,3-Benzotriazol-1-yl)-3,3-diphenyl-2-oxiranyl]-2,2-diphenyl-1-ethanone (5j). White needles (from EtOAc/hexanes); yield, 71%; mp 168−170 °C; ^{1}H NMR δ 7.86−7.83 (m, 1H), 7.74−7.72 (m, 2H), 7.51−7.50 (m, 3H), 7.32−7.30 (m, 3H), 7.20−7.15 (m, 4H), 7.05−6.99 (m, 6H), 6.96−6.92 (m, 2H), 6.86−6.84 (m, 1H), 6.49 (d, J = 6.6 Hz, 2H), 5.18 (s, 1H); ^{13}C NMR δ 198.5, 145.0, 136.4, 135.5, 134.6, 134.5, 133.2, 130.0, 129.7, 129.6, 129.5, 129.0, 128.8, 128.8, 128.2, 128.1, 127.9, 127.3, 126.9, 124.1, 119.8, 110.5, 78.3, 73.9, 60.3 Anal. Calcd for $C_{34}H_{25}N_3O_2$: C, 80.45; H, 4.96; N, 8.28. Found: C, 80.44; H, 5.13; N, 8.45.

General Procedure for the Preparation of 1,7-Octadien-4-ols. To a solution of **2a**,**f** or **2g** (1 mmol) and allyltrimethylsilane (0.48 mL, 3 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added $BF_3{\cdot}OEt_2$ (0.25 mL, 2 mmol), and the reaction mixture was stirred for 10 h at 20 °C. Aqueous $NaHCO_3$ was added, and the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography using EtOAc/hexanes (5:95) as an eluent.

5,5-Diphenyl-1,7-octadien-4-ol (6a). Colorless oil; yield, 75%; ^{1}H NMR δ 7.51−7.46 (m, 10H), 6.19−6.05 (m, 1H), 5.72−5.59 (m, 1H), 5.32−5.18 (m, 4H), 4.68 (t, J = 8.4 Hz, 1H), 3.32 (dd, J = 13.7, 6.9 Hz, 1H), 3.12 (dd, J = 13.9, 7.1 Hz, 1H), 2.73 (dd, J = 14.4, 6.3 Hz, 1H), 1.85−1.72 (m, 2H); ^{13}C NMR δ 144.4, 144.0, 136.1, 134.8, 129.7, 129.7, 127.8, 127.8, 126.5, 126.4, 117.9, 117.5, 73.1, 55.4, 42.9, 37.9; HRMS calcd for $C_{20}H_{20}$ ($M^+ - H_2O$) 261.1643, found 261.1667.

5-(4-Chlorophenyl)-5-phenylocta-1,7-dien-4-ol (6b). Colorless oil; yield, 73%; (isomer mixture 1:1): ^{1}H NMR δ 7.51−7.31 (m, 9H), 6.15−6.01 (m, 1H), 5.68−5.55 (m, 1H), 5.33−5.17 (m, 4H), 4.66−4.61 (m, 1H), 3.25 (dd, J = 13.7, 6.6 Hz, 1H), 3.12−3.03 (m, 1H), 2.75−2.62 (m, 1H), 1.82−1.68 (m, 2H); ^{13}C NMR δ 144.1 (one isomer), 143.5 (other isomer), 143.2 (one isomer), 142.6 (other isomer), 135.8 (one isomer), 135.7 (other isomer), 134.4 (one isomer), 134.3 (other isomer), 132.3 (one isomer), 132.2 (other isomer), 131.2, 131.2, 129.6, 129.5, 128.0, 127.9, 127.9, 126.7 (one isomer), 126.6 (other isomer), 118.3 (one isomer), 118.3 (other isomer), 118.0, 73.0 (one isomer), 72.6 (other isomer), 55.1, 43.0 (one isomer), 42.8 (other isomer), 37.8 (one isomer), 37.7 (other isomer); HRMS Calcd for $C_{20}H_{19}Cl$ ($M^+ - H_2O$) 295.1253, found 295.1237.

5-(4-Methylphenyl)-5-phenylocta-1,7-dien-4-ol (6c). Colorless oil; yield, 68%; (isomer mixture 1:1); ^{1}H NMR δ 7.31−7.20 (m, 5H), 7.18−7.08 (m, 4H), 5.92−5.80 (m, 1H), 5.46−5.34 (m, 1H), 5.06−4.92 (m, 4H), 4.43−4.38 (m, 1H), 3.09−3.00 (m, 1H), 2.89−2.81 (m, 1H), 2.50−2.42 (m, 1H), 2.33 (one isomer) (s, 1.5H), 2.32 (other isomer) (s, 1.5H), 1.58−1.48 (m, 2H); ^{13}C NMR δ 144.6 (one isomer), 144.2 (other isomer), 141.1 (one isomer), 140.9 (other isomer), 136.2 (one isomer), 135.9 (other isomer), 134.9 (one isomer), 134.9 (other isomer), 129.7, 129.6, 129.5, 128.6, 128.5, 127.8, 127.8, 126.4, 126.3, 117.8 (one isomer), 117.4 (other isomer), 73.2 (one isomer), 73.1 (other isomer), 55.1 (one isomer), 55.1 (other isomer), 43.0, 37.9 (one isomer), 37.8 (other isomer), 21.1; HRMS Calcd for $C_{21}H_{22}$ ($M^+ - H_2O$) 275.1799, found 275.1799.

3-Hydroxy-1,3,3-triphenyl-1,2-propanedione (**7a**) and 1-(1-hydroxycyclohexyl)-2-phenyl-1,2-ethanedione (**7b**) were prepared according to the general procedure reported previously.[18a]

3-Hydroxy-1,3,3-triphenyl-1,2-propanedione (7a). Yellow needles (from EtOAc/hexanes); yield, 73%; mp 149−152 °C (lit.[25e] mp 150 °C); ^{1}H NMR δ 7.81 (d, J = 7.3 Hz, 3H), 7.65−7.55 (m, 3H), 7.51−7.47 (m, 5H), 7.41−7.35 (m, 5H); ^{13}C NMR δ 203.8, 197.0, 141.1, 137.8, 135.0, 132.6, 130.3, 129.9, 129.0, 128.7, 128.5, 127.8, 85.6.

1-(1-Hydroxycyclohexyl)-2-phenyl-1,2-ethanedione (7b). Yellow needles (from pentane); yield, 86%; mp 50−52 °C (lit.[25d] mp 52−53 °C); ^{1}H NMR δ 7.89 (d, J = 7.4 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 3.15 (br s, 1H), 2.00−1.83 (m, 4H), 1.79−1.67 (m, 5H), 1.35−1.25 (m, 1H); ^{13}C NMR δ 208.3, 196.1, 135.0, 132.7, 129.8, 129.1, 78.5, 34.1, 25.1, 20.7.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **3** and **6a**−**c**; X-ray structures of compounds **3**, **2g**, **5d**, **5e**, and **5i**; tables of atomic coordinates, thermal parameters, bond lengths, bond angles, anisotropic and isotropic displacement parameters for the X-ray crystal structures of **2g**, **5d**,**e**, and **5i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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