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THE PHOTOCHEMISTRY OF 1-ALKENYLBENZOTRIAZOLES

METHODOLOGY FOR THE SYNTHESIS OF INDOLES

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Abstract—The synthesis of 2-substituted, 3-substituted, and 2,3-disubstituted indoles based on the photolysis of 1-alkenylbenzotriazoles is described along with the application of this method to the synthesis of the 2,3-dihydropyrrolo[1,2-*a*]indole nucleus of the mitomycin antitumor antibiotics.

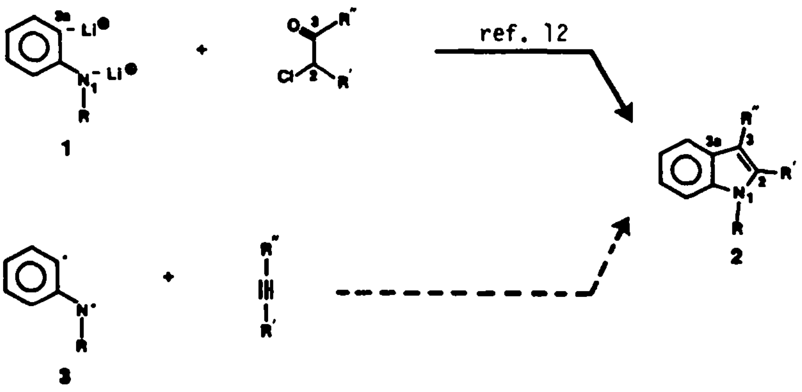
INTRODUCTION

The indole alkaloids comprise a large and structurally diverse class of natural products which, for over a century, has attracted considerable interest. Initially, these heterocycles and their derivatives figured significantly in the early dye industry while, more recently, many indoles have reached clinical importance as anti-inflammatory, antihypertensive, antibiotic and antitumor agents.[1]

Not surprisingly, the development of methods for indole synthesis has been the focus of much research. By far, the most commonly used procedures for the preparation of these heterocycles have been the Fischer indolization reaction, first reported in 1883,[2] and more recently introduced variations on this process.[3] Notwithstanding its versatility, this method is not a panacea for the diverse problems encountered in indole synthesis, particularly in connection with the elaboration of many structurally complex indoles. Accordingly, considerable emphasis has been placed on the development of alternative and complementary routes to indoles, resulting in the methods of Bischler,[4] Batcho–Leimgruber,[5] Madelung,[6] Nenitzescu,[7] and Reissert,[8] as well as other more recently introduced indolization procedures.[9]

Our interest in this area arose during studies on the synthesis of the indole alkaloid reserpine[10] and has been extended by more recent investigations on approaches to the mitomycins (*vide infra*), indole derivatives which have found clinical use as antitumor agents.[11] In connection with the former effort, we reported a method for indole synthesis which is based on the conjunction of a dilithioaniline derivative with a biselectrophile, such as a chloroketone (Scheme 1).[12] In common with the classical Fischer procedure and several others which benefit from the use of aniline derivatives as starting materials, this method develops the N1—C2 and C3—C3a bonds in the construction of the pyrrole subunit of the indole ring but utilizes different chemistry for the formation of these bonds. The synthetic value of this [3+2] annelation procedure prompted our interest in an intriguing alternative notion in which diyl **3**, the diradical analog of the bisnucleophile **1**, would be used to establish the same N1—C2 and C3—C3a bonds of the indole but under non-basic conditions. An attractive and practical feature of such an approach is that the required diradicals could be derived from commercially available or readily prepared benzotriazoles while π-systems would serve as an abundant source of diylophiles.

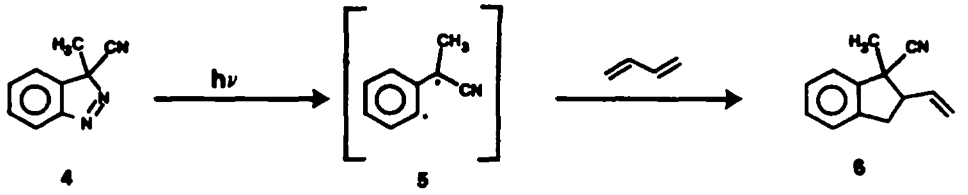
The viability of trapping diyls such as **3** is supported by early work on the carbon analogs in which, for example, photolysis of indazole **4**, in the presence of 1,3-butadiene, is reported to give indane **6** presumably via intermolecular capture of a relatively long-lived diradical **5**.[13] As demonstrated independently by Schmid and co-workers[14] and by Burgess *et al.*,[15] similar results can be obtained with benzotriazoles **7** which

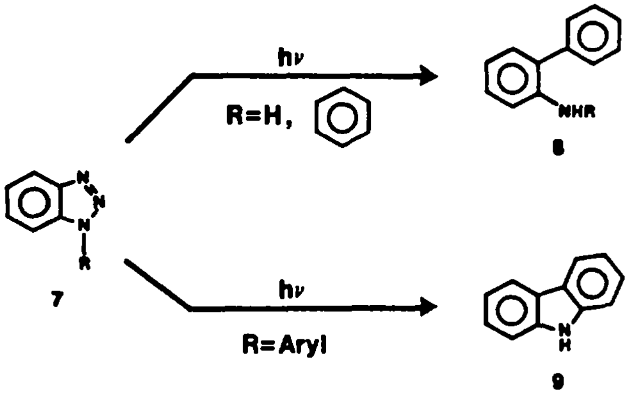


Scheme 1.

upon irradiation in aromatic solvents produce, at low conversion, a high yield of *o*-arylanilines **8**,[14] thereby implicating a diradical sufficiently long-lived for intermolecular reaction with solvent molecules. Furthermore, when the benzotriazole is directly attached to the aromatic ring, as in the case of 1-arylbenzotriazoles, photolysis is reported to afford a high yield of the carbazole product **9**.[15] The corresponding photochemistry of 1-alkenylbenzotriazoles (**7**, R = alkenyl) has received only limited study but in analogy to the 1-arylbenzotriazoles, cyclization to indole products is again observed albeit in variable yields.[16]

through alkylation of a suitably substituted benzotriazole **15**, leading to intermediates **12** or **14**. Photolysis of the former heterocycle could provide directly the mitomycin ring system while the latter intermediate (**14**) would give **13** from which **11** could be derived through intramolecular alkylation. We describe herein our studies directed at testing the viability of this strategy for the construction of the mitomycin dihydropyrroloindole ring system and at investigating the generality and efficiency of N-alkenylbenzotriazole photolysis as a method for the synthesis of indoles.

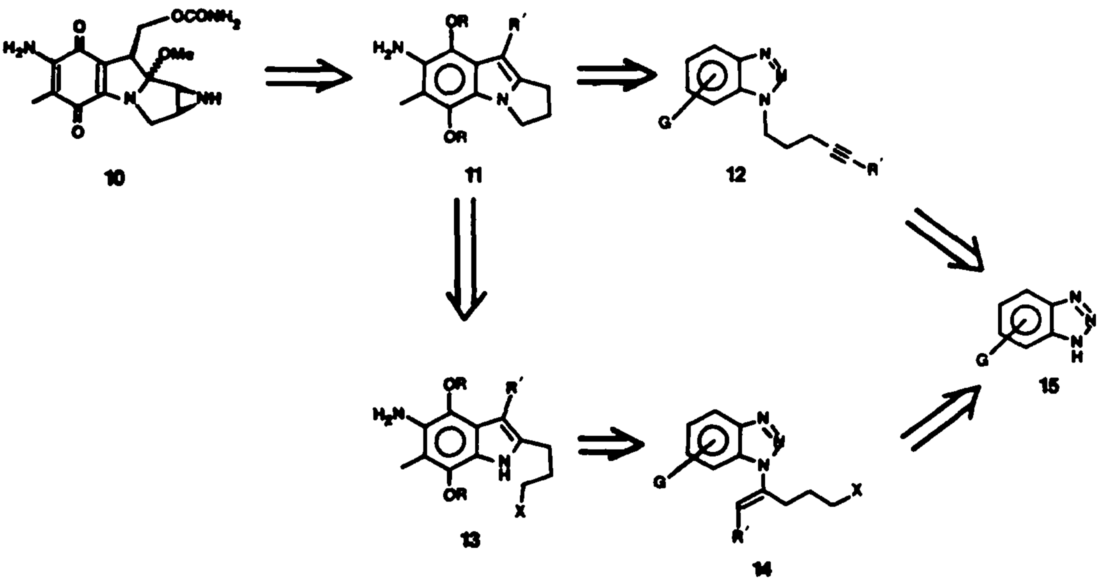




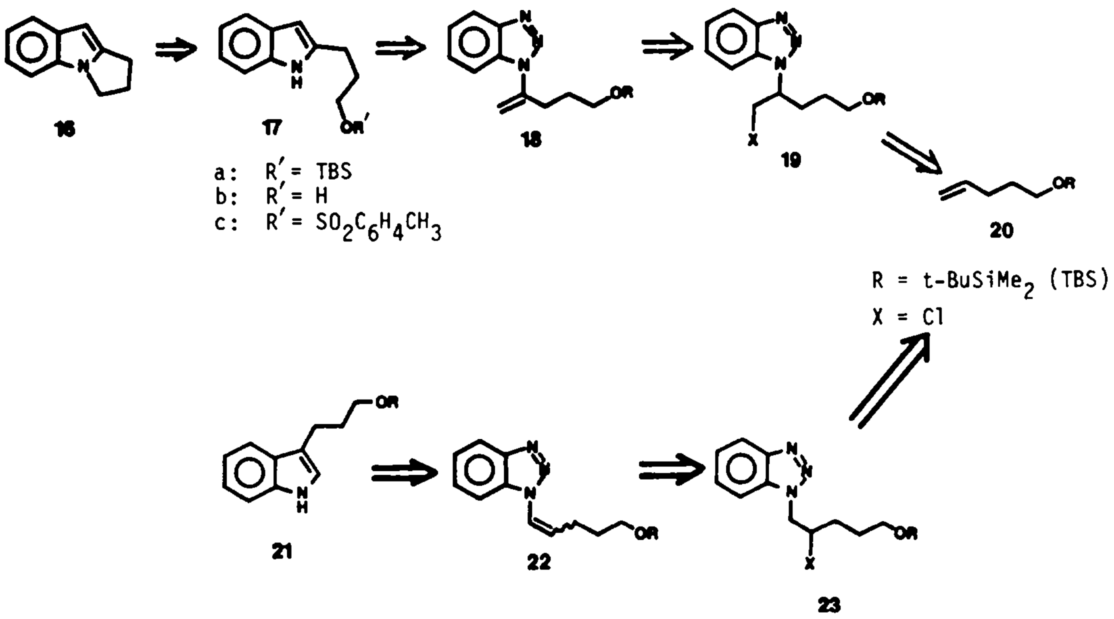
In connection with our interest in the synthesis of mitomycin analogs (Scheme 2), it was presumed on the basis of the above work that a straightforward and convergent route to these heterocycles could arise

RESULTS AND DISCUSSION

Our initial effort in this area was directed at the elaboration of the 2,3-dihydropyrrolo[1,2-*a*]indole



Scheme 2.



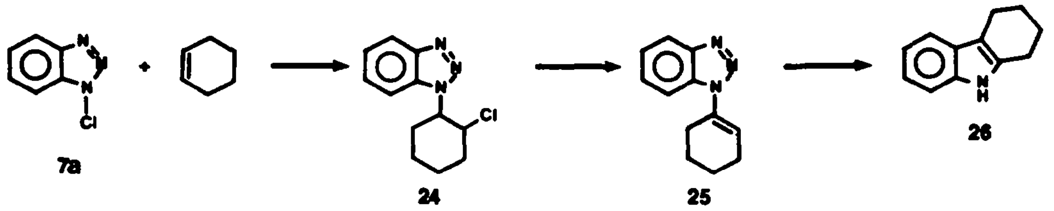
Scheme 3.

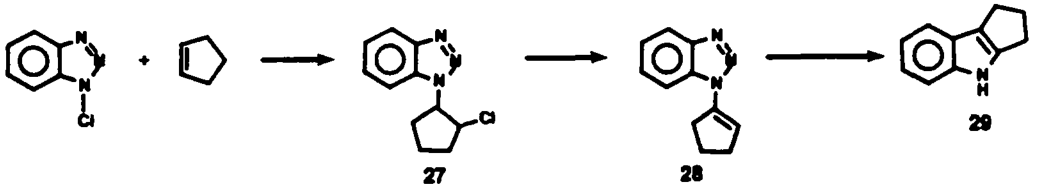
nucleus **16** of the mitomycins.[17] As seen in the retrosynthetic analysis (Scheme 3), this objective required the development of a procedure for the synthesis of N-alkenylbenzotriazoles bearing a functionalized chain attached to the alkenyl group **18** and an examination of whether this substitution and functionality would interfere with the photoextrusion–cyclization process. In connection with the former requirement, Rees and Storr[18] have reported that 1-chlorobenzotriazole (**7a**) reacts with alkenes to provide chlorobenzotriazolyl addition products. It was expected from this report and the mechanistic information described therein, that addition of **7a** to a suitably protected 4-penten-1-ol (**20**) would give addition products **19** and **23** by an ionic addition process. Indeed, when the silyl ether of 4-penten-1-ol (**20**) was treated with 1-chlorobenzotriazole, a 5:2 mixture of **19** and **23** was obtained in 71% yield. The remainder of the reaction material was determined to be a mixture of 2-benzotriazolyl adducts. Because of the difference in polarities of the 1- and 2-benzotriazolyl derivatives (2-substituted benzotriazoles were found to be much less polar than the corresponding 1-benzotriazoles in all cases examined here), the regioisomers were easily separated by column chromatography. Dehydrochlorination of the addition products **19** and **23** using 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in benzene at reflux for extended reaction times (34–41 h) afforded only modest yields of the 1-alkenylbenzotriazoles (16% for **18** and 45% for **22**). However, when adducts **19** and **23** were treated separately with an excess of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at reflux, clean reaction mixtures, consisting only of starting material and product, were obtained from which adducts **18** and **22** could be isolated in yields of 79 and 64%, respectively.

Photolysis (254 nm) of benzotriazole **18** in cyclohexane solvent in a quartz test tube at room temperature for 1.2 h provided a single product (**17a**) in 84% isolated yield (92% yield based on recovered starting material). Similar irradiation of benzotriazole **22** afforded indole **21** again in high isolated yield (88%). In addition to the obvious efficiency of these reactions, it is noteworthy that both processes occur without formation of side products arising from intramolecular hydrogen abstraction reactions.

With the gratifyingly successful transformation of benzotriazole **18** to indole **17**, we were readily able to achieve a synthesis of the dihydropyrroloindole nucleus of the mitomycins. Thus, treatment of **17a** with fluoride afforded alcohol **17b** which was cleanly converted to tosylate **17c** in 55% overall yield. Treatment of this compound with potassium t-butoxide in t-butanol at reflux furnished **16** in 93% yield. Analysis of the crude reaction mixture using TLC, capillary GC, and 300 MHz ^{1}H-NMR indicated that the reaction proceeded without detectable alkylation at C-3.

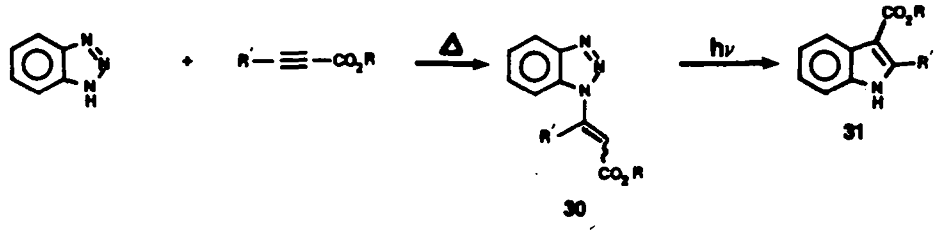
With the success of the above mitomycin model study and in anticipation of the requirements presented by other synthetic applications of this methodology, we next set out to investigate the extension of this chemistry to cycloalkenylbenzotriazoles. Accordingly, derivative **24** was prepared in 94% yield from **7a** and cyclohexene. In contrast to the reaction of **7a** with **20**, the addition involving cyclohexene was quite exothermic and required cooling (−10°) to avoid complications. Subsequent dehydrohalogenation of **24** was sluggish with DBU in toluene at reflux but proceeded rapidly at 0° in N,N-dimethylformamide when potassium t-butoxide was used as a base. Cyclohexenylbenzotriazole **25** was obtained in 72% yield after chromatography. In a similar fashion, cyclopentene was converted to cyclopentenylbenzotriazole **28** in yields of 82% for the addition step and 74% for the elimination reaction. While photolysis of **25** has been reported to provide tetrahydrocarbazole **26** in 25% isolated yield (65% based on recovered starting material),[16] we were gratified to find that this transformation can be effected in 87% isolated yield (96% based on recovered starting material). This significant improvement in efficiency presumably results from the use of a narrow excitation





band (254 nm) instead of the broad band previously employed. However, ring size variations on this process are noteworthy in that cyclopentenylbenzotriazole **28** upon photolysis furnished 1,2,3,4-tetrahydrocyclopent[*b*]indole (**29**) but only in 44% yield.

While the addition–elimination sequence served well in the 1-alkenylbenzotriazole synthesis noted above, we have found a particularly practical one-step route to alkenylbenzotriazoles, such as **30**, based on commercially-available starting materials. Thus, reaction of 1H-benzotriazole with ethyl propiolate in toluene (110°) gave a nearly quantitative yield of ethyl 3-(1-benzotriazolyl)propenoate (**30a**) as a mixture of *cis* and *trans* isomers (*cis*/*trans* = 39:61). When irradiated, this mixture provided ethyl indole-3-carboxylate (**31a**) in 74% yield (93% based on recovered **30a**). Similarly, reaction of benzotriazole with methyl 2-butynoate in *p*-dioxane (102°) with a catalytic amount of cuprous iodide afforded **30b** as a 1:1 mixture of *E* and *Z* isomers in 45% yield. In the absence of CuI, the yield for this transformation was considerably lower (11%) even after longer reaction times. Photolysis of **30b** gave methyl 2-methylindole-3-carboxylate (**31b**) in 72% yield.



a: R′ = H, R = Et
b: R′ = Me, R = Me

In summary, we have found that variously functionalized alkenylbenzotriazoles can be prepared efficiently through an addition–elimination sequence or through conjugate addition to alkynoates and that photolysis of these functionalized triazoles provides indoles in generally good to excellent yields. In the cases examined, neither remote nor conjugated functionality interferes with the photoextrusion–cyclization reaction. Furthermore, this chemistry has been shown to provide a convenient route to the dihydropyrrolo[1,2-*a*]indole nucleus of the mitomycin antitumor antibiotics. Finally, the conjugate addition–photolysis sequence, based on commercially available benzotriazole and alkynoates, represents one of the more practical methods for the synthesis of 3-carboalkoxy substituted indoles.

EXPERIMENTAL

All reactions were performed in flame- or oven-dried glassware under a positive pressure of dry N_2 or Ar. Air- or moisture-sensitive liquids and solns were transferred by syringe or cannula, and were introduced through rubber septa. Air- or moisture-sensitive solids were transferred in a dry glove bag under N_2 or under a funnel of N_2. All solns were dried by shaking with Na_2SO_4, unless otherwise stated. All temperatures are given in degrees Centigrade.

Commercial grade solvents were used without further purification with the following exceptions: hexanes (b.p. 65–69°) were fractionally distilled, CH_2Cl_2 was distilled from CaH_2, and toluene, diethyl ether (ether), and tetrahydrofuran (THF) were distilled from sodium-benzophenone ketyl prior to use. "Flash chromatography" refers to the method of Still *et al.*[19] and was performed with Merck silica gel 60 (40–60 μm) and the solvent system(s) indicated. Chromatotron chromatography was performed with a Harrison Research model 7924 instrument and the indicated solvent system(s). TLC was performed on Merck silica gel 60 F_{254} precoated aluminum sheets (0.2 mm thickness) in an appropriate solvent system.

All b.ps and m.ps reported are uncorrected. M.ps were taken on a Thomas–Hoover capillary m.p. apparatus. Those m.ps denoted (d) indicate that the compound decomposed upon melting.

IR spectra were measured on a Perkin–Elmer model 681 instrument and are reported in wavenumbers (cm^{-1}). UV spectra were run on a Perkin–Elmer Lambda 3 instrument;

absorption maxima are reported in nanometers in the form λ_{max}(log).

^{1}H-NMR spectra were measured at 100 MHz on a Varian XL-100-15 instrument and at 300 MHz on a Nicolet NT-300 instrument. Chemical shifts are reported in ppm downfield from TMS using either TMS or residual $CHCl_3$ as reference. ^{1}H-NMR data are reported in the following form: chemical shift (multiplicity, number of protons, coupling constants in Hz). The following abbreviations are used for spin multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; m, multiplet; b, broad; dd, doublet of doublets, etc.

MS were determined on either a Hewlett-Packard 5970 or 5995 Gas Chromatograph/Mass Spectrometer. Mass spectral data are presented in the following form: parent ion (relative intensity in percent), *m/e* of significant fragments (relative intensity in percent).

Elemental analyses were performed by MicAnal Organic Microanalysis Laboratory, Tucson, Arizona, or the Analytical Laboratory of the Stanford University Chemistry Department.

1 - *Chloro - 2 - (1 - benzotriazolyl) - 5 - t - butyl - dimethylsiloxypentane* **19**. A soln of **7a** (241 mg, 1.57 mmol) and **20**[20] (345 mg, 1.72 mmol) in CH_2Cl_2 (5.0 ml) was stirred at ambient temp in the dark for 3 days. Removal of solvent gave 423 mg of a crude mixture of **19**, **23**, and 1H-benzotriazole, as well as the corresponding 2-benzotriazolyl derivatives. Flash chromatography (20% ether–hexanes) afforded **19** as a colorless oil (283 mg, 51% yield). ^{1}H-NMR ($CDCl_3$): 8.08 (d, 1H, J = 8.3), 7.57–7.38 (m, 3H), 5.01 (m, 1H), 4.14 (dd, 1H, J = 8.6, 11.4), 4.03 (dd, 1H, J = 5.1, 11.4), 3.56 (m, 2H), 2.33 (m, 2H), 1.47–1.26 (m, 2H), 0.86 (s, 9H), 0.01 (s, 6H). IR (CCl_4): 2970, 2940, 1625, 1460, 1260, 1110. Mass spectrum: 298 (36), 296 (96), 194 (24), 148 (25), 143 (32), 123 (53). (Found: C, 57.61; H, 8.13; N, 12.10. Calc for $C_{17}H_{28}ClN_3OSi$: C, 57.69; H, 7.97; N, 11.87%.)

1 - (1 - *Benzotriazolyl) - 2 - chloro - 5 - t - butyl - dimethylsiloxypentane* **23**. Flash chromatography (40% ether–hexanes) of the above reaction mixture afforded pure **23** (98 mg, 20% yield) as white plates, m.p. 56–60° (d). ^{1}H-NMR ($CDCl_3$): 8.08 (d, 1H, J = 8.3), 7.62–7.37 (m, 3H), 4.89 (m, 2H), 4.50 (m, 1H), 3.63 (bt, 2H), 2.02–1.66 (m, 4H), 0.85 (s, 9H), 0.01 (s, 6H). IR (CCl_4): 2965, 1650, 1460, 1130. Mass spectrum: 298 (38), 296 (100), 194 (15), 143 (18), 130 (28), 123 (55), 104 (29). (Found: C, 57.43; H, 7.99; N, 11.61. Calc for $C_{17}H_{28}ClN_3OSi$: C, 57.69; H, 7.97; N, 11.87%.)

1 - t - *Butyldimethylsiloxy - 4 - (1 - benzotriazolyl) - 4 - pentene* **18**. The chloro adduct **19** (107 mg, 0.30 mmol) was dissolved in toluene (5.0 ml) and treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (56 mg, 0.36 mmol) in one portion at ambient temp. The resulting soln was heated to reflux for 16 h with stirring. The mixture was partitioned between ether and water, the layers were separated, and the organic layer was washed successively with water and sat NaCl aq, then dried. Concentration of the ether layer and flash chromatography (15% ether–hexanes) gave **18** (76 mg, 79% yield) as a clear yellow oil. ^{1}H-NMR ($CDCl_3$): 8.10 (d, 1H, J = 8.3), 7.71–7.38 (m, 3H), 5.45 (s, 1H), 5.30 (s, 1H), 3.65 (t, 2H, J = 6.2), 3.00 (bt, 2H, J = 7.5), 1.72 (m, 2H), 0.89 (s, 9H), 0.03 (s, 6H). IR (CCl_4): 1610, 1455, 980. (Found: C, 64.17; H, 8.81; N, 13.27. Calc for $C_{17}H_{27}N_3OSi$: C, 64.31; H, 8.57; N, 13.23%.)

1 - (1 - *Benzotriazolyl) - 5 - t - butyldimethylsiloxy - 1 - pentene* **22**. The chloro adduct **23** (84 mg, 0.24 mmol) was dissolved in toluene (4.0 ml) and treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (54 mg, 0.35 mmol) in one portion at ambient temp. The soln was heated to reflux for 18 h with stirring. The mixture was worked up as described above and the resulting clear amber product mixture was flash chromatographed with 20% ether–hexanes as eluant to furnish **22** (49 mg, 64%) as a yellow-white semi-solid. NMR analysis indicated the product to be a 75:25 mixture of the *trans* and *cis* isomers. ^{1}H-NMR ($CDCl_3$): *trans*-**22**: 8.08 (d, 1H, J = 8.3), 7.66–7.29 (m, 4H), 6.56 (dt, 1H, J = 14.3, 7.1), 3.72 (t, 2H, J = 6.1), 2.43 (m, 2H), 1.81 (m, 2H), 0.91 (s, 9H), 0.04 (s, 6H); *cis*-**22**: 8.07 (d, 1H, J = 8.3), 7.64–7.2 (m, 3H), 7.05 (dt, 1H, J = 10.7, 1.4), 5.88 (bq, 1H, J = 7.8), 3.62 (t, 2H, J = 6.2), 2.59 (dq, 2H, J = 1.3, 7.1), 1.75 (m, 2H).

1 - (1 - *Benzotriazolyl) - 2 - chlorocyclohexane* **24**. To a cooled (−10°) soln of **7a** (0.70 g, 4.56 mmol) in CH_2Cl_2 (10.0 ml) was added cyclohexene (0.45 g, 5.47 mmol) dropwise over 5 min with stirring (NOTE: 1-chlorobenzotriazole reacts *violently* with cyclohexene above 0°). The clear yellow mixture was warmed to ambient temp over 1 h and stirred for an additional 2 h. Following removal of solvent, flash chromatography (30% ether–hexanes) afforded pure **24** (1.01 g, 94% yield) as yellow-white plates, m.p. 73.5–74.0° (lit. 72–73°).[18b] The spectral data for **24** were identical with the previously reported values.[18b] ^{1}H-NMR ($CDCl_3$): 8.08 (d, 1H, J = 8.32), 7.59–7.35 (m, 3H), 4.62–4.56 (m, 2H), 2.54–1.84 (m, 6H), 1.63–1.52 (bt, 2H). IR (CCl_4): 2945, 1730, 1455, 1280, 1160. Mass spectrum: 237 (M+2, 13), 235 (41), 172 (73), 145 (14), 142 (21), 117 (32), 91 (100).

1-(1-*Benzotriazolyl)cyclohexene* **25**. The chloro adduct **24** (0.47 g, 1.85 mmol) was dissolved in N,N-dimethylformamide (DMF, 8.0 ml) at 0° and treated with solid t-BuOK (0.24 g, 2.12 mmol) in one portion. Reaction occurred immediately, giving a clear dark purple soln. After stirring at 0° for 30 min, the reaction was determined to be complete by TLC. The solvent was removed and the heterogeneous product mixture was partitioned between ether and water. The layers were separated and the aqueous phase was re-extracted with ether. The combined organics were washed with 5% HCl aq, sat $NaHCO_3$ aq and sat NaCl aq. The ether layer was dried (Na_2SO_4–K_2CO_3) and concentrated *in vacuo* to give 0.38 g of a heterogeneous yellow oil and white solid. The mixture was flash chromatographed (40% ether–hexanes) to give 0.10 g starting chlorocyclohexane, **24**, and 0.26 g **25** (72% yield) as a white solid, m.p. 45–46° (lit. 44.5–45°).[16] ^{1}H-NMR ($CDCl_3$): 8.08 (d, 1H, J = 8.31), 7.68–7.35 (m, 3H), 6.20 (m, 1H), 2.80 (m, 2H), 2.37 (m, 2H), 1.94 (m, 2H), 1.81 (m, 2H). IR (CCl_4): 1670, 1610, 1590, 1240. UV (95% EtOH): 264 (3.85), 292 (3.74). Mass spectrum: 199 (52), 170 (37), 143 (100), 104 (29), 90 (18).

1 - (1 - *Benzotriazolyl) - 2 - chlorocyclopentane* **27**. A soln of **7a** (300 mg, 1.95 mmol) in CH_2Cl_2 (3.0 ml) was cooled to −10° and treated with cyclopentene (266 mg, 3.91 mmol) dropwise over 2 min. The mixture was stirred at −10° for 12 h, then warmed to ambient temp for an additional 5 h until TLC indicated the reaction to be complete. The solvent was removed and the product mixture was flash chromatographed (50% ether–hexanes) to yield **27** (351 mg, 82% yield) as a clear light yellow oil. ^{1}H-NMR ($CDCl_3$): 8.06 (d, 1H, J = 8.5), 7.61–7.35 (m, 3H), 5.17 (bq, 1H), 4.63 (bq, 1H), 2.53 (m, 3H), 2.14 (m, 3H). IR (CCl_4): 2940, 1465, 1280, 1170. Mass spectrum: 223 (M+2, 8), 221 (23), 158 (57), 143 (10), 131 (14), 130 (69), 117 (20), 104 (32), 103 (19), 91 (100). (Found: C, 59.34; H, 5.15; N, 18.83. Calc for $C_{11}H_{12}ClN_3$: C, 59.60; H, 5.46; N, 18.95%.)

1-(1-*Benzotriazolyl)cyclopentene* **28**. The adduct **27** (72 mg, 0.32 mmol) was dissolved in DMF (3.0 ml), cooled to 0°, and treated with solid t-BuOK (46 mg, 0.41 mmol) in one portion. The clear dark purple soln was stirred at 0° for 30 min. The reaction was partitioned between ether and water, the layers were separated, and the organic phase was washed with sat $NaHCO_3$ aq, and sat NaCl aq. Evaporation of solvent afforded **28** (44 mg, 74% yield) as a yellow solid which was used without further purification. An analytical sample of **28** was obtained by recrystallization from 10:1 pentane–CH_2Cl_2 to give white needles, m.p. 73–75°. ^{1}H-NMR ($CDCl_3$): 8.10 (d, 1H, J = 8.3), 7.76 (d, 1H, J = 8.3), 7.58–7.36 (m, 2H), 6.15 (m, 1H), 3.25 (m, 2H), 2.70 (m, 2H), 2.18 (qn, 2H, J = 8.0). IR (CCl_4): 1665, 1605, 1090. UV (MeOH): 261 (3.74), 288 (3.70). (Found: C, 71.58; H, 6.16; N, 22.38. Calc for $C_{11}H_{11}N_3$: C, 71.34; H, 5.99; N, 22.69%.)

Ethyl 3-(1-benzotriazolyl)propenoate **30a**. 1H-benzotriazole (6.00 g, 50 mmol) and ethyl propiolate (5.43 g, 55 mmol) were dissolved in toluene (50 ml) and heated to reflux for 14 h. The clear yellow soln was concentrated *in vacuo* to yield **30a** (10.55 g, 97% yield) as a yellow solid. NMR indicated the product to be a 61:39 mixture of the *E* and *Z* isomers, respectively. The product mixture was used without further purification. Analytical samples of each isomer were obtained by flash chromatography (60% ether–hexanes). *E*-**30a**, white needles, m.p. 108°. ^{1}H-NMR (CDCl$_3$): 8.52 (d, 1H, J = 14.4), 8.15 (d, 1H, J = 8.3), 7.77–7.47 (m, 3H), 6.76 (d, 1H, J = 14.4), 4.34 (q, 2H, J = 7.1), 1.38 (t, 3H, J = 7.1). IR (CCl$_4$): 1725, 1655, 1275, 1030. Mass spectrum: 217 (68), 144 (36), 117 (100), 116 (58), 90 (59). (Found: C, 60.68; H, 5.22; N, 19.63. Calc for C$_{11}$H$_{11}$N$_3$O$_2$: C, 60.82; H, 5.10; N, 19.34%.) *Z*-**30a**, clear oil. ^{1}H-NMR (CDCl$_3$): 8.11 (d, 1H, J = 8.3), 7.61–7.37 (m, 4H), 6.08 (d, 1H, J = 9.4), 4.18 (q, 2H, J = 7.2), 1.12 (t, 3H, J = 7.2). IR (CCl$_4$): 1730, 1660, 1275, 1020. Mass spectrum: 217 (15), 144 (25), 130 (13), 117 (50), 116 (31), 92 (100). (Found: C, 60.45; H, 5.36; N, 19.58. Calc for C$_{11}$H$_{11}$N$_3$O$_2$: C, 60.82; H, 5.10; N, 19.34%.)

Methyl 3 - (1 - *benzotriazolyl*) - 2 - *butenoate* **30b**. To a soln of 1H-benzotriazole (203 mg, 1.70 mmol) and methyl 2-butynoate (185 mg, 1.86 mmol) in *p*-dioxane (6.0 ml) was added a catalytic amount of CuI (13 mg, 0.068 mmol) at ambient temp. The resulting suspension was heated to reflux for 32 h. The mixture was partitioned between ether and water, the layers were separated, and the aqueous layer was re-extracted with ether. The combined organic layers were washed with sat NaCl aq, dried, and concentrated to give 164 mg of a clear red oil. NMR indicated the product to be a 52:48 mixture of *E* and *Z* isomers, respectively. Chromatotron chromatography (60% ether–hexanes) provided pure *E* and *Z* stereoisomers. *E*-**30b** (86 mg, 23% yield), yellow plates, m.p. 80–83°. ^{1}H-NMR (CDCl$_3$): 8.13 (d, 1H, J = 8.3), 7.78 (d, 1H, J = 8.4), 7.62–7.43 (m, 2H), 6.41 (q, 1H, J = 0.9), 3.83 (s, 3H), 3.04 (d, 3H, J = 0.9). IR (CCl$_4$): 1740, 1250, 1060. Mass spectrum: 217 (24), 186 (10), 131 (14), 130 (100), 129 (32), 103 (29), 91 (28). (Found: C, 60.69; H, 4.99; N, 19.36. Calc for C$_{11}$H$_{11}$N$_3$O$_2$: C, 60.82; H, 5.10; N, 19.34%.) *Z*-**30b** (78 mg, 21% yield), clear colorless oil. ^{1}H-NMR (CDCl$_3$): 8.10 (d, 1H, J = 8.3), 7.54–7.32 (m, 3H), 6.15 (q, 1H, J = 1.3), 3.47 (s, 3H), 2.54 (d, 3H, J = 1.3). IR (CCl$_4$): 1735, 1080. Mass spectrum: 217 (24), 158 (28), 157 (21), 144 (29), 130 (100), 129 (55), 103 (31), 90 (25). (Found: C, 60.93; H, 5.43; N, 19.22. Calc for C$_{11}$H$_{11}$N$_3$O$_2$: C, 60.82; H, 5.10; N, 19.34%.)

General procedure for photolysis of 1-*alkenylbenzotriazoles*

Photolysis experiments were performed in an air-cooled Rayonet Photochemical Reactor equipped with 253.7 nm lamps unless otherwise indicated. All photolysis experiments were conducted in base-washed, oven-dried quartzware. The 1-alkenylbenzotriazole (0.1–5.0 mmol) was dissolved or suspended in cyclohexane (10–50 ml) in a quartz test tube, or in a quartz immersion well flask for large-scale reactions. The soln (suspension) was irradiated under a positive N$_2$ flow for the time indicated. All reactions were worked up by removal of solvent followed by silica gel flash chromatography unless otherwise indicated. Yields in parentheses are based on recovered starting material.

2 - (3′ - t - *Butyldimethylsiloxypropyl*)*indole* **17a**. Compound **18** (47 mg, 0.15 mmol) was dissolved in cyclohexane (20 ml) and irradiated for 1.2 h. Flash chromatography (30% ether–hexanes) afforded the indole **17a** (36 mg, 84% yield (92%)) as a clear yellow oil. ^{1}H-NMR (CDCl$_3$): 8.40 (bs, 1H), 7.54–7.05 (m, 4H), 6.22 (d, 1H, J = 1.3), 3.73 (t, 2H, J = 5.9), 2.88 (t, 2H, J = 7.1), 1.92 (bqn, 2H, J = 6.1), 0.85 (s, 9H), 0.03 (s, 6H). IR (CCl$_4$): 3260, 1600, 1150.

3 - (3′ - t - *Butyldimethylsiloxypropyl*)*indole* **21**. Compound **22** (37 mg, 0.12 mmol) was dissolved in cyclohexane (15 ml) and irradiated for 1.5 h. Flash chromatography (30% ether–hexanes) provided **21** (29 mg, 88% yield) as a yellow oil. ^{1}H-NMR (CDCl$_3$): 8.61 (bs, 1H), 7.83–6.97 (m, 5H), 3.78 (t, 2H, J = 6.0), 2.82 (t, 2H, J = 6.8), 2.07 (qn, 2H, J = 6.3), 0.92 (s, 9H), 0.05 (s, 6H). IR: 3280 (b), 1620, 1245, 1160, 915.

1,2,3,4 - *Tetrahydro* - 9H - *carbazole* **26**. Compound **25** (54 mg, 0.27 mmol) was dissolved in cyclohexane (10 ml) and irradiated for 1.8 h. Flash chromatography (35% ether–hexanes) afforded pure **26** (40 mg, 87% (96%)) as yellow plates, m.p. 114–116° (lit. 117–118°).[21] The spectral data for **26** were identical with that obtained for **26** by a known route.[12] ^{1}H-NMR (CDCl$_3$): 7.67 (bs, 1H), 7.45–7.25 (m, 2H), 7.12–7.06 (m, 2H), 2.72 (m, 4H), 1.90 (m, 4H). IR (CCl$_4$): 3455, 2840, 1470, 1315, 1220. Mass spectrum: 171 (34), 170 (15), 144 (12), 143 (100).

1,2,3,4 - *Tetrahydrocyclopent*[*b*]*indole* **29**. Compound **28** (30 mg, 0.14 mmol) was suspended in cyclohexane (12 ml) and irradiated for 2.1 h. Flash chromatography (50% ether–hexanes) gave **29** (10 mg, 44% yield) as a white solid, m.p. 103–106° (lit. 108°).[12] The spectral data for **29** were identical with the reported values.[12] ^{1}H-NMR (CDCl$_3$): 7.70 (bs, 1H), 7.45–7.02 (m, 4H), 2.98–2.17 (m, 6H). IR (CCl$_4$): 3460, 2925, 1460, 1305, 1040. Mass spectrum: 158 (17), 157 (100), 156 (93), 130 (39), 129 (22), 116 (14).

Ethyl indole-3-*carboxylate* **31a**. Compound **30a** (0.48 g, 2.2 mmol) was suspended in cyclohexane (30 ml) and irradiated for 6.5 h in a water-cooled Ace–Hanovia photolysis reactor employing a 300 W high-pressure mercury-arc UV lamp (no filter). Chromatotron chromatography (75% ether–hexanes) yielded **31a** (0.31 g, 74% (93%)) as a yellow–white solid. Recrystallization from cyclohexane provided an analytical sample of **31a**, m.p. 123–124° (lit. m.p. 124–126°).[22] The spectral data for **31a** were identical with that obtained for **31a** by a known route.[22] ^{1}H-NMR (CDCl$_3$): 8.63 (bs, 1H), 8.20 (m, 1H), 7.93 (d, 1H, J = 3.0), 7.44–7.27 (m, 3H), 4.40 (q, 2H, J = 7.1), 1.43 (t, 3H, J = 7.1). IR (CCl$_4$): 3260 (br), 1660. Mass spectrum: 189 (36), 161 (19), 145 (11), 144 (100), 116 (26), 89 (26).

Methyl 2 - *methylindole* - 3 - *carboxylate* **31b**. *E*-**30b** (65 mg, 0.30 mmol) was suspended in cyclohexane (10 ml) and irradiated for 2.0 h. Concentration of the resulting dark red reaction soln and chromatography (20% CH$_2$Cl$_2$–hexanes) furnished **31b** (41 mg, 72% yield) as a white solid. Recrystallization from 60% benzene–hexane provided pure **31b** as a yellow powder, m.p. 125–128°. ^{1}H-NMR (CDCl$_3$): 8.68 (bs, 1H), 8.10 (m, 1H), 7.17–7.36 (m, 3H), 3.93 (s, 3H), 2.73 (s, 3H). IR (CCl$_4$): 3310, 1650, 1445, 1365, 1100, 1075. Mass spectrum: 189 (63), 174 (12), 159 (11), 158 (100), 157 (21), 130 (26), 129 (19), 103 (14).

2,3-*Dihydro*[1,2-*a*]*pyrroloindole* **16**. A soln of **17a** (36 mg, 0.13 mmol) in THF (3.0 ml) was cooled to 0° and treated with tetra-n-butyl ammonium fluoride (0.5 ml, 1 M THF soln) dropwise over 2 min. The reaction was stirred at 0° for 30 min, then warmed to ambient temp and stirred for an additional 30 min. The clear yellow soln was diluted with 10 ml ether and filtered through a short column of silica gel, eluting with ether. Evaporation of solvent provided **17b**, homogeneous by TLC (16 mg, 73% yield). ^{1}H-NMR (CDCl$_3$): 8.18 (bs, 1H), 7.54–7.04 (m, 4H), 6.26 (d, 1H, J = 1.3), 3.76 (t, 2H, J = 6.1), 2.91 (t, 2H, J = 7.1), 2.42 (bs, 1H), 1.99 (bqn, 2H). Alcohol **17b** was converted to the corresponding *p*-toluenesulfonate ester **17c** by the usual procedure.[23] Tosylate **17c** (11.2 mg, 0.034 mmol) was dissolved in t-BuOH (4.0 ml) and added to a soln of t-BuOK (4 mg, 0.036 mmol) in t-BuOH (2 ml) at ambient temp. The clear yellow soln was heated to reflux for 30 min, then cooled to ambient temp and diluted with 20 ml ether. The organics were washed with sat NaCl aq and dried prior to concentration *in vacuo*. The product mixture was flash filtered through a short column of silica gel, eluting with methylene chloride, to yield the fused indole product **16** (4.5 mg, 92%) as yellow plates, m.p. 75–78° (lit. m.p. 79–80°).[24,25] The spectral data for **16** were identical with that obtained for **16** by a known route.[25] ^{1}H-NMR (CDCl$_3$): 7.54 (d, 1H, J = 7.4), 7.25–7.03 (m, 3H), 6.16 (s, 1H), 4.07 (t, 2H, J = 7.0), 3.02 (t, 2H, J = 7.5), 2.61 (m, 2H). IR (CCl$_4$): 2960, 2920, 1260, 1090, 1015. Mass spectrum: 157 (100), 156 (78), 154 (16), 129 (23), 128 (18). (Found: C, 83.95; H, 7.28; N, 8.77. Calc for C$_{11}$H$_{11}$N: C, 84.04; H, 7.05; N, 8.91%.)

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