Synthesis of 2-Azatricyclo[5.2.1.0^{4,10}]decanes and 2,5-Diazatricyclo[5.2.1.0^{4,10}]decanes by Intramolecular Azomethine Ylide Cycloadditions

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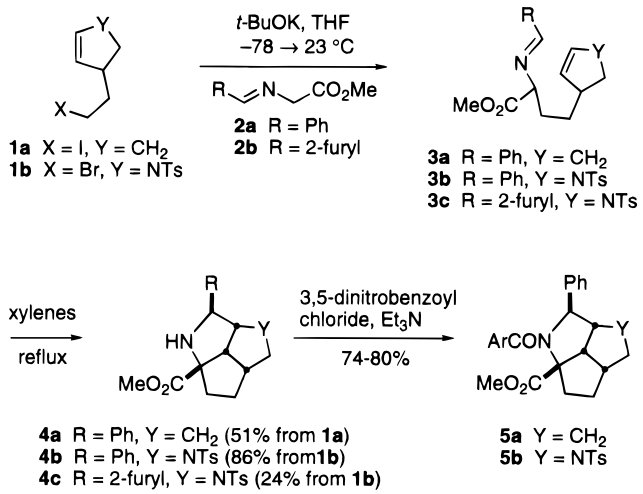
The dipolar cycloaddition of azomethine ylides with suitable dipolarophiles is a powerful method for the synthesis of pyrrolidines, pyrrolines, and pyrroles.[2] The original, and still often-used, method for forming acylic azomethine ylides is thermal ring-opening of substituted aziridines, pioneered by the groups of Heine, Huisgen, and Padwa in the early 1960's. Since that time, many additional methods for generating acyclic azomethine ylides have been disclosed.[2b] One of the simplest of these is tautomerization of α-amino acid ester imines, which has been extensively developed by Grigg and co-workers.[3] Bimolecular cycloadditions of azomethine ylides generated by tautomerization are typically high-yielding only when an electron-deficient dipolarophile is employed. However, intramolecular variants of this reaction proceed efficiently with nonactivated dipolarophiles such as terminal alkenes, providing a convenient synthesis of 2-azabicyclo[3.3.0]octanes.[4] As part of exploratory efforts directed toward the synthesis of several complex guandinium alkaloids,[5] we recently examined the utility of intramolecular azomethine ylide cycloadditions for preparing azahexahydrotriquinacenes. We report here convenient syntheses of the rare 2-azatricyclo[5.2.1.0^{4,10}]-decane and the 2,5-diazatricyclo[5.2.1.0^{4,10}]decane ring systems,[6] which demonstrate that cyclic disubstituted alkenes and related enamine derivatives can participate efficiently as dipolarophiles in Grigg-type intramolecular azomethine ylide cycloadditions.

Results and Discussion

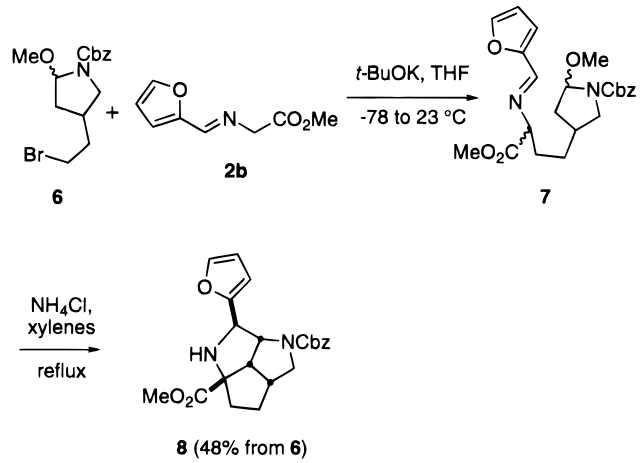
Cycloaddition substrates were prepared by alkylation of methyl glycinate imines **2** with cyclopentenylethyl iodide **1a** or (tosyldihydropyrrolyl)ethyl bromide **1b** (Scheme 1).[7] The resulting crude α-alkyl glycine imines **3** were then heated in refluxing xylenes to generate cycloadducts **4a**−**c** in moderate to good overall yields from **1**. In all cases, only a single cycloadduct was isolated. Cycloadditions of benzaldehyde-derived imines proceeded in higher yield than reactions of the corresponding furfural-derived imines; the latter produced several additional byproducts. The *all-cis* stereochemistry of cycloadducts **4** was signaled by the apparent triplet (J = 9 Hz) observed at 3.3−3.6 ppm for the central methine hydrogen of the hexahydrotriquinacene ring system. Structural assignments for cycloadducts **4a** and **4b** were confirmed by single crystal X-ray analysis of 3,5-dinitrobenzoyl derivatives **5a** and **5b**.[8]

Related enecarbamate electrophiles were prone to decomposition during the alkylation step; thus, we employed an alternate reaction sequence to synthesize the benzyloxycarbonyl-protected cycloadduct **8** (Scheme 2). In this approach, the enecarbamate dipolarophile was generated *in situ* by NH_4Cl-catalyzed elimination of methanol from methyl hemiaminal **7**.[9] As

Scheme 1



Scheme 2



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in the cycloadditions reported in Scheme 1, only the *all-cis* cycloadduct was isolated.

To our knowledge the cycloadditions reported here, and those recently described by Bartlett,[10] are the first examples of dipolar cycloadditions of simple disubstituted and electron-rich alkenes with azomethine ylides generated from α-amino acid ester imines.[11] The two-atom tether linking the dipole and the dipolarophile in these cycloadditions enforces regioselectivity opposite what would be expected from related intermolecular reactions.[2] The *all-cis* stereochemistry observed for cycloadducts **4** and **8** reflects the tendency for monoalkyl glycine-derived ylides to react predominantly in the W-conformation, even with unreactive dipolarophiles.[4a,12] Stereoselection is undoubtedly enforced also by the steric demands of the transition state leading to the rigid tricyclo[5.2.1.$0^{4,10}$]-decane products.

In summary, hexahydrotriquinacenes containing either one or two nitrogen atoms can be prepared conveniently by intramolecular azomethine ylide cycloaddition chemistry. These rigid polycyclic structures are of interest in natural products synthesis and medicinal chemistry.

Experimental Section[13]

General Procedure for Alkylation of Glycine Imines. α-(2-(3-(2,3-Dihydro-1-(*p*-toluenesulfonyl)pyrrolyl)ethyl)-*N*-benzylideneglycine Methyl Ester (3b). A solution of **2a**[7b] (1.67 g, 9.44 mmol) and THF (25 mL) was added over 5 min to a stirring solution of *t*-BuOK (1.02 g, 9.11 mmol) and THF (25 mL) at −78 °C. After 10 min at this temperature, the resulting deep orange mixture was treated dropwise with a solution of **1b**[16] (1.95 g, 5.91 mmol) and THF (15 mL). After 30 min at −78 °C, the mixture was allowed to warm to rt. After an additional 18 h, saturated aqueous NH_4Cl (50 mL) and ether (75 mL) were added. The organic layer was separated, washed with brine (2 × 50 mL), dried ($MgSO_4$), and concentrated to give crude **3b** (3.17 g) as an orange oil, which was used without further purification.

A portion of this sample was purified by rapid chromatography on silica gel (30:15:1 hexanes−EtOAc−Et_3N) to provide a pure specimen of **3b** as a pale yellow oil that was a 1:1 mixture of diastereomers: ^{1}H NMR (300 MHz, C_6D_6) δ 7.91 (br s, 1H), 7.60−7.75 (m, 3H), 7.05−7.2 (m, 3H), 6.76 (d, J = 8 Hz, 1H), 6.75 (d, J = 8 Hz, 1H), 6.34 (m, 1H,), 4.63 (dd, J = 2, 4 Hz, 0.5H), 4.57 (dd, J = 2, 4 Hz, 0.5H), 3.60 (m, 1H), 3.30−3.40 (m, 1H), 3.30 (s, 1.5H), 3.29 (s, 1.5H), 2.95−3.15 (m, 1H), 2.32 (m, 1H), 1.84 (s, 3H), 1.60−1.80 (m, 2H), 0.80−1.10 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6) 171.6, 163.4, 143.4, 136.3, 133.8, 131.2, 130.9, 130.8, 129.7, 128.8, 114.9, 114.8, 73.2, 53.0, 52.9, 51.6, 42.7, 31.6, 30.7, 21.1 ppm; MS (CI) m/z 427.1693 (427.1691 calcd for $C_{23}H_{26}N_2O_4S$, MH).

α-(2-(2-Cyclopentenyl)ethyl)-*N*-benzylideneglycine Methyl Ester (3a). Prepared according to the general procedure for alkylation from **2a**[7b] (1.17 g, 6.61 mmol), *t*-BuOK (737 mg, 6.58 mmol), and **1a**[17] (1.46 g, 6.58 mmol) at −78 °C for 1.5 h, followed by 2 h at rt. Workup gave 1.87 g of crude **3a** as an orange-brown oil, which was used without further purification. This material, a 1:1 mixture of diastereomers, was estimated by ^{1}H NMR analysis to be 80% pure and to be contaminated with a small amount of benzaldehyde: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.79 (dd, J = 2, 9 Hz, 2H), 7.42 (m, 3H), 5.70 (m, 1H), 5.54 (m, 1H), 3.96 (dd, J = 6, 9 Hz, 1H), 3.75 (s, 3H), 2.67 (m, 1H), 2.29 (m, 2H), 1.80-2.10 (m, 3H),1.10−1.45 (m, 3H).

α-(2-(3-(2,3-Dihydro-1-(*p*-toluenesulfonyl)pyrrolyl)ethyl)-*N*-(2-furylidene)glycine Methyl Ester (3c). Prepared according to the general procedure for alkylation from **2b**[18] (530 mg, 3.2 mmol), *t*-BuOK (330 mg, 3.0 mmol), and **1b**[16] (650 mg, 2.0 mmol) at −78 °C for 5 min, followed by 3 h at rt. Workup gave 760 mg of crude **3c** as a brown oil, which was a complex mixture of stereoisomers (^{1}H NMR analysis).

α-(2-(3-(2,3-Dihydro-1-(*p*-toluenesulfonyl)pyrrolyl)ethyl)-*N*-(2-furylidene)glycine Methyl Ester (7). Prepared according to the general procedure for alkylation from **2b**[18] (650 mg, 3.9 mmol), *t*-BuOK (400 mg, 3.6 mmol), and **6**[16] (820 mg, 2.4 mmol) at −78 °C for 5 min, followed by 14 h at rt. Workup gave 1.12 g of crude **7** as a brown oil, which was a complex mixture of stereo- and conformational isomers (^{1}H NMR analysis).

General Procedure for Cycloaddition. (1*R,3*S**,4*S**,7*S**,10*R**)-1-Carbomethoxy-2,5-diaza-3-phenyl-5-(*p*-toluenesulfonyl)tricyclo[5.2.1.$0^{4,10}$]decane (4b).** Dry N_2 was bubbled through a solution of crude **3b** (3.17 g) and xylenes (20 mL) at rt for 10 min. The solution was then heated at reflux (bath temperature 160 °C) for 42 h. The mixture was cooled to rt and concentrated to give a brown residue, which was purified by chromatography on silica gel (2:1 hexanes−EtOAc) to give 2.17 g of **4b** (86% from **1b**) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J = 8 Hz, 2H), 7.20−7.35 (m, 7H), 4.82 (d, J = 2 Hz, 1H), 3.98 (dd, J = 2, 9 Hz, 1H), 3.55 (app t, J = 9 Hz, 1H), 3.48 (s, 3H), 3.44 (dd, J = 3, 10 Hz, 1H), 3.18 (dd, J = 7, 10 Hz, 1H), 2.60 (m, 1H), 2.42 (s, 3H), 1.80−2.10 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) 175.7, 143.7, 141.6, 132.6, 129.5, 128.3, 127.9, 127.1, 126.7, 77.0, 71.0, 68.5, 58.2, 54.9, 52.1, 42.5, 39.0, 30.9, 21.4 ppm; IR (film) 3340, 2947, 2865, 1729, 1596, 1453, 1345, 1214, 1161, 1091, 666 cm^{-1}; MS (EI) m/z 427.1705 (427.1691 calcd for $C_{23}H_{27}N_2O_4S$, MH).

The 3,5-dinitrobenzamide **5b** was prepared from **4b** (10 mg, 0.023 mmol), 3,5-dinitrobenzoyl chloride (50 mg, 0.22 mmol), DMAP (10 mg, 0.082 mmol), Et_3N (200 μL, 1.4 mmol), and CH_2Cl_2 (2.5 mL) at rt for 24 h. Concentration, followed by chromatography of the residue on silica gel (2:1 hexanes−EtOAc) yielded 32 mg (74%) of **5b** as a yellow solid, which crystallized as prisms from hexanes−THF: mp > 230 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (t, J = 2 Hz, 1H), 8.10 (d, J = 2 Hz, 2H), 7.3−7.1 (m, 9H), 5.49 (broad s, 1H), 3.88 (s, 3H), 3.61 (m, 2H), 3.47 (app t, J = 9 Hz, 1H), 3.13 (dd, J = 8, 10 Hz, 1H), 2.97 (m, 1H), 2.70 (m, 1H), 2.36 (m, 2H), 2.35 (s, 3H), 2.02 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 172.3, 165.4, 147.8, 144.5, 140.5, 139.7, 130.7, 129.8, 129.0, 128.3, 128.1, 127.3, 126.4, 118.8, 79.1, 72.9, 72.3, 58.4, 56.9, 53.0, 40.4, 36.8, 33.8, 21.5 ppm; IR (film) 3105, 2953, 2866, 1739, 1732, 1660, 1644, 1543, 1462, 1394, 1345, 1163, 733 cm^{-1}; MS (EI) m/z 620.1571 (621.1577 calcd for $C_{30}H_{29}N_4O_9S$, M). Anal. Calcd for $C_{30}H_{28}N_4O_9S$: C, 58.06; H, 4.55; N, 9.03. Found: C, 58.09; H, 4.59; N, 8.92.

(1*R,3*S**,4*S**,7*S**,10*R**)-2-Aza-1-carbomethoxy-3-phenyltricyclo[5.2.1.$0^{4,10}$]decane (4a).** Prepared according to the general procedure for cycloaddition (reaction time 36 h) from crude **3a** (980 mg). Chromatography on silica gel (3:1 hexanes−EtOAc) gave 482 mg of **4a** (51% from **1a**) as a slightly yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20−7.35 (m, 5H), 3.92 (d, J = 7 Hz, 1H), 3.62 (s, 3H), 3.29 (app t, J = 9 Hz, 1H), 2.61 (m, 2H), 1.45−2.15 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 176.9, 143.2, 128.4, 127.1, 126.9, 76.8, 68.0, 60.6, 52.8, 52.0, 44.9, 37.7, 31.52, 31.50, 31.1 ppm; IR (film) 3350, 3022, 2945, 2862, 1729, 1447,

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(13) General experimental details: The solvents THF, ether, CH_2Cl_2, and toluene were dried by passage through a bed of activated alumina.[14] For reactions requiring anhydrous conditions, substrates were dried by azeotropic distillation using benzene or toluene. High resolution mass spectra were obtained in the CI method with isobutane unless otherwise noted. Chromatography was performed using E. Merck silica gel 60 using standard flash chromatography techniques. Other experimental details were recently described.[15]

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1215, 1158 cm^{-1}; MS (EI) *m/z* 271.1571 (271.1572 calcd for $C_{17}H_{21}NO_2$, M).

The 3,5-dinitrobenzamide **5a** was prepared from **4a** (88 mg, 0.32 mmol), 3,5-dinitrobenzoyl chloride (98 mg, 0.42 mmol), Et_3N (91 μl, 0.65 mmol), and CH_2Cl_2 (2.5 mL) at rt for 10 min. Concentration, chromatography of the residue (3:1 hexanes−EtOAc), and crystallization from hexanes−benzene yielded 120 mg (80%) of **5a** as a slightly yellow solid: mp 174−175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (t, J = 2 Hz, 1H), 8.05 (d, J = 2 Hz, 2H), 6.9−7.2 (m, 5H), 4.37 (broad d, J = 9 Hz, 1H), 3.92 (s, 3H), 3.23 (dd, J = 9, 10 Hz, 1H), 2.83 (m, 2H), 2.25−2.5 (m, 2H), 2.05−2.15 (m, 1H), 1.55−1.9 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 173.0, 164.9, 147.6, 142.7, 140.6, 129.0, 127.6, 126.9, 126.4, 118.4, 79.0, 73.1, 60.2, 54.9, 52.8, 44.4, 37.4, 34.3, 32.8, 31.1 ppm; IR (film) 3104, 2952, 2868, 1738, 1643, 1543, 1456, 1402, 1343, 1170, 1078, 911, 726 cm^{-1}; MS (EI) *m/z* 465.1527 (465.1536 calcd for $C_{24}H_{23}N_3O_7$, M). Anal. Calcd for $C_{24}H_{23}N_3O_7$: C, 61.93; H, 4.98; N, 9.03. Found: C, 61.32; H, 5.02; N, 8.93.

(1*R,3*S**,4*S**,7*S**,10*R**)-1-Carbomethoxy-2,5-diaza-3-(2-furyl)-5-(*p*-toluenesulfonyl)tricyclo[5.2.1.0^{4,10}]decane (4c).** Prepared according to the general procedure for cycloaddition (reaction time 46 h) from **3c** (760 mg). Chromatographic purification on silica gel (1:1 hexanes−EtOAc) gave 201 mg of **4c** (24% from **1b**) as a brown oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8 Hz, 2H), 7.31 (d, J = 8 Hz, 2H), 7.30 (br s, 1H), 6.25 (dd, J = 2, 5 Hz, 1H), 6.05 (d, J = 2 Hz, 1H), 4.99 (s, 1H), 3.75 (d, J = 9 Hz, 1H), 3.62 (t, J = 9 Hz, 1H), 3.50 (s, 3H), 3.46 (d, J = 10 Hz, 1H), 2.91 (dd, J = 6, 10 Hz, 1H), 2.63 (m, 1H), 2.43 (s, 3H), 2.1−1.7 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 175.9, 154.8, 143.9, 141.8, 131.4, 129.6, 128.1, 110.0, 105.8, 77.6, 68.3, 62.3, 57.3, 55.1, 52.2, 41.9, 39.6, 31.1, 21.4 ppm; IR (film) 3359, 3117, 2952, 2863, 1730, 1598, 1500, 1439, 1347, 1273, 1216, 1163, 1092, 1044, 1015, 913, 817, 734, 685 cm^{-1}; MS (CI) *m/z* 417.1480 (417.1484 calcd for $C_{21}H_{25}N_2O_5S$, MH).

(1*R,3*S**,4*S**,7*S**,10*R**)-1-Carbomethoxy-2,5-diaza-3-(2-furyl)-5-(benzyloxycarbonyl)tricyclo[5.2.1.0^{4,10}]decane (8).** Dry N_2 was bubbled for 10 min through a mixture of solid NH_4Cl (500 mg), crude **7** (1.02 g), and xylenes (20 mL), and the mixture was then heated at reflux for 24 h. The cooled mixture was filtered (glass wool) and concentrated, and the residue was purified by chromatography on silica gel (2:1 hexanes−EtOAc) to yield 0.42 g of **8** (48% from **6**) as a brown oil: ^{1}H NMR (300 MHz, toluene-d_8, obtained at 85 °C) δ 6.90−7.20 (m, 6H), 5.99 (dd, J = 2, 3 Hz, 1H), 5.90 (d, J = 3 Hz, 1H), 5.05 (d, J = 12 Hz, 1H), 4.98 (d, J = 12 Hz, 1H), 4.65 (br s, 1H), 4.30 (br d, J = 9 Hz, 1H), 3.56 (app t, J = 9 Hz, 1H), 3.42 (br dd, J = 8, 11 Hz, 1H), 3.28 (dd, J = 4, 11 Hz, 1H), 3.26 (s, 3H), 2.52 (br s, 1H), 2.38 (m, 1H), 1.65−1.80 (m, 4H); ^{13}C NMR (75 MHz, toluene-d_8, obtained at 85 °C; some resonances were obscured by solvent peaks) 175.9, 157.1, 155.1, 141.7, 138.0, 110.3, 105.9, 67.5, 67.1, 64.0, 57.4, 53.6, 51.6, 43.2, 40.8, 32.6, 28.1 ppm; IR (film) 3357, 3031, 2949, 2875, 1730, 1702, 1498, 1440, 1407, 1352, 1272, 1212, 1175, 1110, 738 cm^{-1}; MS (CI) *m/z* 397.1766 (397.1763 calcd for $C_{22}H_{25}N_2O_5$, MH).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new compounds, and detailed experimental procedures and characterization data for the preparation of **1b** and **6** (47 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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