A New Synthesis of 1,2,3,5-Tetrahydroimidazo[2,3-*b*]-[1,3]benzodiazocines

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A new synthesis of 6-carbomethoxy-1,2,3,5-tetrahydroimidazo[2,3-*b*][1,3]benzodiazocines **13** by the intramolecular cycloaddition reaction of methyl 2-(1-aziridinylmethyl)-3-(2-ureidophenyl)propenoates **10** under Appel's dehydration conditions is described. The latter were readily obtained from 2-nitrobenzaldehyde with methyl acrylate through the Baylis-Hillman reaction.

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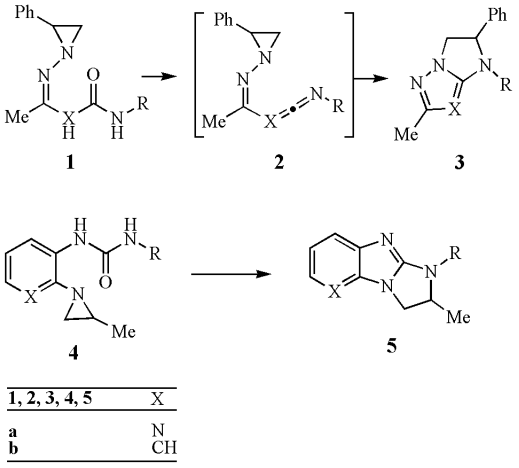
The cycloaddition of three-membered ring heterocycles with heterocumulenes is a useful method for the formation of five-membered ring heterocycles. Aziridines and aziridinium salts are known to undergo ring expansion with a variety of unsaturated functional groups such as aldehydes [1], ketones [2], thioketones [3], imines [4], carbon dioxide [5,6], carbon disulfide [6], isocyanates [7], isothiocyanates [6,7], carbodiimides [8], and sulfur diimides [9].

We recently described new routes to 1,2,4-triazole-, pyrazole-, pyridine- and benzo-fused heterocycles such as 5,6-dihydro-7*H*-imidazo[1,2-*b*][1,2,4]triazoles **3a** [10], 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazoles **3b** [11], 2,3-dihydro-1*H*imidazo[2',3':2,3]imidazo[4,5-*b*]pyridines **5a** [12], and 2,3-dihydro-1*H*-imidazo[1,2-*a*]benzimidazoles **5b** [13], from *N*-aziridinylimino ureas **1a**, *N*-aziridinylimino carboxamides **1b**, 2-(2-methylaziridin-1-yl)-3-ureidopyridines **4a**, and 1-(2-methylaziridin-1-yl)-2-ureidobenzenes **4b** using Appel's dehydration conditions [14], respectively (Scheme I).

Scheme I



1, 2, 3, 4, 5	X
a	N
b	CH

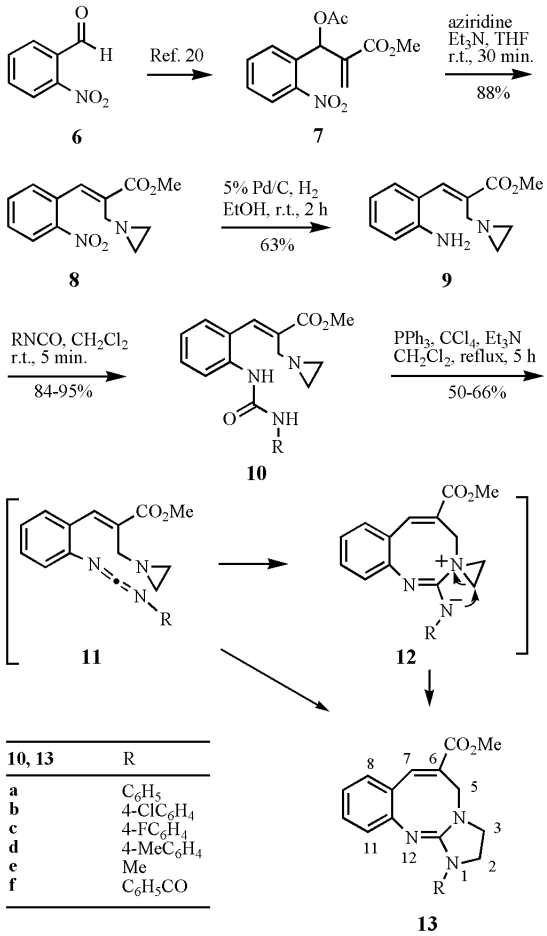
In addition, the Baylis-Hillman reaction has been the subject of recent reviews [15] and continues to elicit attention. We have demonstrated applications of this reaction in the syntheses of 3-oxo-2,3-dihydro-1*H*-isoindoles [16], 4*H*-tetrazolo[1,5-*a*][1]benzazepines [17], 5*H*-1,2,3-triazolo[4,3-*a*][2]benzazepines [18], and anthraquinone derivatives [19]. We herein report a facile synthesis of hitherto unknown 6-carbomethoxy-1,2,3,5-tetrahydroimidazo[2,3-*b*][1,3]benzodiazocines **13** by the intramolecular cycloaddition reaction of 2-(1-aziridinylmethyl)-3-(2-ureidophenyl)acrylic acid methyl esters **10** under Appel's dehydration conditions.

The reaction of known methyl 3-acetoxy-2-methylene-3-(2-nitrophenyl)propanoate (**7**) [20] with aziridine in the presence of triethylamine in tetrahydrofuran at room temperature for 30 minutes afforded a single product methyl 2-(1-aziridinylmethyl)-3-(2-nitrophenyl)propenoate (**8**) as *E*-isomer in 88% yield. The (*E*)-stereochemistry of **8** was determined by the ^{1}H NMR spectral analysis of methine proton in comparison with literature values [21]. Nitrophenylpropenoate **8** on hydrogenation over 5% Pd/C in ethanol gave 63% yield of methyl 3-(2-aminophenyl)-2-(1-aziridinylmethyl)propenoate (**9**). Compound **9** was reacted with an equivalent of isocyanates in dichloromethane at room temperature to give methyl 2-(1-aziridinylmethyl)-3-(2-ureidophenyl)propenoates **10** in 84-95% yields.

Reaction of ureas **10** with triphenylphosphine, carbon tetrachloride, and triethylamine in refluxing dichloromethane for 5 hours afforded 6-carbomethoxy-1,2,3,5-tetrahydroimidazo[2,3-*b*][1,3]benzodiazocines **13** in 50-66% yields, and which constitute unexplored class of compounds. A suitable mechanism for the formation of **13** is depicted in Scheme II. Although the isolation of carbodiimide **11** was unsuccessful under the reaction conditions, a nucleophilic attack of aziridine to carbodiimide gave the zwitterionic aziridinium ion **12** followed by aziridine ring opening by the attack of nitrogen anion to give **13**, or a direct intramolecular cycloaddition reaction of aziridine with carbodiimide in a concerted manner produced **13**.

The structure of **13** was established on the basis of spectroscopic data. In the ^{1}H NMR spectra, the chemical shift of the methine proton of C7 was found at δ = 7.96-8.06 as a singlet and six methylene protons of C2, C3 and C5 were observed at δ = 3.42-3.97 as a broad singlet, δ = 3.21-3.68 as a multiplet and δ = 3.89-4.21 as a broad singlet, and proved to be correlated to the C5 (δ = 44.9), C2 (δ = 45.7), C3 (δ = 47.2) and C7 (δ = 146.7) carbon atoms by two dimensional carbon-proton heteronuclear correlation spec-

Scheme II



10, 13	R
a	C_6H_5
b	4-ClC_6H_4
c	4-FC_6H_4
d	4-MeC_6H_4
e	Me
f	C_6H_5CO

troscopy (HETCOR) and the DEPT ^{13}C NMR spectrum of **13c**. Also in the HMBC spectrum of **13c** C7 methine proton (δ = 8.06) was correlated with C5 carbon (δ = 44.9) and aromatic carbons. The IR spectra showed absorption band in 1712-1719 cm^{-1} assignable for the ester carbonyl bond. The mass spectral data showed all M^+ peaks and characteristic decomposition peak at m/z = (M^+ -CO_2Me) as a base peak except for **13f**.

In conclusion, a new synthesis of tetrahydroimidazo[2,3-*b*][1,3]benzodiazocines **13** by the intramolecular cycloaddition rection of 2-(1-aziridinylmethyl)-3-(2-ureidophenyl)acrylic acid methyl esters **10**, readily obtainable through the Baylis-Hillman adducts, under Appel's conditions was achieved.

EXPERIMENTAL

Aziridine [22] and methyl 3-acetoxy-2-methylene-3-(2-nitrophenyl)propanoate (**7**) [20] were prepared following literature procedures. Isocyanates were purchased from Aldrich and used without further purification. Tetrahydrofuran was distilled from sodium benzophenone ketyl and dichloromethane was distilled from calcium hydride. Silica gel 60 (70-230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical thin layer chromatography (tlc) was carried out on Merck silica gel 60 F_{254} tlc plates. Melting points were taken using an Electrothermal melting point apparatus and are uncorrected. Microanalyses were obtained using a Carlo Erba EA 1180 element analyzer. Mass spectra were obtained using a ThermoQuest Polaris Q mass spectrometer operating at 70 eV. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Gemini 300 spectrometer. The HMBC and DEPT spectra were obtained on a 300 MHz Bruker spectrometer. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane and coupling constants (J) are expressed in Hertz.

Methyl 2-(1-Aziridinylmethyl)-3-(2-nitrophenyl)propenoate (**8**).

To a solution of methyl 3-acetoxy-2-methylene-3-(2-nitrophenyl)propanoate **7** (4.00 g, 14 mmoles) in tetrahydrofuran (20 ml) was added triethylamine (5.78 g, 57 mmoles) and aziridine (2.16 g, 50 mmoles), and the mixture was stirred for 30 minutes at room temperature. The solvent was removed *in vacuo* and the residue was partioned between water (10 ml) and dichloromethane (20 ml x 2). The dichloromethane layer was removed after drying over anhydrous magnesium sulfate to give 3.32 g (88%) of **8** as a pale yellow solid after crystallization with ethyl acetate-petroleum ether; mp 96-98 °C; ir (potassium bromide): 1714, 1636, 1606, 1570, 1513, 1427, 1338 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.29 (m, 2H, CH_2), 1.72 (m, 2H, CH_2), 3.05 (s, 2H, CH_2), 3.88 (s, 3H, OCH_3), 7.56 (dd, 1H, J = 8.2 and 7.6 Hz, aromatic), 7.71 (dd, 1H, J = 7.6 and 7.6 Hz, aromatic), 7.87 (d, 1H, J = 7.6 Hz, aromatic), 8.07 (s, 1H, CH), 8.16 (d, 1H, J = 8.2 Hz, aromatic); ^{13}C nmr (deuteriochloroform): δ 27.6, 52.3, 56.2, 124.7, 129.4, 131.0, 131.4, 132.0, 133.4, 138.5, 147.6, 167.6; ms m/z (%) 262 (M^+, 100), 183 (94), 152 (20), 108 (27).

Anal. Calcd. for $C_{13}H_{14}N_2O_4$: C, 59.54; H, 5.38; N, 10.68. Found: C, 59.21; H, 5.23; N, 10.47.

Methyl 3-(2-Aminophenyl)-2-(1-aziridinylmethyl)propenoate (**9**).

To a solution of the nitro compound **8** (2.62 g, 10 mmoles) in ethanol (50 ml) was added 5% Pd/C (1.31 g, 0.6 mmoles) and the mixture was stirred under hydrogen at atmospheric pressure and room temperature for 2 hours. The reaction mixture was filtered through celite and the filtrate was evaporated *in vacuo* to give an oily residue. The residue was chromatographed on silica gel column and eluted with hexane-ethyl acetate-methanol (V/V = 20:20:1) to give 1.46 g (63%) of **9** as a pale yellow solid after crystallization with petroleum ether; mp 136-138 °C; ir (potassium bromide): 3330, 3206, 1688, 1657, 1618, 1485 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.30 (m, 2H, CH_2), 1.73 (m, 2H, CH_2), 3.16 (s, 2H, CH_2), 3.86 (s, 3H, OCH_3), 3.92 (br s, 2H, NH_2, exchangeable in deuterium oxide), 6.72 (d, 1H, J = 8.2 Hz, aromatic), 6.79 (dd, 1H, J = 7.6 and 7.6 Hz, aromatic), 7.16 (dd, 1H J = 7.9 and 7.6 Hz, aromatic), 7.36 (d, 1H, J = 7.6 Hz, aromatic), 7.75 (s, 1H, CH); ^{13}C nmr (deuteriochloroform): δ 27.7, 52.0, 56.4, 115.6, 118.1, 120.5, 130.1 (two), 131.6, 138.5, 144.7, 163.5; ms m/z (%) 232 (M^+, 4), 201 (57), 188 (75), 158 (49), 130 (100), 103(17).

Anal. Calcd. for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.48; H, 6.71; N, 12.38.

Methyl 2-(1-Aziridinylmethyl)-3-[2-(3-phenylureido)phenyl]-propenoate (**10a**).

To a stirred solution of the amino compound **9** (1.16 g, 5 mmoles) in dichloromethane (10 ml) was added phenyl isocyanate (0.60 g, 5 mmoles) at room temperature. After 5 minutes the solvent was removed *in vacuo*. The residue was crystallized with ether to give 1.49 g (85%) of **10a** as a white solid; mp 132-133 °C; ir (potassium bromide): 3326, 1712, 1650 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.30 (m, 2H, CH_2), 1.64 (m, 2H, CH_2), 3.10 (s, 2H, CH_2), 3.83 (s, 3H, CH_3), 6.95-7.46 (m, 9H, aromatic), 7.74 (s, 1H, CH), 8.19 (s, 1H, NH), 9.04 (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 27.3, 52.6, 56.5, 118.7, 119.8, 122.4, 123.0, 126.4, 129.3, 129.7, 132.2, 137.2, 138.1, 140.1, 141.8, 153.0, 168.4.

Anal. Calcd. for $C_{20}H_{21}N_3O_3$: C, 68.36; H, 6.02; N, 11.96. Found: C, 68.12; H, 5.85; N, 11.73.

Methyl 2-(1-Aziridinylmethyl)-3-[2-(3-*p*-chlorophenylureido)-phenyl]propenoate (**10b**).

Treatment of **9** (1.16 g, 5 mmoles) with 4-chlorophenyl isocyanate (0.77 g, 5 mmoles) following the same procedure described for **10a** afforded 1.68 g (87%) of **10b** as a white solid; mp 154-156 °C; ir (potassium bromide): 3271, 1708, 1632 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.26 (m, 2H, CH_2), 1.59 (m, 2H, CH_2), 3.05 (s, 2H, CH_2), 3.79 (s, 3H, CH_3), 7.11-7.49 (m, 6H, aromatic), 7.71 (s, 1H, CH), 7.74-7.88 (m, 2H, aromatic), 8.20 (s, 1H, NH), 9.13 (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 27.3, 52.6, 56.5, 120.2, 122.5, 123.4, 126.0, 126.6, 129.2, 130.5, 132.3, 137.9, 138.3, 138.4, 139.1, 152.8, 168.3.

Anal. Calcd. for $C_{20}H_{20}ClN_3O_3$: C, 62.26; H, 5.22; N, 10.89. Found: C, 62.49; H, 5.01; N, 10.58.

Methyl 2-(1-Aziridinylmethyl)-3-[2-(3-*p*-fluorophenylureido)-phenyl]propenoate (**10c**).

Treatment of **9** (1.16 g, 5 mmoles) with 4-fluorophenyl isocyanate (0.69 g, 5 mmoles) following the same procedure described for **10a** afforded 1.75 g (95%) of **10c** as a white solide; mp 129-130 °C; ir (potassium bromide): 3311, 1713, 1650 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.26 (m, 2H, CH_2), 1.59 (m, 2H, CH_2), 3.05 (s, 2H, CH_2), 3.79 (s, 3H, CH_3), 7.07-7.39 (m, 6H, aromatic), 7.71 (s, 1H, CH), 7.73-7.91 (m, 2H, aromatic), 8.12 (s, 1H, NH), 8.91 (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 26.8, 52.3, 56.5, 115.0 (d, J_{CF} = 22 Hz), 115.9, 119.5, 120.3, 125.3, 126.0 129.8, 131.8, 132.6, 135.9, 137.6, 152.5, 157.4 (d, J_{CF} = 239 Hz), 168.1.

Anal. Calcd. for $C_{20}H_{20}FN_3O_3$: C, 65.03; H, 5.46; N, 11.38. Found: C, 64.75; H, 5.19; N, 11.17.

Methyl 2-(1-Aziridinylmethyl)-3-[2-(3-*p*-methylphenylureido)-phenyl]propenoate (**10d**).

Treatment of **9** (1.16 g, 5 mmoles) with 4-methylphenyl isocyanate (0.67 g, 5 mmoles) following the same procedure described for **10a** afforded 1.61 g (88%) of **10d** as a white solid; mp 128-130 °C; ir (potassium bromide): 3292, 1708, 1633 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.26 (m, 2H, CH_2), 1.59 (m, 2H, CH_2), 2.24 (s, 3H, CH_3), 3.05 (s, 2H, CH_2), 3.79 (s, 3H, OCH_3), 7.07-7.39 (m, 6H, aromatic), 7.70 (s, 1H, CH), 7.73-7.91 (m, 2H, aromatic), 8.12 (s, 1H, NH), 8.91 (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 20.9, 27.4, 52.6, 56.5, 118.8, 123.1, 126.2, 129.8, 130.0, 130.5, 131.0, 131.3, 132.3, 137.5, 137.7, 138.2, 152.9, 168.4.

Anal. Calcd. for $C_{21}H_{23}N_3O_3$: C, 69.02; H, 6.34; N, 11.50. Found: C, 68.78; H, 6.10; N, 11.21.

Methyl 2-(1-Aziridinylmethyl)-3-[2-(3-methylureido)phenyl]-propenoate (**10e**).

Treatment of **9** (1.16 g, 5 mmoles) with methyl isocyanate (0.29 g, 5 mmoles) following the similar procedure described for **10a** at room temperature for 4 hours afforded 1.32 g (91%) of **10e** as a white solid; mp 114 °C; ir (potassium bromide): 3414, 1698, 1656 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.47 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 2.73 (d, 3H, J = 4.5 Hz, NCH_3), 3.06 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 4.96 (br s, 1H, NH), 7.03-7.35 (m, 3H, aromatic), 7.76 (s, 1H, CH), 7.94-7.96 (m, 1H, aromatic), 8.28 (br s, 1H, NH); ^{13}C nmr (deuteriochloroform): δ 26.7, 27.8, 52.2, 56.0, 122.8, 126.1, 129.3, 129.4, 132.0, 137.1, 140.1, 140.2, 156.6, 167.8.

Anal. Calcd. for $C_{15}H_{19}N_3O_3$: C, 62.27; H, 6.62; N, 14.52. Found: C, 62.53; H, 6.85; N, 14.30.

Methyl 2-(1-Aziridinylmethyl)-3-[2-(3-benzoylureido)phenyl]-propenoate (**10f**).

Treatment of **9** (1.16 g, 5 mmoles) with benzoyl isocyanate (0.74 g, 5 mmoles) following the same procedure described for **10a** afforded 1.59 g (84%) of **10b** as a white solid; mp 158-160 °C; ir (potassium bromide): 3256, 1727, 1704, 1672 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.22 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 3.02 (s, 3H, CH_2), 3.80 (s, 3H, CH_3), 7.21-7.75 (m, 6H, aromatic), 7.79 (m, 1H, CH), 7.85-8.06 (m, 3H, aromatic); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 26.8, 52.3, 56.0, 120.7, 126.6, 127.6, 128.1, 128.3, 128.6, 128.9, 132.2, 133.0, 135.3, 135.9, 139.6, 151.3, 169.0, 170.9.

Anal. Calcd. for $C_{21}H_{21}N_3O_4$: C, 66.48; H, 5.58; N, 11.08. Found: C, 66.23; H, 5.39; N, 10.78.

6-Carbomethoxy-1-phenyl-1,2,3,5-tetrahydroimidazo[2,3-*b*]-[1,3]benzodiazocine (**13a**).

To a stirred solution of urea **10a** (1.05 g, 3 mmoles) in dichloromethane (30 ml) was added triphenylphosphine (1.96 g, 7.5 mmoles), carbon tetrachloride (1.5 ml, 15 mmoles), and triethylamine (1.05 ml, 7.5 mmoles). The mixture was heated to reflux temperature for 5 hours. After cooling to room temperature, the reaction mixture was partitioned between water (10 ml) and dichloromethane (20 ml x 2). After drying over anhydrous magnesium sulfate the solvent was removed and the residue was chromatographed on silica gel column, eluted with hexane-ethyl acetate (V/V = 2:1) to give 0.63 g (63%) of **13a** as a pale yellow solid after crystallization with diethyl ether-hexane; mp 137-138 °C; ir (potassium bromide): 1713, 1658 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.59 (br s, 2H, CH_2), 3.75 (m, 2H, CH_2), 3.85 (s, 3H, CH_3), 4.10 (br s, 2H, CH_2), 6.91-7.03 (m, 4H, aromatic), 7.25-7.32 (m, 3H, aromatic), 7.62-7.64 (m, 2H, aromatic), 8.06 (s, 1H, CH); ^{13}C nmr (deuteriochloroform): δ 44.9, 45.2, 47.2, 52.2, 119.6, 120.5, 122.2, 125.5, 127.5, 128.4, 128.7, 129.7, 130.5, 141.5, 146.7, 148.1, 149.6, 168.2; ms: m/z (%) 333 (M^+, 10), 274 (100), 130 (5).

Anal. Calcd. for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 71.84; H, 5.49; N, 12.38.

6-Carbomethoxy-1-(*p*-chlorophenyl)-1,2,3,5-tetrahydroimidazo[2,3-*b*][1,3]benzodiazocine (**13b**).

Treatment of urea **10b** (1.16 g, 3 mmoles) with Appel's reagents following the same procedure described for **13a** provided 0.73 g (66%) of **13b** as a pale yellow solid; mp 175-176 °C; ir (potassium bromide): 1713, 1656 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.59 (br s, 2H, CH_2), 3.70 (m, 2H, CH_2), 3.85 (s, 3H, CH_3), 4.21 (br s, 2H, CH_2), 6.90-7.02 (m, 3H, aromatic), 7.21-

7.30 (m, 3H, aromatic), 7.56-7.63 (m, 2H, aromatic), 8.06 (s, 1H, CH); ^{13}C nmr (deuteriochloroform): δ 44.8, 45.1, 47.0, 52.3, 120.3, 125.5, 127.0, 127.4, 128.1, 128.3, 128.8, 129.7, 130.6, 140.1, 146.6, 147.7, 149.4, 168.1; ms: m/z (%) 369 (3), 367 (M^+, 8), 310 (34), 308 (100), 130 (9).

Anal. Calcd. for $C_{20}H_{18}ClN_3O_2$: C, 65.31; H, 4.93; N, 11.42. Found: C, 65.59; H, 5.31; N, 11.20.

6-Carbomethoxy-1-(*p*-fluorophenyl)-1,2,3,5-tetrahydroimidazo-[2,3-*b*][1,3]benzodiazocine (**13c**).

Treatment of urea **10c** (1.10 g, 3 mmoles) with Appel's reagents following the same procedure described for **13a** provided 0.53 g (50%) of **13c** as a pale yellow solid; mp 113-114 °C; ir (potassium bromide): 1715, 1657 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.59 (br s, 2H, CH_2), 3.71 (m, 2H, CH_2), 3.86 (s, 3H, CH_3), 4.18 (br s, 2H, CH_2), 6.89-7.01 (m, 5H, aromatic), 7.24-7.29 (m, 1H, aromatic), 7.55-7.59 (m, 2H, aromatic), 8.06 (s, 1H, CH); ^{13}C nmr (deuteriochloroform): δ 44.8, 45.6, 47.2, 52.2, 114.9 (d, J_{CF} = 22 Hz), 120.6, 121.3, 125.5, 127.5, 128.7, 129.7, 130.5, 137.7, 146.6, 147.9, 149.8, 158.3 (d, J_{CF} = 242 Hz), 168.2; ms: m/z (%) 351 (M^+, 10), 292 (100), 130 (9).

Anal. Calcd. for $C_{20}H_{18}FN_3O_2$: C, 68.36; H, 5.16; N, 11.96. Found: C, 68.18; H, 4.89; N, 12.23.

6-Carbomethoxy-1-(*p*-methylphenyl)-1,2,3,5-tetrahydro-imidazo[2,3-*b*][1,3]benzodiazocine (**13d**).

Treatment of urea **10d** (1.09 g, 3 mmoles) with Appel's reagents following the same procedure described for **13a** provided 0.57 g (55%) of **13d** as a pale yellow solid; mp 153-155 °C; ir (potassium bromide): 1712, 1651 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.29 (s, 3H, CH3), 3.58 (br s, 2H, CH_2), 3.71 (m, 2H, CH_2), 3.86 (s, 3H, OCH_3), 4.12 (br s, 2H, CH2), 6.87-7.01 (m, 3H, aromatic), 7.09 (d, 2H, J = 8.4 Hz, aromatic), 7.22-7.28 (m, 1H, aromatic), 7.46 (d, 2H, J = 8.4 Hz, aromatic), 8.06 (s, 1H, CH); ^{13}C nmr (deuteriochloroform): δ 20.7, 44.8, 45.4, 47.3, 52.2, 119.8, 120.3, 125.5, 127.4, 128.7, 128.9, 129.7, 130.4, 131.8, 139.1, 146.7, 148.2, 149.8, 168.2; ms: m/z (%) 347 (M^+, 8), 288 (100), 130 (13).

Anal. Calcd. for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.10. Found: C, 72.43; H, 5.82; N, 11.78.

6-Carbomethoxy-1-methyl-1,2,3,5-tetrahydroimidazo[2,3-*b*]-[1,3]benzodiazocine (**13e**).

Treatment of urea **10e** (0.87 g, 3 mmoles) with Appel's reagents following the same procedure described for **13a** provided 0.51 g (62%) of **13e** as a pale yellow solid; mp 79-80 °C; ir (potassium bromide): 1719, 1657 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.81 (s, 3H, NCH_3), 3.21 (br s, 2H, CH_2), 3.42 (m, 2H, CH_2), 3.83 (s, 3H, OCH_3), 3.89 (br s, 2H, CH_2), 6.86-6.98 (m, 3H, aromatic), 7.22-7.28 (m, 1H, aromatic), 8.03 (s, 1H, CH); ^{13}C nmr (deuteriochloroform): δ 33.6, 44.5, 47.5, 47.7, 52.1, 120.4, 126.0, 127.9, 128.6, 130.1, 130.3, 146.6, 148.9, 154.3, 168.1; ms: m/z (%) 271 (M^+, 9), 212 (100).

Anal. Calcd. for $C_{15}H_{17}N_3O_2$: C, 66.40; H, 6.32; N, 15.49. Found: C, 66.21; H, 6.07; N, 15.78.

1-Benzoyl-6-carbomethoxy-1,2,3,5-tetrahydroimidazo[2,3-*b*]-[1,3]benzodiazocine (**13f**).

Treatment of urea **10f** (1.14 g, 3 mmoles) with Appel's reagents following the same procedure described for **13a** provided 0.60 g (55%) of **13f** as a pale yellow solid; mp 146-148 °C; ir (potassium bromide): 1702, 1698, 1650 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.68 (br s, 2H, CH_2), 3.88 (s, 3H, CH_3), 3.97 (m, 2H, CH_2), 4.19 (br s, 2H, CH_2), 6.34-6.37 (m, 1H, aromatic), 6.83-6.91 (m, 2H, aromatic), 7.08-7.12 (m, 1H, aromatic), 7.31-7,38 (m, 3H, aromatic), 7.55-7.58 (m, 2H, CH_2), 7.96 (s, 1H, CH); ^{13}C nmr (deuteriochloroform): δ 43.2, 44.2, 46.4, 52.3, 121.4, 124.7, 126.7, 127.2, 128.4, 128.7, 129.7, 130.2, 130.4, 136.3, 145.5, 145.9, 146.2, 167.8, 170.5; ms: m/z (%) 361 (M^+, 17), 302 (95), 105 (100), 77 (33).

Anal. Calcd. for $C_{21}H_{19}N_3O_3$: C, 69.79; H, 5.30; N, 11.63. Found: C, 69.47; H, 5.12; N, 11.40.

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