Dibenzo-fused Seven-membered Nitrogen Heterocycles by a Tandem Reduction-Lactamization Reaction

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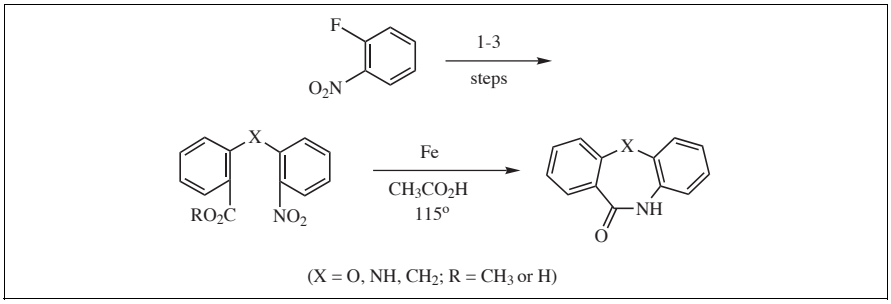

Efficient syntheses of dibenz[*b,f*][1,4]oxazepin-11(10*H*)-one, 5,10-dihydro-11*H*-dibenzo[*b,e*][1,4]-diazepin-11-one and 5,11-dihydro-6*H*-dibenz[*b,e*]azepin-6-one are described using a tandem reduction-lactamization sequence. Precursors for these ring systems are available in 1-3 steps using nucleophilic aromatic substitution and Ullmann coupling methodology. Direct reduction-lactamization of these compounds using iron powder in acetic acid at 115° affords the target heterocycles in ≥90% yield.

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Introduction.

Tandem reactions involving reduction of an aromatic nitro group and trapping the aniline nitrogen with a suitably positioned carbonyl-containing functionality have proven highly useful for the synthesis of a diverse selection of heterocycles [2]. In the current project, we have used this strategy for the synthesis of dibenzo-fused seven-membered nitrogen heterocycles *via* a reduction-lactamization sequence under dissolving metal conditions using iron and acetic acid. We have previously used dissolving metal reduction conditions in a reduction-Michael addition synthesis of 1,2,3,4-tetrahydroquinoline-2-acetic esters [2a] and in a cyclocondensation to prepare 2-alkyl-3-indolecarboxylic esters [2b]. A recent paper by other authors has also reported the use of these conditions for a reduction-lactamization sequence for large-scale production of an important drug precursor [3]. We wish to describe an adaptation of this reaction for the efficient synthesis of dibenz[*b,f*][1,4]oxazepin-11(10*H*)-one, 5,10-dihydro-11*H*-dibenzo[*b,e*][1,4]diazepin-11-one and 5,11-dihydro-6*H*-dibenz[*b,e*]azepin-6-one.

Dibenzo-fused oxazepinones, diazepinones and azepinones have been shown to express a wide range of biological activities. A series of dipyridodiazepinones, pyridobenzoxazepinones and dibenzoxazepinones have been found to be potent non-nucleoside inhibitors of HIV-1 reverse transcriptase [4]. Additionally, several dibenzo-[*b,e*][1,4]diazepin-11-one and dibenzo[*b,e*][1,4]diazepine derivatives have been found to have antiarrhythmic-defibrillatory activity [5]. These ring systems are, thus, valuable targets and short, high-yield syntheses are desirable goal.

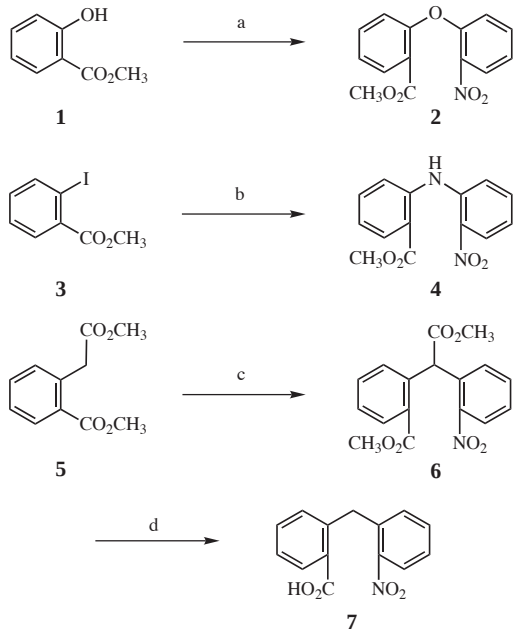
A number of these ring systems have been reported previously by other methods. Most notably are approaches based on the Bischler-Napieralski cyclization [6], the Beckmann rearrangement [7], the Ullmann-Goldberg condensation [8] and the treatment of dilithiated 2-phenoxyanilines and 2-(phenylamino)anilines with carbon dioxide [9]. One earlier report utilized a strategy involving initial lactam formation followed by intra-molecular nucleophilic aromatic substitution [4]. This approach worked well in several cases, but the harsh conditions and high temperatures required for the final cyclization often resulted in side reactions, degradation of the amide linkage and a reduced yield. To overcome these problems, our plan sought to reverse this sequence of steps such that nucleophilic aromatic substitution would be used first to link two functionalized rings, one bearing an *ortho* nitro group and the other an *ortho* carboxylic acid or ester, and then a tandem reduction-lactamization would be used to close the seven-membered ring.

Results and Discussion.

The syntheses of our cyclization substrates are outlined in Scheme 1. Nucleophilic aromatic substitution of the anion derived from methyl salicylate (**1**) with 2-fluoro-1-nitrobenzene [10] afforded the dibenzoxazepinone precursor **2** in 90% yield. Ullmann reaction of 2-nitroaniline (**3**) with methyl 2-iodobenzoate [11] provided the dibenzodiazepinone cyclization substrate **4** in 90%

yield. Finally, nucleophilic aromatic substitution of the anion from methyl 2-[2-(methoxycarbonyl)phenyl]-acetate (**5**) with 2-fluoro-1-nitrobenzene [12] gave diester **6** in 74% yield. Hydrolysis of both esters and selective decarboxylation of the doubly benzylic carboxylic acid group [13] then delivered the dibenzazepinone precursor **7** in 64% yield.

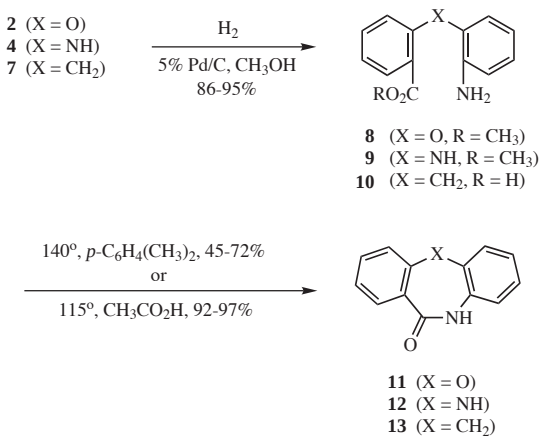
Scheme 1[a]



[a] Key: a) NaH, dimethylformamide, then 2-fluoro-1-nitrobenzene, 60°, 24 hours, 90%; b) 2-nitroaniline, K_2CO_3, copper-bronze, 160°, 6 hours, 90%; c) *tert*-BuOK, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone, then 2-fluoro-1-nitrobenzene, 60°, 24 hours, 74%; d) (i) NaOH, aqueous dioxane; (ii) K_2CO_3, dimethylformamide, 50°, 3 hours, 64%.

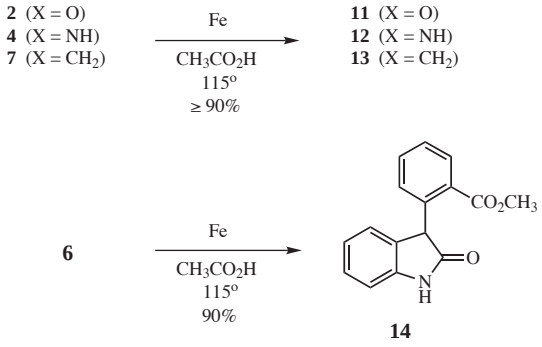
Based on our earlier work [2g], we anticipated that catalytic hydrogenation would not furnish the desired lactams from these substrates. We confirmed this expectation by reduction of **2**, **4** and **7** in methanol under 3 atmospheres of hydrogen using 5% palladium-on-carbon and isolated the amino compounds **8**, **9** and **10** from simple reduction of the nitro group with no further cyclization. Work by others indicated that heating **8**, **9** and **10** in xylene at 140° would effect lactam formation [14]. This was found to be the case and heterocycles **11**, **12**, and **13** were isolated in 72%, 45% and 69% yields, respectively, after 24 hours in boiling xylene. The disadvantages of this procedure were the modest yields and the difficulty in removing xylene from the product. On the other hand, we found that heating **8**, **9** or **10** in acetic acid for 30-60 minutes resulted in nearly quantitative conversion to the dibenzo-fused seven-membered lactams. This suggested that if the nitro reduction could be run in acetic acid, the entire process would occur in a single step.

Scheme 2



In accordance with this observation, the reductions of **2**, **4** and **7** were carried out using 6 equivalents of iron powder in acetic acid at 115° for 30-60 minutes to give **11**, **12** and **13**, respectively, all in ≥90% yield. In each case, the reduction-lactamization proceeded cleanly and the products were easily purified by trituration and filtration. It is well established that these conditions are exceptionally mild and should tolerate a wide variety of

Scheme 3



functional groups [15]. Finally, an attempt to prepare a functionalized dibenzazepinone by reduction of diester **6** gave exclusively the 2-indolinone **14** resulting from preferential five-membered ring closure on the doubly benzylic ester.

Conclusion.

We have developed an efficient route to dibenzoxazepinone (2 steps, 81% yield), dibenzodiazepinone (2 steps, 81% yield) and dibenzoazepinone (4 steps, 45% yield).

The synthesis differs from an earlier route by initially forming the ether, amine or methylene linkage between two functionalized aromatic rings followed by closure of the lactam in a second step. This avoids the necessity of exposing the lactam bond to harsh basic conditions and results in higher overall yields with fewer side products. The products are isolated directly following workup and do not require extensive purification.

EXPERIMENTAL

All reactions were run under dry nitrogen in oven-dried glassware. Reactions were monitored by thin layer chromatography on silica gel GF plates (Analtech no. 21521) with ultraviolet detection. Melting points were uncorrected. Infrared spectra were run as thin films on sodium chloride disks and referenced to polystyrene. Unless otherwise noted, ^{1}H and ^{13}C nuclear magnetic resonance spectra were measured in deuteriochloroform at 300 MHz and 75 MHz, respectively, using tetramethylsilane as an internal standard; coupling constants (J) are given in Hertz. Mass spectra (electron impact/direct probe) were obtained at 70 electron volts.

Methyl 2-(2-Nitrophenoxy)benzoate (**2**).

This compound was prepared from methyl salicylate and 2-fluoro-1-nitrobenzene on a 10-mmole scale according to the general method reported by Bunce and Easton [10]. The yield was 2.45 g (90%) as a white solid, mp 48-49° (ether-hexanes); lit mp 49-50° (no solvent given) [16]. ir: 1727, 1528, 1351 cm^{-1}; ^{1}H nmr: δ 8.00 (dd, 1H, J = 7.9, 1.6), 7.96 (dd, 1H, J = 8.2, 1.6), 7.57 (td, 1H, J = 7.9, 1.9), 7.45 (ddd, 1H, J = 8.5, 7.6, 1.6), 7.31 (tt, 1H, J = 7.9, 0.5), 7.15 (tm, 1H, J = 7.6), 7.12 (dd, 1H, J = 8.2, 0.5), 6.80 (dd, 1H, J = 8.5, 1.1), 3.75 (s, 3H); ^{13}C nmr: δ 165.2, 154.1, 151.5, 148.7, 134.1 (2), 132.5, 125.7, 125.3, 123.4, 122.5, 122.1, 118.4, 52.3; ms: *m/z* 273 (M^+).

Anal. Calcd. for $C_{14}H_{11}NO_5$: C, 61.54; H, 4.03; N, 5.13. Found: C, 61.72; H, 4.09; N, 5.01.

Methyl 2-[(2-Nitrophenyl)amino]benzoate (**4**).

This compound was prepared on a 25-mmole scale according to the method of Black and Rothnie [11]. The yield was 6.15 g (90%) as bright orange crystals, mp 159-160° (aqueous acetone); lit mp 152-153° (aqueous acetone) [11]. ir: 3298, 1696, 1500, 1344 cm^{-1}; ^{1}H nmr: δ 11.1 (br s, 1H), 8.16 (dd, 1H, J = 8.5, 1.1), 8.03 (ddd, 1H, J = 7.9, 1.6, 0.5), 7.60 (dd, 1H, J = 8.5, 1.4), 7.52 (dd, 1H, J = 8.5, 1.4), 7.44, (tm, 2H, J = 7.9), 7.05 (ddd, 1H, J = 8.5, 7.1, 1.4), 6.94 (ddd, 1H, J = 8.5, 7.1, 1.4), 3.96 (s, 3H); ^{13}C nmr: δ 167.4, 147.7, 142.2, 139.0, 134.6, 133.3, 132.0, 126.6, 121.8, 119.9, 119.0, 118.6, 118.5, 52.3; ms: *m/z* 272 (M^+).

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.41; N, 10.29. Found: C, 61.92; H, 4.49; N, 10.12.

2-[(2-Nitrophenyl)methyl]benzoic Acid (**7**).

This compound was prepared *via* compound **6** on a 10-mmole scale according to the method of Bunce and Schammerhorn [12]. The resulting solid was triturated with cold ether and filtered to give 1.18 g (47%, three steps) of **7** as a light yellow solid. The physical and spectral properties matched those reported previously [12].

General Procedure for Hydrogenation: Methyl 2-(2-Aminophenoxy)benzoate (**8**).

To a solution of 0.50 g (1.83 mmoles) of **2** in 150 mL of methanol was added 125 mg of 5% palladium-on-carbon and the mixture was shaken in a stainless steel reaction vessel under 3 atmospheres of hydrogen for 3 hours at 30°. [**Caution**: Though we never experienced any problems, addition of 5% palladium-on-carbon to methanol can cause fires. This operation should be performed under a nitrogen atmosphere.] The crude product was concentrated, diluted with ether and filtered through a plug of Celite topped with a layer of anhydrous magnesium sulfate to remove the catalyst. Following removal of the ether, the crude amino ester was triturated with 2% ether in hexanes to give 0.39 g (86%) of **8** as a light yellow solid, mp 56-57°. This material was spectroscopically pure and was used without further purification. The spectral data were: ir: 3454, 3365, 1718 cm^{-1}; ^{1}H nmr: δ 7.84 (dd, 1H, J = 7.6, 1.9), 7.38 (ddd, 1 H, J = 8.5, 7.4, 1.9), 7.06 (td, 1H, J = 7.6, 1.1), 6.98 (ddd, 1H, J = 7.9, 7.4, 1.6), 6.90 (dd, 1H, J = 8.5, 1.1), 6.88 (dd, 1H, J = 7.9, 1.6), 6.80 (dd, 1H, J = 7.9, 1.6), 6.70 (ddd, 1H, J = 7.9, 7.4, 1.6), 4.04 (br s, 2H), 3.88 (s, 3H); ^{13}C nmr: δ 166.6, 156.8, 142.8, 138.9, 133.4, 131.5, 125.2, 122.4, 121.5, 120.4, 118.3, 117.4, 116.5, 52.1; ms: *m/z* 243 (M^+).

Anal. Calcd. for $C_{14}H_{13}NO_3$: C, 69.14; H, 5.35; N, 5.76. Found: C, 69.36; H, 5.38; N, 5.62.

Methyl 2-[(2-Aminophenyl)amino]benzoate (**9**).

This compound (0.41 g, 92%) was isolated as a light tan solid, mp 102-103°, lit mp 102-103° (ethanol-water) [17]; ir: 3454, 3324, 1682 cm^{-1}; ^{1}H nmr: δ 8.95 (br s, 1H), 7.94 (dd, 1H, J = 7.6, 1.4), 7.26 (ddd, 1H, J = 8.7, 7.6, 1.6), 7.12 (dd, 1H, J = 7.6, 1.4), 7.08 (td, 1H, J = 7.4, 1.6), 6.84-6.60 (complex, 4H), 3.90 (s, 3H), 3.81 (br s, 2H); ^{13}C nmr: δ 169.0, 149.5, 143.3, 134.4, 131.4, 127.7, 127.1, 125.9, 118.8, 116.4, 115.9, 113.7, 110.9, 51.7; ms: *m/z* 242 (M^+).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.42; H, 5.79; N, 11.57. Found: C, 69.32; H, 5.83; N, 11.34.

2-[(2-Aminophenyl)methyl]benzoic Acid (**10**).

This compound (0.40 g, 91%) was isolated as a white solid, mp 124-125°, lit mp 126-127° (80% aqueous ethanol) [18]; ir: 3638-1741, 1701 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 9.1-6.0 (br s, 3H), 7.81 (dd, 1H, J = 7.9, 1.6), 7.43 (td, 1H, J = 7.6, 1.6), 7.30 (td, 1H, J = 7.6, 1.1), 7.12 (d, 1H, J = 7.4), 6.90 (td, 1H, J = 7.9, 1.6), 6.63 (m, 2H), 6.44 (td, 1H, J = 7.4, 1.1), 4.12 (s, 2H); ^{13}C nmr (DMSO-d_6): δ 169.3, 146.2, 140.7, 131.5, 131.3, 130.6, 130.0, 129.5, 126.7, 126.0, 124.0, 116.0, 114.4, 40.3; ms: *m/z* 227 (M^+).

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 74.01; H, 5.73; N, 6.17. Found: C, 73.79; H, 5.67; N, 6.11.

General Procedure for Lactam Closure in High-Boiling Solvents.

p-Xylene: Solutions of 0.50 mmoles of **8**, **9** and **10** in 5 mL of *p*-xylene were heated under reflux for 24 hours. The mixtures were cooled, the solvent was removed under high vacuum, and the residues were triturated with ether-hexanes. This yielded **11**, **12** and **13** in 72%, 45% and 69%, respectively, as dark brown solids.

Acetic Acid: Solutions of 0.50 mmoles of **8**, **9** and **10** in 5 mL of glacial acetic acid were heated at reflux for 30-60

minutes. The mixtures were cooled, poured into water and extracted with ether (two times). The combined ether extracts were washed with water (one time), saturated sodium bicarbonate (two times) and saturated sodium chloride (one time), dried (magnesium sulfate) and concentrated under vacuum. This gave **11**, **12** and **13** in 97%, 92% and 95%, respectively, as light tan solids. The physical and spectral properties for **11**, **12** and **13** are given below.

General Procedure for Reduction-Lactamization: Dibenz[*b*,*f*]-[1,4]oxazepin-11(10*H*)-one (**11**).

A mixture of 273 mg (1.00 mmole) of **2**, 8.0 mL of acetic acid and 335 mg (6.00 mmoles) of iron powder (>100 mesh) was heated with stirring at 115° (oil bath) until thin layer chromatography indicated complete consumption of starting material (30-60 minutes). The crude reaction mixture was cooled and transferred to a separatory funnel containing 50 mL of water. The aqueous layer was extracted with ether (three times). The combined ether layers were washed with water (one time), saturated sodium bicarbonate (three times), sodium chloride (one time), then dried (magnesium sulfate), and concentrated under vacuum. The resulting white solid was triturated with 5% petroleum ether in ether and filtered to give 190 mg (90%) of **11** as a white powder, mp 210-212°; lit mp 210-212° (no solvent given) [19]; ir: 3167, 1665 cm^{-1}; ^1H nmr: δ 9.09 (br s, 1H), 7.96 (dd, 1H, J = 8.2, 1.9), 7.53 (m, 1H), 7.26 (m, 3H), 7.26 (m, 3H); ^{13}C nmr: δ 167.6, 159.6, 150.9, 134.5, 132.0, 130.6, 125.9, 125.8, 125.2, 125.1, 121.7, 121.3, 120.8; ms: *m/z* 211 (M^+).

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.93; H, 4.27; N, 6.64. Found: C, 74.05; H, 4.32; N, 6.51.

5,10-Dihydro-11*H*-dibenzo[*b*,*e*][1,4]diazepin-11-one (**12**).

This compound (189 mg, 90%) was isolated as yellow crystals after recrystallization from methanol, mp 255-256°; lit mp 256-257° (methanol) [8]. ir: 3317, 3160, 1638 cm^{-1}; ^1H nmr (DMSO-d_6): δ 9.86 (s, 1H), 7.86 (s, 1H), 7.70 (dd, 1H, J = 7.6, 0.8), 7.36 (tm, 1H, J = 7.6), 7.06-6.88 (complex, 6H); ^{13}C nmr (DMSO-d_6): δ 167.9, 150.4, 139.9, 133.2, 132.1, 129.8, 124.4, 122.9, 122.7, 121.2, 120.7, 119.7, 119.0; ms: *m/z* 210 (M^+).

Anal. Calcd. for $C_{13}H_{10}N_2O$: C, 74.29; H, 4.76; N, 13.33. Found: C, 74.17; H, 4.79; N, 13.10.

5,11-Dihydro-6*H*-dibenz[*b*,*e*]azepin-6-one (**13**).

This compound (198 mg, 95%) was isolated as a white powder following trituration with 5% petroleum ether in ether, mp 200-201°; lit mp 201° (no solvent given) [7]. ir: 3175, 1652 cm^{-1}; ^1H nmr: δ 9.25 (br s, 1H), 7.94 (dd, 1H, J = 7.6, 1.1), 7.44 (td, 1H, J = 7.4, 1.4), 7.34-7.25 (complex, 3H), 7.23-7.07 (complex, 3H), 3.95 (s, 2H); ^{13}C nmr: δ 170.1, 141.4, 136.2, 133.0, 132.5, 131.8, 130.8, 128.2, 127.5, 127.1, 127.0, 125.3, 120.9, 39.2; ms: *m/z* 209 (M^+).

Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.38; H, 5.26; N, 6.70. Found: C, 80.09; H, 5.14; N, 6.74.

Methyl 2-(2-Oxoindolin-3-yl)benzoate (**14**).

When the reductive cyclization was carried out on 329 mg (1.00 mmole) of **6**, 240 mg (90%) of **12** was isolated as a white solid following trituration with ether and filtration, mp 167-168°. ir: 3224, 1714 cm^{-1}; ^1H nmr: δ 9.34 (br s, 1H), 8.00 (d, 1H, J = 7.6), 7.44 (t, 1H, J = 7.4), 7.37 (td, 1H, J = 7.6, 1.4), 7.19 (t, 1H, J = 7.6), 7.07 (m, 2H), 6.97 (t, 1H, J = 7.4), 6.91 (d, 1H, J = 7.9), 5.82 (br s, 1H), 3.84 (br s, 3H); ^{13}C nmr: δ 179.2, 167.9, 141.5, 137.4, 132.6, 131.1 (2), 130.3, 130.1, 128.0, 127.6, 124.6, 122.5, 109.9, 52.2, 50.3; ms: *m/z* 267 (M^+).

Anal. Calcd. for $C_{16}H_{13}NO_3$: C, 71.91; H, 4.87; N, 5.24. Found: C, 71.85; H, 4.92; N, 5.18.

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