Nucleophilic Annulations of Aromatics. Novel Route to Benzo-Fused Ring Systems via Oxazoline Activation

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The synthesis of three trisubstituted aryloxazolines, **7**, **8**, and **10**, containing an *o*-methoxyl group served as useful precursors to eight benzo-fused ring systems. In this fashion, novel syntheses for tetralins, indans, chromans, benzofurans, indolines, tetrahydroquinolines, benzoxepins, and benzazepins were achieved. The key reaction leading to this variety of benzo-fused systems was based on the facile nucleophilic displacement of an *o*-methoxy group in aryloxazolines.

Several years ago, we reported[1] the highly efficient introduction of a variety of substituents, via organometallics, into the ortho position of an aryloxazoline containing an *o*-methoxy or *o*-fluoro group (**1**). After hydrolytic removal of the oxazoline moiety, a series of substituted benzoic acids **2** and biphenyls **3** were obtained (Scheme I). This process was found to occur by nucleophilic addition of the organometallic to the ortho carbon followed by elimination of the metal methoxide or fluoride. A number of other nucleophiles (nitrogen, silicon, and oxygen) along with the carbon nucleophiles gave reactions which proceeded in good yield. This method also allowed considerable latitude in the preparation of unsymmetrical biphenyls.

We now describe a significant advance in this methodology which demonstrates how these unusual nucleophilic displacements may be utilized in an intramolecular mode to give a wide variety of benzo-fused ring systems. This method may now be added to other well-known aromatic annulations with wide scope such as the Friedel–Crafts, Skraup, Haworth, Bischler–Napieralski, and Pschorr-type reactions. To illustrate this annulation procedure, we have examined three typical trisubstituted benzene derivatives, **7**, **8**, and **10**, prepared from salicyclic acid or anisole in several routine steps (Scheme II). These three precursors possess the requisite functionality and substitution pattern to allow a variety of ring annulated products to form. Thus, **7** was transformed into the alcohol **11** (Scheme III) by hydroboration–oxidation and cyclized to the chroman **15** by simply adding sodium hydride in THF and heating overnight. The yield of **15** was 72%, which, after being heated in acid, gave chroman-8-carboxylic acid **16** in 65% yield. The key intermediate **11** was next converted to the mesylate **12** and treated with lithium bromide in DMF to give a quantitative yield of the bromide **13**. To demonstrate the intramolecular reaction of Grignard reagents analogous to earlier studies in an intermolecular fashion (Scheme I), we added **13** to magnesium metal and heated the mixture to form the in situ Grignard which reacted, as it formed, to produce the indan **17** in 80% yield. Hydrolytic removal of the oxazoline gave indan-4-carboxylic acid **18** (70%). Returning to the mesylate **12**, it was transformed into the amino derivative **14**, by use of potassium phthalimide and subsequent hydrazinolysis, in 73% yield. When the primary amine was treated with lithium diisopropylamide at −45 °C for 1 h, it readily cyclized (78%) to the tetrahydroquinoline **19**. In this instance, hydrolytic removal of the oxazoline was accompanied by decarboxylation and furnished 1,2,3,4-tetrahydroquinoline **20** (61%). Thus, from a single precursor, **7** (or **11**), three different benzo-fused systems became accessible.

By simple ozonolysis of the allyl system **7**, there was obtained in good yield (88%) phenylacetaldehyde derivative **8**, which served as another precursor to annulated benzenes. Sodium borohydride reduction of **8** gave the alcohol **21** (Scheme IV), which upon addition to sodium hydride in THF resulted in cyclization to the benzofuran **23** (82%). After hydrolysis, the carboxylic acid **24** was isolated in 50% yield. An indole synthesis was next attempted with the alcohol **21** by transformation to the amine **22** (72%) via the potassium phthalimide–hydrazine procedure mentioned earlier. Treatment of the amine with LDA at −45 °C gave the indoline **25** (84%) and indoline-7-carboxylic acid (**26**, 68%) after removal of the oxazoline. *Thus, five different benzo-fused systems are accessible from the common trisubstituted benzene 7 as demonstrated herein.*

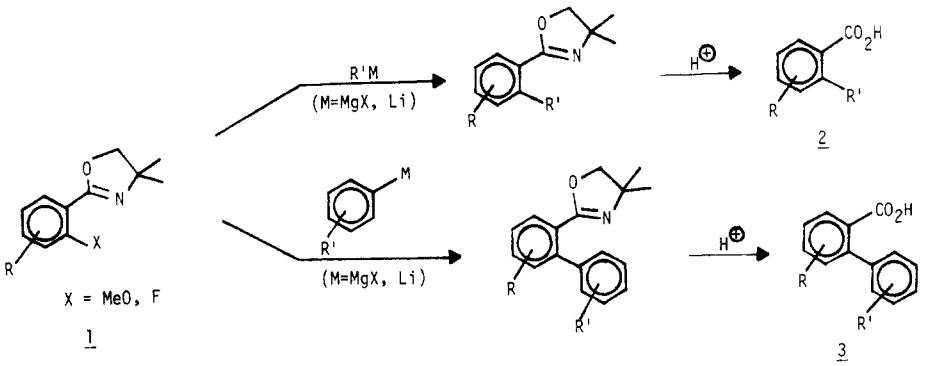
Turning now to the last trisubstituted aromatic investigated in this study, we manipulated the oxazoline **10** in a similar manner. Hydroboration of **10** gave the primary alcohol **27** (85%) which upon treatment with sodium hydride in THF cyclized in 54% yield to the benzoxepin **31** and after hydrolysis led to the carboxylic acid **32** in 64% yield (Scheme V). When the alcohol **27** was treated with methanesulfonyl chloride, the mesylate **28** was formed, which after being stirred with lithium bromide in DMF furnished the bromide **29** (95%). Once again, the in situ Grignard formation of the bromide with magnesium metal led to cyclization which gave the tetralin **33** in 85% yield and the tetralincarboxylic acid **34** (72%) after hydrolysis. To reach the benzazepin systems **35** and **36**, the mesylate **28** was, as before, subjected to the potassium phthalimide–hydrazine procedure, furnishing the amine **30** (70%). The latter was stirred at −45 °C with LDA and gave the benzazepine **35** (48%), and after removal of the oxazoline, a 45% yield of tetrahydrobenzazepin-9-carboxylic acid (**36**) was obtained.

As mentioned at the outset of this report, these displacements of *o*-methoxy groups on aryloxazolines proceed via an addition–elimination process. The side chain must, therefore, be of sufficient length (A, Scheme VI) to approach the aryl ring from an angle close to tetrahedral (B) so that the metal ion can coordinate both to the methoxy group and to the nitrogen–oxygen π system, allowing a "1,4-addition-type reaction" to take place. Elimination of the metal methoxide then reestablishes the ring aromaticity (C). This mechanistic proposal is in complete accord with the earlier proposal for methoxy displacement for the intermolecular sequence. Finally, it should be noted that the wide variety of synthetic transformations described herein had no effect on the carboxylic protecting group,

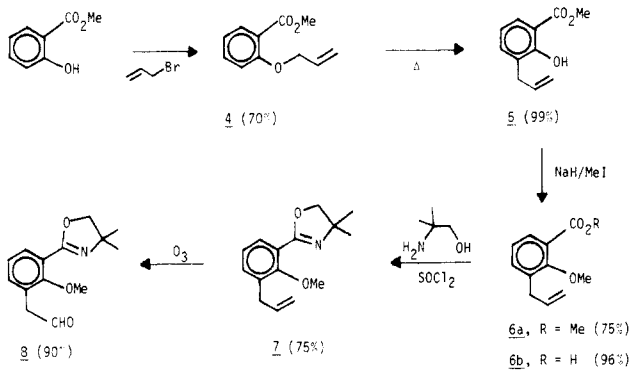
(1) Meyers, A. I.; Gabel, R.; Mihelich, E. D. *J. Org. Chem.* **1978**, *43*, 1372 and references cited therein.

0022-3263/81/1946-0783$01.00/0

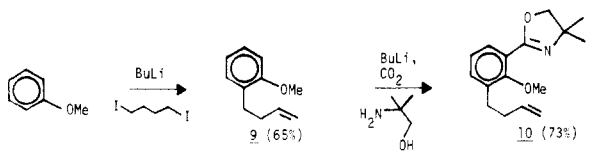
Scheme I



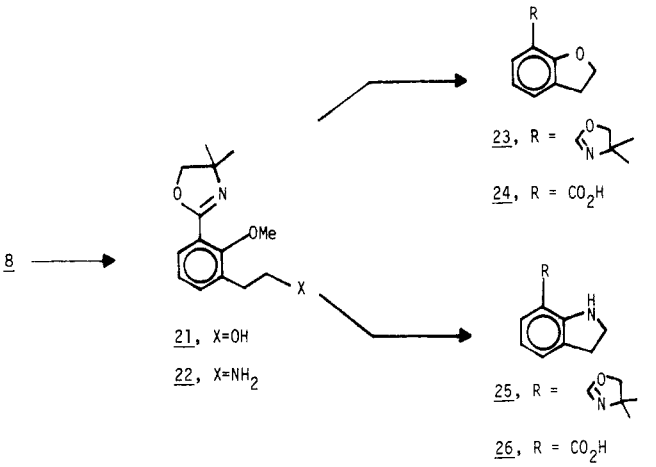
Scheme II



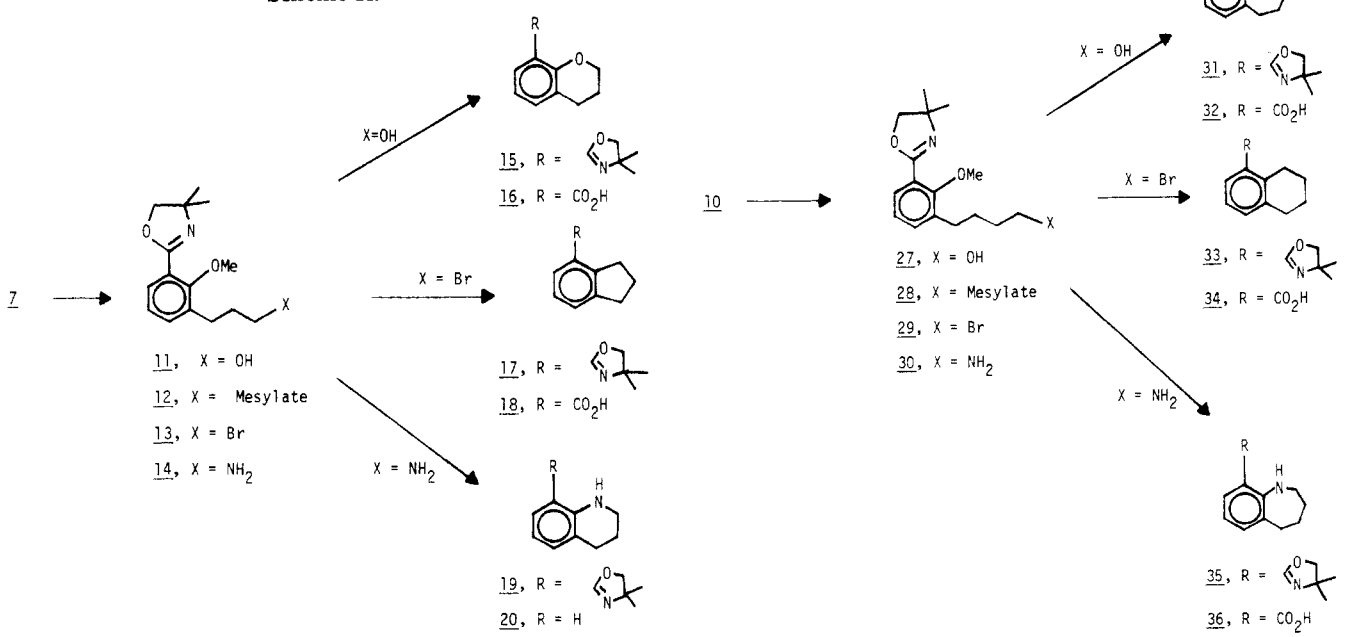
Scheme III



Scheme IV



Scheme V



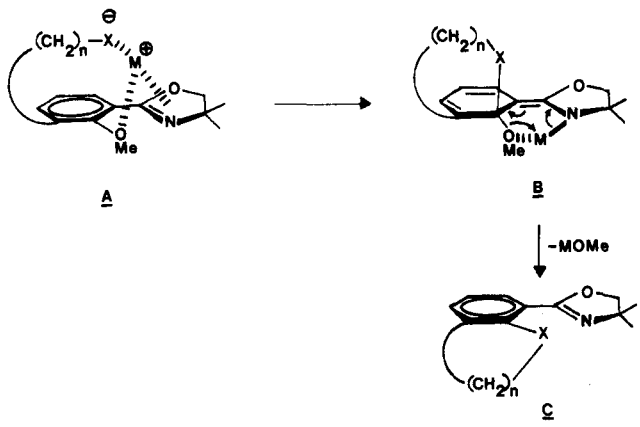
2-oxazoline, which should also enhance its use in many other chemical studies.

Experimental Section

Methyl *o*-Allylsalicylate (4). A mixture of 252 g (1.65 mol) methyl salicylate, 840 mL of acetone, 227 g (1.64 mol) of potassium carbonate and 142 mL (1.64 mol) of allyl bromide was heated to reflux for 10 h. NMR analysis indicated that the reaction had ceased at 60%. An additional 142 mL of allyl bromide and 114 g (0.82 mol) of potassium carbonate were added, and reflux was continued for 60 h. Cooling, filtering, and evaporation of the acetone gave an oily residue which was taken up in ether, washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give the crude allyl ether. Distillation [bp 95–105 °C (3 torr)] gave 220 g (70%) of 4[2] containing a trace of rearranged product 5: ^1H NMR (CCl_4) δ 7.87–6.67 (m, 4), 6.33–5.67 (m, 1), 5.41 (d,

(2) Claisen, L.; Eisleb, O. *Justus Liebigs Ann. Chem.* **1913**, *402*, 21.

Scheme VI



A B C

J = 18 Hz, 1), 5.18 (d, J = 10 Hz, 1), 4.47 (d, 2), 3.78 (s, 3).

2-Allyl-6-(carbomethoxy)phenol (5). The allyl ether 4 from above (220 g) was heated under nitrogen at reflux for 15 h to give 220 g (99.8%) of pure 5: ^{1}H NMR (CCl_4) δ 11.1 (s, 1), 7.25–6.61 (m, 5), 6.25–5.67 (m, 1), 5.15–4.95 (d, 2), 3.93 (s, 3), 3.40 (d, J = 6, 2). Without further purification this material was carried on to the next step.

2-Allyl-6-(carbomethoxy)anisole (6a). Into 1 L of dry THF were added 220 g (1.15 mol) of the phenol 5 and 37 g (1.55 mol) sodium hydride in small portions at 0 °C. Methyl iodide (140 mL, 2.25 mol) was added after 20 min and the mixture heated at reflux for 12 h. Removal of the solvent and other volatiles, taking up the residue in ether, washing with water and brine, drying ($MgSO_4$), and concentration gave 178 g (75%) after distillation: bp 83–86 °C (0.15 torr); ^{1}H NMR (CCl_4) 7.73–6.83 (m, 3), 6.30–5.60 (m, 1), 6.08 (d, J = 10 Hz, 1), 6.00 (d, J = 16 Hz, 1), 3.83 (s, 3), 3.78 (s, 3), 3.43 (d, J = 6 Hz, 2).

2-Methoxy-3-allylbenzoic Acid (6b). The ester 6a was saponified by adding 37.9 g (0.184 mol) of it to 100 mL of 5 N NaOH and heating the mixture just below reflux temperature for 1 h. After the mixture was cooled and acidified with concentrated HCl, the mixture was extracted with ether, and the ethereal extracts were dried ($MgSO_4$) and concentrated to give 34.2 g (96%) as a colorless solid: mp 52–54 °C (hexane); ^{1}H NMR (CCl_4) δ 12.8 (s, 1), 8.00–6.95 (m, 3), 6.41–5.65 (m, 1), 5.06 (d, J = 10 Hz, 1), 4.93 (d, J = 16 Hz, 1), 3.91 (s, 3), 3.45 (d, J = 6 Hz, 2); IR (KBr) 3200–2700, 1680 cm^{-1}.

2-(2-Methoxy-3-allylphenyl)-4,4-dimethyl-2-oxazoline (7). To a single-neck, round-bottomed flask containing 34.2 g (0.18 mol) of the crude acid 6b was added a solution containing 180 mL of $CHCl_3$ and 39 mL (0.64 mol) of thionyl chloride. The mixture was stirred for 17 h, and the $CHCl_3$ and excess thionyl chloride were removed on a rotary evaporator, giving the crude acid chloride. The acid chloride was added to 34 mL (0.36 mol) of 2-amino-2-methyl-1-propanol in 150 mL of CH_2Cl_2 in an ice bath over the period of 1 h. The reaction was slowly warmed to room temperature over 5 h and filtered, and the solvent was removed under reduced pressure to give the amide alcohol. To the amide alcohol was added 39 mL (0.64 mol) of thionyl chloride, and after 30 min, 100 mL of ether was added to the mixture and stirred. The ether was decanted, an additional 100 mL of ether added, and the mixture again stirred. After decantation of the ether, the solid was treated with sufficient 5 M NaOH to make the solution alkaline. The mixture was extracted with ether, washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude oxazoline. Bulb-to-bulb distillation at 90 °C (0.05 mm) gave 29.7 g (73%) of 7: ^{1}H NMR (CCl_4) δ 7.63–6.83 (m, 3 H), 6.35–5.60 (m, 1 H), 5.03 (br d, 2 H), 3.98 (s, 2 H), 3.78 (s, 3 H), 3.41 (d, J = 7 Hz, 2 H), 1.37 (s, 6 H). An elemental analysis was performed on alcohol 21.

2-[2-Methoxy-2-(formylmethyl)phenyl]-4,4-dimethyl-2-oxazoline (8). To a 250-mL, three-necked flask with a stir bar were added 10.0 g (40.8 mmol) of the olefin 7 and 100 mL of methanol. The methanolic solution was cooled to −78 °C with a dry ice–2-propanol bath, and a stream of ozone was passed through the solution until TLC analysis showed that all of the olefin had been consumed. At this point, nitrogen was passed through the solution, 41 mL (56 mmol) of dimethyl sulfide was added, and the mixture was permitted to warm to room temperature overnight. The methanol was removed on a rotary evaporator, and the residue taken up in either, washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum to give 8.88 g (88%) of crude aldehyde 8 as a viscous oil: ^{1}H NMR (CCl_4) δ 9.63 (t, 1 H, J = 2 Hz), 7.58 (dd, 1 H), 7.2–6.8 (m, 2 H), 3.97 (s, 2 H), 3.70 (s, 3 H), 3.57 (d, 2 H, J = 2 Hz), 1.33 (s, 6 H). This compound was air sensitive and reduced immediately to the phenethyl alcohol 21.

2-[2-Methoxy-3-(2-hydroxyethyl)phenyl]-4,4-dimethyl-2-oxazoline (21). A solution of 8.2 g (33 mmol) of aldehyde 8 in 100 mL of absolute ethanol was cooled in an ice bath and 1.25 g (33 mmol) sodium borohydride added. The mixture was stirred for 3 h while slowly warming to ambient temperature and was then poured into water. The aqueous mixture was extracted with ether, dried over $MgSO_4$, and concentrated to give 4.72 g (57%) of a solid which was recrystallized from hexane: mp 72.0–72.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.52 (dd, 1), 7.22 (m, 1), 6.93 (t, 1), 4.03 (s, 2), 3.73 (s, 3), 3.72 (t, 2), 2.90 (br s, 1), 2.82 (t, 2), 1.38 (s, 6); IR (film) 3300, 1627 cm^{-1}.

Anal. Calcd for $C_{11}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.47; H, 7.55; N, 5.62.

2-(3-Butenyl)anisole (9). To 1.08 g (10.0 mmol) of anisole and 1.5 mL (10.0 mmol) of TMEDA in 12 mL of dry ether at reflux was added 4.72 mL (10.5 mmol) of n-BuLi, and the yellow solution was heated at reflux for 1 h. The cloudy white suspension was then added to 4.0 mL (30 mmol) of 1,4-diiodobutane in 10 mL of dry ether at −22 °C. The resulting suspension was stirred overnight. Quenching and extraction gave 2.60 g (90%) of the (4-iodobutyl)anisole after excess diiodobutane was removed by distillation: ^{1}H NMR (CCl_4) δ 6.53–7.25 (m, 4), 3.72 (s, 3), 3.08 (t, J = 7 Hz, 2), 2.57 (t, J = 6 Hz, 2), 1.43–2.10 (m, 4). Without further purification, the (iodobutyl)anisole (32.4 g, 0.112 mol) was added to a hot (90 °C) solution of 12.8 g of potassium *tert*-butoxide in 113 mL of *tert*-butyl alcohol and the mixture stirred at 90 °C for 24 h. The solution was diluted with an equal volume of water and then extracted with ether. The ether solution was washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give an amber liquid. Distillation at 76 °C (2 torr) gave 11.6 g (65%) of the product, 9: ^{1}H NMR (CCl_4) δ 7.3–6.6 (m, 4), 6.2–5.4 (m, 1), 5.20–4.75 (m, 2), 3.73 (s, 3), 2.83–2.00 (m, 4); IR (film) 1640, 750 cm^{-1}.

2-[2-Methoxy-3-(3-butenyl)phenyl]-4,4-dimethyl-2-oxazoline (10). (a) 3-(3-Butenyl)anisic Acid. Lithiation of 9 was formed as described for anisole above. The resulting lithio salt was added to dry ether saturated with carbon dioxide as a continuous stream. After 1 h, the cloudy mixture was extracted with saturated bicarbonate, and the combined extracts were back-extracted with ether. The aqueous phase was carefully neutralized with concentrated HCl and extracted with ether. The ether was washed, dried, and concentrated to give 73% of the anisic acid: mp 74–75 °C (sublimed); IR (film) 2300–3300, 1675, 1590, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.17 (dd, J = 3, 8 Hz, 1), 7.39 (dd, J = 3, 8 Hz, 1), 7.12 (q, J = 8 Hz, 1), 5.47–6.18 (m, 1), 4.77–5.20 (m, 2), 3.87 (s, 3), 2.10–3.00 (m, 4). The acid (1.12 g, 5.4 mmol) was transformed into the amide alcohol by following the procedure given for oxazoline 7. Cyclization to the oxazoline 10 was performed in the following manner. To the amide alcohol was added 3 mL of distilled thionyl chloride. As soon as all the amide alcohol was in solution, the mixture was added to excess 20% NaOH. The layers were separated, and the aqueous phase was extracted with ether. The ether was washed, dried, and evaporated to give 1.29 g (92%) of 10: bp 100 °C (0.1 mm); IR (film) 1646, 1470, 1010 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.51 (dd, J = 2.5, 7 Hz, 1), 7.18 (dd, J = 2.5, 7 Hz, 1), 6.95 (q, J = 7 Hz, 1), 5.45–6.18 (m, 1), 4.75–5.22 (m, 2), 4.23 (s, 2), 3.75 (s, 3), 2.05–3.00 (m, 4), 1.33 (s, 6).

Aryloxazoline 11. To a 250-mL, round-bottomed, three-necked flask under nitrogen with a stir bar, condenser, and addition funnel were added 5.87 g (24 mmol) of oxazoline 7 and 50 mL of THF. To the addition funnel was added 49 mL of 0.98 M (48 mmol) BH_3·THF. The reaction mixture was cooled in ice and the BH_3·THF added over 15 min. The reaction was allowed to warm over 2 h to room temperature and was then cooled in an ice bath. To the cold mixture was slowly added 8 mL of 3 M

NaOH (24 mmol) followed by 2.8 mL of 30% H_2O_2. The mixture was heated at 55–60 °C for 90 min, cooled, poured into ether, and washed with water and brine. The ether layer was stirred 10 h with 500 mL of saturated sodium sulfite. The mixture was rinsed with water and brine and then rinsed three times with 25 mL of 4.5 N HCl, shaking 5 min each time. The aqueous extract was made alkaline with 5 M NaOH, extracted with ether, and dried over $MgSO_4$ to give the crude alcohol. Bulb-to-bulb distillation at 120 °C (0.1 mm) gave 4.29 g (68%) of alcohol **11** as a clear colorless liquid: ^1H NMR (CCl_4) δ 7.63–6.73 (m, 3), 3.97 (s, 2), 3.73 (s, 3), 3.60–3.17 (m, 2), 2.90–2.43 (m, 3), 1.97–1.50 (m, 2), 1.33 (s, 6).

2-(8-Chromanyl)-4,4-dimethyl-2-oxazoline (15). To 20 mg of 50% sodium hydride, previously washed with THF, in 10 mL of THF was added 80 mg of **11**. The mixture was heated to reflux for 20 h and then poured into water, extracted with ether, dried (Na_2SO_4), and concentrated. The residue was placed on a 2-mm-thick silica gel plate (PF_{254}, E. Merck). Elution with 50% ethyl acetate–hexane gave 40 mg (72%) of the product: IR (film) 1640 cm^{-1}; ^1H NMR (CCl_4) δ 7.13 (dd, J = 2, 7 Hz), 6.52–7.18 (m, 2), 4.18 (t, J = 5 Hz, 2), 3.88 (s, 2), 2.75 (t, J = 6 Hz, 2), 1.68–2.22 (m, 2), 1.32 (s, 6).

Chroman-8-carboxylic Acid (16). A solution of 20 mg of **15** in 25 mL of 4.5 M hydrochloric acid was heated to reflux for 18 h and the cooled solution extracted with ether, dried, and concentrated to give 10 mg (65%) of **16**, mp 84–86 °C (lit.[3] mp 85–88 °C).

Mesylate 12. In 10 mL of dry methylene chloride were added 60 mg of alcohol **11** and 0.05 mL of triethylamine. The solution was cooled to −22 °C and 0.025 mL (0.32 mmol) of methanesulfonyl chloride was added. The mixture was stirred over 2.5 h during which time the reaction was allowed to warm to room temperature. The mixture was then extracted with water and brine, dried over Na_2SO_4, and concentrated (<20 °C) to give 66 mg (88%) of **12**: NMR (CCl_4–$CDCl_3$) δ 7.57 (dd, J = 2, 7 Hz, 1), 6.80–7.35 (m, 2), 4.15 (t, J = 6 Hz, 2), 4.02 (s, 2), 3.77 (s, 3), 2.93 (s, 3), 2.50–3.00 (m, 2), 1.38 (s, 6), 0.83–1.50 (m, 2).

Bromide 13. Crude mesylate **12** was dissolved in 1.5 mL of DMF, and 5 equiv of lithium bromide was added. The mixture was stirred overnight. Aqueous workup gave 0.06 g (100%) of bromide **13**: IR (film) 1644 cm^{-1}; ^1H NMR (CCl_4) δ 7.60 (dd, J = 2, 7.5 Hz, 1), 7.25 (dd, J = 2, 7.5 Hz, 1), 7.00 (q, J = 7.5 Hz, 1), 3.97 (s, 2), 3.78 (s, 3), 3.33 (t, J = 6 Hz, 2), 2.78 (t, J = 7 Hz, 2), 1.90–2.37 (m, 2), 1.37 (s, 6).

2-(4-Indanyl)-4,4-dimethyl-2-oxazoline (17). Magnesium (0.002 g, 0.08 mmol) was added to 0.02 g (0.07 mmol) of **13** in 2 mL of dry THF and the mixture heated at reflux for 48 h. Aqueous quench and ether extraction gave 0.01 g (80%) of **17**: IR (film) 1630 cm^{-1}; ^1H NMR (CCl_4) δ 7.38 (dd, J = 2, 8 Hz, 1), 7.12 (dd, J = 2,8 Hz, 1), 6.70 (q, J = 8 Hz, 1), 4.03 (s, 2), 2.40–2.83 (m, 4), 1.50–1.83 (m, 2), 1.40 (s, 6).

Indan-4-carboxylic Acid (18). Standard acidic hydrolysis (4.5 N HCl, reflux) on 0.01 g (0.05 mmol) of **17** for 18 h afforded 0.005 g (67%) of **18**: mp 147–151 °C (lit.[4] mp 153 °C); IR (film) 2400–3600, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.67–7.83 (m, 3), 2.45–2.83 (m, 4), 1.43–1.84 (m, 2).

Amine 14. (a) Reaction of Mesylate 12 with Potassium Phthalimide. To a 100-mL, round-bottomed flask was added 8.51 g (24.9 mmol) of the crude mesylate **3**, followed by 20 mL of DMF and 4.63 g (25 mmol) of potassium phthalimide. A condenser was attached, and the mixture was heated in an oil bath at 60 °C for 2 h. The mixture was cooled, taken up in ether and washed with water. The aqueous layer was extracted with ether, the ether extracts were combined, washed with water and brine, dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure to give 9.23 g (95%) crude phthalimide: ^1H NMR (CCl_4) δ 8.0–6.8 (m, 7), 3.98 (s, 2), 3.76 (s, 3), 3.68 (t, 2), 2.67 (m, 2), 2.23–1.80 (m, 4), 1.37 (s, 6).

(b) Hydrazinolysis of Phthalimide. To a three-necked flask with a stir bar and condenser were added 1.185 g (3.02 mmol) of the above phthalimide, 12 mL of *tert*-butyl alcohol, 165 μL of water (9.2 mmol), and 290 μL (9.1 mmol) of hydrazine. The mixture was heated to reflux for 3.5 h, cooled to ambient temperature, stirred 30 min with ca. 30 mL of 20% Na_2CO_3, and extracted with ether. The ether extracts were washed with 1 M HCl (30 mL, in portions), and the acidic extract was then washed with ether and the ether discarded. The pH of the aqueous layer was adjusted to 5, and it was then washed with additional ether which was discarded. After the water solution was made strongly alkaline and extracted with ether, the ether was brine washed, dried over Na_2SO_4, filtered, and concentrated to give 0.579 g (73%) of the amine: ^1H NMR (CCl_4) δ 7.63 (dd, 1), 7.35–6.85 (m, 2), 4.00 (s, 2), 3.80 (s, 3), 2.63 (m, 4), 1.9–1.3 (m, 2), 1.33 (s, 6), 1.02 (br s, 2).

8-(2-Oxazolinyl)-1,2,3,4-tetrahydroquinoline (19). Under a nitrogen atmosphere, a solution of 0.58 g (2.2 mmol) of **14** in 7 mL of dry THF was added to 4.9 mmol of lithium diisopropyl amide in 22 mL of THF. After the addition was complete, the mixture was stirred for 45 min, quenched with 2 mL of H_2O, allowed to warm to room temperature, extracted with ether and water, brine washed, and dried over anhydrous K_2CO_3. Filtration and concentration under vacuum gave 504 mg of crude material. Preparative layer chromatography using ethyl acetate gave 398 mg (78%) of an oil which crystallized on being allowed to stand. An analytical sample was prepared by recrystallization from ethanol–water: mp 70.5–71.0 °C; ^1H NMR (CCl_4) δ 8.33 (br s, 1), 7.45 (dd, 1), 6.87 (br d, 1), 6.33 (t, 1), 3.85 (s, 2), 3.45 (m, 2), 2.73 (t, 2), 2.08–1.67 (m, 2), 1.35 (s, 6H); IR (KBr) 1622 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88. Found: C, 72.91; H, 8.07.

1,2,3,4-Tetrahydroquinoline (20). A solution containing 101 mg of quinoline–oxazoline **19** in 3 mL of 4.5 M hydrochloric acid was heated to reflux for 24 h. The solution was neutralized, on cooling, with 5 M NaOH and extracted with ether. The ether extracts were dried (Na_2SO_4) and concentrated to give 35.6 mg (61%) of **20**. The IR spectrum was identical with that in the Sadtler file (No. 22130).

7-(Oxazolinyl)dihydrobenzofuran (23). To a 10-mL flask with a condenser were added 274.5 mg (1.10 mmol) of the alcohol **21** and 5 mL of THF, followed by 36 mg (1.5 mmol) of NaH (rinsed with hexane under N_2). The reaction mixture was heated to reflux for 24.5 h, cooled, poured into water, and extracted with ether. The ether extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated to give 248.2 mg of an oil. Preparative layer chromatography using 7.5% THF in CH_2Cl_2 (two elutions) gave 196.3 mg (82%) of liquid which crystallized on being allowed to stand. Recrystallization from hexane gave a white crystalline solid: mp 80.5–81.0 °C; ^1H NMR ($CDCl_3$) δ 7.66 (d, 1), 7.23 (d, 1), 6.80 (t, 1), 4.72 (t, J = 8 Hz, 2), 4.08 (s, 2), 3.22 (t, J = 8 Hz, 2), 1.43 (s, 6).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96. Found: C, 71.89; H, 7.20.

Benzofuran-7-carboxylic Acid (24). To a 10-mL flask with a condenser was added 51.8 mg (0.238 mmol) of the above oxazoline **23** followed by 2 mL of 4.5 M HCl. The mixture was heated to reflux for 24 h, cooled, extracted with ether, brine washed, dried ($MgSO_4$), filtered and concentrated to give 40.4 mg of a white solid. Preparative layer chromatography using 5% methanol in CH_2Cl_2 gave 18.9 mg (49%) of a white crystalline solid, mp 166–169 °C. Recrystallization from ethanol–water gave purified product: mp 168–169 °C; ^1H NMR ($CDCl_3$) δ 8.82 (br s, 1), 7.75 (d, 1), 7.35 (d, 1), 6.87 (m, 1), 4.77 (t, 2), 3.28 (t, 2).

Anal. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 65.75; H, 5.20.

Amine 22. (a) Mesylation of Alcohol 21. To a 50-mL flask were added 3.44 g (13.8 mmol) of the alcohol **21** and 14 mL of pyridine. The solution was cooled in an ice bath, and then 2.15 mL (28 mmol) of mesyl chloride was added. The reaction mixture was placed in a freezer for 1 day and then poured into water and extracted with ether, and the ether extracts were combined, washed with water, saturated $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated under vacuum to give 4.3 g (95%) of the crude mesylate: ^1H NMR (CCl_4) δ 7.53 (dd, 1), 7.2 (br d, 1), 6.9 (t, 1), 4.27 (t, J = 7 Hz, 2), 3.95 (s, 2), 3.77 (s, 3), 3.02 (t, 2, J = 7 Hz), 2.73 (s, 3), 1.33 (s, 6).

The phthalimide was prepared in the following manner. To a 50-mL flask containing 3.41 g (10.4 mmol) of the mesylate was added 10.4 mL of DMF followed by 2.4 g (13 mmol) of potassium

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phthalimide. The mixture was heated at 60–65 °C for 13 h, cooled to ambient temperature, poured into water, and extracted with ether. The ether extracts were combined, washed with water and brine, dried ($MgSO_4$), filtered, and concentrated to give 3.6 g (92%) of crude phthalimide. The crude material was passed through a short column of silica gel by using ethyl acetate–hexanes (1:1). The residue was taken up in $CHCl_3$ (10 mL), hexane (10 mL) was added, and phthalimide crystallized. The mother liquor was concentrated to give an oil which crystallized on addition of hexane to give the phenethylphthalimide as a white solid: 2.48 g (63%); mp 77.5–80.5 °C; ^1H NMR ($CDCl_3$) δ 7.9–6.8 (m, 7), 4.10 (s, 2), 4.0 (m, 2), 3.90 (s, 3), 3.10 (m, 2), 1.43 (s, 6).

(b) Removal of Phthalimide to Amine 22. The phthalimide from above (859 mg, 2.27 mmol) was dissolved in 9 mL of *t*-BuOH, and 124 μL of hydrazine was added. The mixture was heated at reflux for 3 h, cooled to ambient temperature, shaken with ca. 30 mL of 20% Na_2CO_3, and extracted with ether. The ether extracts were washed with 1 M HCl (total 30 mL), the pH of the aqueous layer was adjusted to 6, and then the aqueous layer was washed with ether. The aqueous layer was then made strongly alkaline (pH >11), and the amine was extracted with ether, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum to give 403 mg (72%) of product: ^1H NMR (CCl_4) δ 7.63 (dd, 1), 7.55 (dd, 1), 6.98 (t, 1), 3.98 (s, 2), 3.78 (s, 3), 2.77 (br t, 4), 1.35 (s, 6), 1.02 (br s, 2).

7-(2-Oxazolinyl)indoline (25). To a three-necked, 50-mL flask with an addition funnel and stir bar were added 0.50 mL (3.51 mmol) of diisopropylamine and 22 mL of THF. To the addition funnel was added 403 mg (1.62 mmol) of the amine **22** in THF (3 mL) via cannula under positive nitrogen pressure. The flask was cooled to −45 °C (acetonitrile–dry ice bath), 1.43 mL (3.5 mmol) of *n*-butyllithium was added, and the mixture was stirred for 20 min. The amine was then slowly added (25 min) to the LDA solution, and the mixture was stirred 1 h and then quenched with 2 mL of H_2O. The cooling bath was removed, the mixture was poured into water and extracted three times with ether, and the ether extracts were washed with water and brine, dried (K_2CO_3), filtered, and concentrated to give 349.5 mg of the crude oxazolinylindoline. Preparative layer chromatography using ethyl acetate–hexane (1:1) gave a pale yellow oil which solidified; 293 mg (83.5%). After recrystallization from ethanol–water: mp 48.5–49.0 °C; ^1H NMR ($CDCl_3$) δ 7.49 (br d, 1 H), 7.13 (br d, 1 H), 6.58 (t, 1 H), 6.33 (br s, 1 H), 4.01 (s, 2 H), 3.71 (m, 2 H), 3.05 (m, 2 H), 1.37 (s, 6 H); IR (film) 3360, 1630 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46. Found: C, 72.42; H, 7.51.

Indoline-7-carboxylic Acid (26). To a 10-mL flask with a condenser and stir bar were added 215 mg (1 mmol) of the 7-oxazolinylindoline **25** and 3 mL of 4.5 M HCl. The mixture was heated at reflux for 30 h and cooled to room temperature, the pH was adjusted to approximately 6 by using 5 M NaOH, the mixture was extracted with ether, and the ether extract was dried with anhydrous Na_2SO_4, filtered, and concentrated to give 110 mg (68%) of white crystalline solid: mp 156 °C dec (lit.[5] mp 162–164 °C); ^1H NMR ($CDCl_3$) δ 8.77 (br s, 2 H), 7.63 (d, 1 H), 7.19 (m, 1 H), 6.57 (t, 1 H), 3.93–3.53 (m, 2 H), 3.27–2.83 (m, 2 H); IR (KBr) 3430, 1645 cm^{-1}.

Oxazoline 27. Oxazoline **10** (0.07 g, 0.25 mmol) was dissolved in 2 mL of dry THF and the mixture cooled to 0 °C. Then 0.1 mL (0.1 mmol) of 1 M BH_3–THF was added, and the solution was warmed to 25 °C and stirred 1 h. Water (0.01 mL) was slowly added followed by 0.04 mL of NaOH (12%) and 0.04 mL of H_2O_2 (30%). The solution was heated at 50 °C for 1 h. After cooling, it was poured into water and extracted with ether. A sodium sulfite wash and drying (K_2CO_3) gave 0.064 g of the borane complex of **10** (IR 2370 cm^{-1}). The borane complex was heated in 4.5 N HCl at reflux for 15 min and then made basic and extracted with ether to give 0.053 g (82%) of recovered **10**.

The above was repeated with excess borane (1.00 mmol) to give 95% of the borane complex of **27**. Acid treatment as above yielded a 71% overall yield of **27**. When the borane complex was shaken with HCl for 7 min (instead of heated at reflux), the yield rose to 84%: IR (film) 3350 (br), 1645, cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.55 (dd, J = 2, 7 Hz, 1), 7.24 (dd, J = 2, 8 Hz, 1), 7.03 (dd, J = 7, 8 Hz, 1), 4.05 (s, 2), 3.74 (s, 3), 3.33–3.73 (m, 2), 2.38–2.89 (m, 2), 1.07–2.00 (m, 4), 1.37 (s, 6).

9-(2-Oxazolinyl)-2,3,4,5-tetrahydrobenzoxepin (31). Sodium hydride (0.013 g, 0.21 mmol) was washed with dry THF. To this was added 0.05 g (0.18 mmol) **27** in 3 mL of THF, and the mixture was stirred overnight. The mixture was then heated at reflux for 48 h. Standard workup (preparative LC, two elutions with 50% EtOAc–Hexane) gave 0.024 g (54%) of **31**: IR (film) 1640 cm^{-1}; ^1H NMR (CCl_4) δ 7.41 (dd, J = 2, 7 Hz, 1), 7.06 (dd, J = 2, 7 Hz, 1), 6.88 (q, J = 7 Hz, 1), 3.93 (s, 2), 3.80–4.07 (m, 2), 2.63–3.00 (m, 2), 1.50–2.17 (m, 4), 1.30 (s, 6).

2,3,4,5-Tetrahydrobenzoxapin-9-carboxylic Acid (32). Standard acidic hydrolysis on 0.014 g (0.057 mmol) of **31** overnight resulted in 0.007 g (64%) of **32**: mp 58–59 °C (lit.[6] mp 59–60 °C); IR (film) 2360–3700, 1680 (br), 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00 (dd, J = 2, 7 Hz, 1), 7.38 (dd, J = 2, 7 Hz, 1), 7.14 (q, J = 7 Hz, 1), 4.22 (t, J = 5 Hz, 2), 2.73–3.03 (m, 2), 1.53–2.30 (m, 4).

Mesylate 28. Alcohol **27** (0.41 g, 1.48 mmol) was dissolved in 10 mL of dry methylene chloride (passed through an alumina column) and cooled to −22 °C. Then 0.35 mL (2.22 mmol) triethylamine and 0.17 g (2.11 mmol) methanesulonyl chloride were added in that order. The solution was allowed to warm to ambient temperature and stirred 1 h. Water was then added, and the layers were spearated. The aqueous layer was extracted with methylene chloride and the combined organic phase washed with water and brine, dried over sodium sulfate, and concentrated below 20 °C to give 0.50 g (95%) of **28**: ^1H NMR (CCl_4) δ 6.77–7.78 (m, 3), 4.00–4.30 (m, 2), 3.97 (s, 2), 3.77 (s, 3), 2.87 (s, 3), 2.43–3.17 (m, 2), 1.57–1.93 (m, 4), 1.33 (s, 6). This was used without further purification to reach the bromide, **29**.

Bromide 29. To 0.07 g (0.20 mmol) of crude **28** in 1.5 mL of dry DMF was added 0.07 g (0.79 mmol) lithium bromide, and the mixture was stirred overnight. The mixture was then poured into water, and an ethereal workup gave 0.07 g (94%) of **29**: IR (film) 1655, 1474, 1013 cm^{-1}; ^1H NMR (CCl_4) δ 7.54 (dd, J = 2, 7 Hz, 1), 6.72–7.28 (m, 2), 3.94 (s, 2), 3.73 (s, 3), 3.22–3.58 (m, 2), 2.45–2.90 (m, 2), 1.62–1.98 (m, 4), 1.33 (s, 6).

8-(2-Oxazolinyl)tetralin (33). To 0.03 g (0.09 mmol) of **29** in 2 mL of dry THF was added 0.004 g (0.09 mmol) of magnesium and the mixture stirred overnight. Because the magnesium was not all consumed, the mixture was heated at reflux 24 h. Standard workup gave 0.02 g (84%) of **33**: bp 70 °C (0.03 mm); IR (film) 1632, 1450 cm^{-1}; ^1H NMR (CCl_4) δ 6.32–7.48 (m, 3), 4.00 (s, 2), 2.35–2.92 (m, 4), 1.50–1.92 (m, 4), 1.40 (s, 6).

Tetralin-8-carboxylic Acid (34). Hydrolysis of **33** in 4.5 N HCl at reflux for 18 h, cooling, ether extraction, and concentration gave 72% of acid **34**: mp 148–149 °C (lit.[7] mp 150 °C); IR (film) 2350–3700, 1670, 1450, 764 cm^{-1}; ^1H NMR (CCl_4) δ 7.83 (dd, J = 2, 8 Hz, 1), 7.20–7.53 (m, 1), 6.67–7.10 (m, 1), 2.57–3.03 (m, 4), 1.50 (s, 6).

Amine 30. (a) Reaction of Mesylate 28 with Potassium Phthalimide. To 0.20 g (0.56 mmol) of mesylate **28** in 7 mL of DMF was added 0.42 g (2.24 mmol) of potassium phthalimide, and the mixture was stirred overnight. The product was isolated as described for **14** and **22** and gave 0.19 g (84%) of the phthalimide derivative: ^1H NMR (CCl_4) δ 6.72–7.85 (m, 7), 3.93 (s, 2), 3.72 (s, 3), 3.45–3.83 (m, 2), 2.48–2.95 (m, 2), 1.50–1.90 (m, 4), 1.30 (s, 6).

(b) Removal of the Phthalimide to Amine 30. To 0.65 g (0.160 mmol) of the above phthalimide in 2 mL of ethanol was added 0.06 mL of hydrazine. The solution was heated at reflux for 2 h. After the mixture cooled, a drop of concentrated HCl was added and the solid filtered and washed with ethanol. The pH of the combined filtrate and washings was adjusted to 8, and the excess ethanol was removed in vacuo. The residue was extracted with ether, and it was washed, dried, and concentrated to give 0.041 g (93%) of **30**: IR (film) 3000–3700, 1640 cm^{-1}; ^1H NMR (CCl_4) δ 7.51 (dd, J = 2, 7 Hz, 1), 6.70–7.33 (m, 2), 3.39 (s, 2), 3.73 (s, 3), 2.37–2.83 (m, 4), 1.10–1.73 (m, 4), 1.33 (s, 6).

9-(2-Oxazolinyl)-2,3,4,5-tetrahydrobenzazepin (35). To a 250-mL, three-necked flask with a stir bar and addition funnel

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were added 1.54 mL (11 mmol) of diisopropylamine and 50 mL of THF. To the addition funnel was added 1.38 g (5 mmol) of the amine **30** in 20 mL of THF via cannula. To the diisopropylamine solution at 0 °C was added 4.5 mL (11 mmol) of *n*-butyllithium. After 5 min, the solution was cooled to −45 °C (acetonitrile–dry ice), and **30** was added over 30 min. After being stirred 17 h, the cold mixture was quenched with 5 mL of water, permitted to warm to room temperature, extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated under vacuum to give 1.19 g of crude product. Preparative layer chromatography using ethyl acetate–hexane (1:1) gave 590 mg (48%) of an oil which crystallized after the sides of the flask were scratched. recrystallization from ethanol–water gave a white solid: mp 44.5–45 °C; ^{1}H NMR (CCl_4) δ 8.28 (br s, 1), 7.53 (dd, 1), 7.03 (br d, 1), 6.53 (t, 1), 3.92 (s, 2), 3.18 (m, 2), 2.78 (m, 2), 1.8 (m, 4), 1.37 (s, 6); IR (KBr) 1622 cm^{-1}.

Anal. Calcd for $C_{15}H_{20}N_2O$: C, 73.78; H, 8.25. Found: C, 73.78; H, 8.08.

Benzazepin-9-carboxylic Acid (36). A solution of 50.8 mg of **35** in 1 mL of 4.5 N HCl was heated to reflux for 25 h, cooled, and adjusted to pH 4.5 with 5 M NaOH. The mixture was extracted with dichloromethane, and the extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated to give 17.9 mg (45%) of **36** as a colorless solid. Recrystallization from ethanol–water gave purified product: mp 160–163 °C dec; ^{1}H NMR ($CDCl_3$) δ 9.03 (br s, 2), 7.88 (d, 1), 7.3–6.6 (m, 2), 3.4–3.0 (m, 2), 3.0–2.75 (m, 2), 2.17–1.67 (m, 4).

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 69.09; H, 6.85. Found: C, 69.13; H, 6.77.

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Registry No. **4**, 6282-42-4; **5**, 31456-98-1; **6a**, 75934-00-8; **6b**, 75934-01-9; **7**, 75934-02-0; **8**, 75934-03-1; **9**, 63667-83-4; **10**, 75934-04-2; **11**, 75934-05-3; **12**, 75961-46-5; **12** phthalimide derivative, 75934-06-4; **13**, 75934-07-5; **14**, 75934-08-6; **15**, 75948-75-3; **16**, 31457-16-6; **17**, 75934-09-7; **18**, 4044-54-6; **19**, 75934-10-0; **20**, 635-46-1; **21**, 75934-11-1; **21** mesylate, 75934-12-2; **21** phthalimide derivative, 75934-13-3; **22**, 75934-14-4; **23**, 75934-15-5; **24**, 35700-40-4; **25**, 75934-16-6; **26**, 15861-40-2; **27**, 75934-17-7; **28**, 75948-76-4; **28** phthalimide derivative, 75934-18-8; **29**, 75934-19-9; **30**, 75934-20-2; **31**, 75934-21-3; **32**, 31457-17-7; **33**, 75934-22-4; **34**, 4242-18-6; **35**, 75934-23-5; **36**, 34967-95-8; methyl salicylate, 119-36-8; allyl bromide, 106-95-6; 2-amino-2-methyl-1-propanol, 124-68-5; 1,4-diiodobutane, 628-21-7; (4-iodobutyl)anisole, 75934-24-6; 3-(3-butenyl)anisic acid, 75934-25-7.

Photochemical Reactions of Aromatic Compounds. 35.[1] Photo-Birch Reduction of Arenes with Sodium Borohydride in the Presence of Dicyanobenzene

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Birch-type reduction of phenanthrene, anthracene, naphthalene, and several substituted naphthalenes efficiently occurs upon irradiation of 9:1 acetonitrile–water solutions in the presence of sodium borohydride and *m*- or *p*-dicyanobenzene. The reduction products of phenanthrene and anthracene are the respective 9,10-dihydroarenes, whereas naphthalene, 2,6-dimethylnaphthalene, acenaphthene, and 2-methoxynaphthalene are exclusively photoreduced at C_1 and C_4. With the naphthalenes having alkyl groups on the one ring, the photoreduction gives both the 1,4- and 5,8-dihydronaphthalenes. The exception is the photoreduction of 1-methoxynaphthalene that gives both the 1,2- and 1,4-dihydronaphthalenes. The reaction mechanism has been discussed in terms of electron transfer from the excited singlet state of arenes to the dicyanobenzenes followed by the nucleophilic attack of borohydride anion on the cation radicals of the arenes.

The Birch reduction, one of the most useful synthetic reactions, has now been firmly established to proceed via anion radicals and dianions of substrates;[2] the electron sources are usually alkaline metals in liquid ammonia or amine solvents. For convenience, however, it is desirable that stable electron sources can be used in usual solvents at room temperature. Photochemical electron-transfer reactions of electron donor–acceptor pairs in polar solvents[3] can provide a convenient, elegant method for generation of anion radicals; photoreduction of arenes by amines has been investigated.[4] However, yields of reduction products are usually low because of formation of adducts with amines.[4,5] Sodium borohydride[4,6-8] and sodium sulfite[8] are other candidates as reductants for photoreduction of arenes, though the yields are again low.

Scheme I

$$\mathrm{ArH} + \mathrm{H^-(BH_4^-)} + \mathrm{H^+(H_2O)} \xrightarrow[\mathrm{CH_3CN\text{-}H_2O}]{h\nu/\mathrm{DCNB}} \mathrm{H\text{-}ArH\text{-}H}$$

$$\mathrm{ArH} \xrightarrow{h\nu} {}^1\mathrm{ArH}^* \xrightarrow[\mathrm{DCNB\ DCNB^{-\cdot}}]{} {}^-\mathrm{ArH\text{-}H} \xrightarrow{\mathrm{H^+}} \mathrm{H\text{-}ArH\text{-}H}$$

$$\cdot\mathrm{ArH\text{-}H} \xrightarrow[\mathrm{DCNB\ DCNB}]{} {}^-\mathrm{ArH\text{-}H} \xrightarrow{\mathrm{H^+}} \mathrm{H\text{-}ArH\text{-}H}$$

$$2\cdot\mathrm{ArH\text{-}H} \longrightarrow \mathrm{H\text{-}ArH\text{-}H} + \mathrm{ArH}$$

In a previous paper,[9] we reported that efficient photoreduction of some aromatic hydrocarbons can be accomplished by the use of sodium borohydride and *p*-di-

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