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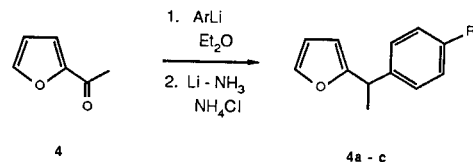
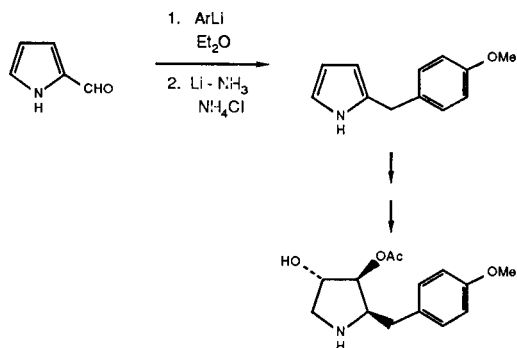
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Tandem arylation-reduction of a series of acyl heterocycles using phenyl-, 4-methylphenyl-, and 4-methoxyphenyllithium reagents followed by lithium-ammonia-ammonium chloride reduction afforded the corresponding benzyl heterocycles. The acyl heterocycles surveyed in this study contained furan, 2,3-dihydro-4*H*-1-benzopyran, 4*H*-1-benzopyran, thiophene, 4,5,6,7-tetrahydrobenzo[*b*]thiophene, 2,3-dihydro-4*H*-1-benzothiopyran, and pyridine nuclei. All acyl heterocycles yielded the corresponding benzyl heterocycles except 2,3-dihydro-4*H*-1-benzothiopyran-4-one, which selectively cleaved during reduction to give the corresponding 2-(1-arylpropyl)benzenethiols.

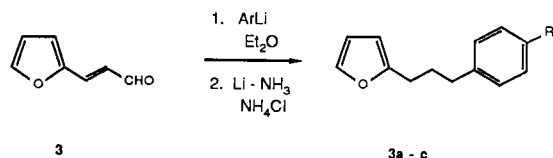
J. Heterocyclic Chem., **24**, 1205 (1987).

In studies extending the usefulness of tandem alkylation-reduction of carbonyl compounds [2], acyl heterocycles had only been superficially examined [3] until the need arose in this laboratory for an efficient synthesis of 2-benzylpyrroles. Subsequently, the arylation-reduction of 2-acylpyrroles were studied in detail and applied in the total synthesis of anisomycin antibiotics [4]. The success of

included 2-furancarboxaldehyde (**1**), 5-methyl-2-furancarboxaldehyde (**2**), 3-(2-furanyl)-2-propenal (**3**), 2-furanyl methyl ketone (**4**), 2,3-dihydro-4*H*-1-benzopyran-4-one (**5**), and 4*H*-1-benzopyran-4-one (**6**). As can be seen, in all cases the method provides an efficient synthesis of the corresponding benzyl oxygen-containing heterocycle where the isolated yields ranged from 63-98%. It should be noted



that in the examples using 3-(2-furanyl)-2-propenal (**3**), the corresponding products **3a-c** are void of the double bond. This is not unexpected since in the intermediate alkoxides the double bond is conjugated with the heterocycle creating styrene-like systems, which are vulnerable to metal-ammonia reducing conditions [5].



the latter study encouraged this group to expand the scope of tandem alkylation-reduction to include a larger selection of acyl heterocycles in an effort to develop a generalized method for the efficient synthesis of benzyl heterocycles and, perhaps, realize the limits of the procedure as it applies to the heterocyclic carbonyl systems. Herewith is described the results of such an undertaking.

The general alkylation-reduction procedure is to add the acyl heterocycle to the aryllithium reagent in ether in a metal-ammonia reaction vessel to generate the intermediate benzyl alkoxide, which is then reduced to the benzyl heterocycle by the sequential addition of ammonia, lithium, and ammonium chloride. The *in situ* generated organolithium reagents used in this study were phenyllithium, 4-methylphenyllithium, and 4-methoxyphenyllithium.

Oxygen-Containing Heterocycles.

Entries 1-6 in Table 1 are a listing of the acyl oxygen-containing heterocycles that were used for the study and

Sulfur-Containing Heterocycles.

Entries 7-14 in Table 1 are a listing of the acyl sulfur-containing heterocycles that were subjected to these tandem arylation-reduction conditions. They included 2-thiophenecarboxaldehyde (**7**), 3-methyl-2-thiophenecarboxaldehyde (**8**), 5-methyl-2-thiophenecarboxaldehyde (**9**), 3-thiophenecarboxaldehyde (**10**), cyclopropyl 2-thienyl ketone (**11**), methyl 3-thienyl ketone (**12**), 4,5,6,7-tetrahydrobenzo[*b*]thiophene-4-one (**13**), and 2,3-dihydro-4*H*-1-benzothiopyran-4-one (**14**) [6]. For the thiophene systems,

Table 1

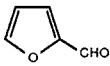
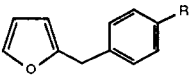
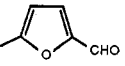
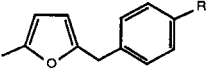
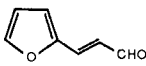
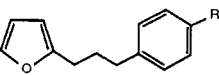
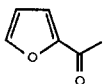
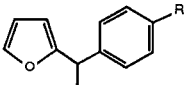
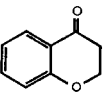
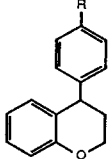
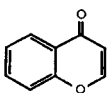
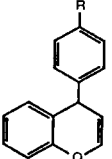
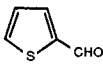
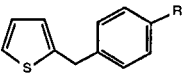
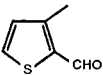
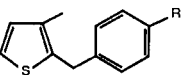
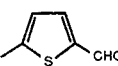
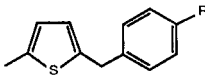

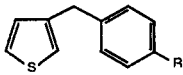
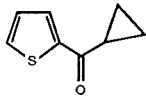
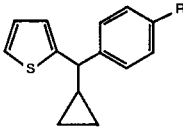
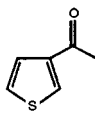
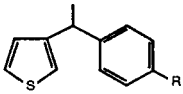
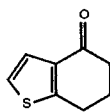
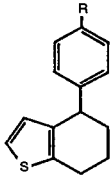
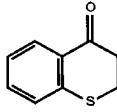
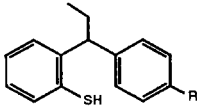
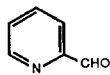
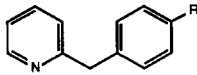
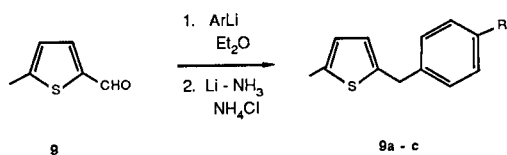
Acyl Heterocycle	Product (% Yield)
	
1	1a , R = H (92) 1b , R = Me (71) 1c , R = OMe (65)
	
2	2a , R = H (95) 2b , R = Me (92) 2c , R = OMe (75)
	
3	3a , R = H (87) 3b , R = Me (77) 3c , R = OMe (72)
	
4	4a , R = H (93) 4b , R = Me (75) 4c , R = OMe (68)
	
5	5a , R = H (98) 5b , R = Me (85) 5c , R = OMe (80)
	
6	6a , R = H (85) 6b , R = Me (72) 6c , R = OMe (63)
	
7	7a , R = H (74) 7b , R = Me (67) 7c , R = OMe (51)
	
8	8a , R = H (79) 8b , R = Me (75) 8c , R = OMe (72)

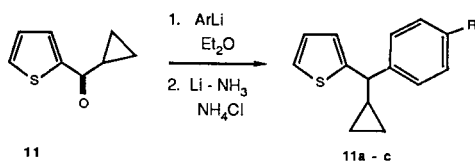
Table 1 continued

Acyl Heterocycle	Product (% Yield)
	
9	9a , R = H (99) 9b , R = Me (87) 9c , R = OMe (86)
	
10	10a , R = H (45) 10b , R = Me (43)
	
11	11a , R = H (94) 11b , R = Me (85) 11c , R = OMe (65)
	
12	12a , R = H (38)
	
13	13b , R = Me (40) 13c , R = OMe (55)
	
14	14a , R = H (85) 14b , R = Me (76) 14c , R = OMe (65)
	
15	15a , R = H (97) 15b , R = Me (92)

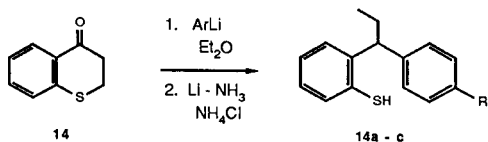
entries 7-13, it was anticipated that the heterocycle would be vulnerable to the reduction conditions [3,7]. In the two cases **7** and **11** where thiophene-ring reduction seemed to be a problem, the isolated yields of the desired benzyl



heterocycle product increased dramatically by simply limiting the exposure time of the intermediate benzyl alkoxide to lithium-ammonia reduction conditions from 15-20 minutes to 2 minutes. In the latter case, **11**, it was equally gratifying to observe that the tenuous cyclopropyl group [8] survived the reduction conditions unscathed, products **11a-c**, 65-94%, as has been observed for the strained-ring group in other selective alkylation-reduction studies [9].

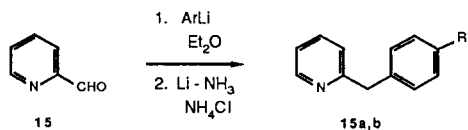


Since alkyl aryl sulfides are cleaved to the aromatic mercaptan and aliphatic hydrocarbon in metal-ammonia conditions [10], it was not surprising with entry 14 to isolate the corresponding 2-(1-arylpropyl)benzenethiols **14a-c**, exclusively, from the arylation-reduction of 2,3-dihydro-4H-1-benzothiopyran-4-one (**14**), in reasonable yields (65-85%).



Nitrogen-Containing Heterocycles.

Since the pyridine ring is vulnerable to metal-ammonia conditions [11] and the yields of the 2-benzylpyridines were low using the standard alkylation-reduction conditions, a modified sequence was developed. Both limiting the reduction exposure time to 10 minutes (from 20 minutes) and performing the entire sequence (alkylation and reduction steps) at -78° resulted in enormous improvements in product yields. For example (entry 15, Table 1), tandem alkylation-reduction of 2-pyridinecarboxaldehyde (**15**) with phenyl- and 4-methylphenyllithium afforded the corresponding 2-benzylpyridines **15a** and **15b** in excellent isolated yields (97 and 92%, respectively) [12].



The tandem arylation-reduction of 2-acylpyrroles to prepare the corresponding 2-benzylpyrroles has been previously reported [4].

For the acyl heterocycles tabulated [13], the tandem arylation-reduction sequence is indeed a convenient and efficient procedure to synthesize benzyl heterocycles. Although the inertness of the furan and pyrrole nuclei to metal-ammonia reduction was anticipated [7d], the surprising resilience of the 2,3-dihydro-4H-1-benzopyran, 4H-1-benzopyran, thiophene, and pyridine ring systems to these reducing conditions was gratifying. Even the selective vulnerability of the 2,3-dihydro-4H-1-benzothiopyran nucleus to metal-ammonia reduction is useful since the arylation-reduction sequence provides synthetic entry to 2-(1-arylpropyl)benzenethiols.

EXPERIMENTAL

Heavy white paraffin oil (Saybolt viscosity 335/365) was from Fisher Scientific Co. Lithium wire for the alloy was from Foote Mineral Co. (3.2-mm diameter, high purity: 0.050% Na, 0.004% K, and 0.010% Ca) and the sodium metal was from Fisher Scientific Co. The *in situ* generation of the aryllithium reagent and subsequent alkylation were performed under an inert argon atmosphere. The reaction assembly consisted of a large Dewar condenser mounted on a sealed 250- or 500-ml, three-necked, indented, round-bottom flask (Morton) containing a magnetic star-head Nalgene stir bar (17-mm diameter). All glassware was oven dried, cooled to ambient temperature in a box desiccator, quickly assembled, and flushed with argon. When ammonia was to be introduced, the inert gas source was disconnected and the reaction protected by attaching a soda-lime trap to the side arm of the Dewar condenser for the duration of the reaction. Anhydrous ether (diethyl ether, Reagent ACS, Fisher Scientific Co.) was used directly from freshly opened 500-g containers. Tetrahydrofuran (THF), which was filtered through an alumina column, was freshly distilled under a nitrogen atmosphere from a dark blue tetrahydrofuran solution containing the sodium-benzophenone ketyl radical. The lithium-sodium alloy was rinsed in hexane, pounded to a thin foil, and cut into thin slivers directly into the reaction vessel with argon sweeping through the flask and out the temporarily opened side-arm joint. 4-Bromotoluene [63° (11 torr)] and 4-bromoanisole [89° (11 torr)] from Aldrich Chemical Co. and bromobenzene [40° (13 torr)] and 2-furan-carboxaldehyde [1, 53° (14 torr)] from Fisher Scientific Co. were redistilled prior to use. Acyl heterocycles **2-15** from Aldrich Chemical Co. were used without further purification. Anhydrous ammonia was passed through a tower of potassium hydroxide pellets and condensed directly into the reaction vessel. Lithium wire for the reduction sequence (Foote Mineral Co., 3.2-mm diameter, high purity: 0.020% Na, 0.002% K, 0.008% Ca., and 0.037% N₂) was wiped free of oil, rinsed in hexane, and cut into 0.5-cm pieces just prior to use. Gas-liquid chromatographic analyses were performed on a 1.1 m × 4 mm (i.d.) glass column packed with 3% silicon gum rubber OV-225 (25% cyanopropyl, 25% phenyl, 50% methyl) supported on 80-100 mesh Chromosorb W HP. Purification by column chromatography was accomplished on 100-200 mesh Floridin magnesium silicate (Florisil) by eluting with ether/hexane or by flash chromatography on 230-400 mesh silica gel 60 (E. Merck) by eluting with ethyl acetate/hexane. Samples for microanalyses were obtained by evaporative distillation in a Kugelrohr oven. Boiling points are uncorrected.

The glc analyses were determined on a Hewlett-Packard Model 7610A (flame detector) chromatograph using a 40 ml/minute carrier gas flow rate. The ir spectra were determined with a Beckman Model 4240 infrared spectrophotometer. The ¹H nmr spectra were determined in deuteriochloroform at 200 MHz with an IBM Instruments Model WP200SY

nmr spectrometer and at 100 MHz with a JEOL Model JNM-PS-FT-100 nmr spectrometer. The chemical shifts are expressed in δ values (parts per million) relative to a TMS internal standard. The ms data were determined either with a Varian Associates Model CH5 mass spectrometer at an ionizing voltage of 70 eV and an emission current of 300 μ A or with a Finnigan Model 100 mass spectrometer at an ionizing voltage of 70 eV and an emission current of 200 μ A.

Lithium-Sodium Alloy (2% Na) [14].

After heating a dry stainless steel beaker (8 \times 12-cm, d \times h), equipped with a 1 \times 5-cm magnetic stir bar, thermometer, and argon atmosphere tent (a dry glass funnel with a 7-cm diameter lip inverted and inserted into the beaker with the funnel's spout attached to an argon source), containing 35 ml of paraffin oil to 210°, 15 g of lithium wire (blotted free of excess oil and cut into ca. 200 pieces) was quickly added. After the lithium metal became molten (15 minutes), 300 mg (2%) of sodium (blotted and cut into 14 pieces) was quickly added and the melt was moderately stirred for 2 hours at 210° before the heating and stirring were stopped. When the oil temperature had dropped to 195°, the molten material was clusted with a spatula, and once the melt was cool, the alloy clump was stored under oil and an argon atmosphere.

2-(Phenylmethyl)furan (1a).

To a vigorously stirred mixture of 107 mg (15.4 mmoles) of lithium-sodium alloy (20 slivers) in 20 ml of anhydrous ether under an argon atmosphere was slowly added (20 minutes) a solution of 1.178 g (7.50 mmoles) of bromobenzene in 10 ml of ether. The mixture turned cloudy grey and within 45 minutes after the addition was completed, the alloy slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 480 mg (5.00 mmoles, 486 mg of a 99% pure sample) of 2-furancarboxaldehyde (1) in 10 ml of ether was slowly added (10 minutes). After 10 minutes the bath was removed and the stirred mixture allowed to return to ambient temperature (40 minutes) during which time the mixture turned pale white. After distilling 100 ml of anhydrous ammonia into the mixture, 174 mg (25.1 mmoles, 9 pieces) of lithium wire was quickly added. Twenty minutes later, the dark-blue-black color of the mixture was discharged by the addition (3 minutes) of 1.5 g of ammonium chloride and then the ammonia was allowed to evaporate. After partitioning the residue between 75 ml of water and 75 ml of ether, the aqueous phase was extracted twice with 50-ml and twice with 25-ml portions of ether. The combined organic phase was dried (magnesium sulfate), filtered, and concentrated at water aspirator pressure (40° water bath) to afford 788 mg of a pale yellow oil. Following chromatography (Florisil), 727 mg (7.60 mmoles, 92%) of 1a was obtained as a colorless oil [3,15]; ir (film): 3170, 3135, 3105, 3080, 3045, 2920, 2860, 1605, 1515, 1505, 1460, 1435, 1155, 1080, 1035, 1015, 940, 885, 795, 770, 730, 705 cm^{-1} ; nmr: (200 MHz) 7.32 (dd, 1, J = 1.9 and 0.9 Hz) superimposed on 7.34-7.18 (m, 5), 6.28 (dd, 1, J = 3.2 and 1.9 Hz), 6.00 (dq, 1, J = 3.2 and 0.9 Hz), 3.97 (s, 2); ms: m/z (relative intensity) 159 (13), 158 (M^+ , 100), 157 (32), 130 (22), 129 (59), 128 (33), 127 (19), 115 (20), 81 (15), 64 (11), 51 (13).

2-[(4-Methylphenyl)methyl]furan (1b).

Similar treatment of 4-bromotoluene and 2-furancarboxaldehyde (1), as described for 1a, afforded 1b (71%) as a colorless oil [15a]; ir (film): 3170, 3130, 3110, 3060, 3035, 3020, 2960, 2930, 2870, 1605, 1520, 1515, 1460, 1443, 1433, 1155, 1075, 1010, 935, 885, 795, 750, 725 cm^{-1} ; nmr: (100 MHz) 7.30 (d, 1, J = 2.0 Hz), 7.11 (s, 4), 6.27 (dd, 1, J = 3.2 and 1.7 Hz), 5.97 (d, 1, J = 3.2 Hz), 3.92 (s, 2), 2.31 (s, 3); ms: m/z (relative intensity) 173 (15), 172 (M^+ , 100), 171 (22), 158 (16), 157 (59), 143 (22), 129 (58), 128 (49), 127 (13), 115 (15), 105 (13), 91 (12), 85 (13), 81 (12), 77 (11).

2-[(4-Methoxyphenyl)methyl]furan (1c).

Similar treatment of 4-bromoanisole and 2-furancarboxaldehyde (1), as described for 1a, afforded 1c (65%) as a colorless oil; ir (film): 3165, 3135, 3080, 3050, 3015, 2965, 2950, 2920, 2850, 1620, 1595, 1520, 1470, 1450, 1435, 1310, 1250, 1180, 1110, 1075, 1040, 1015, 935, 885, 800, 760, 730 cm^{-1} ; nmr: (100 MHz) 7.31 (d, 1, J = 1.0 Hz), 7.15 (d, 2, J = 8.8 Hz),

6.83 (d, 2, J = 8.8 Hz), 6.27 (dd, 1, J = 3.2 and 1.7 Hz), 5.96 (dd, 1, J = 3.1 and 0.9 Hz), 3.90 (s, 2), 3.78 (s, 3); ms: m/z (relative intensity) 189 (14), 188 (M^+ , 100), 187 (29), 173 (15), 159 (32), 157 (40), 145 (19), 144 (31), 129 (27), 128 (22), 127 (15), 115 (27), 91 (15).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_2$: C, 76.57; H, 6.43. Found: C, 76.81; H, 6.41.

2-Methyl-5-(phenylmethyl)furan (2a).

Similar treatment of bromobenzene and 5-methyl-2-furancarboxaldehyde (2), as described for 1a, afforded 2a (95%) as a colorless oil [16]; ir (film): 3135, 3115, 3090, 3050, 3030, 3000, 2970, 2940, 2870, 1630, 1615, 1575, 1505, 1460, 1430, 1390, 1240, 1225, 1165, 1075, 1025, 995, 970, 950, 780, 710, 690 cm^{-1} ; nmr: (100 MHz) 7.24 (s, 5), 5.85 (s, 2), 3.90 (s, 2), 2.24 (s, 3); ms: m/z (relative intensity) 173 (13), 172 (M^+ , 100), 171 (47), 157 (41), 129 (57), 128 (33), 95 (36), 43 (26).

2-Methyl-5-[(4-methylphenyl)methyl]furan (2b).

Similar treatment of 4-bromotoluene and 5-methyl-2-furancarboxaldehyde (2), as described for 1a, afforded 2b (92%) as a colorless oil [17]; ir (film): 3160, 3125, 3070, 3040, 3020, 3000, 2960, 2935, 2880, 1630, 1575, 1522, 1460, 1445, 1430, 1390, 1225, 1165, 1120, 1025, 1000, 970, 950, 845, 815, 780, 755 cm^{-1} ; nmr: (100 MHz) 7.11 (s, 4), 5.83 (s, 2), 3.86 (s, 2), 2.31 (s, 3), 2.23 (s, 3); ms: m/z (relative intensity) 187 (15), 186 (M^+ , 100), 185 (36), 171 (98), 143 (50), 128 (49), 95 (22), 92 (16), 43 (29).

2-[(4-Methoxyphenyl)methyl]-5-methylfuran (2c).

Similar treatment of 4-bromoanisole and 5-methyl-2-furancarboxaldehyde (2), as described for 1a, afforded 2c (75%) as a colorless oil; ir (film): 3140, 3115, 3070, 3040, 3005, 2950, 2920, 2840, 1620, 1590, 1570, 1515, 1465, 1440, 1425, 1300, 1280, 1245, 1220, 1175, 1100, 1035, 1020, 990, 965, 945, 840, 815, 775, 765, 735, 690 cm^{-1} ; nmr: (200 MHz) 7.15 (ddd, 2, J = 8.7, 2.9, and 1.8 Hz), 6.84 (ddd, 2, J = 8.7, 2.9, and 2.0 Hz), 5.84 (d, 1, J = 3.9 Hz), 5.82 (d, 1, J = 3.7 Hz), 3.85 (s, 2), 3.78 (s, 3), 2.74 (s, 3); ms: m/z (relative intensity) 202 (M^+ , 11), 121 (22), 115 (22), 95 (53), 92 (22), 91 (18), 89 (20), 78 (56), 77 (36), 63 (41), 53 (68), 52 (69), 51 (91), 50 (58), 43 (100), 39 (48).

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.20; H, 6.98. Found: C, 77.15; H, 7.00.

2-(3-Phenylpropyl)furan (3a).

To a vigorously stirred solution of 707 mg (4.50 mmoles) of bromobenzene in 30 ml of anhydrous ether under an argon atmosphere was added 67 mg (9.7 mmoles) of lithium-sodium alloy (10 slivers). The mixture turned cloudy grey and within 45 minutes after the addition was completed, the alloy slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 366 mg (3.00 mmoles) of 3-(2-furanyl)-2-propenal (3) in 10 ml of ether was slowly added (10 minutes). After 10 minutes the bath was removed and the stirred mixture allowed to return to ambient temperature (40 minutes) during which time the mixture turned pale grey. After adding an additional 25 ml of anhydrous ether and distilling 100 ml of anhydrous ammonia into the mixture, 146 mg (21.0 mmoles, 7 pieces) of lithium wire was quickly added. Twenty minutes later, the dark blue-black color of the mixture was discharged by the addition (2 minutes) of 1.7 g of ammonium chloride and then the ammonia was allowed to evaporate. Workup, as described for 1a, afforded 622 mg of a pale yellow oil. Following flash chromatography, 486 mg (2.60 mmoles, 87%) of 3a was obtained as a colorless oil [18]; ir (film): 3170, 3135, 3105, 3080, 3045, 2950, 2875, 1608, 1515, 1505, 1460, 1440, 1150, 1085, 1030, 1005, 925, 885, 795, 725, 695 cm^{-1} ; nmr: (200 MHz) 7.30 (dd, 1, J = 1.8 and 0.8 Hz) superimposed on 7.33-7.14 (m, 5), 6.28 (dd, 1, J = 3.1 and 1.9 Hz), 5.99 (dd, 1, J = 3.1 and 0.8 Hz), 2.65 (t, 4, J = 7.2 Hz), 1.97 (quintet, 2, J = 7.6 Hz); ms: m/z (relative intensity) 187 (9), 186 (M^+ , 60), 105 (34), 104 (18), 95 (24), 94 (14), 92 (45), 91 (41), 82 (100), 81 (79), 65 (17), 53 (18).

2-[3-(4-Methylphenyl)propyl]furan (3b).

To a vigorously stirred mixture of 67 mg (9.7 mmoles) of lithium-sodium alloy (10 slivers) in 10 ml of anhydrous ether under an argon atmosphere was slowly added (15 minutes) a solution of 855 mg (5.00 mmoles) of 4-bromotoluene in 10 ml of ether. The mixture turned cloudy grey and

within 50 minutes after the addition was completed, the alloy slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 366 mg (3.00 mmoles) of 3-(2-furanyl)-2-propenal (**3**) in 10 ml of ether was slowly added (5 minutes). After 10 minutes the bath was removed and the stirred mixture allowed to return to ambient temperature (45 minutes) during which time the mixture turned yellow-brown. After adding an additional 25 ml of anhydrous ether and distilling 100 ml of anhydrous ammonia into the mixture, 167 mg (24.0 mmoles, 9 pieces) of lithium wire was quickly added. After 10 minutes, a solution of 36 mg (2.0 mmoles) of water in 5 ml of tetrahydrofuran was slowly added (2 minutes), and 3 minutes later, the dark blue-black color of the mixture was discharged by the addition (2 minutes) of 1.8 g of ammonium chloride and then the ammonia was allowed to evaporate. Workup, as described for **1a**, afforded 684 mg of a pale yellow oil. Following flash chromatography, 463 mg (2.30 mmoles, 77%) of **3b** was obtained as a colorless oil; ir (film): 3135, 3110, 3065, 3035, 2945, 2875, 1605, 1520, 1465, 1150, 1080, 1005, 925, 885, 800, 725 cm^{-1} ; nmr: (200 MHz), 7.30 (dd, 1, $J = 1.9$ and 0.8 Hz), 7.08 (s, 4), 6.28 (dd, 1, $J = 3.0$ and 1.9 Hz), 5.98 (dd, 1, $J = 3.3$ and 0.8 Hz), 2.64 (t, 2, $J = 7.4$ Hz) superimposed on 2.62 (t, 2, $J = 7.6$ Hz), 2.31 (s, 3), 1.94 (quintet, 2, $J = 7.5$ Hz); ms: m/z (relative intensity) 200 (M^+ , 2), 118 (14), 117 (20), 115 (13), 105 (47), 104 (14), 103 (21), 94 (25), 91 (36), 81 (100), 77 (33), 65 (33), 53 (70), 51 (30), 39 (55).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.99; H, 8.10.

2-[3-(4-Methoxyphenyl)propyl]furan (**3c**).

Similar treatment of 4-bromoanisole and 3-(2-furanyl)-2-propenal (**3**), as described for **3b**, except that 312 mg (45.0 mmoles, 16 pieces) of lithium was used for the reduction, and after 10 minutes, 270 mg (15.0 mmoles) of water in 5 ml of tetrahydrofuran was slowly introduced and then 10 minutes later the ammonium chloride interjected, afforded **3c** (72%) as a colorless oil; ir (film): 3170, 3140, 3080, 3050, 3020, 2970, 2950, 2930, 2880, 2850, 1620, 1605, 1590, 1520, 1470, 1445, 1305, 1255, 1180, 1150, 1110, 1080, 1040, 1010, 925, 885, 830, 805, 730 cm^{-1} ; nmr: (200 MHz) 7.30 (dd, 1, $J = 1.8$ and 0.7 Hz), 7.10 (d, 2, $J = 8.7$ Hz), 6.83 (d, 2, $J = 8.7$ Hz), 6.28 (dd, 1, $J = 3.1$ and 1.9 Hz), 5.99 (dd, 1, $J = 3.1$ and 0.7 Hz), 3.79 (s, 3), 2.62 (q, 4, $J = 7.3$ Hz), 1.93 (quintet, 2, $J = 7.6$ Hz); ms: m/z (relative intensity) 216 (M^+ , 3), 134 (22), 121 (46), 94 (23), 91 (33), 81 (100), 78 (35), 77 (31), 65 (30), 53 (65), 51 (29), 39 (50).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.75; H, 7.46. Found: C, 77.55; H, 7.50.

2-(1-Phenylethyl)furan (**4a**).

To a vigorously stirred solution of 786 mg (5.00 mmoles) of bromobenzene in 30 ml of anhydrous ether under an argon atmosphere was added 67 mg (9.7 mmoles) of lithium-sodium alloy (10 slivers). The mixture turned cloudy grey and within 45 minutes after the addition was completed, the alloy slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 330 mg (3.00 mmoles, 334 mg of a 99% pure sample) of 2-furanyl methyl ketone (**4**) in 10 ml of ether was slowly added (10 minutes). After 10 minutes the bath was removed and the stirred mixture allowed to return to ambient temperature (40 minutes) during which time the mixture turned pale grey. After adding an additional 25 ml of anhydrous ether and distilling 100 ml of anhydrous ammonia into the mixture, 187 mg (26.9 mmoles, 9 pieces) of lithium wire was quickly added. Twenty minutes later, the dark blue-black color of the mixture was discharged by the addition (2 minutes) of 1.7 g of ammonium chloride and then the ammonia was allowed to evaporate. Workup, as described for **1a**, afforded 570 mg of a pale yellow oil. Following flash chromatography, 481 mg (2.79 mmoles, 93%) of **4a** was obtained as a colorless oil [15a]; ir (film): 3160, 3130, 3095, 3075, 3040, 2980, 2940, 2880, 1605, 1595, 1505, 1495, 1455, 1180, 1145, 1025, 1005, 915, 795, 725, 690 cm^{-1} ; nmr: (200 MHz) 7.30 (dd, 1, $J = 1.9$ and 1.0 Hz) superimposed on 7.35-7.16 (m, 5), 6.29 (dd, 1, $J = 3.2$ and 2.0 Hz), 6.05 (dt, 1, $J = 3.2$ and 0.9 Hz), 4.12 (q, 1, $J = 7.2$ Hz), 1.59 (d, 3, $J = 7.2$ Hz); ms: m/z (relative intensity): 172 (M^+ , 40), 157 (100), 129 (18), 128 (28), 127 (11).

2-[1-(4-Methylphenyl)ethyl]furan (**4b**).

Similar treatment of 4-bromotoluene and 2-furanyl methyl ketone (**4**), as described for **4a**, afforded **4b** (75%) as a colorless oil; ir (film): 3170, 3140, 3120, 3080, 3045, 2995, 2950, 2895, 1595, 1520, 1460, 1380, 1310, 1235, 1185, 1145, 1065, 1050, 1020, 1010, 920, 885, 815, 800, 730 cm^{-1} ; nmr: (200 MHz) 7.29 (dd, 1, $J = 1.7$ and 0.7 Hz), 7.10 (s, 4), 6.28 (dd, 1, $J = 3.2$ and 1.7 Hz), 6.04 (dt, 1, $J = 3.2$ and 0.9 Hz), 4.08 (q, 1, $J = 7.2$ Hz), 2.31 (s, 3), 1.58 (d, 3, $J = 7.3$ Hz); ms: m/z (relative intensity) 186 (M^+ , 34), 172 (14), 171 (100), 128 (25).

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.93; H, 7.68.

2-[1-(4-Methoxyphenyl)ethyl]furan (**4c**).

Similar treatment of 4-bromoanisole and 2-furanyl methyl ketone (**4**), as described for **4a**, afforded **4c** (68%) as a colorless oil; ir (film): 3160, 3135, 3080, 3050, 3005, 2985, 2945, 2915, 2885, 2845, 1620, 1590, 1515, 1470, 1460, 1450, 1425, 1305, 1270, 1250, 1180, 1145, 1115, 1035, 1010, 915, 825, 800, 725 cm^{-1} ; nmr: (200 MHz) 7.30 (dd, 1, $J = 1.8$ and 0.7 Hz), 7.13 (ddd, 2, $J = 6.6$, 2.9, and 1.9 Hz), 6.84 (ddd, 2, $J = 6.6$, 2.9, and 2.2 Hz), 6.28 (dd, 1, $J = 3.2$ and 1.8 Hz), 6.02 (dt, 1, $J = 3.2$ and 0.9 Hz), 4.07 (q, 1, $J = 7.3$ Hz), 3.77 (s, 3), 1.56 (d, 3, $J = 7.2$ Hz); ms: m/z (relative intensity) 202 (M^+ , 28), 187 (100), 144 (22), 128 (15), 116 (13), 115 (28).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.97; H, 6.96.

3,4-Dihydro-4-phenyl-2H-1-benzopyran (**5a**).

Similar treatment of bromobenzene and 2,3-dihydro-4H-1-benzopyran-4-one (**5**), as described for **1a**, except that 139 mg (20.0 mmoles, 7 pieces) of lithium was used for the reduction, afforded **5a** (98%) as a colorless oil; ir (film): 3115, 3080, 3045, 2980, 2960, 2940, 2890, 1618, 1590, 1495, 1475, 1460, 1315, 1275, 1250, 1230, 1210, 1190, 1160, 1120, 1070, 1055, 1035, 1020, 940, 920, 840, 800, 755, 715, 700 cm^{-1} ; nmr: (100 MHz) 7.38-7.03 (m, 6), 6.93-6.74 (m, 3), 4.16 (t, 2, $J = 5.4$ Hz) superimposed on 4.22-4.10 (m, 1), 2.43-2.03 (two overlapping m, 2; apparent 10-line pattern centered at 2.21, $J = 5.4$ Hz); ms: m/z (relative intensity) 211 (15), 210 (M^+ , 97), 209 (22), 182 (24), 181 (100), 165 (14), 152 (18), 133 (28), 131 (20), 115 (24), 105 (18), 91 (39), 77 (27).

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.72; H, 6.84.

3,4-Dihydro-4-(4-methylphenyl)-2H-1-benzopyran (**5b**).

Similar treatment of 4-bromotoluene and 2,3-dihydro-4H-1-benzopyran-4-one (**5**), as described for **1a**, except that 139 mg (20.0 mmoles, 7 pieces) of lithium was used for the reduction, afforded **5b** (85%, flash chromatography) as a colorless oil; ir (film): 3030, 2975, 2950, 2920, 2875, 1608, 1582, 1512, 1488, 1450, 1305, 1265, 1240, 1220, 1110, 1060, 1045, 1010, 805, 775, 745 cm^{-1} ; nmr: (200 MHz) 7.10 (d, 2, $J = 8.0$ Hz) and 7.01 (d, 2, $J = 8.2$ Hz) superimposed on 7.17-6.99 (m, 1), 6.88-6.76 (m, 3), 4.19-4.12 (m, 3), 2.32 (s, 3) superimposed on 2.32-2.22 (m, 1), 2.12-2.02 (m, 1); ms: m/z (relative intensity) 225 (18), 224 (M^+ , 100), 223 (15), 209 (52), 195 (23), 181 (69), 131 (25), 105 (22), 91 (21).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.59; H, 7.09.

3,4-Dihydro-4-(4-methoxyphenyl)-2H-1-benzopyran (**5c**).

Similar treatment of 4-bromoanisole and 2,3-dihydro-4H-1-benzopyran-4-one (**5**), as described for **1a**, afforded **5c** (80%, flash chromatography) as a white solid; ir (potassium bromide): 3090, 3050, 3020, 2970, 2940, 2900, 2850, 1625, 1590, 1525, 1495, 1475, 1450, 1310, 1290, 1275, 1255, 1227, 1213, 1185, 1115, 1090, 1065, 1040, 1020, 960, 900, 830, 810, 770, 590, 550, 510 cm^{-1} ; nmr: (200 MHz) 7.13-7.03 (m, 3), 6.88-6.78 (m, 5), 4.22-4.09 (m, 3), 3.79 (s, 3), 2.42-2.11 (m, 1), 2.21-1.90 (m, 1); ms: m/z (relative intensity) 240 (M^+ , 56), 211 (63), 209 (22), 197 (24), 181 (100), 168 (16), 152 (17), 132 (21), 131 (40), 121 (15), 115 (40), 91 (21), 77 (33), 63 (20), 51 (21).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.87; H, 7.11.

4-Phenyl-4H-1-benzopyran (**6a**).

To a vigorously stirred mixture of 67 mg (9.7 mmoles) of lithium-sodium alloy (15 slivers) in 10 ml of anhydrous ether under an argon atmosphere was slowly added (25 minutes) a solution of 786 mg (5.00 mmoles) of bromobenzene in 10 ml of ether. The mixture turned cloudy grey and within 45 minutes after the addition was completed, the alloy

slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 438 mg (3.00 mmol, 452 mg of a 97% pure sample) of 4*H*-1-benzopyran-4-one (**6**) in 10 ml of ether was slowly added (5 minutes). After 10 minutes the bath was removed and the stirred mixture allowed to return to ambient temperature (40 minutes). After adding an additional 30 ml of anhydrous ether and distilling 90 ml of anhydrous ammonia into the mixture, 84 mg (12.1 mmol, 4 pieces) of lithium wire was quickly added. After 10 minutes the color of the dark blue-black mixture was discharged by the addition (1 minute) of 1.2 g of ammonium chloride and the ammonia was then allowed to evaporate. Workup, as described for **1a**, afforded 740 mg of a yellow-brown oil. Following flash chromatography, 531 mg (2.55 mmol, 85%) of **6a** was obtained as a pale yellow oil; ir (film): 3075, 3045, 2890, 2855, 2840, 2830, 1675, 1605, 1590, 1490, 1460, 1270, 1245, 1180, 1115, 1060, 750, 735, 695 cm^{-1} ; nmr: (200 MHz) 7.37-7.07 (complex m, 6), 6.95-6.89 (m, 3), 6.64 (dd, 1, $J = 6.2$ and 1.6 Hz), 5.01 (dd, 1, $J = 6.2$ and 3.8 Hz), 4.67 (dd, 1, $J = 3.8$ and 1.6 Hz); ms: m/z (relative intensity) 208 (M^+ , 2), 131 (63), 77 (100), 51 (94), 50 (40), 39 (25).

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{O}$: C, 86.51; H, 5.81. Found: C, 86.10; H, 5.93.

4-(4-Methylphenyl)-4*H*-1-benzopyran (**6b**).

Similar treatment of 4-bromotoluene and 4*H*-1-benzopyran-4-one (**6**), as described for **1a**, except that 139 mg (20.0 mmol, 7 pieces) of lithium was used for the reduction, afforded **6b** (72%, flash chromatography) as a yellow oil; ir (film): 3055, 3035, 2935, 2880, 1750, 1675, 1590, 1520, 1495, 1465, 1270, 1250, 1060, 760, 740 cm^{-1} ; nmr: (200 MHz) 7.17-7.06 (m, 5), 6.94-6.88 (m, 3), 6.62 (1 H, dd, $J = 6.2$ and 1.6 Hz), 4.99 (dd, 1, $J = 6.2$ and 3.8 Hz), 4.63 (dd, 1, $J = 3.8$ and 1.6 Hz), 2.31 (s, 3); ms: m/z (relative intensity) 223 (14), 222 (M^+ , 64), 221 (45), 207 (31), 131 (100), 77 (17).

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{O}$: C, 86.45; H, 6.35. Found: C, 86.04; H, 6.37.

4-(4-Methoxyphenyl)-4*H*-1-benzopyran (**6c**).

Similar treatment of 4-bromoanisole and 4*H*-1-benzopyran-4-one (**6**), as described for **1a**, except that 139 mg (20.0 mmol, 7 pieces) of lithium was used for the reduction, afforded **6c** (63%, flash chromatography) as a yellow oil; ir (film): 3065, 3030, 3000, 2950, 2930, 2900, 2830, 1665, 1610, 1580, 1510, 1485, 1460, 1450, 1300, 1235, 1175, 1110, 1050, 1030, 820, 750 cm^{-1} ; nmr: (200 MHz) 7.20-7.06 (m, 3), 6.95-6.81 (m, 5), 6.62 (dd, 1, $J = 6.2$ and 1.6 Hz), 4.98 (dd, 1, $J = 6.2$ and 3.8 Hz), 4.61 (dd, 1, $J = 3.7$ and 1.4 Hz), 3.77 (s, 3); ms: m/z (relative intensity) 240 (10), 239 (16), 238 (M^+ , 94), 237 (84), 223 (18), 207 (32), 165 (16), 131 (100), 77 (22).

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{O}_2$: C, 80.65; H, 5.92. Found: C, 80.17; H, 5.51.

2-(Phenylmethyl)thiophene (**7a**).

To a vigorously stirred mixture of 67 mg (9.7 mmol) of lithium-sodium alloy (15 slivers) in 10 ml of anhydrous ether under an argon atmosphere was slowly added (25 minutes) a solution of 786 mg (5.00 mmol) of bromobenzene in 10 ml of ether. The mixture turned cloudy grey and within 45 minutes after the addition was completed, the alloy slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 343 mg (3.06 mmol) of 2-thiophenecarboxaldehyde (**7**) in 10 ml of ether was slowly added (5 minutes). After 10 minutes the bath was removed and the stirred mixture allowed to return to ambient temperature (45 minutes). After adding an additional 25 ml of anhydrous ether and distilling 100 ml of anhydrous ammonia into the mixture, 63 mg (9.1 mmol, 4 pieces) of lithium wire was quickly added. Two minutes later, the dark blue-black color of the mixture was discharged by the addition (1 minute) of 1.2 g of ammonium chloride and then the ammonia was allowed to evaporate. Workup, as described for **1a**, afforded 530 mg of a yellow oil. Following flash chromatography, 392 mg (2.25 mmol, 74%) of **7a** was obtained as a colorless oil [19]; ir (film): 3120, 3095, 3075, 3035, 2970, 2910, 2850, 1610, 1500, 1455, 1440, 1250, 1235, 1075, 1040, 1030, 850, 760, 735, 690 cm^{-1} ; nmr: (200 MHz) 7.32-7.19 (m, 5), 7.14 (dd, 1, $J = 5.1$ and 1.2 Hz), 6.92 (dd, 1, $J = 5.1$ and 3.4 Hz), 6.79 (dd, 1, $J = 3.4$ and 1.1 Hz), 4.15 (s, 2); ms: m/z (relative intensity) 175 (17), 174 (M^+ , 100), 173 (84), 129 (21), 97 (64), 45 (18).

2-[(4-Methylphenyl)methyl]thiophene (**7b**).

Similar treatment of 4-bromotoluene and 2-thiophenecarboxaldehyde (**7**), as described for **7a**, afforded **7b** (67%) as a colorless oil; ir (film): 3150, 3130, 3120, 3085, 3065, 3035, 2970, 2935, 2865, 1525, 1465, 1445, 1385, 1305, 1250, 1240, 1190, 1125, 1115, 1075, 1040, 1025, 850, 810, 745, 690 cm^{-1} ; nmr: (200 MHz) 7.12 (apparent s, 4) superimposed on 7.12 (dd, 1, $J = 5.0$ and 1.3 Hz), 6.90 (dd, 1, $J = 5.1$ and 3.4 Hz), 6.78 (dd with further splitting, 1, $J = 3.4$ and 1.1 Hz), 4.11 (s, 2), 2.32 (s, 3); ms: m/z (relative intensity) 189 (16), 188 (M^+ , 100), 187 (49), 173 (78), 97 (39), 45 (28).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{S}$: C, 76.55; H, 6.42. Found: C, 76.83; H, 6.67.

2-[(4-Methoxyphenyl)methyl]thiophene (**7c**).

Similar treatment of 4-bromoanisole and 2-thiophenecarboxaldehyde (**7**), as described for **7a**, afforded **7c** (51%) as a colorless oil; ir (film): 3120, 3080, 3045, 3015, 2970, 2945, 2915, 2845, 1620, 1595, 1515, 1500, 1470, 1445, 1305, 1245, 1180, 1110, 1075, 1035, 850, 815, 750, 690 cm^{-1} ; nmr: (200 MHz) 7.16 (d, 2, $J = 8.7$ Hz), 7.12 (dd, 1, $J = 5.2$ and 1.2 Hz), 6.91 (dd, 1, $J = 5.1$ and 3.4 Hz), 6.84 (d, 2, $J = 8.7$ Hz), 6.77 (dd, 1, $J = 3.4$ and 1.1 Hz), 4.09 (s, 2), 3.78 (s, 3); ms: m/z (relative intensity) 205 (18), 204 (M^+ , 100), 203 (51), 189 (19), 173 (44), 121 (23), 97 (40), 45 (34), 39 (23).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{SO}$: C, 70.55; H, 5.92. Found: C, 70.89; H, 6.15.

3-Methyl-2-(phenylmethyl)thiophene (**8a**).

To a vigorously stirred mixture of 100 mg (14.4 mmol) of lithium-sodium alloy (15 slivers) in 20 ml of anhydrous ether under an argon atmosphere was slowly added (15 minutes) a solution of 1.178 g (7.50 mmol) of bromobenzene in 10 ml of ether. The mixture turned cloudy grey and within 45 minutes after the addition was completed, the alloy slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 631 mg (5.00 mmol) of 3-methyl-2-thiophenecarboxaldehyde (**8**) in 10 ml of ether was slowly added (5 minutes). After 10 minutes the bath was removed and the stirred mixture allowed to return to ambient temperature (45 minutes) during which time the mixture turned pale grey. After adding an additional 80 ml of anhydrous ether and distilling 165 ml of anhydrous ammonia into the mixture, 208 mg (30.0 mmol, 9 pieces) of lithium wire was quickly added. Fifteen minutes later, the dark blue-black color of the mixture was discharged by the addition (2 minutes) of 1.2 g of ammonium chloride and then the ammonia was allowed to evaporate. Workup, as described for **1a**, afforded 916 mg of a pale yellow oil. Following flash chromatography, 744 mg (3.95 mmol, 79%) of **8a** was obtained as a colorless oil; ir (film): 3110, 3095, 3070, 3030, 3005, 2920, 2865, 1610, 1495, 1455, 1435, 1385, 1235, 1160, 1075, 1030, 855, 825, 750, 690 cm^{-1} ; nmr: (100 MHz) 7.22 (s, 5), 7.04 (d, 1, $J = 5.1$ Hz), 6.80 (d, 1, $J = 5.1$ Hz), 4.06 (s, 2), 2.17 (s, 3); ms: m/z (relative intensity) 189 (16), 188 (M^+ , 100), 187 (33), 173 (93), 129 (16), 111 (68), 77 (17), 45 (29).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{S}$: C, 76.55; H, 6.42. Found: C, 76.39; H, 6.63.

3-Methyl-2-[(4-methylphenyl)methyl]thiophene (**8b**).

Similar treatment of 4-bromotoluene and 3-methyl-2-thiophenecarboxaldehyde (**8**), as described for **8a**, except that 243 mg (35.0 mmol, 14 pieces) of lithium was used for the reduction, afforded **8b** (75%) as a colorless oil; ir (film): 3110, 3060, 3030, 3010, 2980, 2920, 2870, 1520, 1455, 1435, 1385, 1300, 1235, 1110, 1075, 1035, 1020, 825, 805, 745, 695 cm^{-1} ; nmr: (100 MHz) 7.08 (s, 4), 7.02 (d, 1, $J = 5.1$ Hz), 6.79 (d, 1, $J = 5.1$ Hz), 4.01 (s, 2), 2.30 (s, 3), 2.16 (s, 3); ms: m/z (relative intensity) 203 (14), 202 (M^+ , 75), 201 (20), 187 (100), 172 (14), 111 (26), 105 (16), 92 (32), 91 (28).

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{S}$: C, 77.18; H, 6.98. Found: C, 77.39; H, 6.93.

2-[(4-Methoxyphenyl)methyl]-3-methylthiophene (**8c**).

Similar treatment of 4-bromoanisole and 3-methyl-2-thiophenecarboxaldehyde (**8**), as described for **8a**, except that 243 mg (35.0 mmol, 14 pieces) of lithium was used for the reduction, afforded **8c** (72%) as a colorless oil; ir (film): 3115, 3075, 3040, 3005, 2960, 2940, 2910, 2870, 2840, 1620, 1590, 1515, 1465, 1445, 1305, 1245, 1180, 1110, 1035, 825, 750, 700 cm^{-1} ; nmr: (200 MHz) 7.12 (d, 2, $J = 8.8$ Hz), 7.03 (d, 1, $J = 5.1$ Hz), 6.83 (d, 2, $J = 8.7$ Hz) superimposed on 6.81 (d, 1, $J = 5.0$ Hz), 4.00 (s, 2), 3.78 (s, 3), 2.71 (s, 3); ms: m/z (relative intensity) 202 (49), 201 (18), 188

(58), 187 (21), 173 (100), 171 (26), 159 (20), 144 (20), 129 (36), 115 (13), 95 (14), 77 (19), 45 (28), 43 (22).

Anal. Calcd. for $C_{13}H_{14}SO$: C, 71.52; H, 6.46. Found: C, 71.58; H, 6.37.

2-Methyl-5-(phenylmethyl)thiophene (9a).

To a vigorously stirred mixture of 67 mg (9.7 mmol) of lithium-sodium alloy (15 slivers) in 10 ml of anhydrous ether under an argon atmosphere was slowly added (25 minutes) a solution of 786 mg (5.00 mmol) of bromobenzene in 10 ml of ether. The mixture turned cloudy grey and within 45 minutes after the addition was completed, the alloy slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 379 mg (3.00 mmol, 386 mg of a 99% pure sample) of 5-methyl-2-thiophenecarboxaldehyde (9) in 10 ml of ether was slowly added (5 minutes). After 10 minutes the bath was removed and the stirred mixture allowed to return to ambient temperature (40 minutes) during which time the mixture turned yellow-brown. After adding an additional 25 ml of anhydrous ether and distilling 100 ml of anhydrous ammonia into the mixture, 125 mg (18.0 mmol, 7 pieces) of lithium wire was quickly added. Fifteen minutes later, the dark blue-black color of the mixture was discharged by the addition (1 minute) of 1.2 g of ammonium chloride and then the ammonia was allowed to evaporate. Workup, as described for **1a**, afforded 682 mg of a pale brown oil. Following flash chromatography, 562 mg (2.99 mmol, 99%) of **9a** was obtained as a colorless oil; ir (film): 3060, 3020, 2900, 2850, 1605, 1495, 1450, 1435, 1235, 1165, 1115, 1070, 1030, 780, 760, 725, 690, 660 cm^{-1} ; nmr: (100 MHz) 7.25 (s, 5), 6.55 (s, 2), 4.06 (s, 2), 2.40 (s, 3); ms: m/z (relative intensity): 189 (16), 188 (M^+ , 100), 187 (46), 173 (69), 111 (60), 45 (21).

Anal. Calcd. for $C_{12}H_{12}S$: C, 76.55; H, 6.42. Found: C, 76.34; H, 6.32.

2-Methyl-5-[(4-methylphenyl)methyl]thiophene (9b).

To a vigorously stirred solution of 1.283 mg (7.50 mmol) of 4-bromotoluene in 30 ml of anhydrous ether under an argon atmosphere was quickly added (2 minutes) 100 mg (14.4 mmol) of lithium-sodium alloy (25 slivers). The mixture turned cloudy grey and within 45 minutes after the addition was completed, the alloy slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 631 mg (5.00 mmol, 644 mg of a 98% pure sample) of 5-methyl-2-thiophenecarboxaldehyde (9) in 10 ml of ether was slowly added (5 minutes). After 10 minutes the bath was removed and the stirred mixture allowed to return to ambient temperature (45 minutes) during which time the mixture turned green-brown. After adding an additional 80 ml of anhydrous ether and distilling 190 ml of anhydrous ammonia into the mixture, 209 mg (30.1 mmol, 11 pieces) of lithium wire was quickly added. Fifteen minutes later, the dark blue-black color of the mixture was discharged by the addition (2 minutes) of 1.8 g of ammonium chloride and then the ammonia was allowed to evaporate. Workup, as described for **1a**, afforded 1.013 g of a yellow-orange oil. Following flash chromatography, 879 mg (4.35 mmol, 87%) of **9b** was obtained as a colorless oil; ir (film): 3050, 3010, 2910, 2855, 1510, 1445, 1430, 1115, 1030, 1015, 780, 740 cm^{-1} ; nmr: (200 MHz) 7.12 (s, 4), 6.54 (s, 2), 4.01 (s, 2), 2.39 (s, 3), 2.31 (s, 3); ms: m/z (relative intensity) 203 (13), 202 (M^+ , 79), 201 (21), 188 (43), 187 (100), 173 (25), 172 (18), 171 (16), 153 (16), 111 (36), 77 (18), 59 (21).

Anal. Calcd. for $C_{13}H_{14}S$: C, 77.18; H, 6.99. Found: C, 77.26; H, 7.21.

2-[(4-Methoxyphenyl)methyl]-5-methylthiophene (9c).

Similar treatment of 4-bromoanisole and 5-methyl-2-thiophenecarboxaldehyde (9), as described for **9b**, except that 244 mg (35.2 mmol, 13 pieces) of lithium was used for the reduction, afforded **9c** (86%) as a colorless oil; ir (film): 3070, 3035, 3000, 2950, 2910, 2835, 1615, 1590, 1510, 1465, 1445, 1300, 1240, 1175, 1115, 1105, 1030, 790, 750, 660 cm^{-1} ; nmr: (100 MHz) 7.15 (d, 2, $J = 8.5$ Hz), 6.82 (d, 2, $J = 8.8$ Hz), 6.54 (s, 2), 3.99 (s, 2), 3.78 (s, 3), 2.40 (s, 3); ms: m/z (relative intensity) 219 (16), 218 (M^+ , 100), 217 (39), 203 (81), 188 (19), 187 (42), 111 (42), 108 (29), 78 (23), 77 (26), 65 (21), 59 (19), 45 (18).

Anal. Calcd. for $C_{13}H_{14}SO$: C, 71.52; H, 6.46. Found: C, 71.11; H, 6.25.

3-(Phenylmethyl)thiophene (10a).

Similar treatment of bromobenzene and 3-thiophenecarboxaldehyde (10), as described for **9b**, except that 244 mg (35.2 mmol, 13 pieces) of lithium was used for the reduction, afforded **10a** (45%) as a colorless oil; ir (film): 3105, 3085, 3065, 3025, 2910, 2850, 1608, 1540, 1497, 1455, 1435, 1415, 1390, 1235, 1150, 1070, 1025, 935, 850, 825, 760, 750, 690, 670, 630 cm^{-1} ; nmr: (200 MHz) 7.34-7.16 (complex m, 6), 6.92-6.89 (m, 2), 3.98 (s, 2); ms: m/z (relative intensity) 175 (16), 174 (M^+ , 100), 173 (92), 141 (13), 129 (23), 128 (14), 97 (53), 45 (25).

Anal. Calcd. for $C_{11}H_{10}S$: C, 75.82; H, 5.78. Found: C, 75.98; H, 5.64.

3-[(4-Methylphenyl)methyl]thiophene (10b).

Similar treatment of 4-bromotoluene and 3-thiophenecarboxaldehyde (10), as described for **9b**, except that the ammonium chloride was intercepted after 20 minutes, afforded **10b** (43%) as a colorless oil; ir (film): 3130, 3080, 3045, 3030, 3000, 2970, 2945, 2880, 1520, 1485, 1444, 1417, 1390, 1305, 1240, 1112, 1080, 1025, 940, 860, 835, 805, 775, 740, 675, 625 cm^{-1} ; nmr: (200 MHz) 7.24 (d, 1, $J = 4.0$ Hz), 7.09 (s, 4), 6.91 (s, 1), 6.89 (d, 1, $J = 4.3$ Hz), 3.93 (s, 2), 2.32 (s, 3); ms: m/z (relative intensity) 189 (18), 188 (M^+ , 100), 187 (47), 173 (85), 139 (24), 97 (34), 93 (17), 77 (18), 51 (15), 45 (35), 39 (20).

Anal. Calcd. for $C_{12}H_{12}S$: C, 76.55; H, 6.42. Found: C, 76.41; H, 6.68.

2-[Cyclopropyl(phenyl)methyl]thiophene (11a).

Similar treatment of bromobenzene and cyclopropyl 2-thienyl ketone (11), as described for **7a**, afforded **11a** (94%) as a colorless oil; ir (film): 3120, 3090, 3040, 3015, 2940, 2880, 1610, 1500, 1460, 1440, 1270, 1235, 1075, 1020, 955, 850, 830, 740, 690 cm^{-1} ; nmr: (200 MHz) 7.32-7.18 (m, 5), 7.15 (dd, 1, $J = 5.1$ and 1.2 Hz), 6.92 (dd, 1, $J = 5.1$ and 3.5 Hz), 6.81 (dd, 1, $J = 3.4$ and 1.0 Hz), 3.37 (d, 1, $J = 9.6$ Hz), 1.50-1.35 (complex m, 1), 0.83-0.69 (complex m, 1), 0.65-0.52 (complex m, 1), 0.49-0.37 (complex m, 1), 0.35-0.23 (complex m, 1); ms: m/z (relative intensity) 214 (M^+ , 12), 187 (46), 186 (84), 185 (52), 173 (20), 171 (27), 153 (25), 137 (28), 129 (21), 128 (17), 115 (19), 110 (100), 97 (16), 92 (18), 91 (29), 77 (21), 45 (22).

Anal. Calcd. for $C_{14}H_{14}S$: C, 78.46; H, 6.58. Found: C, 78.58; H, 6.75.

2-[Cyclopropyl(4-methylphenyl)methyl]thiophene (11b).

Similar treatment of 4-bromotoluene and cyclopropyl 2-thienyl ketone (11), as described for **7a**, afforded **11b** (85%) as a colorless oil; ir (film): 3100, 3070, 3020, 2940, 2880, 1520, 1465, 1445, 1270, 1235, 1110, 1045, 1025, 960, 865, 855, 815, 780, 750, 690 cm^{-1} ; nmr: (200 MHz) 7.18 (d, 2, $J = 8.4$ Hz) and 7.12 (d, 2, $J = 8.1$ Hz) superimposed on 7.23-7.09 (m, 1), 6.91 (dd, 1, $J = 5.1$ and 3.5 Hz), 6.81 (dd, 1, $J = 3.4$ and 0.9 Hz), 3.34 (d, 1, $J = 9.6$ Hz), 2.33 (s, 3), 1.51-1.35 (complex m, 1), 0.82-0.68 (complex m, 1), 0.64-0.51 (complex m, 1), 0.48-0.36 (complex m, 1), 0.34-0.24 (complex m, 1); ms: m/z (relative intensity) 228 (M^+ , 16), 200 (100), 187 (27), 185 (45), 184 (27), 171 (19), 145 (20), 128 (22), 118 (80), 115 (24), 110 (83), 91 (24), 77 (23), 65 (20), 45 (28), 39 (34).

Anal. Calcd. for $C_{15}H_{16}S$: C, 78.90; H, 7.06. Found: C, 78.76; H, 7.13.

2-[Cyclopropyl(4-methoxyphenyl)methyl]thiophene (11c).

Similar treatment of 4-bromoanisole and cyclopropyl 2-thienyl ketone (11), as described for **7a**, afforded **11c** (65%) as a colorless oil; ir (film): 3130, 3100, 3050, 3020, 2980, 2950, 2925, 2890, 2850, 1620, 1590, 1515, 1465, 1445, 1305, 1250, 1180, 1110, 1040, 1020, 955, 865, 850, 820, 690 cm^{-1} ; nmr: (200 MHz) 7.21 (d, 2, $J = 8.7$ Hz), 7.15 (dd, 1, $J = 5.1$ and 1.2 Hz), 6.91 (dd, 1, $J = 5.2$ and 3.5 Hz), 6.85 (d, 2, $J = 8.7$ Hz) superimposed on 6.89-6.79 (m, 1), 3.79 (s, 3), 3.34 (d, 1, $J = 9.5$ Hz), 1.52-1.31 (complex m, 1), 0.85-0.68 (complex m, 1), 0.66-0.51 (complex m, 1), 0.47-0.35 (complex m, 1), 0.33-0.22 (complex m, 1); ms: m/z (relative intensity) 244 (M^+ , 25), 216 (100), 203 (39), 201 (24), 134 (92), 115 (14), 45 (20).

Anal. Calcd. for $C_{15}H_{16}SO$: C, 73.73; H, 6.60. Found: C, 73.99; H, 6.63.

3-(1-Phenylethyl)thiophene (12a).

Similar treatment of bromobenzene and methyl 3-thienyl ketone (12), as described for **9b**, except that 244 mg (35.2 mmol, 13 pieces) of lithium was used for the reduction, afforded **12a** (38%) as a colorless oil; ir

(film): 3120, 3095, 3075, 3040, 2985, 2930, 2880, 2860, 1610, 1500, 1460, 1380, 1082, 1030, 915, 865, 830, 790, 760, 695, 642 cm^{-1} ; nmr: (200 MHz) 7.33-7.15 (m, 6), 6.98-6.95 (m, 1; apparent dt, $J = 2.9$ and 1.2 Hz), 6.89-6.86 (m, 1; apparent ddd, $J = 4.7, 1.2$, and 0.4 Hz), 4.16 (q, 1, $J = 7.2$ Hz), 1.63 (d, 3, $J = 7.2$ Hz); mass: m/z (relative intensity) 189 (9), 188 (M^+ , 55), 173 (100), 129 (22), 77 (11), 45 (21).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{S}$: C, 76.55; H, 6.42. Found: C, 76.55; H, 6.50.

4,5,6,7-Tetrahydro-4-(4-methylphenyl)benzo[b]thiophene (**13b**).

Similar treatment of 4-bromotoluene and 4,5,6,7-tetrahydrobenzo[b]thiophene-4-one (**13**), as described for **7a**, except that 69 mg (10.0 mmoles, 4 pieces) of lithium was used for the reduction and the ammonium chloride was interjected 10 minutes later, afforded **13b** (40%) as a colorless oil; ir (film): 3110, 3060, 3035, 3020, 2940, 2860, 1520, 1455, 1440, 1305, 1250, 1185, 1135, 1115, 1085, 1025, 890, 870, 810, 735, 710, 680, 640 cm^{-1} ; nmr: (200 MHz) 7.09 (d, 2, $J = 8.2$ Hz), 7.00 (d, 2, $J = 8.2$ Hz) superimposed on 6.98 (d, 1, $J = 5.1$ Hz), 6.50 (d, 1, $J = 5.1$ Hz), 3.99-3.93 (m, 1), 2.86 (apparent t, 2, $J = 5.8$ Hz), 2.32 (s, 3), 2.17-2.07 (m, 1), 2.00-1.91 (m, 1), 1.85-1.72 (m, 2); ms: m/z (relative intensity) 229 (19), 228 (M^+ , 100), 213 (28), 200 (54), 195 (17), 185 (99), 137 (24), 136 (28), 135 (21), 91 (30).

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{S}$: C, 78.90; H, 7.06. Found: C, 79.34; H, 7.03.

4,5,6,7-Tetrahydro-4-(4-methoxyphenyl)benzo[b]thiophene (**13c**).

Similar treatment of 4-bromoanisole and 4,5,6,7-tetrahydrobenzo[b]thiophene-4-one (**13**), as described for **7a**, except that 69 mg (10.0 mmoles, 4 pieces) of lithium was used for the reduction and the ammonium chloride was interjected 10 minutes later, afforded **13c** (55%) as a pale yellow solid; ir (potassium bromide): 3130, 3050, 3010, 2955, 2895, 2835, 1610, 1515, 1290, 1275, 1245, 1175, 1035, 835, 800, 740, 680 cm^{-1} ; nmr: (200 MHz) 7.32 (d, 2, $J = 8.9$ Hz), 7.00 (d, 1, $J = 5.1$ Hz), 6.90 (d, 2, $J = 8.9$ Hz), 6.85 (d, 1, $J = 5.1$ Hz), 5.82 (t, 1, $J = 4.6$ Hz), 3.83 (s, 3) superimposed on 3.88-3.78 (m, 1), 2.91 (apparent t, 2, $J = 9.2$ Hz), 2.53 (dd, 2, $J = 9.3$ and 4.6 Hz) superimposed on 2.57-2.45 (m, 1); ms: m/z (relative intensity) 244 (M^+ , 7), 243 (15), 242 (100), 241 (38), 240 (75), 227 (37), 225 (48), 211 (41), 197 (49), 184 (40), 171 (34), 165 (65), 153 (32), 152 (42), 134 (46), 121 (71), 86 (32), 63 (34), 51 (22).

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{SO}$: C, 73.73; H, 6.60. Found: C, 73.70; H, 6.18.

2-(1-Phenylpropyl)benzenethiol (**14a**).

To a vigorously stirred mixture of 67 mg (9.7 mmoles) of lithium-sodium alloy (10 slivers) in 10 ml of anhydrous ether under an argon atmosphere was slowly added (15 minutes) a solution of 786 mg (5.00 mmoles) of bromobenzene in 10 ml of ether. The mixture turned cloudy grey and within 45 minutes after the addition was completed, the alloy slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 493 mg (3.00 mmoles, 508 mg of a 97% pure sample) of 2,3-dihydro-4H-1-benzothio-pyran-4-one (**14**) in 10 ml of ether was slowly added (5 minutes). After 10 minutes the bath was removed and the stirred mixture allowed to return to ambient temperature (45 minutes) during which time the mixture turned yellow-brown. After adding an additional 25 ml of anhydrous ether and distilling 100 ml of anhydrous ammonia into the mixture, 139 mg (20.0 mmoles, 7 pieces) of lithium wire was quickly added. After one minute, 90 mg (5.0 mmoles) of water in 5 ml of tetrahydrofuran was slowly added. One minute later, the dark blue-black color of the mixture was discharged by the addition (1 minute) of 1.1 g of ammonium chloride and then the ammonia was allowed to evaporate. Workup, as described for **1a**, except that the aqueous phase was adjusted to pH 7 with 20% sulfuric acid before extraction with ether, afforded 768 mg of a yellow oil. Following flash chromatography, 582 mg (2.55 mmoles, 85%) of **14a** was obtained as a colorless oil; ir (film): 3120, 3105, 3090, 3045, 2980, 2950, 2890, 2580, 1610, 1595, 1500, 1470, 1460, 1445, 1385, 1090, 1080, 1060, 1040, 1030, 765, 745, 720, 695, 625 cm^{-1} ; nmr: (200 MHz) 7.32-7.12 (m, 8), 7.03 (td, 1, $J = 7.5$ and 1.7 Hz), 4.15 (t, 1, $J = 7.6$ Hz), 3.25 (s, 1), 2.05 (quintet, 2, $J = 7.4$ Hz), 0.93 (t, 3, $J = 7.3$ Hz); ms: m/z (relative intensity) 228 (M^+ , 45), 199 (100), 197 (43), 167 (20), 166 (33), 165 (27).

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{S}$: C, 78.90; H, 7.06. Found: C, 78.75; H, 7.07.

2-[1-(4-Methylphenyl)propyl]benzenethiol (**14b**).

Similar treatment of 4-bromotoluene and 2,3-dihydro-4H-benzothio-pyran-4-one (**14**), as described for **14a**, afforded **14b** (76%) as a colorless oil; ir (film): 3140, 3090, 3060, 3020, 2965, 2930, 2875, 2560, 1590, 1515, 1465, 1440, 1380, 1185, 1110, 1085, 1055, 1040, 1020, 800, 750, 735 cm^{-1} ; nmr: (200 MHz) 7.32-7.24 (m, 2; apparent td at 7.28, $J = 7.7$ and 1.6 Hz), 7.13 (dd, 2, $J = 12.5$ and 1.6 Hz) and 7.06 (dd, 2, $J = 12.4$ and 1.7 Hz) superimposed on 7.20-7.00 (m, 2), 4.10 (t, 1, $J = 7.6$ Hz), 3.26 (s, 1, slowly exchanges with deuterium oxide), 2.29 (s, 3), 2.04 (quintet, 2, $J = 7.4$ Hz), 0.93 (t, 3, $J = 7.3$ Hz); ms: m/z (relative intensity) 242 (M^+ , 35), 213 (100), 211 (26).

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{S}$: C, 79.29; H, 7.49. Found: C, 79.20; H, 7.23.

2-[1-(4-Methoxyphenyl)propyl]benzenethiol (**14c**).

Similar treatment of 4-bromoanisole and 2,3-dihydro-4H-benzothio-pyran-4-one (**14**), as described for **14a**, afforded **14c** (65%) as a colorless oil; ir (film): 3080, 3050, 3020, 2980, 2950, 2890, 2850, 2580, 1610, 1595, 1520, 1500, 1475, 1445, 1295, 1245, 1185, 1165, 1140, 1125, 1110, 1080, 1055, 1035, 785, 755, 700 cm^{-1} ; nmr: (200 MHz) 7.36-6.98 (complex m, 6), 6.92-6.80 (m, 2), 4.56 (t, 1, $J = 7.6$ Hz), 3.81 (s, 3), 3.44 (s, 1), 1.99 (quintet, 2, $J = 7.4$ Hz), 0.94 (t, 3, $J = 7.3$ Hz); ms: m/z (relative intensity) 258 (M^+ , 51), 229 (82), 197 (23), 184 (14), 181 (11), 165 (29), 150 (40), 135 (23), 123 (100), 115 (17), 107 (56), 91 (23), 77 (12).

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{SO}$: C, 74.38; H, 7.02. Found: C, 74.24; H, 7.11.

2-(Phenylmethyl)pyridine (**15a**).

To a vigorously stirred mixture of 67 mg (9.7 mmoles) of lithium-sodium alloy (15 slivers) in 10 ml of anhydrous ether under an argon atmosphere was slowly added (20 minutes) a solution of 786 mg (5.00 mmoles) of bromobenzene in 10 ml of ether. The mixture turned cloudy grey and within 40 minutes after the addition was completed, the alloy slivers had been consumed and the mixture was dark grey. After cooling the mixture (-78° , dry ice-acetone in a Dewar bath), a solution of 321 mg (3.00 mmoles, 325 mg of a 99% pure sample) of 2-pyridinecarboxaldehyde (**15**) in 10 ml of ether was slowly added (5 minutes). After 10 minutes, an additional 25 ml of anhydrous ether was added and 100 ml of anhydrous ammonia was distilled into the mixture, and then 174 mg (25.1 mmoles, 9 pieces) of lithium wire was quickly added without removing the cooling bath. Five minutes later, 270 mg (15.0 mmoles) of water in 5 ml of tetrahydrofuran was slowly introduced, and after 5 minutes, the dark blue-black color of the mixture was discharged by the addition (30 seconds) of 0.8 g of ammonium chloride and then the ammonia was allowed to evaporate. Workup, as described for **1a**, afforded 720 mg of a yellow-brown oil. Following flash chromatography, 494 mg (2.92 mmoles, 97%) of **15a** was obtained as a colorless oil [20]; ir (film): 3090, 3065, 3030, 3010, 2910, 2850, 2810, 1595, 1570, 1495, 1475, 1455, 1435, 1145, 1090, 1070, 1050, 1030, 990, 955, 745, 735, 690, 600 cm^{-1} ; nmr: (200 MHz) 8.55 (dd, 1, $J = 5.1$ and 1.8 Hz), 7.57 (td, 1, $J = 7.7$ and 1.9 Hz), 7.35-7.17 (m, 5), 7.14-7.07 (m, 2), 4.16 (s, 2); ms: m/z (relative intensity) 169 (M^+ , 21), 168 (100), 167 (22), 91 (11), 51 (13), 39 (12).

2-(4-Methylphenyl)methylpyridine (**15b**).

Similar treatment of 4-bromotoluene and 2-pyridinecarboxaldehyde (**15**), as described for **15a**, afforded **15b** (92%) as a colorless oil; ir (film): 3100, 3080, 3065, 3025, 2940, 2880, 1600, 1580, 1525, 1480, 1445, 1150, 1110, 1090, 1050, 1025, 995, 795, 750, 725 cm^{-1} ; nmr: (200 MHz) 8.54 (dd, 1, $J = 5.6$ and 1.9 Hz), 7.55 (td, 1, $J = 7.7$ and 1.9 Hz), 7.16 (d, 2, $J = 8.4$ Hz) and 7.10 (d, 2, $J = 8.6$ Hz) superimposed on 7.18-7.05 (m, 2), 4.11 (s, 2), 2.31 (s, 3); ms: m/z (relative intensity) 183 (M^+ , 29), 182 (100), 168 (10), 167 (29), 77 (11), 51 (10).

Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{N}$: C, 85.21; H, 7.15; N, 7.64. Found: C, 84.79; H, 7.42; N, 7.48.

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