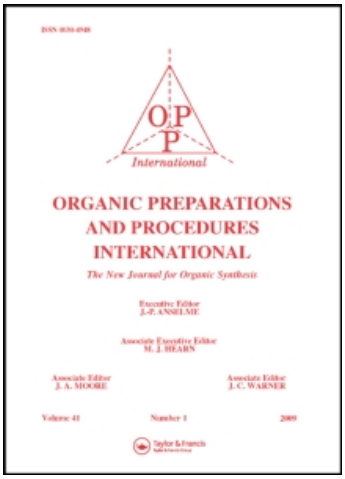

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REDUCTION OF HETEROCYCLIC ALCOHOLS WITH SODIUM BOROHYDRIDE-TRIFLUOROACETIC ACID. PREPARATION OF bis-HETEROCYCLIC METHANES

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REDUCTION OF HETEROCYCLIC ALCOHOLS WITH SODIUM BOROHYDRIDE-TRIFLUOROACETIC ACID. PREPARATION OF bis-HETEROCYCLIC METHANES

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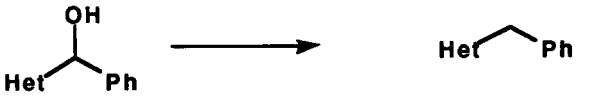
In 1977, Gribble and coworkers[1] reported that di- and triarylcarbinols are conveniently reduced with sodium borohydride-trifluoroacetic acid (TFA) to afford high yields of the corresponding di- and triarylmethanes, respectively. One year later, the same group described the extension of this reaction to the reduction of diarylketones.[2] Recently, we have demonstrated that benzyl alcohols can likewise be converted to the corresponding hydrocarbons through a modification of the Gribble reaction.[3] As these procedures represent simple, clean, and efficient methods for the transformation of an alcohol or ketone to the corresponding hydrocarbon, extension of this methodology to substrates bearing heterocyclic rings appeared to be potentially useful. Previous work in this area includes: reduction of N-benzenesulfonyl-3-acylindoles to N-benzenesulfonyl-3-alkylindoles with sodium borohydride-TFA,[4] reduction of N-benzenesulfonylacylindoles to N-benzenesulfonylalkylindolines with sodium cyanoborohydride-TFA,[5] reduction of N-benzenesulfonylacylpyrroles to N-benzenesulfonylalkylpyrrolines with sodium cyanoborohydride-TFA,[6] and reduction of 2-acylthiophenes and 2-thienylcarbinols to 2-alkylthiophenes with sodium borohydride-TFA.[7] Additionally, it has been shown that N-protected acylpyrroles are reduced to N-protected alkylpyrroles with *tert*-butylamine-borane and aluminum chloride[8] and acylpyrroles or pyrrolyl carbinols are reduced to alkylpyrroles with sodium borohydride in isopropanol.[9]

The applicability of this methodology to other heterocyclic systems or to bis-heterocyclic carbinols has not been described. Extension to the latter substrates would be beneficial as *bis*-heterocyclic methanes are of interest to the food industry as a result of their presence as natural components in food and beverage items such as licorice[10] and coffee.[11] Furthermore, we required compounds of this nature for the synthesis of various heterocyclic [1^n]cyclophanes. Despite these potential applications, a number of structurally simple *bis*-heterocyclic methanes are not known, likely due to a lack of general synthetic procedures. This article reports the results of investigations on the compatibility and reducibility of several heterocyclic alcohols, with respect to sodium borohydride-TFA, and the application of the methodology to the preparation of a variety of symmetric and asymmetric *bis*-heterocyclic methanes.

Thiophenes[7] and N-benzenesulfonylindoles[4] are known to be stable to sodium borohydride-TFA, while unprotected indoles undergo reduction to indolines.[12] As the stability of other heterocycles toward this reducing medium was unknown, initial experiments were aimed at determining which ring systems survive the reaction, and furthermore, which alcohols undergo reduction. The results of these investigations are summarized in Table 1.

TABLE 1. REDUCTION OF DIARYLMETHANOLS TO DIARYLMETHANES



Het	Yield(%)[a,b]
2-Thienyl	85[13a]
3-Thienyl	95[13a]
2-Furyl	46[13b]
3-Furyl	60[13c]
2-Benzo[b]furyl	95[13d]
2-Benzo[b]thienyl	87[13e]
2-(1-Methylimidazolyl)	0[c]
4-(1-Methylimidazolyl)	0[c]
2-Benzothiazolyl	0[c]
2-(1-Methylbenzimidazolyl)	0[c]
2-Oxazolyl	0[c]
3-Pyridyl	0[c]

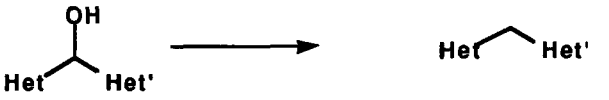
a) Isolated yield after flash chromatography. b) All products exhibited satisfactory proton and carbon NMR. c) Recovered starting material.

Although all of the heterocyclic systems studied survive the reaction conditions, several of them retard reduction of the alcohol, as illustrated in Table 1. The key feature of the compounds that are resistant to reduction is the presence of a basic ring nitrogen which, upon protonation by TFA, will inhibit formation of the benzylic cation, the presumed intermediate of the reaction.[1] In addition to the substrates shown in Table 1, the 2-(1-methylpyrrolyl) analog was studied; owing to the propensity of N-H pyrroles to oligomerize or polymerize in the presence of strong acid,[14] this resulted in a complex product mixture.

These initial experiments demonstrated that benzylic alcohols possessing thienyl, benzo[b]thienyl, furyl, and benzo[b]furyl substituents are amenable to sodium borohydride-TFA reduction. Extension of this methodology to the preparation of bis-heterocyclic methanes possessing various combinations of the compatible aromatic units was also investigated; the results of these

experiments are shown in Table 2.

TABLE 2. REDUCTION OF DIHETEROARYLMETHANOLS TO DIHETEROARYLMETHANES



Het	Het'	Yield(%)[a]
2-Furyl	2-Thienyl	42
3-Furyl	2-Thienyl	64
2-Furyl	3-Thienyl	47
2-Benzo[b]thienyl	3-Thienyl	78
2-Benzo[b]thieny	2-Furyl	45
2-Benzo[b]thienyl	2-Thienyl	76
2-Benzo[b]thienyl	3-Furyl	64
2-Benzo[b]furyl	2-Furyl	32
2-Benzo[b]furyl	3-Furyl	67
2-Benzo[b]furyl	2-Thienyl	75
2-Benzo[b]furyl	3-Thienyl	74
2-Benzo[b]furyl	2-Benzo[b]thienyl	68

a) Isolated yields after flash chromatography.

All of the substrates shown in Table 2 afford the corresponding bis-heterocyclic methanes in moderate to good yield; in all cases, the desired material was the only mobile product evident by TLC, and was readily purified by simple flash chromatography. The lowest yields were consistently realized for those substrates possessing a 2-substituted furan ring, indicating that these materials are the least compatible with the reaction conditions.

In summary, sodium borohydride-TFA reduction of alcohols has been extended to compounds incorporating thiophene, furan, benzo[b]furan and benzo[b]thiophene substituents and proceeds without reduction of the aromatic ring. Additionally, it has been shown that heterocyclic systems containing a basic ring nitrogen survive the strongly acidic reaction conditions, but the alcohols are inert toward reduction. Finally, the procedure has been demonstrated to be quite general for the preparation of various bis-heterocyclic methanes, and should be an attractive alternative to existing methods.[13e,15]

EXPERIMENTAL SECTION

All reactions were performed in oven-dried glassware (120°), and all lithiation reactions were performed under nitrogen. Alkyllithium reagents were purchased from Aldrich and standardized with 2,5-dimethoxybenzyl alcohol.[16] Tetrahydrofuran was distilled from sodium/benzophenone. Thin

layer chromatography was performed on precoated (0.25 mm) silica gel 60 F_{254} plastic sheets; the plates were visualized with 254 nm ultraviolet light. Melting points were determined in open capillary tubes with a Mel-Temp Laboratory Devices apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. Proton and carbon NMR spectra were recorded on a Bruker ACE300 FT-NMR spectrometer; mass spectra were recorded on a Hewlett Packard 5992B GC/MS. Except for α-(3-pyridyl)benzyl alcohol, which was prepared by reduction of 3-benzoylpyridine, all of the alcohols in Table 1 were obtained via standard lithiation procedures;[17] all of these compounds have previously been reported.[18] The alcohols in Table 2 decompose upon standing and should thus be used immediately after flash chromatography purification. Attempts to prepare analytical samples for combustion analysis were not successful due to extensive degradation upon attempted vacuum distillation.

Preparation of 2-Benzo[b]furyl-2-furylmethanol.- To a magnetically stirred solution of benzo[b]furan (1.55 g, 13.1 mmol) in dry THF (50 mL) at -78°C under nitrogen was added over 2 min via syringe n-butyllithium (2.0 M in hexane, 6.60 mL, 13.2 mmol). The solution was allowed to warm over 30 min then recooled to -78°C. To this was added quickly via syringe 2-furaldehyde (1.10 mL, 13.3 mmol) and the resulting solution was allowed to warm to 25°C and stirred at 25°C for 3 hr. The mixture was poured into saturated brine (75 mL) and the resulting aqueous solution was extracted with ether (2 x 75 mL). The combined extracts were dried with sodium sulfate, filtered, and concentrated in vacuo to afford an orange oil. Flash chromatography (5:1 hexane/ether) gave 2-benzo[b]furyl-2-furylmethanol cleanly as a light yellow oil (2.38 g, 85%). ^{1}H NMR($CDCl_3$): δ 7.53-7.50 (m, 1H), 7.44 (br d, 1H), 7.40 (t, 1H), 7.29-7.17 (m, 2H), 6.67 (s, 1H), 6.35 (br s, 2H), 5.92 (d, 1H). ^{13}C NMR($CDCl_3$): δ 155.7, 154.9, 152.65, 142.75, 127.85, 124.4, 122.8, 121.2, 111.3, 110.4, 108.1, 104.2, 64.4. mass spec m/e (rel int %): 214 (M^+, 13.0), 197 (M-OH, 11.6), 145 (23.4), 95 (79.9), 63 (100).

3-Furyl-2-thienylmethanol was analogously prepared from thiophene and 3-furaldehyde (63%). ^{1}H NMR($CDCl_3$): δ 7.40 (s, 1H), 7.39 (t, 1H), 7.25 (dd, 1H), 6.97-6.93 (m, 2H), 6.40 (s, 1H), 5.97 (s, 1H). ^{13}C NMR($CDCl_3$): δ 147.1, 143.4, 139.7, 128.3, 126.6, 125.3, 124.7, 109.0, 65.3. Mass spec m/e (rel int %): 180 (M^+, 12.6), 163 (M-OH, 8.9), 111 (24.9), 95 (41.3), 45 (100).

2-Furyl-3-thienylmethanol was analogously prepared from furan and thiophene-3-carboxaldehyde (48%). ^{1}H NMR($CDCl_3$): δ 7.40 (d, 1H), 7.32-7.26 (m, 2H), 7.08 (dd, 1H), 6.32 (dd, 1H), 6.17 (d, 1H), 5.86 (d, 1H). ^{13}C NMR($CDCl_3$): δ 155.3, 142.3, 142.05, 126.25, 125.9, 122.1, 110.1, 107.1, 66.2. mass spec m/e (rel int %): 180 (M^+, 65.4), 163 (M-OH, 41.4), 111 (65.5), 95 (64.3), 45 (100).

2-Benzo[b]thienyl-2-furylmethanol was analogously prepared from benzo[b]thiophene and 2-furaldehyde (50%). ^{1}H NMR($CDCl_3$): δ 7.80-7.76 (m, 1H), 7.72-7.67 (m, 1H), 7.41 (s, 1H), 7.35-7.26 (m, 2H), 7.20 (s, 1H), 6.36-6.31 (m, 2H), 6.09 (d, 1H). ^{13}C NMR($CDCl_3$): δ 154.3, 145.1, 142.7, 139.7, 139.2, 124.3, 124.2, 123.65, 122.4, 121.6, 110.4, 107.7, 66.7. Mass spec m/e (rel int %): 230 (M^+, 63), 213 (M-OH, 33), 161 (14.7), 135 (100), 95 (57.1).

2-Benzo[b]thienyl-2-thienylmethanol was analogously prepared from benzo[b]thiophene and thiophene-2-carboxaldehyde (61%). ^{1}H NMR ($CDCl_3$): δ 7.80-7.76 (m, 1H), 7.70-7.66 (m, 1H), 7.35-

7.25 (m, 3H), 7.20 (s, 1H), 7.04 (br d, 1H), 6.96 (dd, 1H), 6.31 (s, 1H). ^{13}C NMR($CDCl_3$): δ 147.6, 146.3, 139.7, 139.2, 126.7, 125.7, 125.3, 124.4, 124.3, 123.7, 122.4, 121.3, 68.95. Mass spec m/e (rel int %): 246 (M^+, 53.1), 229 (M-OH, 19.8), 161 (28.3), 135 (100), 111 (61.9).

2-Benzo[b]thienyl-3-furylmethanol was analogously prepared from benzo[b]thiophene and 3-furaldehyde (72%). ^{1}H NMR($CDCl_3$): δ 7.80-7.75 (m, 1H), 7.70-7.65 (m, 1H), 7.45 (s, 1H), 7.4 (t, 1H), 7.35-7.25 (m, 2H), 7.15 (s, 1H), 6.4 (br s, 1H), 6.0 (d, 1H). ^{13}C NMR($CDCl_3$): δ 147.7, 143.5, 139.9, 139.7, 139.3, 127.7, 124.3, 124.2, 123.6, 122.4, 121.1, 109.0, 65.9. Mass spec m/e (rel int %): 230 (M^+, 39.1), 213 (M-OH, 9.1), 161 (10.5), 135 (100), 95 (58.3).

2-Benzo[b]furyl-3-furylmethanol was analogously prepared from benzo[b]furan and 3-furaldehyde (68%). ^{1}H NMR($CDCl_3$): δ 7.55-7.40 (m, 4H), 7.31-7.18 (m, 2H), 6.62 (s, 1H), 6.50 (s, 1H), 5.91 (d, 1H). ^{13}C NMR($CDCl_3$): δ 157.7, 154.95, 143.5, 140.3, 127.9, 125.4, 124.4, 122.9, 121.2, 111.3, 109.2, 103.7, 63.6. Mass spec m/e (rel int %): 214 (M^+, 64.8), 197 (M-OH, 71.7), 145 (19.3), 95 (86.9), 63 (100).

2-Benzo[b]furyl-2-thienylmethanol was analogously prepared from benzo[b]furan and thiophene-2-carboxaldehyde (43%). ^{1}H NMR($CDCl_3$): δ 7.53-7.49 (m, 1H), 7.44 (d, 1H), 7.30-7.16 (m, 3H), 7.05 (br d, 1H), 6.97 (dd, 1H), 6.65 (s, 1H), 6.13 (d, 1H). ^{13}C NMR($CDCl_3$): δ 157.4, 154.9, 143.8, 127.8, 126.7, 125.9, 125.6, 124.4, 122.9, 121.2, 111.3, 103.9, 66.6. Mass spec m/e (rel int %): 230 (M^+, 84.1), 213 (M-OH, 91.7), 145 (27.3), 111 (75.7), 45 (100).

2-Benzo[b]furyl-3-thienylmethanol was analogously prepared from benzo[b]furan and thiophene-3-carboxaldehyde (73%). ^{1}H NMR ($CDCl_3$): δ 7.53-7.49 (m, 1H), 7.44 (br d, 1H), 7.35-7.12 (m, 5H), 6.56 (s, 1H), 5.99 (d, 1H). ^{13}C NMR($CDCl_3$): δ 157.9, 154.95, 141.5, 127.9, 126.3, 126.2, 124.3, 122.8, 122.7, 121.2, 111.3, 103.8, 66.9. Mass spec m/e (rel int %): 230 (M^+, 53.8), 213 (M-OH, 54.7), 145 (20.1), 111 (58.3), 45 (100).

2-Benzo[b]furyl-2-benzo[b]thienylmethanol was analogously prepared from benzo[b]furan and benzo[b]thiophene-2-carboxaldehyde (29%). ^{1}H NMR($CDCl_3$): δ 7.77-7.72 (m, 1H), 7.67-7.63 (m, 1H), 7.51-7.46 (m, 1H), 7.42 (d, 1H), 7.34-7.16 (m, 5H), 6.66 (s, 1H), 6.16 (br s, 1H). ^{13}C NMR($CDCl_3$): δ 156.7, 154.9, 144.3, 139.8, 139.2, 127.75, 124.55, 124.4, 124.3, 123.7, 122.9, 122.4, 122.1, 121.3, 111.3, 104.2, 67.1. Mass spec m/e (rel int %): 280 (M^+, 84.5), 263 (M-OH, 69.2), 161 (28.1), 145 (29.6), 89 (100).

General Reduction Procedure. Preparation of 2-Benzo[b]thienyl-3-thienylmethane.- To a magnetically stirred mixture of 2-benzo[b]thienyl-3-thienylmethanol[15a] (0.34 g, 1.4 mmol) and sodium borohydride powder (0.26 g, 6.9 mmol) in diethyl ether (25 mL) at 25°, TFA (2 mL) was added over 10 min. The mixture was stirred at 25° for 1 hr, then poured into 10% NaOH (25 mL). After 20 min, the aqueous solution was extracted with ether (2 x 50 mL), and the combined extracts were dried with sodium sulfate, filtered and concentrated in vacuo to afford a pale yellow solid. Flash chromatography (hexane) gave 2-benzo[b]thienyl-3-thienylmethane cleanly as a white solid (0.25 g, 78%), mp. 51-53°, lit.[15a] mp. 50-52°. ^{1}H NMR ($CDCl_3$): δ 7.75 (br d, 1H), 7.67 (br d, 1H), 7.36-7.23

(m, 3H), 7.20 (dd, 1H), 7.45-7.00 (m, 2H), 4.24 (s, 2H). ^{13}C NMR($CDCl_3$): δ 144.5, 140.0, 139.7, 128.2, 125.9, 124.1, 123.65, 122.9, 122.15, 121.9, 121.5, 31.5.

2-Furyl-2-thienylmethane[15c] was analogously prepared from 2-furyl-2-thienylmethanol[19] (42%), oil. ^{1}H NMR($CDCl_3$): δ 7.33 (d, 1H), 7.15 (dd, 1H), 6.45-6.91 (m, 1H), 6.89-6.85 (m, 1H), 6.29 (dd, 1H), 6.08 (d, 1H), 4.16 (s, 2H). ^{13}C NMR($CDCl_3$): δ 153.5, 141.6, 140.4, 126.8, 125.5, 124.1, 110.3, 106.2, 28.7.

2-Benzo[b]thienyl-2-furylmethane was analogously prepared from 2-benzo[b]thienyl-2-furylmethanol (45%), mp. 67-69°, lit.[15b] mp. 70-71°. ^{1}H NMR($CDCl_3$): δ 7.74 (d, 1H), 7.67 (dd, 1H), 7.40 (s, 1H), 7.34-7.22 (m, 2H), 7.09 (s, 1H), 6.34 (dd, 1H), 6.18-6.15 (m, 1H), 4.24 (s, 2H). ^{13}C NMR($CDCl_3$): δ 152.7, 141.8, 141.5, 139.9, 139.7, 124.15, 123.8, 123.0, 122.1, 122.0, 110.4, 106.7, 29.6.

2-Benzo[b]thienyl-2-thienylmethane was analogously prepared from 2-benzo[b]thienyl-2-thienylmethanol (76%), mp. 60-62°, lit.[15e] mp. 65-66°. ^{1}H NMR($CDCl_3$): δ 7.71 (br d, 1H), 7.64 (br d, 1H), 7.32-7.14 (m, 3H), 7.04 (br s, 1H), 6.94-6.89 (m, 2H), 4.36 (s, 2H). ^{13}C NMR($CDCl_3$): δ 144.1, 141.9, 139.8, 139.7, 126.8, 125.7, 124.4, 124.1, 123.8, 123.05, 122.15, 121.6, 31.0.

3-Furyl-2-thienylmethane was analogously prepared from 3-furyl-2-thienylmethanol (64%), bp. 60°/0.75 mm (Kugelrohr distillation). ^{1}H NMR($CDCl_3$): δ 7.38-7.36 (m, 1H), 7.30 (br s, 1H), 7.14 (dd, 1H), 6.92 (dd, 1H), 6.85-6.82 (m, 1H), 6.32 (br s, 1H), 4.00 (s, 2H). ^{13}C NMR($CDCl_3$): δ 143.3, 143.0, 139.5, 126.7, 124.8, 123.7, 123.65, 111.0, 25.4. mass spec m/e (rel int %): 166 (M+2, 5.5), 165 (M+1, 13.1), 164 (M^+, 100), 163 (M-1, 39.6), 135 (M-CHO, 79.7), 97 (23.2), 81 (10.4).

Anal. Calcd for C_9H_8OS: C, 65.82; H, 4.91; S, 19.52. Found: C, 65.87; H, 4.94; S, 19.43

2-Furyl-3-thienylmethane was analogously prepared from 2-furyl-3-thienylmethanol (47%), bp. 70°/1.5 mm (Kugelrohr distillation). ^{1}H NMR($CDCl_3$): δ 7.33 (br s, 1H), 7.24 (dd, 1H), 7.01 (br s, 1H), 6.96 (d, 1H), 6.30-6.26 (m, 1H), 6.01 (d, 1H), 4.00 (s, 2H). ^{13}C NMR($CDCl_3$): δ 154.0, 141.35, 138.2, 128.2, 125.6, 121.6, 110.2, 105.9, 29.1. mass spec m/e (rel int %): 166 (M+2, 4.7), 165 (M+1, 10.3), 164 (M^+, 88), 163 (M-1, 27), 135 (M-CHO, 100), 97 (12.6), 81 (16.6).

Anal. Calcd for C_9H_8OS: C, 65.82; H, 4.91; S, 19.52. Found: C, 65.87; H, 4.96; S, 19.37

2-Benzo[b]thienyl-3-furylmethane was analogously prepared from 2-benzo[b]thienyl-3-furylmethanol (64%), mp. 46-48°. ^{1}H NMR ($CDCl_3$): δ 7.73 (br d, 1H), 7.64 (br d, 1H), 7.40-7.20 (m, 4H), 7.03 (s, 1H), 6.33 (br s, 1H), 4.04 (s, 2H). ^{13}C NMR($CDCl_3$): δ 144.3, 143.1, 139.9, 139.7, 139.6, 124.1, 123.6, 122.9, 122.8, 122.1, 121.3, 111.1, 26.3. Mass spec m/e (rel int %): 216 (M+2, 5.6), 215 (M+1, 17.1), 214 (M^+, 100), 185 (M-CHO, 80.7), 147 (16.8), 81 (7.4).

Anal. Calcd for $C_{13}H_{10}OS$: C, 72.87; H, 4.70; S, 14.96. Found: C, 72.99; H, 4.73; S, 14.89

2-Benzo[b]furyl-2-furylmethane was analogously prepared from 2-benzo[b]furyl-2-furylmethanol (32%), bp. 112-20°/1.5 mm (Kugelrohr distillation). ^{1}H NMR($CDCl_3$): δ 7.49-7.39 (m, 2H), 7.35 (br s, 1H), 7.24-7.13 (m, 2H), 6.46 (s, 1H), 6.33 (dd, 1H), 6.16 (d, 1H), 4.16 (s, 2H). ^{13}C NMR($CDCl_3$): δ 154.8, 154.7, 150.6, 141.8, 128.7, 123.6, 122.6, 120.5, 110.9, 110.5, 106.95, 103.5, 27.85. Mass

spec m/e (rel int %): 199 (M+1, 15.6), 198 (M^+, 100), 169 (M-CHO, 91.2), 131 (15.8), 81 (10.4).
Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.08. Found: C, 78.52; H, 5.10

2-Benzo[b]furyl-3-furylmethane was analogously prepared from 2-benzo[b]furyl-3-furylmethanol (67%), bp. 116-124°/3.5 mm (Kugelrohr distillation). ^{1}H NMR($CDCl_3$): δ 7.47-7.33 (m, 4H), 7.22-7.12 (m, 2H), 6.37-6.34 (m, 2H), 3.88 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 157.1, 154.8, 143.1, 140.0, 128.7, 123.4, 122.5, 120.4, 111.2, 110.8, 102.8, 24.5. Mass spec m/e (rel int %): 199 (M+1, 14.4), 198 (M^+, 100), 197 (M-1, 61.1), 169 (M-CHO, 53.9), 131 (16.1), 81 (4.7).
Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.08. Found: C, 78.86; H, 4.95

2-Benzo[b]furyl-2-thienylmethane was analogously prepared from 2-benzo[b]furyl-2-thienylmethanol (75%), bp. 127-36°/1 mm (Kugelrohr distillation). ^{1}H NMR($CDCl_3$): δ 7.47 (br dd, 1H), 7.41 (br d, 1H), 7.24-7.13 (m, 3H), 6.96-6.92 (m, 2H), 6.45 (s, 1H), 4.28 (s, 2H). ^{13}C NMR($CDCl_3$): δ 156.6, 154.8, 139.2, 128.6, 126.9, 126.0, 124.4, 123.6, 122.6, 120.5, 110.9, 103.3, 29.2. Mass spec m/e (rel int %): 216 (M+2, 5.3), 215 (M+1, 17.7), 214 (M^+, 93.5), 213 (M-1, 100), 131 (16.1), 97 (10.2).
Anal. Calcd for $C_{13}H_{10}OS$: C, 72.87; H, 4.70; S, 14.96. Found: C, 72.95; H, 4.75; S, 14.90

2-Benzo[b]furyl-3-thienylmethane was analogously prepared from 2-benzo[b]furyl-3-thienylmethanol (74%), bp. 132-40°/1.5 mm (Kugelrohr distillation). ^{1}H NMR($CDCl_3$): δ 7.48-7.38 (m, 2H), 7.27-7.12 (m, 3H), 7.07 (br d, 1H), 7.00 (d, 1H), 6.36 (s, 1H), 4.08 (s, 2H). ^{13}C NMR($CDCl_3$): δ 157.2, 154.8, 137.1, 128.7, 128.3, 125.8, 123.4, 122.5, 122.1, 120.4, 110.9, 103.0, 29.5. Mass spec m/e (rel int %): 216 (M+2, 6.3), 215 (M+1, 18.1), 214 (M^+, 89.5), 213 (M-1, 100), 131 (18.8), 97 (10).
Anal. Calcd for $C_{13}H_{10}OS$: C, 72.87; H, 4.70; S, 14.96. Found: C, 73.10; H, 4.72; S, 14.76

2-Benzo[b]furyl-2-benzo[b]thienylmethane was analogously prepared from 2-benzo[b]furyl-2-benzo[b]thienylmethanol (68%), mp. 97-99°. ^{1}H NMR ($CDCl_3$): δ 7.73 (br d, 1H), 7.68-7.63 (m, 1H), 7.50-7.40 (m, 2H), 7.32-7.13 (m, 4H), 7.12 (br s, 1H), 6.52 (s, 1H), 4.32 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 155.7, 154.9, 140.3, 139.8, 139.7, 128.5, 124.2, 123.9, 123.7, 123.1, 122.65, 122.55, 122.1, 120.6, 111.0, 103.75, 30.0. Mass spec m/e (rel int %): 266 (M+2, 7.1), 265 (M+1, 22.6), 264 (M^+, 100), 147 (4.7), 131 (10.1).
Anal. Calcd for $C_{17}H_{12}OS$: C, 77.24; H, 4.58; S, 12.13. Found: C, 77.40; H, 4.59; S, 12.08

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