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Synthesis and Diels–Alder reactions of the furo[3,4-*b*]pyrrole ring system. A new indole ring synthesis

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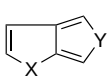
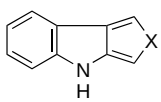
Abstract—The previously unknown furo[3,4-*b*]pyrrole ring system has been synthesized from the appropriate pyrrolo hydroxyketones by acid-catalyzed cyclodehydration. Diels–Alder reactions of these furo[3,4-*b*]pyrroles affords a new synthesis of indoles.

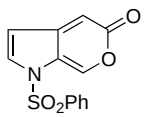
Fused bicyclic heterocycles that are isoelectronic with pentalene dianion have proven to be synthetically useful,[1–7] particularly those that can be viewed as stable analogues of hetero-*o*-quinodimethanes,[8] and they are also of intrinsic theoretical interest.[9] Pioneered by the early work of Wynberg,[1a,2a] these known ring systems include thieno[3,4-*b*]thiophene (**1a**),[1] thieno[2,3-*c*]pyrrole (**1b**),[2] thieno[2,3-*c*]furan (**1c**),[3] furo[3,4-*b*]furan (**1d**),[4] thieno[3,4-*b*]furan (**1e**),[5] furo[2,3-*c*]pyrrole (**1f**),[6] and thieno[3,4-*b*]pyrrole (**1g**).[7] Two conspicuously missing members of these condensed heterocycles are the furo[3,4-*b*]pyrrole (**1h**) and pyrrolo[3,4-*b*]pyrrole (**1i**) ring systems.



1a; X = Y = S
1b; X = S, Y = NR
1c; X = S, Y = O
1d; X = Y = O
1e; X = O, Y = S
1f; X = O, Y = NR
1g; X = NR, Y = S
1h; X = NR, Y = O
1i; X = Y = NR



2a; X = O
2b; X = NR



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In continuation of our work with the corresponding furo[3,4-*b*]indole (**2a**)[10] and pyrrolo[3,4-*b*]indole (**2b**)[11] ring systems, both of which serve admirably as indole-2,3-quinodimethane mimics,[12] we now describe the synthesis and Diels–Alder trapping of the previously unknown furo[3,4-*b*]pyrrole (**1h**) ring system, to afford a new indole ring synthesis.[13] In a related strategy, Moody[14] has crafted the pyrano[3,4-*b*]pyrrole (**3**) ring system and utilized it in a new synthesis of indoles via Diels–Alder reactions.

Our synthesis of furo[3,4-*b*]pyrrole **11** is summarized in Schemes 1 and 2. The known *N*-(phenylsulfonyl)pyrrole (**4**)[15] was acylated under the usual conditions to give ketone **5**.[16] Reduction of **5** affords alcohol **6**[17] in high yield. Lithiation of **6** with LDA at −78°C followed by quenching at low temperatures with acetaldehyde gave the C-5 substituted diol[18] in 60% yield along with a sultone[19] (10–20% yield) formed by *ortho*-lithiation of the phenyl ring and subsequent cyclization and nucleophilic cleavage of the S–N bond. However, allowing the lithiation mixture to warm to room temperature and then quenching at −78°C with acetaldehyde gave the desired diol **7**[20] as a mixture of diastereomers in 90% yield. The differing hydroxy side chains in **7** (propyl and ethyl) were deliberately chosen so as to make subsequent NMR characterization of the hydroxy ketones facile. Oxidation of **7** with PCC yielded an equal mixture of hydroxy ketones **8**[21] and **9**[21] (74%) and a small amount of diketone **10**.[22] The isomeric hydroxy ketones **8** and **9** were readily distinguishable by proton NMR (e.g. methyl ketone versus ethyl ketone). Interestingly, we discovered that **8** is rapidly converted completely to **9** upon exposure to trifluoroacetic acid at room temperature or acetic acid at 100°C. This transformation would seem to represent a novel vinylogous acyloin isomerization.

Keywords: furo[3,4-*b*]pyrrole; Diels–Alder reaction; indole ring synthesis.
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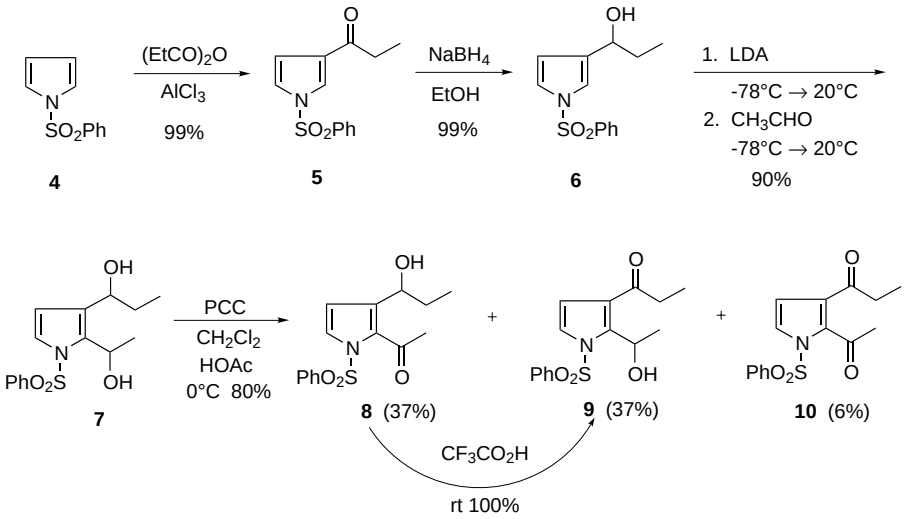
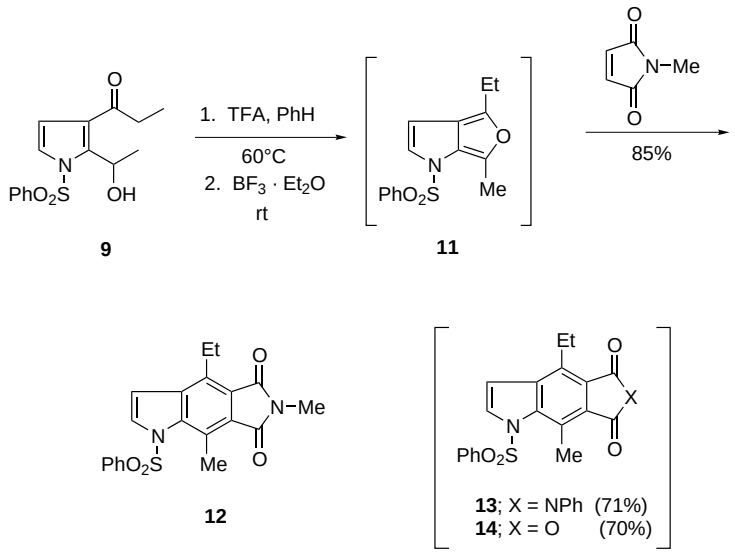


Scheme 1.

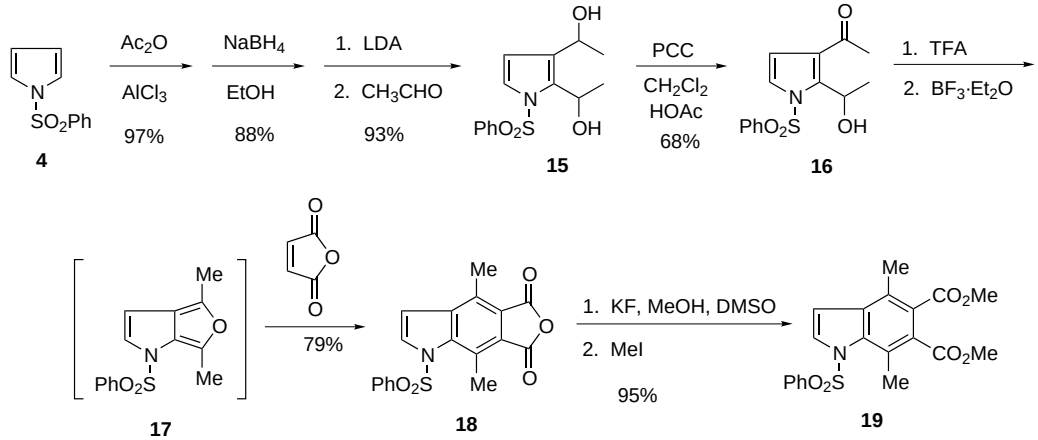


Scheme 2.

After some experimentation, we found that treating hydroxy ketone **9** with trifluoroacetic acid (benzene, 60°C, 1 h) followed by boron trifluoride etherate (rt) in the presence of *N*-methylmaleimide gave indole **12**[23] in 85% yield, presumably via the desired furopyrrole **11** (Scheme 2). Similarly, *N*-phenylmaleimide and maleic anhydride gave indoles **13**[24] and **14**,[25] respectively. An X-ray crystal structure of indole **13** confirmed its identity.[26] The two maleimides are notably more reactive than maleic anhydride in the presence of $BF_3{\cdot}Et_2O$ (rt, few minutes versus rt, 30 min). Somewhat surprising was the fact that both diethyl maleate and dimethyl fumarate gave indole anhydride **14** (50–55%) in the presence of $BF_3{\cdot}Et_2O$ at higher temperatures (70°C/40 min and 140°C/10 min, respectively), rather than the expected diesters.

A similar sequence was used to generate the dimethylfuro[3,4-*b*]pyrrole **17** (Scheme 3). Trapping with maleic anhydride afforded indole **18**[27] in 79% yield. Both anhydrides **14** and **18** were quite resistant to alcoholysis and could be recrystallized unchanged from ethanol. This lack of reactivity may be a consequence of the twin *peri*-interactions which block access to the carbonyl groups in **14** and **18**. Nevertheless, under more vigorous conditions, **18** could be converted to the known dimethyl ester **19**,[28] identical with authentic spectra (IR, NMR, MS) of this compound[14] kindly provided by Professor Moody.

The reaction of in situ generated **11** with ethyl acrylate (TFA, 75°C, 12 h) afforded a 1.5:1 mixture of indoles **20** and **21** (50% yield).[29] This ester mixture was distinguished by the respective deshielding effects of the carbonyl group on the adjacent methyl and methylene protons. A similar mixture of esters was obtained in a 1:1 ratio by Moody in the reaction between a dimethylpyrano[3,4-*b*]pyrrole and ethyl propiolate.[14] Our proton NMR data and isomer assignments are in agreement with those of Moody for similar indoles.[14]



Scheme 3.

After much experimentation, we have isolated furopyrrole **11**. Thus, a mixture of hydroxy ketones **8** and **9** (75 mg) and hydroquinone (3 mg) in THF was treated at room temperature with phosphorus pentoxide. After 15 min, a standard work-up and flash chromatography through basic alumina and then silica gel afforded **11** in 71% yield as an unstable solid, mp 87–89°C.[30] A solution of **11** in chloroform slowly decomposes to a mixture of **11**, **8**, **9**, and diketone **10** (6.4:1:8:1.3) after 4 h by NMR. After one day this ratio is 1.4:0:12:3.5, and after 2 days only **9** and **10** are present in a 14:5 ratio. This decomposition can also be followed by UV spectroscopy. Analysis by TLC was consistent with these NMR and UV results. Furopyrrole **11** is more stable in the solid state, but after ten days in an open vial it had been transformed into **9** and **10**.

Our work with this new fused heterocyclic ring system is continuing, particularly with regard to the synthesis of indole-containing natural products.

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17. Compound **6**: oil; IR (film) ν_{max} 3553, 3384, 1583, 1476, 1369, 1174, 1061 cm^{-1}; λ_{max} ($CHCl_3$) 256 nm; ^1H NMR ($CDCl_3$) δ 7.90 (m, 2H), 7.65–7.50 (m, 3H), 7.16 (m, 1H), 7.13 (m, 1H), 6.32 (m, 1H), 4.04 (t, 1H), 1.74 (q, 3H), 0.91 (t, 3H); MS *m*/*z* 265 (M^+, 5%), 247, 236, 141, 77, 58 (100%): HRMS *m*/*z* calcd for $C_{13}H_{15}NO_3S$ (M^+): 265.0773; found: 265.0776.
18. This diol (1-[5-(1-hydroxyethyl)-1-(phenylsulfonyl)-1*H*-pyrrol-3-yl]-1-propanol) is an oil; ^1H NMR ($CDCl_3$) δ 7.84 (m, 2H), 7.70–7.40 (m, 3H), 7.25 (m, 1H), 6.35 (m, 1H), 5.02 (q, 1H), 4.54 (t, 1H), 1.74 (q, 3H) (overlapping with OH), 1.50 (d, 3H), 0.94 (t, 3H).
19. This sultone (3-methyl-2,1-λ^6-benzoxathiole-1,1-(3*H*)-dione) has mp 85–87°C; ^1H NMR ($CDCl_3$) δ 7.83 (d, 1H, 7.8), 7.73 (m, 1H), 7.60 (m, 1H), 7.42 (d, 1H, 7.8), 5.84 (q, 1H, 6.6), 1.81 (d, 3H, 6.6). Anal. calcd for $C_8H_8O_3S$: C, 52.16; H, 4.38; S, 17.40. Found: C, 52.47; H, 4.33; S, 17.46.
20. Compound **7** (1-[2-(1-hydroxyethyl)-1-(phenylsulfonyl)-1*H*-pyrrol-3-yl]-1-propanol): mp 106–108°C; ^1H NMR ($CDCl_3$) δ 7.78 (m, 2H), 7.68–7.50 (m, 3H), 7.28 (d, 1H, 3.6), 6.30 (d, 1H, 3.6), 5.40 (q, 1H), 4.81 (t, 1H), 3.39 (br s, 1H), 2.95 (br s, 1H), 1.79 (m, 2H), 1.42 (d, 3H), 0.96 (t, 3H); MS *m*/*z* 332 (MNa^+). Anal. calcd for $C_{15}H_{19}NO_4S$: C, 58.25; H, 6.15; N, 4.53; S, 10.36. Found: C, 58.46; H, 6.14; N, 4.62; S, 10.43.
21. Compound **8** (1-[3-(1-hydroxypropyl)-1-(phenylsulfonyl)-1*H*-pyrrol-2-yl]-1-ethanone): mp 60°C (dec.); ^1H NMR ($CDCl_3$) δ 7.80 (m, 2H), 7.67–7.48 (m, 3H), 7.31 (d, 1H, 3.3), 6.36 (d, 1H, 3.3), 4.57 (m, 1H), 2.64 (s, 3H), 2.40 (d, 1H), 1.74 (m, 2H), 0.90 (t, 3H).
Compound **9** (1-12-(1-hydroxyethyl)-1-(phenylsulfonyl)-1*H*-pyrrol-3-yl]-1-propanone): mp 86° (dec.); IR (film) ν_{max} 3300, 1723, 1656, 1542, 1404, 1170, 1138, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90 (m, 2H), 7.75–7.57 (m, 3H), 7.38 (d, 1H, 3.6), 6.71 (d, 1H, 3.6), 6.06 (d, 1H), 5.39 (m, 1H), 2.90 (q, 2H), 2.70 (s, 3H), 1.16 (t, 3H); MS *m*/*z* 330 (MNa^+).
22. Compound **10** (1-[2-acetyl-1-(phenylsulfonyl)-1*H*-pyrrol-3-yl]-1-propanone): mp 80–81°C; IR (film) ν_{max} 3054, 2985, 1709, 1678, 1264 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80 (m, 2H), 7.74–7.56 (m, 3H), 7.20 (d, 1H, 3.3), 6.57 (d, 1H, 3.3), 2.78 (q, 2H), 2.70 (s, 3H), 1.16 (t, 3H); MS *m*/*z* 306 (MH^+).
23. Compound **12** (4-ethyl-6,8-dimethyl-1-(phenylsulfonyl)-pyrrolo[3,4-*f*]indole-5,7-(1*H*,6*H*)-dione): mp 166–167°C; IR (Nujol) ν_{max} 1752, 1693, 1457, 1377, 1269 cm^{-1}; λ_{max} ($CHCl_3$) 254, 344 nm; ^1H NMR ($CDCl_3$) δ 8.07 (d, 1H, 3.6), 7.76–7.54 (m, 5H), 6.96 (d, 1H, 3.6), 3.34 (q, 2H), 3.14 (s, 3H), 2.90 (s, 3H), 1.31 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 169.6, 168.5, 139.6, 137.9, 136.6, 136.2, 134.4, 133.1, 129.8, 126.7, 126.1, 125.0, 123.6, 107.1, 23.9, 21.5, 15.3, 14.9; MS *m*/*z* 382 (M^+, 96%), 241 (100%), 234, 141, 85, 77. Anal. calcd for $C_{20}H_{18}N_2O_4S$: C, 62.81; H, 4.74; N, 7.33; S, 8.38. Found: C, 62.88; H, 4.82; N, 7.26; S, 8.37.
24. Compound **13** (4-ethyl-8-methyl-6-phenyl-1-(phenylsulfonyl)pyrrolo[3,4-*f*]indole-5,7-(1*H*,6*H*)-dione): mp 158–160°C; IR (Nujol) ν_{max} 1757, 1713, 1597, 1502, 1451, 1377 cm^{-1}; λ_{max} ($CHCl_3$) 256, 346 nm; ^1H NMR ($CDCl_3$) δ 8.12 (d, 1H, 3.9), 7.77–7.44 (m, 10H), 7.02 (d, 1H, 3.9), 3.40 (q, 2H), 2.96 (s, 3H), 1.35 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 168.4, 167.3, 139.6, 138.2, 137.1, 136.8, 134.4, 132.1, 129.9, 129.1, 128.1, 127.0, 126.7, 125.6, 125.5, 123.2, 107.1, 21.7, 15.2, 15.0; MS *m*/*z* 444 (M^+, 70%), 303 (100%), 259, 141, 83, 77. Anal. calcd for $C_{25}H_{20}N_2O_4S$: C, 67.55; H, 4.54; N, 6.30; S, 7.21. Found: C, 67.33; H, 4.66; N, 6.28; S, 7.13.
25. Compound **14** (4-ethyl-8-methyl-1-(phenylsulfonyl)-1*H*-furo[3,4-*f*]indole-5,7-dione): mp 195–196°C; IR (Nujol) ν_{max} 1823, 1762, 1460, 1377, 1286 cm^{-1}; λ_{max} ($CHCl_3$) 256, 340 nm; ^1H NMR ($CDCl_3$) δ 8.20 (d, 1H, 3.9), 7.79–7.58 (m, 5H), 7.04 (d, 1H, 3.9), 3.34 (q, 2H), 2.90 (s, 3H), 1.34 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 163.9, 162.9, 139.3, 138.7, 138.6, 138.4, 134.8, 134.7, 130.0, 127.0, 126.8, 124.9, 122.4, 106.9, 21.9, 15.2, 15.1; MS *m*/*z* 369 (M^+, 37%), 141 (100%), 77. Anal. calcd for $C_{19}H_{15}NO_5S$: C, 61.78; H, 4.09; N, 3.79; S, 8.68. Found: C, 61.48; H, 4.08; N, 3.76; S, 8.54.
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27. Compound **18** (4,8-dimethyl-1-(phenylsulfonyl)-1*H*-furo[3,4-*f*]indole-5,7-dione): mp 209–211°C; IR (Nujol) ν_{max} 1827, 1761, 1371, 1290 cm^{-1}; λ_{max} ($CHCl_3$) 258, 340

nm; ^{1}H NMR ($CDCl_3$) δ 8.19 (d, 1H, 4.2), 7.77–7.54 (m, 5H), 7.03 (d, 1H, 4.2), 2.91 (s, 3H), 2.88 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 163.8, 163.2, 139.2, 139.1, 138.3, 134.8, 134.7, 132.1, 130.0, 126.9, 126.7, 124.6, 123.1, 107.2, 15.2, 14.2; MS m/z 355 (M^+, 36%), 215, 141, 77 (100%). Anal. calcd for $C_{18}H_{13}NO_5S$: C, 60.84; H, 3.69; N, 3.94; S, 9.02. Found: C, 60.75; H, 3.81; N, 3.87; S, 8.96.

28. Compound **19** (dimethyl 4,7-dimethyl-1-(phenylsulfonyl)-1*H*-indole-5,6-dicarboxylate): oil; IR (film) ν_{max} 1729, 1440, 1368, 1296, 1178 cm^{-1}; λ_{max} ($CHCl_3$) 254, 310 nm; ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 1H, 3.9), 7.67–7.40 (m, 5H), 6.84 (d, 1H, 3.9), 3.90 (s, 3H), 3.88 (s, 3H), 2.56 (s, 3H), 2.54 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.6, 168.8, 139.5, 135.8, 134.14, 134.10, 132.3, 131.2, 130.0, 128.6, 127.1, 126.5, 121.8, 107.7, 52.7, 52.6, 18.2, 16.3; MS m/z 401 (M^+, 27%), 370, 369, 304, 228 (100%), 77; HRMS m/z calcd for $C_{20}H_{19}NO_6S$ (M^+): 401.0933; found: 401.0930. These spectra agreed well with those provided by Professor Moody for **19**.[14]
29. Compounds **20** and **21** (ethyl 4-ethyl-7-methyl-1-(phenylsulfonyl)-1*H*-indole-5- and 6-carboxylate): oil; IR (film) ν_{max} 1713, 1573, 1350, 1260 cm^{-1}; λ_{max} ($CHCl_3$) 252, 308 nm; ^{1}H NMR ($CDCl_3$) δ 7.89 (m, 1H), 7.72–7.46 (m, 5H), 6.90 (d, 1H, 3.9), 6.78 (d, 1H, 3.9), 4.40 (m, 2H), 3.20 (q, 2H), 2.84 (q, 2H), 2.70 (s, 3H), 2.53 (s, 3H), 1.42 (m, 3H), 1.27 (m, 3H); MS m/z 371 (M^+, 100%), 326, 230, 202, 184, 158, 77; HRMS m/z calcd for $C_{20}H_{21}NO_4S$ (M^+): 371.1191; found: 371.1194.
30. Compound **11** (4-ethyl-6-methyl-1-(phenylsulfonyl)-1*H*-furo[3,4-*b*]pyrrole): mp 87–89°C; IR (Nujol) ν_{max} 1671, 1526, 1456, 1350 cm^{-1}; λ_{max} ($CHCl_3$) 246, 276, 292 nm; ^{1}H NMR ($CDCl_3$) δ 7.80 (m, 2H), 7.60–7.46 (m, 3H), 6.98 (d, 1H, 3.9), 6.14 (d, 1H, 3.9), 2.68 (q, 2H), 2.63 (s, 3H), 1.25 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 140.9, 137.6, 133.5, 132.3, 130.4, 129.3, 127.2, 122.3, 105.4, 30.5, 21.4, 12.6, 12.0; MS m/z 289 (M^+, 65%), 274, 148, 106, 77 (100%); HRMS m/z calcd for $C_{15}H_{15}NO_3S$ (M^+): 289.0773; found: 289.0768.