SUPPLEMENTARY DATA

OL0525359

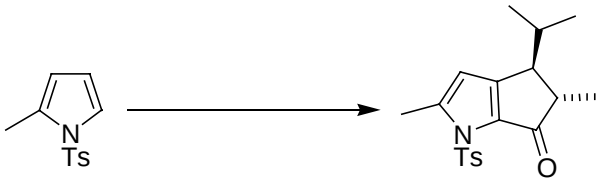
The first examples of Nazarov cyclisations leading to annulated pyrroles"

David W. Knight, Chuanjun Song and Maria A. Whatton,

School of Chemistry, Cardiff University, Main College, Park Place, Cardiff, CF10 3 AT, UK.

[knightdw@cf.ac.uk]

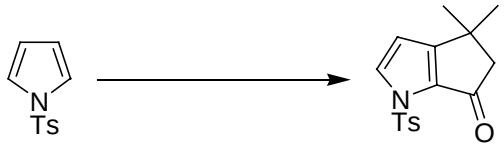
A typical procedure is as follows: ***trans*-4,5-Dihydro-2,5-dimethyl-4-isopropyl-1-(4'-methylphenyl-sulfonyl)cyclopenta[b]-pyrrol-6(1H)-one 24d.**



23 **24d**

A solution of 2-methyl-*N*-tosylpyrrole [**23**; R^1 = Me] (55 mg, 0.23 mmol), 2,4-dimethylpent-2-enoic acid (118 mg, 0.92 mmol) and trifluoroacetic anhydride (0.5 ml) in dry dichloromethane (10 ml) was stirred at ambient temperature for 48 h then diluted with dicloromethane (20 ml). The resulting solution was washed with saturated aqueous sodium carbonate (10 ml) and brine (10 ml) then dried ($MgSO_4$), filtered and evaporated. Column chromatography of the residue over silica gel eluted with petrol-ethyl acetate (4:1) separated the *cyclopentapyrrolone* **24d**. as a clear, colourless oil (51 mg, 64%), which showed ν_{max} (film) 1694, 1597, 1494, 1451, 1377, 1193, 1137, 1089, 1042 cm^{-1}, δ_H ($CDCl_3$, 400 MHz) 0.90 (3H, d, *J* 6.8 Hz, ^{i}Pr-Me), 0.91 (3H, d, *J* 6.8 Hz, ^{i}Pr-Me), 1.25 (3H, d, *J* 7.4 Hz, 5-Me), 1.19-1.88 (1H, m, ^{i}Pr-H), 2.41-2.43 (4H, m, Ts-Me and 4-H), 2.55 (1H, qd, *J* 7.4 and 2.3 Hz, 5-H), 2.59 (3H, s, 2-Me), 6.00 (1H, s, 3-H), 7.31 (2H, d, *J* 8.3 Hz, 2 x Ar-H), 8.05 (2H, d, *J* 8.3 Hz, 2 x Ar-H), δ_C ($CDCl_3$, 100 MHz) 15.7, 17.3, 19.9, 20.3 (all Me), 21.7 (Ts-Me), 31.3 (*C*HMe_2), 48.8 (4-CH), 51.1 (5-CH), 110.4 (3-CH), 127.8 (2 x Ar-CH), 129.9 (2 x Ar-CH), 133.4, 136.0, 145.3, 145.9, 158.0 (all C), 190.4 (CO), m/z (APCI) 346 (M^+ + H, 100%). [Found: M^+ + H, 346.1474. $C_{19}H_{24}NO_3S$ requires 346.1471].

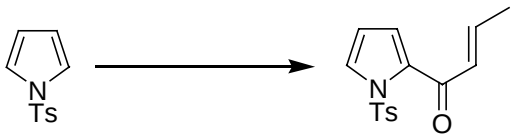
4,5-Dihydro-4,4-dimethyl-1-(4'-methylphenylsulfonyl)cyclopenta[*b*]pyrrol-6(1*H*)-one (17)



14 **17**

A brown oil, which showed: R_f 0.19 (petroleum ether-ethyl acetate 3:1); ν_{max}/cm^{-1} [film] 1694 (C=O), 1596, 1447, 1422, 1370, 1177, 1154 and 1057; δ_H 8.01 (2H, d, *J* 8.3, 2'- and 6'-H), 7.53 (1H, d, *J* 3.1, 2-H), 7.26 (2H, d, *J* 8.3, 3'- and 5'-H), 6.14 (1H, d, *J* 3.1, 3-H), 2.64 (2H, s, 5-CH_2), 2.35 (3H, s, *Ts*-Me) and 1.23 (6H, s, 2 x (4-Me)); δ_C 187.7 (C=O), 167.7, 145.7, 134.9 (all C), 133.6 (2-CH), 131.3 (C), 129.9 (2'- and 6'-CH), 128.4 (3'- and 5'-CH), 106.4 (3-CH), 57.5 (5-CH_2), 34.5 (4-C), 29.0 (2 x (4-Me)) and 21.8 (*Ts*-Me); m/z (APCI) 304 (M^+ + H, 80%), 112 (15), 86 (15) and 72 (100) [Found: M^+ + H, 304.1000. $C_{16}H_{18}NO_3S$ requires 304.1002].

(*E*)-1-[1'-(4''-Methylphenylsulfonyl)pyrrol-2'-yl]but-2-en-1-one (18a)

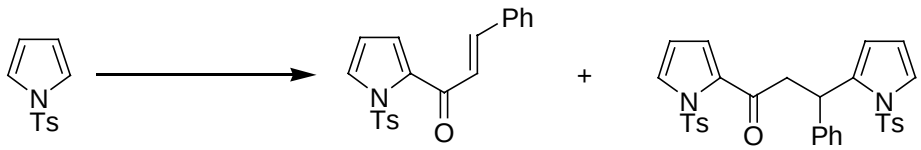


14 **18a**

A orange oil, which showed: R_f 0.29 (petroleum ether-ethyl acetate 3:1); ν_{max}/cm^{-1} [film] 1668 (C=O), 1625, 1597, 1541, 1494, 1440, 1401, 1367, 1302, 1245, 1174, 1145, 1091 and 1053; δ_H 7.85 (2H, d, *J* 8.3, 2''- and 6''-H), 7.70 (1H, dd, *J* 3.2 and 1.7, 5'-H), 7.24 (2H, d, *J* 8.3, 3''- and 5''-H), 6.92 (1H, dd, *J* 3.8 and 1.7, 3'-H), 6.86 (1H, dq, *J* 15.4 and 6.9, 3-H), 6.50 (1H, dq, *J* 15.4 and 1.6, 2-H), 6.26 (1H, *app.* t, *J ca.* 3.4, 4'-H), 2.33 (3H, s, *Ts*-Me) and 1.82 (3H, dd, *J* 6.9 and 1.6, 3-Me); δ_C 179.1 (C=O), 144.7 (C), 144.1 (3-CH), 136.2, 133.9 (both C), 130.0 (5'-CH), 129.4 (2''- and 6''-CH), 128.2 (3''- and 5''-CH), 128.1, 123.1 (both CH),

110.4 (4'-CH), 21.7 (*Ts*-Me) and 18.4 (3-Me); m/z (APCI) 290 (M^+ + H, 100%) [Found: M^+ + H, 290.0846. $C_{15}H_{16}NO_3S$ requires 290.0845].

(*E*)-1-[1'-(4''-Methylphenylsulfonyl)pyrrol-2'-yl]-3-phenylprop-2-en-1-one (18b) and 3-phenyl-1,3-bis[1'-(4''-methylphenylsulfonyl)pyrrol-2'-yl]propan-1-one (19)



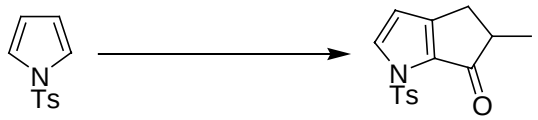
14 **18b** **19**

The p*ropenone* **18b** showed: R_f 0.24 (petroleum ether-ethyl acetate 3:1); mp 111-113 ^oC; ν_{max}/cm^{-1} [KBr] 1658 (C=O), 1605, 1435, 1401, 1348, 1184, 1146, 1054 and 975; δ_H 7.85 (2H, d, *J* 8.3, 2''- and 6''-H), 7.72 (1H, dd, *J* 3.1 and 1.7, 5'-H), 7.55 (1H, d, *J* 15.8, 3-H), 7.42-7.40 (2H, m, both Ar-H), 7.25-7.23 (3H, m, all Ar-H), 7.20 (2H, d, *J* 8.3, 3''- and 5''-H), 7.09 (1H, d, *J* 15.8, 2-H), 7.03 (1H, dd, *J* 3.7 and 1.7, 3'-H), 6.26 (1H, *app*. t, *J ca.* 3.4, 4'-H) and 2.27 (3H, s, *Ts*-Me); δ_C 178.6 (C=O), 144.9 (C), 143.8 (3-CH), 136.2, 134.6, 134.4 (all C), 130.5, 130.4 (both CH), 129.5 (2 x CH), 129.0 (2 x CH), 128.4 (2 x CH), 128.3 (2 x CH), 123.5, 122.8 (both CH), 110.7 (4'-CH) and 21.8 (*Ts*-Me); m/z (APCI) 352 (M^+ + H, 100%) and 108 (70) [Found: M^+ + H, 352.1003. $C_{20}H_{18}NO_3S$ requires 352.1002].

The *dipyrrylpropanone* **19** showed: R_f 0.19 (petroleum ether-dichloromethane 1:10); ν_{max}/cm^{-1} [film] 1676 (C=O), 1596, 1438, 1365, 1174, 1145, 1091 and 1063; δ_H 7.71-7.68 (3H, m, $5_{\alpha\text{-pyrrole}}$-, $2_{\alpha\text{-}Ts}$- and $6_{\alpha\text{-}Ts}$-H), 7.29 (2H, d, *J* 8.3, $2_{\beta\text{-}Ts}$- and $6_{\beta\text{-}Ts}$-H), 7.15-7.13 (3H, m, $3_{\alpha\text{-}Ts}$-, $5_{\alpha\text{-}Ts}$- and $5_{\beta\text{-pyrrole}}$-H), 7.03-6.96 (5H, m, all Ar-H), 6.86 (1H, dd, *J* 3.6 and 1.6, $3_{\alpha\text{-pyrrole}}$-H), 6.83-6.81 (2H, m, both Ar-H), 6.19 (1H, t, *J* 3.6, $4_{\alpha\text{-pyrrole}}$-H), 6.08 (1H, t, *J* 3.4, $4_{\beta\text{-pyrrole}}$-H), 5.98-5.97 (1H, m, *br.res*., $3_{\beta\text{-pyrrole}}$-H), 5.08 (1H, t, *J* 7.5, 3-H), 3.16 (1H, dd, *J* 15.9 and 7.5, 2-H_α), 3.06 (1H, dd, *J* 15.9 and 7.5, 2-H_β), 2.34 (3H, s, *Ts*-Me_α) and 2.27 (3H, s, *Ts*-Me_β); δ_C 185.1 (C=O), 144.7, 144.3, 142.3, 136.6, 136.2, 135.5, 133.0 (all C), 130.3 (CH), 129.7 (2 x CH), 129.2 (2 x CH), 128.4 (2 x CH), 128.2 (2 x CH), 127.8 (2 x CH), 126.8 (2 x CH), 126.3, 123.4, 123.0, 112.9 111.3, 110.2 (all CH), 46.6 (2-CH_2), 38.8 (3-CH), 21.8 and 21.6 (both *Ts*-Me); m/z (APCI) 573 (M^+ + H, 25%), 310

(10), 261 (10), 250 (10), 156 (20), 140 (30), 123 (45) and 108 (100) [Found: M^+ + H, 573.1517. $C_{31}H_{29}N_2O_5S_2$ requires 573.1512].

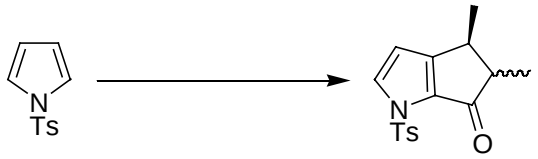
4,5-Dihydro-5-methyl-1-(4'-methylphenylsulfonyl)cyclopenta[*b*]pyrrol-6(1*H*)-one (21a)



14 **21a**

A pale orange solid, which showed: R_f 0.25 (petroleum ether-ethyl acetate 3:1); mp 126-128 ^oC; ν_{max}/cm^{-1} [KBr] 1697 (C=O), 1377, 1174 and 1136; δ_H 7.99 (2H, d, *J* 8.3, 2'- and 6'-H), 7.57 (1H, d, *J* 3.1, 2-H), 7.23 (2H, d, *J* 8.3, 3'- and 5'-H), 6.15 (1H, d, *J* 3.1, 3-H), 2.93 (1H, dd, *J* 17.1 and 6.6, 4-H$_\alpha$), 2.84-2.76 (1H, m, 5-H), 2.32 (3H, s, *Ts*-Me), 2.29 (1H, dd, *J* 17.1 and 2.5, 4-H$_\beta$) and 1.18 (3H, d, *J* 7.5, 5-Me); δ_C 191.7 (C=O), 157.2, 145.7, 134.9 (all C), 133.7 (2-CH), 132.8 (C), 129.9 (2'- and 6'-CH), 128.3 (3'- and 5'-CH), 108.9 (3-CH), 47.6 (5-CH), 29.4 (4-CH_2), 21.7 (*Ts*-Me) and 16.9 (5-Me); m/z (APCI) 290 (M^+ + H, 100%) [Found: M^+ + H, 290.0844. $C_{15}H_{16}NO_3S$ requires 290.0845].

***trans*- and *cis*-4,5-Dihydro-4,5-dimethyl-1-(4'-methylphenylsulfonyl)cyclopenta[*b*]pyrrol-6(1*H*)-one (21b)**

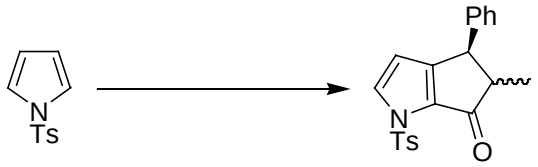


14 **21b**

A mixture of *cis*- and *trans*-isomers in a ratio of 1:2, as a syrup, which showed: R_f 0.29 (petroleum ether-dichloromethane 1:3); ν_{max}/cm^{-1} [film] 1694 (C=O), 1596, 1447, 1425, 1378, 1227, 1175, 1146, 1130, 1089, 1062, 1018 and 921; δ_H 8.01-7.97 (2H, m, 2'- and 6'-H, both isomers), 7.55 (1H, d, *J* 3.0, 2-H, both isomers), 7.24 (2H, d, *J* 8.2, 3'- and 5'-H, both isomers), 6.17-6.15 (1H, m, 3-H, both isomers), 3.12 (0.33H, *app.* quint, *J ca.* 7.0, 5-H, *cis*-isomer), 2.89 (0.33H, *app.* quint, *J ca.* 7.2, 4-H, *cis*-isomer), 2.58 (0.67H, qd, *J* 7.0 and 2.7, 5-H, *trans*-isomer), 2.35-2.32 (3.67H, m, 4-H for *trans*-isomer and *Ts*-Me for both isomers), 1.19 (2H, d, *J* 7.0, 5-Me, *trans*-isomer), 1.16 (2H, d, *J* 7.5, 4-Me, *trans*-isomer), 1.07 (1H, d, *J* 7.7, 4-Me, *cis*-

isomer) and 1.04 (1H, d, *J* 7.3, 5-Me, *cis*-isomer); δ_C 191.6 (C=O, *cis*-isomer), 190.8 (C=O, *trans*-isomer), 163.1 *(cis*-isomer), 161.5 (*trans*-isomer), 145.7 (*trans*-isomer), 145.7 (*cis*-isomer), 134.9 (*cis*-isomer), 134.9 (*trans*-isomer) (all C), 133.6 (2-CH, *trans*-isomer), 133.6 (2-CH, *cis*-isomer), 132.0 (C, *trans*-isomer), 131.9 (C, *cis*-isomer), 129.9 (2'- and 6'-CH, both isomers), 128.3 (3'- and 5'-CH, *trans*-isomer), 128.3 (3'- and 5'-CH, *cis*-isomer), 107.9 (3-CH, *cis*-isomer), 107.7 (3-CH, *trans*-isomer), 56.6 (5-CH, *trans*-isomer), 51.0 (5-CH, *cis*-isomer), 37.0 (4-CH, *trans*-isomer), 31.7 (4-CH, *cis*-isomer), 21.7 (*Ts*-Me, both isomers), 18.7 (5-Me, *trans*-isomer), 16.3 (5-Me, *cis*-isomer), 14.8 (4-Me, *trans*-isomer) and 11.9 (4-Me, *cis*-isomer); m/z (APCI) 304 (M^+ + H, 100%) [Found: M^+ + H, 304.1004. $C_{16}H_{18}NO_3S$ requires 304.1002].

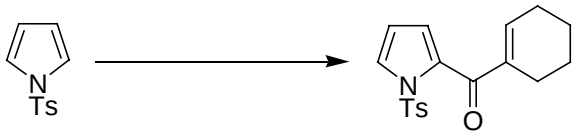
trans- and _cis_-4,5-Dihydro-5-methyl-1-(4'-methylphenylsulfonyl)-4-phenylcyclopenta[_b_]-pyrrol-6(1_H_)-one (21c)



14 **21c**

A mixture of *trans*- and *cis*-isomers in a ratio 6:1, as a syrup, which showed: R_f 0.33 (petroleum ether-ethyl acetate 3:1); ν_{max}/cm^{-1} [film] 1698 (C=O), 1596, 1494, 1454, 1423, 1376, 1192, 1175, 1139, 1088, 1047 and 1004; δ_H 8.04-8.01 (2H, m, 2'- and 6'-H, both isomers), 7.63 (0.14H, d, *J* 3.1, 2-H, *cis*-isomer), 7.60 (0.86H, d, *J* 3.0, 2-H, *trans*-isomer), 7.29-7.13 (5H, m, all Ar-H, both isomers), 7.04-7.01 (2H, m, Ar-H, both isomers), 6.09 (0.14H, d, *J* 3.1, 3-H, *cis*-isomer), 6.04 (0.86H, d, *J* 3.0, 3-H, *trans*-isomer), 4.32 (0.14H, d, *J* 6.8, 4-H, *cis*-isomer), 3.69 (0.86H, d, *J* 3.3, 4-H, *trans*-isomer), 3.12 (0.14H, *app.* quint, *J ca.* 7.3, 5-H, *cis*-isomer), 2.65 (0.86H, qd, *J* 7.4 and 3.3, 5-H, *trans*-isomer), 2.36 (0.43H, s, *Ts*-Me, *cis*-isomer), 2.34 (2.57H, s, *Ts*-Me, *trans*-isomer), 1.24 (2.57H, d, *J* 7.4, 5-Me, *trans*-isomer) and 0.65 (0.43H, d, *J* 7.7, 5-Me, *cis*-isomer); δ_C 191.2 (C=O, *cis*-isomer), 190.3 (C=O, *trans*-isomer), 159.1 (*cis*-isomer), 158.7 (*trans*-isomer), 145.9 (*trans*-isomer), 141.2 (*trans*-isomer), 134.9 (*trans*-isomer) (all C), 134.1 (CH, *cis*-isomer), 133.9 (CH, *trans*-isomer), 132.9 (C, *trans*-isomer), 130.1 (2 x CH, both isomers), 128.9 (2 x CH, *cis*-isomer), 128.9 (2 x CH, *trans*-isomer), 128.4 (2 x CH, *trans*-isomer), 128.4 (2 x CH, *cis*-isomer), 127.3 (2 x CH, both isomers), 127.1 (CH, both isomers), 109.0 (3-CH, *cis*-isomer), 108.6 (3-CH, *trans*-isomer), 58.5 (4-CH, *trans*-siomer), 52.4 (4-CH, *cis*-isomer), 48.4 (5-CH, *trans*-isomer), 43.9 (5-CH, *cis*-isomer), 21.8 (*Ts*-Me, both isomers), 14.8 (5-Me, *trans*-isomer) and 13.9 (5-Me, *cis*-isomer); m/z (APCI) 366 (M^+ + H, 100%) [Found: M^+ + H, 366.1161. $C_{21}H_{20}NO_3S$ requires 366.1158].

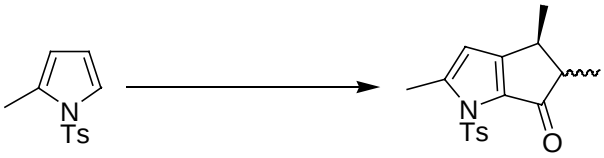
Cyclohex-1’’-en-1’’-yl-[1-(4’-methylphenylsulfonyl)pyrrol-2-yl]methanone (22)



14 **22**

A pale orange solid, which showed: R_f 0.32 (petroleum ether-ethyl acetate 5:1); mp 126-128 ^oC; ν_{max}/cm^{-1} [KBr] 1638 (C=O), 1596, 1448, 1366, 1311, 1249, 1171, 1146, 1088 and 1059; δ_H 7.97 (2H, d, *J* 8.3, 2’- and 6’-H), 7.59 (1H, dd, *J* 3.1 and 1.7, 5-H), 7.34 (2H, d, *J* 8.3, 3’- and 5’-H), 6.81-6.79 (1H, m, 2’’-H), 6.60 (1H, dd, *J* 3.5 and 1.7, 3-H), 6.27 (1H, *app.* t, *J ca.* 3.4, 4-H), 2.41 (3H, s, *Ts*-Me), 2.33-2.31 (2H, m, *br. res*., 6’’-CH_2), 2.26-2.24 (2H, m, *br. res*., 3’’-CH_2) and 1.71-1.63 (4H, m, 4’’- and 5’’-CH_2); δ_C 186.9 (C=O), 144.9 (C), 144.0 (2’’-CH), 139.5, 136.3, 133.0 (all C), 129.5 (2’- and 6’-CH), 128.2 (3’- and 5’-CH), 127.6 (5-CH), 122.0 (3-CH), 110.5 (4-CH), 26.1 (6’’-CH_2), 23.6 (3’’-CH_2), 21.9 (CH_2), 21.7 (*Ts*-Me) and 21.6 (CH_2); m/z (APCI) 330 (M^+ + H, 100%) [Found: M^+ + H, 330.1163. $C_{18}H_{20}NO_3S$ requires 330.1158].

***trans*- and *cis*-4,5-Dihydro-1-(4’-methylphenylsulfonyl)-2,4,5-trimethylcyclopenta[*b*]-pyrrol-6(1*H*)-one (24a)**

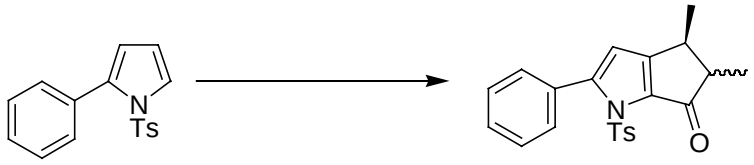


23a **24a**

A mixture of *trans*- and *cis*-isomers in a ratio 6:1, as a syrup, which showed: R_f 0.22 (petroleum ether-ethyl acetate 3:1); ν_{max}/cm^{-1} [film] 1695 (C=O), 1597, 1493, 1459, 1375, 1277, 1239, 1181, 1141, 1091, 1049, 1010, 985, 927 and 816; δ_H 8.00-7.96 (2H, m, 2’- and 6’-H, both isomers), 7.23-7.21 (2H, m, 3’- and 5’-H, both isomers), 5.91 (0.14H, s, 3-H, *cis*-isomer), 5.90 (0.86H, s, 3-H, *trans*-isomer), 3.04 (0.14H, *app.* quint, *J ca.* 7.0, 5-H, *cis*-isomer), 2.86 (0.14H, *app.* quint, *J ca.* 7.6, 4-H, *cis*-isomer), 2.49 (0.86H, qd, *J* 7.2 and 2.9, 5-H, *trans*-isomer), 2.49 (2.57H, s, 2-Me, *trans*-isomer), 2.48 (0.43H, s, 2-Me, *cis*-isomer), 2.31 (2.57H, s,

Ts-Me, *trans*-isomer), 2.30 (0.43H, s, *Ts*-Me, *cis*-isomer), 2.29 (0.86H, qd, *J* 7.4 and 2.9, 4-H, *trans*-isomer), 1.15 (2.57H, d, *J* 7.4, 4-Me, *trans*-isomer), 1.14 (2.57H, d, *J* 7.2, 5-Me, *trans*-isomer), 1.06 (0.43H, d, *J* 7.6, 4-Me, *cis*-isomer) and 0.99 (0.43H, d, *J* 7.4, 5-Me, *cis*-isomer); δ_C 190.6 (C=O, *cis*-isomer), 189.8 (C=O, *trans*-isomer), 161.7 (*cis*-isomer), 160.1 (*trans*-isomer), 146.2 (*trans*-isomer), 146.1 (*cis*-isomer), 145.4 (*trans*-isomer), 145.3 (*cis*-isomer), 136.0 (*cis*-isomer), 136.0 (*trans*-isomer), 132.6 (*trans*-isomer), 132.5 (*cis*-isomer) (all C), 129.9 (2'- and 6'-CH, both isomers), 127.8 (3'- and 5'-CH, *trans*-isomer), 127.8 (3'- and 5'-CH, *cis*-isomer), 109.1 (3-CH, *cis*-isomer), 109.0 (3-CH, *trans*-isomer), 56.2 (5-CH, *trans*-isomer), 50.7 (5-CH, *cis*-isomer), 36.5 (4-CH, *trans*-isomer), 31.2 (4-CH, *cis*-isomer), 21.7 (*Ts*-Me, both isomers), 18.8 (Me, *trans*-isomer), 16.2 (Me, *cis*-isomer), 15.6 (Me, both isomers), 15.1 (Me, *trans*-isomer) and 12.0 (Me, *cis*-isomer); m/z (APCI) 318 (M^+ + H, 100%) [Found: M^+ + H, 318.1157. $C_{17}H_{20}NO_3S$ requires 318.1158].

trans- and _cis_-4,5-Dihydro-4,5-dimethyl-1-(4'-methylphenylsulfonyl)-2-phenyl-cyclopenta[_b_]pyrrol-6(1_H_)-one (24b)

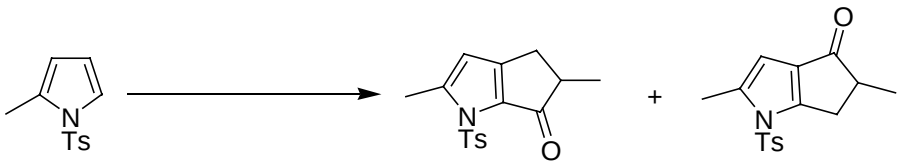


23b **24b**

A mixture of *trans*- and *cis*-isomers in a ratio of 6:1, as a syrup, which showed: R_f 0.17 (petroleum ether-ethyl acetate 5:1); ν_{max}/cm^{-1} [film] 1699 (C=O), 1596, 1464, 1383, 1192, 1180, 1127, 1090 and 1019; δ_H 7.77-7.73 (2H, m, 2'- and 6'-H, both isomers), 7.39-7.22 (5H, m, all Ar-H, both isomers), 7.18 (2H, d, *J* 8.1, 3'- and 5'-H, both isomers), 6.09 (0.14H, s, 3-H, *cis*-isomer), 6.08 (0.86H, s, 3-H, *trans*-isomer), 3.14 (0.14H, *app.* quint, *J ca.* 7.1, 5-H, *cis*-isomer), 2.96 (0.14H, *app.* quint, *J ca.* 7.5, 4-H, *cis*-isomer), 2.59 (0.86H, qd, *J* 7.1 and 2.9, 5-H, *trans*-isomer), 2.40 (0.86H, qd, *J* 7.4 and 2.9, 4-H, *trans*-isomer), 2.32 (3H, s, *Ts*-Me, both isomers), 1.22 (2.57H, d, *J* 7.4, 4-Me, *trans*-isomer), 1.21 (2.57H, d, *J* 7.1, 5-Me, *trans*-isomer), 1.12 (0.43H, d, *J* 7.6, 4-Me, *cis*-isomer) and 1.06 (0.43H, d, *J* 7.4, 5-Me, *cis*-isomer); δ_C 191.8 (C=O, *cis*-isomer), 191.1 (C=O, *trans*-isomer), 162.1 (*cis*-isomer), 160.5 (*trans*-isomer), 149.7 (both isomers), 145.3 (both isomers), 135.9 (both isomers), 134.4 (both isomers), 131.6 (both isomers) (all C), 129.8 (2 x CH, both isomers), 129.7 (2 x CH, both isomers), 129.3 (Ar-CH, both isomers), 128.1 (2 x CH, both isomers), 127.7 (2 x CH, both isomers), 111.3 (3-CH, *cis*-isomer), 111.1 (3-CH, *trans*-isomer), 56.3 (5-CH, *trans*-isomer), 50.9 (5-CH, *cis*-isomer), 36.7 (4-CH, *trans*-isomer), 31.5 (4-CH, cis-*isomer*), 21.8 (*Ts*-Me, both isomers), 18.9

(Me, *trans*-isomer), 16.3 (Me, *cis*-isomer), 15.2 (Me, *trans*-isomer) and 12.1 (Me, *cis*-isomer); m/z (APCI) 380 (M^+ + H, 100%) [Found: M^+ + H, 380.1313. $C_{22}H_{22}NO_3S$ requires 380.1315].

4,5-Dihydro-2,5-dimethyl-1-(4'-methylphenylsulfonyl)cyclopenta[*b*]pyrrol-6(1*H*)-one (24c) and 5,6-dihydro-2,5-dimethyl-1-(4'-methylphenylsulfonyl)cyclopenta[*b*]pyrrol-4(1*H*)-one



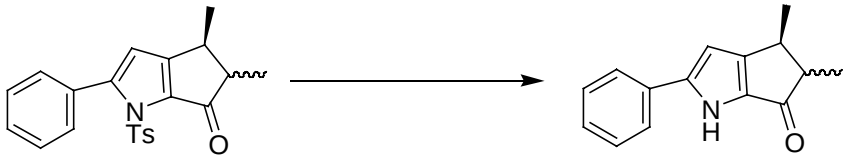
23a **24c**

A solution of 2-methyl-*N*-tosylpyrrole **23a** (70 mg, 0.3 mmol, 1.0 eq), methacrylic acid (77 mg, 0.9 mmol, 3.0 eq) and trifluoroacetic anhydride (0.5 ml) in 1,2-dichloroethane (5 ml) was refluxed for 21 hours, before work-up as described in the general procedure for pyrrole acylation. The crude product was separated by column chromatography (petroleum ether-ethyl acetate 5:2) to give the *cyclopentapyrrole-6-one* **24c** (75 mg, 82%) as a colourless solid and the *cyclopentapyrrole-4-one* (8 mg, 9%) as a sticky oil.

The *cyclopentapyrrole-6-one* **24c** showed: R_f 0.21 (petroleum ether-ethyl acetate 3:1); mp 106-108 ^oC; ν_{max}/cm^{-1} [KBr] 1738 (C=O), 1666, 1627, 1444, 1404, 1261, 1049, 998, 922 and 862; δ_H 7.98 (2H, d, *J* 8.3, 2'- and 6'-H), 7.23 (2H, d, *J* 8.3, 3'- and 5'-H), 5.89 (1H, s, 3-H), 2.86 (1H, dd, *J* 16.9 and 6.7, 4-H_α), 2.82-2.75 (1H, m, 5-H), 2.51 (3H, s, 2-Me), 2.33 (3H, s, *Ts*-Me), 2.21 (1H, dd, *J* 16.9 and 2.2, 4-H_β) and 1.19 (3H, d, *J* 7.4, 5-Me); δ_C 190.8 (C=O), 155.9, 146.3, 145.3, 136.1, 133.5 (all C), 129.9 (2'- and 6'-CH), 127.8 (3'- and 5'-CH), 110.1 (3-CH), 47.3 (5-CH), 29.1 (4-CH_2), 21.7 (*Ts*-Me), 17.2 (Me) and 15.7 (Me); m/z (APCI) 304 (M^+ + H, 100%) [Found: M^+ + H, 304.1003. $C_{16}H_{18}NO_3S$ requires 304.1002].

The *cyclopentapyrrole-4-one* showed: R_f 0.13 (petroleum ether-ethyl acetate 3:1); ν_{max}/cm^{-1} [film] 1694 (C=O), 1597, 1538, 1493, 1428, 1259, 1164, 1089 and 1026; δ_H 7.66 (2H, d, *J* 8.3, 2'- and 6'-H), 7.30 (2H, d, *J* 8.3, 3'- and 5'-H), 6.00 (1H, s, 3-H), 3.43 (1H, dd, *J* 18.1 and 6.5, 6-H_α), 2.90-2.82 (1H, m, 5-H), 2.77 (1H, dd, *J* 18.1 and 2.2, 6-H_β), 2.39 (3H, s, 2-Me), 2.27 (3H, s, *Ts*-Me) and 1.25 (3H, d, *J* 7.5, 5-Me); δ_C 199.7 (C=O), 159.7, 146.0, 138.1, 135.6 (all C), 130.4 (2'- and 6'-CH), 128.1 (C), 127.1 (3'- and 5'-CH), 105.2 (3-CH), 46.3 (5-CH), 32.8 (6-CH_2), 21.8 (*Ts*-Me), 16.9 (Me) and 14.6 (Me); m/z (APCI) 304 (M^+ + H, 100%) [Found: M^+ + H, 304.1001. $C_{16}H_{18}NO_3S$ requires 304.1002].

***trans*- and *cis*-4,5-Dihydro-4,5-dimethyl-2-phenylcyclopenta[*b*]pyrrol-6(1*H*)-one (25)**



24b **25**

***trans* and *cis*-4,5-Dihydro-4,5-dimethyl-2-phenyl-1-cyclopenta-[b]pyrrol-6(1H)-one 25:** A solution of the *N*-tosyl cyclopenta[b]pyrrolone **24b** (30 mg, 0.08 mmol) as a 6:1 ratio (*trans*/*cis*) in 10 M aqueous sodium hydroxide (5 ml) and methanol (5 ml) was refluxed for 5 h then cooled and the bulk of the methanol evaporated. The aqueous residue was acidified to pH 6 using 1 M hydrochloric acid then extracted with ether (2 x 50 ml). The combined extracts were dried ($MgSO_4$), filtered and evaporated. The residue was purified by coloun chromatography [petrol-EtOAc, 3:1] to give the *cyclopenta[b]pyrrol-6-one* **25** (17 mg, 95%) as a colourless solid and a 6:1 mixture of *trans* and *cis* isomers, which showed m.p. 168-171 ^{o}C, R_f 0.24 [petrol-EtOAc, 3:1], ν_{max} ($CHCl_3$) 3193, 1653, 1365, 1455, 1290, 1266 cm^{-1}, δ_H ($CDCl_3$, 400 MHz) 1.16 (0.43 H, d, *J* 7.2 Hz, 5-Me), 1.19 (0.43 H, d, *J* 7.8 Hz, 4-H), 1.29 (2.57 H, d, *J* 7.4 Hz, 4-Me), 1.32 (2.57 H, d, *J* 7.1 Hz, 5-Me), 2.47 (0.86 H, qd, *J* 7.4 and 2.6 Hz, 4-H), 2.75 (0.86 H, qd, *J* 7.1 and 2.6 Hz, 5-H), 3.06 (0.14 H, app. quintet, *J ca.* 7.4 Hz, 4-H), 3.31 (0.14 H, app. quintet, *J ca*. 7.0 Hz, 5-H), 6.41-6.42 (1H, m, 3-H, both isomers), 7.25-7.28 (1H, m), 7.34-7.38 (2H, m), 7.76-7.78 (2H, m) δ_C ($CDCl_3$, 100 MHz) *trans*-iosmer: 15.3, 19.6 (both Me), 37.7 (4-CH), 56.5 (5-CH), 102.4 (3-CH), 125.7 (2 x CH), 128.4 (CH), 128.9 (2 x CH), 131.7, 133.1, 146.7, 157.9 (all C), 193.9 (CO) [the *cis*-isomer could be identified by δ_C 12.3, 16.9 (both Me) and 32.1 (4-CH)], m/z (APCI) 226 (M^+ + H, 100%). [Found: M^+ + H, 226.1226. $C_{15}H_{16}NO$ requires 226.1226].