2-Bromo-*N*-(*p*-toluenesulfonyl)pyrrole: A Robust Derivative of 2-Bromopyrrole

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Abstract: 2-Bromo-*N*-(*p*-toluenesulfonyl)pyrrole (**2**), a crystalline stable derivative of 2-bromopyrrole (**1**) has been prepared in 80% yield by bromination of pyrrole, followed by conversion to the *N*-(*p*-toluenesulfonyl) derivative. This compound is stable indefinitely at ambient temperature. Compound **2** is an excellent substrate for Suzuki coupling with arylboronic acids.

Key words: 2-arylpyrroles, radical reactions, Suzuki coupling, palladium catalysis, *p*-toluenesulfonyl protecting group

Several years ago our group described the synthesis and pharmacology of a series of *N*-alkyl-3-(1-naphthoyl)pyrroles which are ligands for the cannabinoid central nervous system (CB_1) receptor.[1] Relative to similarly substituted cannabimimetic indoles, these compounds show at best modest affinity for the CB_1 receptor and have corresponding diminished potency in vivo.[1,2] Both these indoles and pyrroles were designed on the basis of a hypothesis that the 3-acyl group which is present in these compounds is involved in a hydrogen bonding interaction with the receptor.[1,2] However, subsequent experiments have provided convincing evidence that the 3-acyl group is not essential for binding to the CB_1 receptor and suggest that cannabimimetic indoles and indenes interact with the receptor primarily by aromatic stacking.[3] This hypothesis suggested that *N*-alkyl-2-aryl-4-(1-naphthoyl)pyrroles should have greater receptor affinity than the *N*-alkyl-3-(1-naphthoyl)pyrroles reported previously due to the presence of an additional aromatic ring.

The synthesis of the target *N*-alkyl-2-aryl-4-(1-naphthoyl)pyrroles requires a convenient source of 2-arylpyrroles. Substituted pyrroles are frequently tedious to prepare, and many of the syntheses are plagued by low yields and difficult purification of the final product. Most of the reported methods center around either ring expansion of a suitably substituted precursor[4–6] or addition to conjugated systems followed by ring closure.[7–9] Arylketoximes have been alkylated then cyclized to a 2-arylpyrrole under basic conditions.[10–12] Cycloaddition of 2,3-butadienoates and dimethyl acetylenedicarboxylate with imines can also be used to form substituted pyrrolidines that can be oxidized to the pyrrole using DDQ or TBAF.[13] However, these linear methods are ill-suited to a rapid parallel synthesis, because they require that each starting 2-arylpyrrole must be prepared individually.

Previous workers have employed Suzuki chemistry to prepare 2-arylpyrroles, employing either *N*-BOC-pyrrole-2-boronic acid[14] or *N*-BOC protected 2-bromopyrrole.[15] Although *N*-BOC-pyrrole-2-boronic acid is reported to be be readily available by the procedure of Martina et al.,[16] in which initial lithiation followed by quenching with trimethyl borate, and hydrolysis provides the boronic acid, this approach did not appear appealing due to reported instability of *N*-BOC-pyrrole-2-boronic acid.[17] Also, the reported yields for the Suzuki reactions of this boronic acid are variable (16–98%) and in the case of several simple aryl halides with electron releasing or weakly electron withdrawing groups the yields are at the lower end of this range.[14] *N*-Phenylsulfonyl-pyrrole-2-boronic acid has also been employed in Suzuki couplings, however the reported yield for the preparation of the boronic acid is less than 10%.[17]

An alternative route employing *N*-BOC protected 2-bromopyrrole is reported to give excellent yields (90–99%) in Suzuki couplings with four simple arylboronic acids.[15] However, *N*-BOC-2-bromopyrrole as previously described by Cava, et al.[18] is a quite sensitive compound which is best stored as a 20–25% solution in hexane at –10 °C, under which conditions it is stable for several months. In order to obtain a more robust derivative of 2-bromopyrrole, an *N*-*p*-toluenesulfonyl group was investigated as an alternative to *N*-BOC, since the toluenesulfonyl group should prove to be considerably less sensitive to subsequent conversions.[19]

Two groups have previously reported the preparation of 2-bromo-*N*-arylsulfonylpyrroles.[20,21] Groenendaal et al. employed the stannylation of 2-lithio-*N*-benzenesulfonylpyrrole using trimethyltin chloride.[20] This procedure is not attractive for the preparation of gram quantities of 2-bromo-*N*-*p*-toluenesulfonylpyrrole due to the toxicity and cost of trimethyltin chloride. In an initial approach to the preparation of *N*-tosyl-2-bromopyrrolehe the direct bromination of pyrrole with NBS, followed by in situ protection of nitrogen was attempted. This procedure gave complex mixtures of products of variable composition and although the desired product could be detected spectroscopically, pure material could not be isolated. Subsequently, Koike et al. reported the preparation of *N*-tosyl-2-bromopyrrole by a route similar to that which we had explored.[21] Repetition of the experimental procedure re-

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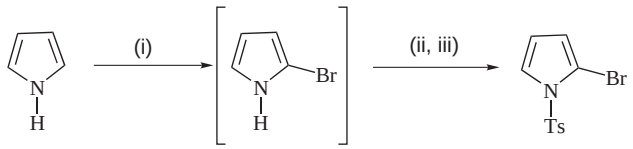
ported by these workers gave a complex mixture. Chromatography of this mixture gave a major fraction, analysis of which by GC/MS indicated that it contained an approximately eqimolar mixture of *N*-tosyl-2-bromopyrrole and a dibrominated compound, plus several other compounds.

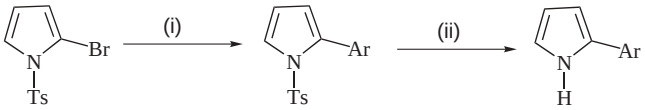


Scheme 1 *Reagents*: (i) 1,3-Dibromo-5,5-dimethylhydantoin, THF, –78 °C, AIBN or ambient light; (ii) *n*-Bu_3N, Et_2O; (iii) TsCl, NaH.

N-Tosyl-2-bromopyrrole was finally prepared reproducibly by a modification of Cava's procedure in which pyrrole was treated with 1,3-dibromo-5,5-dimethylhydantoin in the presence of AIBN at –78 °C to effect regioselective bromination at the 2-position (Scheme 1).[18] Treatment of the cold mixture with ether and Bu_3N precipitated the residual hydantoin and its reduction products. Subsequent addition of *p*-toluenesulfonyl chloride and sodium hydride initially gave a low yield of **2**. GC-MS analysis of the crude mixture showed the presence of a significant quantity of unprotected 2-bromopyrrole (**1**). This unprotected compound turns black within minutes upon concentration from solution. Increasing the equivalents of *p*-toluenesulfonyl chloride from 1.1 to 2.0 and the equivalents of sodium hydride from 1.5 to 3.0 gives **2** in a reproducible yield of 80% as a gray crystalline solid of sufficient purity for use in subsequent reactions. This material is stable to light and air for several months at ambient temperature. Recrystallization from isopropyl alcohol provides the pure material as white crystals, mp 105–106 °C. The ^1H and ^{13}C NMR spectra of **2** are consistent with the assigned structure (see Experimental) and the structure was confirmed by X-ray crystallography.[22,23]

A study of the bromination step was carried out in order to determine if the reaction proceeds via a free radical or ionic mechanism. Removal of the AIBN catalyst had no effect on the overall yield of **2**, however, exclusion of light resulted in a mixture of **2** and *N*-tosylpyrrole. One minute of irradiation by shortwave (254 nm) UV light followed by exclusion of all light for the duration of the bromination step resulted in moderate yields of **2**. These results indicate that the reaction is best catalyzed by the continual exposure to ambient light, and is thus probably radical-mediated. The addition of Bu_3N minimizes the extent of dibromination and the amount of unbrominated *N*-*p*-toluenesulfonylpyrrole. Also, polymeric materials are obtained if the reaction temperature is allowed to increase above –50 °C.

N-Tosyl-2-bromopyrrole (**2**) was employed in Suzuki coupling reactions (Scheme 2) and is an excellent substrate for this reaction. Table 1 provides examples of Suzuki coupling products (**3**) synthesized utilizing this synthon under standard Suzuki conditions using commercially available arylboronic acids.[24,25] This procedure gives moderate to good yields of the corresponding *N*-tosyl-2-arylpyrrole, except with 3-nitrophenylboronic acid, which provides only a 24% yield (entry 7). All Suzuki products have ^1H and ^{13}C NMR spectra, which are consistent with the assigned structures, and all gave satisfactory analytical data. In order to determine the feasability of removing the *N*-*p*-toluenesulfonyl group, the base hydrolysis of *N*-tosyl-2-(4-methoxyphenyl)pyrrole was carried out to provide the 2-arylpyrrole (**4**, Ar = 4-methoxyphenyl) in excellent yield.[26]



Scheme 2 *Reagents*: (i) $ArB(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3, toluene, EtOH, H_2O, reflux; (ii) NaOH, EtOH, reflux.

Table 1 Suzuki Reactions of *N*-*p*-Toluenesulfonyl-2-bromopyrrole[a]

Entry	**3**	Yield[b]
1	Ar = 4-MeC_6H_4	68
2	Ar = 3-ClC_6H_4	76
3	Ar = 4-ClC_6H_4	60
4	Ar = 4-$MeOC_6H_4$	80
5	Ar = 1-Naphthyl	52
6	Ar = Phenyl	75
7	Ar = 3-$NO_2C_6H_4$	24

[a] For the general experimental procedure and characterization data see ref.[25,]
[b] Isolated yield.

In summary, *N*-tosyl-2-bromopyrrole provides a robust derivative of 2-bromopyrrole, which promises to be a versatile precursor for substituted pyrroles. This compound is an excellent substrate for Suzuki reactions, and should also prove useful in other metal-mediated coupling reactions.

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(23) **Experimental Procedure for the Preparation of 2.** To a solution of 3.1 mL of **1** (44.7 mmol) in 120 mL of freshly distilled THF in a flame-dried flask under N_2 at –78 °C was added 6.53 g (22.4 mmol) of 1,3-dibromo-5,5-dimethylhydantoin. The mixture was stirred for 30 min and allowed to stand for an additional 3.5 h under ambient room light at –78 °C. To this solution were added 4 mL of Bu_3N and 180 mL of freshly distilled Et_2O and the mixture was stirred for 10 min at –78 °C. The resulting gray precipitate was removed by filtration(vacuum) and the solution was concentrated in vacuo to remove the Et_2O. To this solution was added 17.04 g (89.4 mmol) of *p*-toluenesulfonyl chloride and the inert atmosphere was reestablished. The solution was cooled to 0 °C and 5.36 g (134.0 mmol) of NaH (60% in mineral oil) was added cautiously. The mixture was stirred for 18 h at ambient temperature and 60 mL of H_2O were added. The mixture was extracted with Et_2O and the ether extracts were washed with successive portions of 1 M HCl and sat. aq $NaHCO_3$. This mixture was combined with an equal volume of 2 M NaOH and was stirred for 2 h at r.t. The layers were separated and the organic extract was washed repeatedly with H_2O and 2 M NaOH. The organic layer was dried ($MgSO_4$) and concentrated in vacuo to give a light brown solid. Recrystallization from isopropyl alcohol gave 10.73 g (80%) of 2-bromo-1-(*p*-toluenesulfonyl)pyrrole as a white crystalline solid: mp 105–106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 6.23–6.29 (m, 2 H), 7.32 (d, *J* = 8.3 Hz, 2 H), 7.46 (dd, *J* = 2.0, 3.5 Hz, 1 H), 7.81 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 145.5, 135.1, 129.9, 127.8, 124.2, 117.9, 113.5, 112.5, 100.0, 21.7. MS (EI): *m/z* (%) = 301 (27), 299 (28), 155 (56), 91 (100). Anal. Calcd for $C_{11}H_{10}BrNO_2S$: C, 44.02; H, 3.36; N, 4.67. Found: C, 44.65; H, 3.36; N, 4.67. Although this compound is homogeneous to TLC, GC/MS, ^{1}H and ^{13}C NMR, aceptable analytical data could not be obtained.
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(25) **Experimental Procedure for the Preparation of 4 (Ar = 4-Methoxyphenyl).** A mixture of 0.020 g (0.02 mmol) of $Pd(PPh_3)_4$ and 4.4 mL of distilled toluene was stirred under an inert atmosphere for 5 min at ambient temperature, and 0.470 g (1.6 mmol) of 2-bromo-*N*-*p*-toluenesulfonylpyrrole was added as a solid, followed by 0.256 g (2.4 mmol) of Na_2CO_3 in 2.2 ml of H_2O. To this mixture was added 0.250 g (1.6 mmol) of 4-methoxyphenylboronic acid in 3 mL of 95% EtOH. The mixture was heated at reflux for 6 h, cooled to ambient temperature, and extracted into EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated in vacuo to give a brown solid. Recrystallization from 2-propanol gave 0.412 g (80%) of 2-(4-methoxyphenyl)-*N*-tosylpyrrole as a white crystalline solid: mp 120–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 3.84 (s, 3 H), 6.10 (dd, *J* = 1.8, 3.0 Hz, 1 H), 6.28 (t, *J* = 3.4 Hz, 1 H), 6.81–6.86 (m, 2 H), 7.09–7.17 (m, 4 H), 7.25–7.26 (m, 2 H), 7.41 (dd, *J* = 1.8, 3.1 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.5, 55.2, 111.9, 112.7, 115.3, 123.7, 127.1, 129.3, 132.2. MS (EI): *m/z* (%) = 327 (17), 172 (100). Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23; N, 4.28. Found: C, 66.27; H, 5.31; N, 4.31.
Compound 3 (Ar = Phenyl): mp 123–124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 6.15 (dd, *J* = 1.7, 3.2 Hz, 1 H), 6.30 (t, *J* = 3.3 Hz, 1 H), 7.09 (d, *J* = 8.3 Hz, 2 H), 7.21–7.38 (m, 7 H), 7.44 (dd, *J* = 1.7, 3.3 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.6, 112.0, 115.7, 124.1, 127.1, 127.3, 128.2, 129.3, 130.9, 131.4, 135.6, 136.0, 144.6. MS (EI): *m/z* (%) = 297 (38), 142 (100). Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08, N, 4.71. Found: C, 68.39; H, 5.03, N, 4.56.
Compound 3 (Ar = 4-Methylphenyl): mp 120–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 2.39 (s, 3 H), 6.11 (dd, *J* = 1.7, 3.2 Hz, 1 H), 6.28 (t, *J* = 3.3 Hz, 1 H), 7.06–7.12 (m, 6 H), 7.24–7.16 (m, 2 H), 7.41 (dd, *J* = 1.8, 3.3 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.3, 21.5, 112.0, 115.5, 123.9, 127.0, 128.0, 128.5, 129.3, 130.7, 135.7, 136.1, 138.0, 144.5. MS (EI): *m/z* (%) = 311 (40), 156 (100). Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.43; H, 5.50, N, 4.50. Found: C, 69.69; H, 5.51, N, 4.42.
Compound 3 (Ar = 3-Chlorophenyl): mp 91–92 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 6.16–6.17 (m, 1 H), 6.30 (t, *J* = 3.2 Hz, 1 H), 7.04–7.34 (m, 8 H), 7.45–7.46 (m, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.5, 111.9, 116.1, 124.4, 127.0, 128.2, 128.7, 129.2, 129.4, 130.6, 133.1, 134.1, 135.4, 145.0. MS (EI): *m/z* (%) = 331 (37), 176 (100). Anal. Calcd for $C_{17}H_{14}ClNO_2S$: C, 61.53; H, 4.25; N, 4.22. Found: C, 61.25; H, 4.34; N, 4.25.
Compound 3 (Ar = 1-Naphthyl): mp 146–147 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3 H), 6.26 (dd, *J* = 1.7, 2.2 Hz, 1 H), 6.41 (t, *J* = 3.3 Hz, 1 H), 6.79 (d, *J* = 8, 2 Hz, 2

H), 7.03 (d, *J* = 8.3 Hz, 2 H), 7.09–7.26 (m, 2 H), 7.33–7.44 (m, 3 H), 7.59 (dd, *J* = 1.7, 3.3 Hz, 1 H), 7.77 (d, *J* = 8.2 Hz, 1 H), 7.86 (d, *J* = 8.2 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.3, 111.0, 116.5, 122.8, 124.4, 125.3, 125.8, 127.2, 127.6, 128.6, 129.0, 129.1, 130.5, 131.9, 132.9, 133.7, 135.0, 144.4. MS (EI): *m/z* (%) = 347(34), 192(100); Anal. Calcd for $C_{21}H_{17}NO_2S$: C, 72.60; H, 4.93; N, 4.03. Found: C, 72.36; H, 4.96; N, 3.99.

Compound 3 (Ar = 3-Nitrophenyl): pale pink gum. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 6.27 (dd, *J* = 1.7, 3.1 Hz, 1 H), 6.36 (t, *J* = 3.3 Hz, 1 H), 7.14 (d, *J* = 8.3 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 7.49 (dd, *J* = 1.6, 3.9 Hz, 1 H), 7.53 (d, *J* = 7.9 Hz, 1 H), 7.68 (dt, *J* = 1.3, 7.7 Hz, 1 H), 7.94 (t, *J* = 1.9 Hz, 1 H), 8.18–8.22 (m, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.5, 112.4, 117.1, 122.9, 125.0, 125.1, 126.8, 128.3, 129.6, 133.0, 135.3, 136.9, 145.3, 147.3. MS (EI): *m/z* (%) = 342 (100), 203 (26). HRMS calcd for $C_{17}H_{14}N_2O_4S$: 342.0674. Found: 342.0670.

(26) A mixture of 0.050 g (0.15 mmol) of 2-(4-methoxyphenyl)-*N*-tosylpyrrole in 0.6 mL of EtOH and 0.2 mL of 15% ethanolic NaOH was stirred at reflux temperature for 3 h. The solution was concentrated in vacuo; the residue was dissolved in CH_2Cl_2 and washed with H_2O. The organic layer was dried ($MgSO_4$) and concentrated in vacuo to give 0.025 g (97%) of 2-(4-methoxyphenyl)pyrrole as a white solid: mp 143–144 °C (lit. mp 147 °C[27]). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 6.27 (dd, *J* = 2.8, 5.7 Hz, 1 H), 6.40 (t, *J* = 3.5 Hz, 1 H), 6.79 (dd, *J* = 2.4, 3.9 Hz, 1 H), 6.88–6.91 (m, 2 H), 7.36–7.39 (m, 2 H), 8.32 (br s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.3, 104.8, 109.9, 114.3, 118.1, 125.2, 125.9, 132.1, 158.2. MS (EI): *m/z* (%) = 245 (7), 173 (70), 158 (100). The spectroscopic data agree with those reported previously.[27]

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