SHORT PAPER

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A facile synthesis of functionalised 3*H*-pyrroles promoted by magnesium and a catalytic amount of iodine†

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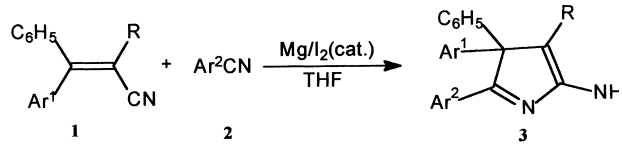
The intermolecular reductive coupling cyclisation of 3,3-diaryl-2-cyanoacrylonitriles or ethyl 3,3-diaryl-2-cyanoacrylates with aromatic nitriles with magnesium and catalytic iodine in THF afforded 3*H*-pyrroles in good yields under neutral and mild conditions.

Keywords: 3*H*-pyrroles, magnesium, acrylonitriles, acrylate esters, reductive coupling

3*H*-Pyrroles constitute a little-known ring system with a potentially rich chemistry in terms of rearrangement, addition, and cycloaddition reactions.[1] Although other types of pyrroles have been described in the literature, the 3*H* compounds have been positively characterised only several years ago[2] and have received little attention since. Some 3*H* compounds showed antimicrobial activity against gram-positive bacteria, and some have antitumor activity.[3] The methods for preparing 3*H*-pyrroles are by reaction of electrophiles with 1*H*-pyrroles;[4] cyclisation of open-chain compounds;[5] 1,3-dipolar cycloadditions using nitrile ylides[6] and preparation from pyrrolines[2,7], but the above methods usually have low yields, the reaction conditions are often inconvenient and the starting materials are not easily accessible.

Samarium diiodide, a versatile single-electron transfer reagent, is widely used in synthetic organic chemistry.[8] Recently, we reported the preparation of polysubstituted 3*H*-pyrroles from 3,3-diaryl-2-cyanoacrylonitriles or ethyl 3,3-diaryl-2-cyanoacrylates and aromatic nitriles mediated by this compound.[9] Although SmI_2 is a useful reagent, its storage is difficult because it is very sensitive to air oxidation. Furthermore, it is costly and not easily available. On the other hand, metallic magnesium is stable in air and has strong reducing power. This stimulated us to use the more convenient and cheaper metallic magnesium directly instead of samarium(II) iodide in the above mentioned reaction. According to the literature, many types of additives ($HgCl_2$,[10] $HgBr_2$,[11] $(NH_4)_2SO_4$,[12] $TiCl_4$,[13] I_2,[14] *etc*.) should be added because of the low reactivity of metallic magnesium. In addition, the direct utilisation of magnesium in methanol can also promote several types of reaction.[15] In this paper, we describe a novel method for the synthesis of functionalised 3*H*-pyrroles from 3,3-diaryl-2-cyanoacrylonitriles and ethyl 3,3-diaryl-2-cyanoacrylates with aromatic nitriles using magnesium with a catalytic quantity of iodine as a promoter in THF. To the best of our knowledge there is no prior report on the synthesis of 3*H*-pyrroles in this way.



Scheme 1

In our experiments, when 3,3-diaryl-2-cyanoacrylonitriles or ethyl 3,3-diaryl-2-cyanoacrylates (**1**) and aromatic nitriles (**2**) were treated with magnesium / iodine in dry THF at reflux under a nitrogen atmosphere, the reductive cyclisation products, the 3*H*-pyrroles (**3**) were obtained in good yields (Scheme 1). Table 1 summarises our results. The reactions are completed in 20–140 minutes at reflux. When the substrates are diethyl 3,3-diaryl-2-cyanoacrylate and aromatic nitriles, the cyclisation takes place to the C≡N bond, rather than the C=O bond. At the same time, fluoro, chloro, bromo, alkoxyl groups, *N*,*N*-disubstituted amino groups bearing on the aromatic rings were not reduced and have no influence on the rate of intermolecular reductive cyclisation. It should be noted that when the substrate **2** is 4-chlorobenzonitrile or 3-bromobenzonitrile, the desired products were obtained without contamination by any product of a Grignard reaction. However, when ethyl 3,3-diaryl-2-cyanoacrylate was used as substrate, the yields were comparatively low. Unlike the aromatic nitriles, which react smoothly with substrates **1** in the Mg/I_2 system, benzyl cyanide and acetonitrile turned out to be less reactive, and the desired functionalised 3*H*-pyrroles were not obtained. In addition, 1-phenyl-2,2-dicyanoethylene and 1-phenyl-1-methyl-2,2-dicyanoethylene failed to react with benzonitrile to give the corresponding product under the same conditions.

Though the detailed mechanism of the above reaction has not yet been clarified, according to the previous literature,[9,16] a possible mechanism for the formation of the 3*H*-pyrroles may be proposed as is shown in Scheme 2.

In conclusion, the present procedure is an efficient method for the synthesis of 3*H*-pyrroles. With its simplicity and milder reaction conditions, this procedure will offer an easy access to substituted 3*H*-pyrroles with varied substitution patterns in moderate to good yields.

Experimental

General experimental details: Melting points were obtained on an electrothermal melting point apparatus and were uncorrected. Infrared spectra were recorded on a Bruker Vector 22 spectrometer using KBr pellets. ^1H and ^{13}C NMR: spectra were recorded on a Bruker 400MHz instrument as $CDCl_3$ or DMSO-d_6 solutions using TMS as internal standard. Chemical shifts (δ) were expressed in ppm downfield from internal standard TMS and coupling constants *J* were given in Hz. Mass spectra were recorded on a HP 5989B MS spectrometer. Elemental analyses were performed on an EA-1110 instrument. Metallic magnesium and all solvents were purchased from commercial sources, without further purification before use.

General procedure for the preparation of 3H-pyrroles (**3**): To Mg turnings (96 mg, 4 mmol), 3,3-diaryl-2-cyanoacrylonitriles[17]or ethyl 3,3-diaryl-2-cyanoacrylates[18] (1mmol) and nitrile (1.2mmol) in anhy-

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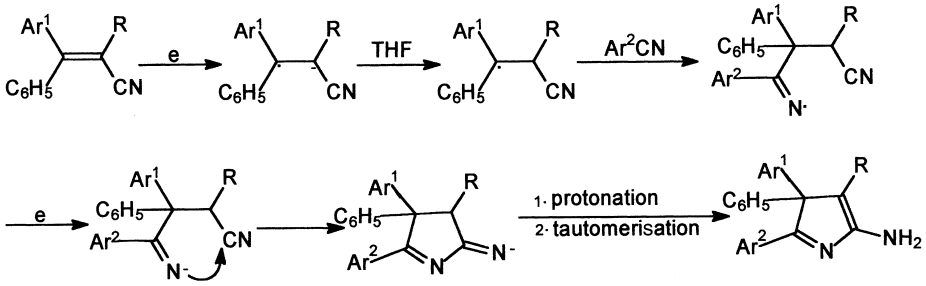
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 2

drous THF (15 ml) was added I_2 (100 mg, 0.4 mmol) under a nitrogen atmosphere. The resultant orange slurry was stirred vigorously at reflux. After being stirred for a given time (Table 1; the reaction was monitored by TLC), the reaction was quenched with dilute HCl (0.1 mol/l, 15 ml) and extracted with ethyl acetate (3 × 30 ml). The organic phase was washed with water (20ml), brine (15 ml), and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure to give the crude product, which was purified by preparative TLC using ethyl acetate and cyclohexane (1: 4) as eluant.

2-Amino-4,5-diphenyl-4-(4-methylphenyl)-4H-pyrrole-3-carbonitrile (**3a**): m.p. 205–206 °C; IR: 3354, 3187, 3057, 2188, 1651, 1601 cm^{-1}; ^1H NMR: δ 7.82–7.84 (2H, d), 7.26–7.42 (9H, m), 7.10–7.19 (4H, m), 5.15 (2H, br s), 2.31 (3H, s); ^{13}C NMR: δ 185.9 165.5, 139.5, 137.2, 136.2 132.5 131.6, 130.1, 129.9, 129.3, 129.0, 128.4, 127.9, 118.8, 80.2, 73.1, 21.1; MS: *m/z* (%) 349 (M^+, 100), 334 (4.89), 231 (30.61), 104 (27.24), 77 (45.80); Anal. Calcd. For $C_{24}H_{19}N_3$: C, 82.49; H, 5.48; N, 12.03; Found: C, 82.33; H, 5.21; N, 12.21.

2-Amino-5-(3-bromophenyl)-4-(4-methylphenyl)-4-phenyl-4H-pyrrole-3-carbonitrile (**3b**): m.p. 157–159 °C; IR: 3343, 3279, 2184, 1672, 1651, 1594 cm^{-1}; ^1H NMR: δ 8.11 (1H, s), 7.60–7.62 (1H, d), 7.48–7.50 (1H, d), 7.09-7.31 (10H, m), 5.22 (2H, br s), 2.32 (3H, s); ^{13}C NMR: δ 185.6, 163.8, 137.8, 137.7, 134.7, 134.4, 133.5, 132.5, 129.7, 129.6, 128.9, 128.7, 128.3, 128.2, 127.9, 122.6, 117.1, 84.7, 74.1, 21.0; MS: *m/z* (%) 427 (M^+, 100), 429 (M^++2, 100), 412 (6.54), 414 (7.01), 245 (46.46), 231 (74.62), 91(18.67), 77(36.31); Anal. Calcd. For $C_{24}H_{18}BrN_3$: C, 67.30; H, 4.24; N, 9.81; Found: C, 67.22; H, 4.09; N, 9.91.

2-Amino-5-(4-methoxyphenyl)-4-(4-methylphenyl)-4-phenyl-4H-pyrrole-3-carbonitrile (**3c**): m.p. 188–190 °C; IR: 3344, 3242, 2930, 2183, 1646, 1604 cm^{-1}; ^1H NMR: δ 7.81–7.83 (2H, d), 7.25–7.30 (5H, m), 7.16–7.18 (2H, d), 7.10–7.12 (2H, d), 6.75–6.77 (2H, d), 5.18 (2H, br s), 3.77 (3H, s), 2.31 (3H, s); ^{13}C NMR: δ 186.7, 164.5, 162.7, 138.6, 137.3, 135.3, 132.2, 129.5, 128.7, 128.4, 128.3, 127.5, 124.3, 117.7, 113.7, 83.5, 73.5, 55.3, 21.0; MS: *m/z* (%) 379 (M^+, 100), 364 (14.44), 246 (30.94), 231 (40.94), 91 (22.40), 77 (23.54); Anal. Calcd. For $C_{25}H_{21}N_3O$: C, 79.13; H, 5.58; N, 11.07; Found: C, 79.25; H, 5.45; N, 11.01.

2-Amino-5-(4-chlorophenyl)-4-(4-methylphenyl)-4-phenyl-4H-pyrrole-3-carbonitrile (**3d**): m.p. 178–179 °C; IR: 3332, 3186, 2193, 1678, 1648, 1608 cm^{-1}; ^1H NMR: δ 7.76–7.78 (2H, d), 7.22–7.32 (7H, m), 7.06–7.14 (4H, m), 5.23 (2H, br s), 2.31 (3H, s); ^{13}C NMR: δ 186.0, 164.1, 138.4, 137.9, 137.7, 134.6, 131.3, 129.9, 129.6, 128.9, 128.6, 128.3, 128.2, 127.8, 117.2, 84.4, 73.9, 21.0; MS: *m/z* (%) 383 (M^+, 100), 385 (M^++2, 37.32), 368 (7.40), 231 (40.55), 77 (12.37). Anal. Calcd. For $C_{24}H_{18}ClN_3$: C, 75.09; H, 4.73; N, 10.95; Found: C, 75.17; H, 4.85; N, 11.04.

2-Amino-5-(4-fluorophenyl)-4-(4-methylphenyl)-4-phenyl-4H-pyrrole-3-carbonitrile (**3e**): m.p. 183–185 °C; IR: 3354, 3191, 2188, 1673, 1653, 1603 cm^{-1}; ^1H NMR: δ 7.85–7.86 (2H, m), 7.26–7.31 (5H, m), 7.12–7.16 (4H, m), 6.94–6.97 (2H, m), 5.14 (2H, br s), 2.32 (3H, s); ^{13}C NMR: δ 186.0, 166.2, 164.0, 163.6, 138.0, 137.6, 134.7, 132.5, 132.4, 129.6, 128.9, 128.3, 128.2, 127.9, 127.8, 117.2, 115.7, 115.5, 84.3, 73.9, 21.0; MS: *m/z* (%) 367 (M^+, 4.0), 352 (7.68), 245 (20.58), 231 (34.68), 77 (8.38); Anal. Calcd. For $C_{24}H_{18}FN_3$: C, 78.45; H, 4.94; N, 11.43; Found: C, 78.37; H, 4.87; N, 11.59.

2-Amino-5-(3,4-methylenedioxyphenyl)-4-(4-methylphenyl)-4-phenyl-4H-pyrrole-3-carbonitrile (**3f**): m.p. 203–205 °C; IR: 3480, 3377, 2908, 2183, 1645, 1606 cm^{-1}; ^1H NMR: δ 7.40 (1H, s), 7.25–7.39 (6H, m), 7.10–7.17 (4H, q), 6.63–6.65 (1H, d), 5.94 (2H, s), 5.15 (2H, br s), 2.31 (3H, s); ^{13}C NMR: δ 186.4, 164.3, 150.9, 147.7, 138.5, 137.4, 135.2, 129.5, 128.8, 128.4, 128.3, 127.6, 126.5, 125.9, 117.6, 109.5, 107.9, 101.7, 83.9, 73.6, 21.0; MS: *m/z* (%)393 (M^+, 100), 378 (7.56), 246 (23.54), 231 (37.21), 77 (8.12); Anal. Calcd. For $C_{24}H_{19}N_3O_2$: C, 76.32; H, 4.88; N, 10.68; Found: C, 76.45; H, 4.93; N, 10.47.

2-Amino-5-(3-bromophenyl)-4,4-diphenyl-4H-pyrrole-3-carbonitrile (**3g**): m.p. 208–209 °C (lit.[9] 209–211 °C); IR: 3462, 3270, 2192,

Table 1 Preparation of 3*H*-pyrroles promoted by magnesium / iodine[a]

Product	Mol. formula	Ar^1	Ar^2	R	T/min	Yield/%[b]
3a	$C_{24}H_{19}N_3$	4-$CH_3C_6H_4$	C_6H_5	CN	90	85
3b	$C_{24}H_{18}BrN_3$	4-$CH_3C_6H_4$	3-BrC_6H_4	CN	40	79
3c	$C_{25}H_{21}N_3O$	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	CN	95	73
3d	$C_{24}H_{18}ClN_3$	4-$CH_3C_6H_4$	4-ClC_6H_4	CN	60	81
3e	$C_{24}H_{18}FN_3$	4-$CH_3C_6H_4$	4-FC_6H_5	CN	20	92
3f	$C_{25}H_{19}N_3O_2$	4-$CH_3C_6H_4$	3,4-$OCH_2OC_6H_3$	CN	120	65
3g	$C_{23}H_{16}BrN_3$	C_6H_5	3-BrC_6H_4	CN	40	77
3h	$C_{24}H_{19}N_3$	C_6H_5	3-$CH_3C_6H_4$	CN	90	79
3i	$C_{24}H_{19}N_3O$	C_6H_5	4-$CH_3OC_6H_4$	CN	90	81
3j	$C_{23}H_{17}N_3$	C_6H_5	C_6H_5	CN	90	76
3k	$C_{25}H_{22}N_4$	C_6H_5	4-$Me_2NC_6H_4$	CN	120	69
3l	$C_{24}H_{14}N_3O_2$	C_6H_5	3,4-$OCH_2OC_6H_3$	CN	120	65
3m	$C_{23}H_{16}ClN_3$	C_6H_5	4-ClC_6H_4	CN	55	82
3n	$C_{30}H_{25}N_3O$	4-$C_6H_5C_6H_4$	4-$CH_3OC_6H_4$	CN	90	75
3o	$C_{27}H_{22}N_2O_2$	C_6H_5	C_6H_5	CO_2Et	80	52
3p	$C_{28}H_{24}N_2O_2$	C_6H_5	3-$CH_3C_6H_4$	CO_2Et	75	56
3q	$C_{28}H_{24}N_2O_3$	C_6H_5	4-$CH_3OC_6H_4$	CO_2Et	90	47
3r	$C_{29}H_{27}N_3O_2$	C_6H_5	4-$Me_2NC_6H_4$	CO_2Et	7.5	50
3s	$C_{28}H_{22}N_2O_4$	C_6H_5	3,4-$OCH_2OC_6H_3$	CO_2Et	120	43
3t		C_6H_5	$C_6H_5CH_2$	CN	140	0
3u		C_6H_5	CH_3	CN	180	0
3v		H	C_6H_5	CN	120	0
3w		CH_3	C_6H_5	CN	120	0

[a]1 equiv. of **1**, 1.2 equiv. of **2**, 4 equiv. of magnesium turnings and 0.4 equiv. of iodine were used.
[b]Yields of isolated products.
[c]5 equiv of acetonitrile was used.

1653, 1592 cm^{-1}; ^{1}H NMR: δ 7.70 (1H, s), 7.20–7.22 (1H, d), 7.11–7.09 (1H, d), 6.94-6.85 (10H, m), 6.75-6.71 (1H, t), 5.29 (2H, br s). ^{13}C NMR: δ 185.57, 163.89, 137.56, 134.78, 133.39, 132.49, 129.66, 128.96, 128.65, 128.28, 127.93, 122.57, 117.53, 84.58, 74.31.

2-Amino-4,4-diphenyl-5-(3-methylphenyl)-4H-pyrrole-3-carbonitrile (**3h**): m.p. 186–187 °C (lit.[9] 186–188 °C); IR: 3348, 3195, 2185, 1670, 1598 cm^{-1}; ^{1}H NMR: δ 7.73 (1H, s), 7.50–7.45 (1H, d), 7.24–7.30 (10H, m), 7.21–7.17 (1H, d), 7.08–7.12 (1H, t), 5.32 (2H, br s), 2.25 (3H, s).

2-Amino-4,4-diphenyl-5-(4-methoxylphenyl)-4H-pyrrole-3-carbonitrile (**3i**): m.p. 200–201 °C (lit.[9] 199–200 °C); IR: 3460, 3205, 2188, 1654, 1600 cm^{-1}; ^{1}H NMR: δ 7.78–7.80 (2H, d), 7.23–7.29 (10H, m), 6.73–6.75 (2H, d), 5.33 (2H, br s), 3.75 (3H, s).

2-Amino-4,4,5-triphenyl-4H-pyrrole-3-carbonitrile (**3j**): m.p. 217–219 °C (lit.[9] 218–220 °C); IR: 3348, 3192, 2191, 1670, 1602 cm^{-1}; ^{1}H NMR: δ 7.78-7.80 (2H, m), 7.21–7.37 (13H, m), 5.48 (2H, br s).

2-Amino-5-(4-dimethylaminophenyl)-4,4-diphenyl-4H-pyrrole-3-carbonitrile (**3k**): m.p. 230–232 °C (lit.[9] 230–232 °C); IR: 3395, 3205, 2182, 1648, 1606 cm^{-1}; ^{1}H NMR: δ 7.73–7.76 (2H, d), 7.21–7.31 (10H, m), 6.49–6.47 (2H, d), 5.31 (2H, br s), 2.97 (6H, s).

2-Amino-4,4-diphenyl-5-(3,4-methylenedioxyphenyl)-4H-pyrrole-3-carbonitrile (**3l**): m.p. 191–192 °C (lit.[9] 190–191 °C); IR: 3346, 3189, 2184, 1670, 1597 cm^{-1}; ^{1}H NMR: δ 7.39 (1H, s), 7.25–7.38 (11H, m), 6.63-6.65 (1H, d), 5.94 (2H, s), 5.19 (2H, br s).

2-Amino-5-(4-chlorophenyl)-4,4-diphenyl-4H-pyrrole-3-carbonitrile (**3m**): m.p. 196–198 °C (lit.[9] 195–197 °C); IR: 3341, 3210, 2188, 1652, 1592 cm^{-1}; ^{1}H NMR: δ 7.75–7.77 (2H, d), 7.21–7.33 (12H, m), 5.30 (2H, br s).

2-Amino-5-(4-methoxyphenyl)-4-phenyl-4-(4-phenylphenyl)-4H-pyrrole-3-carbonitrile (**3n**): m.p. 127–128 °C (lit.[9] 128–130 °C); IR: 3385, 3200, 2183, 1647, 1604 cm^{-1}; ^{1}H NMR: δ 7.81-7.84 (2H, m), 7.53–7.81 (4H, m), 7.30–7.41 (10H, m), 6.96 (2H, br s), 6.77–6.80 (2H, d), 3.76 (3H, s).

Ethyl 2-amino-4,4,5-triphenyl-4H-pyrrole-3-carboxylate (**3o**): m.p. 186–189 °C (lit.[9] 186–188 °C); IR: 3471, 3292, 1750, 1688, 1645 cm^{-1}; ^{1}H NMR: δ 7.66–7.68 (2H, m), 7.19–7.37 (13H, m), 6.29 (2H, br s), 4.01–3.96 (2H, q, *J* = 7.20 Hz), 1.02–0.98 (3H, t, *J* = 7.20 Hz).

Ethyl 2-amino-4,4-diphenyl-5-(3-methylphenyl)-4H-pyrrole-3-carboxylate (**3p**): m.p. 155–156 °C (lit.[9] 155–157 °C); IR: 3476, 3312, 1744, 1652, 1575 cm^{-1}; ^{1}H NMR: δ 7.59 (1H, s), 7.13–7.37 (12H, m), 7.05–7.08 (1H, t), 6.24 (2H, br s), 4.01–3.96 (2H, q, *J* = 7.04 Hz), 2.24 (3H, s), 1.03–0.99 (3H, t, *J* = 7.04 Hz).

Ethyl 2-amino-4,4-diphenyl-5-(3-methoxyphenyl)-4H-pyrrole-3-carboxylate (**3q**): m.p. 175–177 °C (lit.[9] 174–176 °C); IR: 3472, 3290, 1747, 1661, 1585 cm^{-1}; ^{1}H NMR: δ 7.71–7.69 (2H, d), 7.40–7.37 (4H, m), 7.25–7.17 (6H, m), 6.74–6.71 (2H, d), 6.26 (2H, br s), 4.01–3.96 (2H, q, *J* = 7.08 Hz), 3.74 (3H, s), 1.03–0.99 (3H, t, *J* = 7.04 Hz).

Ethyl 2-amino-5-(dimethylaminophenyl)-4,4-diphenyl-4H-pyrrole-3-carboxylate (**3r**): m.p. 190–191 °C (lit.[9] 190–192 °C); IR: 3470, 3198, 1749, 1655, 1608 cm^{-1}; ^{1}H NMR: δ 7.67–7.69 (2H, d), 7.41–7.43 (4H, m), 7.15–7.25 (6H, m), 6.44–6.46 (2H, d), 6.32 (2H, br s), 4.01–3.96 (2H, q, *J* = 7.12 Hz), 2.94 (6H, s), 1.03–0.99 (3H, t, *J* = 7.08 Hz).

Ethyl 2-amino-5-(3,4-methylenedioxyphenyl)-4,4-diphenyl-5-(3-methylphenyl)-4H-pyrrole-3-carboxylate (**3s**): m.p. 209–211 °C (lit.[9] 208–209 °C); IR: 3470, 3220, 1755, 1684, 1644 cm^{-1}; ^{1}H NMR: δ7.36-7.38 (4H, m), 7.20–7.26 (8H, m), 6.61–6.63 (1H, d), 6.18 (2H, br s), 5.91 (2H, s), 3.95–4.01 (2H, q, *J* = 7.08 Hz), 1.02–0.99 (3H, t, *J* = 7.00 Hz).

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