Convenient preparations of polysubstituted 3*H*-pyrroles promoted by SmI_2

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The intermolecular reductive coupling of 1,1-diaryl-2,2-dicyanoethylenes or 1,1-diaryl-2-cyano-2-ethoxycarbonylethylenes with aromatic nitriles induced by samarium(II) iodide has been studied. Polysubstituted 3*H*-pyrroles were prepared in good to excellent yields under neutral and mild conditions.

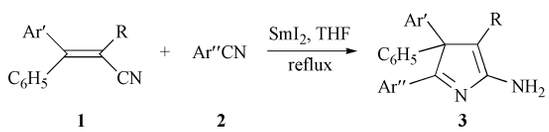
Introduction

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 pyrrole have been described in the literature, the 3*H* compounds, which were positively characterized several years ago,[2] have received little attention since. Some 3*H* compounds showed antimicrobial activity against Gram-positive bacteria, and some have antitumor activity.[3] To date, no general synthetic approaches to these compounds have been reported. The methods for preparing 3*H*-pyrroles are: reaction of electrophiles with 1*H*-pyrroles;[4] cyclization of open-chain compounds;[5] 1,3-dipolar cycloadditions using nitrile ylides[6] and preparation from pyrrolines.[2,7] However, the above methods usually have low yields, the reaction conditions are often inconvenient and the starting materials are not easily accessible. Therefore, development and introduction of a convenient, mild and efficient method for the preparation of polysubstituted 3*H*-pyrroles is of practical importance and is still in demand.

Since its introduction by Kagan *et al.*,[8] samarium diiodide (SmI_2) has been applied to a multitude of important synthetic transformations, which generally proceed with high chemoselectivity and high levels of stereochemical control.[9] A large variety of functional groups such as organic halides, carbonyl compounds, α-hetero-substituted carbonyl compounds, cyclopropyl ketones, epoxides, amine oxides, sulfoxides, phosphine oxides, sulfones, sulfonates, nitro and nitroso compounds, azo compounds, allyl acetates, and isoxazoles have been chemoselectively reduced by SmI_2.[9] Recently, Hong and Kang reported the decyanation of α-alkoxylcarbonyl substituted nitrile derivatives by samarium diiodide.[10] Yacovan and coworkers reported that 1,1-diaryl-2,2-dicyanoethylenes were quantitatively reduced to diphenylmethylmalononitrile without contamination by any dimeric products by this reagent.[11] 1,1-Diaryl-2,2-dicyanoethylenes can form radical anions like diaryl ketones due to the similarity between the $C{=}C(CN)_2$ and the C=O groups.[11,12] Our group has reported the cyclodimerization of arylmethylidenemalononitrile[13a] and the reductive coupling reactions of ketones and nitriles[13b] promoted by SmI_2.

Results and discussion

Here, we wish to report our preliminary results on a novel reductive cyclization of 1,1-diaryl-2,2-dicyanoethylenes or 1,1-diaryl-2-cyano-2-ethoxycarbonylethylenes with nitriles promoted by samarium(II) iodide to give polysubstituted 3*H*-pyrroles in good to excellent yields under mild conditions.



1 **2** **3**

Scheme 1

Table 1 summarizes our results on intermolecular reductive cyclization of 1,1-diaryl-2,2-dicyanoethylenes or 1,1-diaryl-2-cyano-2-ethoxycarbonylethylenes with nitriles. Chloro, bromo, alkoxy groups, and *N,N*-disubstituted amino groups could not be reduced under the reaction conditions and have no influence on the rate of intermolecular reductive cyclization. The reactions are complete within 2–3 hours at reflux. When the substrates are 1,1-diaryl-2-cyano-2-ethoxycarbonylethylenes and nitriles, the cleavage takes place between the C≡N bond, rather than the C=O bond. However, in this case, the reactivity of the starting materials and the yields of the reaction were almost the same either in the presence or absence of HMPA.

Though the detailed mechanism of the above reaction has not been clarified yet,[11–14] a possible mechanism for the formation of polysubstituted 3*H*-pyrroles may be postulated as shown in Scheme 2.

In the initial step, an electron is transferred from SmI_2 to substrate **1** resulting in the formation of radical anion **A**, which is then protonated by THF to form radical **B**. The radical **B** attacks another substrate nitrile **2** to form the carbon–carbon bond and generates **C**. The latter could follow two pathways to the intramolecular formation of a carbon–nitrogen bond and produce intermediate **D**. Form **D** could be isomerized to product **3**.

In conclusion, polysubstituted 3*H*-pyrrole derivatives are readily obtained *via* intermolecular reductive cyclization of 1,1-diaryl-2,2-dicyanoethylenes or 1,1-diaryl-2-cyano-2-ethoxycarbonylethylenes with nitriles promoted by samarium(II) iodide. The advantages of our method are convenient manipulation, easily accessible starting materials and good to excellent yields. Further studies to develop other new reactions using SmI_2 are in progress.

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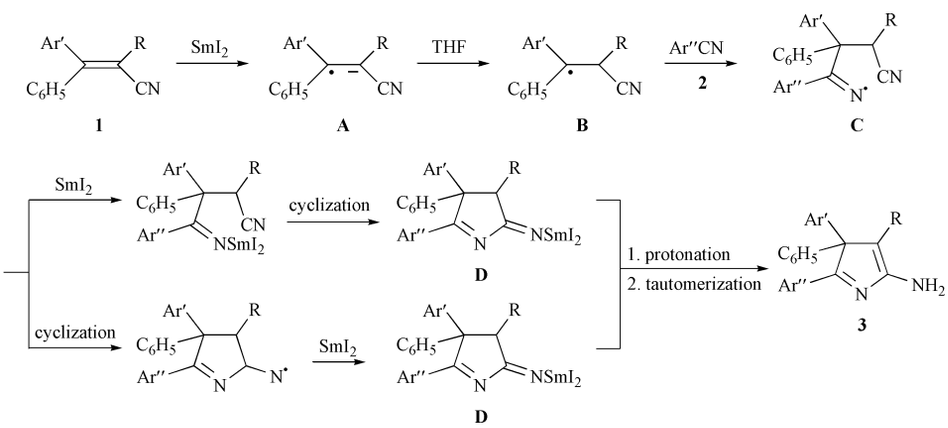
Table 1 Intermolecular reductive cyclization of 1,1-diaryl-2,2-dicyanoethylenes or 1,1-diaryl-2-cyano-2-ethoxycarbonylethylenes with nitriles

Entry	Ar′	Ar″	R	*t*/h	Yield (%)[a]
3a	C_6H_5	3-BrC_6H_4	CN	2	90,[b] 89[c]
3b	C_6H_5	3-$CH_3C_6H_4$	CN	2.5	87, 87[c]
3c	C_6H_5	4-ClC_6H_4	CN	2	81
3d	C_6H_5	4-$CH_3OC_6H_4$	CN	3	85
3e	C_6H_5	C_6H_5	CN	2.5	80
3f	C_6H_5	4-$Me_2NC_6H_4$	CN	3	78
3g	C_6H_5	3,4-$OCH_2OC_6H_3$	CN	3	85
3h	4-ClC_6H_4	3-BrC_6H_4	CN	2	89
3i	4-ClC_6H_4	3-$CH_3C_6H_4$	CN	2.5	84
3j	4-ClC_6H_4	4-$CH_3OC_6H_4$	CN	3	84
3k	4-$C_6H_5C_6H_4$	4-$CH_3OC_6H_4$	CN	3	87
3l	C_6H_5	C_6H_5	COOEt	2	72[b], 71[c]
3m	C_6H_5	3-$CH_3C_6H_4$	COOEt	2.5	77,[b] 78[c]
3n	C_6H_5	4-ClC_6H_4	COOEt	2	81
3o	C_6H_5	4-$CH_3OC_6H_4$	COOEt	2.5	75
3p	C_6H_5	3-BrC_6H_4	COOEt	2	78
3q	C_6H_5	4-$Me_2NC_6H_4$	COOEt	3	73
3r	C_6H_5	3,4-$OCH_2OC_6H_3$	COOEt	3	76

[a] Yield of isolated products. [b] 25 ml THF used as solvent. [c] 25 ml THF and 1 ml HMPA used as solvent.



Scheme 2

Experimental

Tetrahydrofuran was distilled from sodium–benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 400 MHz instrument for $CDCl_3$ or DMSO-d_6 solutions using TMS as internal standard. Chemical shifts (δ) are reported in ppm and coupling constants J are given in Hz. IR spectra were recorded using KBr disks with a Bruker Vector-22 infrared spectrometer. Elemental analyses were performed on an EA-1110 instrument. Metallic samarium and all solvents were purchased from commercial sources, without further purification before use.

General procedure for the syntheses of polysubstituted 3*H*-pyrroles

A solution of 1,1-diaryl-2,2-dicyanoethylenes (1 mmol) and nitrile (1 mmol) or 1,1-diaryl-2-cyano-2-ethoxycarbonylethylenes (1 mmol) and aromatic nitrile (1.2 mmol) in dry THF (3 ml) was added dropwise to the solution of SmI_2 (2.2 mmol) in THF (25 ml) at 65 °C under a nitrogen atmosphere. Immediately upon mixing of the reductants, the deep blue color of the solution vanished and a red color appeared. 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^{-1}, 5 ml) and extracted with ethyl acetate (3 × 30 ml). The organic phase was washed with water (20 ml) and saturated 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 the eluant.

2-(3-Bromophenyl)-3,3-diphenyl-4-cyano-5-amino-3*H*-pyrrole (3a). Mp 209–211 °C. ν_{max}(KBr)/cm^{-1} 3462, 3270, 2192, 1653, 1592; δ_H($CDCl_3$) 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); *m*/*z* (%) 415 (M^+, 98), 413 (M^+, 100), 232 (66), 231 (79), 155 (36). Anal. $C_{23}H_{16}BrN_3$. Calcd. C, 66.68; H, 3.89; N, 10.14. Found C, 66.79; H, 4.05; N, 10.03%.

2-(3-Methylphenyl)-3,3-diphenyl-4-cyano-5-amino-3*H*-pyrrole (3b). Mp 186–188 °C. ν_{max}(KBr)/cm^{-1} 3348, 3195, 2185, 1670, 1598; δ_H($CDCl_3$) 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); *m*/*z* (%) 349 (M^+, 100), 232 (37), 231 (41), 155 (17). Anal. $C_{24}H_{19}N_3$. Calcd. C, 82.49; H, 5.48; N, 12.03. Found C, 82.61; H, 5.58; N, 11.91%.

2-(4-Chlorophenyl)-3,3-diphenyl-4-cyano-5-amino-3*H*-pyrrole (3c). Mp 195–197 °C. ν_{max}(KBr)/cm^{-1} 3341, 3210, 2188, 1652, 1592; δ_H($CDCl_3$) 7.75–7.77 (2H, d), 7.21–7.33 (12H, m), 5.30 (2H, br s); *m*/*z* (%) 371 (M^+, 35), 369 (M^+, 100), 232 (22), 231 (33), 155 (11). Anal. $C_{23}H_{16}ClN_3$. Calcd. C, 74.69; H, 4.36; N, 11.36. Found C, 74.75; H, 4.44; N, 11.28%.

2-(4-Methoxyphenyl)-3,3-diphenyl-4-cyano-5-amino-3*H*-pyrrole (3d). Mp 199–200 °C. ν_{max}(KBr)/cm^{-1} 3460, 3205, 2188, 1654, 1600; δ_H($CDCl_3$) 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); *m*/*z* (%) 365 (M^+, 100), 350 (12), 232 (26), 231 (30), 155 (11). Anal. $C_{24}H_{19}N_3O$. Calcd. C, 75.59; H, 5.24; N, 11.50. Found C, 75.83; H, 5.32; N, 11.45%.

2,3,3-Triphenyl-4-cyano-5-amino-3*H*-pyrrole (3e). Mp 218–220 °C. ν_{max}(KBr)/cm^{-1} 3348, 3192, 2191, 1670, 1602; δ_H($CDCl_3$) 7.78–7.80 (2H, m), 7.21–7.37 (13H, m), 5.48 (2H, br s); *m*/*z* (%) 335 (M^+, 100), 334 (17), 232 (22), 231 (29), 155 (11). Anal. $C_{23}H_{17}N_3$. Calcd. C, 82.36; H, 5.11; N, 12.53. Found C, 82.41; H, 5.17; N, 12.47%.

2-(4-Dimethylaminophenyl)-3,3-diphenyl-4-cyano-5-amino-3*H*-pyrrole (3f). Mp 230–232 °C. ν_{max}(KBr)/cm^{-1} 3395, 3205, 2182, 1648, 1606; δ_H($CDCl_3$) 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); *m*/*z* (%): 378 (M^+, 100), 377 (21), 301 (33), 147 (27), 231 (22). Anal. $C_{25}H_{22}N_4$. Calcd. C, 79.34; H, 5.86; N, 14.80. Found C, 79.41; H, 5.99; N, 14.65%.

2-(3,4-Methylenedioxyphenyl)-3,3-diphenyl-4-cyano-5-amino-3*H*-pyrrole (3g). Mp 190–191 °C. ν_{max}(KBr)/cm^{-1} 3346, 3189, 2184, 1670, 1597; δ_H($CDCl_3$) 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); *m*/*z* (%): 379 (M^+, 100), 378 (19), 232 (20), 231 (24). Anal. $C_{24}H_{17}N_3O_2$. Calcd. C, 75.97; H, 4.52; N, 11.07. Found C, 76.09; H, 4.69; N, 10.96%.

2-(3-Bromophenyl)-3-phenyl-3-(4-chlorophenyl)-4-cyano-5-amino-3*H*-pyrrole (3h). Mp 188–189 °C. ν_{max}(KBr)/cm^{-1} 3426, 3205, 2187, 1649, 1533; δ_H($CDCl_3$) 8.09 (1H, s), 7.58–7.11 (12H, m), 5.29 (2H, br s); *m*/*z* (%): 451 (M^+, 27), 449 (M^+, 100), 447 (M^+, 75), 265 (20), 232 (20), 231 (67). Anal. $C_{23}H_{15}BrClN_3$. Calcd. C, 61.56; H, 3.37; N, 9.36. Found C, 61.71; H, 3.60; N, 9.19%.

2-(3-Methylphenyl)-3-phenyl-3-(4-chlorophenyl)-4-cyano-5-amino-3*H*-pyrrole (3i). Mp 166–168 °C. ν_{max}(KBr)/cm^{-1} 3339, 3197, 2190, 1653, 1600; δ_H($CDCl_3$) 7.71 (1H, s), 7.46–7.48 (1H, d), 7.20–7.30 (10H, m), 7.10–7.14 (1H, t), 5.34 (2H, br s), 2.27 (3H, s); *m*/*z* (%) 385 (M^+, 37), 383 (M^+, 100), 266 (16), 265 (16), 231 (56). Anal. $C_{24}H_{18}ClN_3$. Calcd. C, 75.09; H, 4.73; N, 10.95. Found C, 74.88; H, 4.97; N, 10.81%.

2-(4-Methoxyphenyl)-3-phenyl-3-(4-chlorophenyl)-4-cyano-5-amino-3*H*-pyrrole (3j). Mp 207–208 °C. ν_{max}(KBr)/cm^{-1} 3334, 3187, 2188, 1673, 1603; δ_H($CDCl_3$) 7.77–7.79 (2H, d), 7.21–7.31 (9H, m), 6.76–6.78 (2H, d), 5.25 (2H, br s), 3.78 (3H, s); *m*/*z* (%) 401 (M^+, 39), 399 (M^+, 100), 266 (20), 265 (18), 231 (69). Anal. $C_{24}H_{18}ClN_3O$. Calcd. C, 72.09; H, 4.54; N, 10.51. Found C, 72.26; H, 4.70; N, 10.43%.

2-(4-Methoxyphenyl)-3-phenyl-3-(4-phenylphenyl)-4-cyano-5-amino-3*H*-pyrrole (3k). Mp 128–130 °C. ν_{max}(KBr)/cm^{-1} 3385, 3200, 2183, 1647, 1604; δ_H(DMSO) 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); *m*/*z* (%) 441 (M^+, 100), 440 (9), 426 (12), 308 (12), 307 (14). Anal. $C_{30}H_{23}N_3O$. Calcd. C, 81.61; H, 5.25; N, 9.52. Found C, 81.79; H, 5.43; N, 9.67%.

2,3,3-Triphenyl-4-ethoxycarbonyl-5-amino-3*H*-pyrrole (3l). Mp 186–188 °C. ν_{max}(KBr)/cm^{-1} 3471, 3292, 1750, 1688, 1645; δ_H($CDCl_3$) 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), 1.02–0.98 (3H, t, *J* 7.20); *m*/*z* (%) 382 (M^+, 34), 310 (27), 309 (100). Anal. $C_{25}H_{22}N_2O_2$. Calcd. C, 78.51; H, 5.80; N, 7.32. Found C, 78.65; H, 5.98; N, 7.11%.

2-(3-Methylphenyl)-3,3-diphenyl-4-ethoxycarbonyl-5-amino-3*H*-pyrrole (3m). Mp 155–157 °C. ν_{max}(KBr)/cm^{-1} 3476, 3312, 1744, 1652, 1575; δ_H($CDCl_3$) 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), 2.24 (3H, s), 1.03–0.99 (3H, t, *J* 7.04); *m*/*z* (%) 396 (M^+, 36), 324 (27), 323 (100). Anal. $C_{26}H_{24}N_2O_2$. Calcd. C, 78.76; H, 6.10; N, 7.07. Found C, 78.94; H, 5.98; N, 7.23%.

2-(4-Chlorophenyl)-3,3-diphenyl-4-ethoxycarbonyl-5-amino-3*H*-pyrrole (3n). Mp 169–170 °C. ν_{max}(KBr)/cm^{-1} 3411, 3195, 1760, 1675, 1529; δ_H($CDCl_3$) 7.62–7.64 (2H, d), 7.17–7.36 (12H, m), 6.28 (2H, br s), 4.02–3.96 (2H, q, *J* 7.08), 1.02–0.99 (3H, t, *J* 7.08); *m*/*z* (%) 418 (M^+, 13), 416 (M^+, 35), 345 (36), 343 (100). Anal. $C_{25}H_{21}ClN_2O_2$. Calcd. C, 72.02; H, 5.08; N, 6.72. Found C, 71.87; H, 5.21; N, 6.64%.

2-(4-Methoxyphenyl)-3,3-diphenyl-4-ethoxycarbonyl-5-amino-3*H*-pyrrole (3o). Mp 174–176 °C. ν_{max}(KBr)/cm^{-1} 3472, 3290, 1747, 1661, 1585; δ_H($CDCl_3$) 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), 3.74 (3H, s), 1.03–0.99 (3H, t, *J* 7.04); *m*/*z* (%) 412 (M^+, 35), 340 (27), 339 (100). Anal. $C_{26}H_{24}N_2O_3$. Calcd. C, 75.71; H, 5.86; N, 6.79. Found C, 75.59; H, 5.98; N, 6.64%.

2-(3-Bromophenyl)-3,3-diphenyl-4-ethoxycarbonyl-5-amino-3*H*-pyrrole (3p). Mp 148–150 °C. ν_{max}(KBr)/cm^{-1} 3468, 3275, 1747, 1694, 1647; δ_H($CDCl_3$) 7.94 (1H, s), 7.47–7.49 (1H, d), 7.42–7.46 (1H, d), 7.20–7.35 (10H, m), 7.01–7.05 (1H, t), 6.29 (2H, br s), 4.02–3.97 (2H, q, *J* 7.08), 1.02–0.98 (3H, t, *J* 7.04); *m*/*z* (%) 462 (M^+, 37), 460 (M^+, 36), 389 (98), 388 (30), 387 (100). Anal. $C_{25}H_{21}BrN_2O_2$. Calcd. C, 65.08; H, 4.59; N, 6.07. Found C, 65.22; H, 4.73; N, 5.89%.

2-(4-Dimethylaminophenyl)-3,3-diphenyl-4-ethoxycarbonyl-5-amino-3*H*-pyrrole (3q). Mp 190–192 °C. ν_{max}(KBr)/cm^{-1} 3470, 3198, 1749, 1655, 1608; δ_H($CDCl_3$) 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), 2.94 (6H, s), 1.03–0.99 (3H, t, *J* 7.08); *m*/*z* (%) 425 (M^+, 30), 353 (28), 352 (100). Anal. $C_{27}H_{27}N_3O_2$. Calcd. C, 76.21; H, 6.40; N, 9.87. Found C, 76.35; H, 6.64; N, 10.03%.

2-(3,4-Methylenedioxyphenyl)-3,3-diphenyl-4-ethoxycarbonyl-5-amino-3*H*-pyrrole (3r). Mp 208–209 °C. ν_{max}(KBr)/cm^{-1} 3470, 3220, 1755, 1684, 1644; δ_H($CDCl_3$) 7.36–7.38 (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), 1.02–0.99 (3H, t, *J* 7.00); *m*/*z* (%) 426 (M^+, 31), 353 (100), 354 (28). Anal. $C_{26}H_{22}N_2O_4$. Calcd. C, 73.21; H, 5.20; N, 6.57. Found C, 73.47; H, 5.39; N, 6.35%.

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