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New and clean synthesis of *N*-substituted pyrroles under microwave irradiation

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Abstract—*N*-Substituted homochiral pyrrole derivatives were synthesized by the ring-closure reaction of *cis*-1,4-dichloro-2-butene with various amine compounds on a silica surface under microwave irradiation.

1. Introduction

Pyrrole derivatives have great importance in organic chemistry because they are present in many natural, medicinal and agricultural products, and semiconductor polymers. They are also very convenient precursors for biologically important compounds such as indolizidine alkaloids, bicyclic lactams, and unsaturated γ-lactams.[1] There are various pyrrole syntheses in the literature.[2] The most widely used method is the Paal–Knorr synthesis, which involves the reaction of 1,4-dicarbonyl compounds and their masked equivalents, such as 2,5-dimethoxytetrahydrofuran, with primary amines. Most of these methods are multistep reactions, and their main problem is racemization. Therefore, the development of effective and selective methods for obtaining pyrrole derivatives is desirable.

The use of microwaves for carrying out reactions is advantageous for the synthesis of numerous types of compound. The most evident improvements with this technique are reduced reaction time, cleaner reactions due to fewer side reactions, and the use of minimal quantities of solvent.[3] Thus, microwave-assisted synthesis can be considered as being more economical and environmentally friendly.

As a part of our ongoing research on the synthesis and reactions of pyrrole derivatives,[4] we wish to report here the synthesis of homochiral pyrrole derivatives from the reaction of *cis*-1,4-dichloro-2-butene, which is a commercially available and inexpensive starting material, with various amines, amino alcohols, and amino acid esters under microwave conditions.

Keywords: Pyrrole; Microwave; *cis*-1,4-Dichloro-2-butene; Silica gel.
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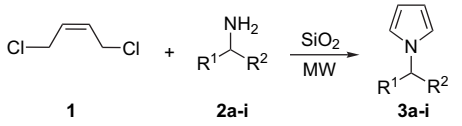
2. Results and discussion

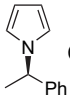
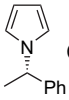
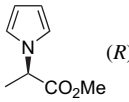
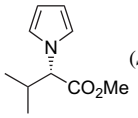
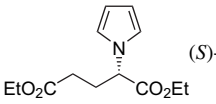
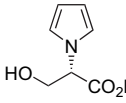
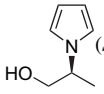
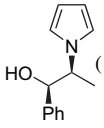
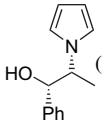
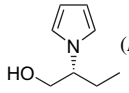
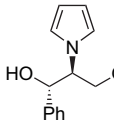
The reaction of *cis*-1,4-dichloro-2-butene with several amines has been studied by several groups.[5] These reactions were carried out in different solvents, such as toluene, DMF, methanol, and benzene, at 50–60 °C in the presence of pyridine, triethylamine, and sodium hydride, to give 3-pyrroline derivatives in 60–75% yield, as expected. But when we carried out the reaction of *cis*-1,4-dichloro-2-butene with various amines, amino alcohols, and amino acid esters under microwave irradiation on silica gel, we obtained pyrrole derivatives instead of the expected 3-pyrrolines (Scheme 1).



Scheme 1.

We tried several different reaction conditions under microwave irradiation, and found that the reaction took place on a silica-gel surface without solvent quickly in good yield. In a typical reaction procedure, a mixture of *cis*-1,4-dichloro-2-butene, amine, and triethylamine adsorbed on the silica-gel surface was irradiated in a microwave oven for a period of time long enough to complete the reaction. The reaction mixture was washed with a minimum amount of ether, and evaporation of the solvent furnished a crude product that was purified by column chromatography. Using this procedure, various chiral amine compounds were converted to their pyrrole derivatives through a one-step operation in 49–69% yield, as summarized in Table 1. All the spectroscopic data of the pyrrole compounds are in full agreement with their structures.

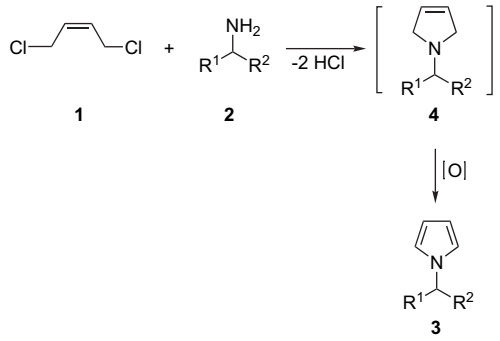
Table 1. The synthesis of pyrrole derivatives

Amine **2**	Pyrrole **3**	Reaction time (min)	Yield[a] (%)
 (*R*)-**2a**	 (*R*)-**3a**[6]	2	63
 (*S*)-**2a**	 (*S*)-**3a**	2	65
 (*R*)-**2b**	 (*R*)-**3b**[7–11]	3	49
 (*S*)-**2c**	 (*S*)-**3c**[7–9]	2	51
 (*S*)-**2d**	 (*S*)-**3d**[1e,2b]	4	52
 (*S*)-**2e**	 (*S*)-**3e**	2	55
 (*S*)-**2f**	 (*S*)-**3f**	2	58
 (1*R*, 2*S*)-**2g**	 (1*R*, 2*S*)-**3g**[10]	2	66
 (1*S*, 2*R*)-**2g**	 (1*S*, 2*R*)-**3g**[10]	2	62
 (*R*)-**2h**	 (*R*)-**3h**	2	61
 (1*S*, 2*S*)-**2i**	 (1*S*, 2*S*)-**3i**	2	69

[a] Isolated yield.

It is obvious that the reaction takes place via simple substitution of chlorine by nitrogen, followed by dehydrogenation (Scheme 2). The reaction of *cis*-1,4-dichloro-2-butene with (*R*)-phenylethylamine has also been carried out in toluene or DMF at 55–60 °C in the presence of pyridine or triethylamine without microwave irradiation. The GC–MS analysis of the crude products obtained from these reactions showed that trace amounts of the pyrrole derivatives were formed,

but that the 3-pyrroline was the main product. This result showed that the oxidation of pyrroline to pyrrole can take place in atmospheric oxygen and supported our mechanism.



Scheme 2.

3. Conclusion

A new microwave-assisted one-pot synthesis of *N*-substituted pyrrole derivatives has been achieved on a silica-gel surface under solvent-free conditions from commercially available materials. This environmentally friendly method provides various advantages, such as reasonably good yield, fast reaction under mild and solvent-free reaction conditions, and no racemization.

4. Experimental

4.1. General

All reagents were of commercial quality and reagent quality solvents were used without further purification. IR spectra were determined on a Perkin–Elmer, Spectrum One FTIR spectrometer. NMR spectra were recorded on Mercury VX-400 MHz and Varian Unity-Inova 500 MHz spectrometers. Chemical shifts δ are reported in parts per million relative to $CHCl_3$ (^{1}H: δ=7.27), $CDCl_3$ (^{13}C: δ=77.0) and TMS as internal standard. Column chromatography was carried out on silica gel 60 (40–63 μM). TLC was carried out on aluminum sheets precoated with silica gel $60F_{254}$ (Merck). MS were determined on Thermo Finnigan multi Mass (EI, 70 eV). Elemental analyses were carried out on Thermo Flash EA 1112 series apparatus. Optical rotations were measured with AA-55 Polarimeter. The reactions were carried out in Milestone-Start microwave instrument.

4.2. General procedure

A mixture of amine (1.0 mmol), *cis*-1,4-dichloro-2-butene (1.0 mmol), and triethylamine (2.0 mmol) was uniformly adsorbed on the surface of silica gel (5 g) in a Pyrex round bottomed flask at rt. The flask was then placed on a bed of silica gel in a porcelain basin and irradiated in a microwave oven at 500 W for 2–4 min (TLC). The reaction mass was eluted with ether and the ether extract was evaporated to leave the crude product, which was purified by column chromatography over silica gel (EtOAc/hexane 1:2, 1:6 or 1:10) to afford pure product.

4.2.1. (*R*)-1-(1-Phenylethyl)-1*H*-pyrrole (*R*)-3a. Colorless liquid (107 mg, 63%). $[\alpha]_D^{20}$ −6.6 (*c* 2.7, $CHCl_3$); lit.[6] $[\alpha]_D^{20}$ −14.4 (*c* 1.2, $CHCl_3$); IR (neat): ν 3029, 2963, 1603, 1377 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.75 (d, *J*=7.02 Hz, 3H, CH_3), 5.20 (q, *J*=7.02 Hz, 1H, N–CH), 6.11 (br s, 2H, =CH), 6.68 (br s, 2H, =CH), 7.01 (d, *J*=7.80 Hz, 2H, ArH), 7.14 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 57.0, 106.9, 118.4, 124.7, 126.3, 127.5, 142.5; MS (*m*/*z*) (rel abund): 171 [M$^+$] (57), 105 (100), 77 (26), 67 (27). Anal. Calcd for $C_{12}H_{13}N$ (171.24): C, 84.17; H, 7.65; N, 8.18. Found: C, 84.25; H, 7.57; N, 8.21.

4.2.2. (*S*)-1-(1-Phenylethyl)-1*H*-pyrrole (*S*)-3a. Colorless liquid (111 mg, 65%). $[\alpha]_D^{20}$ +6.8 (*c* 2.7, $CHCl_3$); IR (neat): ν 3027, 2965, 1603, 1377 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.75 (d, *J*=7.02 Hz, 3H, CH_3), 5.20 (q, *J*=7.02 Hz, 1H, N–CH), 6.11 (br s, 2H, =CH), 6.68 (br s, 2H, =CH), 7.01 (d, *J*=7.80 Hz, 2H, ArH), 7.14 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 57.0, 106.9, 118.4, 124.7, 126.3, 127.5, 142.5; MS (*m*/*z*) (rel abund): 171 [M$^+$] (57), 105 (100), 77 (26), 67 (27). Anal. Calcd for $C_{12}H_{13}N$ (171.24): C, 84.17; H, 7.65; N, 8.18. Found: C, 84.24; H, 7.59; N, 8.21.

4.2.3. (*R*)-Methyl 2-(1*H*-pyrrol-1-yl)propanoate (*R*)-3b. Colorless oil (75 mg, 49%). $[\alpha]_D^{20}$ +12.83 (*c* 1.1, $CHCl_3$); IR (neat): ν 3102, 2992, 2954, 1747, 1378, 1282 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65 (d, *J*=7.33 Hz, 3H, CH_3), 3.64 (s, 3H, OCH_3), 4.69 (q, *J*=7.33 Hz, 1H, N–CH), 6.11 (apparent t, *J*=2.44, 1.96 Hz, 2H, =CH), 6.67 (apparent t, *J*=2.44, 1.95 Hz, 2H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.6, 53.0, 57.4, 109.4, 120.6, 171.9; MS (*m*/*z*) (rel abund): 153 [M$^+$] (71), 94 (100), 79 (26), 67 (56), 52 (49), 40 (92). Anal. Calcd for $C_8H_{11}NO_2$ (153.18): C, 62.73; H, 7.24; N, 9.14. Found: C, 62.59; H, 7.26; N, 9.17.

4.2.4. (*S*)-Methyl 3-methyl-2-(1*H*-pyrrol-1-yl)butanoate (*S*)-3c. Colorless oil (92 mg, 51%). $[\alpha]_D^{20}$ −2.8 (*c* 4.2, $CHCl_3$); IR (neat): ν 3055, 2986, 1727, 1372, 1285 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.67 (d, *J*=6.65 Hz, 3H, CH_3), 0.91 (d, *J*=6.65 Hz, 3H, CH_3), 2.32 (m, 1H, CH), 3.63 (s, 3H, CH_3), 4.00 (d, *J*=10.23 Hz, 1H, N–CH), 6.02 (br s, 2H, =CH), 6.63 (br s, 2H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.7, 19.4, 32.0, 51.9, 68.8, 108.5, 120.1, 171.0. Anal. Calcd for $C_{10}H_{15}NO_2$ (181.23): C, 66.27; H, 8.34; N, 7.73. Found: C, 66.25; H, 8.36; N, 7.75.

4.2.5. (*S*)-Diethyl 2-(1*H*-pyrrol-1-yl)pentandioate (*S*)-3d. Colorless oil (117 mg, 52%). $[\alpha]_D^{20}$ −12.3 (*c* 1.3, $CHCl_3$); lit.[1e] $[\alpha]_D^{20}$ −12.2 (*c* 1.3, $CHCl_3$); IR (neat): ν 3062, 2985, 1732, 1284 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19–1.25 (m, 6H, CH_3), 2.09–2.36 (m, 3H, CH_2 and CH_A), 2.38–2.42 (m, 1H, CH_B), 4.12 (q, *J*=7.32 Hz, 2H, CH_2), 4.19 (q, *J*=7.25 Hz, 2H, CH_2), 4.75 (m, 1H, N–CH), 6.19 (apparent t, *J*=2.24 Hz, 2H, =CH), 6.72 (apparent t, *J*=2.24 Hz, 2H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 14.1, 28.0, 29.9, 60.5, 60.7, 61.6, 108.9, 120.1, 170.1, 173.2. Anal. Calcd for $C_{13}H_{19}NO_4$

(253.29): C, 61.64; H, 7.56; N, 5.53. Found: C, 61.67; H, 7.49; N, 5.51.

4.2.6. (*S*)-Ethyl 3-hydroxy-2-(1*H*-pyrrol-1-yl)propanoate (*S*)-3e. Yellow oil (101 mg, 55%). $[\alpha]_D^{20}$ +4.63 (*c* 1.7, $CHCl_3$); IR (neat): *ν* 3532, 3099, 2982, 2934, 1738, 1371, 1281 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* 1.95 (t, *J*=7.32 Hz, 3H, CH_3), 1.95 (br s, 1H, OH), 3.97 (apparent q, *J*=6.83 Hz, 1H, H_A), 4.06 (apparent q, *J*=5.85 Hz, 1H, H_B), 4.15 (q, *J*=7.32 Hz, 2H, CH_2), 4.66 (apparent t, *J*=6.83, 5.86 Hz, 1H, N–CH), 6.13 (apparent t, *J*=2.44, 1.95 Hz, 2H, =CH), 6.69 (apparent t, *J*=2.44, 1.96 Hz, 2H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 13.0, 60.8, 62.3, 62.4, 107.9, 119.4, 168.2; MS (*m*/*z*) (rel abund): 183 [M^+] (39), 110 (55), 81 (100), 66 (41), 52 (42), 40 (22). Anal. Calcd for $C_9H_{13}NO_3$ (183.20): C, 59.00; H, 7.15; N, 7.65. Found: C, 59.19; H, 7.06; N, 7.62.

4.2.7. (*S*)-2-(1*H*-Pyrrol-1-yl)propan-1-ol (*S*)-3f. Colorless oil (73 mg, 58%). $[\alpha]_D^{20}$ +8.25 (*c* 2.2, $CHCl_3$); IR (neat): *ν* 3524, 3098, 2982, 1558, 1378, 1280 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.37 (d, *J*=7.02 Hz, 3H, CH_3), 1.63 (br s, 1H, OH), 3.59 (m, 2H, CH_2), 4.09 (m, 1H, N–CH), 6.10 (br s, 2H, =CH), 6.67 (br s, 2H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 17.6, 57.7, 67.7, 108.4, 119.1; MS (*m*/*z*) (rel abund): 125 [M^+] (84), 94 (95), 79 (23), 67 (59), 52 (56), 40 (100). Anal. Calcd for $C_7H_{11}NO$ (125.17): C, 67.17; H, 8.86; N, 11.19. Found: C, 67.22; H, 8.83; N, 11.23.

4.2.8. (1*R*,2*S*)-1-Phenyl-2-(1*H*-pyrrol-1-yl)propan-1-ol (1*R*,2*S*)-3g. Yellow oil (133 mg, 66%). $[\alpha]_D^{20}$ +26.8 (*c* 3.6, $CHCl_3$); IR (neat): *ν* 3523, 3055, 2992, 1605, 1376, 1283 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.32 (d, *J*=7.00 Hz, 3H, CH_3), 2.11 (br s, 1H, OH), 4.08 (m, 1H, N–CH), 4.61 (d, *J*=4.68 Hz, 1H, O–CH), 5.93 (br s, 2H, =CH), 6.47 (br s, 2H, =CH), 7.04 (d, *J*=7.60 Hz, 2H, ArH), 7.17 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 14.9, 60.8, 77.8, 107.9, 119.2, 126.0, 127.7, 128.2, 140.9; MS (*m*/*z*) (rel abund): 201 [M^+] (21), 115 (7), 106 (16), 94 (100), 77 (63), 66 (45), 50 (49), 40 (78). Anal. Calcd for $C_{13}H_{15}NO$ (201.26): C, 77.58; H, 7.51; N, 6.96. Found: C, 77.59; H, 7.56; N, 6.88.

4.2.9. (1*S*,2*R*)-1-Phenyl-2-(1*H*-pyrrol-1-yl)propan-1-ol (1*S*,2*R*)-3g. Yellow oil (124 mg, 62%). $[\alpha]_D^{20}$ −26.5 (*c* 3.6, $CHCl_3$); IR (neat): *ν* 3526, 3053, 2989, 1605, 1377, 1283 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.32 (d, *J*=7.00 Hz, 3H, CH_3), 2.11 (br s, 1H, OH), 4.08 (m, 1H, N–CH), 4.61 (d, *J*=4.68 Hz, 1H, O–CH), 5.93 (br s, 2H, =CH), 6.47 (br s, 2H, =CH), 7.04 (d, *J*=7.60 Hz, 2H, ArH), 7.17 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 14.9, 60.8, 77.8, 107.9, 119.2, 126.0, 127.7, 128.2, 140.9; MS (*m*/*z*) (rel abund): 201 [M^+] (21), 115 (7), 106 (16), 94 (100), 77 (63), 66 (45), 50 (49), 40 (78). Anal. Calcd for $C_{13}H_{15}NO$ (201.26): C, 77.58; H, 7.51; N, 6.96. Found: C, 77.61; H, 7.54; N, 6.87.

4.2.10. (*R*)-2-(1*H*-Pyrrol-1-yl)butan-1-ol (*R*)-3h. Colorless oil (85 mg, 61%). $[\alpha]_D^{20}$ +14.3 (*c* 0.4, $CHCl_3$); IR (neat): *ν* 3517, 3048, 2998, 1602, 1376, 1282 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 0.85 (t, *J*=7.41 Hz, 3H, CH_3), 1.68 (br s, 1H, OH), 1.77 (m, 2H, CH_2), 3.73 (m, 2H, CH_2), 3.85 (m, 1H, N–CH), 6.18 (apparent t, *J*=2.34, 1.95 Hz, 2H, =CH), 6.70 (apparent t, *J*=2.34, 1.95 Hz, 2H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 10.8, 25.1, 64.1, 66.3, 108.4, 119.3. Anal. Calcd for $C_8H_{13}NO$ (139.19): C, 69.03; H, 9.41; N, 10.06. Found: C, 68.97; H, 9.45; N, 10.08.

4.2.11. (1*S*,2*S*)-1-Phenyl-2-(1*H*-pyrrol-1-yl)propane-1,3-diol (1*S*,2*S*)-3i. Yellow oil (149 mg, 69%). $[\alpha]_D^{20}$ +93.5 (*c* 0.5, $CHCl_3$); IR (neat): *ν* 3525, 3050, 1605, 1375, 1284 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.00 (br s, 1H, OH), 2.45 (br s, 1H, OH), 3.72 (m, 2H, CH_2), 4.06 (m, 1H, N–CH), 4.92 (d, *J*=6.6 Hz, 1H, O–CH), 6.15 (apparent t, *J*=1.95 Hz, 2H, =CH), 6.70 (apparent t, *J*=2.34, 1.95 Hz, 2H, =CH), 7.19 (m, 2H, ArH), 7.31 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 63.1, 67.7, 74.7, 108.8, 120.7, 126.6, 128.6, 128.8, 140.4; MS (*m*/*z*) (rel abund): 217 [M^+] (7), 168 (7), 111 (14), 106 (42), 93 (100), 77 (33), 67 (32), 51 (39). Anal. Calcd for $C_{13}H_{15}NO_2$ (217.26): C, 71.87; H, 6.96; N, 6.45. Found: C, 71.83; H, 7.02; N, 6.42.

References and notes

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