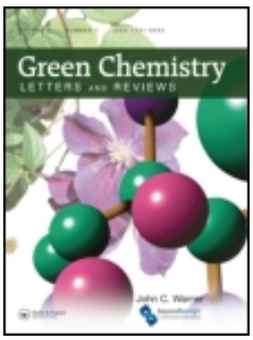

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RESEARCH LETTER

Synthesis of highly substituted pyrroles using ultrasound in aqueous media

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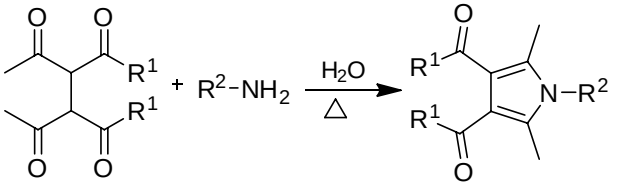
A two-step protocol for the synthesis of highly substituted pyrroles in aqueous media and without catalyst is described. The first step is the dimerization of a 1,3-dicarbonyl compound by ceric ammonium nitrate/ultrasound to produce a tetracarbonyl derivative. This derivative is then combined with an amine in the absence of any catalysts to obtain the pyrrole via a Paal–Knorr reaction. This route is an improvement when compared with classical methodologies toward Green Chemistry objectives.



Keywords: pyrroles; Green Chemistry; aqueous media

Introduction

Pyrroles are heterocycles, which are present in natural molecules such as porphyrins and bilirubins (*1–4*) and many other compounds that possess antioxidant (*5*), antitumor (*6–8*), and anticancer (*9, 10*) properties. The classic methods for the synthesis of pyrroles described in the literature are Knorr (*11–14*), Hantzsch (*15*), Paal–Knorr (*16–20*), and Barton–Zard (*21, 22*) reactions. The Paal–Knorr reaction, in which 1,4-dicarbonyl compounds react with primary amines under slightly acidic conditions, is a very attractive approach. Ranu et al. reported a process in aqueous media catalyzed by a water-tolerant Lewis acid that can lead to penta-substituted pyrroles (*23*).

In the literature, there is an effort to optimize this methodology leading to environmentally friendly processes. Current publications describe the use of solvent-free conditions with Lewis acid catalysts (*24*), microwave heating (*25, 26*), ionic liquids (*27*), and ultrasound (*28*). Most of these processes lead to tri- and tetra-substituted pyrroles.

Currently, the study of organic reactions that use water as a solvent is considered an important strategy for developing more environmentally friendly methodologies. Water is an innocuous solvent and is both more abundant and less expensive than organic solvents (*29–39*).

The effect of a solvent in a chemical reaction in relation to the formation of products and their speed is very important. The change of solvent can modify the activation energy, the solvation energy of reactants, and the transition state (*40*).

Rideout and Breslow demonstrated in 1980 the advantages of organic reactions in aqueous media (*41, 42*) and the properties of water considering that the speed of Diels Alder reaction is related with the hydrophobic effect, which is the tendency of nonpolar species to aggregate in water due to the high cohesion energy of this solvent. This effect leads to a decrease in the contact surface between hydrophobic molecules and water, reducing the system energy (*31*).

In this paper we present a simple and efficient methodology for the synthesis of penta-substituted pyrroles without catalysts using water as a solvent.

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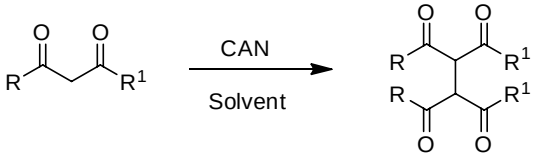
Results and discussion

The penta-substituted pyrroles (**IV**) were obtained via a two-step protocol in aqueous media. The first step was the dimerization of 1,3-dicarbonyl compounds (**I**) by ceric ammonium nitrate (CAN) to produce tetracarbonyl derivatives (**II**) in high yields using ultrasound (Scheme 1). Finally, the pyrroles were obtained by reacting these compounds with amines (**III**), without catalysts, via a Paal–Knorr reaction (Scheme 2). The first step is a modification of Romero (*43*) methodology for dimerization of 1,3-dicarbonyl compounds, substituting the methanol by water, either with or without ultrasound (Scheme 1).

The CAN is widely used in oxidative transformations. Its low toxicity, ease of handling, experimental simplicity, and solubility in different solvents, including water, turn it an oxidant even more valuable (*44*).

Classic methods to obtain these compounds include the use of: (1) reflux with acetic acid for long periods of time (*45*); (2) alkaline fusion at 155°C (*46*); (3) acetylation reaction of pyrroles with aluminum chloride and carbon disulfide (*47*); and (4) cyclocondensation of enamines using diacetoxyiodobenzene (*48*). Some of these methods use methanol as a solvent and water resistant catalysts (*23*) as in the

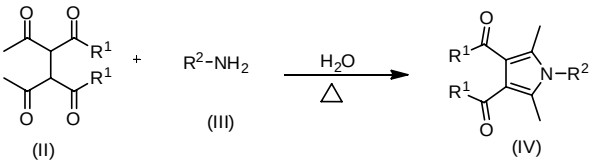


(I) (II)

Ia - R = R^1 = Me
IIb - R = Me; R^1 = OEt
IIIc - R = R^1 = OMe

I	Conditions	Time	Yield (II)/%
a	MeOH/ CAN[43]	1h	80
	H_2O/ CAN/ silent	1h	51
	H_2O/ CAN/ ultrasound	2min	87
b	H_2O/ CAN/ silent	1h	45
	H_2O/ CAN/ ultrasound	5min	62
c	MeOH/ CAN[43]	1h	61
	H_2O/ CAN/ silent	1h	56
	H_2O/ CAN/ ultrasound	2min	76

Scheme 1. Dimerization of 1,3-dicarbonyl compounds.



IV	R^1	R^2	Time/h	yield/%
a	Me	Ph	1	47
b	Me	4-Me(Ph)	1	40
c	Me	4-OMe(Ph)	1	70
d	Me	$PhCH_2$	1	37
e	OEt	Ph	1	55
f	OEt	4-Me(Ph)	1	50
g	OEt	4-OMe(Ph)	1	70
h	OEt	4-Cl(Ph)	2	60
i	OEt	$PhCH_2$	1	42

Scheme 2. Synthesis of penta-substituted pyrroles using water as a solvent.

synthesis of the penta-substituted pyrrol (IVd), obtained in yields as low as 10% (*49*). As can be seen in Scheme 2 electron donating groups on the amines are accelerating the pyrroles formation. This can be explained by the increase on the nucleophilicity of these amines. By other side, the lower yield when using benzylamine (IIId and IIIi) when compared with aniline (IIIa and IIIe) cannot be explained by steric effects. It means that in the case of aniline the aromatic ring helps the reaction by acquiring some electron density.

In opposite, the methodology developed in this paper uses only water as a solvent and milder conditions leading to highly functionalized pyrroles, being the pirrol 3,4-(diethyloxycarbonyl)-2,5-dimethyl-1-(4-methylphenyl)-1*H*-pyrrole (IVf), a novel penta-substituted pyrrole, not yet described in the literature.

Experimental

Dimerization of 1,3-dicarbonyl compounds

Silent methodology

First, 11 mmol CAN in 30 mL of water was added, dropwise, to 5 mmol 1,3-dicarbonyl compound **I** in a stirred water bath at 5°C. After this addition, the

reaction was allowed to proceed at room temperature until the initial deep red color of the CAN disappeared. The product was extracted with CH_2Cl_2 (2×10 mL) and dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The product **IIa** was recrystallized from ethanol. Products **IIb** and **IIc** were recrystallized from hexane.

Ultrasound methodology

First, 11 mmol of CAN in 30 mL of water was added, dropwise, to 5 mmol of the 1,3-dicarbonyl compound **I** in an ultrasound bath with ice and water at 5°C, until the initial deep red color of the CAN disappeared. The product **II** were filtered. Product **IIa** was recrystallized from ethanol, product **IIb** was recrystallized from hexane, and **IIc** was obtained pure.

3,4-Diacetylhexane-2,5-dione (IIa): Solid (silent – 500 mg, 51%; ultrasound – 860 mg, 87%), m.p. 158–160°C; IR (KBr) 3007, 2971, 2927, 1600, 1410, 1254, 1017, 997, 913, 678, 540, 482 cm^{-1}; MS *m*/*z* (%) 198 (M^+, 12), 180 (75), 165 (100), 123 (40), 43 (75); ^1H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 6*H*), 2.35 (s, 6*H*), 4.75 (s, 1*H*), 16.79 (s, 1*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8, 31.0, 67.9, 108.3, 192.9, 201.2.

Diethyl-2,3-diacetylsuccinate (IIb): Solid (silent – 580 mg, 45%; ultrasound – 800 mg, 62%), m.p. 88–89°C; IR (KBr) 3410, 2993, 2966, 2951, 1725, 1710, 1355, 1297, 1253, 1183, 1018, 871, 549, 504 cm^{-1}; MS *m*/*z* (%) 258 (M^+, 1), 213 (2), 198 (25), 173 (48), 167 (28), 145 (20), 127 (50), 99 (35), 43 (100); ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, 6*H*, $J = 7.0$ Hz), 2.43 (s, 6*H*), 4.16 (q, 4*H*, $J = 7.0$ Hz), 4.49 (s, 2*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 31.0, 57.9, 62.3, 167.2, 201.8.

Tetramethyl ethane-1,1,2,2-tetracarboxylate (IIc): Solid (silent – 730 mg, 56%; ultrasound – 990 mg, 76%), m.p. 134–135°C; IR (KBr) 3449, 3045, 3025, 2968, 1750, 1720, 1441, 1315, 1282, 1175, 1156, 999, 889, 657, 601, 575 cm^{-1}; MS *m*/*z* (%) 231 (10), 203 (10), 171 (100), 159 (70), 113 (5), 59 (60); ^1H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 6*H*), 4.18 (s, 1*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.1, 53.2, 167.5.

*1-Substituted-3,4-diacetyl-2,5-dimethyl-1*H*-pyrrole*

The mixture of 1 mmol of 3,4-diacetylhexane-2,5-dione **IIa**, 1 mmol of amine **IIIa–d,** and 1 mL of water was refluxed for 1 h. The solid product **IVa–d** was extracted with CH_2Cl_2 (3×5 mL) and dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The product **IVa–d** was recrystallized from ethanol.

3,4-Diacetyl-2,5-dimethyl-1-phenyl-1*H*-pyrrole(IVa): Solid (120 mg, 47%), m.p. 96–98°C; MS *m*/*z* (%) 255 ($M^{+\cdot}$, 36), 240 (100), 212 (8), 77 (15), 51 (5), 43 (6); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.11 (s, 6*H*), 2.45 (s, 6*H*), 7.18 (dd, *J* 1.4, 8.1 Hz, 2*H*), 7.52 (m, 3*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.5, 31.7, 123.5, 128.3, 129.4, 129.9, 133.0, 136.8, 197.6.

3,4-Diacetyl-2,5-dimethyl-1-(4-methylphenyl)-1*H*-pyrrole (IVb): Solid (108 mg, 40%), m.p. 135–136°C; MS *m*/*z* (%) 269 (M^+, 38), 254 (100), 226 (6), 91 (12), 65 (6), 43 (6); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.10 (s, 6*H*), 2.44 (s, 3*H*), 2.45 (s, 6*H*), 7.05 (d, *J* 8.2 Hz, 2*H*), 7.32 (d, *J* 8.2 Hz, 2*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.5, 21.3, 31.2, 123.4, 128.0, 130.5, 133.2, 134.1, 139.5, 197.7.

3,4-Diacetyl-2,5-dimethyl-1-(4-methoxyphenyl)-1*H*-pyrrole(IVc): Solid (200 mg, 70%), m.p. 115–117°C; MS *m*/*z* (%) 285 (M^+, 45), 270 (100), 242 (7), 77 (7), 43 (8); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.10 (s, 6*H*), 2.44 (s, 6*H*), 3.88 (s, 3*H*), 7.02 (d, *J* 9.0 Hz, 2*H*), 7.09 (d, *J* 9.0 Hz, 2*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 12.5, 31.2, 55.7, 115.0, 123.3, 125.3, 129.3, 133.5, 160.1, 197.7.

1-Benzyl-3,4-diacetyl-2,5-dimethyl-1*H*-pyrrole(IVd): Solid (100 mg, 37%), m.p. 84–85°C; MS *m*/*z* (%) 269 (M^+, 60), 254 (55), 226 (10), 178 (20), 91 (100), 65 (15), 43 (10); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 6*H*), 2.42 (s, 6*H*), 5.06 (s, 2*H*), 6.93 (d, *J* 7.5 Hz, 2*H*), 7.29 (d, *J* 7.5 Hz, 1*H*), 7.34 (t, *J* 7.5 Hz, 2*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.5, 31.4, 47.1, 123.5, 125.7, 128.0, 129.3, 132.4, 135.9, 197.8.

*1-Substituted-3,4-(diethyloxycarbonyl)-2,5-dimethyl-1*H*-pyrrole*

The mixture of 1 mmol of diethyl-2,3-diacetylsuccinate **IIb**, 1 mmol of amine **IIIe–i**, and 1 mL of water was refluxed for 1 h (or 2 h for 4-chloroaniline **IIIh**). The solid product **IVe–i** was extracted with CH_2Cl_2 (3×5 mL) and dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The product **IVe–i** was purified by column chromatography using hexane:ethyl acetate (8:2).

3,4-(Diethyloxycarbonyl)-2,5-dimethyl-1-phenyl-1*H*-pyrrole(IVe): Yellow oil (173 mg, 55%); MS *m*/*z* (%) 315 (M^+, 30), 269 (100), 242 (40), 169 (40), 77 (30), 51 (10); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.34 (t, *J* 7.2 Hz, 6*H*,), 2.14 (s, 6*H*), 4.30 (q, *J* 7.2 Hz, 4*H*), 7.16 (dd, *J* 1.4, 8.0 Hz, 2*H*), 7.47–7.54 (m, 3*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.9, 14.5, 60.3, 112.7, 128.7, 129.2, 129.8, 134.3, 136.9, 165.8.

3,4-(Diethyloxycarbonyl)-2,5-dimethyl-1-(4-methylphenyl)-1*H*-pyrrole(IVf): Brown oil (165 mg, 50%); MS *m*/*z* (%) 329 (M^+, 30), 283 (100), 256 (40), 254 (50), 183 (40), 91 (25), 77 (2), 65 (10), 43 (2); ^1H

NMR ($CDCl_3$, 400 MHz) δ 1.34 (t, *J* 7.1 Hz, 6*H*), 2.13 (s, 6*H*), 2.43 (s, 3*H*), 4.30 (q, *J* 7.1 Hz, 4*H*), 7.03 (d, *J* 8.2 Hz, 2*H*), 7.29 (d, *J* 8.2 Hz, 2*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.9, 14.4, 21.3, 60.2, 112.6, 127.9, 130.3, 134.3, 134.4, 139.2, 165.8.

3,4-(Diethyloxycarbonyl)-2,5-dimethyl-1-(4-methoxyphenyl)-1*H*-pyrrole(IVg): Yellow oil (242 mg, 70%); MS *m*/*z* (%) 345 (M^+, 40), 299 (100), 270 (50), 227 (30), 199 (30), 148 (20), 77 (10), 43 (5); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.34 (t, *J* 7.1 Hz, 6*H*), 2.13 (s, 6*H*), 3.87 (s, 3*H*), 4.30 (q, *J* 7.1 Hz, 4*H*), 7.00 (d, *J* 8.8 Hz, 2*H*), 7.07 (d, *J* 8.8 Hz, 2*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.9, 14.5, 55.7, 60.3, 112.6, 114.9, 129.3, 129.6, 134.7, 160.0, 165.9.

3,4-(Diethyloxycarbonyl)-2,5-dimethyl-1-(4-chlorophenyl)-1*H*-pyrrole (IVh): Brown oil (210 mg, 60%); MS *m*/*z* (%) 349 (M^+, 20), 303 (100), 276 (50), 231 (25), 203 (25), 168 (30), 152 (40), 111 (25), 51 (5), 43 (3); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.34 (t, *J* 7.1 Hz, 6*H*), 2.14 (s, 6*H*), 4.30 (q, *J* 7.1 Hz, 4*H*), 7.11 (d, *J* 8.6 Hz, 2*H*), 7.49 (d, *J* 8.6 Hz, 2*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.9, 14.4, 60.4, 113.1, 129.6, 130.1, 134.1, 135.4, 135.5, 165.7.

1-Benzyl-3,4-(diethyloxycarbonyl)-2,5-dimethyl-1*H*-pyrrole(IVi): Yellow oil (138 mg, 42%); MS *m*/*z* (%): 329 (M^+, 35), 284 (52), 283 (90), 256 (10), 91 (100), 65 (10); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, *J* 7.1 Hz, 6*H*), 2.31 (s, 6*H*), 4.28 (q, *J* 7.1 Hz, 4*H*), 5.04 (s, 2*H*), 6.92 (d, *J* 7.1 Hz, 2*H*), 7.27 (d, *J* 7.1 Hz, 1*H*), 7.32 (t, *J* 7.1 Hz, 2*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.0, 14.5, 47.1, 60.3, 112.9, 125.7, 127.8, 129.1, 133.6, 136.1, 165.9.

Conclusions

The dimerization of 1,3-dicarbonyl compounds (**I**) by CAN can be performed by substituting the methanol solvent with water. Furthermore, the use of ultrasound as an alternative energy supply significantly increases the yield and decreases the reaction time in aqueous media. The methodology we have developed, based on the Paal–Knorr reaction in water without catalysts, is simple and efficient, specifically for the synthesis of penta-substituted pyrroles (**IV**). These modifications represent an improvement to the classic synthesis methodology toward a Green Chemistry alternative.

Supplementary Data

Supplementary data associated with this paper contains NMR spectra (^1H and ^{13}C) for the compounds (**II**) and (**IVa-i**) as a PDF file.

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