Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron
Tetrahedron 60 (2004) 1625–1630

Microwave mediated facile one-pot synthesis of polyarylpyrroles from but-2-ene- and but-2-yne-1,4-diones

H. Surya Prakash Rao,[a,*] S. Jothilingam[a] and Hans W. Scheeren[b]

[a]*Department of Chemistry, Pondicherry University, Pondicherry 605 014, India*
[b]*Department of Organic Chemistry, NSR Center for Molecular Structure, Design and Synthesis, University of Nijmegen, Toernooiveld 1, Nijmegen 6525 ED, The Netherlands*

Received 10 September 2003; revised 31 October 2003; accepted 28 November 2003

Dedicated to Professor Goverdhan Mehta, I.I.Sc., Bangalore, on the occasion of his 60th birthday

Abstract—Several pyrrole derivates with multiple aryl substituents were prepared conveniently in a one pot-reaction from but-2-ene-1,4-diones and but-2-yne-1,4-diones via hydrogenation of the carbon–carbon double bond/triple bond followed by amination–cyclization. The reaction could be performed with ammonium formate or alkyl/arylammonium formates under Pd/C in polyethylene glycol-200 (PEG-200) under microwave irradiation. Using this procedure, different aryl-substituted pyrroles were prepared. Furthermore, studies on microwave vs thermal conditions indicate faster heating under microwave conditions was responsible for rate enhancement.

1. Introduction

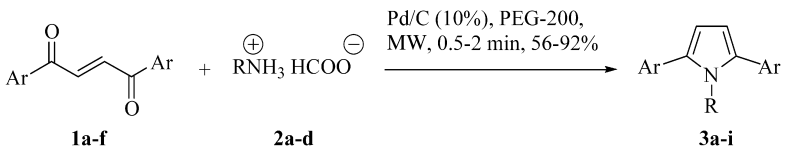
The pyrrole ring is one of the fundamental heterocycles. It is a widely distributed structural unit in a variety of natural and biologically important molecules such as porphyrins, bile pigments, co-enzymes and alkaloids.[1] Since fundamental molecules for energy trapping from sunlight embody a porphyrin nucleus with four pyrrole units, there has been a continuous quest to synthesize this heterocycle with different substituents efficiently and from readily available starting materials.[2] In recent years, there has been an enhanced interest in the synthesis of pyrrole and its oligomers due to their potential application as conducting materials.[3] Furthermore, pyrrole ring with multiple aromatic ring substitutions have applications as electroluminescent devices.[4] For this reason we became interested in developing a versatile synthesis of pyrrole derivatives from readily available starting materials.

The 2,5-disubstituted pyrroles can be synthesized by the classical Paal–Knorr method involving the reaction of 1,4-butanediones with amines.[5] Even though this procedure is versatile and applicable for the synthesis of a wide variety of pyrrole derivatives, it is limited to the availability of 1,4-diketones. On the other hand, but-2-ene-1,4-diones, the precursors to 1,4-butanediones can be prepared easily from readily available starting materials. For example, 1,4-diarylbut-2-ene-1,4-diones can be prepared by Friedel–Crafts acylation of arenes with fumaroyl chloride.[6] The 1,2,4-triarylbut-2-ene-1,4-diones can be prepared by condensation of benzil and its derivatives with acetophenone.[7] The 1,2,3,4-tetraarylbut-2-ene-1,4-diones can be prepared by deoxygenative dimerization of benzil and its derivatives via carbene intermediates.[8] The 1,4-butanediones can also be prepared by hydrogenation of the triple bond present in the but-2-yne-1,4-diones. The but-2-yne-1,4-diones of interest in the present study, the diaroylacetylenes, can be prepared from the corresponding diaroylethylenes by bromination followed by dehydrobromination.[9]

We reasoned that a simple and versatile route for the synthesis of pyrrole derivatives from 1,4-enediones could be developed if the two steps, viz. reduction and amination–cyclization can be combined in a single pot operation. For this purpose, ammonium formate can be employed as it behaves as a reducing agent of the double bond and also as a source of ammonia. There are several reports in the literature on the utility of ammonium formate as a source of hydrogen in the transfer hydrogenation reaction.[10] In the preliminary communication we disclosed the utility of ammonium formate for one-pot transformation of (*E*)-1,4-diarylbut-2-ene-1,4-diones to 2,5-diaryl-1*H*-pyrroles (Scheme 1).[11] We found that the reaction was greatly accelerated under microwave irradiation and required only 2–3 min. for completion. We also found that polyethylene glycol-200 (PEG-200) can be employed as a convenient solvent for the microwave promoted reactions. Now, we wish to report that this versatile method can be extended for the preparation of 2,5-diaryl and 1,2,5-triaryl-1*H*-pyrrole

Keywords: Pyrrole synthesis; Microwave assisted organic synthesis; Alkyl and aryl ammonium formates; Reduction; Amination–cyclization.
* Corresponding author. Tel.: +91-413-2655991x411; fax: +91-413-2655265; e-mail address: hspr@yahoo.com

0040–4020/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2003.11.087



1a-f **2a-d** **3a-i**

1a: Ar = C_6H_5
1b: Ar = 4-ClC_6H_4
1c: Ar = 4-BrC_6H_4
1d: Ar = 4-$CH_3C_6H_4$
1e: Ar = 4-$OCH_3C_6H_4$
1f: Ar = 4-Cl-3-$CH_3C_6H_3$

2a: R = H
2b: R = n-C_4H_9
2c: R = $CH_2C_6H_5$
2d: R = C_6H_5

3a: Ar = C_6H_5, R = H;
3b: Ar = 4-ClC_6H_4, R = H
3c: Ar = 4-BrC_6H_4, R = H
3d: Ar = 4-$CH_3C_6H_4$, R = H
3e: Ar = 4-$OCH_3C_6H_4$, R = H
3f: Ar = 4-Cl-3-$CH_3C_6H_3$, R = H
3g: Ar = C_6H_5, R = n-C_4H_9
3h: Ar = C_6H_5, R = $CH_2C_6H_5$
3i: Ar = R = C_6H_5.

Scheme 1.

derivatives from 1,4-diarylbut-2-yne-1,4-diones and also for the synthesis of 2,3,5-triaryl, 1,2,3,5-tetraaryl and 2,3,4,5-tetraaryl-1*H*-pyrroles. We also report our studies on comparison of yield of the selected pyrrole derivative when synthesized by microwave or conventional heating techniques.

2. Results and discussion

The 1,4-diarylbut-2-ene-1,4-diones (dibenzoyl ethylenes) **1a–f** were smoothly converted into 2,5-diaryl-1*H*-pyrroles **3a–f** when they were subjected to reductive amination–cyclization with ammonium formate **2a** in the presence of 5% Pd/C in PEG-200 under microwave irradiation for 2 min (Scheme 1). In this method the ene-dione was being reduced to the 1,4-dione in the initial transformation via palladium catalyzed catalytic transfer hydrogenation. The resulting 1,4-dione moiety was further transformed into 2,5-diaryl-1*H*-pyrroles in a domino fashion through amination–cyclization by utilizing in situ generated ammonia. The results of the transformation of differently phenyl substituted 1,4-diarylbut-2-ene-1,4-diones **1a–f** to pyrrole derivatives **3a–f** are gathered together in Table 1. It can be seen from the Table that when the reaction was conducted under microwave irradiation in PEG-200 the transformation of 1,4-diphenylbut-2-ene-1,4-dione **1a** into 2,5-diphenyl-1*H*-pyrrole **3a** was over in 30 s whereas the reaction required 30 min for completion in methanol reflux. However, the transformation of 1,4-di(4-methoxyphenyl)-but-2-ene-1,4-dione **1e** into 2,5-di(4-methoxyphenyl)-1*H*-pyrrole **3e** required comparatively longer time both under microwave conditions or under methanol reflux indicating the influence of the electron donating 4-methoxy group in the transformation. The yield of the pyrrole derivative **3e** was 89% under microwave irradiation but only 37% in methanol reflux. In addition to the pyrrole product, the double bond reduced product 1,4-diphenyl-1,4-butanedione was obtained in 45% yield in refluxing in methanol. Prolonged reflux did not increase the yield of the pyrrole product. However, the yield of **3e** rose to 85% when the reaction was conducted in diethylene glycol at 150 °C for 10 min. This result indicated that the reduction of the double bond in **1e** with ammonium formate was efficient and was not affected by the electron donating methoxy substituent on the phenyl ring. On the other hand, subsequent steps in the sequence, the formation of the hemiaminal intermediates and cyclisation to pyrrole rings appears to be highly influenced by the presence of the methoxy group. Amarnath and co-workers made similar observations in the mechanistic studies on Paal–Knorr pyrrole synthesis.[12]

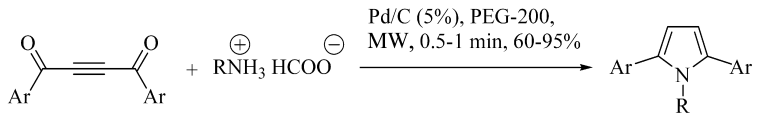
Table 1. Transformation of ene-diones **1a–e** to pyrroles **3a–i**

Entry	Enedione	Formate derivatives	Pyrrole	Time (min)	Power (W)	Yield (%)
1	**1a**	**2a**	**3a**[a]	0.5	200	92
2	**1b**	**2a**	**3b**[b]	1.0	200	80
3	**1c**	**2a**	**3c**[c]	1.0	200	85
4	**1d**	**2a**	**3d**[b]	1.5	200	85
5	**1e**	**2a**	**3e**[d]	2.0	200	89
6	**1f**	**2a**	**3f**[e]	2.0	200	84
7	**1a**	**2b**	**3g**[f]	2.0	200	56
8	**1a**	**2c**	**3h**[g]	2.0	200	63
9	**1a**	**2d**	**3i**[h]	2.0	200	60

[a] Ref. 13.
[b] Ref. 14.
[c] Ref. 15.
[d] Ref. 12.
[e] Ref. 11.
[f] Ref. 16.
[g] Ref. 17.
[h] Ref. 18.

The *N*-alkyl or *N*-aryl pyrrole derivatives **3g–i** was prepared by employing alkyl/aryl ammonium formates **2b–d** as reagents for the reduction, amination–cyclization of enedione **1a**. In general the reaction of alkyl/aryl ammonium formates was found to be difficult and only moderate yields of the pyrrole products **3g–i** were realized in the reaction (Table 1, entry 7–9). Whereas with the microwave heating conditions, the yield of the pyrroles **3g–i** was around 60%, the yield was only about 28% in methanol reflux. It appears that the steric and electronic effects on the amino group of the alkyl/aryl amines play a role in the rate-determining step during the pyrrole formation. Similar to our observation previously, Sammes and Chiu have shown that the Paal–Knorr reaction may follow different pathways depending on whether the reactant is ammonia or an alkyl amine.[19]

Next, we sought to demonstrate utility of the present procedure in the one-pot synthesis of 2,5-disubstituted



4a-f **2a-d** **3a-i**

4a: Ar = C_6H_5
4b: Ar = 4-ClC_6H_4
4c: Ar = 4-BrC_6H_4
4d: Ar = 4-$CH_3C_6H_4$
4e: Ar = 4-$OCH_3C_6H_4$
4f: Ar = 4-Cl-3-$CH_3C_6H_3$

2a: R = H
2b: R = n-C_4H_9
2c: R = $CH_2C_6H_5$
2d: R = C_6H_5

3a: Ar = C_6H_5, R = H
3b: Ar = 4-ClC_6H_4, R = H
3c: Ar = 4-BrC_6H_4, R = H
3d: Ar = 4-$CH_3C_6H_4$, R = H
3e: Ar = 4-$OCH_3C_6H_4$, R = H
3f: Ar = 4-Cl-3-$CH_3C_6H_3$, R = H
3g: Ar = C_6H_5, R = n-C_4H_9
3h: Ar = C_6H_5, R = $CH_2C_6H_5$
3i: Ar = R = C_6H_5

Scheme 2.

Table 2. Transformation of yne-diones **4a–f** to pyrroles **3a–i**

Entry	Ynedione	Formate derivatives	Pyrrole	Time (min)	Power (W)	Yield (%)
1	**4a**	**2a**	**3a**	0.5	200	95
2	**4b**	**2a**	**3b**	1.0	200	92
3	**4c**	**2a**	**3c**	1.0	200	94
4	**4d**	**2a**	**3d**	1.0	200	90
5	**4e**	**2a**	**3e**	1.0	200	91
6	**4f**	**2a**	**3f**	1.0	200	90
7	**4a**	**2b**	**3g**	1.0	200	60
8	**4a**	**2c**	**3h**	1.0	200	65
9	**4a**	**2d**	**3i**	1.0	200	61

pyrroles from 1,4-diphenylbut-2-yne-1,4-diones wherein complete hydrogenation of the triple bond in ynedione to 1,4-dione is followed by an amination cyclization reaction. Thus, in the palladium mediated microwave assisted reaction of ammonium formate with **2a**, 1,4-diarylbut-2-yne-1,4-diones **4a–f** resulted in the 2,5-disubstituted pyrrole derivatives **3a–f** in over 90% yield within one min (Scheme 2). Similar reaction with alkyl/aryl ammonium formate **2b–d** also resulted in the pyrrole derivatives **3g–i** in 60–95% yield (Table 2). It appears that the reactivity of ynediones **4a–f** towards the formation of pyrrole derivatives is similar to enediones **1a–f**. Since there is little difference in the reactivity of similarly substituted ynediones and enediones it can be concluded that hydrogenation of the triple bond to the corresponding fully saturated derivatives is facile and the steps involving amination–cyclization determine the rate of formation of pyrrole derivatives.

Having demonstrated a facile 2,5-diarylpyrrole synthesis from enediones **1a–f** and ynediones **4a–f**, we extended the method for the preparation of pyrroles with multiple aryl substitution. The reaction of (*E*)-1,2,4-triphenylbut-2-ene-1,4-dione (1,2-dibenzoylstyrene) **5a** with ammonium formate **2a** and Pd/C in PEG-200 under microwave irradiation resulted in the known[20] 2,3,5-triphenyl-1*H*-pyrrole **6a** in near quantitative yield within 1 min (Scheme 3; Table 3, entry 1). We conducted this reaction on a 10 mmol scale and found smooth transformation to the pyrrole derivative in 92% yield. Thus, the present procedure is amenable for scaling up. The reaction of **5a** with anilinium formate **2d** resulted in 1,2,3,5-tetraphenyl-1*H*-pyrrole[21] **6b** within 1 min (Scheme 3; Table 3, entry 2). Similarly, the reaction of (*E*)-1,2,3,4-tetraphenylbut-2-ene-1,4-dione (1,2-dibenzoylstilbene) **5b** with ammonium formate furnished 2,3,4,5-tetraphenyl-1*H*-pyrrole[22] **6c** (Scheme 3; Table 3, entry 3). However, the reaction of **5b** with anilinium formate did not yield the expected 1,2,3,4,5-pentaphenyl-1*H*-pyrrole[23] **6d**. The ^{1}H NMR and IR spectra of the crude product from this reaction indicated that reduction of the double bond and formation of imine

Table 3. Transformation of ene-dione **5a**,**b** to pyrroles **6a–c**

Entry	Enedione	Formate derivatives	Pyrrole	Time (min)	Power (W)	Yield (%)
1	**5a**	**2a**	**6a**[a]	1.0	200	95
2	**5a**	**2b**	**6b**[b]	1.0	200	65
3	**5b**	**2a**	**6c**[c]	5.0	200	95

[a] Ref. 20.
[b] Ref. 21.
[c] Ref. 22.

5a,b **2a,d** **6a-d**

5a: $R^1 = R^2 = R^4 = C_6H_5$, R^3 = H
5b: $R^1 = R^2 = R^3 = R^4 = C_6H_5$

2a: R^5 = H
2d: $R^5 = C_6H_5$

6a: $R^1 = R^2 = R^4 = C_6H_5$, $R^3 = R^5$ = H
6b: $R^1 = R^2 = R^4 = R^5 = C_6H_5$, R^3 = H
6c: $R^1 = R^2 = R^3 = R^4 = C_6H_5$, R^5 = H
6d: $R^1 = R^2 = R^3 = R^4 = R^5 = C_6H_5$

Scheme 3.

Table 4. The effect of reaction conditions on the transformation of **5a** to **6a**

S. No.	Vessel	Solvent	Time (min)	Power (W)	Temperature (°C)	Yield (%)
1	Glass (open)[a]	PEG-200	1.0	200	126	96
2	Glass (open)	PEG-200	5.0	–	126	90
3	Teflon (capped)	Methanol	2.0	200	–	96
4	Glass (open)	Ethylene glycol	2.0	200	116	88

[a] The vessel was kept in silica gel bath.

intermediates have occurred but the anticipated cyclization to the pyrrole ring did not take place. It appears that the steric factors play a major role in preventing the open chain intermediates to go through an entropically unfavorable cyclization step.

Next, we sought to find out if there were any non-thermal microwave effects in the conditions employed in the conversion of 1,4-butanediones to the pyrrole derivatives. The transformation of (*E*)-1,2,4-triphenylbut-2-ene-1,4-dione (1,2-dibenzoylstyrene) **5a** to 2,3,5-triphenyl-1*H*-pyrrole **6a** was taken as a representative example. The results in the study are gathered together in Table 4. We found that microwave irradiation at 200 W the temperature of the reaction mixture in PEG-200 reached 126 °C in 1 min (Table 4, entry 1). When the same reaction was conducted in a preheated oil bath maintained at 126 °C it took 5 min. for completion (Table 4, entry 2). However, the yield of the desired product was marginally lower possibly due to decomposition of the product. When the reaction was conducted in methanol in a screw-capped Teflon vessel the reaction took 2 min indicating that methanol is also a good solvent for the reaction (Table 4, entry 3). The microwave-mediated transformation of **5a** to **6a** was equally facile in the high boiling solvent, ethylene glycol (Table 4, entry 4). Thus, similar to the observations made by many groups,[24] in the present transformation microwave energy is used only for rapid heating of the reaction mixture to furnish the desired pyrrole derivatives in near quantitative yield within few min. Even tough the reaction worked well in methanol; obviously, PEG-200 is a better solvent for conducing the microwave-assisted reactions due to precautions one need to take while conducing them in the sealed vessels.

3. Conclusion

In conclusion we have shown that various aryl substituted pyrrole derivatives can be synthesized readily from enediones and ynediones in a microwave mediated one-pot synthesis using ammonium and alkylammonium formates in the presence of palladium. In the future, we plan to use the polyaryl pyrroles for the synthesis of flat dendrimers incorporating the pyrrole core.

4. Experimental

4.1. General

All reagents and solvents were purchased form E-Merck and Sisco Chemicals, India. Microwave reactions were carried out using BPL-Sanyo, India; mono-mode and multi-power (power source: 230 V, 50 Hz, microwave frequency: 2450 MHz) microwave oven. The TLC (pre-coated silica gel 60 F_{254}, Merck) method was used to monitor the progress of the reaction and the products were isolated by short column chromatography on silica gel (100–200 mesh, Acme Synthetic Chemicals, India) using hexanes/dichloromethane (DCM) mixture as the eluent. Melting points were noted using a Gallenkamp melting point apparatus. The IR spectra were recorded as KBr pellets using Bomem MB104 spectrometer. The frequencies at which the ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or in CCl_4:$CDCl_3$ (1:1) with Bruker 300 MHz, Bruker 400 MHz, JEOL 400 MHz or Varian 300 MHz are noted in the spectral data. TMS was used as internal standard. Mass spectra were recorded on HP MS-engine S989A (EI, electron impact, 70 eV). We have given in the experimental section only those spectral data (IR, ^{1}H NMR, ^{13}C NMR or MS), which have not been described in literature.

4.1.1. General procedure for the synthesis of di, tri and tetraarylpyrroles from enediones: 2,5-diphenyl-1*H*-pyrrole (3a). A 25 mL conical flask, charged with enedione **1a** (100 mg, 0.42 mmol), ammonium formate **2a** (267 mg, 4.2 mmol), 5% Pd/C (2 mg) and PEG-200 (2 mL), was irradiated in the microwave oven at 200 W for 30 s. After completion of the reaction (TLC) cooled (rt) contents of the flask were charged on the short column of silica (5 cm×1 cm) and eluted with hexane/DCM (90:10 to 50:50). Removal of solvent from pooled fractions yielded pyrrole **3a** as a white solid (85 mg, 92%). An analytically pure sample was obtained by recrystallization from DCM/hexanes (2:98); mp 142-144 °C (lit:[13] 143 °C). ^{13}C NMR ($CDCl_3$): δ=108.0, 123.8, 126.3, 128.9, 132.6, 133.0 ppm.

4.1.2. 2,5-Di(4-chlorophenyl)-1*H*-pyrrole (3b). Following the above general procedure, enedione **1b** (100 mg, 0.33 mmol) was transformed to pyrrole **3b** with ammonium formate **2a** (206 mg, 3.3 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 1 min. Yield: 76 mg (80%; white solid); mp 180–182 °C (lit.[14] 181 °C). ν_{max}=3460 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=6.50 (d, J=2.7 Hz, 2H), 7.33 (d, J=8.4 Hz, 4H), 7.42 (d, J=8.4 Hz, 4H), 8.44 (br s, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ=108.6, 125.0, 129.2, 130.9, 132.3, 132.4 ppm.

4.1.3. 2,5-Di(4-bromophenyl)-1*H*-pyrrole (3c). Following the above general procedure, enedione **1c** (100 mg, 0.25 mmol) was transformed to pyrrole **3c** with ammonium formate **2a** (160 mg, 2.5 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 1 min. Yield: 81 mg (85%, white solid); mp 212–214 °C (lit.[15] 214–216 °C). ^{13}C NMR ($CDCl_3$): δ=108.1, 123.8, 126.4, 128.9, 132.7, 133.1 ppm.

4.1.4. 2,5-Di(4-methylphenyl)-1*H*-pyrrole (3d). Following the above general procedure, enedione **1d** (100 mg, 0.38 mmol) was transformed to pyrrole **3d** with ammonium formate **2a** (238 mg, 3.8 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 1.5 min. Yield: 80 mg (85%, white solid); mp 202–204 °C (lit.[14] 203 °C). ^{1}H NMR ($CDCl_3$): δ=2.35 (s, 6H), 6.45 (br s, 2H), 7.14 (d, J=7.8 Hz, 4H), 7.37 (br d, J=7.8 Hz, 4H), 8.42 (s, br, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ=21.3, 107.5, 123.8, 130.0, 132.0, 132.9, 135.7 ppm.

4.1.5. 2,5-Di(4-methoxyphenyl)-1*H*-pyrrole (3e). Following the above general procedure, enedione **1e** (100 mg, 0.34 mmol) was transformed to pyrrole **3e** with ammonium formate **2a** (213 mg, 3.4 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 2 min. Yield: 84 mg (89%, white solid); mp 230–232 °C (lit.[12] 232 °C).

4.1.6. 2,5-Di(4-chloro-3-methylphenyl)-1*H*-pyrrole (3f). Following the above general procedure, enedione **1f** (100 mg, 0.3 mmol) was transformed to pyrrole **3f** with ammonium formate **2a** (189 mg, 3.0 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 2 min. Yield: 80 mg (84%, white solid); mp 190–192 °C (lit.[11] 190 °C).

4.1.7. 2,3,5-Triphenyl-1*H*-pyrrole (6a). Following the above general procedure, enedione **5a** (1000 mg, 3.2 mmol) was transformed to pyrrole **6a** with ammonium formate **2a** (2019 mg, 32 mmol) and 5% Pd/C (5 mg) in PEG-200 (5 mL) under microwave irradiation at 200 W for 2 min. Yield: 901 mg (95%, white solid); mp 138–140 °C (lit.[20] 135–137 °C).

4.1.8. 2,3,4,5-Tetraphenyl-1*H*-pyrrole (6c). Following the above general procedure, enedione **5a** (500 mg, 1.29 mmol) was transformed to pyrrole **6c** with ammonium formate **2a** (812 mg, 12.9 mmol) and 5% Pd/C (5 mg) in PEG-200 (5 mL) under microwave irradiation at 200 W for 7 min. Yield: 453 mg (95%, white solid); mp 212–214 °C (lit.[22] 214–216 °C). ^{13}C NMR ($CDCl_3$): δ=123.4, 126.1, 126.7, 127.2, 128.0, 128.2, 128.6, 128.9, 130.1, 131.0, 132.9, 135.4, 138.6 ppm.

4.1.9. 1-Butyl-2,5-diphenyl-1*H*-pyrrole (3g). To butylamine (155 mg, 2.1 mmol) and formic acid (0.1 mL, 2.1 mmol) were taken in a 25 mL conical flask at 5 °C, enedione **1a** (100 mg, 0.42 mmol), 5% Pd/C (2 mg) and PEG-200 (2 mL), were added, This reaction mixture was irradiated by microwaves in the microwave oven at 200 W for 2 min. After completion of the reaction (TLC), the mixture was cooled to room temperature and chromatographed on silica (5 cm×1 cm) using hexanes/DCM as the eluent. Removal of solvent from pooled fractions yielded pyrrole **3g** as white solid (65 mg, 56%). An analytically pure sample was obtained by recrystallization from DCM/hexanes (2:98); mp 112–114 °C (lit.[16] 113 °C). ^{1}H NMR ($CDCl_3$): δ=0.50 (t, J=7.3 Hz, 3H), 0.81 (sextet, J=7.3 Hz, 2H), 1.14 (pentet, J=7.3 Hz, 2H), 4.03 (t, J=7.3 Hz, 2H), 6.22 (s, 2H), 7.27 (br t, J=7.2 Hz, 2H), 7.37 (br t, J=7.2 Hz, 4H), 7.42 (br d, J=7.2 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$): δ=13.3, 19.3, 32.7, 44.9, 109.3, 126.8, 128.4, 129.0, 134.2, 136.5 ppm.

4.1.10. 1-Benzyl-2,5-diphenyl-1*H*-pyrrole (3h). Following the above general procedure, enedione **1a** (100 mg, 0.42 mmol) was transformed to pyrrole **3h** with benzyl amine (227 mg, 2.1 mmol), formic acid (0.1 mL, 2.1 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 2 min. Yield: 81 mg, (63%); mp 144–146 °C (lit.[17] 144 °C).

4.1.11. 1,2,5-Triphenyl-1*H*-pyrrole (3i). Following the above general procedure, enedione **1a** (100 mg, 0.42 mmol) was transformed to pyrrole **3i** with aniline (197 mg, 2.1 mmol), formic acid (0.1 mL, 2.1 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 2 min. Yield: 75 mg, (60%); mp 228–230 °C (lit.[18] 229 °C).

4.1.12. 1,2,3,5-Tetraphenyl-1*H*-pyrrole (6b). Following the above general procedure, enedione **5a** (624 mg, 2 mmol) was transformed to pyrrole **6b** with aniline (931 mg, 1 mmol), formic acid (0.45 mL, 10 mmol) and 5% Pd/C (5 mg) in PEG-200 (3 mL) under microwave irradiation at 155 W for 8 min. Yield: 485 mg, (65%); mp 200–202 °C (lit.[21] 200–1 °C).

4.1.13. General procedure for the synthesis of di and triarylpyrroles from ynediones: synthesis of 2,5-diphenyl-1*H*-pyrrole (3a). A 25 mL conical flask, charged with ynedione **4a** (100 mg, 0.43 mmol), ammonium formate (269 mg, 4.3 mmol), 5% Pd/C (2 mg) and PEG-200 (2 mL), was irradiated in the microwave oven at 200 W for 30 s. After completion of the reaction (TLC) the cooled (rt) reaction mixture was loaded on a short column of silica (5 cm×1 cm) and eluted with hexanes/DCM (90:10 to 50:50). Removal of solvent from pooled fractions resulted in pyrrole **3a** as the white solid (89 mg, 95%) after removal of the solvent.

4.1.14. 2,5-Di(4-chlorophenyl)-1*H*-pyrrole (3b). Following the above general procedure, ynedione **4b** (100 mg, 0.33 mmol) was transformed to pyrrole **3b** with ammonium formate (207 mg, 3.3 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 60 s. Yield: 87 mg (92%).

4.1.15. 2,5-Di(4-bromophenyl)-1*H*-pyrrole (3c). Following the above general procedure, ynedione **4c** (100 mg, 0.26 mmol) was transformed to pyrrole **3c** with ammonium formate (161 mg, 2.6 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 60 s. Yield: 90 mg (94%).

4.1.16. 2,5-Di(4-methylphenyl)-1*H*-pyrrole (3d). Following the above general procedure, ynedione **4d** (100 mg, 0.38 mmol) was transformed to pyrrole **3d** with ammonium formate (240 mg, 3.8 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 60 s. Yield: 85 mg (90%).

4.1.17. 2,5-Di(4-methoxyphenyl)-1*H*-pyrrole (3e). Following the above general procedure, ynedione **4e**

(100 mg, 0.34 mmol) was transformed to pyrrole **3e** with ammonium formate (214 mg, 3.4 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 60 s. Yield: 86 mg (91%).

4.1.18. 2,5-Di(4-chloro-3-methylphenyl)-1*H*-pyrrole (3f). Following the above general procedure, ynedione **4f** (100 mg, 0.3 mmol) was transformed to pyrrole **3f** with ammonium formate (190 mg, 3 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 60 s. Yield: 86 mg (90%).

4.1.19. 1-Butyl-2,5-diphenyl-1*H*-pyrrole (3g). To butyl amine (155.9 mg, 2.13 mmol) and formic acid (0.1 mL, 2.13 mmol) taken in a 25 mL conical flask at 5 °C, ynedione **4a** (100 mg, 0.43 mmol), 5% Pd/C (2 mg) and PEG-200 (2 mL) were added. This reaction mixture was irradiated by microwaves in the microwave oven at 200 W for 60 s. After completion of the reaction (TLC) the mixture was cooled to room temperature and chromatographed on silica (5 cm×1 cm) using hexanes/DCM as the eluent. Removal of solvent from pooled fraction yielded pyrrole **3g** as white solid (70 mg, 60%).

4.1.20. 1-Benzyl-2,5-diphenyl-1*H*-pyrrole (3h). Following the above general procedure, ynedione **4a** (100 mg, 0.43 mmol) was transformed to pyrrole **3h** with benzyl amine (228.6 mg, 2.13 mmol), formic acid (0.1 mL, 2.13 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 60 s. Yield: 80 mg, (61%).

4.1.21. 1,2,5-Triphenyl-1*H*-pyrrole (3i). Following the above general procedure, ynedione **4a** (100 mg, 0.43 mmol) was transformed to pyrrole **3i** with aniline (198.7 mg, 2.13 mmol), formic acid (0.1 mL, 2.13 mmol) and 5% Pd/C (2 mg) in PEG-200 (2 mL) under microwave irradiation at 200 W for 60 s. Yield: 82 mg, (65%).

Acknowledgements

S. J. thanks CSIR for a fellowship. H. S. P. R. thanks the UGC-SAP program and CSIR, India, for financial support. We thank Professor A. Srikrishna, for spectra and helpful discussions. We also thank RSIC, IITM, Chennai and SIF, IISc, Bangalore, for recording the spectra.

References and notes

1. (a) Jones, R. A.; Bean, G. P. *The chemistry of pyrroles*; Academic: London, 1977; pp 1–5. (b) Sundberg, R. J. *Comprehensive heterocyclic chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 4, p 370. (c) Sundberg, R. J. *Comprehensive heterocyclic chemistry II*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1996; Vol. 2, p 149. (d) Boger, D. L.; Boyce, C. W.; Labrili, M. A.; Sehon, C. A.; Jin, Q. *J. Am. Chem. Soc.* **1999**, *121*, 54, and references cited therein.
2. *The chemistry of heterocyclic compounds*; Jones, R. A., Ed.; Wiley: Toronto, 1990; part 1 and 2.
3. (a) Tietze, L. F.; Nordmann, G. *Synlett* **2001**, 337. (b) Groenendaal, L.; Meijer, E.-W.; Vekemans, J. A. J. M. In *Electronic materials: the oligomer approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1997.
4. Sakon, Y.; Ohnuma, T.; Hashimoto, M.; Saito, S.; Tsutsui, T.; Adachi, C. US Patent 5,077,142 A 19,911,231; **1991** CA 117:16862.
5. (a) Paal, C. *Chem. Ber.* **1884**, *17*, 2756. (b) Knorr, L. *Chem. Ber.* **1884**, *17*, 2863.
6. (a) Conant, J. B.; Lutz, R. E. *J. Am. Chem. Soc.* **1923**, *45*, 1303. (b) Conant, J. B.; Lutz, R. E. *J. Am. Chem. Soc.* **1925**, *47*, 881. (c) Coampaigne, E.; Foye, W. O. *J. Org. Chem.* **1952**, *17*, 1405.
7. Demirdji, S. H.; Haddadin, M. J.; Issidorides, C. H. *J. Heterocycl. Chem.* **1985**, *22*, 495.
8. Wilson, R. M.; Hengge, A. C.; Ataei, A.; Ho, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 7240.
9. Zhang, J.-J.; Schuster, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 7149.
10. (a) Ram, S.; Ehrenkaufer, R. E. *Synthesis* **1988**, 91. (b) Rao, H. S. P.; Reddy, K. S. *Tetrahedron Lett.* **1994**, *35*, 171.
11. Rao, H. S. P.; Jothilingam, S. *Tetrahedron Lett.* **2001**, *42*, 6595.
12. Amarnath, V.; Anthony, D. C.; Amarnath, K.; Valentine, W. M.; Wetterau, L. A.; Graham, D. G. *J. Org. Chem.* **1991**, *56*, 6924.
13. Patterson, J. N.; Soedigdo, S. *J. Org. Chem.* **1968**, *33*, 2057.
14. Tsuge, O.; Tashiro, M.; Hokama, K.; Yamada, K. *Kogyo Kagaku Zasshi* **1968**, *71*, 1667. CA 70:37587.
15. Alper, H.; Prickett, J. E. *Inorg. Chem.* **1977**, *16*, 67.
16. Schulte, K. E.; Reisch, J.; Walker, H. *Chem. Ber.* **1965**, *98*, 98.
17. Alickmann, D.; Frohlich, R.; Maulitz, A. H.; Wurthwein, E. *Eur. J. Org. Chem.* **2002**, 1523.
18. Periasamy, M.; Srinivas, G.; Bharathi, P. *J. Org. Chem.* **1999**, *64*, 4204.
19. Chiu, P. K.; Samme, M. P. *Tetrahedron* **1988**, *44*, 3531.
20. Furstner, A.; Weintritt, H.; Hupperts, A. *J. Org. Chem.* **1995**, *60*, 6637.
21. Lee, C.; Yang, L.; Hwu, T.; Feng, A.; Tseng, J.; Luh, T. *J. Am. Chem. Soc.* **2000**, *122*, 4992.
22. Sera, A.; Fukumoto, S.; Yoneda, T.; Yamada, H. *Heterocycles* **1986**, *24*, 697.
23. Hong, P.; Yamazaki, H. *J. Organomet. Chem.* **1989**, *373*, 133.
24. Kuhnert, N. *Angew Chem. Int. Ed.* **2002**, *41*, 1863.