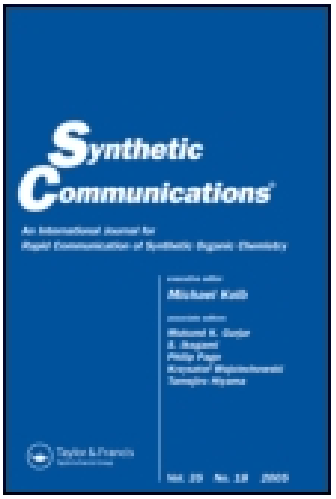

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SOLVENT-FREE SYNTHESIS OF *N*-ARYLFULLEROPYRROLIDINE DERIVATIVES WITHOUT USING PHASE-TRANSFER CATALYST UNDER MICROWAVE IRRADIATION

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Several N-arylfulleropyrrolidine derivatives were synthesized via the direct solvent-free reactions of N-unsubstituted fulleropyrrolidines and nitrochlorobenzenes under microwave irradiation in the absence of phase-transfer catalysts. Their structures were confirmed by ultraviolet–visble, Fourier transform–infrared, ^{1}H NMR, and mass spectrometry.

Keywords: *N*-Arylation; fullerene; fulleropyrrolidine; microwave irradiation; solvent-free

Because of fullerene's unique geometrical shape and chemical properties, its chemical derivatization is an important frontier of active research, immediately after the discovery and availability in macroscopic amounts of the most abundant fullerene.[1–7] Various methods have been developed for functionalizing fullerene and an impressive number of fullerene derivatives have been synthesized.[8–13] Among the wide variety of organofullerene compounds that have been synthesized and studied, the family of fulleropyrrolidines has played a prominent role.[14–16] The reaction between azomethine ylide and fullerene is one of the first reported fullerene reactions and has been widely studied to prepare fulleropyrrolidine derivatives.[17] To obtain the *N*-substituted fulleropyrrolidines, either an *N*-substituted amino acid was used or the *N*-unsubstituted fulleropyrrolidines were modified at the *N*-H functionality.[18–20] Because *N*-nitrophenylfulleropyrrolidine derivatives cannot be easily obtained by cycloaddition reactions with the corresponding *N*-substituted amino acid as starting materials, the *N*-arylation of *N*-unsubstituted fulleropyrrolidines is regarded as the better approach.

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Microwave irradiation is a clean methodology for introducing energy into reactions, and microwave-assisted organic synthesis can remarkably decrease reaction time and improve yields of products.[21–23] De la Cruz et al. first reported the *N*-alkylation of *N*-unsubstituted fulleropyrrolidines to afford *N*-alkylfulleropyrrolidines under microwave irradiation by phase-transfer catalysis in the absence of solvent.[19] Nevertheless, microwave irradiation has not been successfully applied to the *N*-arylation of *N*-unsubstituted fulleropyrrolidines.[24,25] In this article, we report the *N*-arylation of *N*-unsubstituted fulleropyrrolidines with 2,4-dinitrochlorobenzene and 2,4,6-trinitrochlorobenzene under microwave irradiation without using solvent or phase-transfer catalysts. To the best of our knowledge, this is the first example of application of microwave irradiation without using phase-transfer catalyst and solvent for *N*-arylation of *N*-unsubstituted fulleropyrrolidines.

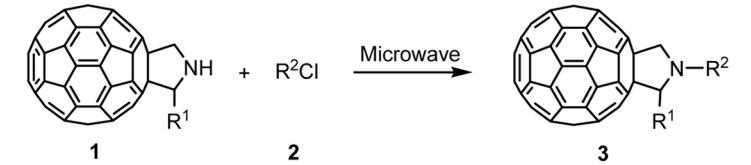
RESULTS AND DISCUSSION

Microwave-irradiated, solvent-free, phase-transfer catalysis has been successfully applied to *N*-alkylation of *N*-unsubstituted fulleropyrrolidines.[19] Our previous work was to synthesize some *N*-nitrophenylfulleropyrrolidine derivatives using this method. Initially, a mixture of 2-(3-nitrophenyl)fulleropyrrolidine **1a** (9.2 mg), 2,4,6-trinitrochlorobenzene (TNCB) (12.6 mg), potassium carbonate (14.2 mg), and tetrabutylammonium chloride (TBAC) (16.6 mg) was homogenized in an ultrasonic bath for 10 min and irradiated at 693 W for 5 min to prepare *N*-(2,4,6-trinitrophenyl)-2-(3-nitrophenyl)fulleropyrrolidine **3a**, but only 10% of the starting material, 20% of C_{60}, and other unidentified decomposition products were obtained. Various irradiation powers (297–900 W) and times (0.5–15 min) were studied, and product **3a** was not obtained. We thought it might be caused by the phase-transfer catalyst TBAC, so we tried directly reacting **1a** and TNCB without using TBAC and potassium carbonate. When a binary mixture of **1a** (18.0 mg) and TBAC (35.0 mg) was homogenized in an ultrasonic bath for 10 min and heated to 150°C for 8 h, no starting material was recovered and only some unidentified decomposition products were obtained, which were not dissolved in organic solvents such as toluene, carbon bisulfide, dimethylsulfoxide, and chloroform. To our delight, when a binary mixture of **1a** (35.4 mg) and TNCB (224.1 mg) was homogenized in an ultrasonic bath for 10 min and irradiated at 693 W for 15 min, the aim product **3a** was obtained (Scheme 1).

To probe the generality of the reaction for other *N*-unsubstituted fulleropyrrolidines and nitrophenyl chloride, compounds **1b–d** and **2a–b** were used in the reaction. As we expected, when the binary mixtures of **1b–d** and **2a, b** were irradiated at 693 W for 15 min, the corresponding products **3b–e** were obtained, as shown in Scheme 1 and Table 1.

Benzyl halides were also used in the reaction to see if the *N*-benzyl fulleropyrrolidines could be obtained. When the binary mixtures of **1d** (0.04 mmol) and **2c, d** (0.90 mmol) were irradiated at 693 W for 15 min and then isolation by flash-column chromatography on silica gel using a mixture of *n*-hexane and toluene as eluents, **3f** and **3 g** were afforded in 23% and 80% yields respectively (Scheme 1, Table 1).

For the sake of comparison with microwave irradiation, traditional heating has been chosen to synthesize the products **3a–e** with **1a–d** and **2a, b** as starting materials. The binary mixtures of **1a–d** and **2a, b** were heated to 150°C for 8 h, then the



1 2 3

1a: R^1=3-$NO_2C_6H_4$ **2a**: R^2X=2,4-$(NO_2)_2C_6H_3$Cl **3a**: R^1=3-$NO_2C_6H_4$, R^2=2,4,6-$(NO_2)_3C_6H_2$
1b: R^1=2-$NO_2C_6H_4$ **2b**: R^2X=2,4,6-$(NO_2)_3C_6H_2$Cl **3b**: R^1=2-$NO_2C_6H_4$, R^2=2,4-$(NO_2)_2C_6H_3$
1c: R^1=4-$NO_2C_6H_4$ **2c**: R^2X=4-$NO_2C_6H_4CH_2$Br **3c**: R^1=2-$NO_2C_6H_4$, R^2=2,4,6-$(NO_2)_3C_6H_2$
1d: R^1=C_6H_5 **2d**: R^2X=$C_6H_5CH_2$Cl **3d**: R^1=4-$NO_2C_6H_4$, R^2=2,4,6-$(NO_2)_3C_6H_2$
3e: R^1=C_6H_5, R^2=2,4,6-$(NO_2)_3C_6H_2$
3f: R^1=C_6H_5, R^2=4-$NO_2C_6H_4CH_2$
3g: R^1=C_6H_5, R^2=$C_6H_5CH_2$

Scheme 1. Synthesis of **3a–g** by the *N*-arylation of **1a–d** with **2a–d** under microwave irradiation.

mixtures were cooled to room temperature and purified by flash chromatography with hexane/toluene (1:2) as eluent to afford products **3a–e**. The results of the reaction are shown in Table 2.

As shown in Tables 1 and 2, *N*-arylfulleropyrrolidine derivatives **3a–e** were obtained in less reaction time and better yields under microwave irradiation conditions than with the traditional heating method.

The structures of products **3a–g** were characterized by ultraviolet–visible (UV-vis), ^{1}H NMR, Fourier transform–infrared (FT-IR), and mass (MS) spectral data. The spectral data of adducts **3f, g** are fully consistent with those reported previously.[19] The UV-vis spectra of products **3a–e** have absorption bands around 257, 318, and 430 nm. The ^{1}H NMR spectra of **3a–e** in $CDCl_3$ solution show typical signals of the 2-arylfulleropyrrolidine system, a singlet at $\delta = 6.06$–7.33 for H–2, and two doublets at $\delta = 4.94$–5.57 for CH_2–5 with $J_{AB} = 9.6$–10.8 Hz. Products **3a** and **3c–e** exhibit a singlet at $\delta = 8.73$–8.78 in their ^{1}H NMR spectra for *N*-substituted 2,4,6-trinitrophenyl group in the pyrrole ring. Product **3b** shows a doublet at $\delta = 8.87$ ($J = 2.4$ Hz), a double doublet at $\delta = 8.47$ ($J = 2.4$, 9.0 Hz), and a doublet at $\delta = 8.00$ ($J = 9.0$ Hz) in their ^{1}H NMR spectra for *N*-substituted 2,4-dinitrophenyl group in the pyrrole ring. The IR spectra are very complex, and more than 20 absorption bands were observed. The absorption around 526, 577, 1183, and

Table 1. Reaction results of **1a–d** and **2a–d** under microwave irradiation[a]

Entry	Reactants	Products	Yields (%)[b]
1	0.04 mmol **1a**, 0.90 mmol **2b**	**3a**	33
2	0.04 mmol **1b**, 0.90 mmol **2a**	**3b**	29
3	0.04 mmol **1b**, 0.90 mmol **2b**	**3c**	18
4	0.04 mmol **1c**, 0.90 mmol **2b**	**3d**	56
5	0.04 mmol **1d**, 0.90 mmol **2b**	**3e**	37
6	0.04 mmol **1d**, 0.90 mmol **2c**	**3f**	23[c]
7	0.04 mmol **1d**, 0.90 mmol **2d**	**3g**	80

[a]Irradiation power and time are 693 W and 15 min, respectively.
[b]Isolated yields.
[c]89% based on consumed **2c** (74% **2c** was recovered).

Table 2. Reaction results of **1a–d** and **2a–b** under traditional heating[a]

Entry	Reactants	Products	Yields (%)[b]
1	0.04 mmol **1a**, 0.90 mmol **2b**	**3a**	23
2	0.04 mmol **1b**, 0.90 mmol **2a**	**3b**	24
3	0.04 mmol **1b**, 0.90 mmol **2b**	**3c**	17
4	0.04 mmol **1c**, 0.90 mmol **2b**	**3d**	45
5	0.04 mmol **1d**, 0.90 mmol **2b**	**3e**	29

[a]Reaction temperature and time are 150°C and 8h respectively.
[b]Isolated yields.

1460 cm^{-1} are attributed to the vibration of fullerene core. Bands at 3022–2848 cm^{-1} show the carbon hydrogen (C−H) stretching vibration, and the absorptions around 1500 and 1605 cm^{-1} are attributed to the stretch vibration of benzene ring. The absorptions around 1530 and 1343 cm^{-1} are assigned to asymmetric and symmetric NO_2 stretching modes, respectively. The MS of products **3b** and **3c** show peaks at m/z 1050 and 1096, respectively, corresponding to their M^+ and MH^+. Products **3a, 3d**, and **3e** reveal peaks at m/z 855, 855, and 810, respectively, corresponding to their molecular ion minus $(NO_2)_3C_6H_2NCH_2$ unit.

CONCLUSION

In summary, we have developed a general and efficient microwave-assisted approach for the synthesis of *N*-arylfulleropyrrolidine derivatives without solvent and phase-transfer catalyst. Compared with the traditional heating method, microwave-assisted, solvent-free reaction has advantages in improved yield and enhanced reaction rates.

EXPERIMENTAL

General Methods

Reactions were performed in a domestic microwave oven (Midea model KJ23C-AN). ^{1}H NMR spectra were recorded on a Bruker Ac 300/600 spectrometer with $CS_2/CDCl_3$ as the solvent. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS were taken on a Bruker BiFlexIII mass spectrometer using 4-hydroxy-α-cyanocinnamic acid as the matrix. The IR spectra were measured on a Nicolet 380 FT-IR spectrometer (KBr pellet) with a resolution of 4 cm^{-1}, in the range of 4000–400 cm^{-1}. UV-vis spectra were recorded on Unicon UV-2102 PCS spectrometer using $CHCl_3$ as the solvent. Chromatographic purifications were carried out with 200- to 300-mesh silica gel. C_{60} was prepared by arc discharge method.[26] *N*-Unsubstituted fulleropyrrolidines **1a–d** were afforded by the Prato reaction.[17] All other commercial reagents are of analytical grade.

Synthesis of *N*-Arylfulleropyrrolidine Derivatives Under Microwave Irradiation—General Procedure

A mixture of corresponding *N*-unsubstituted fulleropyrrolidine (0.04 mmol) and nitrophenyl chloride (0.90 mmol) was homogenized in an ultrasonic bath for

10 min and irradiated at 693 W for 15 min. Then the mixture was cooled to room temperature and washed with carbon disulfide. The solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography [SiO_2, hexane/toluene (1:2)] to give the reaction product and the unreacted *N*-unsubstituted fulleropyrrolidine.

Synthesis of *N*-Arylfulleropyrrolidine Derivatives Under Traditional Heating—General Procedure

A mixture of corresponding *N*-unsubstituted fulleropyrrolidine (0.04 mmol) and nitrophenyl chloride (0.90 mmol) was homogenized in an ultrasonic bath for 10 min and heated in an oil bath at 150°C for 8 h. Then the mixture was cooled to room temperature and washed with carbon disulfide. The solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography [SiO_2, hexane/toluene (1:2)] to give the reaction product and the unreacted *N*-unsubstituted fulleropyrrolidine.

Selected Data

***N*-(2,4,6-Trinitrophenyl)-2-(3-nitrophenyl)fulleropyrrolidine 3a.** UV-vis($CHCl_3$) λ_{max}: 257 (s), 318 (m), 430 (w)nm; ^{1}H NMR (CS_2/$CDCl_3$, 400 MHz) δ: 8.75 (s, 2H), 8.48 (s, 1H), 8.18 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 8.0$ Hz, 1H), 6.17 (s, 1H), 5.56 (d, $J = 10.4$ Hz, 1H), 5.42 (d, $J = 10.8$, 1H) ppm; IR (KBr) υ: 3022, 2920, 2848, 1608, 1530, 1462, 1399, 1351, 1183, 1089, 838, 779, 719, 682, 574, 563, 553, 527 cm^{-1}; MS (MALDI-TOF) m/z: 855 $[M\text{-}(NO_2)_3C_6H_2NCH_2]^+$, 720 $[C_{60}]^+$.

***N*-(2,4-Dinitrophenyl)-2-(2-nitrophenyl)fulleropyrrolidine 3b.** UV-vis($CHCl_3$) λ_{max}: 257 (s), 317 (m), 431 (w)nm; ^{1}H NMR (CS_2/$CDCl_3$, 600 MHz) δ: 8.87 (d, $J = 2.4$ Hz, 1H), 8.47 (dd, $J = 2.4$, 9.0 Hz, 1H), 8.27 (d, $J = 7.8$ Hz, 1H), 8.00 (d, $J = 9.0$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 1H), 7.64 (t, $J = 7.8$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 1H), 7.33 (s, 1H), 5.56 (d, $J = 9.6$ Hz, 1H), 4.94 (d, $J = 9.6$, 1H) ppm; IR (KBr) υ: 3019, 2923, 2848, 1604, 1528, 1486, 1463, 1400, 1344, 1187, 1071, 767, 737, 575, 562, 553, 527 cm^{-1}; MS (MALDI-TOF) m/z: 1050 $[M]^+$, 720 $[C_{60}]^+$.

***N*-(2,4,6-Trinitrophenyl)-2-(2-nitrophenyl)fulleropyrrolidine 3c.** UV-vis($CHCl_3$) λ_{max}: 257 (s), 320 (m), 431 (w)nm; ^{1}H NMR (CS_2/$CDCl_3$, 600 MHz) δ: 8.77 (s, 2H), 8.05 (t, $J = 7.8$ Hz, 2H), 7.58 (t, $J = 7.8$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.13 (s, 1H), 5.56 (d, $J = 10.8$ Hz, 1H), 5.45 (d, $J = 10.8$, 1H) ppm; IR (KBr) υ: 3020, 2927, 2852, 1608, 1540, 1461, 1400, 1343, 1187, 1088, 858, 767, 737, 574, 562, 553, 527 cm^{-1}; MS (MALDI-TOF) m/z: 1096 $[M + H]^+$, 720 $[C_{60}]^+$.

***N*-(2,4,6-Trinitrophenyl)-2-(4-nitrophenyl)fulleropyrrolidine 3d.** UV-vis($CHCl_3$) λ_{max}: 257 (s), 318 (m), 430 (w)nm; ^{1}H NMR (CS_2/$CDCl_3$, 600 MHz) δ: 8.78 (s, 2H), 8.19 (d, $J = 9.0$ Hz, 2H), 7.83 (d, $J = 9.0$ Hz, 2H), 6.20 (s, 1H), 5.57 (d, $J = 10.8$ Hz, 1H), 5.43 (d, $J = 10.8$, 1H) ppm; IR (KBr) υ: 3018, 2924, 2848, 1606, 1538, 1493, 1462, 1400, 1343, 1187, 1085, 860, 842, 729, 574, 562, 553, 527 cm^{-1}; MS (MALDI-TOF) m/z: 855 $[M\text{-}(NO_2)_3C_6H_2NCH_2]^+$, 720 $[C_{60}]^+$.

***N*-(2,4,6-Trinitrophenyl)-2-phenylfulleropyrrolidine 3e.** UV-vis($CHCl_3$) λ_{max}: 257 (s), 315 (m), 431 (w)nm; ^{1}H NMR ($CS_2/CDCl_3$, 300 MHz) δ: 8.73 (s, 2H), 7.55–7.52 (m, 2H), 7.32–7.28 (m, 3H), 6.06 (s, 1H), 5.56 (d, $J = 10.3$ Hz, 1H), 5.39 (d, $J = 10.2$, 1H) ppm; IR (KBr) υ: 2923, 2851, 1605, 1537, 1456, 1403, 1338, 1183, 1085, 904, 877, 729, 705, 574, 563, 553, 527 cm^{-1}; MS (MALDI-TOF) m/z: 810 $[M\text{-}(NO_2)_3C_6H_2NCH_2]^+$, 720 $[C_{60}]^+$.

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