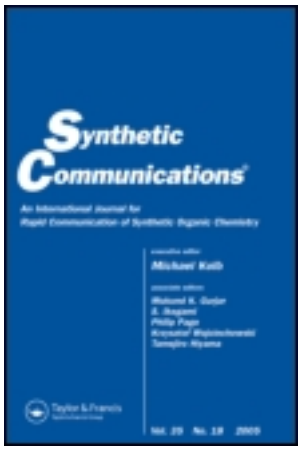

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ABSTRACT

A convenient synthetic method for the title compounds are described. Heating 1, 2 and 3 under microwave irradiation for 3–5 min to afford **4**. The structure of the compound **4c** has been thoroughly studied by X-ray crystallographic analysis.

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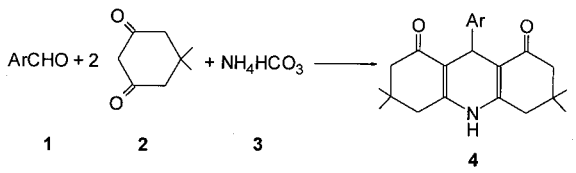
Since microwave heating was used for organic synthesis by Gedye[1] in 1986, the microwave organic chemistry has been a topic of continuing interest. Another area that has been drawing many researches in organic synthesis is organic reaction under dry condition.[2] We are currently studying new synthetic methods for heterocyclic compounds by taking advantage of both microwave irradiation and dry reaction condition. 1,4-Dihydropyridines (1,4-DHPs) are well-known compounds as a consequence of their pharmacological profile as calcium channel modulators.[3] The chemical modifications carried out on the DHP ring such as the presence of different substituents,[4] heteroatoms[5] have allowed expansion of the receptor level. However, bearing three fused ring have been less well studied. By refluxing dimedone, aromatic aldehyde in ammonium hydroxide solution **4** was obtained,[6] and the yields were poor. Margarita Suarez et al. reported that **4** was synthesized by reaction of aromatic aldehyde, dimedone, ammonium (acetate using two types of alumina (neutral or basic) as mineral solid supports, DMF as energy transfer medium under microwave irradiation, only five products were synthesized.[7] Here, we would like to report another method, thus, using ammonium bicarbonate instead of ammonium acetate under microwave irradiation without solid supports and energy transfer medium, and the yields were higher. We also present a structure study of **4c** by X-ray analysis.



1 2 3 4

The results were listed in Table 1.

All the compounds obtained gave analysis for C, H, N in good agreement with calculated values. The structures were established on the basis of spectroscopic data and confirmed by X-ray diffraction studies on monocrystal of **4c** (Figure 1).[8]

EXPERIMENTAL

Melting points were determined in a capillary tube and are uncorrected. The ^{1}H NMR spectra were recorded on a DPX 300 MHz spectrometer with TMS as internal standard. The IR spectra were obtained with

Table 1. The Synthesis of **4**

Entry	Ar	Time (min)	Yield (%)
4a	C_6H_5	5	90
4b	2-ClC_6H_4	4	85
4c	4-ClC_6H_4	4	92
4d	4-$(CH_3)_2NC_6H_4$	7	91
4e	3-$O_2NC_6H_4$	4	83
4f	3,4-$(CH_3O)_2C_6H_3$	6	89
4g	3,4-$(OCH_2O)C_6H_3$	6	91
4h	4-$CH_3OC_6H_4$	7	89

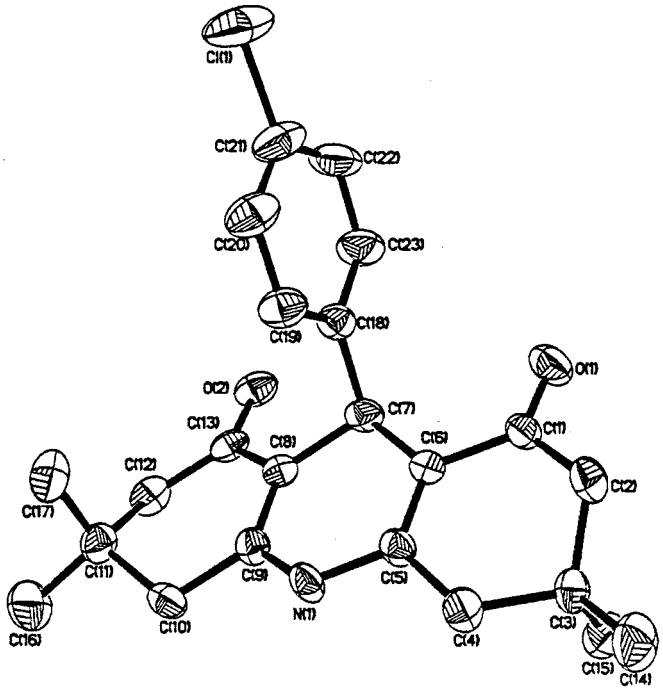


Figure 1. X-ray crystal structure of **4c**.

SE-1730 instrument as potassium bromide pellets. Elemental analyses were determined by using Perkin-Elmer 240c elemental analyser. Crystal structure was obtained with CAD4 diffractometer. Benzaldehyde was distilled before used, all other reagents were commercially available used without

further purification. Microwave irradiation was carried out with a modificatory commercial microwave oven (2450 MHz, 650 W) under atmospheric pressure.

General Procedure

A dry flask (25 mL) was charged with the aromatic aldehyde **1** (5 mmol), dimedone **2** (10 mmol) and ammonium bicarbonate **3** (7.5 mmol). The flask was then connected with refluxing equipment. After microwave irradiation for $4 \sim 7$ min, the reaction mixture was cooled and washed with ethanol (3 mL). The crude products were purified by recrystallization from 95% ethanol to afford **4**.

4a: M.p. 190–192°C. (lit. 190–192°C).[6]

4b: M.p. 221–223°C. (lit. 222–224°C).[7]

4c: M.p. 296–298°C, IR (KBr, ν, cm^{-1}): 3383 (NH), 1623 (C=O), 1603 (N-C=O); ^{1}H NMR ($CDCl_3$, δ, ppm): 0.93 (s, 6H, $2CH_3$), 1.05 (s, 6H, $2CH_3$), 2.21–2.25 (m, 8H, 4CH), 5.06 (s, 1H, CH), 7.12–7.32 (m, 4H, ArH), 7.72 (s, 1H, NH). Elementary analysis: found (%): C, 72.03, H, 6.72, N, 3.50; Calcd. for: $C_{23}H_{26}ClNO_2$: C, 71.96, H, 6.83, N, 3.65.

4d: M.p. 263–265°C. (lit. 264–266°C).[6]

4e: M.p. 283–285°C. (lit. 285–286°C).[7]

4f: M.p. 258–260°C. IR (KBr, ν, cm^{-1}): 3384 (NH), 1623 (C=O), 1602 (N-C=O); ^{1}H NMR ($CDCl_3$, δ, ppm): 0.934 (s, 6H, $2CH_3$), 1.05 (s, 6H, $2CH_3$), 2.10–2.30 (m, 8H, 4CH), 3.76 (s, 6H, $2CH_3O$), 5.05 (s, 1H, CH), 6.74–6.93 (m, 3H, ArH), 8.18 (s, 1H, NH). Elementary analysis: found (%): C, 73.43, H, 7.54, N, 3.31; Calcd. for: $C_{25}H_{31}NO_4$: C, 73.32, H, 7.63, N, 3.42.

4g: M.p. 324–326°C. IR (KBr, ν, cm^{-1}): 3280 (NH), 1620 (C=O), 1601 (N-C=O); ^{1}H NMR ($CDCl_3$, δ, ppm): 1.00 (s, 6H, $2CH_3$), 1.10 (s, 6H, $2CH_3$), 2.16–2.40 (m, 8H, 4CH), 5.00 (s, 1H, CH), 5.85 (s, 2H, OCH_2O), 6.63–6.85 (m, 3H, ArH), 7.27 (s, 1H, NH). Elementary analysis: found (%): C, 73.42, H, 6.81, N, 3.44; Calcd. for: $C_{24}H_{27}NO_4$: C, 73.26, H, 6.92, N, 3.56.

4h: M.p. 269–270°C. (lit. 270–272°C).[6]

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8. X-ray analysis of **4c:** Empirical formula $C_{23}H_{26}ClNO_2$, F.W. 383.90, $T = 293(2)$ K, orthorhombic, space group Pna2(1), $a = 14.125(3)$ Å, $b = 14.118(3)$ Å, $c = 10.719(2)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2137.5(7)$ Å^3, $Z = 4$, $D_c = 1.193$ Mg/m^3, $F(000) = 816$, λ (MoKα) $= 0.71073$ Å, $\mu = 0.195$ mm^{-1}, $2.04^\circ < \theta < 24.96^\circ$, $R = 0.0507$, $wR = 0.1536$. S = 1.034, largest diff. peak and hole: 0.341 and -0.317 eÅ^3.

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