Research Article

Clauson Kaas Pyrrole Synthesis Catalyzed by Acidic Ionic Liquid under Microwave Irradiation

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A new procedure to synthesize the N-substituted pyrrole derivatives by Clauson Kaas reaction catalyzed by acidic ionic liquid under microwave irradiation was developed. This procedure provides several advantages such as high yield, clean product formation, and short reaction time.

Dedicated to the memory of Professor Ayhan S. Demir

1. Introduction

Pyrrole derivatives have great importance in organic chemistry, because they are present in many compounds which were natural, medicinal, and agricultural products and semiconductor polymers [1–3]. They are also very useful starting materials for biologically important compounds such as indolizidine alkaloids, bicyclic lactams, and unsaturated γ -lactams [4–7]. Various pyrrole syntheses have been reported in the literature [8–15]. One of these methods is Clauson Kaas pyrrole synthesis which uses 2,5-dimethoxytetrahydrofuran as four-carbon source. Although this reaction provides an important and useful way for synthesis of N-substituted pyrroles, the necessity of high temperature and acidic conditions is resulted by the decomposition of product so low yields and difficult product separation are the main problems with this method [16, 17]. To overcome the problems with classical Clauson Kaas reaction, new synthetic methods such as using two phase system [16], initial aqueous hydrolysis of 2,5-dimethoxytetrahydrofuran [17], and using acetic acid, water, or sodium acetate buffer under microwave irradiation [18] and new catalysts [19–21] have been still developed successfully.

Using microwaves for carrying out reactions is advantageous for the synthesis of numerous types of compound.

The most important improvements with this technique are reduced reaction time, cleaner reactions due to fewer side reactions, and the use of minimal quantities of solvent [22, 23]. So, microwave-assisted synthesis is more economical and environmentally friendly method.

Ionic liquids (ILs) have been widely used in organic reactions as solvent due to their advantages such as negligible vapor pressure, variable polarity, and good solvating ability [24–26]. Recently, they have also attracted the researchers' attention due to their significant role in organic reactions as catalyst [27–32]. After the first use of imidazolium chloroaluminate as catalyst in Friedel-Crafts acylations [33], various ionic liquids have been developed and used in many types of organic reactions as catalyst. Many Lewis acidic and Bronsted acidic ionic liquids have been successfully used as acid catalysts in organic synthesis with advantages such as solvent-free reaction conditions, easy product separation, and recycling [34–39]. As far as we know, acidic ionic liquids have not been used to promote Clauson Kaas reaction, and only a few methods have been developed for this reaction under microwave irradiation [18, 40, 41]. So, we wish to report here the clean, short time synthesis of N-substituted pyrrole derivatives by the Clauson Kaas reaction catalyzed by acidic ionic liquid, 1-hexyl-3-methylimidazolium hydrogen sulfate ([hmim][HSO₄]), under microwave irradiation.

TABLE 1: Comparison of the catalytic activity of the catalysts.

Catalyst	Time (min)	Yield (%)
CH ₃ CO ₂ H	80	52
[bmim][BF ₄]	30	56
[hmim][H ₂ PO ₄]	30	61
[hmim][HSO ₄] ^a	60	73
[hmim][HSO ₄]	4	85

^aWithout MW.

2. Experimental

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 FT-IR spectrometer. NMR spectra were recorded on Mercury VX-400 MHz and Bruker Avance III 500 MHz spectrometer. Chemical shifts δ are reported in ppm relative to CDCl₃ (¹H: δ = 7.27) and TMS as internal standard. Column chromatography was conducted on silica gel 60 (40–63 μ m). TLC was carried out on aluminum sheets precoated with silica gel 60F₂₅₄ (Merck). Elemental analysis was carried out on Thermo Flash EA 1112 series apparatus. Optical rotations were measured with Bellingham Stanley ADP-410 Polarimeter. Microwave-assisted reactions were carried out on an Arcelik MD 554 household oven.

2.1. General Procedure for Clauson Kaas Reaction. Amine (1 mmol) was added to 2,5-dimethoxytetrahydrofuran (1 mmol or 2 mmol for amine 2b) in [hmim][HSO₄] (1 mmol) and mixed thoroughly. The mixture was then exposed to microwave irradiation (90 W) for a period of time enough to complete the reaction. The reaction mixture was dissolved in water, and the product was extracted with diethyl ether (3 $\times$ 5 mL), and the combined organic phases were dried over MgSO₄. The crude product obtained after evaporation of the solvent was purified by column chromatography over silica gel (EtOAc:hexane 1:2, 1:6, or 1:10).

2.1.1. (S)-1-(1-Phenylethyl)-1H-pyrrole (S)-3a. Colorless liquid (85% yield). $[\alpha]_D^{20}$ = +6.6; Lit. +6.8 [42] (c 2.7, CHCl₃); IR (neat): ν 3027, 2965, 1603, and 1377 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.75 (d, J = 7.02 Hz, 3H, CH₃), 5.20 (q, J = 7.02 Hz, 1H, N-CH), 6.11 (brs, 2H, =CH), 6.68 (brs, 2H, =CH), 7.01 (d, J = 7.80 Hz, 2H, ArH), and 7.14 (m, 3H, ArH). Anal. Calcd for C₁₂H₁₃N (171.24): C, 84.17; H, 7.65; N, 8.18. Found: C, 84.22; H, 7.61; N, 8.15.

2.1.2. 1-(4-(1H-Pyrrol-1-yl)butyl)-1H-pyrrole 3b. Colorless oil (91% yield). IR (neat): ν 3098, 2929, 2872, 1498, 1279, and 1087 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.75 (m, 4H, CH₂), 3.85 (t, J = 6.64 Hz, 4H, CH₂), 6.15 (apparent t, J = 1.95, 1.95 Hz, 4H, =CH), and 6.63 (apparent t, J = 2.34, 1.95 Hz, 4H, =CH). Anal. Calcd for C₁₂H₁₆N₂ (188.13): C, 76.55; H, 8.57; N, 14.88. Found: C, 76.49; H, 8.58; N, 14.86.

2.1.3. (R)-Methyl 2-(1H-Pyrrol-1-yl)propanoate (R)-3c. Colorless oil (73% yield). $[\alpha]_D^{20}$ = +12.7; Lit. +12.83 [42] (c 1.1, CHCl₃); IR (neat): ν 3102, 2992, 2954, 1747, 1378, and 1282 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.65 (d, J = 7.33 Hz, 3H, CH₃), 3.64 (s, 3H, OCH₃), 4.69 (q, J = 7.33 Hz, 1H, N-CH), 6.11 (apparent t, J = 2.44, 1.96 Hz, 2H, =CH), and 6.67 (apparent t, J = 2.44, 1.95 Hz, 2H, =CH). Anal. Calcd for C₈H₁₁NO₂ (153.18): C, 62.73; H, 7.24; N, 9.14. Found: C, 62.76; H, 7.21; N, 9.15.

2.1.4. (S)-Methyl 3-Methyl-2-(1H-pyrrol-1-yl)butanoate (S)-3d. Colorless oil (69% yield). $[\alpha]_D^{20}$ = -2.7; Lit. -2.8 [42] (c 4.2, CHCl₃); IR (neat): ν 3055, 2986, 1727, 1372, and 1285 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.67 (d, J = 6.65 Hz, 3H, CH₃), 0.91 (d, J = 6.65 Hz, 3H, CH₃), 2.32 (m, 1H, CH), 3.63 (s, 3H, CH₃), 4.00 (d, J = 10.23 Hz, 1H, N-CH), 6.02 (brs, 2H, =CH), and 6.63 (brs, 2H, =CH). Anal. Calcd for C₁₀H₁₅NO₂ (181.23): C, 66.27; H, 8.34; N, 7.73. Found: C, 66.28; H, 8.40; N, 7.69.

2.1.5. (S)-2-(1H-Pyrrol-1-yl)propan-1-ol (S)-3e. Colorless oil (89% yield). $[\alpha]_D^{20}$ = +8.3; Lit. +8.25 [42] (c 2.2, CHCl₃); IR (neat): ν 3524, 3098, 2982, 1558, 1378, and 1280 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.37 (d, J = 7.02 Hz, 3H, CH₃), 1.63 (brs, 1H, OH), 3.59 (m, 2H, CH₂), 4.09 (m, 1H, N-CH), 6.10 (brs, 2H, =CH), and 6.67 (brs, 2H, =CH). Anal. Calcd for C₇H₁₁NO (125.17): C, 67.17; H, 8.86; N, 11.19. Found: C, 67.21; H, 8.84; N, 11.16.

2.1.6. (R)-2-(1H-Pyrrol-1-yl)butan-1-ol (R)-3f. Colorless oil (91% yield). $[\alpha]_D^{20}$ = +14.3; Lit. +14.3 [42] (c 0.4, CHCl₃); IR (neat): ν 3517, 3048, 2998, 1602, 1376, and 1282 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.85 (t, J = 7.41 Hz, 3H, CH₃), 1.68 (brs, 1H, OH), 1.77 (m, 2H, CH₂), 3.73 (m, 2H, CH₂), 3.85 (m, 1H, N-CH), 6.18 (apparent t, J = 2.34, 1.95 Hz, 2H, =CH), and 6.70 (apparent t, J = 2.34, 1.95 Hz, 2H, =CH). Anal. Calcd for C₈H₁₃NO (139.19): C, 69.03; H, 9.41; N, 10.06. Found: C, 69.01; H, 9.42; N, 9.96.

2.1.7. (1R, 2S)-1-Phenyl-2-(1H-pyrrol-1-yl)propan-1-ol (1R, 2S)-3g. Yellow oil (83% yield). $[\alpha]_D^{20}$ = +26.6; Lit. +26.8 [42] (c 3.6, CHCl₃); IR (neat): ν 3523, 3054, 2994, 1605, 1376, and 1283 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.33 (d, J = 7.00 Hz, 3H, CH₃), 2.11 (brs, 1H, OH), 4.08 (m, 1H, N-CH), 4.61 (d, J = 4.68 Hz, 1H, O-CH), 5.94 (brs, 2H, =CH), 6.47 (brs, 2H, =CH), 7.04 (d, J = 7.60 Hz, 2H, ArH), and 7.16 (m, 3H, ArH). Anal. Calcd for C₁₃H₁₅NO (201.26): C, 77.58; H, 7.51; N, 6.96. Found: C, 77.51; H, 7.60; N, 7.01.

2.1.8. (1S, 2S)-1-Phenyl-2-(1H-pyrrol-1-yl)propane-1,3-diol (1S, 2S)-3h. Yellow oil (81% yield). $[\alpha]_D^{20}$ = +93.2; Lit. +93.5 [42] (c 0.5, CHCl₃); IR (neat): ν 3525, 3050, 1605, 1375, and 1284 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 2.00 (brs, 1H, OH), 2.45 (brs, 1H, OH), 3.72 (m, 2H, CH₂), 4.06 (m, 1H, N-CH), 4.92 (d, J = 6.6 Hz, 1H, O-CH), 6.15 (apparent t, J = 1.95, 1.95 Hz, 2H, =CH), 6.70 (apparent t, J = 2.34, 1.95 Hz, 2H, =CH), 7.19 (m, 2H, ArH), and 7.31 (m, 3H, ArH). Anal. Calcd

TABLE 2: The synthesized pyrrole derivatives.

Amine (2)	Pyrrole (3)	Reaction time (min)	Yield (%) ^a
(S)-2a	(S)-3a [42]	4	85
2b	3b [43]	4	91
(R)-2c	(R)-3c [42]	3	73
(S)-2d	(S)-3d [42]	3	69
(S)-2e	(S)-3e [42]	5	89
(R)-2f	(R)-3f [42]	5	91
(1R, 2S)-2g	(1R, 2S)-3g [42]	5	83
(1S, 2S)-2h	(1S, 2S)-3h [42]	5	81
2i	3i [44]	25	72

^a Isolated yield.

for $C_{13}H_{15}NO_2$ (217.26): C, 71.87; H, 6.96; N, 6.45. Found: C, 71.82; H, 6.97; N, 6.41.

2.1.9. 1-(4-Methyl-2-pyrimidinyl)-1H-pyrrole 3i. White solid, mp. 44–45°C; Lit. 44.5–46°C [44] (72% yield). IR (neat): ν 2917, 1583, 1475, 1434, and 1384 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$): δ 2.51 (s, 3H, CH_3), 6.32 (apparent t, $J = 2.25$ Hz, 2H, =CH), 6.90 (d, $J = 5.00$ Hz, 1H, ArH), 7.79 (apparent t, $J = 2.25$ Hz, 2H, =CH), and 8.44 (d, $J = 5.05$ Hz, 1H, ArH). Anal. Calcd for $C_9H_9N_3$ (159.19): C, 67.90; H, 5.70; N, 26.40. Found: C, 67.86; H, 5.72; N, 26.41.

3. Results and Discussion

The acidic ionic liquid [hmim][HSO_4] was prepared under microwave irradiation starting from [hmim][Br] according to the literature procedure [45], and the spectral data of the compound were in accordance with the reported data [46]. We started the research with (S)-phenylethylamine as a representative reactant to see if the acidic IL would catalyze the Clauson Kaas reaction and to achieve optimum reaction conditions such as microwave irradiation power, IL amount, and the necessity of cosolvent such as diethyl ether, chloroform. It was found that the reaction was completed within 4 min in the presence of equimolar amount of acidic ionic liquid under solvent-free conditions without any decomposition of product. The reaction was also carried out without microwave irradiation by stirring the reaction mixture at room temperature. It was found that the reaction completed in 1 hour with the decomposition of small amount product.

The catalytic activity of [hmim][HSO_4] was compared with those of acetic acid, [bmim][BF_4], and [hmim][H_2PO_4], which was prepared by the same procedure with [hmim][HSO_4], under the optimum conditions. As one can see from the results shown in the Table 1, [hmim][HSO_4] was found to be best catalyst providing 85% yield of product.

In a typical reaction procedure, 2,5-dimethoxytetrahydrofuran (1 mmol), equimolar amount of amine, and [hmim][HSO_4] were mixed, and the mixture was exposed to microwave irradiation (90 W) for a period of time enough to complete the reaction. The reaction mixture was dissolved in water, and the product was extracted with diethyl ether and purified by column chromatography. To check the reusability of the ionic liquid, water was removed from the aqueous layer under vacuum, and the residue was washed with diethyl ether and dried under vacuum. Decreasing in the yield of pyrrole was seen after recycling of ionic liquid. The main problem with the Clauson Kaas reaction is the decomposition of acid sensitive derivatives, especially derived from amino acids. Using this procedure, various amine compounds such as aliphatic amines, amino acid esters, amino alcohols, and heteroaromatic amine were converted to their pyrrole derivatives without any significant decomposition (Scheme 1) in 69–91% yield, as summarized in Table 2. Some of the amines were chiral, and any racemization was not observed with these amines. All of the pyrrole derivatives are known in the

SCHEME 1: The synthesis of N-substituted pyrroles catalyzed by [hmim][HSO_4].

literature, and their spectroscopic data are in full agreement with their structures.

4. Conclusion

In conclusion, efficient synthesis of N-substituted pyrrole derivatives has been achieved by Clauson Kaas reaction catalyzed by acidic ionic liquid under microwave irradiation. This new method provides a clean, fast, high yielded, environmentally friendly, and effective way to pyrroles without any significant decomposition of acid sensitive derivatives.

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