



ORIGINAL ARTICLE

Comparative Studies between Conventional Techniques and Green Chemistry to Synthesis of Novel Piperidinium Salts Ionic Liquids (PBSILs)

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KEYWORDS

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Introduction

ABSTRACT: Comparative studies between conventional technique, method (A) and green chemistry (microwave irradiation), method (B) to synthesis of four novel unsymmetrical alkyl piperidinium salts ionic liquids (PBSILs) by the addition of alkyl halides (methyl or allyl) to piperidine with yields more than (90%) in method (A) and less than (70%) in method (B) respectively with decrease reaction time. These novel organic salts are characterized by elemental analysis, ¹H NMR, FTIR and mass spectrometry.

INTRODUCTION

The six membered nitrogenous heterocyclic Piperidinium salts have received high attention as part of continuous program directed toward the synthesis of important heterocyclic compounds; exogenous and nitrogenous five and six membered ring [1, 2], Substituted pyridinium derivatives bearing benzyl, ethyl phenyl or propyl phenyl groups [3-5] on the quaternary nitrogen atom of pyridine salt were prepared and study for their activity against bacteria and fungus, also stereochemistry of polymer synthesis [6], as liquid crystals [7], also it is found that the facile synthesis of significant quantities of a piperidinium-cyclooctene monomer [8], In addition to microwave irradiation which was introduced as a useful alternative to the traditional heating for the synthesis of several heterocyclic derivatives with high yields and short reactions time [9-11]. The method of ionic liquids and Deep eutectic solvents (Reline) has been used to improve the number of products in organic reactions and increase

their efficiency [12, 13]. In recent studies, the researchers took advantage of the protection of the amine group by using acetyl to obtain new heterocyclic compounds [14]. The importance of the heterocyclic compounds lies in that they gave effectiveness against viruses and bacteria compared to the known antibiotics. In a theoretical study, the heterocyclic compounds proved that they had the effectiveness of repelling the Corona virus-19 [15], and also in another study that gave the compensators effective against bacteria [16].

A comparative study between conventional techniques and green chemistry to synthesis of novel piperidinium salts ionic liquids (PBSILs). The microwave synthetic technique is described, which produces the target salts with comparable high yield and low reaction time to conventional reported traditional organic synthetic techniques.

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MATERIALS AND METHODS

All the chemicals used were purchased from Fluka Chemical Co. (Switzerland), Aldrich-Sigma Chemical Co. (Milwaukee, WI, USA) and Alfa Aesar Europe (Karlsruhe, Germany), and used without further purification. All melting points are uncorrected. They determined by the open capillary method using Thomas Hoover melting point apparatus. The FT-IR spectra were determined in (nujol) mulls using Perkin – Elmer 590B, Unicam SP 1025 Infrared spectrophotometer. The ¹H NMR and ¹³C-NMR spectra were carried out on Bruker 400MHz spectrometer using DMSO-d₆ as solvents, tetramethylsilane (T.M.S.) was used as an internal reference.

Finally, the microanalysis was performed at the Alfred Bernhardt Mulheim Laboratories, West Germany.

Synthesis of alkyl piperidinium salts ionic liquids (PBSILs) (2a-e): Method (A) (conventional technique) [17]

To a solution of proper N-alkylpiperidine (0.01 mole) in (10ml) ethanol is added dropwise an equimolecular weight solution of appropriate alkyl halide. The mixture is refluxed for 8 hours.

After cooling, the mixture which is extracted by n-hexane (3-5) times is lifted for one day. Light yellow powder is obtained, filtered and washed several times by diethyl ether. This solid is recrystallized from tetrahydrofuran, to afford the title salts. Some physical properties and elemental analysis are outlined in Table 1.

Method (B) (Microwave irradiation) [18]

To a solution of proper N-alkylpiperidine (513 m. moles) is added dropwise an equimolecular weight solution of appropriate alkyl bromide. The mixture is placed in a flask and exposed to irradiation for 20 min at 70 °C using a microwave irradiation. After cooling, the solid which is formed is worked up as in Method (A) without recrystallization. Percentage yields are outlined in Table 1.

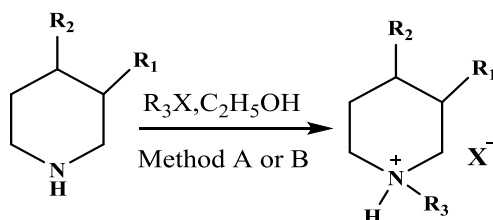
Table 1. Physical properties for compounds (2a-e)

Com. No.	Molecular Formula	Molecular weight	Melting Point (°C)	Yield% method		Elemental analysis % theory (Calculate)		
				A	B	C	H	N
2a	C ₉ H ₁₈ BrN	220.108	157-159	69	94	49.10 (48.24)	8.24 (8.22)	6.36 (6.33)
2b	C ₇ H ₁₆ N	241.07	133-135	69	94	34.87 (35.89)	6.69 (6.84)	5.81 (5.51)
2c	C ₇ H ₁₆ BrN	192.06	117-119	65	90	49.10 (40.39)	8.24 (7.86)	6.36 (7.76)
2d	C ₇ H ₁₆ N	241.07	122-123	66	92	34.87 (35.89)	6.69 (6.84)	5.81 (5.51)
2e	C ₈ H ₁₇ N	254.9	147-148	68	91	37.33 (37.81)	6.68 (6.73)	5.73 (5.51)

RESULTS AND DISCUSSION

Ionic liquids have several properties which could make them an ideal reaction media for chemical reactions performed on a large scale and there are few reports on the uses in many fields especially in industrial application. Accordingly, we will prepare some new

organic salts with different captions such as bromide and iodide. A suitable synthesis of target salts is accomplished by the route outlined in Figure 1. In addition to elemental analysis that comes with agreement of those salts structures, Table 1.



Method (A): Conventional; stirring , 24 hrs at 60 °C

Method (B): Microwave; solvent free; 20mins at 60°C

(2a):R₁= Methyl; R₂=H; R₃=Allyl and X=Br

(2b):R₁= H; R₂=R₃ =Methyl and X=I

(2c):R₁= H; R₂=Methyl ; R₃=Allyl and X=Br

(2d):R₁= R₃=Methyl ; R₂=H and X=I

(2e) R₁= R₂=R₃ =Methyl and X=I

Figure 1. The rout of target salts (2a-e) synthesis.

Also, the structure of compounds (2a-e) was identified by, FT IR and ¹H-NMR spectral data.

The FT-IR spectra showed the stretching bands which belongs to the most important active groups in these compounds, which are shown in the Table 2, Structures of these salts confirmed by ¹HNMR were measured by using DMSO-d₆ as solvent, these values were come in agreement with the proposed structure in the literatures [9] and [10]. Where ¹H NMR spectra for compounds (2a-

e) showed absorptions singlet bands in the range (0.873-0.91ppm) belong to methyl groups protons on carbon atom, also around (0.96-2.77 ppm) assigned to the proton of methylene attached with methyl group (CH-CH₃), broad bands at (8.48-9.59ppm) due to (NH) protons. In addition to the other peaks mentioned in the Table 2. All These values were come in agreement with the literatures [19, 20].

Table 2. Spectral data for synthesized compounds (2a-e).

Comp. No.	IR(KBr) γ cm ⁻¹			¹ H-NMR δ (ppm)
	C- N	C-H	NH	DMSO-d ₆
2a	1586	1660	3422	0.88(s,3H,C-CH ₃),1.066(bs,1H,CH-C),1.06,1.73,3.29.3.70 each of them(bs,cyclic,2H,CH ₂), 4.010(d,2H,CH ₂ in allylic system),5.74(bs,1H,=CH),3.70(bs,2H,terminal CH ₂),9.59(s,1H,NH)
2b	1586	1642	3419	0.91(s,3H,C-CH ₃),1.25(bs,1H,CH-C),1.66(s,,3H,N-CH ₃),2.75,3.10 each of them(bs,cyclic,2H,CH ₂),8.29(s,1H,NH)
2c	1592	1635	3398	0.90(s,3H,C-CH ₃),1.066(bs,1H,CH-C) ,1.06,1.73,3.29.3.70 each of them(bs,cyclic,2H,CH ₂ CH ₂),3.21(d,2H,CH ₂ in allylic system), 5.38(bs, 1H,=CH),5.18(bs,2H,terminal CH ₂),8.53(s,1H,NH)
2d	1570	1635	3412	0.873(s,3H,C-CH ₃),1.045(bs,1H,CH-C),1.747(s,,3H,N-CH ₃),2.75,3.10 each of them(bs,cyclic,2H,CH ₂),8.48(s,1H,NH)
2e	1590	1635	3434	0.88(bs,6H,C-2CH ₃),1.25(bs,2H,2CH-C),1.815(s,,3H,N-CH ₃),2.75,3.10 each of them(bs,cyclic,2H,CH ₂),9.18(s,1H,NH).

The GC-Mass study approves the chemical structures of salts (1) and (3) (as representative for these serious) as shown in the suggested cations GC –Mass fragmentation

mechanism Figures 2 and 3 respectively, which become agree with the references [21] and [22].

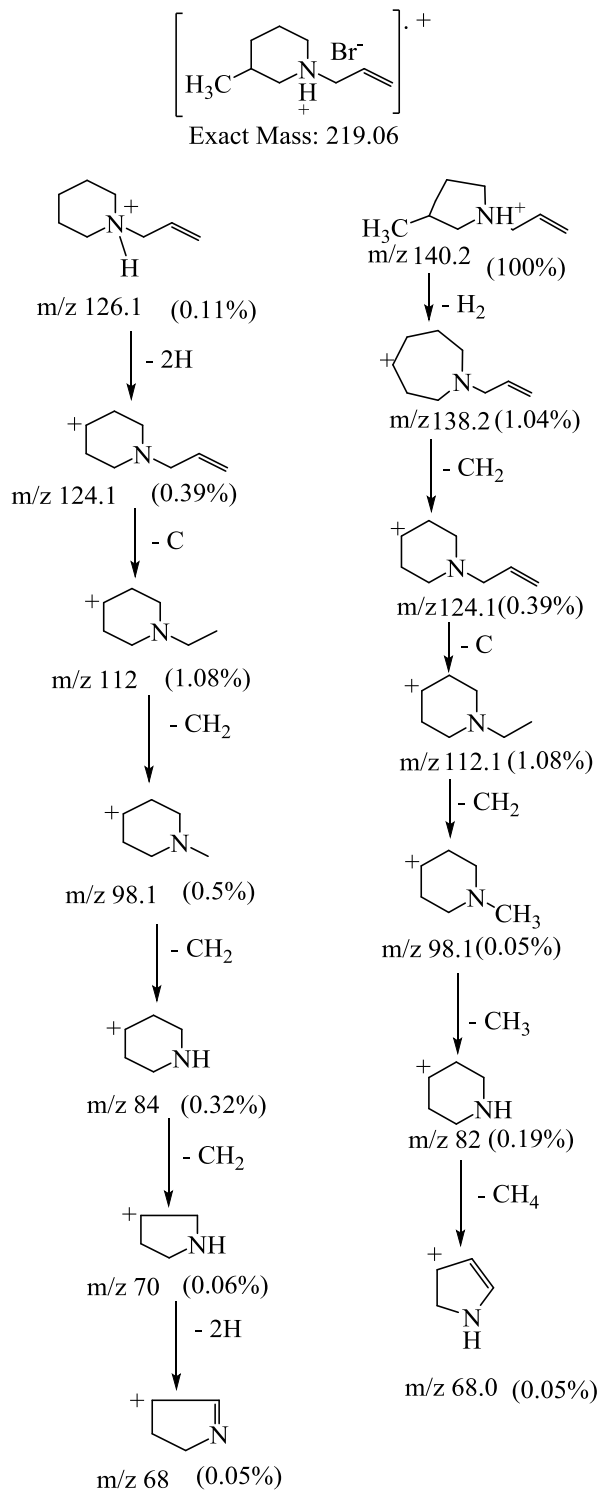


Figure 2. The suggested cation GC-Mass Fragmentation mechanism of salt (2a)

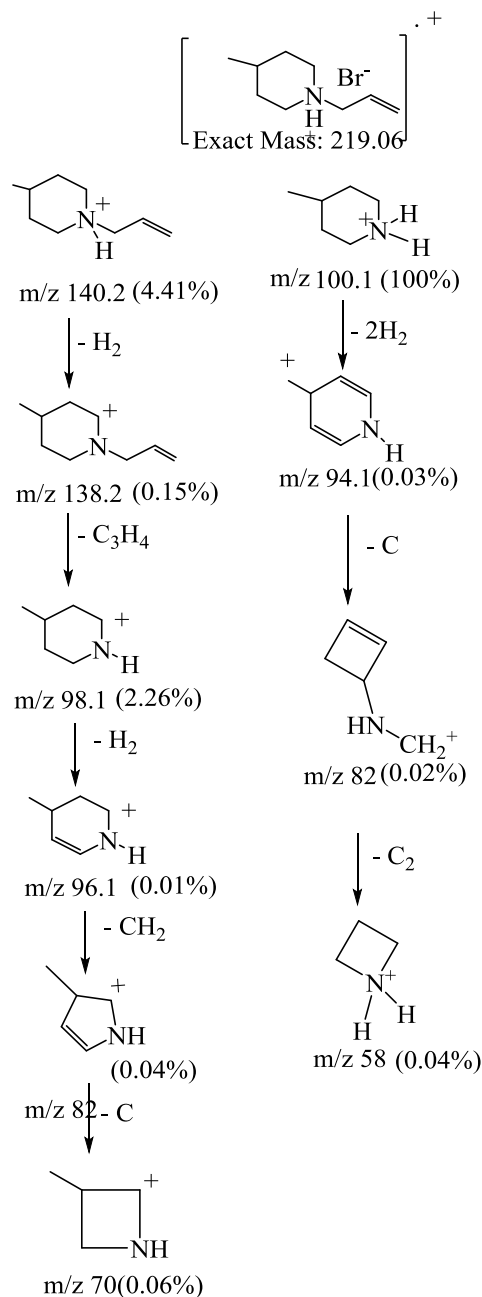


Figure 2. The suggested cation GC-Mass Fragmentation mechanism of salt (3)

CONCLUSIONS

From the experiment it was concluded that method (B), the microwave irradiation has several advantages over conventional one provided significantly low reaction

times, no solvent procedure, and high reaction yields observed. Microwave energy offers many assistances for

carrying out preparation including improved reaction rates, income enhancements, and chemically cleaner.

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Conflict of interests

The author declares no conflict of interest.

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