



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS AND CHARACTERIZATION OF QUATERNARY
AMMONIUM SALTS CONTAINING CARBONYL FUNCTIONALITY**

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**SYNTHESIS AND CHARACTERIZATION OF QUATERNARY AMMONIUM
SALTS CONTAINING CARBONYL FUNCTIONALITY**

By

NORAZLINALIZA BINTI SALIM

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Master of Science**

June 2007



This thesis is dedicated to my family, whose name:

Salim b Abd. Rahman

Lailawati bt M. Roseli

Tengku Muhamad Azlin b Tuan Siri

Nor Azreen bt Salim

Nor Arianti bt Salim

Nor Amira bt Salim

for their support and understanding.

“THANKS FOR YOUR LOVE AND PRAYERS”

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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June 2007

Chairman : Professor Badri Muhammad, PhD

Faculty : Science

This study is mainly focused on the synthesis of quaternary ammonium salts (QASs) derived from long-chain ketones as starting materials. The procedure used in this study is an extension of a new procedure for the preparation of iodinated acetone successfully developed in our lab and shown to be a generalized procedure for the preparation of iodinated ketones (Wong (2002), Badri (2000)), used to produce a class of quaternary amines containing a carbonyl functionality. Eight new QASs were produced; *N*-acetyl-3-methylpyridinium iodide (**17**), *N*-acetyl-4-methylpyridinium iodide (**18**), *N*-(2-oxoheptan-3-yl)pyridinium iodide (**19**), 2-methyl-*N*-(2-oxoheptan-3-yl)pyridinium iodide (**20**), *N*-2-oxoundecanylpyridinium iodide (**21**), 3-methyl-*N*-(2-oxoundeca-3-yl)pyridinium iodide (**22**), *N*-(2-oxododecyl)pyridinium iodide (**23**) and *N*-acetyltriethylammonium iodide (**24**). These compounds were characterized by FT-IR, ¹H and ¹³C NMR and CHN elemental analysis. Single crystal x-ray analysis was used to solve the structures of **17** and **18**. The crystal systems for both compounds were



monoclinic. In the surface tension study, it was found that all of the QASs prepared lower the surface tension of water. The critical micelles concentration (CMC) value for the compound **24** (0.0339 mM) is the lowest of all the quaternary ammonium compounds prepared. Qualitative and quantitative antimicrobial assays showed that not all of the QASs prepared were active against bacteria and fungi tested. Only some of them were found to be active against the microorganisms. The compound **23** was strongly active (diameter > 15 mm) against *Salmonella choleraesuis* and *Bacillus subtilis* wild type with 20 mm and 25 mm diameter inhibition zones, respectively. There are higher than the control, Streptomycin (17 mm and 15 mm respectively). The presence of long-chain ketones moderately increases the inhibiting effect against the selected microorganisms. The MIC value for the compound **23** against *Salmonella choleraesuis* is 12500 $\mu\text{g ml}^{-1}$. The MIC value for the compound **23** (1560 $\mu\text{g ml}^{-1}$) against *Bacillus subtilis* is higher than the control, Streptomycin (48.8 $\mu\text{g ml}^{-1}$).



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**SINTESIS DAN PENCIRIAN GARAM KUATERNARI AMINA YANG
MENGANDUNGI KUMPULAN BERFUNGSI KARBONIL**

Oleh

NORAZLINALIZA BINTI SALIM

Jun 2007

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Penyelidikan ini khususnya mengkaji sintesis sebatian garam kuaternari amina (QASs) yang dihasilkan daripada keton berantai panjang sebagai bahan pemula. Prosedur yang digunakan dalam kajian ini adalah sambungan daripada kaedah baru dan telah berjaya dimajukan untuk menghasilkan aseton teriodin ((Wong (2002), Badri (2000)) dan ini telah digunakan untuk menghasilkan satu kelas kuaternari amina yang mengandungi kumpulan berfungsi karbonil. Terdapat lapan QAS baru yang telah dihasilkan iaitu; *N*-asetonil-3-metilpiridinium iodida (**17**), *N*-asetonil-4-metilpiridinium iodida (**18**), *N*-(2-oksoheptan-3-il)piridinium iodida (**19**), 2-metil-*N*-(2-oksoheptan-3-il)piridinium iodida (**20**), *N*-2-oksoundekasilpiridinium iodida (**21**), 3-metil-*N*-(2-oksoundeka-3-il)piridinium iodida (**22**), *N*-(2-oksododesil)piridinium iodida (**23**) dan *N*-asetoniltrioktilammonium iodida (**24**). Kesemua sebatian yang telah dihasilkan dicirikan melalui FT-IR, ¹H-, ¹³C-NMR dan juga analisis unsur CHN. Analisis kristal X-ray telah digunakan untuk membuktikan struktur-struktur sebatian **17** dan **18**. Didapati bahawa sistem kristal bagi



kedua-dua sebatian ini adalah monoklinik. Bagi kajian tegangan permukaan, didapati bahawa kesemua sebatian kuaternari amina yang dihasilkan telah merendahkan tegangan permukaan air. Nilai CMC bagi sebatian **24** (0.0339 mM) adalah yang paling kecil jika dibandingkan nilai CMC bagi sebatian-sebatian yang lain. Secara analisis kualitatif dan kuantitatif antimikrob menunjukkan tidak kesemua sebatian yang dihasilkan adalah aktif terhadap bakteria dan fungi. Sebatian **23** adalah yang paling aktif (Diameter > 15 mm) terhadap *Salmonella choleraesuis* and *Bacillus subtilis* jenis liar dengan diameter zon perencatan masing-masing 20 mm dan 25 mm. Nilai ini lebih tinggi daripada Streptomycin (17 mm dan 15 mm masing-masing). Dengan kehadiran keton berantai panjang, ia akan meningkatkan kesan perencatan terhadap mikroorganisma terpilih. Nilai MIC bagi sebatian **23** terhadap *Salmonella choleraesuis* adalah 12500 $\mu\text{g ml}^{-1}$. Manakala nilai MIC bagi sebatian **23** (1560 $\mu\text{g ml}^{-1}$) terhadap *Bacillus subtilis* jenis liar adalah melebihi nilai MIC bagi Streptomycin (48.8 $\mu\text{g ml}^{-1}$).

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I certify that an Examination Committee met on 13th June 2007 to conduct the final examination of Norazlinaliza Binti Salim on her Master of Science thesis entitled “Synthesis and Characterization of Quaternary Ammonium Salts Containing Carbonyl Functionality” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institution.

NORAZLINALIZA BINTI SALIM

Date: 24 July 2007

TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	v
ACKNOWLEDGEMENTS	vii
APPROVAL	viii,ix
DECLARATION	x
LIST OF TABLES	xiv
LIST OF FIGURES	xvi
LIST OF ABBREVIATIONS	xxi
CHAPTER	
I INTRODUCTION	1
Quaternary Ammonium Salts (QASs), their application and uses	1
Halogenation of Ketones	3
The Physical Properties of Iodine	10
Surfactants	11
Critical Micelles Concentration (CMC)	12
Biological Properties	14
II LITERATURE REVIEW	17
Preparation of Quaternary Ammonium Salts (QASs)	17
Objectives	22
III MATERIAL AND METHODS	23
Chemicals	23
Reagents	23
Solvents	23
Physical Measurements and Elemental Analyses	24
Melting Point (°C)	24
CHN Elemental Analysis	24
Thin Layer Chromatography (TLC)	24
Fourier Transform-Infrared (FT-IR) Spectral Analysis	25
¹ H-NMR and ¹³ C-NMR Spectral Analysis	25
Gas Chromatographic-Mass Spectral (GC-MS) Analysis	25
X-ray Structure Analysis	25
Iodination of Ketones	26
Iodination of Acetone	26
Iodination of 2-Heptanone	27
Preparation of Quaternary Ammonium Salts (QASs)	27
<i>N</i> -acetyl-3-methylpyridinium iodide (17)	27
<i>N</i> -acetyl-4-methylpyridinium iodide (18)	28



<i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19)	29
2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20)	30
<i>N</i> -2-oxoundecanylpyridinium iodide (21)	31
3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide (22)	32
<i>N</i> -(2-oxododecyl)pyridinium iodide (23)	33
<i>N</i> -acetonyltriocylammonium iodide (24)	34
General Procedure for Surface Tension Measurement	36
Surface Tension Measurement for Samples	37
Antimicrobial Activity	37
Qualitative Antimicrobial Assay	38
Quantitative Antimicrobial Assay	38
IV RESULTS AND DISCUSSION	39
Characterization of Quaternary Ammonium Salts (QASs)	44
<i>N</i> -acetyl-3-methylpyridinium iodide (17)	44
FT-IR analysis	44
¹ H NMR analysis	45
¹³ C NMR analysis	45
X-ray Structure Analyses	46
<i>N</i> -acetyl-4-methylpyridinium iodide (18)	52
FT-IR analysis	52
¹ H NMR analysis	52
¹³ C NMR analysis	53
X-ray Structure Analyses	54
<i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19)	59
FT-IR analysis	59
¹ H NMR analysis	60
¹³ C NMR analysis	60
2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20)	66
FT-IR analysis	67
¹ H NMR analysis	67
¹³ C NMR analysis	67
<i>N</i> -2-oxoundecanylpyridinium iodide (21)	74
FT-IR analysis	74
¹ H NMR analysis	75
¹³ C NMR analysis	75
3-methyl- <i>N</i> -(2-oxoundecan-3-yl)pyridinium iodide (22)	82
FT-IR analysis	82
¹ H NMR analysis	82
¹³ C NMR analysis	83
<i>N</i> -(2-oxododecyl)pyridinium iodide (23)	90
FT-IR analysis	90
¹ H NMR analysis	91
¹³ C NMR analysis	91
<i>N</i> -acetonyltriocylammonium iodide (24)	99
FT-IR analysis	99



¹ H NMR analysis	100
¹³ C NMR analysis	100
CHN Elemental Analyses	106
Gas Chromatography and Mass Spectra (GC-MS) Analyses	107
<i>N</i> -acetyl-3-methylpyridinium iodide (17) and <i>N</i> -acetyl-4-methylpyridinium iodide (18)	107
<i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19)	109
<i>N</i> -2-oxoundecanylpyridinium iodide (21)	111
3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide (22)	113
<i>N</i> -(2-oxododecyl)pyridinium iodide (23)	115
<i>N</i> -acetyltrioctylammonium iodide (24)	118
Surface Tension Measurement	118
Qualitative and Quantitative Antimicrobial Assays	125
V CONCLUSIONS	130
REFERENCES	133
APPENDICES	140
BIODATA OF STUDENT	153



LIST OF TABLES

Table		Page
1	The pK_a Values for Hydrogen Attached to Carbon	4
2	Dissociation Energies of Halogenation Molecules	11
3	Electron Affinity of Halogens	11
4	The pK_a of Alkylpyridine	41
5	NMR spectral data of <i>N</i> -acetyl-3-methylpyridinium iodide (17)	46
6	NMR spectral data of <i>N</i> -acetyl-4-methylpyridinium iodide (18)	54
7	NMR spectral data of <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19)	61
8	NMR spectral data of 2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20)	68
9	NMR spectral data of <i>N</i> -2-oxoundecanylpyridinium iodide (21)	76
10	NMR spectral data of 3-methyl- <i>N</i> -(2-oxoundecan-3-yl)pyridinium iodide (22)	84
11	NMR spectral data of <i>N</i> -(2-oxododecyl)pyridinium iodide (23)	92
12	NMR spectral data of <i>N</i> -acetyltrioctylammonium iodide (24)	101
13	Elemental Analysis of Quaternary Ammonium Salts	106
14	The CMC Value for the QASs Prepared	120
15	Qualitative Antimicrobial Assay of the Quaternary Ammonium Salts (100mg cm ⁻³)	128
16	Quantitative Antimicrobial Assay (MIC value, µg ml ⁻¹)	129
A2.1	Crystal data and structure refinement for sample <i>N</i> -acetyl 3-methylpyridinium iodide (17)	143
A2.2	Bond Lengths (Å) and Angles (°) for <i>N</i> -acetyl-3-methylpyridinium iodide (17)	144
A2.3	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å ² $\times 10^3$) for <i>N</i> -acetyl-3-methylpyridinium iodide (17)	144



A2.4	Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA} \times 10^3$) for <i>N</i> -acetyl-3-methylpyridinium iodide (17)	145
A2.5	Anisotropic displacement parameters ($\text{\AA} \times 10^3$) for <i>N</i> -acetyl-3-methylpyridinium iodide (17)	145
A2.6	Crystal data and structure refinement for sample <i>N</i> -acetyl-4-methylpyridinium iodide (18)	146
A2.7	Bond Lengths (\AA) and Angles ($^\circ$) for <i>N</i> -acetyl-4-methylpyridinium iodide (18)	147
A2.8	Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA} \times 10^3$) for <i>N</i> -acetyl-4-methylpyridinium iodide (18)	147
A2.9	Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA} \times 10^3$) for <i>N</i> -acetyl-4-methylpyridinium iodide (18)	148
A2.10	Anisotropic Displacement Parameters ($\text{\AA} \times 10^3$) for <i>N</i> -acetyl-4-methylpyridinium iodide (18)	148
A3.1	Surface Tension Data of <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19)	149
A3.2	Surface Tension Data of 2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20)	150
A3.3	Surface Tension Data of <i>N</i> -2-oxoundecanylpyridinium iodide (21)	151
A3.4	Surface Tension Data of 3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide (22)	124
A3.5	Surface Tension Data of <i>N</i> -(2-oxododecyl)pyridinium iodide (23)	152
A3.6	Surface Tension Data of <i>N</i> -acetyltriethylammonium iodide (24)	152



LIST OF FIGURES

Figure		Page
1	Example of Quaternary Ammonium Salt (Cetyltrimethylammonium Bromide)	1
2	Mechanism of the Acid and Base-Catalyzed Halogenation of Ketones	6
3	Graph of Surface Tension vs Log of Concentration of Surfactant	13
4	FT-IR spectrum of 3-iodo-2-heptanone (16)	43
5	FT-IR Spectrum of <i>N</i> -acetyl-3-methylpyridinium iodide (17)	45
6	The X-Ray Structure of <i>N</i> -acetyl-3-methylpyridinium iodide (17)	47
7	¹ H NMR spectrum of <i>N</i> -acetyl-3-methylpyridinium iodide (17) (400 MHz, DMSO)	49
8	¹ H NMR spectrum of <i>N</i> -acetyl-3-methylpyridinium iodide (17) (400 MHz, DMSO) (expanded)	50
9	¹³ C NMR spectrum of <i>N</i> -acetyl-3-methylpyridinium iodide (17) (100 MHz, DMSO)	51
10	FT-IR spectrum of <i>N</i> -acetyl-4-methylpyridinium iodide (18)	53
11	The X-Ray Structure of <i>N</i> -acetyl-4-methylpyridinium iodide (18)	55
12	¹ H NMR spectrum of <i>N</i> -acetyl-4-methylpyridinium iodide (18) (400 MHz, DMSO)	56
13	¹ H NMR spectrum of <i>N</i> -acetyl-4-methylpyridinium iodide (18) (400 MHz, DMSO) (expanded)	57
14	¹³ C NMR spectrum of <i>N</i> -acetyl-4-methylpyridinium iodide (18) (100 MHz, DMSO)	58
15	FT-IR spectrum of <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19)	59
16	¹ H NMR spectrum of <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19) (400 MHz, (CD ₃) ₂ C=O)	62



17	¹ H NMR spectrum of <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19) (400 MHz, (CD ³) ² C=O) (Expanded)	63
18	¹³ C NMR spectrum of <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19) (100 MHz, (CD ³) ² C=O)	64
19	¹³ C NMR spectrum of <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19) (100 MHz, (CD ³) ² C=O) (Expanded)	65
20	FT-IR spectrum of 2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20)	66
21	¹ H NMR spectrum of 2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20) (400 MHz, DMSO)	69
22	¹ H NMR spectrum of 2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20) (400 MHz, DMSO) (Expanded)	70
23	¹ H NMR spectrum of 2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20) (400 MHz, DMSO) (Expanded)	71
24	¹³ C NMR spectrum of 2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20) (100 MHz, DMSO)	72
25	¹³ C NMR spectrum of 2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20) (100 MHz, DMSO) (Expanded)	73
26	FT-IR spectrum of <i>N</i> -2-oxoundecanylpyridinium iodide (21)	75
27	¹ H NMR spectrum of <i>N</i> -2-oxoundecanylpyridinium iodide (21) (400 MHz, DMSO)	77
28	¹ H NMR spectrum of <i>N</i> -2-oxoundecanylpyridinium iodide (21) (400 MHz, DMSO) (Expanded)	78
29	¹ H NMR spectrum of <i>N</i> -2-oxoundecanylpyridinium iodide (21) (400 MHz, DMSO) (Expanded)	79
30	¹³ C NMR spectrum of <i>N</i> -2-oxoundecanylpyridinium iodide (21) (100 MHz, DMSO)	80
31	¹³ C NMR spectrum of <i>N</i> -2-oxoundecanylpyridinium iodide (21) (100 MHz, DMSO) (Expanded)	81
32	FT-IR spectrum of 3-methyl- <i>N</i> -(2-oxoundecan-3-yl)pyridinium iodide (22)	83



33	¹ H NMR spectrum of 3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide (22) (400 MHz, (CD ₃) ₂ C=O)	85
34	¹ H NMR spectrum of 3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide (22) (400 MHz, (CD ₃) ₂ C=O) (Expanded)	86
35	¹ H NMR spectrum of 3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide (22) (400 MHz, (CD ₃) ₂ C=O) (Expanded)	87
36	¹³ C NMR spectrum of 3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide (22) (100 MHz, (CD ₃) ₂ C=O)	88
37	¹³ C NMR spectrum of 3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide (22) (100 MHz, (CD ₃) ₂ C=O) (Expanded)	89
38	FT-IR spectrum of <i>N</i> -(2-oxododecyl)pyridinium iodide (23)	91
39	¹ H NMR spectrum of <i>N</i> -(2-oxododecyl)pyridinium iodide (23) (400 MHz, DMSO)	93
40	¹ H NMR spectrum of <i>N</i> -(2-oxododecyl)pyridinium iodide (23) (400 MHz, DMSO) (Expanded)	94
41	¹ H NMR spectrum of <i>N</i> -(2-oxododecyl)pyridinium iodide (23) (400 MHz, DMSO) (Expanded)	95
42	¹³ C NMR spectrum of <i>N</i> -(2-oxododecyl)pyridinium iodide (23) (100 MHz, DMSO)	96
43	¹³ C NMR spectrum of <i>N</i> -(2-oxododecyl)pyridinium iodide (23) (100 MHz, DMSO) (Expanded)	97
44	¹³ C NMR spectrum of <i>N</i> -(2-oxododecyl)pyridinium iodide (23) (100 MHz, DMSO) (Expanded)	98
45	FT-IR spectrum of <i>N</i> -acetyltrioctylammonium iodide (24)	100
46	¹ H NMR spectrum of <i>N</i> -acetyltrioctylammonium iodide (24) (400 MHz, DMSO)	102
47	¹³ C NMR spectrum of <i>N</i> -acetyltrioctylammonium iodide (24) (100 MHz, DMSO)	103
48	¹³ C NMR spectrum of <i>N</i> -acetyltrioctylammonium iodide (24) (100 MHz, DMSO) (Expanded)	104



49	Expected structure for the compound 25, 26 and 27	105
50	The FT-IR Spectra for the compound 25, 26 and 27	105
51	DI-MS Spectrum of <i>N</i> -acetyl-3-methylpyridinium iodide (17)	108
52	DI-MS Spectrum of <i>N</i> -acetyl-4-methylpyridinium iodide (18)	108
53	Mass fragmentation patterns of <i>N</i> -acetyl-4-methylpyridinium iodide (18)	109
54	DI-MS Spectrum of <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19)	110
55	DI-MS Chromatogram of Mass Fragment for the Compound 19 Detected at Low Intensity	110
56	Mass fragmentation patterns of <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19)	111
57	DI-MS Spectrum of <i>N</i> -2-oxoundecanylpyridinium iodide (21)	112
58	DI-MS Chromatogram of Mass Fragment for the Compound 21 Detected at Low Intensity	112
59	Mass fragmentation patterns of <i>N</i> -2-oxoundecanylpyridinium iodide (21)	113
60	DI-MS Spectrum of 3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide (22)	114
61	DI-MS Chromatogram of Mass Fragment for the Compound 22 Detected at Low Intensity	114
62	Mass fragmentation patterns of 3-methyl- <i>N</i> -(2-oxoundeca-3-yl)-pyridinium iodide (22)	115
63	DI-MS Spectrum of <i>N</i> -(2-oxododecyl)pyridinium iodide (23)	116
64	DI-MS Chromatogram of Mass Fragment for the Compound 23 Detected at Low Intensity	116
65	Mass fragmentation patterns of <i>N</i> -(2-oxododecyl)pyridinium iodide (23)	117
66	DI-MS Spectrum of <i>N</i> -acetyltriocylammonium iodide (24)	118



67	Graph Surface Tension versus Logarithm Molarity of <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (19)	122
68	Graph Surface Tension versus Logarithm Molarity of 2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide (20)	122
69	Graph Surface Tension versus Logarithm Molarity of <i>N</i> -2-oxoundecanylpyridinium iodide (21)	123
70	Graph Surface Tension versus Logarithm Molarity of 3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide (22)	123
71	Graph Surface Tension versus Logarithm Molarity of <i>N</i> -(2-oxodecyl)pyridinium iodide (23)	124
72	Graph Surface Tension versus Logarithm Molarity of <i>N</i> -acetyl-trioctylammonium iodide (24)	124
A1.1	FT-IR Spectra of the Products (Oily Solution) between Iodoketones with 2-methylpyridine.	140
A1.2	FT-IR Spectra of the Products (Oily Solution) between Iodoketones with 3-methylpyridine.	141
A1.3	FT-IR Spectra of the Products (Oily Solution) between Iodoketones with 4-methylpyridine.	142



LIST OF ABBREVIATIONS

δ	Chemical shift in ppm
μg	Microgram
17	<i>N</i> -acetyl-3-methylpyridinium iodide
18	<i>N</i> -acetyl-4-methylpyridinium iodide
19	<i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide
20	2-methyl- <i>N</i> -(2-oxoheptan-3-yl)pyridinium iodide
21	<i>N</i> -2-oxoundecanylpyridinium iodide
22	3-methyl- <i>N</i> -(2-oxoundeca-3-yl)pyridinium iodide
23	<i>N</i> -(2-oxododecyl)pyridinium iodide
24	<i>N</i> -acetyltrioctylammonium iodide
CHN	Carbon, Hydrogen, Nitrogen Analyses
CMC	Critical Micelles Concentration
d	Doublet
dd	Doublet of doublet
DI-MS	Direct Injection-Mass Spectroscopy
DMSO	Dimethylsulphoxide
EI-MS	Electron Impact-Mass Spectroscopy
FT-IR	Fourier Transform-Infrared
Hz	Hertz
<i>J</i>	Coupling constant in Hz
m	Multiplet



m.p.	Melting point
MIC	Minimum Inhibitory Concentration
ml	Milliliter
NMR	Nuclear Magnetic Resonance
°C	Degree in Celsius
ORTEP	Oak Ridge Thermal Ellipsoid Plot (from the program for Crystal Structure Illustration)
s	Singlet
t	Triplet



CHAPTER I

INTRODUCTION

Quaternary Ammonium Salts (QASs), their application and uses

Amine compounds in which the nitrogen is bound to four carbon atoms through covalent bonds are known as quaternary ammonium salts (QASs). Originally, it was considered that the R groups were only hydrocarbon radicals attached to the nitrogen by a C-N bond. The alkyl radicals may be substituted or unsubstituted, saturated or unsaturated, aliphatic or aromatic, or branched or normal chains. QASs are stable compounds that are not converted to amines by treatment with base and generally show good water solubility because of their ionic structure.

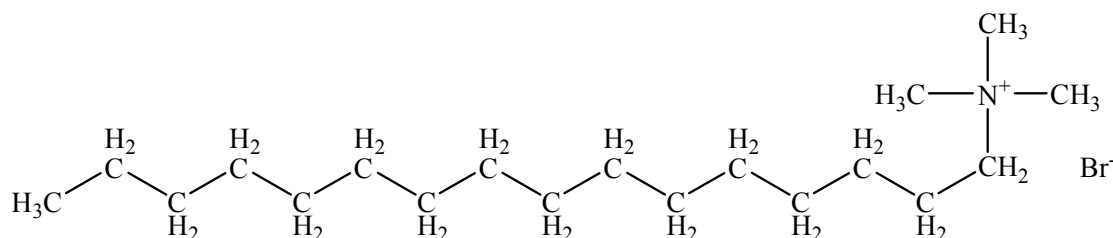
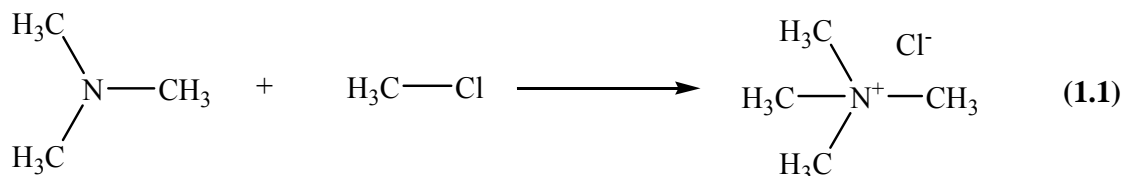


Figure 1: Example of Quaternary Ammonium Salt (Cetyltrimethylammonium bromide)

QASs are made by reacting tertiary amines with halogenated compounds; for example, trimethylamine with chloromethane gives tetramethylammonium chloride (1.1). QASs of this type do not liberate the free amine when alkali is added, and

quaternary hydroxides (such as $(\text{CH}_3)_4\text{N}^+\text{OH}^-$) can be isolated. Such compounds are strong alkalis, comparable to sodium hydroxide (Daintith, 2000).



QASs constitute a huge group of organic compounds. N-substituted salts of pyridine and related compounds are one of the most important and versatile being investigated in chemical synthesis (Sliwa, 1996). They are widely used as cationic surfactants, drugs, and herbicides. Because of the formal positive charge on the nitrogen atom, these compounds possess many unique properties, which have been utilized in numerous applications (Bluhm and Li, 1998). For example, a number of molecular recognition systems for nucleotide triphosphates are based on quaternary ammonium compound (Li and Disderich, 1992).

The fabric softening agents for example, widely used now are nitrogen-containing cationic compounds. The existence of positively charged nitrogen atoms leads to a marked difference in the nature of the surface active properties compared to the anionic and nonionic compounds. The positively charged nitrogen atom enables the molecule to be absorbed onto negatively charged surfaces. Also, positively charged fabric softening agents possess antistatic properties. The various types of softening agents in the market mostly are high molecular weight i.e. dialkyl dimethyl quaternary ammonium compounds (1) and diamidoamine quaternaries (2) (Idris, 1998).