The Preparation And Use Of Ionic Liquids - Solvents For Clean Catalysis

Thesis submitted in accordance with the requirements of the
University of Liverpool
for the degree of Doctor in Philosophy

by

Craig Nicholas Chatterton
[B.Sc.(Hons), M.Sc., University of Liverpool]

December 2000

In loving memory of

Peter Walkden, Mary Walkden and Alice Chatterton

For Mum, Dad, Andrew

and Grandpa

without whose help none of this would have been possible, and

to whom I am eternally grateful

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Craig Nicholas Chatterton, Ph.D. Thesis, University Of Liverpool, 2000

Abstract.

Various ways of preparing several different ionic liquids were investigated with specific regard given to the purity obtained. These ionic liquids prepared were subsequently used as solvents for both hydroformylation and Heck reactions. Variations in the choice of ionic liquid used and the effect this had on the catalytic reactions involving these ionic liquids as solvents, was investigated.

Ionic liquids based on the methyl imidazolium cation were successfully prepared in high yield and excellent purity using a new, modified approach based on the initial work carried out by Bonhote *et al.* (1996). The ionic liquids were easy to prepare and handle. They possessed exceptional qualities making them an ideal choice as solvents for homogeneous catalysis.

Rhodium catalysed hydroformylation of olefins 1-decene and 1-pentene was carried out using the prepared ionic liquids as solvents. Under various reaction conditions, the olefins were successfully hydroformylated to their corresponding aldehydes in high yield. The effect on the reaction of varying the choice of ionic liquid solvent was investigated, showing that optimum hydroformylation conditions were achieved when a $[BF_4]$-based ionic liquid solvent was used.

Under the relevant reaction conditions, the palladium catalysed Heck reaction, involving the arylation of several acrylates, was achieved using various aryl halides in ionic liquid solvent. Further investigation into this reaction revealed the preferred choice of ionic liquid solvent, and provided interesting information regarding the specific active catalytic mechanism involved in Heck reactions of this type. Under no circumstances was there evidence of catalyst degradation, showing again the remarkable solvent effects of these ionic liquids.

These observations show that ionic liquids are not only designer solvents, they are an integral part of catalytic chemistry, now and for the future.

ACKNOWLEDGEMENTS

I am grateful to the Leverhulme Centre For Innovative Catalysis, University Of Liverpool, for giving me the opportunity to do this interesting research and for their financial support. I would like to sincerely thank Dr. Jianliang Xiao, for his supervision throughout this project and his assistance in the preparation of this thesis. Thanks to all members of the academic staff, in particular Dr. Rafiq Siddiqui and Dr. Masihul Hasan. Your valued support and advice was been extremely welcome and greatly appreciated.

"I have to say" a huge 'thank-you' to Dave Harrison for the unbelievable amount of help, advice and not surprisingly criticism! he's given me during my time as a Ph.D. student and also as an undergraduate. Without Dave, this certainly would not have been possible. Cheers Harro!

Finally, I would like to give special thanks to all my family and friends, who have helped me in any number of ways. Special thanks go to all members of Liverpool University Mens Hockey Club, past and present, for allowing me to cram in as much hockey as possible in my spare time (and the occasional pint!). Good luck fellas!

ABBREVIATIONS

UNITS and SYMBOLS

bp	boiling point
bar	pressure
bu	butyl
bmim	1-butyl-3-methyl imidazolium
cm	centimeter
cm^3	centimeters cubed
cm^{-1}	reciprocal centimeters
^{o}C	degrees Celcius
δ	Delta (NMR)
d_6	deuterated
$CDCl_3$	deuterated chloroform
d	doublet (NMR)
et	ethyl
emim	1-ethyl-3-methyl imidazolium
g	gravitational acceleration
Hz	Hertz (Frequency)
SbF_6	hexafluoroantimonate
PF_6	hexafluorophosphate
h	hour(s)
K	degrees Kelvin
L	unit length
MHz	Mega Hertz (10^6 Hertz)
Mp	melting point
μ	micro (10^{-6})
meq/g	milli equivalents per gram (10^{-3} equivalents per gram)
mg	milligram (10^{-3} gram)
ml	millilitre (10^{-3} litre)
mm	millimeter (10^{-3} meter)
mmol	milli moles (10^{-3} moles)
mp	millipiosse (10^{-3} poisse)
mol	moles
m	multiplet (NMR)
oc	octyl
omim	1-octyl-3-methyl imidazolium
ppm	parts per million (NMR)

p	pressure
q	quartet (NMR)
r	radius
s	singlet (NMR)
BF_4	tetrafluoroborate
t	triplet (NMR)
t	unit time
u	velocity
η	viscosity
V	volts
v	unit volume
w/v	weight per unit volume

OTHER

GC	Gas Chromatography
IR	Infrared (Spectroscopy)
NMR	Nuclear Magnetic Resonance (Spectroscopy)
PTFE	Poly Tetrafluoroethylene
RTP	Room temperature and pressure
TGA	Thermogravimmetric Analysis
TOF	Turn-Over Frequency
TON	Turn-Over Number
XRD	X-Ray Diffraction

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Chapter 1

Introduction

1.1. Introduction To Ionic Liquids

The existence of molten salts (ionic liquids) dates back to the early 1950's. Since the discovery of the first ambient temperature ionic liquid (a *N*-ethylpyridinium bromide - aluminium chloride melt) in 1951 many classes of molten salts have been investigated.[1] The generally highly conductive tetrachloroaluminates and heptachlorodialuminates of cations as 1,3-dialkylimidazolium[2] or triazolium,[3] tetraalkylammonium or phosphonium, and trialkylsulphonium[4] are water reactive and thus difficult to handle. Molten salts containing low symmetry tetraalkylammonium cation associated to tetraalkylboride,[5] perchlorate or bromide are either difficult to prepare or weakly conducting. Ionic liquids such as 1-ethyl-3-alkylimidazolium trifluoromethane-sulphonate (triflate, TfO^-) exhibit large electrochemical windows ($> 4V$), good conductivity, and excellent thermal stability.[6] The acetate of the same cation is reported to melt at -45 °C.[7] Rajeshwar *et al.*[8] reported the application of dialkylimidazolium tetrachloroaluminate in photoelectrochemical cells, but the sensitivity of that material to water precludes its application to solar cells. 1,3-dialkylimidazolium salts ($RR'Im^+X^-$) appear to be up to now the most stable and conductive ionic liquids.[9]

Ionic liquids based on methylimidazolium are favourable species for investigation because of their air and water stability, their wide liquidus range, the fact that they remain liquid at room temperature, and their relatively favourable viscosity and density characteristics.[7,10]

Room temperature ionic liquids are quite simply, liquids that are comprised entirely of ions. In reality, room temperature ionic liquids can be liquid as low as -96 °C and are colourless, fluid, and easily handled.[11] In this sense alone they resemble the ionic melts which may be produced by heating normal metallic salts such as sodium chloride to high temperature (e.g., NaCl to over 800 °C).[12]

1.2. Choice Of Solvent

The solvent in homogeneous catalysis can influence the course of a reaction by increasing reaction rates and allowing better control of the chemo-, regio-, stereo-, and enantioselectivities of the reaction. In transition metal-based catalysis, as well as in ionic catalysis, the solvent has to solubilize the active species, but it must not be reactive toward the transition metal carbon-bond intermediate and cannot compete with the reactant for the coordination centre.

The major disadvantage of using solvent is the need to separate it from the catalyst and the products without decomposition of the catalyst itself. This is why, despite the benefits, many homogeneous processes are carried out without solvent, and the active species is dissolved in the reactant(s) and products. An approach dating back to the early 1970's utilized the use of molten salts as stable, non-volatile solvents from which organic products were readily separated by distillation.[28]

1.2.1. Industrial Application

Volatile organic solvents are the normal media for the industrial synthesis of organic chemicals (petrochemical and pharmaceutical), with a current world-wide usage estimated at £4,000,000,000 p.a. However, the environmental impact of these solvents is significant, and the Montreal Protocol has resulted in a compelling need to re-evaluate many chemical processes that have proved otherwise satisfactory for much of this century. A conspicuous example is the recent closure of one of the DuPont Hypalon © plants in Northern Ireland, which had been operating with chlorinated hydrocarbon solvents.

The design of safe and environmentally benign separation processes has an increasingly important role in the development of clean manufacturing processes and in the remediation of sites contaminated by an older generation of manufacturing technologies. Fused salts that are liquid at room temperature are an unconventional but interesting class of aprotic solvents for studying the chemistry of inorganic, organometallic and organic solutes. The R group of the cation (in the ionic liquids based on methylimidazolium) is variable and may be used to fine tune the properties of the ionic liquid. Such liquids are able to solvate a wide range of species including inorganic, organometallic and organic compounds. They are also miscible with a number of organic solvents such as benzene and toluene.[2] The use of room temperature ionic liquids as solvents for industrial catalytic reactions, including polymerisation, alkylations and acylations[12-15] allows the controlled production of desired products from reactants with a minimum of waste production through side reactions due to the tendency of ionic liquids to suppress conventional solvation and solvolysis phenomena.[12,13]

Clean technology is concerned with reducing the waste from an industrial chemical process to zero. Its implementation will lead to a cleaner environment, and more cost-effective use of starting materials. It requires, in the majority of cases, the rethinking and redesign of many chemical processes that we currently think of as an industrial norm. Catalysis clearly has a central role to play in the process, with its potential for both high yield and high specificity.

The *E*-factor of a process is the ratio (by weight) of the by-products to the desired product(s). Table 1.2.1a illustrates that contrary to popular perception, the 'dirty' end of the chemical industry, oil-refining and bulk chemicals, is remarkably waste conscious. It is, surprisingly, the fine chemicals and pharmaceutical companies that are using inefficient, dirty, processes, albeit on a much smaller scale, and there will be increasing demand (political, economic, social and environmental) for the introduction of new clean technology. Industries that do not respond will die.[11]

TABLE 1.2.1a By-Products As A Proportion Of Production For The Chemical Industry.[13]

Industry	**Production / Tons p.a.**	***E*-Factor**
Oil Refining	10^6 - 10^8	0.1
Bulk Chemicals	10^4 - 10^6	1 - 5
Fine Chemicals	10^2 - 10^4	5 - 50
Pharmaceuticals	10^1 - 10^3	25 - 100

There appear to be four main alternative 'solvent-strategies' to industrial synthesis:

1. Solvent-free synthesis.
2. The use of water as a solvent.
3. The use of supercritical fluids as solvents.
4. The use of ionic liquids as solvents.

Ionic liquids may in themselves be suitable, and indeed favourable, media for the design of novel liquid-liquid extraction systems. Features of these ionic liquid systems, such as the high solubilities of organic species, the prevalence of high coulombic forces resulting in the practical absence of any significant vapour pressure,[12] and the availability of air and moisture stable, water immiscible ionic liquids (e.g. imidazolium salts of PF_6^- or [partially miscible BF_4^-]) may recommend such systems as being uniquely suited to the development of completely novel liquid-liquid extraction processes.[16]

Unlike water and other hydroxylic solvents, they will dissolve a wide range of organic molecules to an appreciable extent (benzene, for example, will form up to 50% (v/v) solutions), meaning much lower volumes of solvent are required for a given process. Exploratory work has demonstrated that a wide range of catalyzed organic reactions (including oligomerizations, polymerisations, alkylations and acylations) occurs in room temperature ionic liquids, and that these are serious candidates for commercial processes.[1,26] The reactions observed represent the tip of the iceberg - all the indications are that room temperature ionic liquids are the basis of a new industrial technology. They are truly designer solvents.[27]

1.2.2. Properties Of Ionic Liquids

Room temperature chloroaluminate(III) ionic liquids are attracting much academic[14,16,17] and industrial[13,19-23] interest as, in addition to an extended liquid range, they exhibit superacidity,[13] remarkable solubility properties[24] and unique catalytic behaviour[20,22,23]. The most widely studied systems are $AlCl_3$-[emim]Cl, $AlCl_2Et$-[bmim]Cl and $AlCl_3$-[*N*-Bupy]Cl, where [emim]$^+$, [bmim]$^+$ and [*N*-Bupy]$^+$ are 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium and *N*-butylpyridinium cations respectively.[25]

Compared to most convenient molecular solvents, room temperature haloaluminate ionic liquids are difficult to purify and must be protected from the atmosphere in order to avoid degradation by atmospheric moisture, which is believed to react with the aluminium halide species to produce aluminium oxide halide complexes and protonic impurities. However, since these melts are completely ionic, they are, like many other molten salts, superb solvents for highly charged complex ions and as solvents for absorption spectroscopy.[14]

Table 1.2.2a shows some typical cation / anion combinations that can be used as ionic solvents. It outlines the solvation and coordination ability of ionic liquids according to the complexing ability of their anions. Other cations that are used are also mentioned, such as *N*-alkylpyridinium, phosphonium, and sulphonium. In a similar way to aluminium halides, cuprous halides form polynuclear anions.[13]

TABLE 1.2.2a Some Typical Cation / Anion Combinations That Can Be Used As Ionic Solvents.

CATIONS	ANIONS	COORDINATING ABILITY
NR_4^{+a}	Cl^-	Strong (basic)
PR_4^+		
SR_3^+	BF_4^-	Weak (neutral)
	PF_6^-	
	SbF_6^-	
	$CF_3SO_3^-$	
	$CuCl_2^-$	
	$AlCl_4^-$	
	$Cu_2Cl_3^-$, $Cu_3Cl_4^-$	None (acidic)
	$Al_2Cl_7^-$, $Al_3Cl_{10}^-$	

[a] *N*-Alkylpyridinium, 1-3-dialkylimidazolium

Ionic liquids possess the following desirable properties:

1. They have a liquid range of 300 °C (*cf.* water, which has a liquid range of 100 °C, and ammonia, with a liquid range of only 44 °C.)

2. They have no effective vapour pressure.

3. Their water sensitivity does not restrict their industrial applications.

4. They are thermally stable up to 200 °C.

5. They are relatively cheap and easy to prepare.

Ionic liquids are potentially useful as electrolytes in batteries, photoelectrochemical cells, and electroplating. The class of organochloroaluminate ionic liquids, typically a mixture of a quartenary ammonium salt such as 1,3-dialkylimidazolium chloride with aluminium chloride has been most widely explored.[14] These liquids have been studied primarily for their applications as electrolytes in electrochemistry technologies such as electroplating, batteries, and alloy preparations. These systems are also excellent solvents for highly charged complex ions of high- or low-oxidation states and have been widely used for electronic absorption spectra of inorganic complexes (no solvolysis).[29]

Melts of the type aluminium chloride or 1-alkylpyridinium chlorides, which are molten at or near room temperature are easily prepared.[11] The aluminium chloride / 1-butylpyridinium chloride system has a wide Lewis acidity attainable, as expressed by chloride concentration.[12,23]

Molten salts have been used in many catalytic reactions.[26] Wilkes *et al.*[2] revealed that the 1,3-dialkylimidazolium salts were attractive candidates as solvents, particularly for electrochemistry, spectroscopy and synthesis, since their reduction potentials were predicted to be about 0.8V lower than the 1-alkylpyridinium salts, and they could be prepared readily from commercially available starting materials. However, their use has been limited by their physical properties. Rony[27], studying homogeneous catalytic reactions of olefins, found that many of the conventional molten electrolytes were corrosive and presented mass transfer problems.

A considerable drawback of ambient ionic liquids concerns the need to protect rigorously the ionic liquids from moisture and other oxide impurities. While many organic cations would probably have sufficient size to produce low melting chloroaluminate salts, the cations must also have reduction potentials more negative than Al(III) in the melts in order to be unreactive toward Al and to improve the electrochemical window. There is a tendency of many substrates to react with haloaluminates. Initially, therefore work involving ambient temperature ionic liquids was limited to a narrow range of organic substrates, typically those that reacted with Lewis acids such as Friedel-Crafts substrates.[30]

A novel aspect of these ionic solvents is their adjustable Lewis acidity; substantial variations in acidity can be effected simply by varying the molar ratio of the two components. These variations in acidity can be used to induce substantial changes in the coordination of complex solutes present in the melt. The acid-base properties of these ionic liquids are dictated by the species present at a given molar ratio.

When an aluminium halide, AlX_3 is combined with an organic salt, R^+X^-, the constituents of the resulting ionic liquid are determined by the molar ratio of these components, q/p, according to the following reactions, which proceed essentially to completion:

$$pR^+X^- \;+\; qAlX_3 \;\text{-------->}\; qR^+AlX_4^- \;+\; (p-q)R^+X^-, (q/p<1) \qquad [1]$$

$$pR^+X^- \;+\; qAlX_3 \;\text{-------->}\; (2p-q)R^+AlX_4^- \;+\; Al_2X_7^-, (1<q/p,2) \qquad [2]$$

If q/p is less than 1, these melts consist of essentially R^+X^- and $R^+AlX_4^-$ [31-33]; they are 'basic' because they contain halide ions that are not bound to aluminium. When q/p is greater than 1 but less than 2, $R^+AlX_4^-$ and $R^+Al_2X_7^-$ [31-33] are the principle constituents of the system, and these molten salts are 'acidic' due to the presence of the latter species, which is a halide ion acceptor. These ionic liquids for which q/p = 1 are considered 'neutral' because they contain only $R^+AlX_4^-$. However, finite concentrations of X^+ and $Al_2X_7^-$ are always present in neutral melts as a consequence of the following autosolvolysis reaction:

$$2R^+AlX_4^- \text{ -------->} \; R^+Al_2X_7^- \; + \; R^+X^- \qquad [3]$$

Likewise, very small amounts of X^- and $Al_2X_7^-$ are always present in acidic and basic ionic liquids, respectively, for the same reason. The equilibrium constant for equation [3] has been estimated to be of the order of 10^{-16} to 10^{-18} for the $AlCl_3$.MeEtImCl and $AlCl_3$.BupyCl systems at 40 °C.[34,35]

1.3. Structure Of Imidazolium Based Ionic Liquids

The ability of the 1-ethyl-3-methylimidazolium cation $[emim]^+$ to produce room temperature molten salts with $AlCl_4^-$ and BF_4^- is an intriguing and useful property and is rooted in the cation-anion interactions. Although several salt structures containing $[emim]^+$ have been reported, all these contain anions which form substantial hydrogen bonds with the cation.[7,36] $[emim][PF_6]$ was used to investigate the interionic interactions of $[emim][AlCl_4]$ and $[emim][BF_4]$, as, like the BF_4^- room temperature melt, $[emim][PF_6]$ is also air stable and may be useful as an electrolyte for operation at moderately elevated temperatures. Because PF_6^- is a weakly complexing anion, $[PF_6]^-$ was expected to interact with $[emim]^+$ in a similar manner as $AlCl_4^-$ and BF_4^-.

Through proper spectroscopic comparisons, the structure of $[emim][PF_6]$ can be related to the liquid state local structure found for the room temperature molten salts $[emim][AlCl_4]$ and $[emim][BF_4]$.

Figure 1.3a shows the molecular structure of [emim][PF_6], and the ion packing is shown in figures 1.3b and 1.3c. The organic cations are positioned in pairs with a centroid to centroid separation of 5.39 Å, and a plane to plane separation of 4.53 Å. The cations are not in a stacked arrangement, they show a large parallel offset. The hexafluorophosphate anions in [emim][PF_6] surround the organic cations, and the fluorine atoms partially penetrate the region between the two cations at sites away from the ethyl groups, which extend into the region between the two cations. The structure appears to be accommodating to both hydrophobic molecules and other ionic species.

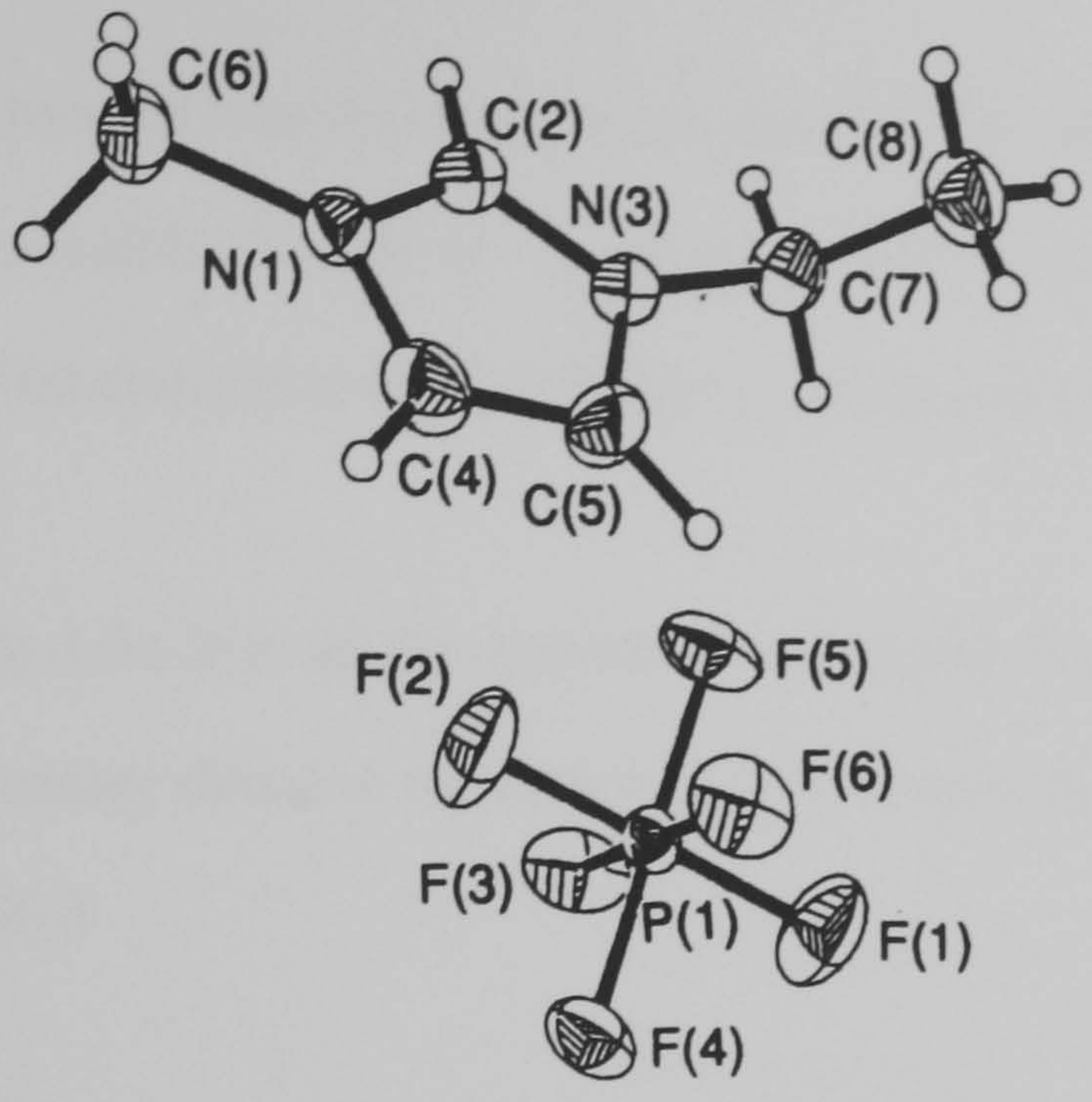


FIGURE 1.3a Molecular Structure Of [emim][PF_6]

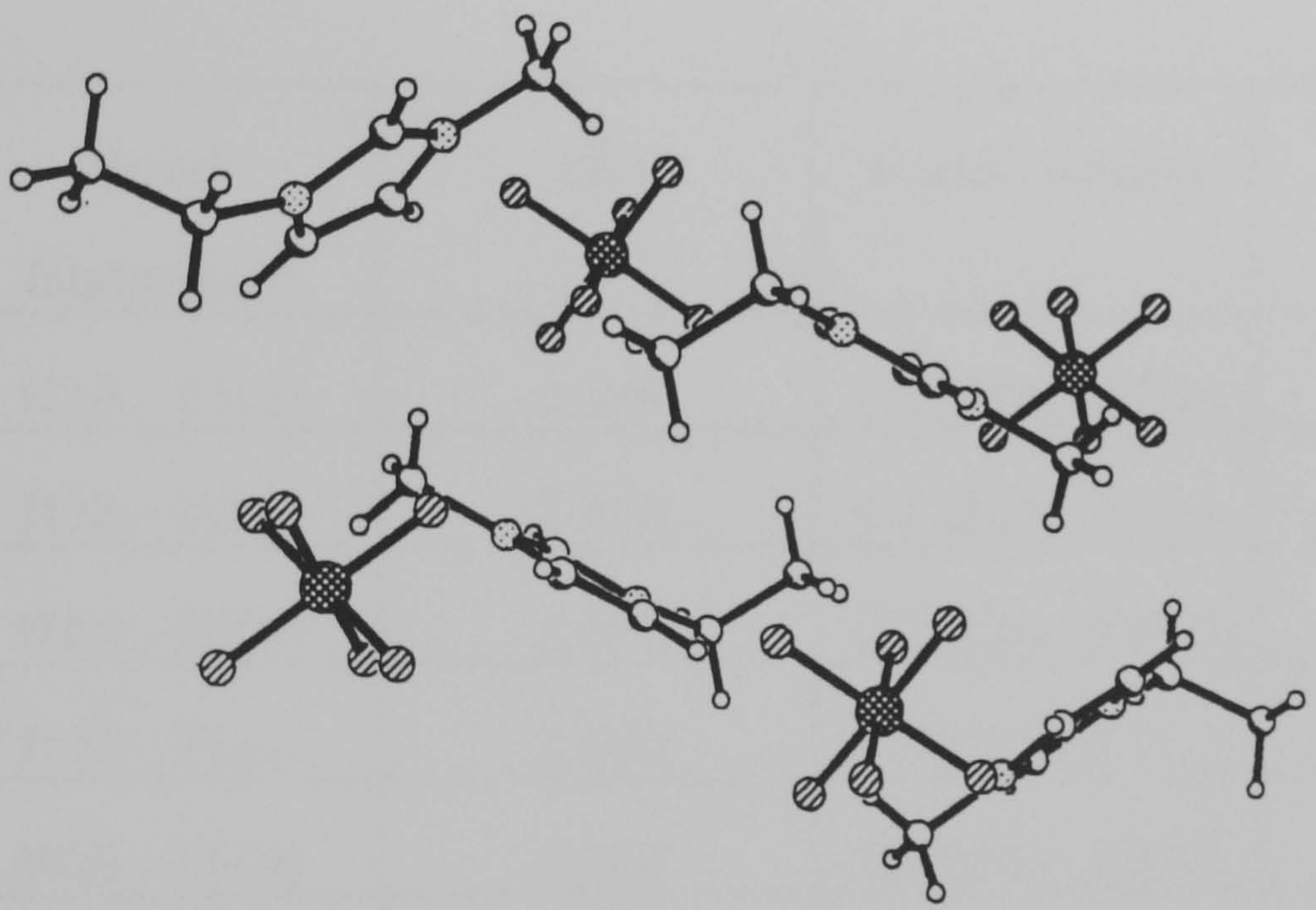


FIGURE 1.3b View Of [emim][PF_6] Showing The PF_6^- Anions Surrounding The Organic Cations

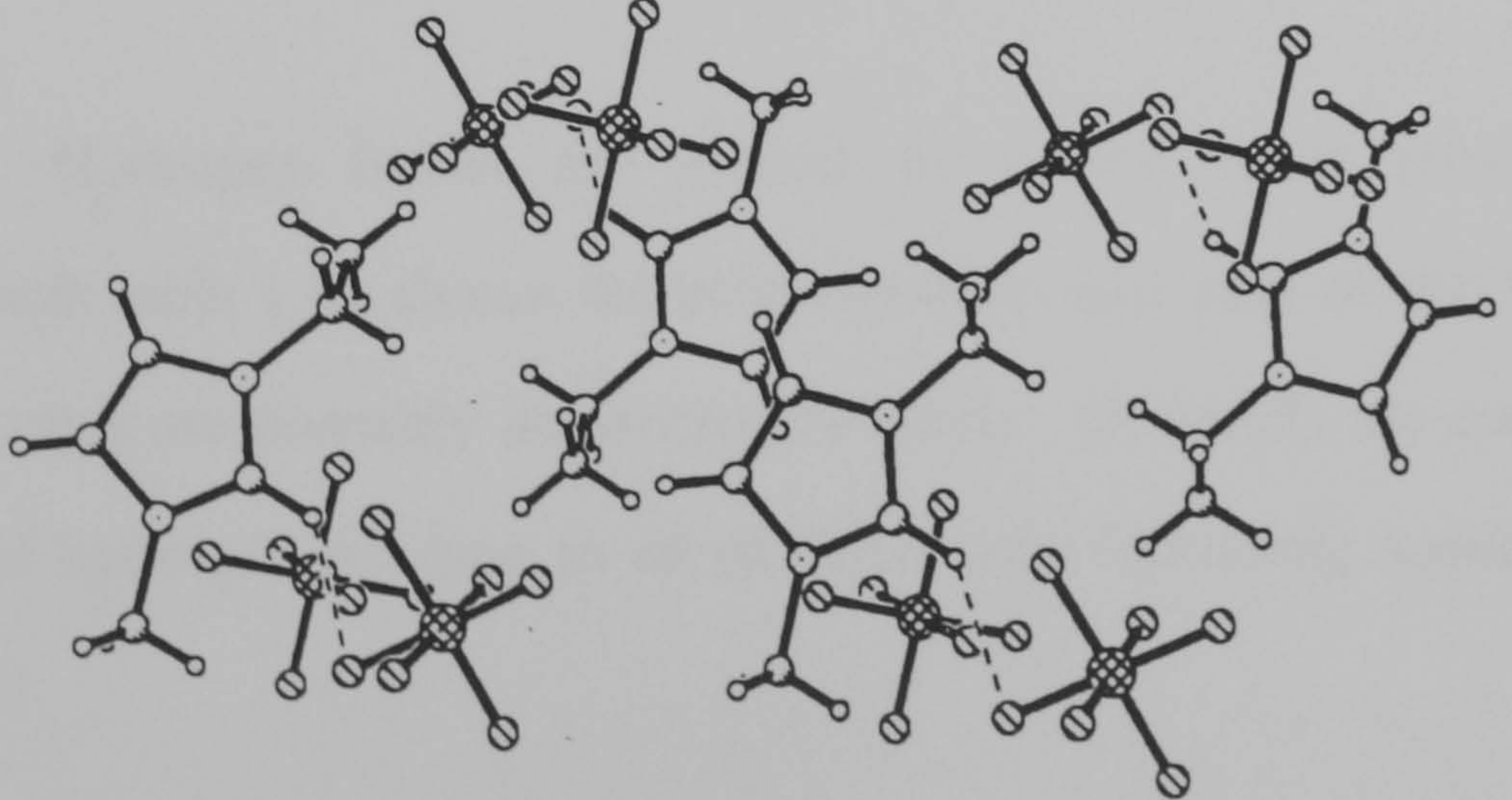


FIGURE 1.3c View Of [emim][PF_6] Showing The Parallel Offset Of The Two Cations And The Weak Hydrogen Bonding Between The C-(2) Hydrogen And A Fluorine Atom

The long distances between cations and the lack of a stacked structure makes it impossible for any π - π aromatic interactions, as has been proposed for 1-methylimidazolium salts containing cation-anion hydrogen bonding.[37]

Table 1.3a lists all the distances and angles for H···F distances less than 2.70 Å (necessary distance to substantiate hydrogen bonding involving C-H···F radii.)

TABLE 1.3a Hydrogen Bond Lengths And Angles For [emim][PF_6].[10]

Bond Distances[a]	**(Å)**	**Bond Angles**	**(Degrees)**
H2A···F5(a)	2.559	C2-H2A···F5(a)	128.8
H2A···F2(a)	2.678	C2-H2A···F2(a)	157.1
H2A···F3(b)	2.697	C2-H2A···F3(b)	106.9
H5A···F1(c)	2.690	C5-H5A···F1(c)	132.8
H6B···F6(d)	2.644	C6-H6B···F6(d)	119.2
H6A···F5(a)	2.652	C6-H6A···F5(a)	135.7

[a] Letter in parentheses indicates PF_6^- units related by symmetry elements.

Hydrogen bonds are formed in several other [emim]$^+$ salts.[7,36] Although table 1.3a shows the bond distances (the sum of the van der Waals radii), they are probably not hydrogen bonds. IR results are consistent with a lack of hydrogen bonding in all of these salts containing weakly complexing anions.

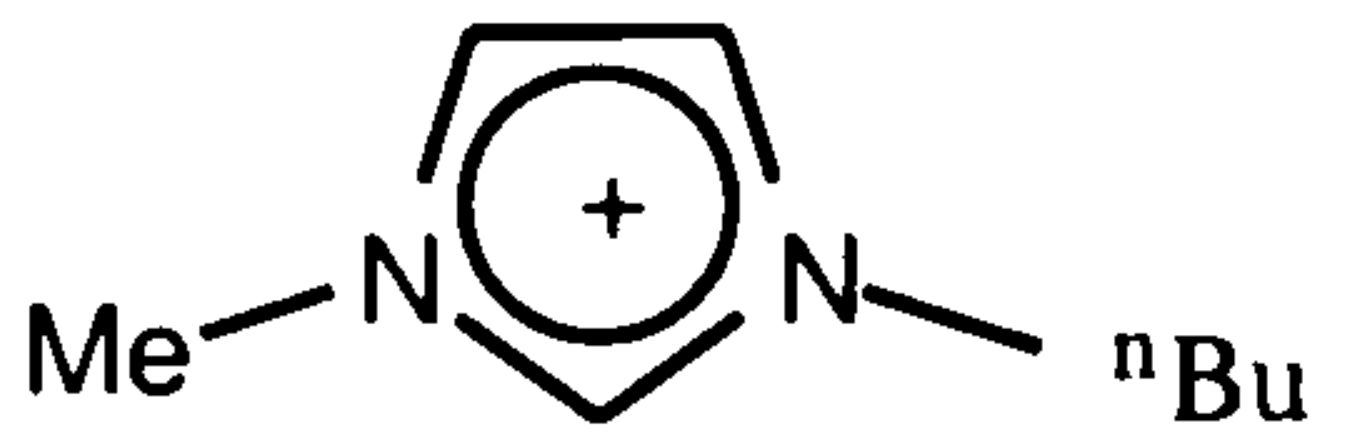
It is possible that hydrophobic effects play a role in the orientation of the ethyl groups of [emim][PF_6], and the lack of hydrogen bonding and aromatic

π - π stacking leads to the conclusion that cation-anion coulombic attraction is driving the overall crystal structure, with local steric effects influencing the final orientations.[10]

1.4. Catalysis

The separation of the products from the reaction mixture is still a major drawback of homogeneous catalysis by transition-metal complexes. It is now well recognized that the use of two-phase catalysis in water or high-polar organic solvents is one of the best approaches to solve this basic problem.[38] The use of two-phase solvent systems, especially those based on water-soluble ligands and their transition metal complexes, has emerged in the last decade as an important alternative for both homogeneous and heterogeneous catalysis.[21,39] Although several processes such as hydroformylation[40] and oligomerization[41] of olefins have been already developed, the application of these systems is limited due to the sensitivity of the organometallic catalytic species towards acids and bases. In this respect, the use of room temperature molten salts (ionic liquids) as solvents has proved to be particularly useful for these types of two-phase catalytic reactions.[21,39]

Room temperature ionic liquids of the sort:-



X^- $X = BF_4^-, PF_6^-, SbF_6^-$.

have been used as non-aqueous solvents for the rhodium (Rh) - catalysed two-phase hydrogenation, isomerization and hydroformylation of unsaturated substrates. In these solvents the catalyst can be 'immobilized' either because of their ionic character or by using polar modified ligands.

1.4.1. Hydrogenation Reactions

Hydrogenation of 1-pentene has been carried out in these solvents, using the Osborn complex **1** ($[Rh(nbd)(PPh_3)_2]^+PF_6^-$) as the cationic precursor,[42] (nbd = norbornadiene.) Remarkable solvent effects were observed. Hydrogenation rates were nearly five times higher than for the comparable homogeneous reaction in acetone. (See Table 1.4.1a)[20]

TABLE 1.4.1a Rh-Catalysed Hydrogenation Of 1-pentene[a].

Entry	Solvent	Conversion (%) 1-pentene	Yield (%) Pentane	Yield (%) Pent-2-ene	TOF (min^{-1})[b]
1[c]	acetone	99	38	61	0.55
2	$[bmim][SbF_6]$	96	83	13	2.54
3	$[bmim][PF_6]$	97	56	41	1.72
4	$[bmim][BF_4]$	10	5	5	0.15
5[d]	[bmim][Cl] : CuCl	18	0	18 (98% cis)	0
6[e]	$[bmim][PF_6]$	99	25	74	0.73

[a] 1: 0.05 mmol; 1-pentene: 18.4 mmol; solvent: 4 ml; $T = 30\ ^oC$; $p(H_2) = 0.1$ MPa; $t = 2h$

[b] Turnover frequency (TOF) defined as mol (pentane) per mol (rhodium) per min. [c] Acetone: 10 ml; 1-pentene: 9.2 mmol. [d] Molten salt prepared by reacting 1.5 eq. of [bmim][Cl].

[e] Acetone (2 ml) added.

It is interesting to note that conjugated diolefins, which are more stable in ionic liquids than the corresponding monoalkenes, could also be hydrogenated. Hydrogenation of cyclohexa-1,3-diene in $[bmim][SbF_6]$ gave results showing reaction activity comparable to that observed in organic solvents.[20]

The interaction between the Wilkinson catalyst [$RhCl(PPh_3)_3$] and [bmim][BF_4] and [bmim][PF_6] ionic liquids, produces a stable solution from which the transition metal complexes cannot be removed by non-polar organic solvents. The rhodium complexes [$RhCl(PPh_3)_3$] and [$Rh(cod)_2$][BF_4] are completely soluble in both [bmim][BF_4] and [bmim][PF_6]. As a result, they are able to catalyse the hydrogenation of cyclohexene in a typical two-phase catalysis. (See Table 1.4.1b) The ionic liquids acting as solvents in these hydrogenation systems do not show any noticeable difference in the turnover rate with the Wilkinson catalyst. These ionic liquids can be used as solvents in classical rhodium complex catalysis.

TABLE 1.4.1b Two-Phase Hydrogenation Catalysis Of Cyclohexene.[38]

Entry	Ionic Liquid	Complex	[Rh] (M)	[olefin] [Rh]	Conv[c]	TOR[d]
1[a]	[bmim][$AlCl_4$]	$RhCl(PPh_3)_3$	0.0018	15,000	-	-
2[b]	[bmim][$AlCl_4$]	$RhCl(PPh_3)_3$	0.0018	15,000	40	0.83
3	[bmim][BF_4]	$RhCl(PPh_3)_3$	0.0018	15,000	40	0.93
4	[bmim][BF_4] - EtOH[e]	$RhCl(PPh_3)_3$	0.0018	15,000	40	0.83
5	[bmim][PF6]	$RhCl(PPh_3)_3$	0.0018	15,000	40	0.83
6	[bmim][BF4]	[Rh(cod)$_2$][BF_4]	0.0064	6,400	65	0.50

Reaction conditions : room temperature, 10 atm of H_2, 120 h.

[a] Aluminium molar fraction in the ionic liquid = 0.56; only cyclohexene polymerisation was observed. [b] Aluminium molar fraction in the ionic liquid = 0.45. [c] Cyclohexene conversion in %. [d] Turnover rate in min-1. [e] 1 : 1 v / v.

1.4.2. Dimerization

It has been known for a long time that the active species involved in olefin dimerization catalyzed by nickel is a cationic nickel complex of the type $[LNi - CH_2R']^+[AlCl_4]^-$ where L = PR_3[43] (See Figure 1.4.2a). This complex is quite soluble and particularly active in aromatic and chlorinated hydrocarbons such as toluene and chlorobenzene. Ionic liquids favour the dissociation of ionic transition metal complexes and demonstrate poor solubility of aliphatic hydrocarbons. Therefore, these particular properties of ionic liquids suggest that they would be superb solvents for stabilizing active nickel catalysts.

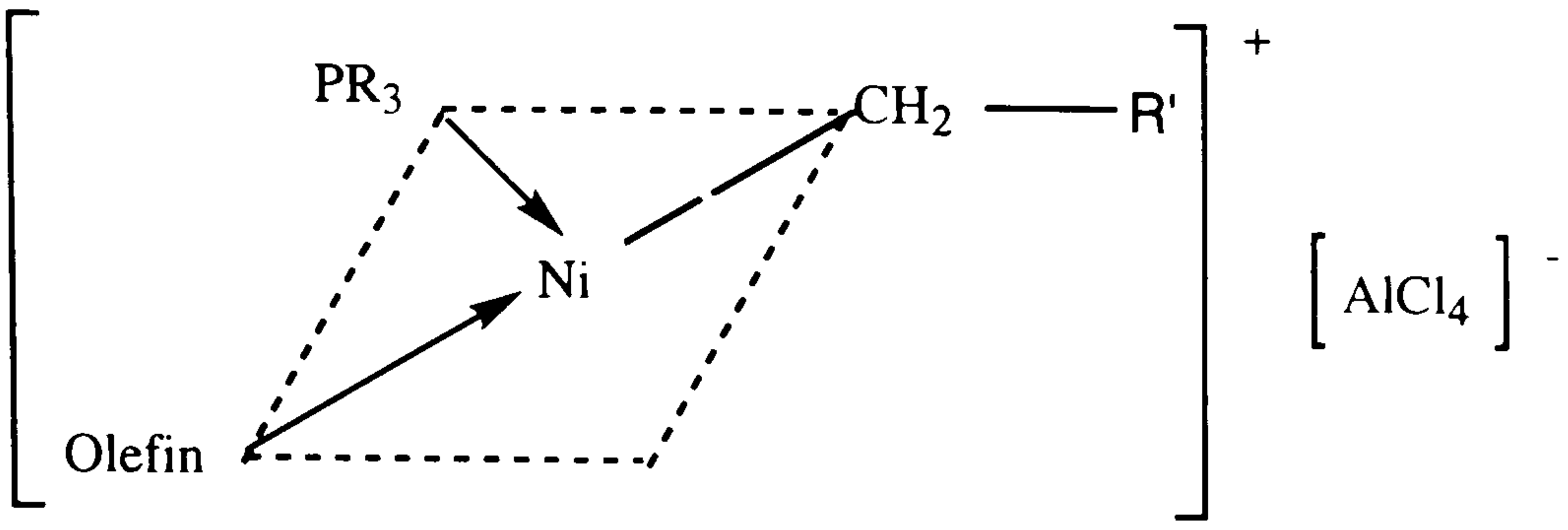


FIGURE 1.4.2a

Nickel complexes are catalytically active only in acidic ionic liquids and the use of such liquids containing ethyl aluminium dichloride in addition to aluminium trichloride ([bmim][Cl] / $AlCl_3$ / $EtAlCl_2$ = 1 / 1.2 / 0.25) makes it possible to use $NiCl_2.2L$ complexes (L = pyridine or phosphine) as catalyst precursors. In basic ionic liquids no activity is observed. The active nickel - carbon bond (Figure 1.4.2a : R' = Me) is formed, in situ, by a metathetic exchange between the chloride anion of the nickel dichloride precursor and the Et^- anion of the ethyl aluminium dichloride present in the ionic liquid.

Using ionic liquids as solvent, the dimerization of propene has been catalyzed by cationic nickel complexes, producing isomeric hexenes with high activity. (See Figure 1.4.2b.) At 5 ^{o}C and under atmospheric pressure, the propene dimerization reaction productivity was > 250 kg of dimers per gram of nickel (much greater than that obtained with organic solvents.) Butene and ethene have also been dimerized to the corresponding dimers using ionic liquid solvents. In both cases high selectivity was observed due to their low solubility in the ionic liquid. In all of the reactions the products formed a second phase that could be easily separated by simple decantation and the catalyst remained in the ionic phase, although in some cases catalyst deactivation was observed.[21] It was possible to re-use this ionic phase several times.[13]

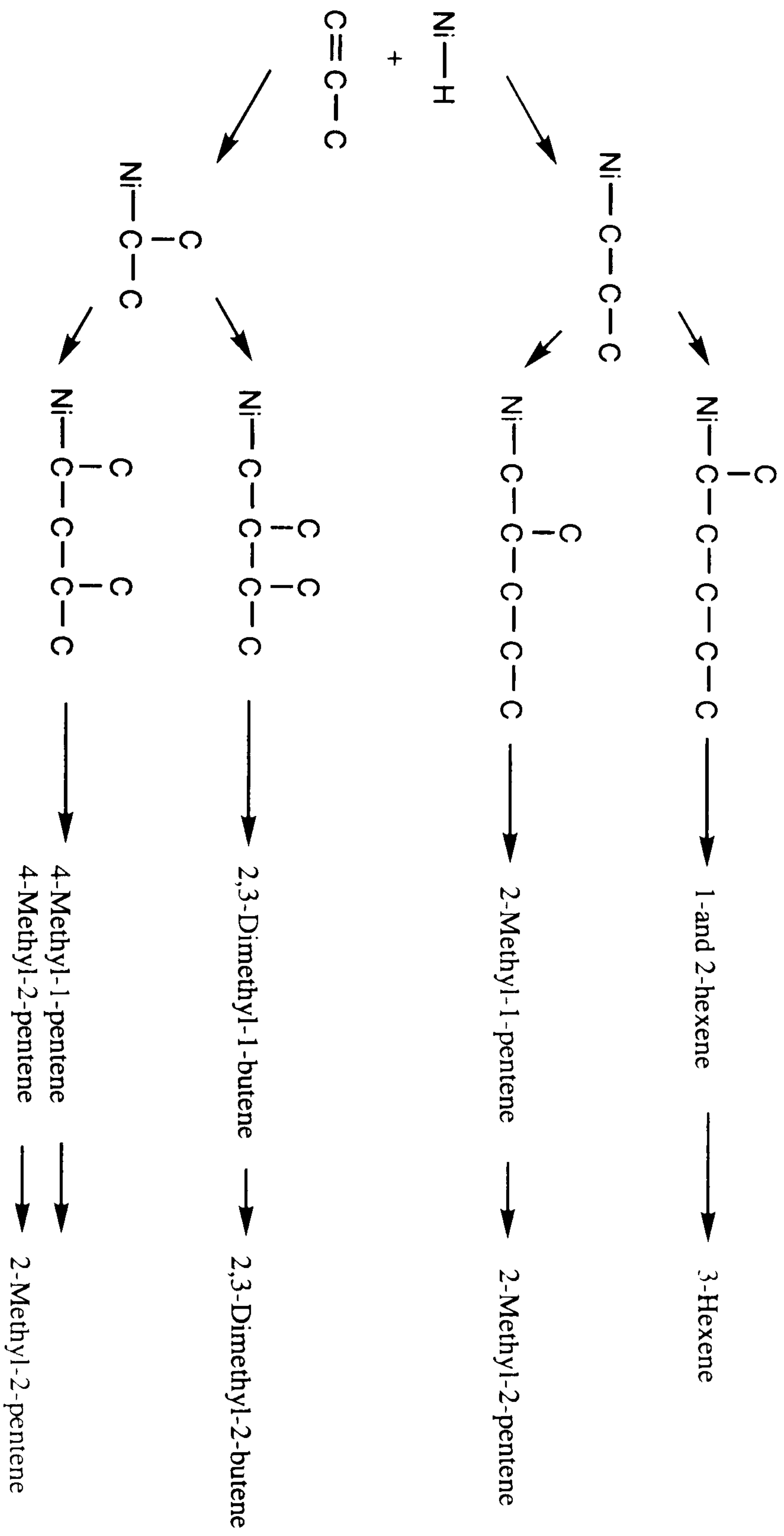
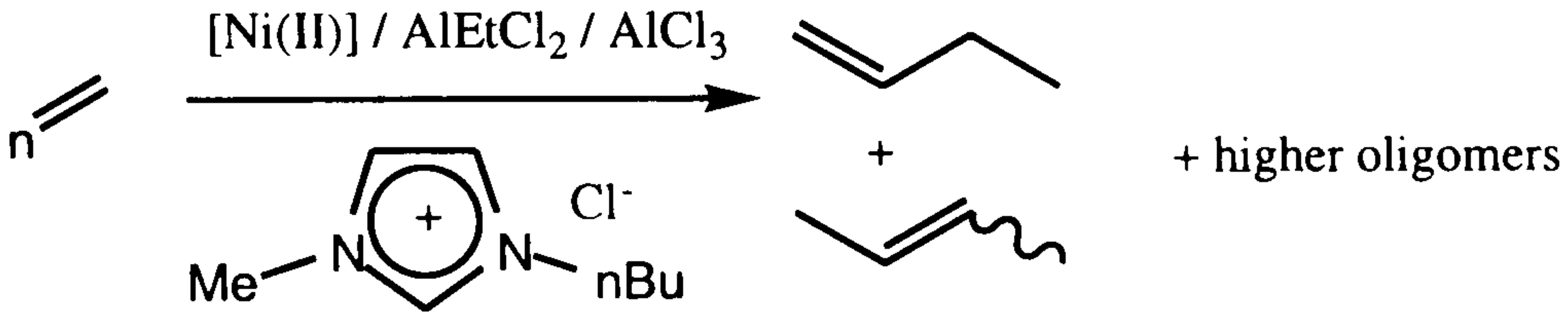


FIGURE 1.4.2b. Reaction Pathways Of Propene Dimerization Catalysed By Cationic Nickel Complexes.[21]

Dupont *et al* have also carried out dimerization reactions using nickel catalysts in ionic liquid solvents.[44] They showed that nickel (II) complexes dissolved in [bmim][Cl] / $AlCl_3$ molten salt in the presence of $AlEtCl_2$ and aromatic solvents catalyse the dimerization of ethylene into butenes in a typical two-phase catalytic reaction, and that the nature of the nickel catalyst precursor has a strong influence on the reactions activity and selectivity. The reaction rates of the system (two liquid layers) are strongly dependant on the mass transfer. (Physical parameters such as stirring probably limit the rate.)



The dissolution of the complexes NiF_2 (**1**), $NiCl_2(PCy_3)_2$ (**2**) or $[Ni(MeCN)_6][BF_4]_2$ (**3**) in the ionic liquids produced the catalytic system. The results obtained are shown in table 1.4.2a.

TABLE 1.4.2a Selective Two-Phase Catalytic Ethylene Dimerization By Ni^{II} Complexes / $AlEtCl_2$ Dissolved In Organoaluminate Ionic Liquids.[44]

Entry	Nickel Complex	Temp (°C)	Ethylene P (atm)	But-1-ene	Selectivity (%) But-2-enes	Hexenes	TOF[a] (h^{-1})
1	**1**	25	8	18	49	33	326
2	**2**	25	2	-	63	37	2653
3	**2**	-10	8	10	53	37	7595
4[b]	**3**	25	8	5	51	38	5954
5	**3**	-10	8	68	32	-	488
6	**3**	-10	14	80	20	-	575
7	**3**	-10	18	83	17	-	1731
8[c]	**3**	0	10	9	66	19	$>1.10^5$
9	None	25	18	-	-	-	-

[a] Turnover frequency = mol (product) mol (Ni) $^{-1}$ h^{-1}. [b] Formation of 6 % of octenes.

[c] In heptane; formation of 4 % of octenes and 2 % of decenes.

In these reactions > 98 % of the nickel was retained in the ionic liquid and the products (oligomers) were easily removed by decantation at the end of the reaction. It was possible to re-use the catalyst system several times without noticeable changes in selectivity or turn over frequency. It was suggested that the mechanism for this reaction was an analogy to the classical one proposed by Muthukumaru et al,[45] for the oligomerization of olefins by nickel complexes in the presence of alkyl aluminium compounds in homogeneous media.

In 1998 Dupont *et al* used palladium (II) compounds dissolved in [bmim][BF_4] ionic liquid to catalyse the hydrodimerization of 1,3-butadiene into octa-2,7-dien-1-ol. It was found that 1,3-butadiene conversion was achieved with a new catalyst precursor, $[bmim]_2PdCl_4$ dissolved in [bmim][BF_4]. The products' selectivity and catalytic activity depended on the reaction conditions, with increasing conversions and TOF in the presence of CO_2. Again the ionic liquid catalytic solution could be re-used several times (> 97 % palladium retained in the ionic phase) without significant changes in catalytic performance. As with the other reactions outlined, the products were removed by simple decantation.[46]

1.4.3. Friedel-Crafts Acylation

The use of low-melting ionic liquids composed of an organic chloride and aluminium chloride as solvent and catalyst for Friedel-Crafts reactions at ambient temperatures was first reported in 1976.[47] The Friedel-Crafts alkylation and acylation of benzene has also been studied in room-temperature ionic liquids.[48]

1-ethyl-3-methylimidazolium halogenaluminate melts have been used as reaction media for the Friedel-Crafts acylation of the organometallic complex ferrocene. The monoacylated product, acetylcyclopentadienyl (cyclopentadienyl) iron (II) was formed in good to excellent yields under the appropriate conditions.

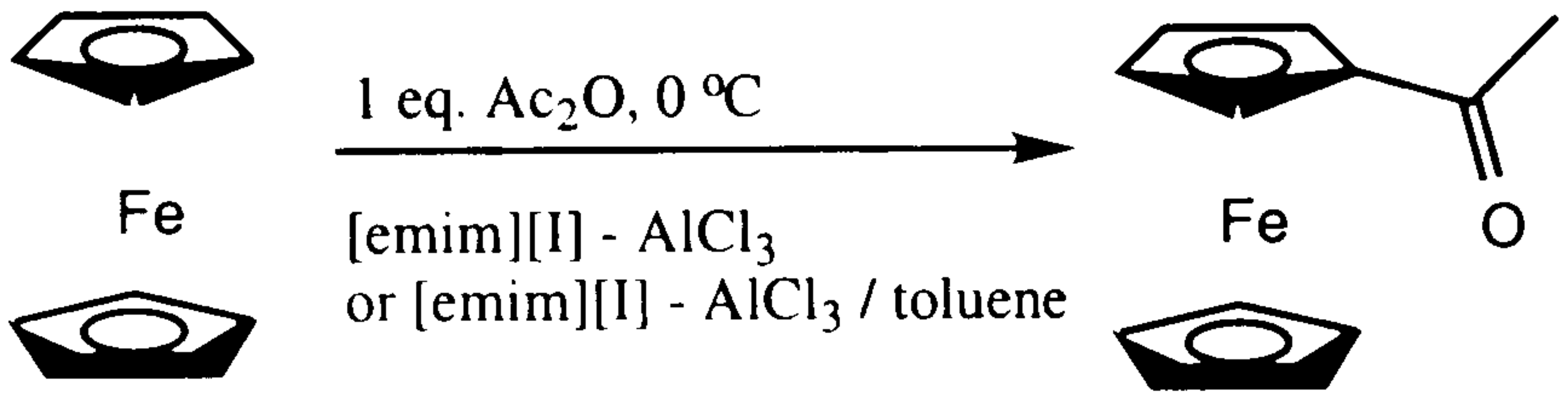


TABLE 1.4.3a Friedel-Crafts acylation of ferrocene in [emim][I] - $AlCl_3$ or [emim][I] - $AlCl_3$ / toluene.[49]

Entry	Reaction Medium	Mole Ratio Ac_2O : $Fe(\eta-C_5H_5)_2$	Reaction time (hours)	Yield (%)
1	[emim][I]-$AlCl_3$	3:1	2	72
2		2:1	2	62
3			4	84
4		1:1	2	31
5			4	71
6		2:1	2	0[a]
7	[emim][I] - $AlCl_3$ / toluene	6.6:1	2	90
8		3:1	2	96
9		2:1	2	90
10		1:1	2	80

[a] Reaction performed in neutral melt containing 1 : 1 ratio of [emim][I] - $AlCl_3$.

Table 1.4.3a shows that synthetically useful yields of the monoacetylated product, acetylferrocene, are obtained in the molten salt either when an excess of acetic anhydride is used (entries 1-3) or when extended reaction times are used (entries 3 and 5). No diacylated product, bis(acetylcyclopentadienyl)iron(II), was observed under the conditions used in any of these reactions.

The physical properties of the molten salts and the high solubility of the organometallic reactants (and other organic compounds) in these solvents make them an extremely useful media and contribute to the facility at which these reactions take place. Ionic liquids undoubtedly impart unique solvent effects on any reaction involving charged intermediates along their reaction pathways.

The 'built-in' Lewis catalyst and the potential to recycle the solvent make them an ideal choice for Friedel-Crafts reactions.[49]

1.4.4. Hydroformylation

Hydroformylation is one of the most versatile methods for the functionalisation of C=C bonds. Asymmetric hydroformylation provides a potential synthetic tool for the preparation of enantiomerically pure aldehydes useful as precursors of many biologically active compounds.[50] Although the pioneering work in asymmetric hydroformylation of olefins involved the use of platinum catalysts in the presence of Lewis acids,[51] rhodium systems have since been demonstrated to provide excellent chemoselectivity and regioselectivity in the hydroformylation reaction.[52,53] The platinum systems downfall being the modest results they produced.

1.4.5. Rhodium Catalysed Hydroformylation

In 1993, Claver *et al.* showed that rhodium (I) complexes containing the atropisomeric sulphur ligands 1,1'-binaphthalene-2,2'-dithiol (binas) or the relevant dimethyl sulphide (Me_2binas) were efficient catalysts for the highly regioselective hydroformylation of styrene. In the presence of PPh_3 a dinuclear neutral complex (produced by the addition of a stoichiometric amount of binas to a dichloromethane solution of $[Rh(\mu\text{-}OMe)(cod)]_2$ (cod = cycloocta-1,5-diene)) was able to promote the hydroformylation of styrene under mild conditions with excellent yield and regioselectivity, but with low enantiomeric excess (e.e.). This was the first time that hydroformylation was achieved under conditions catalysed by a complex which contained only sulphur derivatives as the hetero-donor ligands.[54]

Sakai *et al.* carried out successful asymmetric hydroformylation of 1,2-disubstituted olefins using chiral phosphinephosphite-rhodium (I) complexes. They showed that hydroformylation of internal olefins such as (E)- and (Z)-but-2-ene, (E)- and (Z)- 1-phenylprop-1-ene, indene, and 1,2-dihydronaphthalene, catalysed by (R,S)-binaphos-Rh^I complex {(R,S)-binaphos = (R)-[2[(diphenylphisphino)-1,1'-binaphthalen-2'-yl][(S)-1,1'-binaphthalen-2,2'-diyl]phosphite} or its enantiomer, gave the corresponding oxo-aldehydes in up to 97 % enantiomeric excess, e.e.[55] The results of their work showed that the catalysis involved provided a new, powerful means for the synthesis of a variety of physiologically active compounds.

Alper has carried out hydroformylation of olefins,[56] α, β-unsaturated esters[57,58] and allyl acetates[59] using zwitterionic rhodium complexes as catalysts. He showed that a zwitterionic rhodium complex (see FIGURE 1.4.5a), obtained from rhodium chloride, sodium tetraphenylborate, and 1,5-cyclooctadiene in aqueous methanol, [60] was of genuine use for the hydroformylation of a wide range of olefins under exceptionally mild conditions, resulting in highly regioselective, and in some cases regiospecific products. The zwitterionic complex was not a useful catalyst for hydroformylation of simple monosubstituted olefins, since the branched / linear aldehyde ratio was near to unity. However, if the substituent was bulky (e.g., 3,3-dimethyl-1-hexene), then regiospecific hydroformylation occurred leading to the linear aldehyde as the only product. The reaction was essentially insensitive to electronic effects.

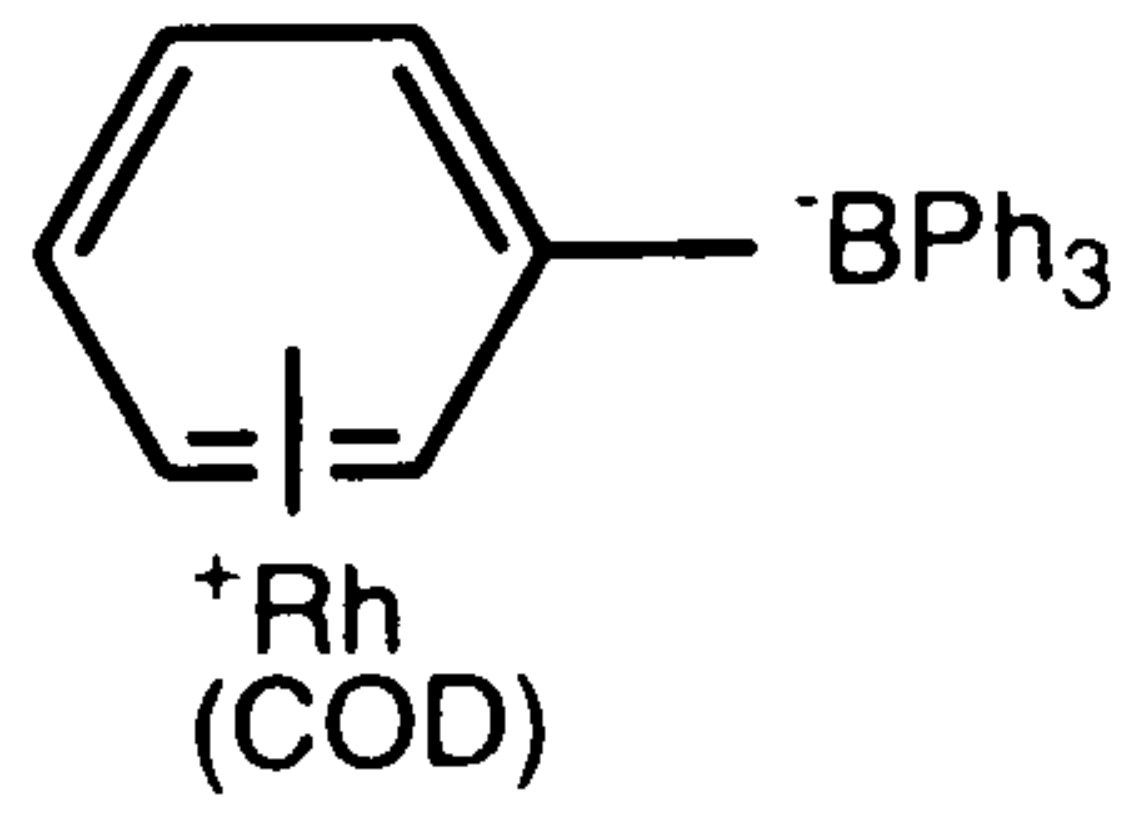
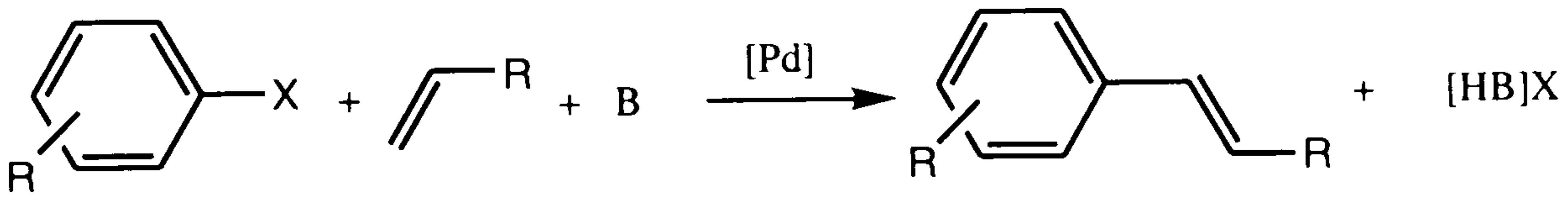


FIGURE 1.4.5a : Zwitterionic Rhodium Complex.[56]

Continued work using this complex in conjunction with 1,4-bis(diphenylphosphino) butane (dppb) as an added ligand, produced a catalytic system for the hydroformylation of α,β-unsaturated esters, resulting in excellent regioselectivity for the branched-chain aldehydic ester. Comparing the results of this zwitterionic hydroformylation with existing literature on the regioselectivity of the hydroformylation of α,β-unsaturated esters, showed that the regiochemistry control of the zwitterionic complex-dppb catalytic system was consistently superior to that of $[Rh(CO)_2Cl]_2$-dppb or other bidentate phosphines.[57]

1.4.6. The Heck Reaction

The Heck reaction has developed into a standard method of organic synthesis since its discovery in 1971.[61,62] Styrene derivatives, amongst others, can be prepared as vinyl C-C coupling products in one step from iodo- and bromoarenes. The Heck reaction has enormous synthetic potential, for generating C-C bonds. The Heck reaction is also beginning to make headway in polymer chemistry.[63]



X = Br, I

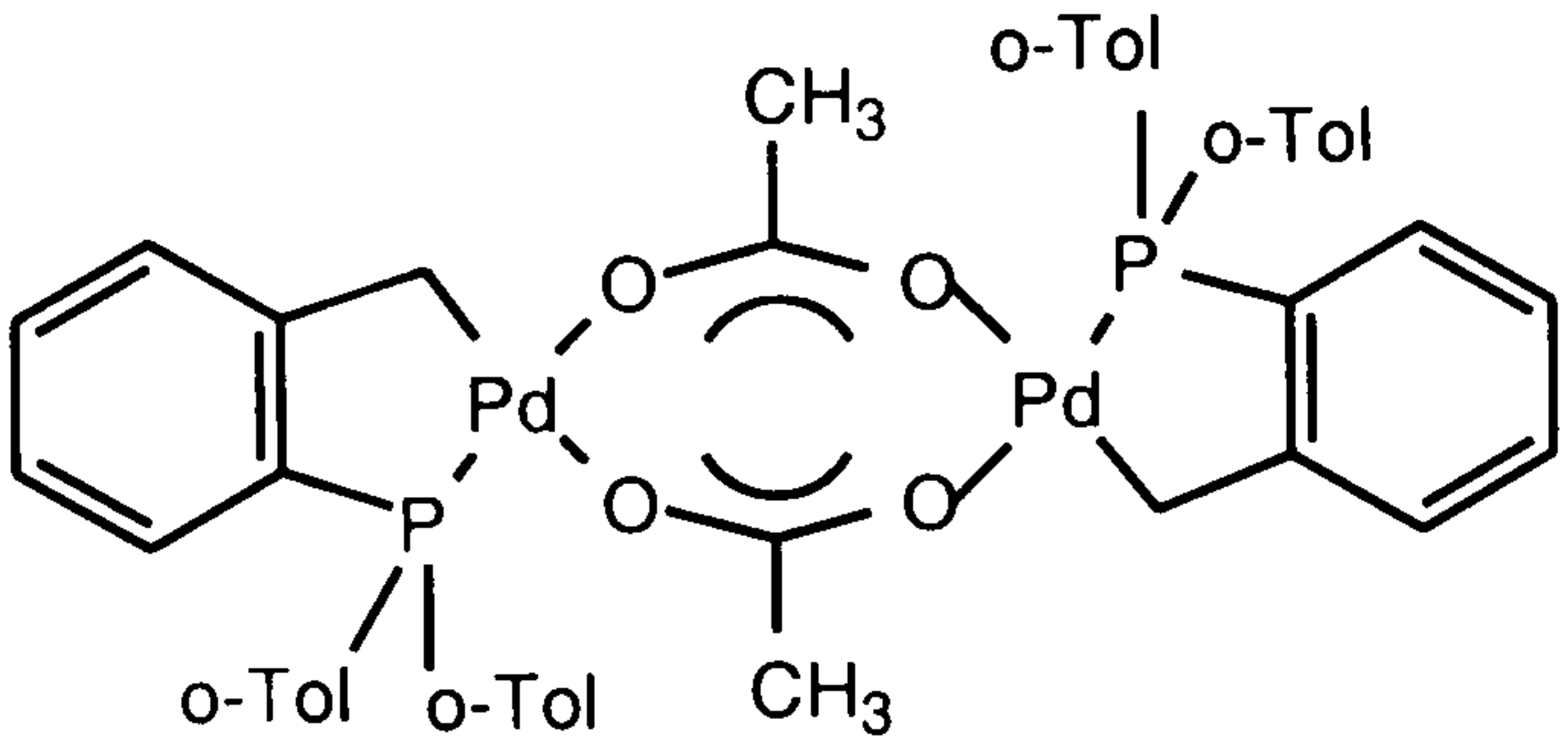
[Pd] = $Pd(OAc)_2$ / PPh3

B = Base, e.g. $N(C_2H_5)_3$, K_2CO_3, Na(OAc)

(Ref. [64])

The traditional catalyst mixture of palladium (II) acetate and hindered tertiary amine in the presence of triarylphosphine suffers from a number of drawbacks, including catalyst decomposition and lack of regioselectivity. Bidentate phosphine ligands have been shown to provide increased regioselectivity by virtue of their chelate effect and the possibility of phosphine dissociation preceding oxidative addition of the olefin to the palladium during the rate determining step of the catalytic cycle.[65]

Phospha-palladacycles are among the most powerful palladium catalyst systems for the Heck reaction. Non aqueous ionic liquids are an alternative solvent to the traditional molecular solvents for this reaction.[66] The use of ionic liquids would provide ideal alternative solvents if the products could de distilled from the 'solvent' and the still active, stable catalyst thus giving the opportunity to recycle the whole catalyst-solvent system.



1 *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II)

The cyclometallated complex *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) has been used as an efficient catalyst for the Heck reaction with aryl bromides and electron-deficient aryl chlorides. Using catalyst **1** did not lead to visible palladium black formation in most of reaction media, even in the reaction of chlorobenzene with styrene at 150 °C. The addition of tetraphenylphosphonium chloride, $[PPh_4]Cl$, caused an increase in TON with chlorobenzene. The stability of **1** in molten $[NBu_4]Br$ suggested a possible recycling procedure and recycling of the solvent and the catalyst **1** was achieved by distillation of the reactants and products from solvent and catalyst in vacuo. After a fourth run, visible palladium black formation occurred and after the sixth run the melt became more viscous but catalysis could still be performed with excellent yields in further runs.[66]

Different molten salts have also been used as solvents for palladium catalysed C-C coupling reactions. Hexadecyltributylphosphonium bromide (Hdtbpb), tetrabutylammonium bromide (Tbab) and tetraoctylammonium bromide (Toab) have all been used as solvents, successfully producing high efficiency results. (See TABLE 1.4.6a)

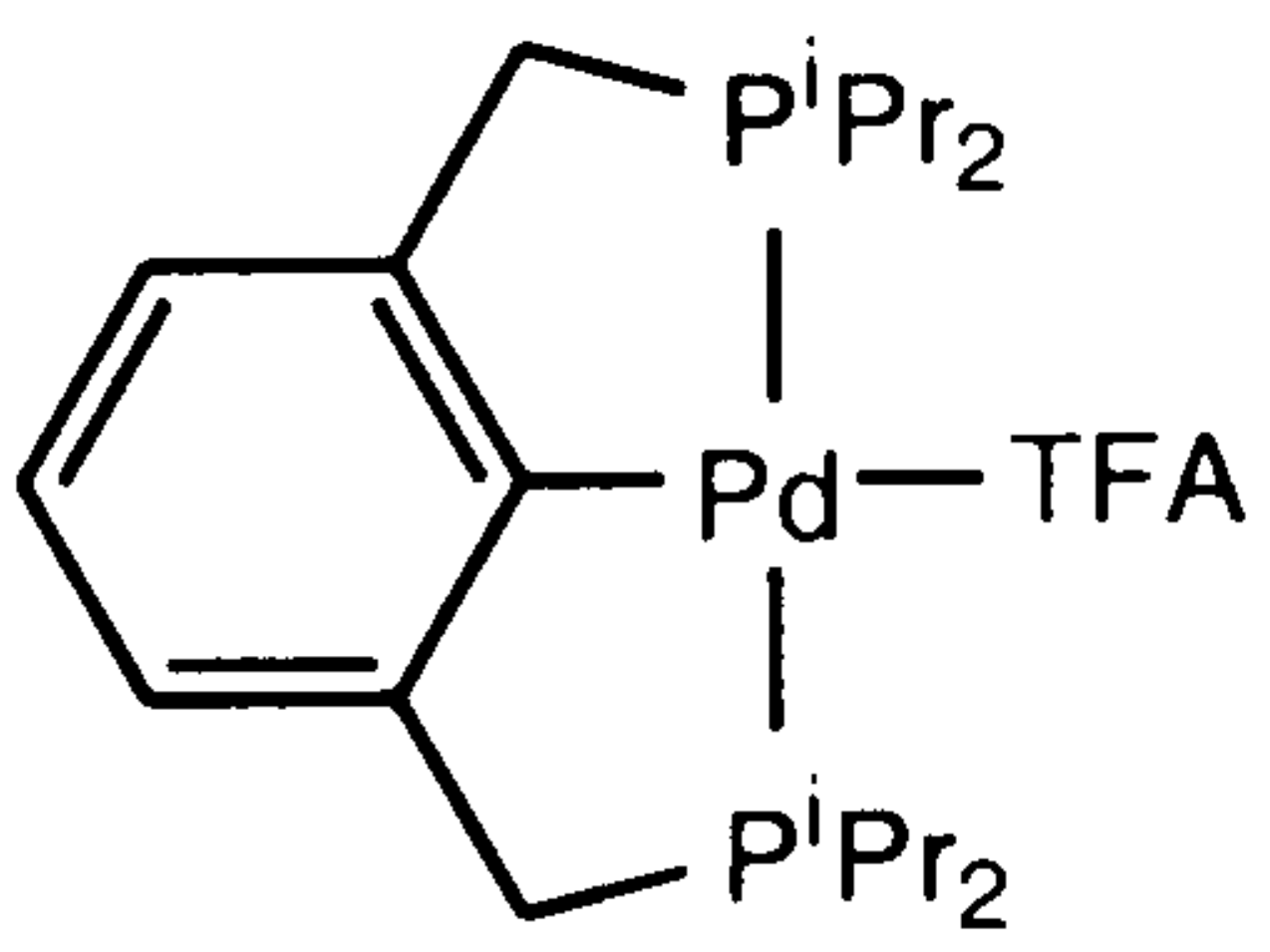
TABLE 1.4.6a Heck Reaction Of Aryl Halides With Butyl Acrylate In The Presence Of Triethylamine.[67]

No	Molten Salt	Aryl Halide	Catalyst [1 mol %]	t (h)	conversion (%)[b]	Yield[3] (%)[b,d]
1	Hdtbpb[a]	1a	$Cl_2Pd(PPh_3)_2$	24	>99	>99
2	Hdtbpb	1a	$PdCl_2$	16	84	81
3	Hdtbpb	1a	$Pd(OAc)_2$, 1.5 molequiv. NaOAc	17	>99	81
5	Hdtbpb	1a	$Pd(OAc)_2$	43	>99	>99
4	Hdtbpb	1b	$Cl_2Pd(PPh_3)_2$	16	>99	51
6	Hdtbpb	1c	$Cl_2Pd(PPh_3)_2$	16	97	52
7	Tbab[c]	1a	$Cl_2Pd(PPh_3)_2$ 3.0 molequiv LiBr	6	95	90
8	Tbab[c]	1a	$Cl_2Pd(PPh_3)_2$	24	86	51

[a] Hexadecyltributylphosphonium bromide. [b] The conversion rates (bromobenzene) and the yields were determined by GC (internal standard 2-methyl-napthalene). [c] Tetrabutylammonium bromide. [d] The products were characterised by 1H NMR, GC and GC-MS.

Having distilled off the products, the remaining catalyst showed comparable catalytic activity in the melt in two following runs. By using melts of aluminium or phosphonium halide salts as an alternative reaction medium, a simple, efficient and practical procedure for the generation of long term active palladium (0) was achieved. When running the Heck reaction, no additional phosphine ligands were needed to get high yields of C-C coupling products. The catalyst stayed stable for several reaction runs.[67]

Milstein *et al.*[65]reported catalysis of the Heck reaction with aryl chlorides using electron-rich trigonal biphosphine palladium (0) complexes. They showed that, although at a moderate rate, these reactions exhibited a remarkable chelate effect and enabled Heck coupling under reducing conditions in the absence of base. They have since showed that three new complexes (see FIGURES **2**, **3** & **4** below) are highly active in the catalytic arylation of olefins with aryl iodides and bromides. These complexes are extraordinarily thermally stable and showed no signs of decomposition at temperatures up to 180 °C. They were not sensitive to oxygen and moisture, therefore reactions involving them could be carried out in air with no change in efficiencies. The evidence also suggested that this catalysis may not involve the classical Pd (0) cycle.[68]



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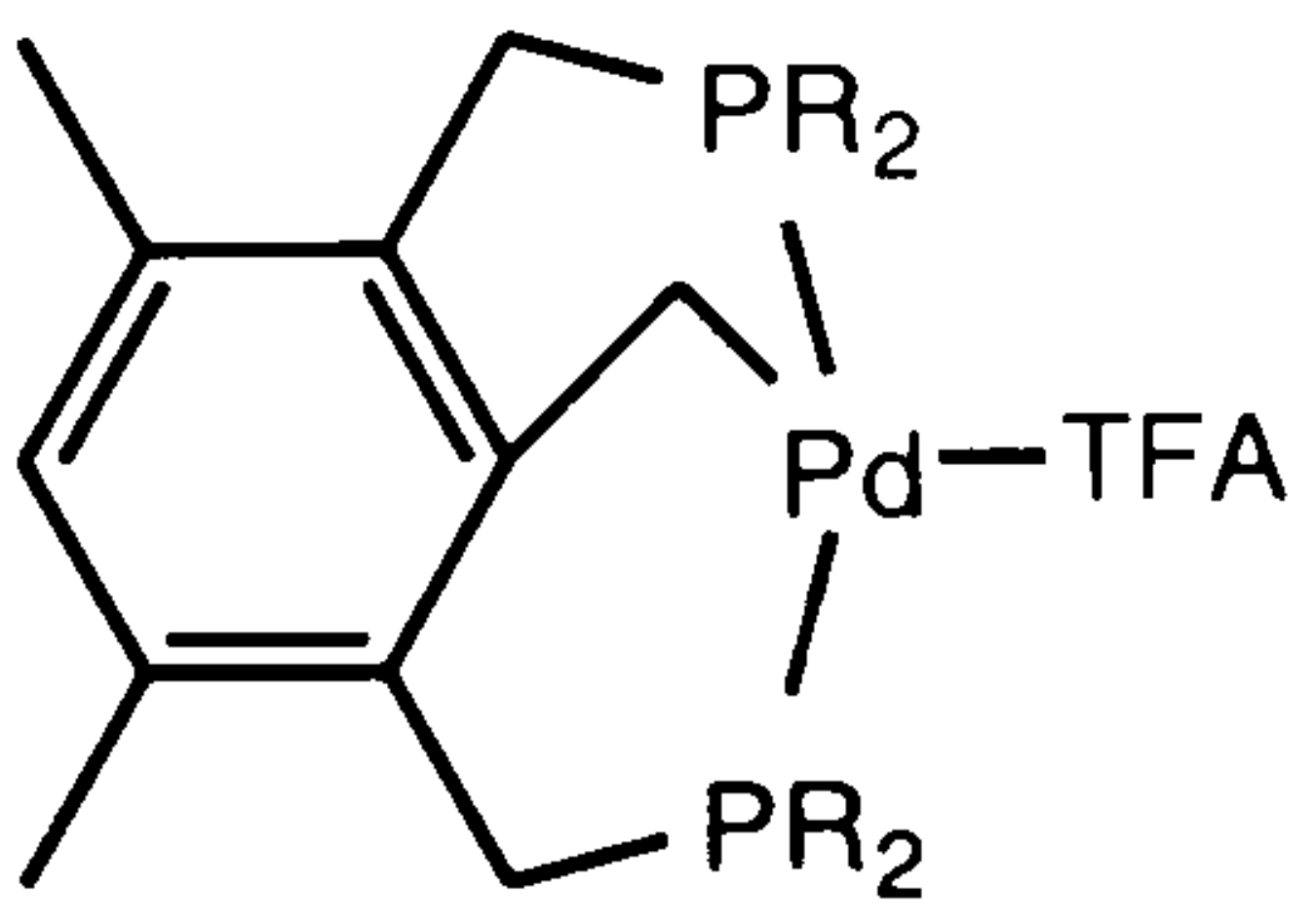

3, R = i-Pr
4, R = t-Bu

1.5. Aims And Objectives

The overall aim of this research was to investigate how well-known catalytic, chemical reactions would be affected by using ionic liquids as solvents, as opposed to the conventional organic solvents generally used for such reactions. Research would be carried out to determine whether or not it is possible to alter the outcome of a specific chemical reaction, simply by varying the nature of the ionic liquid chosen as solvent.

Initial research would involve the development of a suitable technique for preparing these ionic liquids. Several different techniques would be investigated with the emphasis on achieving good purity and high yield. These properties along with their 'ease of handling' would determine the way in which these ionic liquids would be used as solvents for future experiments.

Other objectives would involve investigation into the specific reaction mechanisms and the various catalytic species involved in the hydroformylation of olefins in ionic liquid solvents. The effect on the reaction of varying the choice of solvent would be investigated to determine the optimum reaction conditions and necessary requirements for ionic liquid based rhodium catalysed hydroformylation.

The palladium catalysed Heck reaction would also be investigated in ionic liquid solvents. By varying the solvent, and also the aryl halides involved, research would be carried out to investigate what specific catalytic species were involved during the Heck reaction, and also determine whether the choice of solvent could directly effect the outcome of the Heck reaction under such conditions.

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Chapter 2

Preparation Of Ionic Liquids

2.1. Introduction

Ionic liquids may in themselves be suitable, indeed favourable, media for the design of novel liquid-liquid extraction systems. Some features of these ionic liquid systems, the high solubilities of organic species, the prevalence of high coulombic forces resulting in the practical absence of any significant vapour pressure,[1] and the availability of air and moisture stable, water immiscible ionic liquids (e.g. imidazolium salts of PF_6) may recommend such systems as being uniquely suited to the development of completely novel liquid-liquid extraction processes[2]

Synthesis of the imidazolium based salts was initially performed using procedures developed by Bonhote *et al.* Pure ionic liquids were essential for future experimental work, therefore it was necessary to modify the standard preparation techniques outlined by Bonhote *et al*, who described the preparation as difficult.[3] Where necessary new, alternative methods of preparation were attempted, such methods are described in this chapter. The ionic liquids used in this research were prepared in the main from their corresponding imidazolium based salts.

This chapter deals with the experimental work and techniques used for the initial preparation of imidazolium based salts and the subsequent work involved in converting them into the desired ionic liquids. It outlines the equipment required and how it was used and also explains the various methods chosen to prepare, in some cases the same, and in other, different ionic liquids.

This chapter goes on to explain the subsequent characterisation techniques used to identify such liquids and verify their purity. Explanations are given of how certain catalysts were used and, where necessary, how they were prepared, purified and characterised. The final section of this particular chapter shows the results obtained from such work and includes all relevant data.

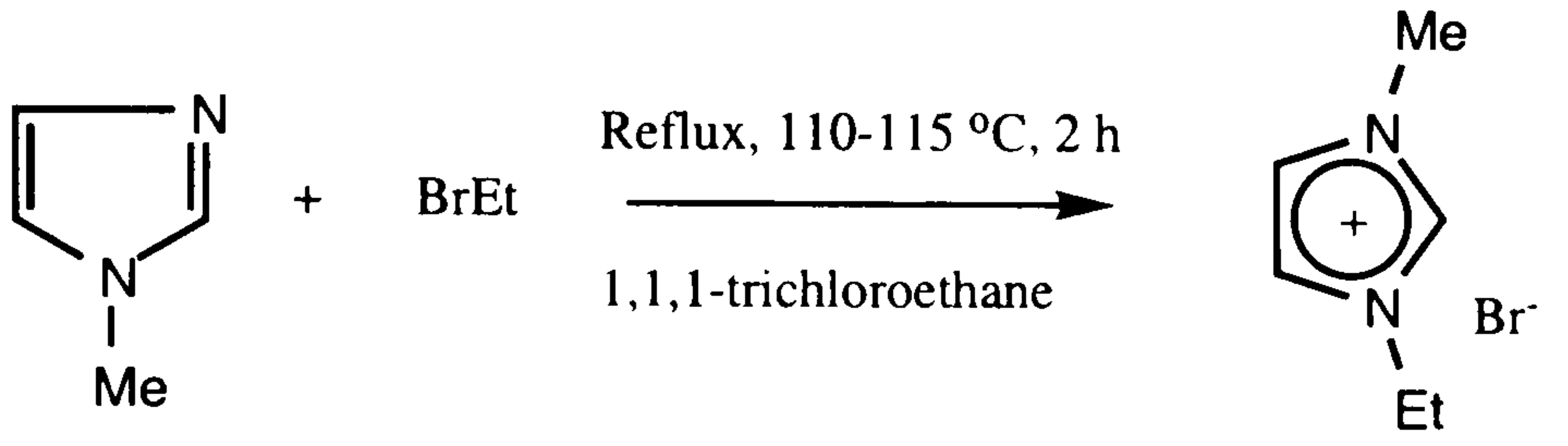
2.2. General Experimental

The imidazolium based salts were prepared using oven-dried standard glassware equipment. Initial preparation involved the use of, in most cases, three-necked round-bottomed flasks of varying size depending on the scale of the particular experiment. Pressure vessels (autoclaves) were occasionally used during preparation, yet in each of these cases a PTFE stirrer bar was used along with a digital magnetic hot-plate. All the solvents were degassed and dried (1-methylimidazole was dried over CaH_2) before use, reagents were used as received. NMR spectra were recorded on a Bruker 200 MHz spectrometer in ppm with reference to TMS internal standard in $CDCl_3$ or d_6-acetone. The TGA of [bmim][BF_4] was performed using a Perkin-Elmer TGA 7 Analyser. The carrier gas was air, and the sample (30.05 mg) was heated from 30 to 600 ^oC at a heating rate of 20 ^oC / minute. The TGA was calibrated using iron , nickel and perkalloy curie point. The melting point was measured using standard equipment and the viscosity was calculated from measurements made using an ASTM Kinematic Viscometer. Explanations of the techniques used are given in sections 2.9. and 2.9.2.

Solutions were generally mixed by dropwise addition from a standard dropping funnel, and where necessary a heating mantle was used to provide the correct experimental conditions. In certain cases a reflux condenser fitted with calcium hydride (CaH_2) drying tube was used. The molten salts were often decanted using a separating funnel and a rotary evaporator was used to dry the products. During air-free synthesis a vacuum line was used as too were schlenk tubes. It was also necessary in certain situations to use columns to purify some of the products obtained. In these cases the columns ranged between 45 cm-60 cm in height and from 15 mm to 30 mm in width. In all cases they were filled with celite and again calcium hydride drying tubes were attached to the top.

2.3. Detailed Experimental Procedures : Halide Salt Preparation

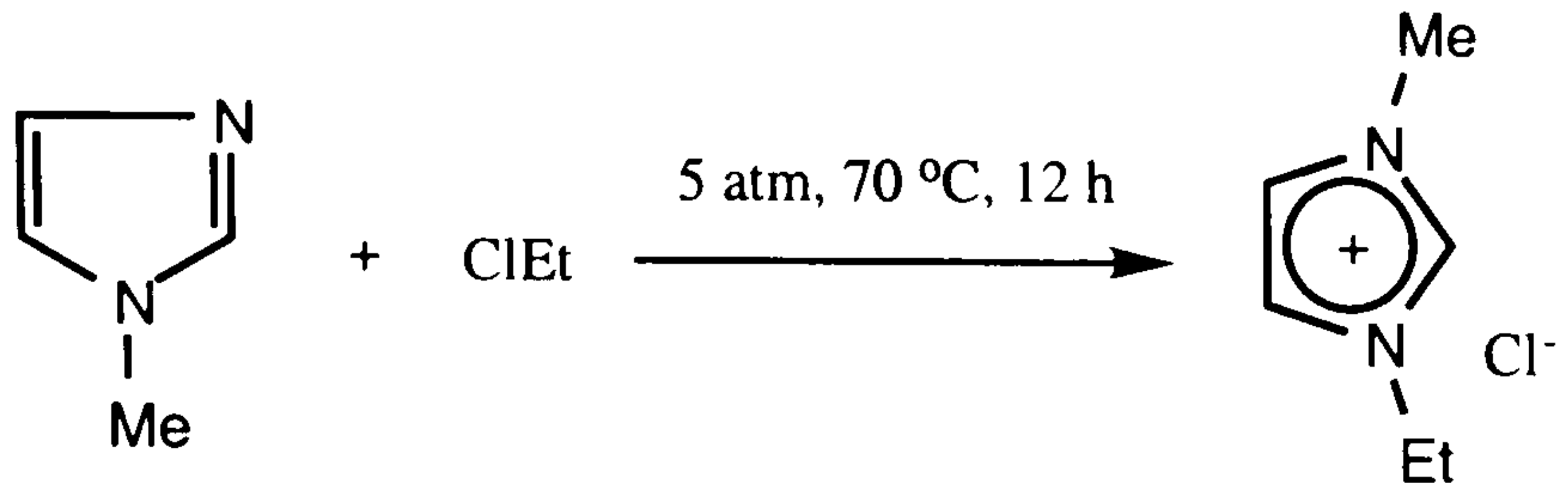
2.3.1. 1-ethyl-3-methylimidazolium bromide [emim][Br]



In a round bottomed flask equipped with a reflux condenser, bromoethane (3.11 cm^3, 0.0285 mol), 1,1,1-trichloroethane (20 cm^3) and 1-methyl imidazole (2.26 cm^3, 0.0283 mol) were mixed together and refluxed at 110-115 °C for 2 h. The cloudy mixture began to change appearance and a light orange oil formed at the bottom of the flask. The light orange oil was washed twice with 1,1,1-trichloroethane (2 x 10 cm^3) and dried, initially for 1h at 70 °C, then for 30 minutes on a vacuum line at 70 °C. An orange crystalline product appeared which was stored under nitrogen and a sample was submitted for ^{1}H NMR analysis in d$_6$-acetone. The melting point was recorded.

^{1}H NMR (d$_6$-acetone) δ 10.24 (s, 1H), 7.96 (t, 1H), 7.86 (t, 1H), 4.46 (q, 2H), 4.08 (s, 3H), 1.53 (t, 3H). m.p. 81 °C. Yield: 52.4%

2.3.2. 1-ethyl-3-methylimidazolium chloride [emim][Cl]

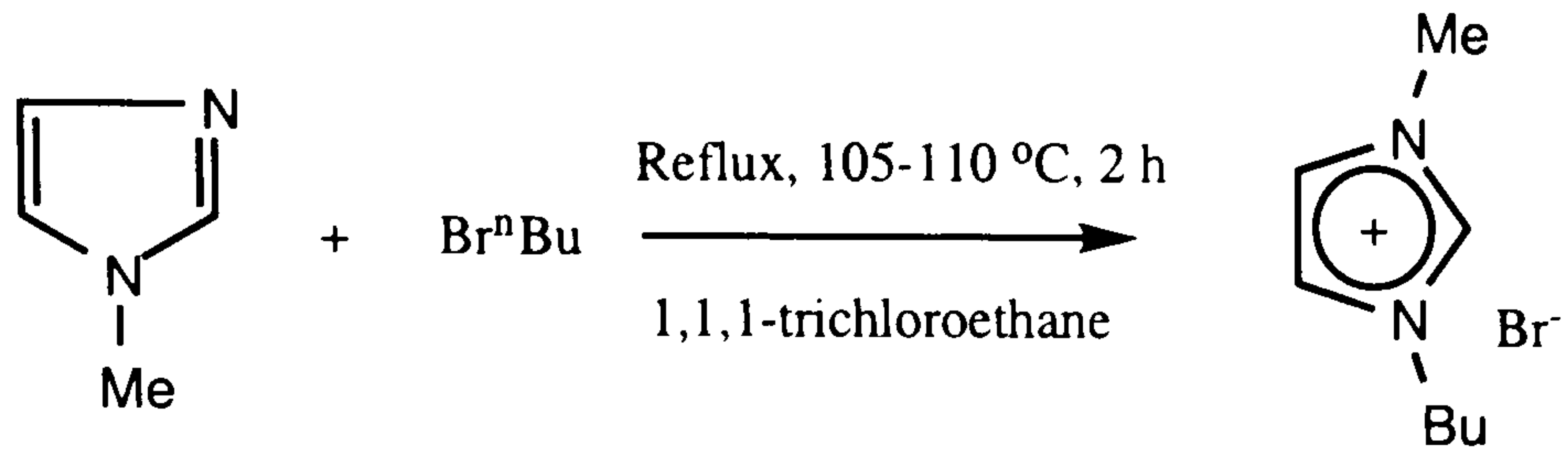


This salt preparation is slightly more complicated due to the fact that the chloroethane is significantly more volatile (bp 15 °C) and hence more difficult to handle than bromoethane. Generally, chloroethane is contained in pressurised containers and stored in diethyl ether. It is possible to handle the chloroethane relatively easily under liquid nitrogen conditions.

Into a pressurised container 1-methyl imidazole (100 cm^3) distilled from calcium hydride (CaH_2) was poured at atmospheric pressure. Chloroethane (125 cm^3) was added. (The amount of chloroethane was determined initially then the corresponding quantity of 1-methyl imidazole required was calculated. For ease of experimental procedure, due to the high volatility of chloroethane, the 1-methyl imidazole was initially added to the pressure vessel, then the chloroethane solution was added as quickly as possible. The solutions were 'poured' into the pressure vessel by means of vacuum techniques using liquid nitrogen.) The vessel was immediately sealed and the pressure raised to 5 atmospheres. The mixture was stirred vigorously at 70 °C. As the desired temperature was being reached, the pressure reading was monitored regularly. After 12 h the excess chloroethane (g) was evaporated off. A single phase, almost colourless liquid was produced which, on cooling solidified to form a creamy, off-white solid. A sample was submitted for ^1H NMR analysis in d_6-acetone and the melting point was recorded.

^1H NMR (d_6-acetone) δ 10.52 (s, 1H), 8.04 (t, 1H), 7.96 (t, 1H), 4.46 (q, 2H), 4.09 (s, 3H), 1.48 (t, 3H). m.p. 80-85 °C. Yield: 55.4%

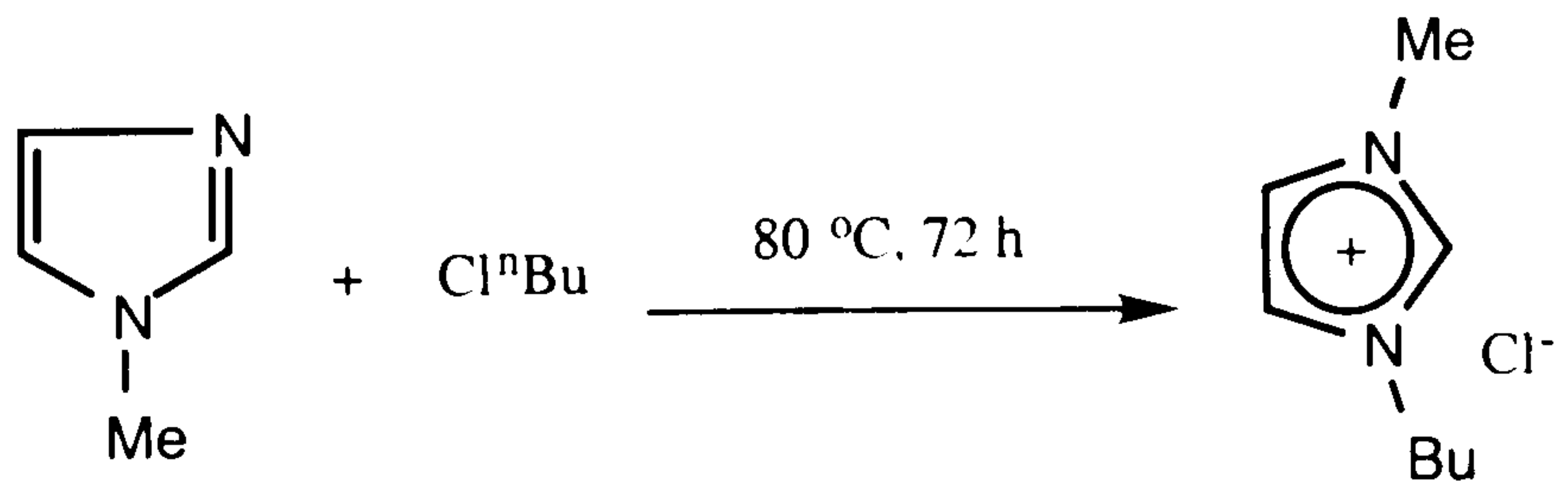
2.3.3. 1-butyl-3-methylimidazolium bromide [bmim][Br]



In a round bottomed flask, equipped with a reflux condenser fitted with a calcium hydride drying tube, bromobutane (30.6 cm^3, 0.285 mol) and 1,1,1-trichloroethane (100 cm^3) were added to 1-methyl imidazole (22.6 cm^3, 0.283 mol) and 1,1,1-trichloroethane (100 cm^3) dropwise over 25-30 minutes. The mixture was refluxed at 105-110 °C for 2 h during which time the liquid turned extremely viscous. The caramel coloured molten salt, forming the top layer, was decanted from the hot solution and washed twice with trichloroethane (2 x 100 cm^3). It was dried on a rotary evaporator at 70 °C for 1 h. The product was analysed by ^{1}H NMR spectroscopy in d$_6$-acetone and the melting point was recorded.

^{1}H NMR (d$_6$-acetone) δ 9.99 (s, 1H), 7.89 (t, 1H), 7.83 (t, 1H), 4.43 (t, 2H), 4.08 (s, 3H), 1.91 (m, 2H), 1.36 (m, 2H), 0.92 (t, 3H). m.p. 63 °C. Yield: 71.1%

2.3.4. 1-butyl-3-methylimidazolium chloride [bmim][Cl]



In a large pressure vessel 1-methyl imidazole (140 cm^3, 1.76 mol) and chlorobutane (200 cm^3, 1.92 mol) were heated to 80 °C and stirred vigorously at 80 °C for 72 h. The orange / brown viscous liquid was transferred to a large round bottomed flask and allowed to cool. The resulting solid was washed with diethyl ether (3 x 50 cm^3) and dried under reduced pressure. A sample was submitted for ^{1}H NMR analysis in d_6-acetone and its melting point was recorded.

^{1}H NMR (d_6-acetone) δ 10.90 (s, 1H), 8.01 (t, 1H), 7.92 (t, 1H), 4.45 (t, 2H), 4.10 (s, 3H), 1.93 (m, 2H), 1.35 (m, 2H), 0.92 (t, 3H). m.p. 68 °C. Yield: 65.2%

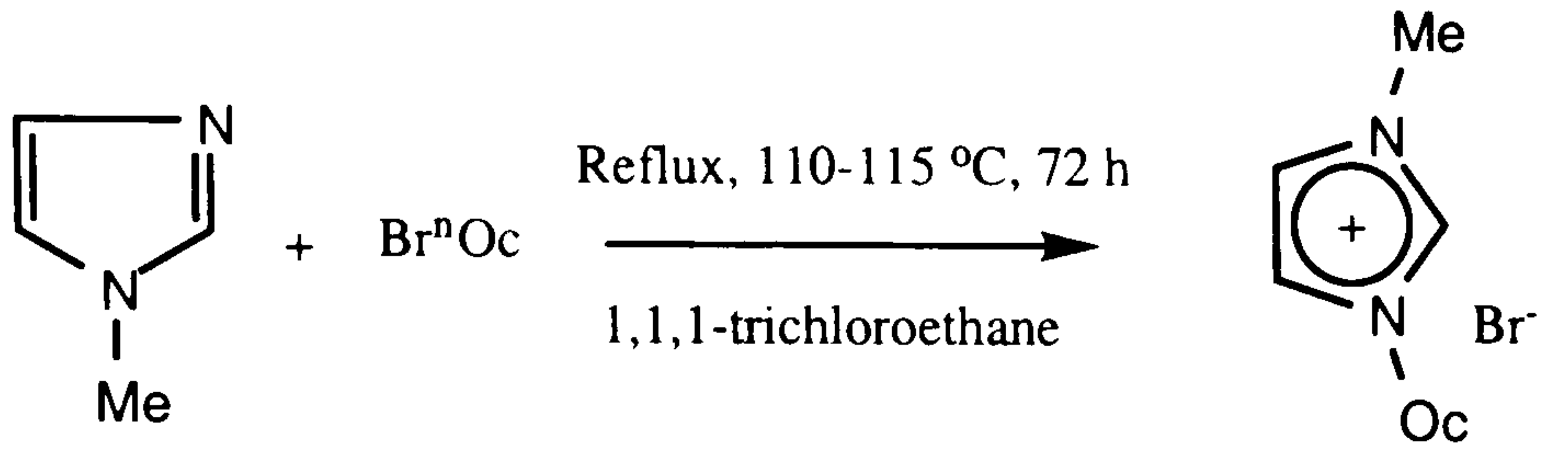
2.3.4.1. Problems Encountered During ^{1}H NMR Analysis

All of these molten salts solidified during stirring under reduced pressure. It proved extremely difficult to dissolve these solids, [emim][Br], [emim][Cl], [bmim][Br] and [bmim][Cl] in the small amount of d_6-acetone required for NMR analysis. Therefore, whilst these samples were in the 5 mm NMR tube containing d_6-acetone, gentle heating was applied to the tube by means of a heat gun. As soon as the solid molten salt melted, forming a homogeneous solution with the d_6-acetone, the sample was analysed.

2.3.4.2. Problems Encountered During Separation Of Products

It was extremely time consuming waiting for the relevant liquids to separate into two distinct layers, especially as the systems were often susceptible to moisture. Directly resulting from this, all samples were washed with diethyl ether and then dried on a vacuum line at 50 °C for several hours.

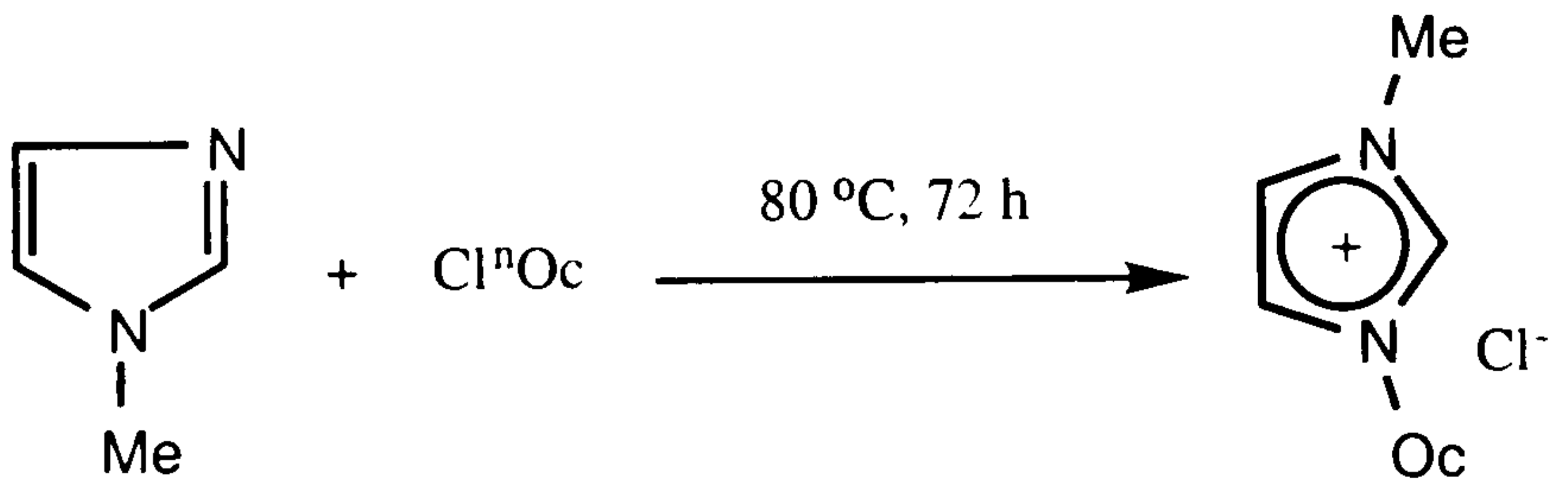
2.3.5. 1-octyl-3-methylimidazolium bromide [omim][Br]



In a large round bottomed flask equipped with a reflux condenser and calcium hydride drying tube, bromooctane (60.0 cm^3, 0.347 mol), 1-methyl imidazole (26.0 cm^3, 0.326 mol) and 1,1,1-trichloroethane (50 cm^3) were mixed via dropwise addition over 1 h and refluxed at 110-115 °C for 72 h. The resulting deep red / brown extremely viscous liquid was separated from the excess trichloroethane using a separating funnel and washed three times with diethyl ether (3 x 50 cm^3). The liquid was dried on a rotary evaporator at 70 °C for 2 h and then on a vacuum line for several hours (due to the high viscosity of the liquid). A sample was submitted for ^{1}H NMR analysis in d$_6$-acetone.

^{1}H NMR (d$_6$-acetone) δ 10.28 (s, 1H), 7.96 (t, 1H), 7.88 (t, 1H), 4.44 (t, 2H), 4.10 (s, 3H), 1.94 (m, 2H), 1.30 (m, 10H), 0.84 (t, 3H). Yield: 40.4%

2.3.6. 1-octyl-3-methylimidazolium chloride [omim][Cl]



In a large pressure vessel 1-methyl imidazole (75 cm^3, 0.94 mol) and chlorooctane (100 cm^3) were stirred vigorously at 80 °C for 72 h. The deep brown viscous liquid was washed three times with diethyl ether (3 x 50 cm^3) and dried on a rotary evaporator at 70 °C for 2 h then on a vacuum line for a further 2 h. A sample was then submitted for ^{1}H NMR analysis in d$_6$-acetone.

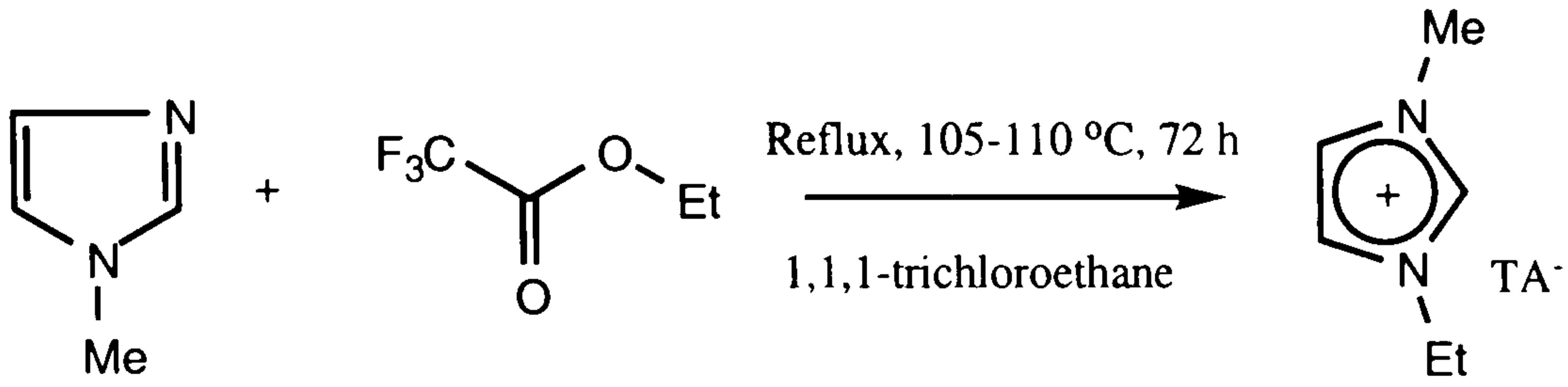
^{1}H NMR (d_6-acetone) δ 10.72 (s, 1H), 8.18 (t, 1H), 8.11 (t, 1H), 4.47 (t, 2H), 4.11 (s, 3H), 1.96 (m, 2H), 1.28 (m, 2H), 0.83 (t, 3H). Yield: 33.4%

2.3.7. Unreacted Starting Material

Peaks in the ^{1}H NMR spectra of [bmim][Br] at δ 7ppm and δ 3.1ppm indicate the presence of unreacted starting material, 1-methyl imidazole and excess water respectively in the product sample (see TABLE 2.9.3a.) A 10% excess of haloalkane was added to all future repeat synthesis experiments in the hope of pushing the experiments further to completion. (For example, 0.313 mol bromobutane was used as opposed to the initial 0.285 mol. See 2.3.3.)

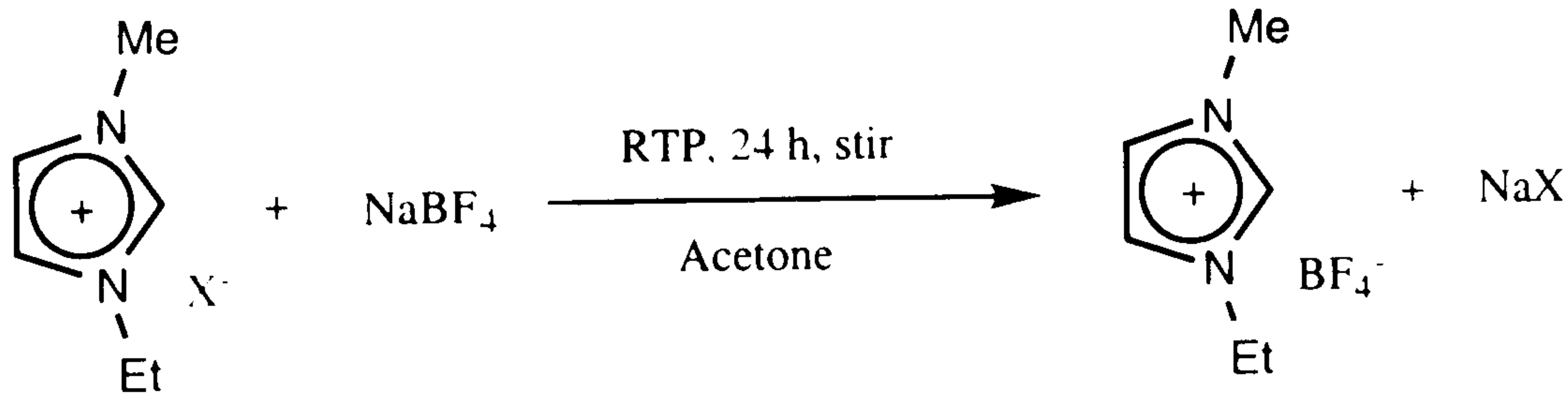
2.3.8. Detailed Experimental Procedures : Ionic Liquid Preparation

2.3.8.1. 1-ethyl-3-methylimidazolium trifluoroacetate [emim][TA]



In a round bottomed flask, 1-methyl imidazole (32.5 cm^3, 0.408 mol), ethyltrifluoroacetate (97.1 cm^3, 0.816 mol) and 1,1,1-trichloroethane (120 cm^3) were refluxed at 105-110 °C for 72 h. The brown viscous solution was washed twice with 1,1,1-trichloroethane (2 x 75 cm^3) and once with diethyl ether (75 cm^3). Excess solvents were removed using rotary evaporation and subsequent drying on a vacuum line at 50 °C for 2 h led to the formation of a brown solution. A sample was submitted for ^{1}H NMR analysis in d$_6$-acetone. ^{1}H NMR (d$_6$-acetone) δ 8.94 (s, 1H), 7.73 (t, 1H), 7.62 (t, 1H), 4.31 (q, 2H), 3.99 (s, 3H), 1.44 (t, 3H). Yield: 45.5%

2.3.8.2. 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF$_4$]

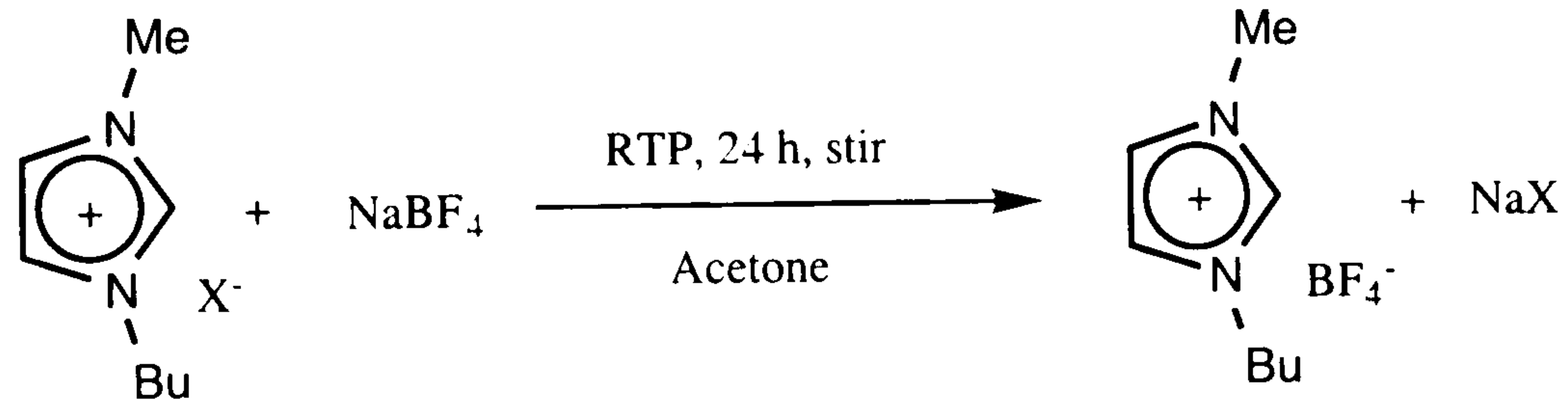


In a large round bottomed flask solid [emim][X] (0.047 mol ; X = halide) dissolved in acetone solution (45 cm^3) and 1.1 eq. of sodium tetrafluoroborate (NaBF$_4$, 0.052 mol) were mixed together. Immediately a white precipitate formed, insoluble in the acetone solution. The mixture was stirred vigorously for 24 h at room temperature and the resulting biphasic mixture was filtered through a gauge 4, glass sintered funnel removing the insoluble precipitate. A small sample of the yellow solution was tested with silver nitrate ($AgNO_3$) forming an immediate white precipitate, indicating the presence of halide ions. The solution was then diluted with dichloromethane (DCM, 25 cm^3) and again filtered. The excess solvent was removed by rotary evaporation from the pale yellow liquid and dried on a vacuum line at 50 °C for 2 h. A sample was submitted for ^1H NMR analysis in d_6-acetone solution.

^1H NMR (d_6-acetone) δ 8.90 (s, 1H), 7.71 (t, 1H), 7.63 (t, 1H), 4.32 (q, 2H), 3.97 (s, 3H), 1.50 (t, 3H). Yield: 57.5%

Note: The ^1H NMR spectra obtained for the ionic liquid was identical regardless of which halide was used during preparation.

2.3.8.3. 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4]

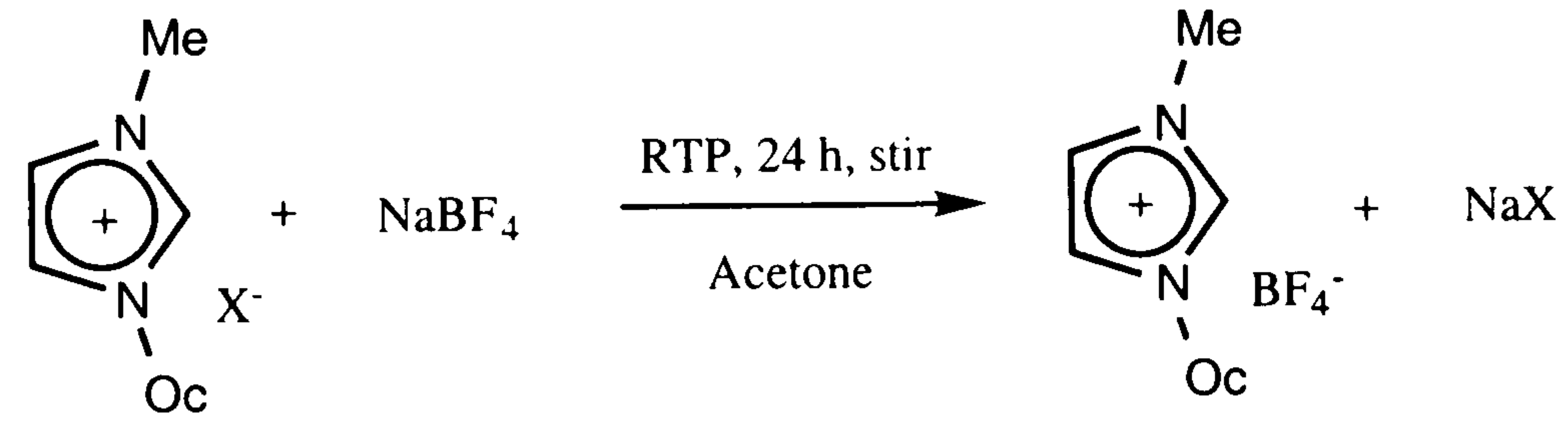


In a round bottomed flask, [bmim][X] (4.75 mmol ; X = Halide) was dissolved at room temperature in acetone solution (15 cm^3). Immediate precipitation occurred on addition of sodium tetrafluoroborate (5.225 mmol ; 1.1 eq) and the creamy reaction mixture was stirred vigorously for 24 h. A light brown oily liquid, pipetted from the insoluble white precipitate was run through a celite column (3 cm) using acetone solution as the solvent. The filtrate was collected and the excess solvent removed by rotary evaporation at

40 °C for 30-45 minutes. The resulting liquid was dried on a vacuum line for a further 30 minutes during which time tiny crystals appeared in the light brown oily solution. Dichloromethane (DCM, 10 cm^3) was added and the cloudy liquid was filtered under reduced pressure using a gauge 4 glass sintered funnel. The excess solvents were removed on a vacuum line. The sample remained in the liquid phase throughout, even on cooling to -78 °C. A sample of the liquid was submitted for ^{1}H NMR analysis in d_6-acetone and the viscosity measured.

^{1}H NMR (d_6-acetone) δ 8.93 (s, 1H), 7.73 (t, 1H), 7.68 (t, 1H), 4.32 (t, 2H), 4.00 (s, 3H), 1.89 (m, 2H), 1.35 (m, 2H), 0.91 (t, 3H). Viscosity 1140 mp. Yield: 85.4%

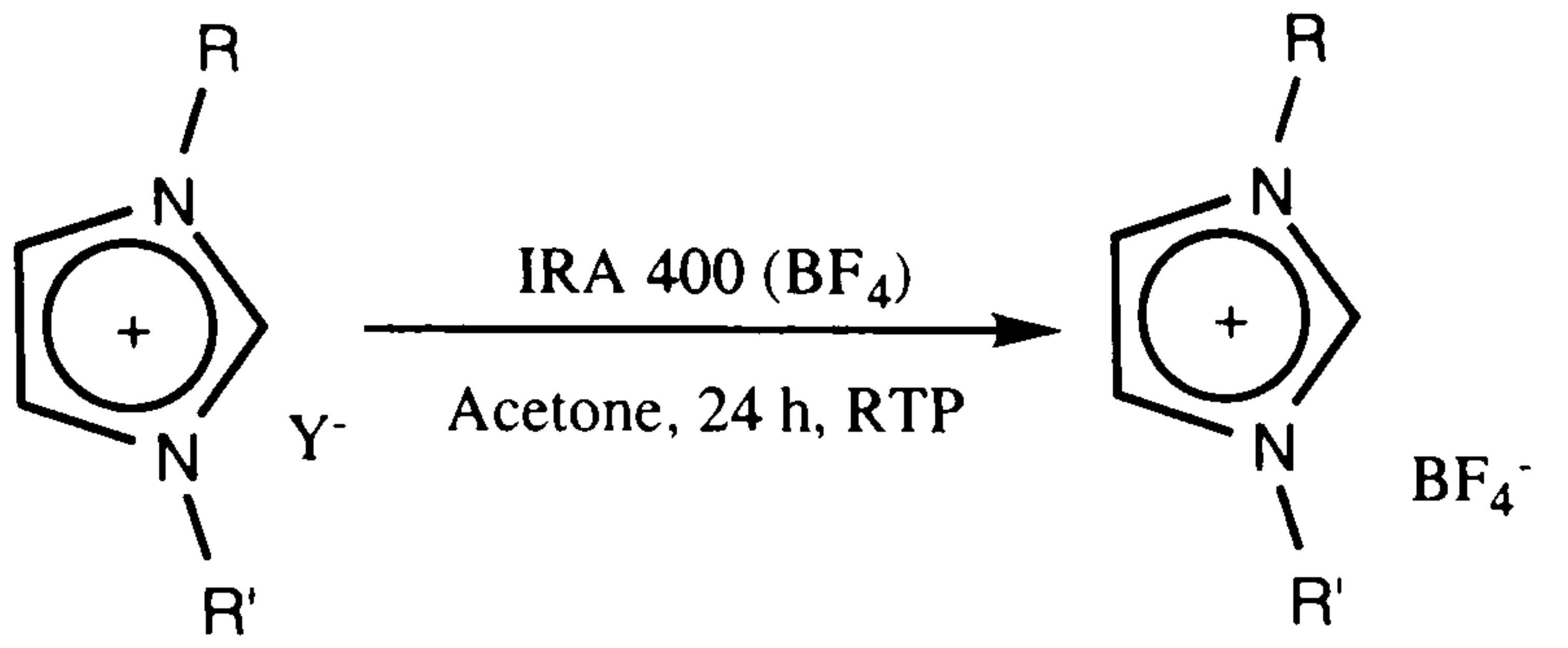
2.3.8.4. 1-octyl-3-methylimidazolium tetrafluoroborate [omim][BF$_4$]



The preparation technique used here was identical to that of [bmim][BF$_4$] (see 2.3.8.3). The only difference was during filtration through a sintered funnel where in this case a gauge 3 sintered funnel was used as opposed to the gauge 4 sintered funnel used in the [bmim][BF$_4$] synthesis. The reason for this change was due to the apparent added viscosity of the [omim][BF$_4$] ionic liquids. A sample of the product was submitted for ^{1}H NMR analysis in d_6-acetone and the viscosity was also measured.

^{1}H NMR (d_6-acetone) δ 8.96 (s, 1H), 7.73 (t, 1H), 7.68 (t, 1H), 4.31 (t, 2H), 4.00 (s, 3H), 1.91 (m, 2H), 1.29 (m, 10H), 0.84 (t, 3H). Viscosity 1141 mp. Yield: 55.2%

2.4. Ion Exchange Resins : General Experiment

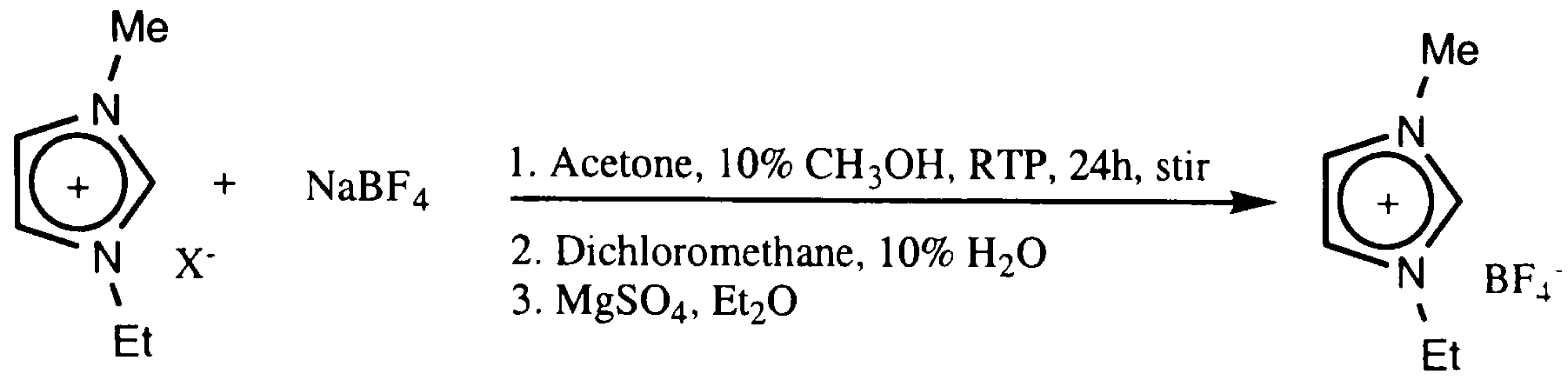


In a preliminary test, in a large round bottomed flask, [emim][Br] (1.92g, 0.01 mol) dissolved in acetone solution and 1.1 eq. of IRA 400 (BF_4) were stirred vigorously for 1 h. A small sample was removed and tested with silver nitrate ($AgNO_3$). An immediate precipitate formed on contact indicating the presence of halide ions, therefore the mixture was left stirring for a further 23 h after which time a sample was again tested with silver nitrate. There was no visible precipitate and the light brown, oily liquid was separated from the resin by simple filtration under reduced pressure. A sample was submitted for ^1H NMR analysis in d_6-acetone to confirm that the expected ionic liquid had formed.

It should be noted that this is the first time that ionic liquids have been synthesised free of halides using ion-exchange techniques. Synthesis of pure, halide free, ethyl, butyl and octyl imidazolium tetrafluoroborates ([emim][BF_4], [bmim][BF_4] and [omim][BF_4]) has been successfully achieved using these ion exchange techniques.

2.5. Alternative Preparation Of [xmim][BF_4] (x = ethyl, butyl or octyl)

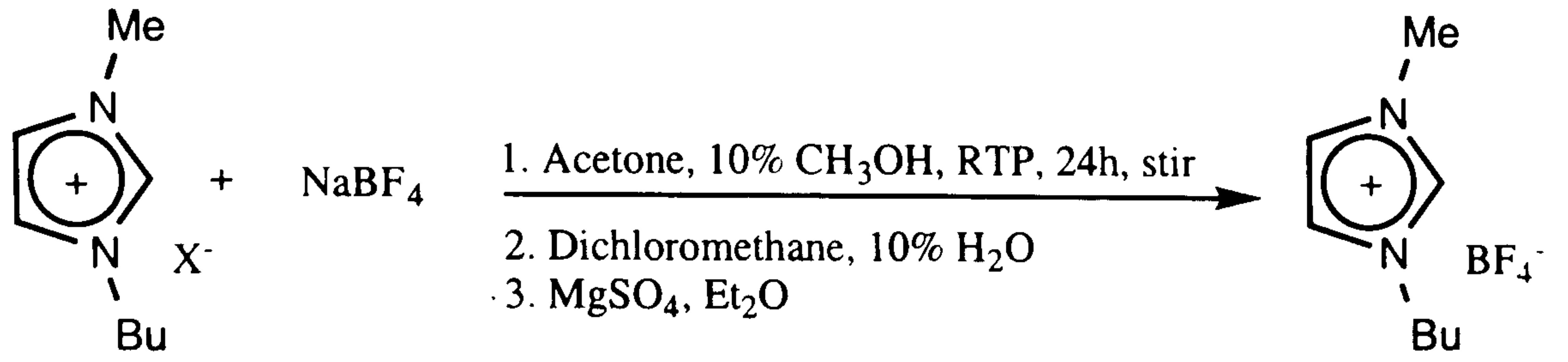
2.5.1. 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF4]



In a round bottomed flask solid [emim][X] (0.4 mol) was dissolved in a solution containing acetone (100 cm^3) and approximately 10% methanol (CH_3OH) solution - added to aid with the dissolving process. The slow addition of sodium tetrafluoroborate (48.31g, 0.44 mol, 1.1 eq) to this light brown solution caused immediate precipitation of white, solid sodium halide. The reaction mixture was stirred at room temperature for 24 h and the product filtered through a gauge 4 glass sintered funnel. A light brown solution containing ionic liquid, acetone and methanol remained. The excess solvent was removed on a rotary evaporator. Dichloromethane (DCM, 50 cm^3) and distilled water (H_2O, 5 cm^3) were added to the cloudy brown solution. The water was added to dissolve any excess halide that may remain from the above synthesis. The two-phase solution was separated using a separating funnel and the organic layer dried over magnesium sulphate ($MgSO_4$) and filtered under reduced pressure using a gauge 4 sintered funnel. The organic layer (containing the ionic liquid) was now washed three times with diethyl ether (Et_2O, 3 x 15 cm^3). The light brown oily liquid was dried on a vacuum line for 1 h and a sample was submitted for ^1H NMR analysis in d_6-acetone.

^1H NMR (d_6-acetone) δ 8.90 (s, 1H), 7.71 (t, 1H), 7.63 (t, 1H), 4.32 (q, 2H), 3.97 (s, 3H), 1.50 (t, 3H).

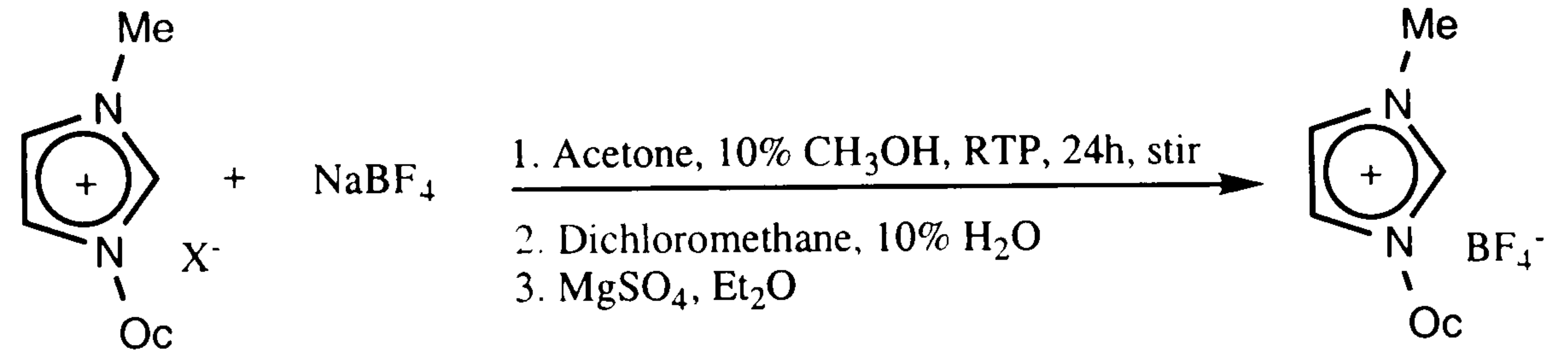
2.5.2. 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4]



The experimental methodology used here was identical to that outlined in section 2.5.1. The same molar equivalents and molecular quantities were used and identical reaction conditions were applied. The only variation was in the appearance of the respective ionic liquid produced.

^1H NMR (d_6-acetone) δ 8.93 (s, 1H), 7.73 (t, 1H), 7.68 (t, 1H), 4.32 (t, 2H), 4.00 (s, 3H), 1.89 (m, 2H), 1.35 (m, 2H), 0.91 (t, 3H).

2.5.3. 1-octyl-3-methylimidazolium tetrafluoroborate [omim][BF_4]

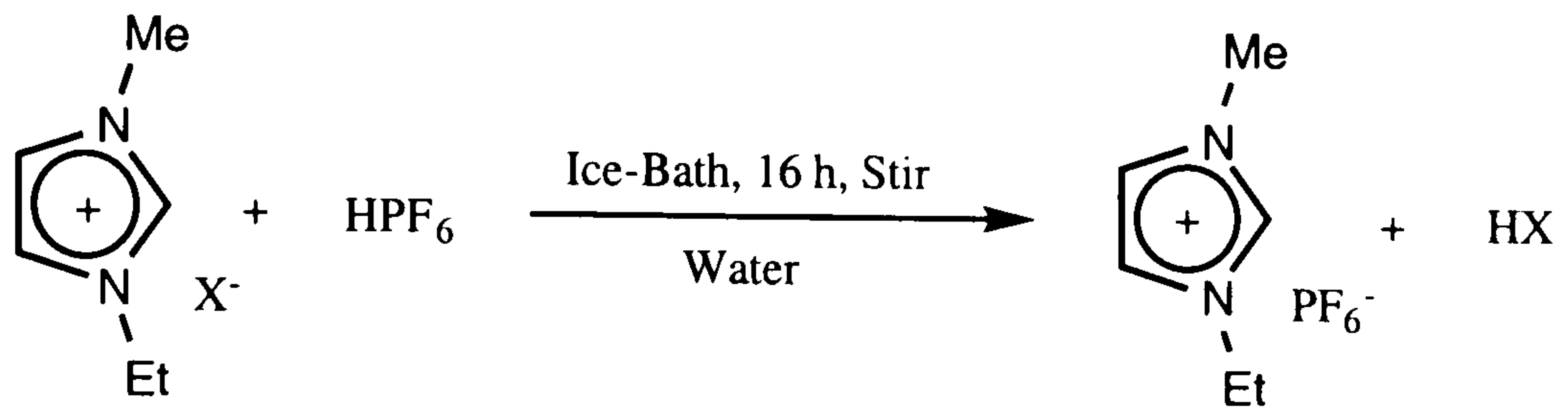


The experimental methodology used in the preparation of [omim][BF_4] was exactly the same as for [bmim][BF_4] (above). Again, the only variation was in the appearance of the ionic liquids produced and there was a visible increase in viscosity with an increase in the side-chain length. The viscosity increased in the order [emim][BF_4] < [bmim][BF_4] < [omim][BF_4].

^1H NMR (d_6-acetone) δ 8.96 (s, 1H), 7.73 (t, 1H), 7.68 (t, 1H), 4.31 (t, 2H), 4.00 (s, 3H), 1.91 (m, 2H), 1.29 (m, 10H), 0.84 (t, 3H).

This preparation technique worked extremely well and produced the desired pure, ionic liquids. All future preparation of these three particular ionic liquids was done using the method outlined in section 2.5.1.

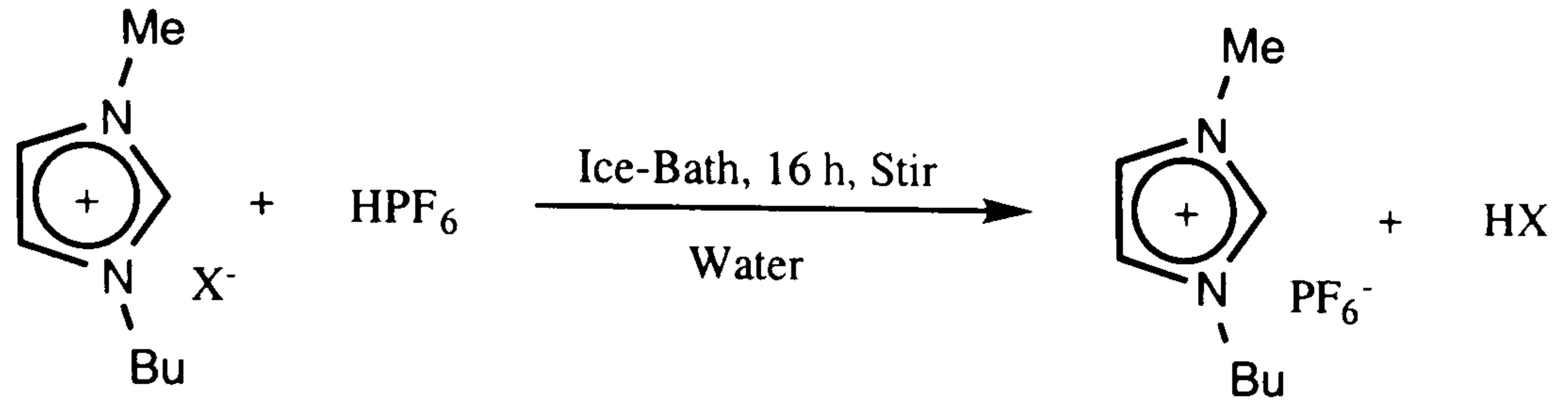
2.5.4. 1-ethyl-3-methylimidazolium hexafluorophosphate [emim][PF$_6$]



A round bottomed flask containing [emim][X], (96g, 0.5 mol [emim][Br] : 73.25g, 0.5 mol [emim][Cl]) dissolved in distilled water (250-300 cm^3) was placed in an ice-bath and hexafluorophosphoric acid (60 % w/v aqueous solution, 182.5 cm^3, 0.75 mol) solution was added extremely slowly, over approximately 30 minutes. There was much effervescence and the mixture was stirred vigorously for 16 h, resulting in the formation of a biphasic solution. The excess water formed the upper layer whilst the light brown oily ionic liquid formed the lower layer. The excess water was removed initially by a pipette then finally by placing the flask on a vacuum line for 2 h. The cloudy liquid was washed three times with diethyl ether (3 x 25 cm^3) and dried on the vacuum line for 1 h. A sample of the light brown oily liquid was submitted for ^{1}H NMR analysis in d$_6$-acetone solution.

^{1}H NMR (d$_6$-acetone) δ 8.91 (s, 1H), 7.74 (t, 1H), 7.66 (t, 1H), 4.33 (q, 2H), 4.00 (s, 3H), 1.47 (t, 3H). Yield: 60.1%

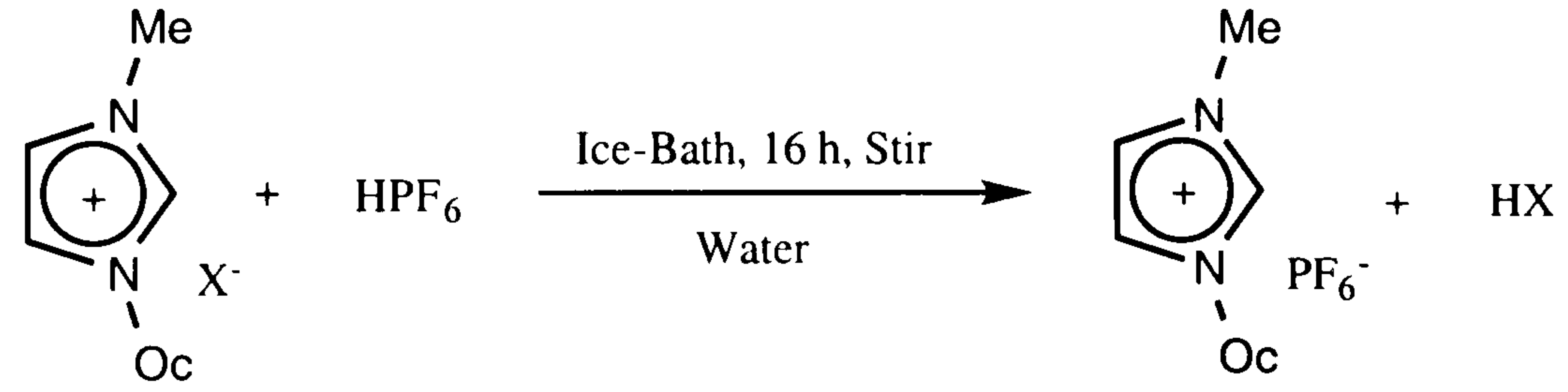
2.5.5. 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6]



The experimental methodology used here was identical to that outlined in section 2.5.4. The same molar equivalents and molecular quantities were used and identical reaction conditions were applied. The only variation was in the appearance of the respective ionic liquid produced.

1H NMR (d_6-acetone) δ 8.92 (s, 1H), 7.71 (t, 1H), 7.66 (t, 1H), 4.36 (t, 2H), 4.02 (s, 3H), 1.90 (m, 2H), 1.36 (m, 2H), 0.92 (t, 3H).

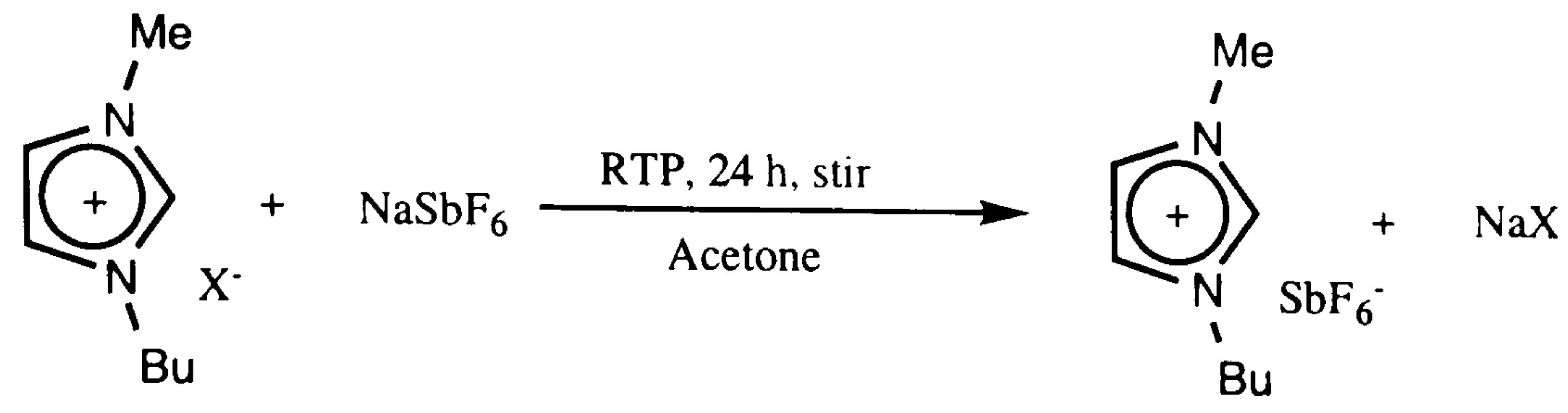
2.5.6. 1-octyl-3-methylimidazolium hexafluorophosphate [omim][PF_6]



The reaction methodology used here was identical to that outlined above (2.5.5.) Again the only variations were in the appearance of the ionic liquid which was a darker brown colour and more viscous than the [bmim][PF_6].

1H NMR (d_6-acetone) δ 8.94 (s, 1H), 7.73 (t, 1H), 7.66 (t, 1H), 4.33 (t, 2H), 4.02 (s, 3H), 1.93 (m, 2H), 1.30 (m, 10H), 0.84 (t, 3H).

2.5.7. 1-butyl-3-methylimidazolium hexafluoroantimonate [bmim][SbF_6]



In a round bottomed flask [bmim][X] (4.6 mmol) was dissolved in acetone solution (10 cm^3) at room temperature. Slow addition of sodium hexafluoroantimonate ($NaSbF_6$, 1.31g, 5.06 mmol, 1.1 eq) to the light brown solution resulted in the formation an immediate insoluble creamy white precipitate of sodium halide. The mixture was stirred vigorously at room temperature for 24 h. Excess acetone was removed under vacuum and the mixture was redissolved in dichloromethane (DCM, 2 x 10 cm^3) solution. The organic layer was washed twice with water (2 x 5 cm^3), which was subsequently removed by simple separation using a separating funnel. The organic phase was dried under vacuum and a sample was sent for ^1H NMR analysis in d_6-acetone solution.

^1H NMR (d_6-acetone) δ 8.95 (s, 1H), 7.72 (t, 1H), 7.67 (t, 1H), 4.34 (t, 2H), 4.03 (s, 3H), 1.91 (m, 2H), 1.36 (m, 2H), 0.92 (t, 3H). Yield: 67.2%

2.6. RESULTS and DISCUSSION

2.6.1. Problems Encountered During Preparation

2.6.1.1. Separation Problems

The preparation of ionic liquids described in section 2.3.8. produced the inevitable precipitation of sodium halides, it became increasingly difficult to separate the liquid phase from the solid precipitate as the chain length in the ionic liquids increased. The increased carbon content of the [omim] ionic liquids in particular made them significantly more viscous and therefore much more difficult to handle. Each time separation of product from precipitate resulted in reduced yields of respective products. The more viscous the ionic liquid, the greater the % loss.

2.6.1.2. Trace Quantities Of Halide

The ionic liquids were left standing for several days, after which time many of them appeared cloudy. Subsequent testing with more silver nitrate revealed that halide was still present in some of these liquids and those that did not produce a precipitate were quite clearly not pure, simply due to their changed appearance. The cloudiness could be as a result of absorbed moisture.

2.6.1.3. Purification

The ionic liquids were washed, extracted, dried etc. and the whole synthetic routes were repeated several times in attempts to purify the liquids. Unfortunately every time there appeared to be halide impurities. A main problem is the fact that extraction was difficult. Polar solvents such as water and acetone are miscible or partially miscible with the ionic liquids used here and thus could not be used to extract the halide salts. The technique employed by Bonhote *et al.*[2] was therefore modified and an alternative preparation route was chosen involving the use of ion-exchange resins. IRA 400 was chosen and repeat synthesis of the ionic liquids along with purification experiments were attempted.

2.7. The Use Of Ion Exchange Resins

The ion exchange resin chosen was 'IRA 400'. This resin was purchased in the chloride (Cl^-) form so it was initially have transformed to the tetrafluoroborate (BF_4^-) before attempting ionic liquid preparation.

Ion exchange techniques were attempted as a relatively straightforward way to synthesise the desired ionic liquids. Either stirring the imidazolium salts in a solution containing the IRA 400, or running the imidazolium salts through an IRA 400 column resulted in a simple exchange where the ion contained within the resin (in this case tetrafluoroborate (BF_4^-) 'exchanged places' with the counter-ion of the respective imidazolium salts (both chloride (Cl^-) and bromide (Br^-)). The halide ion remained within the ion exchange resin and therefore played no further part in the reaction mechanism, nor did it interfere with the newly formed ionic liquid.

2.7.1. Preparing The IRA 400

As mentioned, IRA 400 was purchased in the chloride form. The capacity of the resin is 3.8 meq/g. 1g contains 3.8 mmol chloride. The IRA 400 was converted to the active tetrafluoroborate form by simple exchange with $NaBF_4$.

2.7.2. Exchanging The IRA 400

In a large round bottomed flask, IRA 400 (25.07g, 95.27 mmol Cl^-) and distilled water (100 cm^3) were stirred at room temperature for 1 h. $NaBF_4$, (20.8g, 0.189 mol, 2 eq) dissolved in water (100 cm^3) was slowly added at room temperature to the IRA 400 / water mixture and the slightly cloudy mixture stirred at room temperature for 24 h. The contents of the flask were filtered through a glass sintered funnel to remove the small traces of fragmented resin. A small sample of the resin was tested for halide ions with silver nitrate ($AgNO_3$). There was no evidence of precipitation therefore it could be assumed that successful exchange had occurred and that the resin was now in the BF_4 form.

2.7.3. Ionic Liquid Preparation Using BF_4 Modified Resin IRA 400

There was a choice of preparation technique to use. The imidazolium salt [xmim][Y] (where x = ethyl, butyl or octyl and Y = Br or Cl) would simply be in contact with the IRA 400 (BF_4^-) resin in the appropriate solvent and exchange would theoretically occur. This reaction could therefore be performed using a column or simply a round bottomed flask. As the original modification of IRA 400 (Cl^-) to IRA 400 (BF_4^-) had readily occurred using a round bottomed flask with vigorous stirring, it seemed foolish not to replicate such conditions.

2.7.4. Problems Encountered

Although tests indicated that there was no halide present in the ionic liquids produced using ion exchange techniques, the liquids themselves had a slightly cloudy appearance possibly due to absorbed moisture, however the result of vigorous stirring was fragmentation of the resin, also potentially causing the cloudy appearance. This was soon resolved by running the ionic liquids through a column, (containing IRA 400(BF_4) resin) with a cotton wool filter at the bottom. This successfully removed any small resin broken-down fragments. As the IRA 400 resin had been exchanged initially in aqueous conditions it was essential to dry the newly synthesised ionic liquids for 3 h at elevated temperature (70 °C) on a vacuum line to ensure that all trace amounts of water would be removed.

2.7.5. Continued Work

Although the ion exchange resins worked well for the preparation of tetrafluoroborate ionic liquids, there was always the chance that although halide impurity had been removed, one could never be 100% certain as to the undetectable trace impurities that the ion exchange resin itself may have introduced. The resins undoubtedly contained undetectable impurities, such as lanthanides, that could well have been introduced into the ionic liquids. It was therefore necessary to attempt to find a new preparation route for halide-free, ionic liquid synthesis without the use of ion exchange resins.

2.8. Preparation Of Hexafluorophosphate Ionic Liquids

There were very few problems encountered during the synthesis of the hexafluorophosphate ionic liquids (See sections 2.5.4., 2.5.5. and 2.5.6.) Most difficulty arose from simple handling procedures. The HPF_6 solution was extremely corrosive and much care had to be taken not only in the personal handling of the material but with the chosen glassware.

During initial attempted synthesis of [xmim][PF_6] ionic liquids (x = ethyl, butyl or octyl), often after the 16 h 'stir period' in an ice-bath, the round bottom flask had dissolved and therefore the reaction had to be scrapped. The reason for this is due to the build up of the extremely corrosive hydrofluoric acid (HF) during the course of the reaction. Future experiments were therefore performed in plastic round bottomed flasks and all the 'glassware' equipment required during handling of HPF_6 was exchanged for the corresponding plastic equipment.

The viscosity of the [omim] ionic liquid in particular, often caused problems during separation processes. It was extremely difficult to stir the liquid vigorously, especially whilst drying under vacuum and separation itself was not only difficult but also an extremely time consuming process.

2.8.1. Continued Work 2

Much of the future work, involving the ionic liquids as solvents for catalytic reactions, concentrated predominantly on reactions in four of the ionic liquids, [bmim][BF_4], [bmim][PF_6], [omim][BF_4] and [omim][PF_6]. Synthesis of another ionic liquid ([bmim][SbF_6]) was attempted, however similar problems were encountered as with the initial synthesis of the tetrafluoroborate liquids. [bmim][SbF_6] was synthesised from $NaSbF_6$ in exactly the same way as [bmim][BF_4] from $NaBF_4$ (see section 2.5.2.), yet after several purification attempts, sodium (Na) levels of almost 5% were still present in the ionic liquid (see figure 2.8.1a). Impurities proved difficult to remove and extract for the same reasons as outlined in section 2.6.1.

2.9. Melting Point Data

Only the short chain compounds, [emim] and [bmim] (C_2-mim and C_4-mim) are low melting point solids. On increasing the chain length the melting point decreases steadily. This point is reinforced by the fact that the [omim] halide salts are liquid at room temperature.

All the respective melting points were obtained using standard melting point apparatus. Each melting point was recorded three times then the mean value was calculated. (See TABLE 2.9a)

TABLE 2.9a. 'Melting Points Of Prepared Imidazolium Salts'

Imidazolium Salt	Mp 1 (°C)	Mp 2 (°C)	Mp 3 (°C)	Mp (average)	Reported[4] Mp
[emim][Br]	80	81	81	81	**81**
[emim][Cl]	79-84	80-85	80-85	80-85	**82-87**
[bmim][Br]	60	61	66	63	-
[bmim][Cl]	66	71	68	68	**65-69**

The data here for [bmim][Br] is shown as the upper temperature reading over a wide range of recorded melting points. It is feasible that there were trace amounts of impurity in the halide salts. Any impurity would undoubtedly have a direct effect on the measured melting point, and in this case would cause an initial lower value in the recorded melting point due to the presence of 1-methylimidazole.

From these results it is possible to draw two conclusions.

1. The $[emim]^+$ salts have a higher melting point than their corresponding $[bmim]^+$ salts, therefore increasing the chain length decreases the melting point.

2. Chlorides have higher melting points than bromides.

The variation in the melting point when changing the anion could be for several reasons. One major possibility is structure related. (See FIGURE 2.9a)

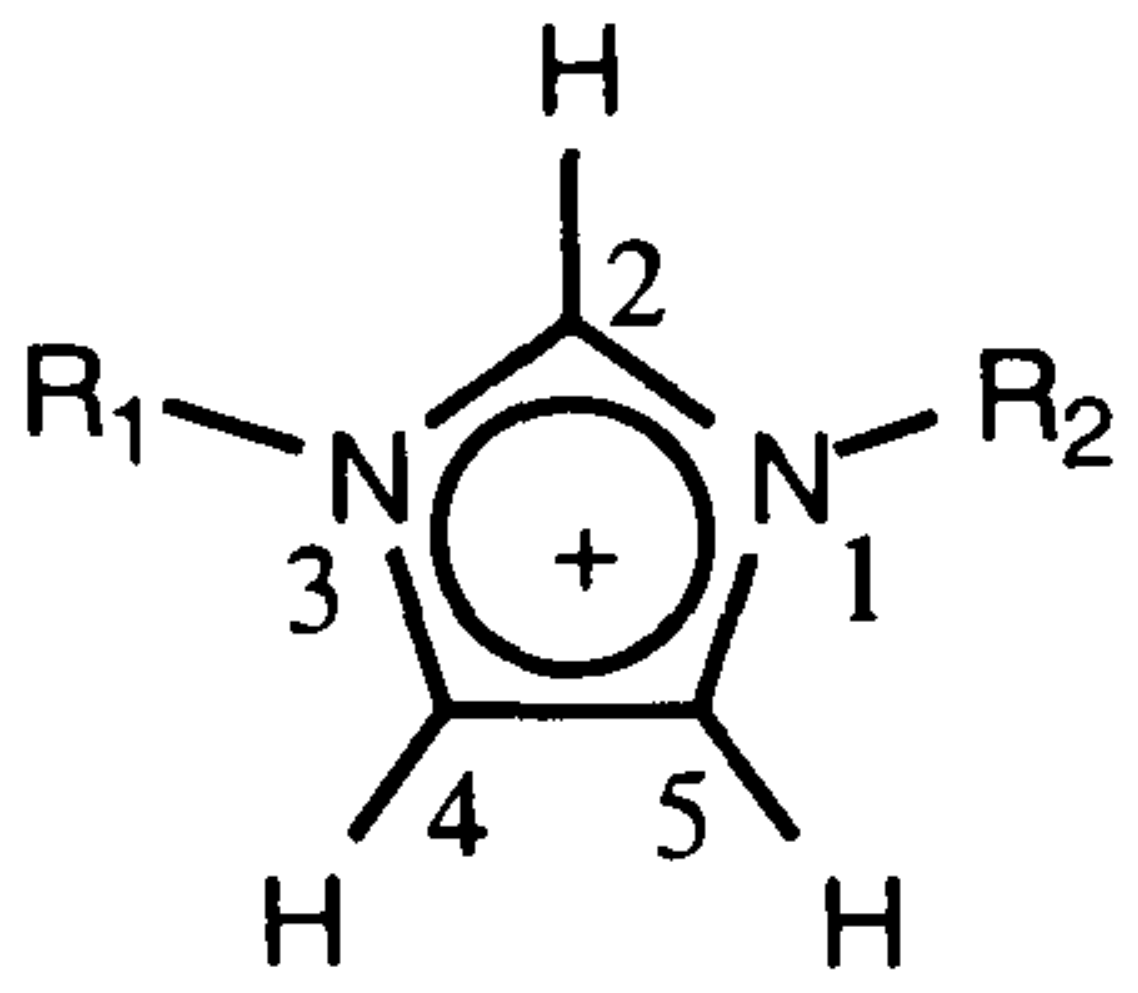


FIGURE 2.9a. Imidazolium cation ring numbering.[5]

In [emim][Br] there is only one unique cation and one unique anion, whereas in [emim][Cl] there are four unique cations and four unique anions. In [emim][Br] each anion is hydrogen bonded to three cations, one by the H^2, one by the H^4 and one by the H^5 proton of the imidazolium ring. However, in [emim][Cl] the arrangement is considerably more complicated. Each of the crystallographic distinct chloride ions is hydrogen bonded to three cations, but to different ring protons. One chloride ion is bonded to the H^4 proton of one cation and to the H^2 protons of two other cations, the next is bonded to the H^4 protons of two cations and to the H^2 proton of the third cation, the next is bonded to the H^4 proton of one cation and to the H^5 protons of two cations and the final chloride is bonded to the H^2 proton of one cation and to the H^5 proton of two cations. This leads to an overall structure that is considerably more disordered than that of the bromide. It is unlikely that the chloride salt has a low temperature polymorph which is isostructural with the bromide.[6]

It can be safely assumed that hydrogen bonding is responsible for the different structures adopted by these salts, and therefore could be responsible for the variations in the observed melting points. It is possible however than the size of the halides could also play a significant role in structure determination.

2.9.1. Density Measurements

As the ionic liquids were viscous materials it was relatively difficult to accurately measure their respective densities. Accurate pipetting of the liquids extremely difficult. In an attempt to simplify this process several small sample tubes were graduated by accurately pipetting 2.0 cm^3 and 2.2 cm^3 distilled water into the tubes and physically marking the water level on the side of the tubes. The ionic liquids were then 'dripped' into the now clean, dry sample tubes until the level reached indicated that 2.0 cm^3 and 2.2 cm^3 had been added. The tubes were accurately weighed before and after ionic liquid addition so the respective densities of the ionic liquids could subsequently be calculated.

Density **d** = mass **m** / volume **v**

TABLE 2.9.1a. 'Ionic Liquid Density Data'

Ionic Liquid	Mass Of 2.0 cm^3 (g)	Mass Of 2.2 cm^3 (g)	Density (2.0 cm^3) d_1	Density (2.2 cm^3) d_2	Mean Density d_m
[bmim][BF$_4$]	2.6	3.0	1.3	1.3	1.3
[omim][BF$_4$]	2.2	2.8	1.1	1.3	1.2
[bmim][PF$_6$]	2.9	3.6	1.4	1.6	1.5
[omim][PF$_6$]	3.0	3.9	1.5	1.8	1.6

2.9.2. Viscosity Measurements

The apparatus used here was a ASTM Kinematic Viscometer. The direct measurement of viscosity is based on the Poiseuille equation (1)

(1) **Viscosity** $\eta = \pi r^4 t p / 8 v L$

where **v** is the volume of liquid flowing in **t** seconds through a narrow tube of radius **r** cm and length **L** cm, under a driving pressure of **p** dynes per sq cm.

If a solid body is falling through a liquid, the effect of viscosity is to exert a drag on the falling body. Instead of a continued increase in its rate of fall, the body acquires a constant velocity, called the terminal velocity, when the gravitational pull downwards just balances the upward drag due to viscosity. For a falling sphere of radius **r** this steady velocity **u** is related to the viscosity η by the Stokes's Law equation

(2) $u = 2gr^2(d' - d) / 9\eta$

where **g** is the gravitational acceleration, **d'** is the density of the sphere and **d** is that of the liquid. If **d** is small in comparison with **d'**, equation (2) reduces to the simple form

(3) $u = 2gr^2d / 9\eta$

which is particularly applicable when the medium is a gas instead of a liquid.

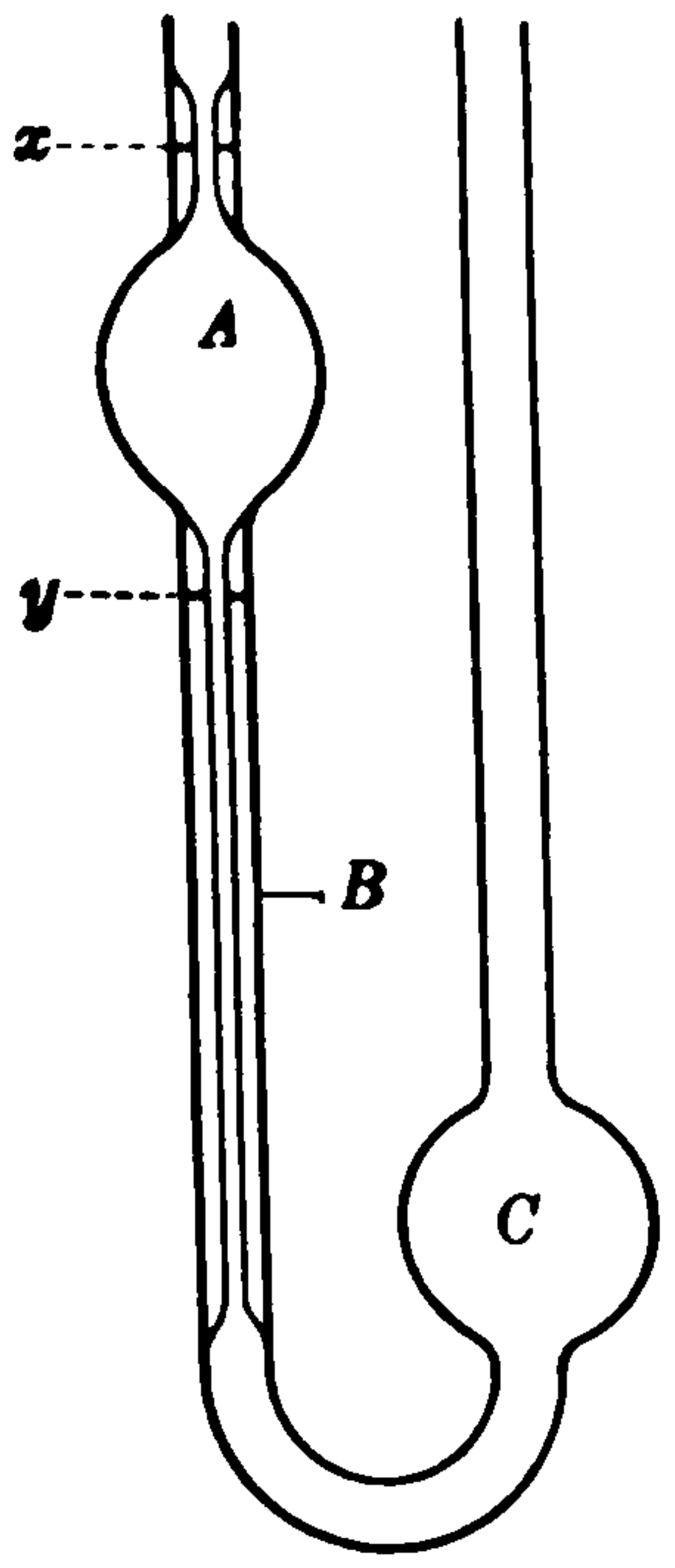


FIGURE 2.9.2b. Ostwald Viscometer.[7]

To determine the viscosity of a liquid the rate of flow of the liquid, under a definite pressure, through a capillary tube is determined. A definite volume of liquid is introduced into the bulb **C** and is then sucked into **A** ; the time **t** is observed for the liquid to flow through the capillary tube **B**, between the marks **x** and **y**. The measurement is then repeated with the same volume of another liquid whose viscosity is known. The relative viscosity can then be calculated by referring to (1), it is seen that, since the same viscometer is used for the two liquids, the radius **r** and length **L** of the capillary tube, and the volume **v** of the bulb **A**, are the same in both cases. The pressure **p** depends on the head of the liquid and its density ; the former is constant but the latter varies for the two liquids. If η_1 and η_2 are the viscosities of the two liquids of density $\mathbf{d_1}$ and $\mathbf{d_2}$ respectively, and $\mathbf{t_1}$ and $\mathbf{t_2}$ are the times of flow in the given viscometer, then by substituting these values in (1) for each liquid and dividing, the result is

$$(4) \quad \eta_1 / \eta_2 = d_1 t_1 / d_2 t_2$$

For viscous liquids, such as hydrocarbon oils, the falling sphere method, which is based on the Stokes equation (2), is frequently employed for the determination of viscosity. A small steel sphere is introduced below the surface of the liquid in a tall cylinder, and the time taken for it to fall between two marks is noted. The observation is then repeated with the same sphere and another liquid of known viscosity. The distance fallen is the same in each case, and so the rate of fall **u** is inversely proportional to the time of fall **t**; it follows, therefore, from equation (2), since **g** and **r** are constant, that

$$\eta 1 / \eta 2 = t_1(d'-d_1) / t_2(d'-d_2)$$

where **d'** is the density of the steel ball, and d_1 and d_2 are the densities of the two liquids. Since the viscosity of one liquid is known, that of the other can be determined from observations on the falling sphere.

To determine the viscosities of the ionic liquids using equation (4), the time **t** was measured for several known liquids and also for the respective ionic liquids. The values obtained are given in tables 2.9.2a. and 2.9.2b. If the viscosity coefficient η_2 and density d_2 of one liquid are known, the viscosity of the other can be calculated from the density and flow times. (See TABLES 2.9.2a and 2.9.2b)

TABLE 2.9.2a. 'Viscosity Calibration Values'

Solution	**Flow Time t_1 (sec)**	**Flow Time t_2 (sec)**	**Flow Time t_3 (sec)**	**Average t (sec)**	**Density d (gcm^{-3})**
Water	11.93	11.84	11.87	11.88	1.00
Ethanol (C_2H_5OH)	17.40	17.75	17.68	17.61	0.801
Methanol (CH_3OH)	9.65	9.90	9.93	9.83	0.791

The volume of liquids used was constant at 20.0 cm^3.

These values were recorded for calibration purposes. Combining the flow times obtained from the relevant ionic liquids with these values, using equation (4), the viscosities of the respective ionic liquids could be calculated as outlined in section 2.9.2. (See TABLE 2.9.2c)

TABLE 2.9.2b. 'Ionic Liquid Flow Times'

Ionic Liquid	**Temp °C**	**Flow Time t_1 (sec)**	**Flow Time t_2 (sec)**	**Flow Time t_3 (sec)**	**Mean t (sec)**	**Density d (gcm^{-3})**
[bmim][BF_4]	23	1001	1016	1014	1010	**1.33**
[omim][BF_4]	23	1095	1135	1135	1122	**1.20**
[bmim][PF_6]	20	4769	4798	4782	4783	**1.53**
[omim][PF_6]	24	8510	8387	8701	8533	**1.63**

The volume of liquids used was constant at 20.0 cm^3.

The density values used here are those calculated in section 2.9.1.

The quoted value of viscosity for water at 20 °C is η = 10.09 mp. Assuming this to be η_2, the viscosity η_1 of ethanol can be calculated to test the accuracy of the measurements.

Ethanol: $\eta_1 / \eta_2 = d_1 t_1 / d_2 t_2$

η_1 = (10.09 mp x 0.801 x 17.61s)/ (1.00 x 11.88s)

η_1 = 11.98 mp. (Data indicates that at 20 °C, η_1 = 12.0)[7]

(Error in experiment of +/- 0.167%)

The viscosity of ethanol was calculated primarily to verify the accuracy of the viscometer. This value showed good correlation with the expected result. Obviously there were significant errors in the experimental values obtained:-

1. The temperature was not 20 °C, it fluctuated between 20 and 24 °C.
2. Pipetting inaccuracy of 2-5% can be expected.
3. Human error in time measurements for movement of liquid through the viscometer.

The viscosity of methanol and water were also calculated using the same method as for ethanol. The viscosity of methanol was calculated to be η = 6.60 mp (compared to the reference value of 5.93 mp) and water was calculated as η = 10.09 mp (compared to the reference value of 10.09 mp). These obtained values were used to calculate the viscosities of the ionic liquids. (See TABLE 2.9.2c)

TABLE 2.9.2c. Table Of Ionic Liquid Calculated Viscosities

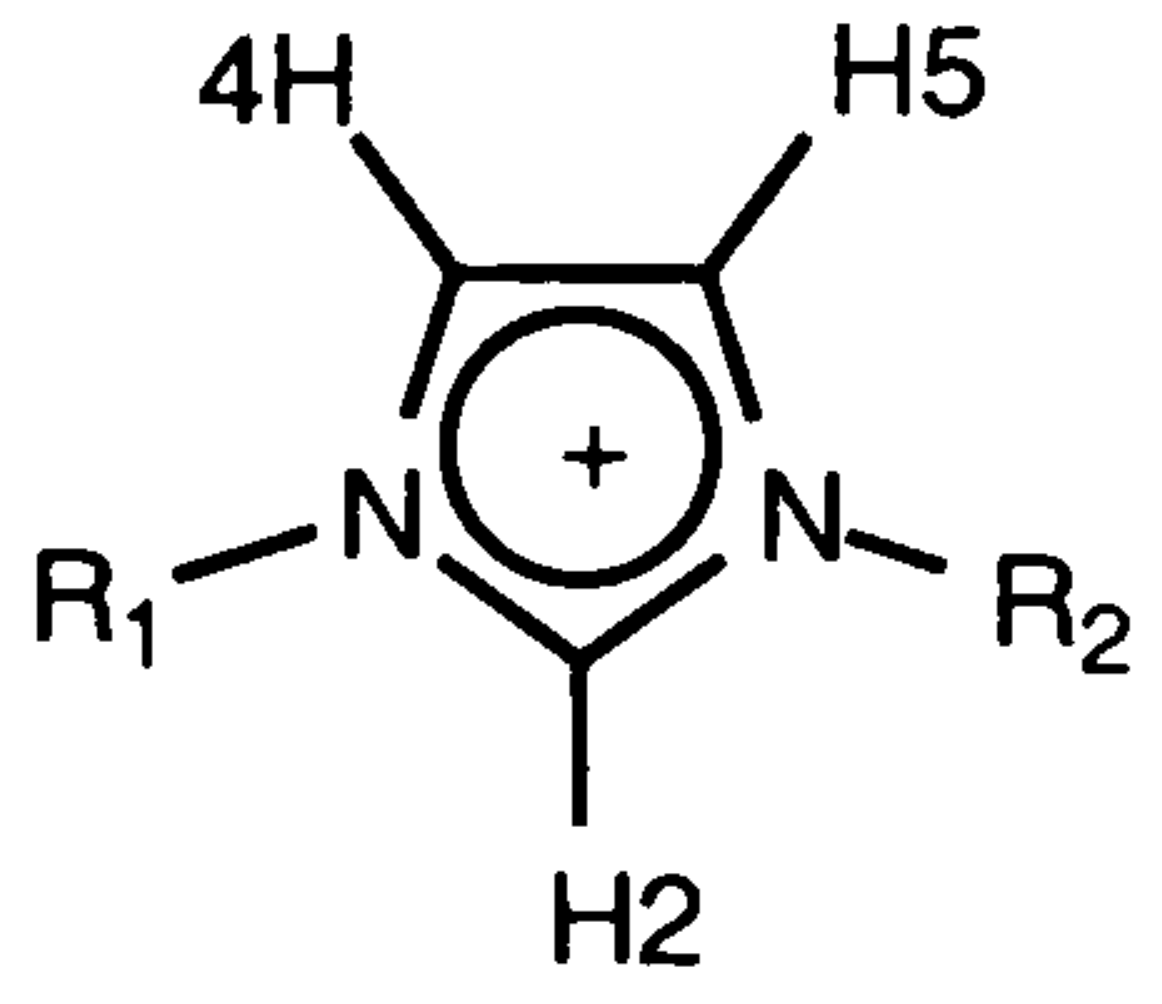
Ionic Liquid	Viscosity (mp)
[bmim][BF_4]	1140.78
[omim][BF_4]	1140.82
[bmim][PF_6]	6229
[omim][PF_6]	11780

During the preparation of the individual ionic liquids it was significantly more difficult to handle the [omim] ionic liquids due to their added viscosity. The calculated viscosity values of the [BF_4] ionic liquids is therefore slightly surprising as there appears to be little difference in the calculated viscosity of the [bmim] and [omim] salts. There appears to be little effect, if any, on the viscosity with an increase in chain length. Although the [omim][BF_4] ionic liquid is of greater density than the corresponding [bmim] liquid, the flow time observed for calculating the viscosity is reduced. However in the [PF_6] salts there is a notable variation in calculated viscosity. When changing from tetrafluoroborate [BF_4] to hexafluorophosphate [PF_6] anion, both the [bmim] and [omim] ionic liquids are found to be significantly more viscous in their [PF_6] form. The reason for this dramatic increase in viscosity could perhaps be structure related.

Investigation into the structure of [emim][PF_6] showed that the [PF_6^-] anions surround the organic cations, and the fluorine atoms partially penetrate the region between the two cations at sites away from the ethyl groups. The long distances between cations, and the lack of a stacked structure, precludes any possibility of π - π aromatic interactions. The lack of hydrogen bonding and aromatic π - π stacking indicates that cation - anion coulombic attraction is driving the overall crystal structure, with local steric effects influencing the final orientation. The result is that the local liquid structure of the analogous [emim][BF_4] resembles the solid state structure of the [emim][PF_6]. If the same is assumed for the [bmim][PF_6] and [omim][PF_6] liquids then it is perhaps feasible that this is the reason for the observed increase in viscosity.[8]

2.9.3. ^{1}H NMR Data

The ionic liquids synthesised in this chapter were identified in the main using ^{1}H NMR spectroscopy techniques. (See TABLE 2.9.3a)



General structure, $R_1 = CH_3$, $R_2 = C_2H_5$, C_4H_9 or C_8H_{17}.

Table 2.9.3a shows the chemical shifts of the hydrogen atoms which are most affected by a change in anion. Although these three shifts alone do not provide enough information regarding the conversion to product, they do allow us to clarify whether ionic liquid has been successfully synthesised by enabling a direct comparison between 1-methylimidazole and the new compound being analysed. The remaining peaks in the ^{1}H NMR spectra (at lower field shifts) are from the aliphatic side chains hydrogens of the imidazolium cation, therefore providing information regarding the actual, individual structure of the ionic liquids synthesised, and allowing, where possible, comparison to literature[3] to confirm successful synthesis. (If the compound has already been previously synthesised and is therefore 'a known compound.')

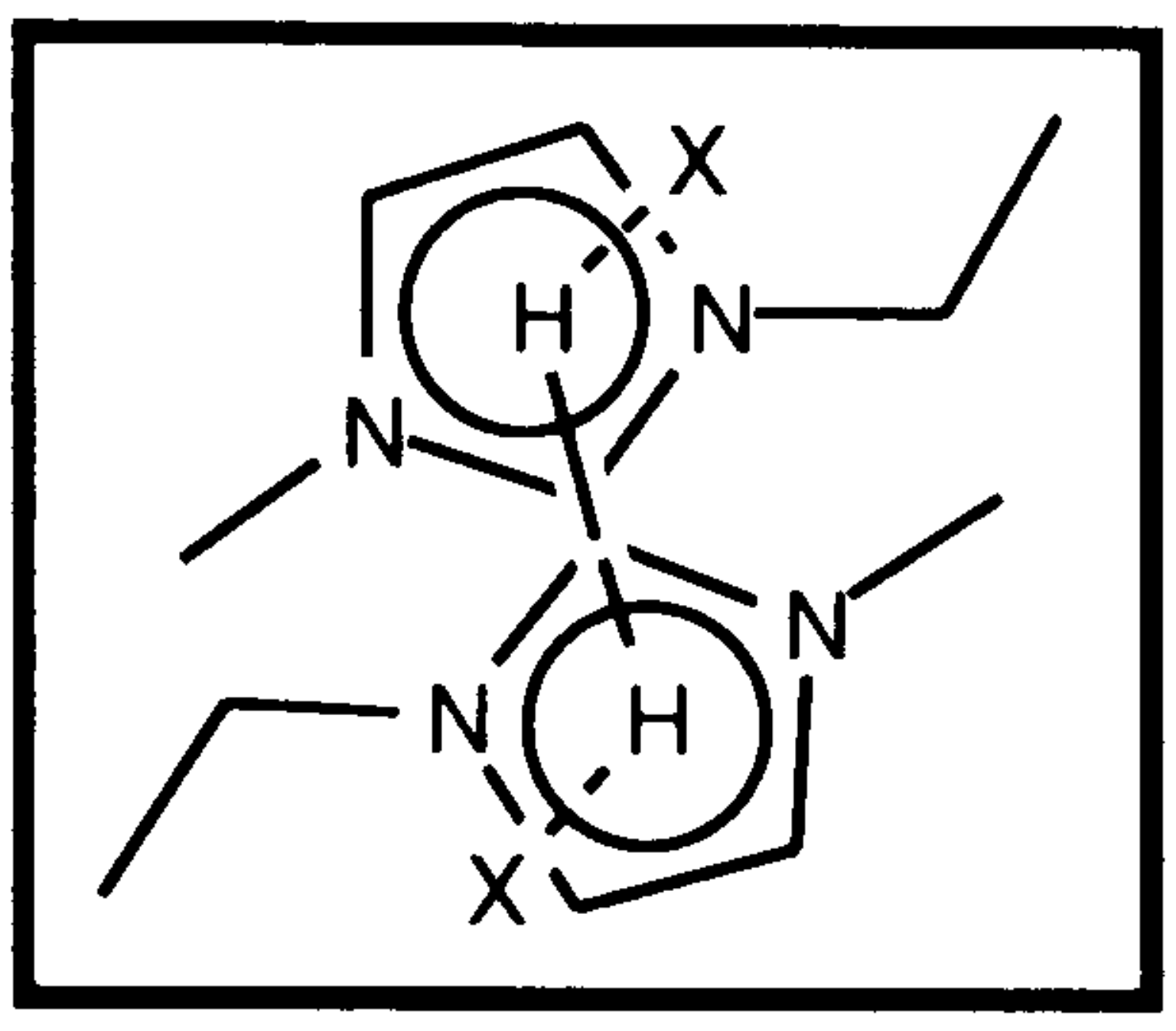
TABLE 2.9.3a Relevant Proton Chemical Shifts In d_6-acetone (ppm)

Compound	**C(2)-H**	**C(4)-H**	**C(5)-H**
1-methyl imidazole	*7.46*	*7.00*	*6.90*
[emim][Br]	10.24	7.96	7.86
[emim][Cl]	10.52	8.04	7.96
[bmim][Br]	10.14	8.00	7.97
[bmim][Cl]	10.90	8.01	7.92
[omim][Br]	10.28	7.96	7.88
[omim][Cl]	10.72	8.18	8.11
[emim][BF_4]	8.90	7.71	7.63
[emim][PF_6]	8.91	7.74	7.66
[bmim][BF_4][a]	8.93	7.73	7.68
[bmim][PF_6][b]	8.92	7.71	7.66
[omim][BF_4]	8.96	7.73	7.68
[omim][PF_6]	8.94	7.73	7.66

[a] See FIGURE 2.9.3a. [b] See FIGURE 2.9.3b.

There were notable shifts in the position of the C(2)-H in the spectra caused by a change of anion and subsequent change in the acidic nature of the imidazolium hydrogens. With a concentration increase, the C(2)-H of the imidazolium ring entering the shielding core of the neighbouring imidazolium moves to high field, while the C(4)-H and C(5)-H, pointing outside, remain only influenced by hydrogen bonding strengthening. (See FIGURE 2.9.3c) In 1-methyl imidazole we have a simple structure whereas in the more complicated [emim], [bmim] and [omim] salts the structures consist of layers of anions and cations which are interconnected by an extended network of hydrogen bonds. Each cation is hydrogen bonded to three anions and each anion is hydrogen bonded to three cations. The C(4)-H···X$^-$ and C(5)-H···X$^-$ contacts are considerably shorter than the C(2)-H···X$^-$, indicating weaker hydrogen bonds, hence the difference in respective chemical shifts.[6] Although this refers to the solid state structure of these salts, it was assumed to be the same structure in the liquid phase.

TABLE 2.9.3a shows the relevant shifts in these respective protons and provides good evidence that there has been production of the desired ionic liquids.



(FIGURE 2.9.3c): Imidazole Ring Stacking.[3]

The variations in the chloride and bromide C(2)-H shifts show that the chloride ionic liquids are slightly more acidic than their corresponding bromides. Likewise, the BF_4 salts appear to be ever so slightly more acidic than the corresponding PF_6 salts, however, both remain significantly less acidic than their halide counterparts.

2.9.4. TGA Analysis (See FIGURE 2.9.4a)

The TGA of [bmim][BF_4] shows no evidence to suggest even trace amounts of water are present in the ionic liquid. It further shows the stability of

$[bmim][BF_4]$ up to 400 °C, where upon it loses weight completely by 500 °C - showing complete decomposition of the ionic liquid. From this data it can be concluded that $[bmim][BF_4]$ behaves as ionic liquid from room temperature up to approximately 400 °C.

This determined thermal stability value of $[bmim][BF_4]$ compares well with those reported for both $[emim][TfO^-]$ and $[emim][TF_2N^-]$. These liquids are stable up to 400 °C, and decompose rapidly between 440 and 480 °C. [emim][TA] is thermally less stable, starting to decompose at temperatures of approximately 150 °C, the process lasting up to 250 °C.[3]

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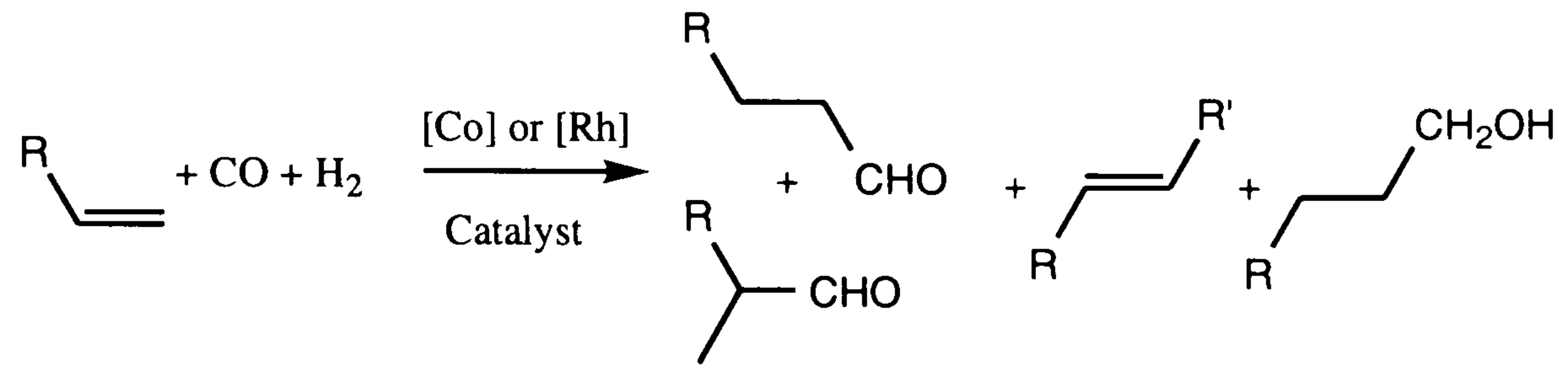
Chapter 3

Hydroformylation Of Olefins In Ionic Liquid Solvent

3.1. Introduction



Olefins can be hydroformylated by treatment with carbon monoxide and hydrogen over a catalyst to produce their corresponding aldehydes. The order of reactivity is straight-chain terminal olefins > straight-chain internal olefins > branched-chain olefins. It is also possible under certain conditions for internal isomerisation to occur during the reaction, the result of which can produce internal alkenes and alcohols.

Hydroformylation of higher olefins is an important industrial process, as the resulting long chain aldehydes can be converted into plasticizer alcohols (C_6-C_{11}) and biodegradable detergent alcohols (C_{12}-C_{20}), of which the latter are of high commercial value.[1] Long chain aldehydes also find applications in perfumery and fragrance industries. The use of cobalt catalysts for the hydroformylation of higher olefins is a high pressure and high temperature process. The separation and recycling of the catalyst are costly. Rhodium catalysts cannot readily be applied to the hydroformylation of olefins of carbon lengths greater than C_6 or C_7, due to the difficulty in catalyst / product separation in a conventional homogeneous catalytic process, or the low solubility of the olefins in water under reaction conditions comparable to those used in the Rhone-Poulenc / Ruhrchemie aqueous-organic biphasic process.[1]

The most common hydroformylation catalysts are cobalt carbonyls and rhodium complexes (e.g., hydridocarbonyltris(triphenylphosphine)rhodium). Cobalt catalysts are less active than the rhodium type, and catalysts of other metals are less active still.[2] Polymer-supported rhodium catalysts including those that are water soluble have been investigated for the hydroformylation of olefins.[3-6] Fluorous soluble polymer catalysts have also been used for the fluorous biphase hydroformylation of olefins. When combined with rhodium, they were found to be both highly active and selective.[7,8]

Conventional organic solvents such as toluene are generally chosen for hydroformylation. However the use of ionic liquids provides a much cleaner, attractive alternative, not only synthetically but also environmentally with the added incentive of ease of product separation. Reactions, occurring in the ionic liquid phase are straightforward in their methodology, and, when complete, the products, forming a completely separate phase can be removed by simple decantation.

Room temperature ionic liquids based on 1-butyl-3-methylimidazolium salts have been used as non-aqueous solvents for the Rh-catalysed two-phase hydroformylation of 1-pentene. Using the [Rh(acac)$(CO)_2$ / PPh_3] uncharged molecular system as catalyst pre-cursor, 1-pentene was successfully hydroformylated in [bmim][PF_6] with a reaction yield of 99 %, TOF 333, and although the catalytic rates were lower when [Rh(acac)$(CO)_2$] / tppms or [Rh(acac)$(CO)_2$] / tppts systems were used in [bmim][PF_6] or [bmim][BF_4], reasonable TOF values were still obtained.[9] (See TABLE 3.1a)

TABLE 3.1a Rh-catalysed hydroformylation of 1-pentene.[a]

Entry	Solvent	Ligand	Rh / P	Yield %	n:i [b]	TOF h^{-1} [c]
1	toluene	PPh_3	0.106	95	2	297
2	[bmim][PF_6]	PPh_3	0.106	99	3	333
3 [d]	[bmim][PF_6]	tppms	0.106	16	3.9	59
4 [e]	[emim][BF_4]	tppts	0.33	33	2.8	103

[a] [Rh(acac)$(CO)_2$] : 0.075 mmol; 1-pentene : 68 mmol; solvent : 4 ml; T = 80 °C; $p(H_2$ / CO 1/1) = 2 MPa; t = 2h; 2 ml heptane. [b] n:i = n aldehyde / i aldehyde.

[c] Turnover frequency (TOF) defined as mol (converted 1-pentene) per mol (rhodium) per hour.

[d] THF (1 ml) added. [e] $p(H_2$ / CO 1/1) = 4 MPa, 5 ml heptane, 0.2 ml H_2O, $[emim]^+$ = 1-ethyl-3-methylimidazolium.

Chauvin *et al.* noted that although a small part of the active Rh catalyst was extracted into the organic phase, after removal of the organic phase, the ionic phase could be reused, and gave similar activity.[9]

This chapter reports the experimental work carried out, specifically hydroformylation of olefins by a rhodium catalyst, involving those ionic liquids prepared in Chapter 2. The aim of the research was to carry out successful hydroformylation reactions using the ionic liquids as solvents. Investigating how the choice of ionic liquid effected the overall rate of hydroformylation and the reaction regioselectivity was the main priority. Variation in the olefin used and its subsequent effect on the overall hydroformylation was also investigated. Reaction conditions such as temperature and pressure were varied in attempts to find the optimum conditions for hydroformylation. Chauvin *et al.*[9] suggest that the triphenylphosphine (PPh_3) additive is used as the uncharged [Rh(acac)$(CO)_2$] catalyst precursor has to be immobilised in the salt by a polar ligand. Reactions were carried out in the absence of triphenylphosphine to clarify this hypothesis. The ratio of rhodium to phosphine (Rh : PPh_3) was also varied until an optimum value for hydroformylation was determined.

The experimental equipment used and the procedures chosen for successful hydroformylation of olefins are outlined together with the characterisation techniques and subsequent results obtained. This chapter explains how hydroformylation occurs and goes on to explain how and why variables such as ionic liquid chain length and different ionic liquid anions effect the rate of hydroformylation and the observed regioselectivity. Where necessary explanations are given on how to prepare and handle certain catalysts involved during the procedures outlined. The final section of this particular chapter discusses the results obtained and the relevant characterisation data.

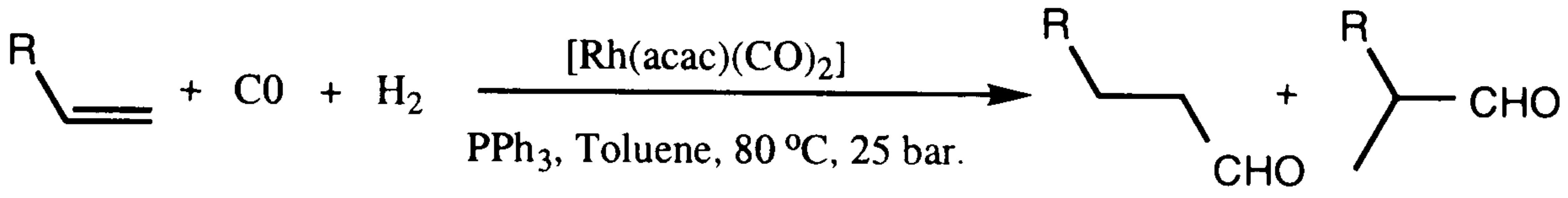
3.2. General Experimental

As hydroformylation occurs at elevated temperature and pressure, much of the experimental work was carried out in oven-dried autoclaves using PTFE stirrer bars, however on the rare occasions where simple glassware was sufficient, this too was oven-dried prior to use. All the solvents were degassed and dried before use, reagents were used as received. The liquids involved were generally handled in oven-dried syringes and the apparatus was heated by means of digital magnetic hot-plates. Many of the chosen chemicals were air-sensitive, therefore schlenk tubes and vacuum lines were used to provide air-free conditions. Characterisation of the products (and in some cases the starting materials) was conducted using a Bruker 200MHz ^1H NMR spectrometer and the data was recorded in ppm with reference to TMS internal standard in $CDCl_3$ or d_6-acetone solution. Infra-red (IR) spectroscopy was used where necessary.

Initial work was carried out using the technique described by Chauvin *et al.*[9] However, future work involving investigation into the effects of varying the ionic liquids and olefins chosen involved making changes to Chauvins original technique.

3.3. Detailed Experimental Procedures

3.3.1. Hydroformylation In Toluene



In a stainless steel autoclave equipped with a glass lining, $[Rh(acac)(CO)_2]$ (19.4 mg, 0.075 mmol) and triphenylphosphine (98.4 mg, 0.375 mmol, 5 eq) were dissolved in distilled toluene solution (4 cm^3). The rhodium species dissolved readily producing a pale yellow solution. The autoclave was purged with CO / H_2 (1:1) and 1-decene (12.9 cm^3, 68 mmol) was added. The autoclave was placed in an oil bath at 80 °C, 25 bar and stirred for 2 h. There was a noticeable change on the autoclave pressure reading dial during the 2 h reaction period. A visible decrease in the pressure reading was observed after a short time (< 30 mins) due to the absorption of CO / H_2 into the reaction system. After the 2 h had passed, the reaction was stopped and the system was allowed to cool. When sufficiently cool the pressure was slowly released from the autoclave. There were no visible signs of undissolved rhodium catalyst in the resulting deep brown, pungent homogeneous solution. A sample was submitted for ^1H NMR analysis in $CDCl_3$ containing TMS. Chloroform was chosen as the NMR solvent in preference to d_6-acetone which, due to its chemical shift of δ 2.04, would interfere with integral spectral peaks necessary for characterisation. The whole process was then repeated replacing

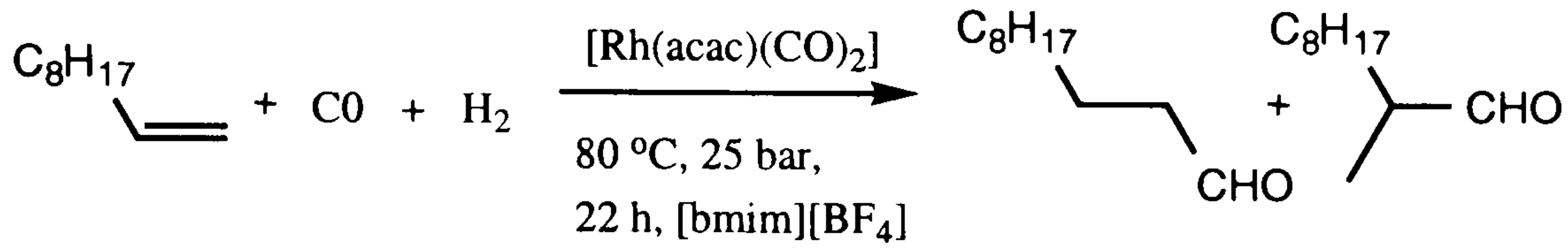
1-decene with 1-pentene. All the experimental conditions were unchanged as were the analytical techniques used.

(PPh_3 : Rh = 4.98[a]). (n : i) = 2.94[a]. Conversion: 100%[a]. Selectivity to aldehyde: 100%[a]. TOF = 421.

(PPh_3 : Rh = 4.81[b]). (n : i) = 2.78[b]. Conversion: 100%[b]. Selectivity to aldehyde: 100%[b]. TOF = 403. [a] 1-Decene. [b] 1-Pentene.

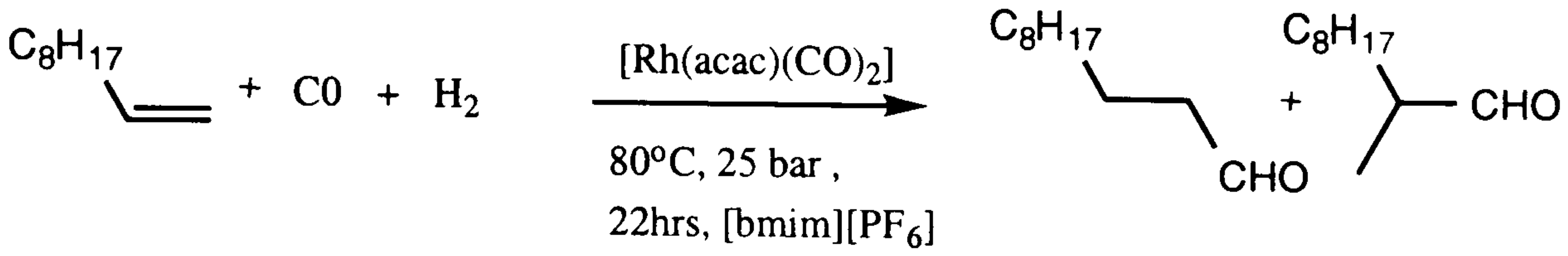
(See Results, sections 3.9.3., 3.9.4.)

3.3.2. Hydroformylation Of 1-Decene in [bmim][BF_4]



In a stainless steel autoclave equipped with a glass lining, [Rh(acac)(CO)$_2$] (1.6 mg, 6.18 μmol) was dissolved in [bmim][BF_4] ionic liquid (2 cm^3). The autoclave was purged with CO / H_2 (1:1) and 1-decene (2 cm^3, 10.6 mmol) was added. The autoclave was placed in an oil bath and stirred at 80 °C under 25 bar CO / H_2 for 22 h, after which time the reaction was stopped and the system cooled in an ice bath. When sufficiently cool the pressure was slowly released. There were no visible signs of undissolved rhodium catalyst, with the orange ionic liquid separate from the olefin on the outside of the glass liner. A sample of both layers was submitted for ^1H NMR analysis. The ionic liquid was analysed in d_6-acetone whilst the olefin layer was analysed in $CDCl_3$ containing TMS. The ^1H NMR results of the ionic liquid showed no change to that of the liquid prior to reaction. The ^1H NMR of the olefin indicated the presence of 1-decene only. There was no evidence of the expected triplet, doublet peaks at approximately δ 10-9 respectively, characteristic of the straight (n) and branched (i) chained aldehydes produced as a result of successful hydroformylation. The experiment was therefore completely repeated using identical quantities and experimental conditions. The same method was employed as outlined above. Identical ^1H NMR data was obtained from this repeat experiment also. (See FIGURE 3.9.1a.)

3.3.3. Hydroformylation Of 1-Decene in [bmim][PF_6]

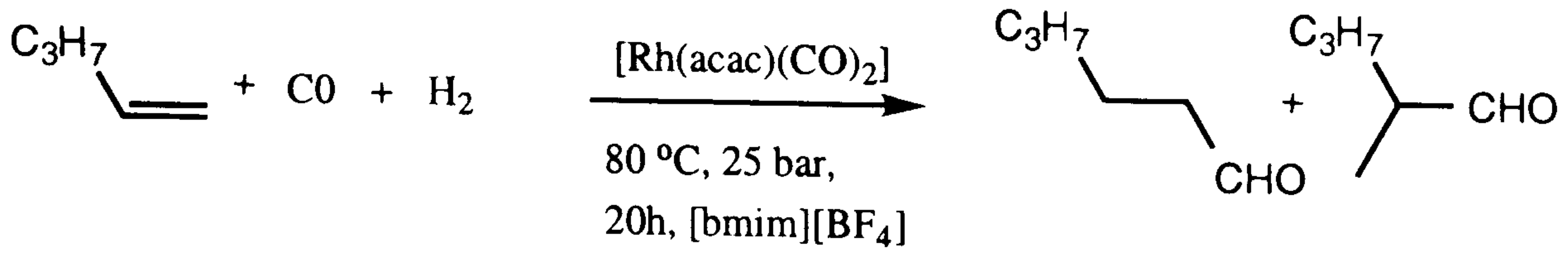


[Rh(acac)(CO)$_2$] (1.9 mg, 7.34 μmol) was dissolved in [bmim][PF_6] (2 cm^3) to which 1-decene (2 cm^3, 10.6 mmol) was added. All the other reaction conditions were identical to those used with [bmim][BF_4]. At the end of this reaction, after the system had cooled, a two-phase solution resulted. The upper layer was dark brown in colour, whereas the lower layer (containing the ionic liquid) appeared pale yellow. There were no signs of undissolved catalyst. The reaction was repeated (using [Rh(acac)(CO)$_2$] 1.6 mg, 6.18 μmol), with identical observed results, both visually and spectroscopically.

The ^1H NMR results obtained here were slightly more promising than those using the [bmim][BF_4] as solvent. Although the NMR spectra was mainly that of starting material 1-decene, there was evidence to suggest that slight conversion to desired product had occurred. A triplet and a doublet were evident between δ 9.80 and δ 9.60ppm however they were too small to accurately measure.

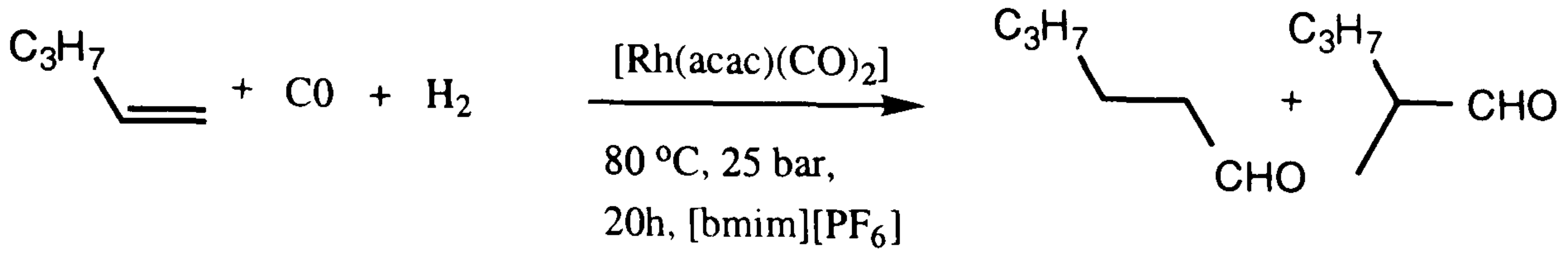
Conversion: 1%.

3.3.4. Hydroformylation Of 1-Pentene In [bmim][BF$_4$]



In a stainless steel autoclave equipped with a glass lining, [Rh(acac)(CO)$_2$] (1.8 mg, 6.95 μmol) was dissolved in [bmim][BF$_4$] ionic liquid (2 cm^3). The autoclave was purged with CO / H_2 (1:1) and 1-Pentene (2 cm^3, 18.3 mmol) was added. The autoclave was placed in an oil bath and stirred at 80 °C under 25 bar CO / H_2 for 22 h, after which time the reaction was stopped and the system cooled by placing the autoclave in a dry-ice bath. When sufficiently cool the pressure was released extremely slowly due to the high volatility of the 1-pentene. There were no visible signs of undissolved rhodium catalyst in the two-phase solution. The upper olefin layer was orange in colour whilst the lower, ionic liquid layer appeared a much darker, deep brown. A sample of both layers was submitted for ^1H NMR analysis. The ionic liquid was analysed in d_6-acetone whilst the olefin layer was analysed in $CDCl_3$ containing TMS. The complete synthesis was again repeated (using [Rh(acac)(CO)$_2$] 1.6 mg, 6.18 μmol), with almost identical results. The two liquid phases this time were very similar in appearance. There was no sign of any undissolved catalyst. A sample of both layers was submitted for ^1H NMR analysis. The ^1H NMR results of the ionic liquid showed that there was no apparent change from that of the liquid prior to reaction. The ^1H NMR of the olefin layer indicated the presence of 1-pentene only. As with the results of 1-decene hydroformylation in [bmim][BF$_4$], (See section 3.3.2.) there was no evidence to conclude that hydroformylation had occurred. An experiment was next attempted in [bmim][PF$_6$].

3.3.5. Hydroformylation Of 1-Pentene In [bmim][PF_6]



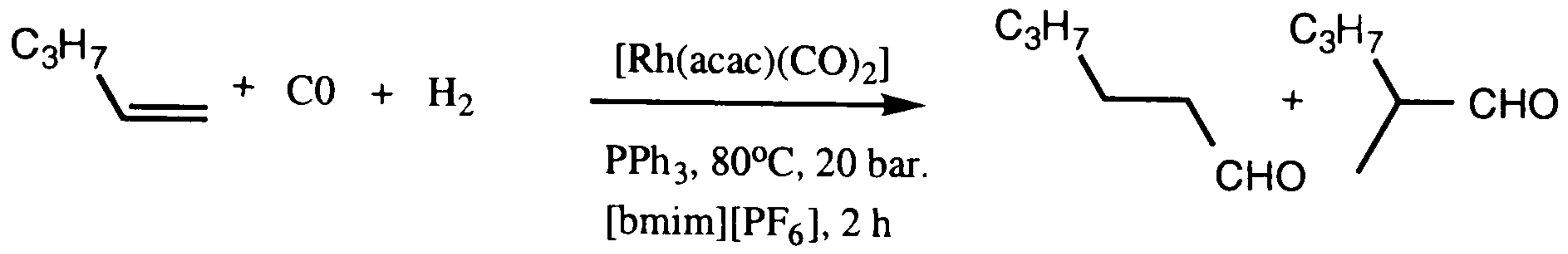
The method used was identical to that for [bmim][BF_4] The quantities used of the respective chemicals again varied slightly. [Rh(acac)(CO)$_2$] (1.6 mg, 6.18 μmol) was dissolved in [bmim][PF_6] (2 cm^3) to which 1-pentene (2 cm^3, 18.3 mmol) was added. All the other reaction conditions were identical to those in [bmim][BF_4]. At the end of this reaction, again after cooling, a two-phase solution resulted. The upper layer was brown in colour, whereas the lower layer appeared yellow. There were no signs of undissolved catalyst. Repeating the synthesis using [Rh(acac)(CO)$_2$] (1.7 mg, 6.57 μmol) gave identical results. A sample of both layers was sent for ^1H NMR analysis. The ^1H NMR spectra showed no visible change in the ionic liquids throughout the course of the reactions. As with the [bmim][PF_6] / 1-decene reactions there were only minute traces of possible desired product. The amounts monitored were so tiny that they could be deemed negligible.

Conversion: 1%.

3.4. Hydroformylation Of 1-Pentene In Ionic Liquids - PPh_3 Addition

The hydroformylation reactions outlined in this section were carried out in exactly the same way as those in section 3.3.5. The only variations were the addition of triphenylphosphine to the reaction mixture, a slight decrease in the reaction pressure from 25 bar atm CO / H_2 to 20 bar atm CO / H_2 and an altered reaction time. The ionic liquids and products were analysed in the same way using ^1H NMR spectroscopy in d_6-acetone solution and $CDCl_3$ containing TMS respectively.

3.4.1. 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6]



In a dry, clean stainless steel autoclave, a mixture of [Rh(acac)$(CO)_2$] (10 mg, 0.04 mmol) and triphenylphosphine (50 mg, 0.19 mmol, 5 eq) PPh_3) was dissolved in [bmim][PF_6] ionic liquid (2 cm^3). The autoclave was purged with CO / H_2 (1:1) and 1-pentene (3.7 cm^3, 34 mmol) was added. The autoclave was placed in an oil bath and stirred at 80 °C under 20 bar CO / H_2 for 2 h, after which time the reaction was stopped and cooled by placing the autoclave in a dry-ice bath at -78 °C. When sufficiently cool the pressure was very slowly released due to the high volatility of the 1-pentene. There were no visible signs of undissolved rhodium catalyst and the pungent, two-phase solution was collected. The orange ionic liquid formed the lower layer whilst the pale orange olefin formed the upper layer. A sample of both layers was submitted for ^1H NMR analysis.

(Rh : PPh_3 = 0.203). (n : i) = 2.88. Conversion: 83%. Selectivity to aldehyde: 67.1%. TOF = 406. (See FIGURE 3.4.1a)

This method was followed exactly for the subsequent hydroformylation reactions involving 1-pentene in [bmim][BF_4], [omim][PF_6] and [omim][BF_4]. It was also used when attempting hydroformylation of 1-decene using the various ionic liquid solvents.

During the course of each individual reaction there was a noticeable decrease in the autoclave pressure dial reading, indicating perhaps that successful hydroformylation had occurred. There was slight variation in the colours of the products obtained. The pungent smell was evident in all samples to a certain degree. The [omim][PF_6] ionic liquid reaction product was less pungent than the other ionic liquid reaction products. Ionic liquid [omim][BF_4] produced a single-phase product whereas the other ionic liquids resulted in two-phase reaction products. There was no evidence of undissolved catalyst in any of the products. ^1H NMR spectroscopy was used to analyse each product, with particular attention paid to the % conversion and the (n : i) observed selectivity.

3.4.2. 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4]

(Rh : PPh_3 = 0.204). (n : i) = 2.95. Conversion: 97%. Selectivity to aldehyde: 84.6%. TOF = 427.

3.4.3. 1-octyl-3-methylimidazolium hexafluorophosphate [omim][PF_6]

(Rh : PPh_3 = 0.207). (n : i) = 2.48. Conversion: 22%. Selectivity to aldehyde: 99.9%. TOF = 101.

3.4.4. 1-octyl-3-methylimidazolium tetrafluoroborate [omim][BF_4]

(Rh : PPh_3 = 0.203). (n : i) = 2.97. Conversion: 94%. Selectivity to aldehyde: 99.9%. TOF = 416.

3.4.5. Hydroformylation Of 1-Decene In Ionic Liquid Solvent - PPh_3 Addition

3.4.6. 1-butyl-3-methylimidazolium hexafluorophosphate $[bmim][PF_6]$

(Rh : PPh_3 = 0.207). (n : i) = 2.73. Conversion: 86%. Selectivity to aldehyde: 99.9%. TOF = 369.

3.4.7. 1-butyl-3-methylimidazolium tetrafluoroborate $[bmim][BF_4]$

(Rh : PPh_3 = 0.193). (n : i) = 3.38. Conversion: 96%. Selectivity to aldehyde: 99.9%. TOF = 433.

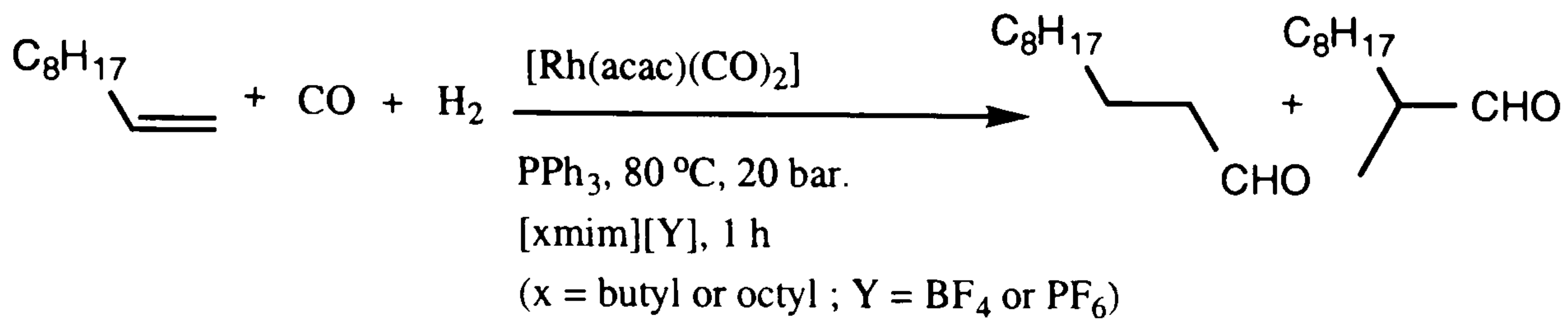
3.4.8. 1-octyl-3-methylimidazolium hexafluorophosphate $[omim][PF_6]$

(Rh : PPh_3 = 0.202). (n : i) = 3.16. Conversion: 20%. Selectivity to aldehyde: 99.9%. TOF = 97.

3.4.9. 1-octyl-3-methylimidazolium tetrafluoroborate $[omim][BF_4]$

(Rh : PPh_3 = 0.207). (n : i) = 3.16. Conversion: 96%. Selectivity to aldehyde: 99.9%. TOF = 403.

3.5. Hydroformylation Of 1-Decene In Ionic Liquid Solvents - 1 Hour Reactions



The hydroformylation was performed using the same method as for the reactions outlined in section 3.4., the only variation being that of the reaction time. The results obtained from these experiments would provide useful information regarding the preferred ionic liquid solvent for hydroformylation.

3.5.1. 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF$_4$]

(Rh : PPh$_3$ = 0.198). (n : i) = 3.20 Conversion: 91%. Selectivity to aldehyde: 97.9%. TOF = 812. (See FIGURE 3.5.1a)

3.5.2. 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF$_6$]

(Rh : PPh$_3$ = 0.199). (n : i) = 1.54 Conversion: 9%. Selectivity to aldehyde: 99.9%. TOF = <1.

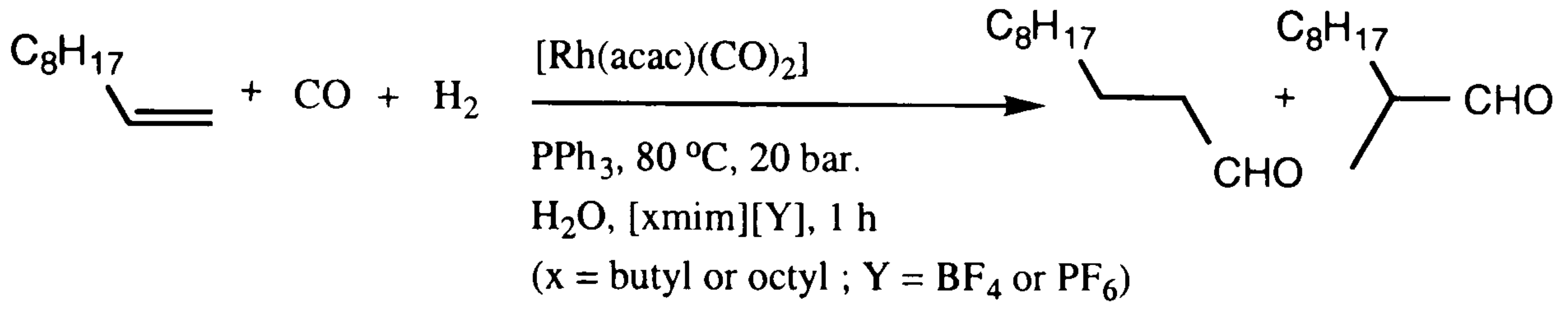
3.5.3. 1-octyl-3-methylimidazolium tetrafluoroborate [omim][BF$_4$]

(Rh : PPh$_3$ = 0.200). (n : i) = 3.21 Conversion: 99%. Selectivity to aldehyde: 99.9%. TOF = 861.

3.5.4. 1-octyl-3-methylimidazolium hexafluorophosphate $[omim][PF_6]$

(Rh : PPh_3 = 0.197). (n : i) = n/a Conversion: 0%. Selectivity to aldehyde: 0%. TOF = 0.

3.6. The Effect Of Water On The Hydroformylation Of 1-Decene In Ionic Liquids.



Experiments were carried out under identical conditions to those outlined in section 3.5. The methodology was completely replicated, the only variation being the addition of 1 cm^3 H_2O. It was decided to use 1-decene in preference to 1-pentene as the choice of olefin had no noticeable effect on the results so far observed.

The products resulting from these experiments were analysed by ^1H NMR spectroscopy and directly compared to the corresponding results obtained in 'water-free' hydroformylation (section 3.5.) Experiments were repeated until concordant results were obtained.

3.6.1. 1-butyl-3-methylimidazolium tetrafluoroborate $[bmim][BF_4]$

(Rh : PPh_3 = 0.207). (Rh : H_2O = 7.07 x 10^{-4}). (n : i) = 3.16. Conversion: 98%. Selectivity to aldehyde: 92.3%. TOF = 860. (See FIGURE 3.6.1a)

3.6.2. 1-butyl-3-methylimidazolium hexafluorophosphate $[bmim][PF_6]$

(Rh : PPh_3 = 0.207). (Rh : H_2O = 7.09 x 10^{-4}). (n : i) = n/a Conversion: 0%. Selectivity to aldehyde: 0%. TOF = 0.

3.6.3. 1-octyl-3-methylimidazolium tetrafluoroborate $[omim][BF_4]$

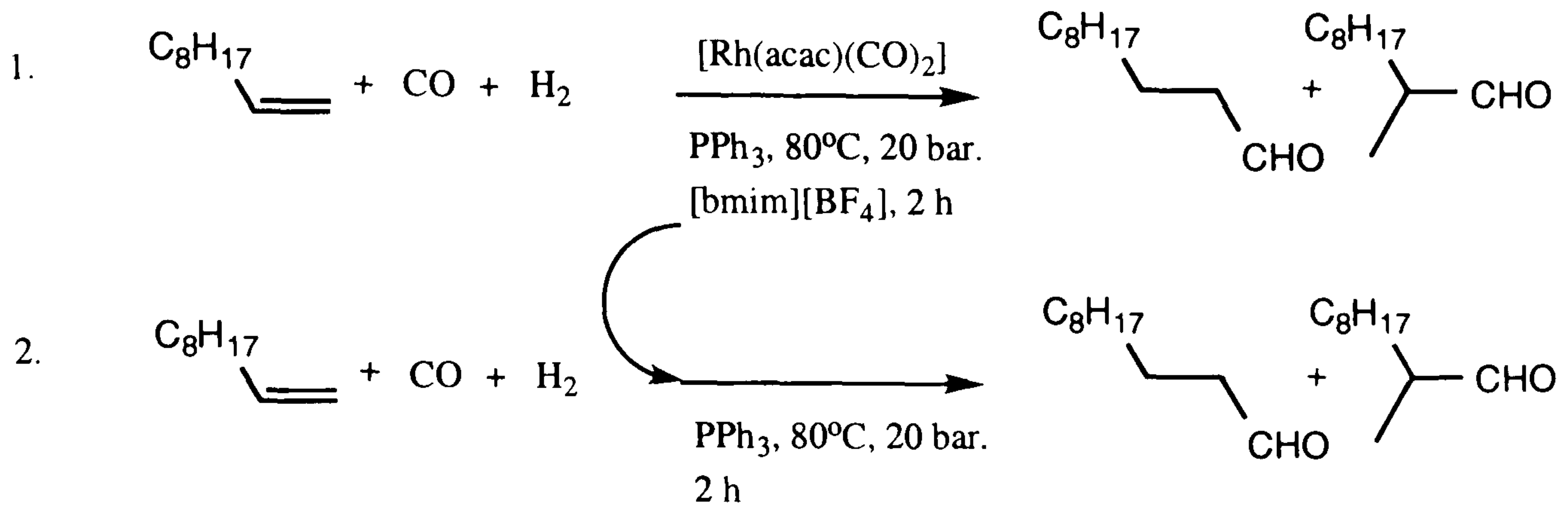
(Rh : PPh_3 = 0.202). (Rh : H_2O = 6.95 x 10^{-4}). (n : i) = 3.41. Conversion: 99.9%. Selectivity to aldehyde: 99.9%. TOF = 881.

3.6.4. 1-octyl-3-methylimidazolium hexafluorophosphate $[omim][PF_6]$

(Rh : PPh_3 = 0.206). (Rh : H_20 = 3.5 x 10^{-4}). (n : i) = 3.12 Conversion: 5%. Selectivity to aldehyde: 98.3%. TOF = 50.

3.7. Catalyst / Solvent Recycle

As ionic liquid [bmim][BF_4] seemed the 'preferred' solvent for successful hydroformylation, initial experiments were conducted using [bmim][BF_4] as solvent.



3.7.1. Stage 1

In a stainless steel autoclave equipped with a glass lining, a mixture of [Rh(acac)(CO)$_2$] (10.0 mg, 0.0386 mmol) and PPh$_3$ (50.8 mg, 0.194 mmol, 5 eq) was dissolved in [bmim][BF_4] ionic liquid (2 cm^3). The autoclave was purged with CO / H_2 (1:1) and 1-decene (6.4 cm^3, 34 mmol) was added. The autoclave was placed in an oil bath and stirred at 80 °C under 20 bar CO / H_2 for 2 h, after which time the reaction was stopped and the system cooled. When sufficiently cool the pressure was slowly released. There were no visible signs of undissolved rhodium catalyst and a pungent, two-phase solution was collected. A sample of both layers was sent for ^{1}H NMR analysis.

3.7.2. Stage 2

The remaining [bmim][BF_4] from the first experiment was carefully transferred under nitrogen to a clean stainless steel autoclave which was subsequently purged with CO / H_2 (1:1) and 1-decene (6.4 cm^3, 34 mmol) added. The autoclave was placed in an oil bath and stirred at 80 °C under 20 bar CO / H_2 for 2 h. After cooling the system, the pressure was slowly released. A sample of each liquid phase was analysed by ^1H NMR analysis.

3.8. Catalytic Species Investigation

In a stainless steel autoclave, in a glove-box, $[Rh(acac)(CO)_2]$ (0.50g, 1.93 mmol) and triphenylphosphine (2.5g, 9.53 mmol) were dissolved in $[bmim][BF_4]$ ionic liquid (35 cm^3). The autoclave was sealed and initially purged with CO / H_2 (1:1), then subsequently pressurised to 20 bar CO / H_2. The autoclave was then transferred to an oil bath where it was stirred vigorously at 80 °C for 2 h. After this time the system was cooled. Whilst remaining in the glove-box the pressure was slowly released from the autoclave and the resulting bright yellow, glue-like product was transferred to a two-necked round bottomed flask. This species was dissolved in distilled toluene, producing a bright yellow solution. The toluene layer was separated from the ionic liquid layer and the excess solvent removed under vacuum. A small amount of n-hexane was added and the subsequent, careful removal of this, under a slight vacuum, lead to the formation of a yellow crystalline material. This crystalline material was submitted for ^1H NMR analysis and IR analysis in nujol.

^1H NMR ionic liquid : (d_6-acetone) δ 8.89 (s, 1H), 7.68 (t, 1H), 7.62 (t, 1H), 4.29 (t, 2H), 3.97 (s, 3H), 1.86 (m, 2H), 1.32 (m, 2H), 0.90 (t, 3H).

(See FIGURE 3.8a.)

3.9. RESULTS and DISCUSSION

Due to the volatile nature of the olefins used, 1-pentene in particular, it was essential to thoroughly cool the system after reaction using a dry-ice bath before releasing any pressure. Problems still arose however, and during the course of the reactions involving 1-pentene in particular, significant amounts of the respective olefins 'spilled-over' from inside the glass lining, subsequently occupying the space between the lining and the autoclave itself. Future experiments were therefore conducted without a glass lining. Extreme care was taken to ensure that the autoclave was clean and dry before each individual experiment to rule out the risk of contamination. The experiments were attempted in both [bmim][PF_6] and [bmim][BF_4] ionic liquids. Preliminary tests indicated that the rhodium catalyst appeared more soluble in the hexafluorophosphate ionic liquid, therefore it was a realistic possibility that this could make the ionic liquid a more suitable choice of solvent.

The results obtained from the hydroformylation of olefins, initially in toluene then subsequently in ionic liquid solvent are outlined in this section. All the reaction products were analysed by ^1H NMR spectroscopy and the data obtained is recorded here. Relevant NMR spectra are presented at the end of this thesis. The numerical data obtained from the respective NMR spectra is outlined here.

3.9.1. Hydroformylation Of Olefins In [bmim][X], (X = [BF_4], [PF_6])

TABLE 3.9.1a. Hydroformylation Of Olefins 1-Decene and 1-pentene In [bmim][X], (X = [BF_4], [PF_6]) - Without PPh_3.

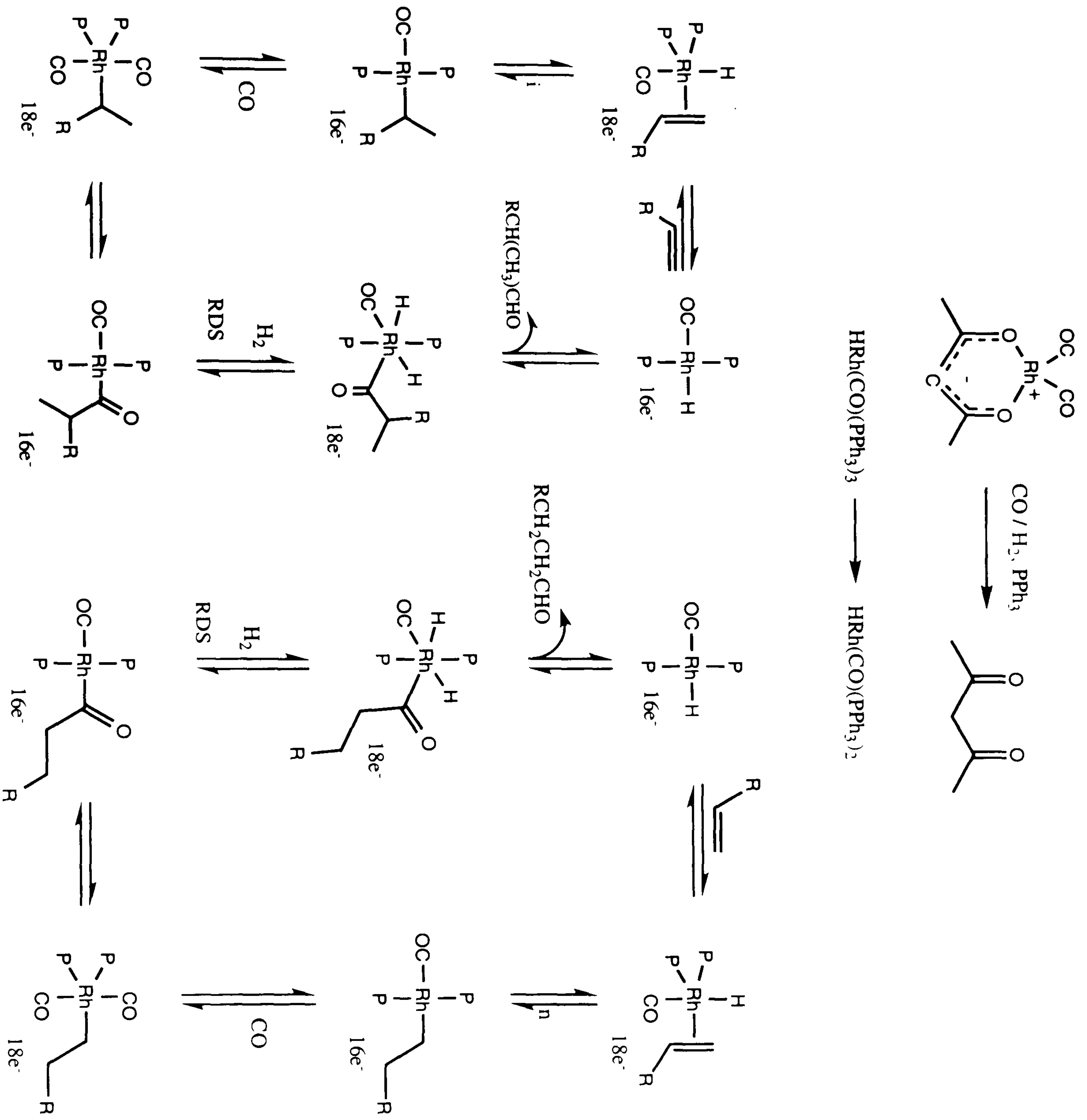
Solvent	% Conversion	% Selectivity[c]	(n : i)	TOF
[bmim][BF_4][a]	0.0	0.0	-	-
[bmim][PF_6][a]	1.0	-	-	-
[bmim][BF_4][b]	0.0	0.0	-	-
[bmim][PF_6][b]	1.0	-	-	-

[a] 1-Decene. [b] 1-pentene. [c] To aldehyde. (See FIGURE 3.9.1a)

It can be clearly seen from these results that rhodium catalysed hydroformylation of olefins, 1-decene and 1-pentene, in the ionic liquid solvents used is unsuccessful. A conversion of 1% (observed in [bmim][PF_6]) is not an acceptable value and therefore the method used cannot be deemed an appropriate way of producing the relevant aldehyde products. It was not possible to calculate the selectivity to aldehyde in any of the [bmim][PF_6] reactions as the conversion was simply too low. Successful, high-conversion hydroformylation in the absence of triphenylphosphine, appears to be an unrealistic objective in these particular ionic liquid solvents.

A reason for the lack of hydroformylation observed is possibly due to the general mechanism involved in hydroformylation itself. Although [Rh(acac)$(CO)_2$] is itself an active species without PPh_3, in these experiments it was hoped that the imidazolium cation (of the ionic liquid) would form a Rh - carbene species, therefore producing an active catalyst. This has not occurred, and it can therefore be said that these results show that the ionic liquids themselves are not capable of replacing the phosphine ligands, under these conditions, to form an active catalytic species via a Rh - carbene. The result is no observed reaction. PPh_3 is required if hydroformylation in ionic liquid solvent is to occur. (See section 3.9.2)

3.9.2. [Rh(acac)(CO)$_2$] / PPh$_3$ Catalysed Hydroformylation Of Olefin (Mechanism)



3.9.3. Hydroformylation Of 1-Pentene In [xmim][Y], (x = butyl, octyl : Y = [BF$_4$], [PF$_6$]) In The Presence Of PPh$_3$.

During the course of this research these particular experiments were repeated numerous times. Table 3.9.3a. displays the reaction results for two specific experiments and an additional entry shows the overall mean results from all of these particular experiments. The results of using toluene as solvent are also listed. (See FIGURE 3.4.1a.)

TABLE 3.9.3a. Hydroformylation Of 1-Pentene In [xmim][Y], (x = butyl, octyl : Y = [BF$_4$], [PF$_6$]) In The Presence Of PPh$_3$.

Solvent	Rh / P	% Conversion	% Selectivity[a]	(n : i)	TOF
Toluene	0.208	100	100	2.78	403
[bmim][BF$_4$]	0.211	98	82.0	2.94	430
[bmim][BF$_4$]	0.202	98	88.1	2.78	430
[bmim][BF$_4$]	*0.204*	*97*	*84.6*	*2.95*	*427*
[bmim][PF$_6$]	0.191	87	70.3	2.86	407
[bmim][PF$_6$]	0.209	84	65.4	2.89	410
[bmim][PF$_6$]	*0.203*	*83*	*67.1*	*2.88*	*406*
[omim][BF$_4$]	0.211	100	99.9	3.03	421
[omim][BF$_4$]	0.196	91	99.9	3.03	417
[omim][BF$_4$]	*0.203*	*94*	*99.9*	*2.97*	*416*
[omim][PF$_6$]	0.203	32	99.9	2.63	152
[omim][PF$_6$]	0.207	23	99.9	2.44	99
[omim][PF$_6$]	*0.207*	*22*	*99.9*	*2.48*	*101*

[a] To aldehyde. *Italic* entries indicate mean values obtained from ALL experiments using these conditions.

3.9.4. Rh Catalysed Hydroformylation Of 1-Decene In [xmim][Y], (x = butyl, octyl : Y = [BF_4], [PF_6]) In The Presence Of PPh_3.

During the course of this research these particular experiments were repeated numerous times. Table 3.9.4a. displays the reaction results for two specific experiments and an additional entry shows the overall mean results from all of these particular experiments. The results of using toluene as solvent are also listed.

TABLE 3.9.4a. Rh Catalysed Hydroformylation Of 1-Decene In [xmim][Y], (x = butyl, octyl : Y = [BF_4], [PF_6]) In The Presence Of PPh_3.

Solvent	**Rh / P**	**% Conversion**	**% Selectivity**[a]	**(n : i)**	**TOF**
Toluene	0.201	100	100	2.94	421
[bmim][BF_4]	0.194	100	99.9	3.13	439
[bmim][BF_4]	0.193	96	99.9	3.57	440
[bmim][BF_4]	*0.193*	*96*	*99.9*	*3.38*	*433*
[bmim][PF_6]	0.211	87	99.9	2.86	366
[bmim][PF_6]	0.202	85	99.9	2.33	370
[bmim][PF_6]	*0.207*	*86*	*99.9*	*2.73*	*369*
[omim][BF_4]	0.205	93	99.9	3.23	394
[omim][BF_4]	0.206	99	99.9	3.13	416
[omim][BF_4]	*0.207*	*96*	*99.9*	*3.16*	*403*
[omim][PF_6]	0.201	27	99.9	3.23	116
[omim][PF_6]	0.203	16	99.9	3.13	70
[omim][PF_6]	*0.202*	*20*	*99.9*	*3.16*	*97*

[a] To aldehyde. *Italic* entries indicate mean values obtained from ALL experiments using these conditions.

3.9.5. Rh Catalysed Hydroformylation Of 1-Decene In Ionic Liquid Solvents - In The Presence Of PPh_3 - 1 Hour Reactions.

As some of the reactions outlined in section 3.4. had gone to completion in the 2 h reaction time, making comparisons based on TOF difficult, it was decided to cut the reaction time down from 2 h to 1 h. This would help verify which ionic liquid would afford higher TOF's. The TOF value of each ionic liquid could then be calculated. 1-decene was used in preference to 1-pentene. Results so far indicated that the choice of olefin had little effect hydroformylation. 1-decene was chosen as it was much less volatile than its C_5, lower boiling-point equivalent, making it significantly easier to handle.

Table 3.9.5a. displays the reaction results for two specific experiments and an additional entry shows the overall mean results from all of these particular experiments. The results of using toluene as solvent are also listed. (See FIGURE 3.5.1a)

TABLE 3.9.5a. Rh Catalysed Hydroformylation Of 1-Decene In Ionic Liquid Solvents - In The Presence Of PPh$_3$ - 1 Hour Reactions.

Solvent	Rh / P	% Conversion	% Selectivity[a]	(n : i)	TOF
Toluene	0.200	90	100	3.03	804
[bmim][BF$_4$]	0.192	90	95.2	3.33	827
[bmim][BF$_4$]	0.210	94	94.0	3.03	806
[bmim][BF$_4$]	*0.198*	*91*	*93.5*	*3.20*	*812*
[bmim][PF$_6$]	0.207	1	-	-	-
[bmim][PF$_6$]	0.191	1	-	-	-
[bmim][PF$_6$]	*0.199*	*1*	-	-	-
[omim][BF$_4$]	0.195	95	98.4	3.45	864
[omim][BF$_4$]	0.199	95	99.9	2.94	848
[omim][BF$_4$]	*0.200*	*96*	*99.0*	*3.21*	*861*
[omim][PF$_6$]	0.197	0	0	0	0
[omim][PF$_6$]	0.203	0	0	0	0
[omim][PF$_6$]	*0.197*	*0*	*0*	*0*	*0*

[a] To aldehyde. *Italic* entries indicate mean values obtained from ALL experiments using these conditions.

3.9.6. The Effect Of Water On The Hydroformylation Of 1-Decene In Ionic Liquid.

Data collected thus far indicated that hydroformylation occurred more readily in the presence of PPh$_3$ in tetrafluoroborate ionic liquids. In these tetrafluoroborate ionic liquids, results suggested that the preferred imidazolium based cation was the 1-butyl-3-methylimidazolium ([bmim]) cation.

A new, modified hydroformylation process was now used to see if the addition of water to the system would have an altered effect on the pattern of results obtained. The addition of water could cause several alterations, possibly enhancing the PF_6 reactions whilst inhibiting the BF_4 reactions, due to the significant differences in the miscibilities of these ionic liquids with water. PF_6 is immiscible in water whereas BF_4 is slightly miscible. The presence of water may also have a direct effect on the hydrogen bonding that occurs within the ionic liquid. A result of this could cause an alteration in the nature of the ionic liquid itself and hence the way in which it acts as a solvent for hydroformylation. The overall effect of water addition could therefore directly change the final hydroformylation results. It was also possible however that the addition of water may have no noticeable effect at all on observed hydroformylation.

Table 3.9.6a. displays the reaction results for two specific experiments and an additional entry shows the overall mean results from all of these particular experiments. (See FIGURE 3.6.1a)

TABLE 3.9.6a. Rh Catalysed Hydroformylation Of 1-Decene In Ionic Liquid Solvents - In The Presence Of PPh_3 and H_20. 1 Hour Reactions.

Solvent	**Rh / P**	**% Conversion**	**% Selectivity**[a]	**(n:i)**	**TOF**
[bmim][BF$_4$]	0.205	99	94.0	3.13	870
[bmim][BF$_4$]	0.211	98	92.1	3.33	838
[bmim][BF$_4$]	*0.207*	*98*	*92.3*	*3.16*	*860*
[bmim][PF$_6$]	0.205	1	99.1	2.83	1
[bmim][PF$_6$]	0.211	1	98.5	2.87	1
[bmim][PF$_6$]	*0.207*	*1*	*98.7*	*2.85*	*1*
[omim][BF$_4$]	0.211	99	99	3.57	855
[omim][BF$_4$]	0.204	99	99	3.33	870
[omim][BF$_4$]	*0.202*	*99*	*99*	*3.41*	*881*
[omim][PF$_6$]	0.201	6	98.0	3.13	52
[omim][PF$_6$]	0.213	6	98.1	3.13	48
[omim][PF$_6$]	*0.206*	*5*	*98.3*	*3.12*	*50*

a To aldehyde. *Italic* entries indicate mean values obtained from ALL experiments using these conditions.

Several conclusions can de drawn from the results outlined in sections 3.9.1. to 3.9.6. regarding the hydroformylation of olefins in ionic solvents.

It is clear to see that the presence of triphenylphosphine is essential, under these conditions, if successful hydroformylation is to occur. The phosphine ligands, in the presence of syn-gas (CO / H_2) attach to the Rh catalyst forming the active pre-catalytic species $HRh(CO)(PPh_3)_3$. This species then alternates between 16 and 18 electron pairs, during which hydroformylation occurs. (See SECTION 3.9.2.) This particular pathway is of course not possible in the absence of triphenylphosphine.

It was hoped that perhaps the ionic liquid, through interaction of the imidazolium ring with the rhodium, would act as an alternative ligand to PPh_3. The hypothesis that a carbene species, formed by the possible interaction of the ionic liquid and rhodium catalyst, would mean the ionic liquid effectively replaces the need for PPh_3 as it would be acting in the same way as PPh_3 does in conventional hydroformylation catalysis.[10,11,12] However, the results of section 3.7., varying the methodology and introducing such techniques as pre-heating the autoclave prior to pressurising, had no observed effect on hydroformylation. The results obtained from these experiments were identical to those obtained from the reactions performed in the absence of PPh_3 - they showed no signs of successful hydroformylation. However, when PPh_3 was present, hydroformylation occurred readily as previously described.

It can be seen also from these results that hydroformylation occurs with higher conversion to aldehyde in the tetrafluoroborate $[BF_4^-]$ ionic liquids. The average % conversion for all the reactions in $[BF_4^-]$ ionic liquid solvent is 95.9%, compared to an average 27.3% conversion value of % for the $[PF_6^-]$ liquids. Of course, the significantly lower values of the $[omim][PF_6]$ ionic liquids have a detrimental effect on this mean value.

It is also evident that the addition of water to the system has very little effect on the observed hydroformylation. Although the $[BF_4^-]$ ionic liquids are partially miscible with water, suggesting perhaps that the addition of water to such solvents could effect the way in which they operate in the system, there is no observed detrimental effect on the system at all when water is introduced. In fact, there is a very slight increase in the % conversion in both the $[bmim][BF_4]$ and $[omim][BF_4]$ cases. There is also evidence of hydroformylation in the $[omim][PF_6]$ solvent. Where originally there were no signs of conversion, with the addition of water, 5% conversion, 98% selectivity to aldehyde is observed.

There appears to be little difference in the hydroformylation results, regardless of which olefin is used. Both 1-decene and 1-pentene are readily hydroformylated, with good selectivity, to their corresponding aldehydes. It is noticeable however that 1-pentene is more susceptible to isomerisation than 1-decene, especially in [bmim][PF_6]. The reason for this could be due to the fact that the boiling point of 1-pentene is significantly lower than that of its C_{10} equivalent, and under high temperature, high pressure conditions, some of the reaction could take place in the gas phase, where the catalyst is without PR_3, leading to an increase in % isomerisation.

It is noticeable that when using [bmim][PF_6] ionic liquid, a two hour reaction time is required for hydroformylation to occur. In reaction times of less than two hours, conversion values of only 1-2% are observed. Significant reductions in hydroformylation in [omim][PF_6] are also observed for reduced-time reactions. No reaction is observed after one hour, whereas 20% conversion can be seen in two hour reactions.

In all cases, a straight : branched ratio of approximately 3 : 1 is observed. The ratio of (n : i) is slightly higher in BF_4^- ionic liquids than in PF_6^- ionic liquids.

3.9.7. Catalyst / Solvent Recycle

The hydroformylation reactions performed in ionic liquid as opposed to the conventional solvents such as toluene, result in two phase reaction products. This is one of the main advantages of using ionic liquids as solvents for catalysis. The two layers are easily separated and individually analysed, and the ionic layer that contains the rhodium catalyst could be recycled for new reactions.[9] Experiments were carried out using the ionic liquid layer at the end of the reaction as the starting material for repeat experiments. It would be interesting to see how the % conversion values were effected in these reactions where there was no addition of catalyst other than that already present in the ionic liquid solution.

3.9.8. Variations In Experimental Method : Effects On Hydroformylation

Work done so far has concentrated on the hydroformylation of two olefins, 1-decene and 1-pentene to their corresponding aldehydes, both with and without the addition of triphenylphosphine in ionic liquid solvent. The general method used is outlined in section 3.4. It can effectively be broken down into four systematic steps:-

Step 1. Add reactants to autoclave. (a: Without PPh_3 : b: With PPh_3)
Step 2. Purge with CO / H_2.
Step 3. Heat to 80 °C.
Step 4. Pressurise the autoclave to 20 bar atm CO / H_2.

As the system is purged with CO / H_2 prior to heating and final pressurisation it is feasibly possible that hydroformylation could occur immediately. Another potential outcome could be the formation and involvement of a Rh - carbene species in the hydroformylation process. When heated, $[Rh(acac)(CO)_2]$ may react with $[bmim][BF_4]$, whose C(2)-H proton is acidic and can be easily deprotonated by bases such as acac to form *N*-heterocyclic carbene complexes of rhodium in the presence of H_2 / CO.

Previous studies have shown that such reactions easily proceed in the presence of co-ordinating halide ions.[10,11,12]

Potentially, as the ionic liquid / catalyst mixture becomes active on initial contact with the purged CO / H_2, the imidazolium ring may form a carbene species with the catalyst. The system outlined above was therefore modified to verify this hypothesis.

3.9.8a. Modified System Outline (1)

Step 1. Add reactants to autoclave. (a: Without PPh_3 : b: With PPh_3)
Step 2. Heat system to 80 °C under inert atmosphere
Step 3. Pressurise the autoclave to 20 bar CO / H_2.

3.9.8b. Modified System Outline (2)

Step 1. Add reactants to autoclave. (a: Without PPh_3 : b: With PPh_3)
Step 2. Pressurise the autoclave to 20 bar CO / H_2.
Step 3. Heat system to 80 °C.

A sample of each reaction products from section 3.7. was analysed by ^1H NMR spectroscopy.

The method outlined in section 3.7. involved re-using of the ionic liquid layer of a particular experiment and attempting further hydroformylation without further addition of catalyst. None of the experiments attempted using this method were successful and there was no evidence to suggest that second, and subsequent hydroformylation had occurred. The ionic liquid layer did not allow re-use, possibly due to leaching of the catalytic species from the ionic liquid into the olefin layer. A sample of the ionic liquid layer and the product layer, used for successful hydroformylation were analysed for the presence of rhodium to see if indeed leaching had occurred. The results obtained showed no detectable traces of rhodium in the olefin layer indicating that leaching had not occurred, however, 0.08 % rhodium was detected in the ionic liquid layer. This very low percentage of rhodium in the ionic liquid layer explains why re-use of the ionic liquid for hydroformylation proved unsuccessful.

3.9.8.1. Variation In Experimental Method

Results of varying the methodology of hydroformylation as outlined in section 3.9.8., introducing such techniques as pre-heating the autoclave prior to pressuring had no observed effect on the observed hydroformylation. Identical results were observed to those shown in sections 3.4. and 3.4.5. Reactions performed in the absence of triphenylphosphine showed no signs of successful hydroformylation. However when triphenylphosphine was present, hydroformylation occurred readily as previously described. These results are technically the same as those described in section 3.9.1.

3.9.8.2. Catalytic Species Investigation

The yellow crystalline material produced using the method outlined in section 3.8. was analysed using IR spectroscopy. The mulling agent used was nujol. The ionic liquid layer was analysed using ^{1}H NMR spectroscopy (d_6-acetone).

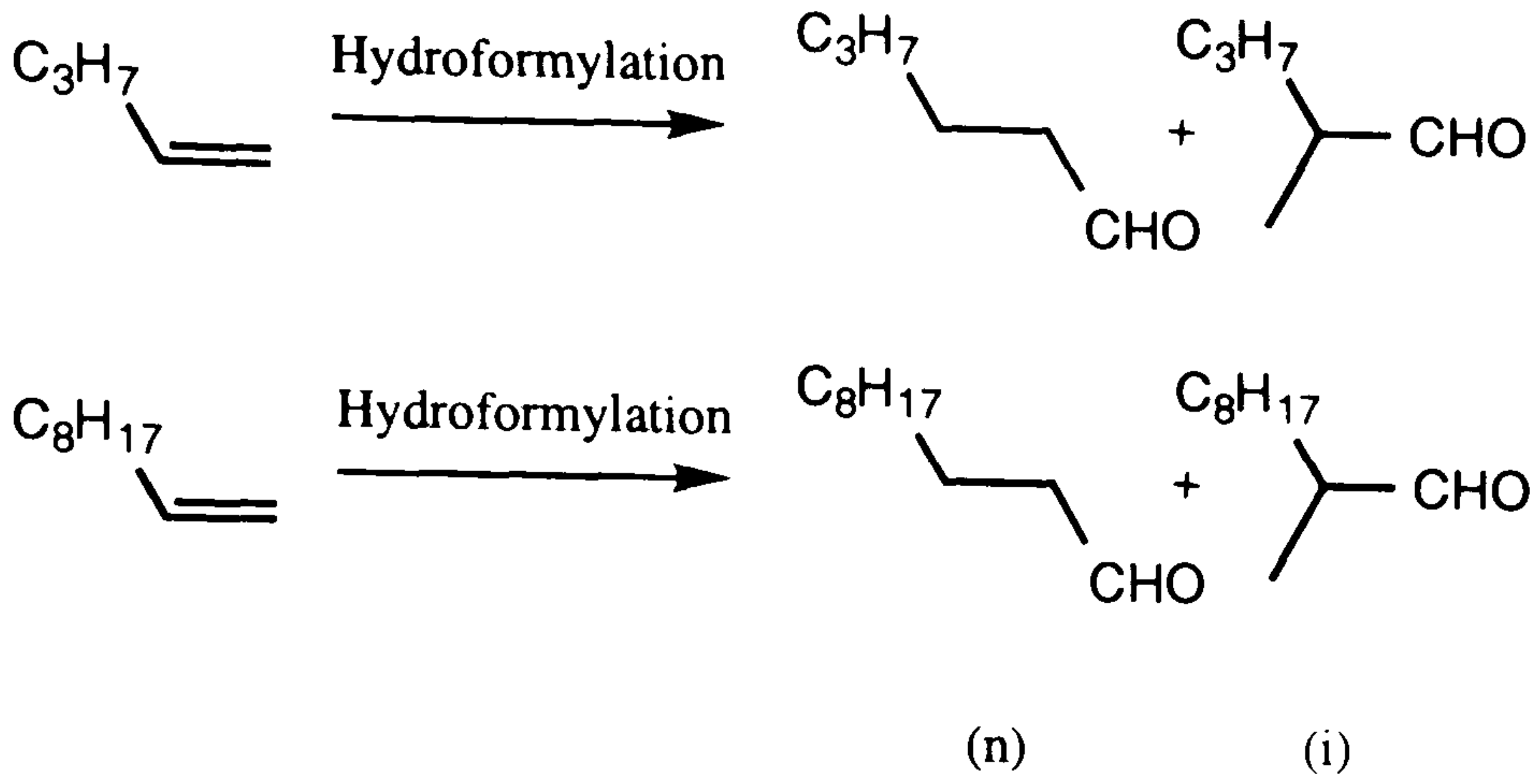
The NMR spectra obtained for the ionic liquid layer was basically that of [bmim][BF_4]. However, there were additional peaks indicating the presence of toluene in the ionic liquid layer, hence showing that separation of the two liquid layers had not been performed successfully.

The IR spectra of the rhodium species showed no evidence of C=C stretching. If, as hoped, a carbene species was formed by the interaction of the ionic liquid imidazolium ring and the rhodium catalyst, one would expect to see the resulting, characteristic C=C stretching frequency at approximately $1400cm^{-1}$. Unfortunately the IR analysis of the yellow crystalline product revealed very few characteristic stretches, for example, there was no evidence of a the CO stretch which would be expected in a catalytic species of the kind expected. The only stretches that were strong enough to be accurately characterised were due to the nujol mulling agent. (See FIGURE 3.8a.) It could be concluded from this data that a Rh-carbene species had not been formed.

3.9.9. Result Accuracy - ^1H NMR Clarification

The main analytical technique used in the hydroformylation work was ^1H NMR spectroscopy. Data analysis involved the calculation of the % conversion, % selectivity to aldehyde and the regioselectivity of the system. It was essential therefore to verify the accuracy of the analysis.

The major products of 1-pentene and 1-decene hydroformylation are shown overleaf :-



Therefore taking a single sample containing a known amount, and hence a known exact ratio of both the (n) and (i) products and analysing it by ^1H NMR spectroscopy in exactly the same manner as the individual reaction products were analysed, enables the % error in the NMR integration values of the products to be calculated. This technique was therefore carried out using authentic samples of the products shown above. The accuracy of the NMR data collected, and the subsequent results obtained using this NMR data, was then calculated. (See TABLE 3.9.9a)

TABLE 3.9.9a. ^1H NMR Clarification Results

Authentic Sample Actual Ratio (n : i)	**^1H NMR Observed Ratio (n : i)**	**% Error**
1.00	0.97	2.80
1.01	0.95	5.36
0.99	0.95	4.23
1.84	1.61	12.3
1.99	2.18	8.37
1.99	2.08	4.51
2.95	2.86	3.15
3.01	2.78	7.68
2.97	2.70	8.96

The ratios chosen of the authentic samples was between the range of (1:1) - (3:1), (n : i) as this was the observed ratio of the majority of the products obtained. It can be seen from these results that an error range of 3 - 12 % is possible.

^{1}H NMR Data : Re-Use Of Ionic Liquid Layer

3.9.9b. [bmim][BF4] Ionic Liquid Re-Use Reaction

^{1}H NMR ionic liquid : (d_6-acetone) δ 8.94 (s, 1H), 7.69 (t, 1H), 7.63 (t, 1H), 4.27 (t, 2H), 3.96 (s, 3H), 1.83 (m, 2H), 1.33 (m, 2H), 0.87 (t, 3H).

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.81 (m, 1H), 4.95 (m, 2H), 2.04 (dt, $^3J_{HH}$ = 7.14Hz, 2H), 1.28 (m, 12H), 0.88 (t, $^3J_{HH}$ = 6.6Hz, 3H).

^{1}H NMR Data : Catalytic Species Investigation

3.9.9c. [bmim][BF_4] / Rh Catalyst Mixture

^{1}H NMR ionic liquid : (d_6-acetone) δ 8.89 (s, 1H), 7.68 (t, 1H), 7.62 (t, 1H), 4.29 (t, 2H), 3.97 (s, 3H), 1.86 (m, 2H), 1.32 (m, 2H), 0.90 (t, 3H).

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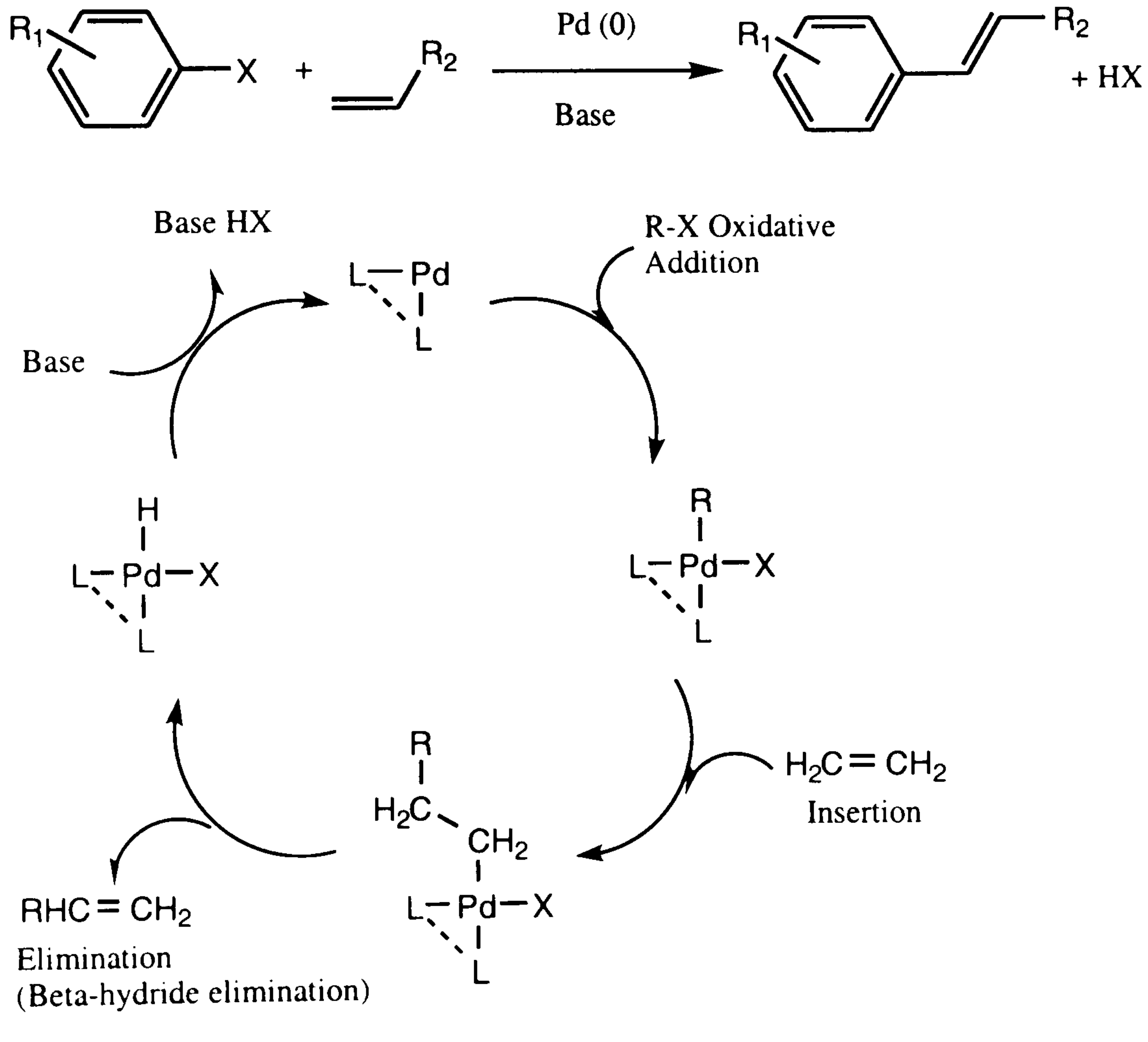
Chapter 4

The Heck Reaction In Ionic Liquid Solvents

4.1. Introduction

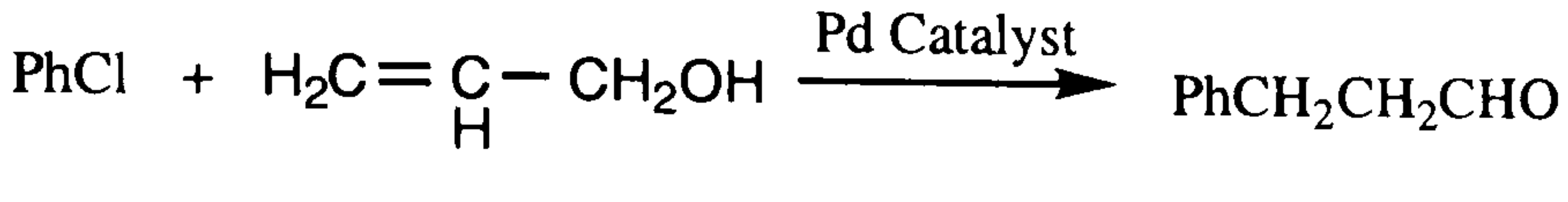
The Heck reaction usually involves the interaction of an aromatic halide or anhydride with an alkene, in the presence of a palladium catalyst and base to give aryl alkene. The Heck reaction is of major importance in synthetic organic chemistry because of its enormous potential for generating carbon-carbon bonds and its tolerance towards a wide range of functional groups.[1,2]



SCHEME 4.1a. Heck Reaction Mechanism Outline.[3]

The catalyst is a 14 electron Pd^0L_2 species, where L is usually a mono or bi-dentate phosphine.

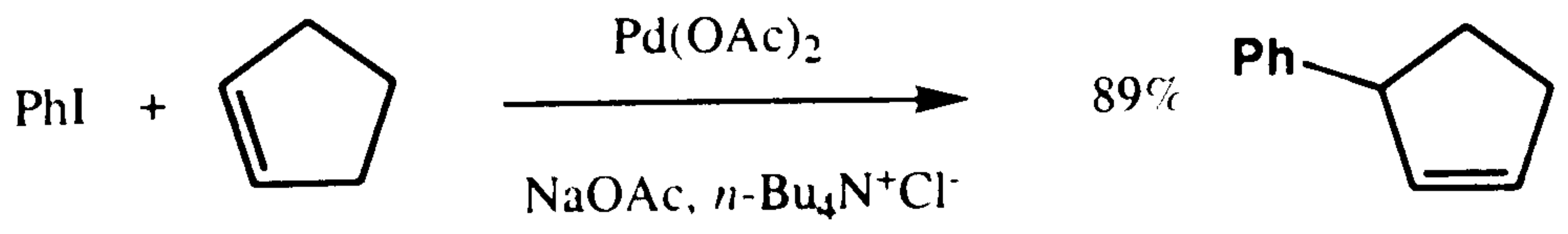
The substrate can be a simple olefin, or it can contain a variety of functional groups, such as ester, ether[4], carboxyl, phenolic, or cyano groups.[5] For example, primary and secondary allylic alcohols (and even nonallylic unsaturated alcohols[6]) give aldehydes or ketones that are products of double-bond migration,[7] e.g.,



$$PhCl + H_2C{=}\underset{H}{C}{-}CH_2OH \xrightarrow{\text{Pd Catalyst}} PhCH_2CH_2CHO$$

Ethylene is the most reactive olefin. Increasing substitution lowers reactivity. Substitution therefore takes place at the less highly substituted side of the double bond.[8] Alkylation can also be accomplished, but only if the alkyl group lacks a ß hydrogen, e.g., the reaction is successful for the introduction of methyl, benzyl, and neopentyl groups.[9] Vinylic groups, even those possessing ß hydrogens, have been successfully introduced (to give 1,3-dienes) by the reaction of the olefin with the vinylic halide in the presence of a trialkylamine and a catalyst composed of palladium acetate and a triarylphosphine at 100 to 150 °C.[10] The reaction has also been done with terminal alkynes as substrates.[11]

The evidence is in accord with the addition-elimination mechanism (addition of ArPdX followed by elimination of HPdX) in most cases.[12] The reactions are stereospecific, yielding products expected from syn addition followed by syn elimination.[13] Because the product is formed by an elimination step, with suitable substrates the double bond can go the other way, resulting in allylic rearrangement, e.g., [14]



The Heck reaction, although well studied still has several problems to overcome. One of these problems is the fact that the Heck reaction only truly works well with active arylhalides such as aryliodide and less so with arylbromide. The arylchlorides are significantly less active, however Herrman and Bohm have demonstrated that, by the use of phospha-palladacycles in non aqueous ionic liquids, by recycling and using more active catalysts, it is possible to overcome these problems and the technical application for generating C-C bonds, using the Heck reaction, can indeed involve all aryl halides.[15]

Catalyst deactivation can also occur causing problems during the Heck reaction, and often 'palladium black' results due to decomposition of the active palladium catalyst. One of the reasons for this is due to the high temperatures at which the Heck reaction operates.

The Heck reaction has been successfully carried out using several different experimental techniques. Variations in both the catalysts, and solvents used have been investigated and the results thereof published.[3,16-30]

This chapter deals with the experimental work using the ionic liquids synthesised in Chapter 2, involving their specific use as Heck reaction solvents. A major problem with the Heck reaction is that the palladium catalyst if often lost at the end of the reaction.[31] However, the use of a biphasic ionic liquid system enables the simple separation of catalysts from products and could also allow the Heck reaction to proceed under much milder conditions.

The experimental techniques and equipment used for Heck reaction chemistry are outlined along with the characterisation techniques chosen to analyse the products obtained. This chapter initially explains how the Heck reaction occurs and goes on to explain why variations in the chosen ionic liquids effect the outcome of specific Heck reactions. The final section of this particular chapter shows and discusses the results obtained from these reactions, including the respective characterisation data. Explanations are suggested as to why such results have occurred.

4.2. General Experimental

Here we investigate how variation in the ionic liquids chosen as solvents affect the overall Heck reaction. Variations in the experimental conditions, such as overall reaction time and reaction temperature, along with the choice of aryl halide and olefin were all investigated.

Initial work concentrated on the reaction of iodobenzene with butyl acrylate. Further experiments were carried out replacing the butyl acrylate with ethyl and subsequently methyl acrylate to see the overall effect on the Heck reaction. Reactions were performed in the main in the 1-butyl-3-methylimidazolium [bmim] ionic liquids, namely the bromide and analogous tetrafluoroborate salts. Heck reactions were also attempted in the hexafluorophosphate salts and in the longer chain 1-octyl-3-methyl imidazolium [omim] salts.

Generally the Heck reactions were performed in clean, oven-dried two-necked round bottomed flasks fitted with reflux condensers. Vacuum lines, to allow air-free conditions, were used where necessary and the apparatus was heated and monitored using digital, magnetic hot-plates. Chemicals were dried and distilled prior to handling using syringes. Reagents were used as received. PTFE stirrer bars were used to stir the reaction mixtures. Standard glassware such as separating and sintered funnels were oven-dried prior to being used during purification of products. The products themselves were analysed and characterised using a Bruker 200MHz ^1H NMR spectrometer.

4.3. Detailed Experimental Procedures

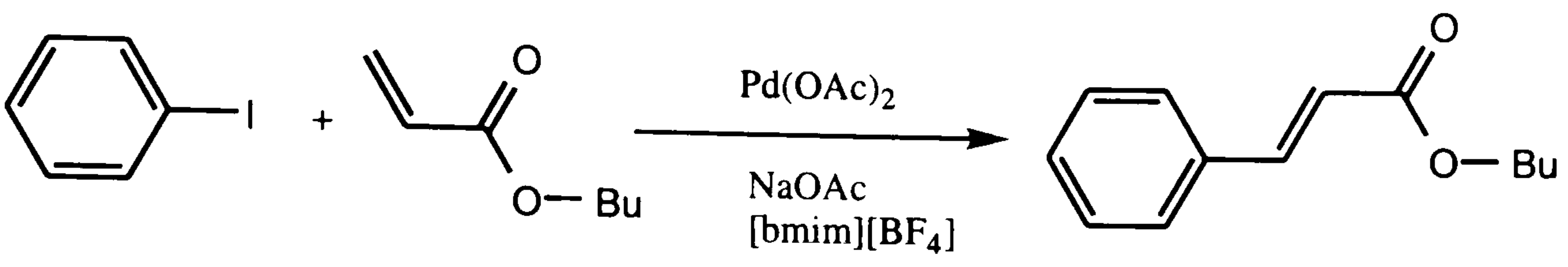
4.3.1. Preliminary Test For Catalyst Degradation

In a degassed schlenk tube, [bmim][BF_4] (5 cm^3) and $Pd(OAc)_2$ (5 mg, 0.022 mmol) were stirred vigorously at 150 °C for 12 h in an attempt to see whether deposits of the inactive palladium black species would be formed. After this time the ionic liquid was analysed by ^1H NMR spectroscopy in d_6-acetone.

There were no visible signs of black deposits, indicative of decomposed active palladium, on the sides of the schlenk tube, nor in the ionic liquid layer. The catalyst appeared to be completely dissolved and the ^1H NMR data revealed that the ionic liquid was unchanged. ^1H NMR ionic liquid : (d_6-acetone) δ 8.93 (s, 1H), 7.73 (t, 1H), 7.68 (t, 1H), 4.32 (t, 2H), 4.00 (s, 3H), 1.89 (m, 2H), 1.35 (m, 2H), 0.91 (t, 3H). Investigation into the Heck reaction could therefore begin.

4.4. The Heck Reaction In Ionic Liquid Solvents

4.4.1 Arylation Of Butyl Acrylate By Iodobenzene In [bmim][BF$_4$]



In a two-necked round bottomed flask equipped with a septum and reflux condenser, iodobenzene (2.04g, 10 mmol), anhydrous sodium acetate (0.902g, 11 mmol), palladium acetate (4.5 mg, 0.02 mmol, 0.2 mol % of the aryl halide) and [bmim][BF$_4$] (5 cm^3) were mixed and repeatedly degassed under oil pump vacuum and flushing with nitrogen. Butyl acrylate (1.79g, 14 mmol) was injected through the septum and the mixture was stirred for 14 h at 100 ^{o}C. After cooling to room temperature, distilled water (50 cm^3) was added and the product was extracted with ethyl acetate (2 x 10 cm^3). The organic layers were combined and washed with water (2 x 20cm^3) and brine (20 cm^3), then dried over magnesium sulphate (MgSO$_4$). The excess solvent was removed under reduced pressure and a sample of the crude product was analysed by ^{1}H NMR spectroscopy (CDCl$_3$ / TMS). This experimental procedure outlined was carried out several times until the optimum conditions for that particular reaction were obtained. Changes such as the reaction temperature and the time taken for the overall reaction, along with slight variations in molar quantities and equivalents resulted in higher conversion to the desired product. These 'new' reactions were repeated several times.

^{1}H NMR : (200 MHz, $CDCl_3$)

δ 6.48 (d, $^3J_{HH}$ = 15.94Hz, 1H), 6.41 (d, $^3J_{HH}$ = 15.94Hz, 1H), 4.22 (t, $^3J_{HH}$ = 6.6Hz, 2H), 1.68 (m, $^3J_{HH}$ = 7.14Hz, 2H), 1.44 (m, $^3J_{HH}$ = 7.42Hz, 2H), 0.97 (t, $^3J_{HH}$ = 7.14Hz, 3H).

14 h Reaction, 100 °C : Conversion[a]: 5%. Selectivity[b]: 65%.

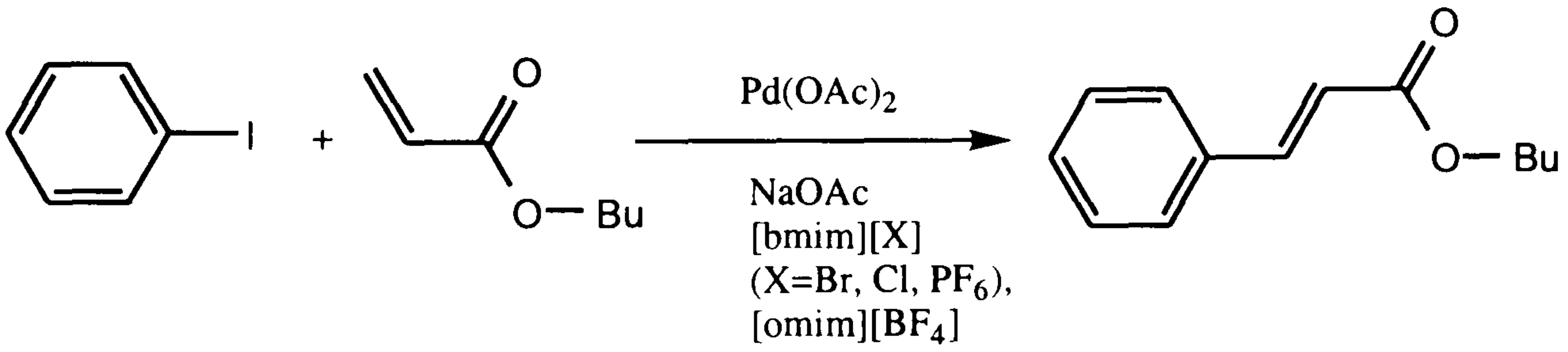
24 h Reaction, 90 °C : Conversion[a]: 20%. Selectivity[b]: 65%.

24 h Reaction, 100 °C : Conversion[a]: 15%. Selectivity[b]: 65%.

72 h Reaction, 100 °C : Conversion[a]: 22%. Selectivity[b]: 65%.

[a] Of The Halide. [b] To *trans-* product.

4.4.2. Arylation Of Butyl Acrylate By Iodobenzene In [bmim][X] (X = Br, Cl, PF_6) and [omim][BF_4]



The methodology used here was identical, in the main, to that outlined in section 4.4.1. As in section 4.4.1., each individual reaction was repeated several times (until the optimum conditions were discovered and subsequent concordant results obtained.)

Iodobenzene / Butyl Acrylate / [bmim][Br]

24 h Reaction, 90 °C : Conversion[a]: 50%. Selectivity[b]: 99%.

24 h Reaction, 100 °C : Conversion[a]: 75%. Selectivity[b]: 99%.

[a] Of The Halide. [b] To *trans-* product.

Iodobenzene / Butyl Acrylate / [bmim][Cl]

24 h Reaction, 100 °C : Conversion[a]: 35%. Selectivity[b]: 99%.

[a] Of The Halide. [b] To *trans-* product.

Iodobenzene / Butyl Acrylate / [bmim][PF_6]

24 h Reaction, 100 °C : Conversion[a]: 18%. Selectivity[b]: 70%.

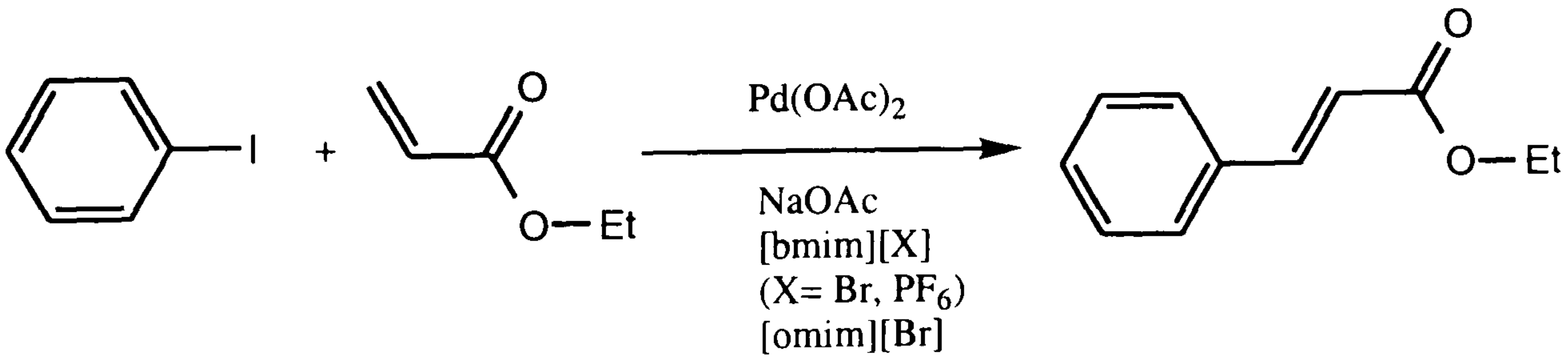
[a] Of The Halide. [b] To *trans-* product.

Iodobenzene / Butyl Acrylate / [omim][BF_4]

72 h Reaction, 100 °C : Conversion[a]: 16%. Selectivity[b]: 98%.

[a] Of The Halide. [b] To *trans-* product.

4.4.3. Arylation Of Ethyl Acrylate By Iodobenzene In [bmim][X] (X = Br, Cl, PF_6) and [omim][Br]



These reactions were carried out in exactly the same way as that outlined in section 4.4.1.

Iodobenzene / Ethyl Acrylate / [bmim][Br]

^{1}H NMR olefin : (200 MHz, $CDCl_3$) δ 6.48 (d, $^3J_{HH}$ = 15.94Hz, 1H), 6.40 (d, $^3J_{HH}$ = 15.94Hz, 1H), 4.27 (q, $^3J_{HH}$ = 7.14Hz, 2H), 1.33 (t, $^3J_{HH}$ = 7.14Hz, 3H).

24 h Reaction, 90 °C : Conversion[a]: 5.8%. Selectivity[b]: 99%.

24 h Reaction, 100 °C : Conversion[a]: 43%. Selectivity[b]: 99%.

[a] Of The Halide. [b] To *trans*- product.

Iodobenzene / Ethyl Acrylate / [bmim][PF_6]

24 h Reaction, 100 °C : Conversion[a]: 12%. Selectivity[b]: 99%.

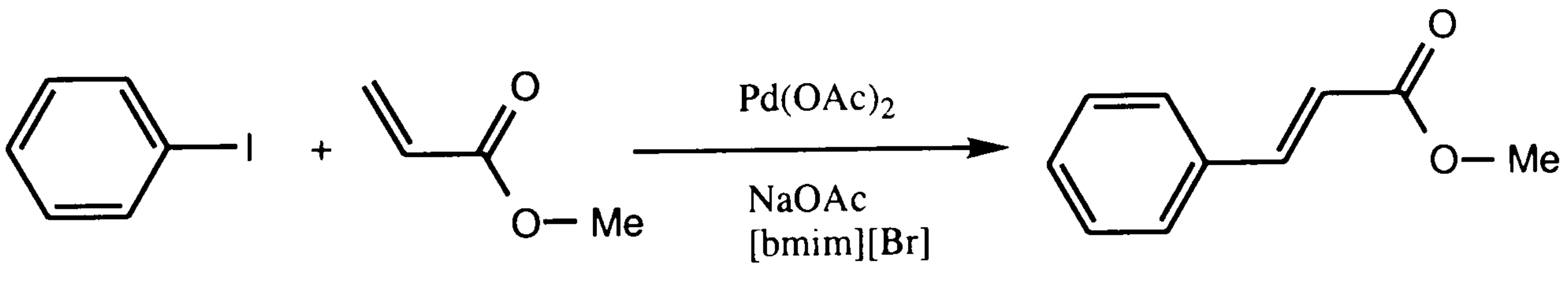
[a] Of The Halide. [b] To *trans*- product.

Iodobenzene / Ethyl Acrylate / [omim][Br]

24 h Reaction, 90 °C : Conversion[a]: 27%. Selectivity[b]: 99%.

[a] Of The Halide. [b] To *trans*- product.

4.4.4. Arylation Of Methyl Acrylate By Iodobenzene In [bmim][Br]



The same methodology was used as in section 4.4.1.

^{1}H NMR olefin : (200 MHz, $CDCl_3$) δ 6.48 (d, $^3J_{HH}$ = 15.94Hz, 1H), 6.41 (d, $^3J_{HH}$ = 15.94Hz, 1H), 3.81 (s, 3H).

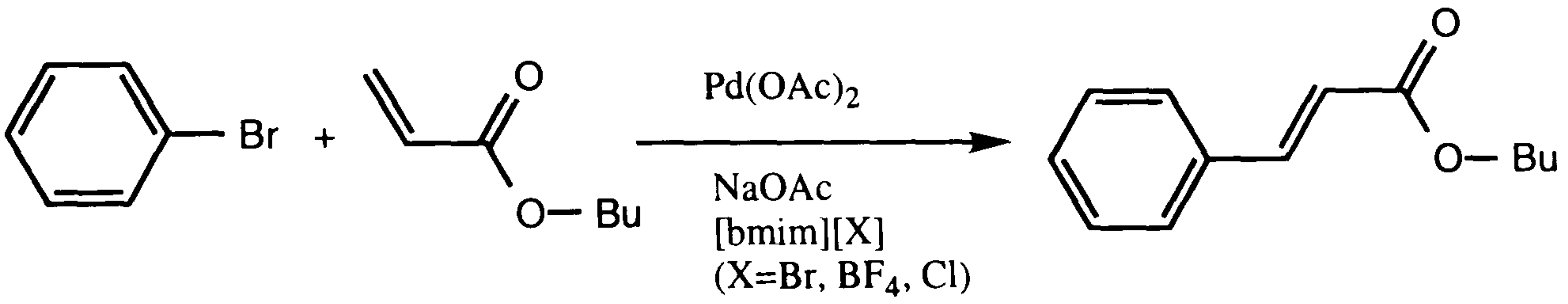
24 h Reaction, 90 °C : Conversion[a]: 36%. Selectivity[b]: 99%.

[a] Of The Halide. [b] To *trans*- product.

4.5. The Choice Of Halide

The choice of halide in the Heck reaction has a marked effect on the overall rate of reaction. The addition of the aryl halide to the palladium species is important in the catalytic mechanism of the Heck reaction, and it is also essential that halide separation from its aromatic occurs readily to help with the oxidative addition step. (See SCHEME 4.1a) Different halide substrates were now investigated to see their effect on the overall Heck reaction.

4.5.1. Arylation Of Butyl Acrylate By Bromobenzene In [bmim][X] : (X = Br, BF_4, Cl)



The same methodology was used as in section 4.4.1.

Bromobenzene / Butyl Acrylate / [bmim][Br] : ^1H NMR olefin : (200 MHz, $CDCl_3$) δ 6.47 (d, $^3J_{HH}$ = 15.94Hz, 1H), 6.41 (d, $^3J_{HH}$ = 15.94Hz, 1H), 4.21 (t, $^3J_{HH}$ = 6.6Hz, 2H), 1.69 (m, $^3J_{HH}$ = 7.14Hz, 2H), 1.40 (m, $^3J_{HH}$ = 7.42Hz, 2H), 0.96 (t, $^3J_{HH}$ = 7.14Hz, 3H).

24 h Reaction, 100 °C : Conversion[a]: 3.2%. Selectivity[b]: 89%.

[a] Of The Halide. [b] To *trans-* product.

Bromobenzene / Butyl Acrylate / [bmim][Cl]

24 h Reaction, 100 °C : Conversion[a]: 2.0%. Selectivity[b]: 89%.

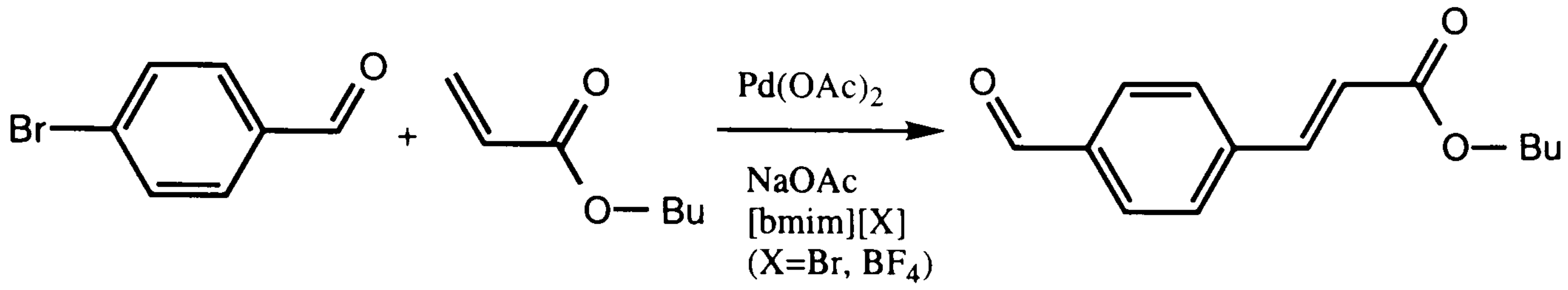
[a] Of The Halide. [b] To *trans-* product.

Bromobenzene / Butyl Acrylate / [bmim][BF_4]

24 h Reaction, 100 °C : Conversion[a]: 1.1%.

[a] Of The Halide.

4.5.2. Arylation Of Butyl Acrylate By 4-bromobenzaldehyde In [bmim][X] : (X = Br, BF_4)



The same methodology was used as in section 4.4.1., however 1 mol % $Pd(OAc)_2$ was used as opposed to the 0.2 mol % $Pd(OAc)_2$ used in all previous work. All other reaction quantities remained unchanged as did the overall reaction methodology.

4-bromobenzaldehyde / Butyl Acrylate / [bmim][Br] : ^1H NMR olefin : (200 MHz, $CDCl_3$) δ 6.48 (d, $^3J_{HH}$ = 15.94Hz, 1H), 6.41 (d, $^3J_{HH}$ = 15.94Hz, 1H), 4.20 (t, $^3J_{HH}$ = 6.6Hz, 2H), 1.68 (m, $^3J_{HH}$ = 7.14Hz, 2H), 1.38 (m, $^3J_{HH}$ = 7.42Hz, 2H), 0.94 (t, $^3J_{HH}$ = 7.14Hz, 3H).

24 h Reaction, 125 °C : Conversion[a]: 72%. Selectivity[b]: 95%.

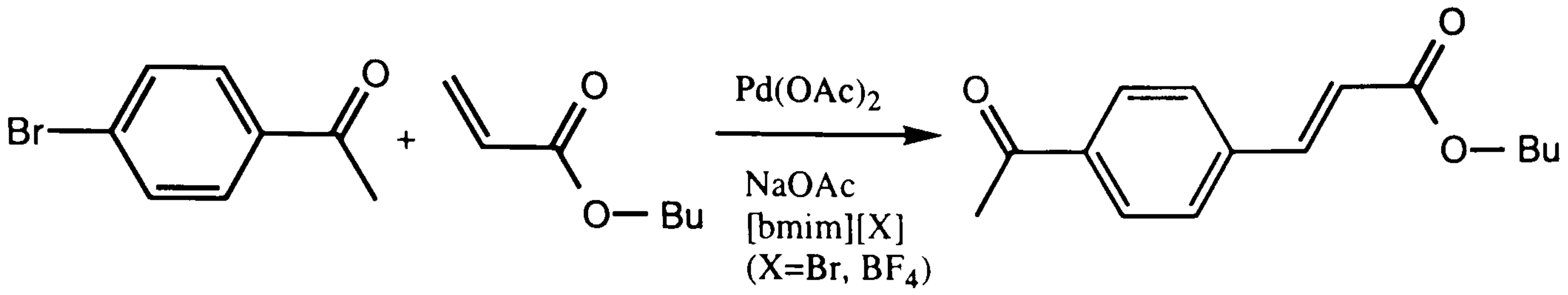
[a] Of The Halide. [b] To *trans*- product.

4-bromobenzaldehyde / Butyl Acrylate / [bmim][BF_4]

24 h Reaction, 125 °C : Conversion[a]: 14%. Selectivity[b]: 80%.

[a] Of The Halide. [b] To *trans*- product.

4.5.3. Arylation Of Butyl Acrylate By 4-bromoacetophenone In [bmim][X] : (X = Br, BF_4)



The same methodology was used as in section 4.4.1., however 1.1 mol % $Pd(OAc)_2$ was used as opposed to the 0.2 mol % $Pd(OAc)_2$ used in all previous work. All other reaction quantities remained unchanged as did the overall reaction methodology.

4-bromoacetophenone / Butyl Acrylate / [bmim][Br] : ^1H NMR olefin : (200 MHz, $CDCl_3$) δ 6.48 (d, $^3J_{HH}$ = 15.94Hz, 1H), 6.41 (d, $^3J_{HH}$ = 15.94Hz, 1H), 4.20 (t, $^3J_{HH}$ = 6.6Hz, 2H), 1.68 (m, $^3J_{HH}$ = 7.14Hz, 2H), 1.38 (m, $^3J_{HH}$ = 7.42Hz, 2H), 0.94 (t, $^3J_{HH}$ = 7.14Hz, 3H).

24 h Reaction, 110 °C : Conversion[a]: 85%. Selectivity[b]: 97%.

[a] Of The Halide. [b] To *trans*- product.

4-bromoacetophenone / Butyl Acrylate / [bmim][BF_4]

24 h Reaction, 110 °C : Conversion[a]: 28%. Selectivity[b]: 84%.

[a] Of The Halide. [b] To *trans*- product.

4.6. RESULTS and DISCUSSION

This section deals with the results obtained from various Heck reactions performed in the ionic liquids prepared in chapter 2. The products obtained from these reactions were analysed by ^{1}H NMR spectroscopy and the relevant data obtained from this analysis is presented in tabulated form.

As deactivation of the palladium catalyst is often a problem during Heck reactions, (palladium deposits [palladium black] are often formed because of the high temperatures at which the system operates), a small test reaction was performed using ionic liquid [bmim][BF_4] and palladium (II) acetate. (See section 4.3.1). As shown in section 4.3.1. 'no palladium black' was observed therefore the Heck reactions were attempted. The reason for this lack of 'palladium black' could be attributed to the ionic liquids presence.

4.6.1. Arylation Of Butyl Acrylate By Iodobenzene.

Table 4.6.1a shows the results of the Heck reactions described in sections 4.4.1. and 4.4.2.

TABLE 4.6.1a. Arylation Of Butyl Acrylate By Iodobenzene In [bmim][X] - (X = BF_4, Br, Cl, PF_6) and [omim][BF_4]

Substrate	Ionic Liquid	Temp °C	Reaction Time (h)	Conversion[a,b] %
iodobenzene	[bmim][BF_4]	90	24	20
		100	14	5
		100	24	15
		100	72	22
iodobenzene	[bmim][Br]	90	24	50
		100	24	75
iodobenzene	[bmim][Cl]	100	24	35
iodobenzene	[bmim][PF_6]	100	24	18
iodobenzene	[omim][BF_4]	100	72	16

[a] Of the halide. Determined by simple ^1H NMR calculation. (See section 4.8)

[b] All values are the mean results of several repeated experiments.

4.6.2. Arylation Of Ethyl Acrylate By Iodobenzene.

Table 4.6.2a shows the results of the Heck reaction outlined in section 4.4.3.

TABLE 4.6.2a. Arylation Of Ethyl Acrylate By Iodobenzene In [bmim][X] - (X = Br, PF_6) and [omim][Br]

Substrate	Ionic Liquid	Temp °C	Reaction Time (h)	Conversion[a,b] %
iodobenzene	[bmim][Br]	90	24	5.8
		100	24	43
iodobenzene	[bmim][PF_6]	100	24	12

[a] Of the halide. Determined by simple ^1H NMR calculation. (See section 4.8)

[b] All values are the mean results of several repeated experiments.

4.6.3. Arylation Of Methyl Acrylate By Iodobenzene.

Table 4.6.3a shows the results of the Heck reaction described in section 4.4.4a.

TABLE 4.6.3a. Arylation Of Methyl Acrylate By Iodobenzene In [bmim][Br]

Substrate	Ionic Liquid	Temp °C	Reaction Time (h)	Conversion[a,b] %
iodobenzene	[bmim][Br]	90	24	36

[a] Of the halide. Determined by simple ^1H NMR calculation. (See section 4.8)

[b] All values are the mean results of several repeated experiments.

4.6.4. The Effect Of Variation In The Choice Of Halide On The Heck Reaction.

Tables 4.6.4a, 4.6.5a and 4.6.6a shows the results of the Heck reactions attempted in section 4.5.1., 4.5.2. and 4.5.3.

TABLE 4.6.4a. Arylation Of Butyl Acrylate By Bromobenzene In [bmim][X] - (X = Br, BF_4, Cl)

Substrate	Ionic Liquid	Temp °C	Reaction Time (h)	Conversion[a,b] %
bromobenzene	[bmim][Br]	100	24	3.2
bromobenzene	[bmim][Cl]	100	24	2.0
bromobenzene	[bmim][BF_4]	100	24	1.1

[a] Of the halide. Determined by simple ^1H NMR calculation. (See section 4.8)

[b] All values are the mean results of several repeated experiments.

TABLE 4.6.5a. Arylation Of Butyl Acrylate By 4-bromobenzaldehyde In [bmim][X] - (X = Br, BF_4)

Substrate	Ionic Liquid	Temp °C	Reaction Time (h)	Conversion[a,b] %
4-bromo-benzaldehyde	[bmim][Br]	125	24	72
4-bromo-benzaldehyde	[bmim][BF_4]	125	24	14

[a] Of the halide. Determined by simple ^1H NMR calculation. (See section 4.8)

[b] All values are the mean results of several repeated experiments.

TABLE 4.6.6a. Arylation Of Butyl Acrylate By 4-bromoacetophenone In [bmim][X] - (X = Br, BF_4)

Substrate	Ionic Liquid	Temp °C	Reaction Time (h)	Conversion[a,b] %
4-bromo-acetophenone	[bmim][Br]	110	24	85
4-bromo-acetophenone	[bmim][BF_4]	110	24	28

[a] Of the halide. Determined by simple ^1H NMR calculation. (See section 4.8)

[b] All values are the mean results of several repeated experiments.

Generally, the systems outlined operated most efficiently over a period of 24 hours, with a mixture of 10.0 mmol of the aryl halide, 1.4 eq acrylate, 1.1 eq of base (NaOAc) and 0.2 mol% $Pd(OAc)_2$ in 5.0 ml ionic liquid, heated to 100 °C.

These results confirm and support those recently published that the Heck reaction can be performed without additive phosphine ligands in ionic liquids.[31,32,33]

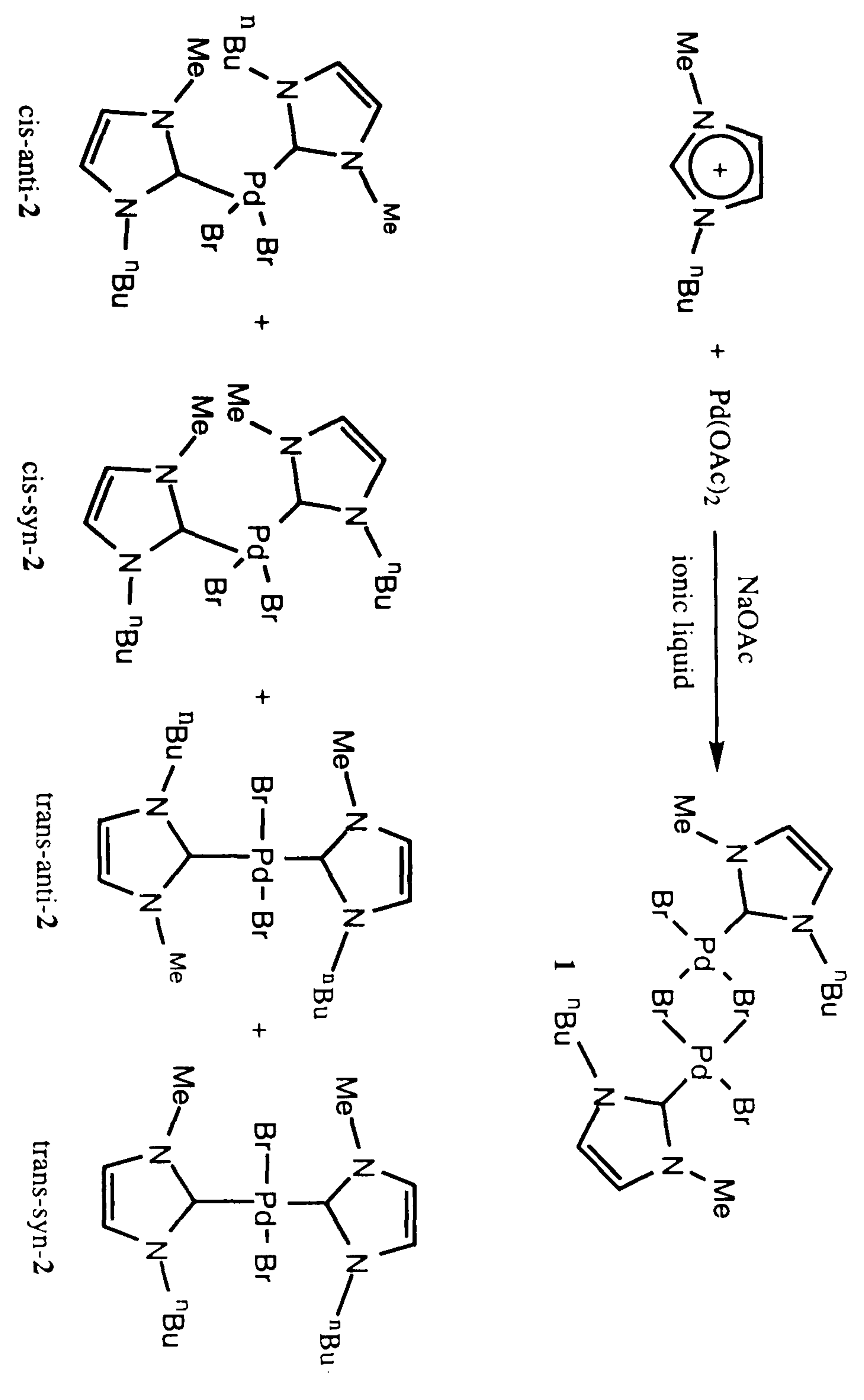
It can clearly be seen from these results that the Heck reaction was found to proceed markedly more efficiently in the ionic liquid 1-butyl-3-methylimidazolium bromide [bmim][Br] than in the analogous [bmim][BF_4] and [bmim][PF_6] ionic liquids. The Heck reaction is also markedly more efficient in [bmim][Br] than in the 1-octyl-3-methylimidazolium [omim] -based ionic liquids. Although the conversion values for all the ionic liquid solvents are relatively low (less than 50%), the few cases where conversion is greater than 50% all involve the use of [bmim][Br] as solvent. It can also be seen from these results than the Heck reaction proceeded more efficiently with aryl iodides and activated aryl bromides in the ionic liquids. The less reactive bromobenzene showed much lower conversion (< 5%) under the same conditions.

The variation in coupling reaction efficiency between [bmim][Br] and the analogous [bmim][BF_4] and [bmim][PF_6] is due to differences in the catalytically active palladium species formed during the respective reactions.

When the ionic liquid [bmim][Br] is used as a solvent for the Heck reaction, it reacts readily with the $Pd(OAc)_2$ to produce *N*-heterocyclic carbene complexes of palladium. No such carbene complexes are produced when using the [bmim][BF_4] ionic liquid. Results of heating $Pd(OAc)_2$ in [bmim][Br] in the absence of olefin and aryl halide have resulted in the formation of palladium 1-butyl-3-methylimidazol-2-ylidene (bmiy) complexes. Heating $Pd(OAc)_2$ in [bmim][BF_4] under the same conditions yielded no such carbene species.

Scheme 4.6a outlines that the imidazolium ion can react with a catalyst precursor to form *N*-heterocyclic carbene complexes *via* deprotonation in the imidazolium-based ionic liquids under catalytic conditions. The carbene complexes so generated are active for C-C bond coupling reactions. The higher activity and stability of palladium in the Heck reaction in [bmim][Br] than in [bmim][BF_4] is explained, partly, in terms of the easy formation of stable palladium carbene complexes in the former. The activity of the carbene complexes towards Heck coupling varies with the choice of an ionic liquid; they are active in [bmim][Br] but much less so in the analogous [bmim][BF_4]. Ionic liquids therefore not only function as solvating media but can also act as reactive reagents, and so a catalyst in an ionic liquid may completely differ from its established form in molecular solvents.

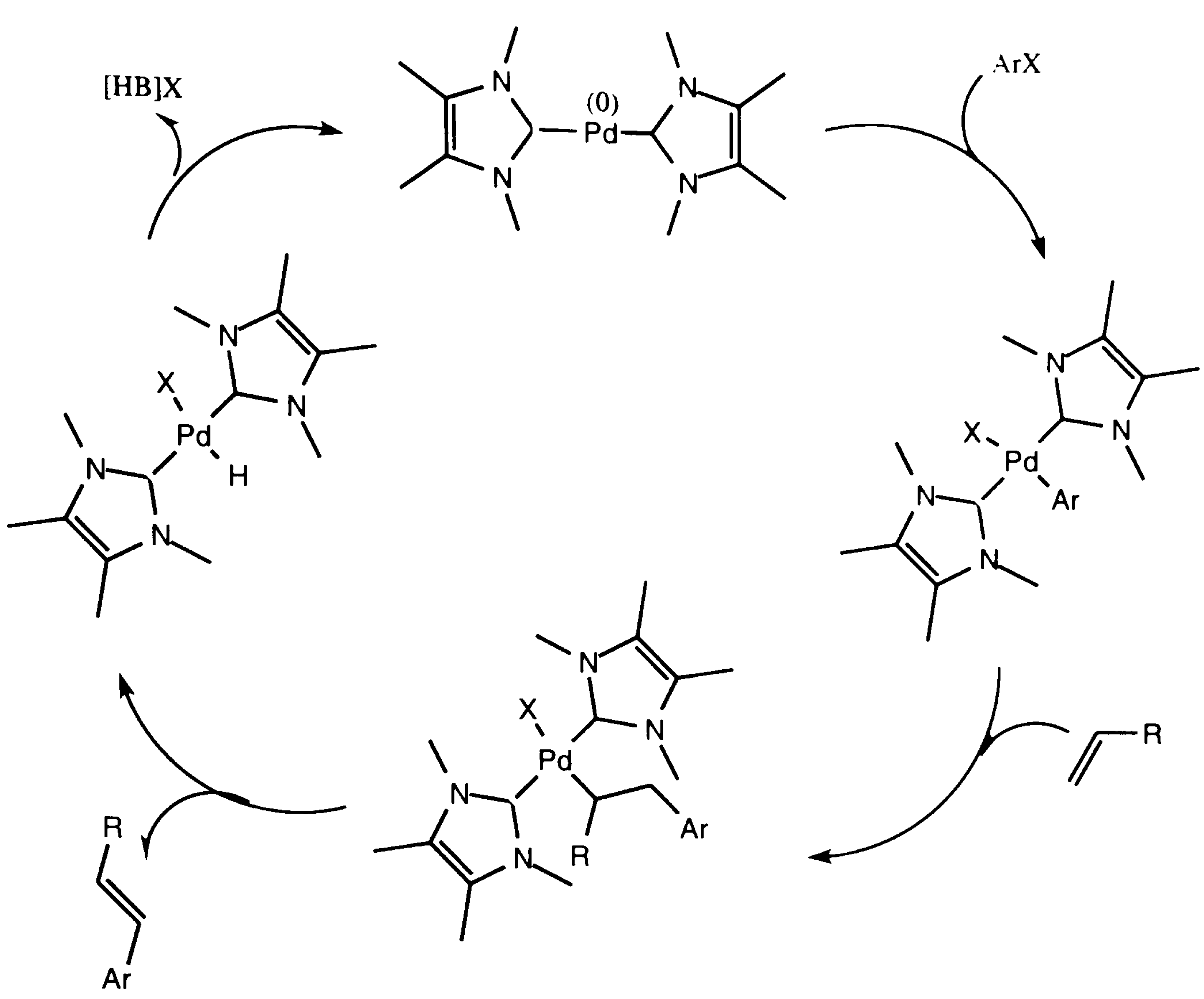
1-butyl-3-methylimidazol-2-ylidene complexes of palladium [PdBr(μ-Br)(bmiy)]$_2$ (**1**) and [PdBr$_2$(bmiy)$_2$] (**2**) have been isolated in [bmim][Br] but not in [bmim][BF$_4$] under conditions similar to those employed for the Heck reaction. In both the ionic liquid [bmim][Br] and molecular solvents, complex **2** was formed *via* the intermediate **1**. **2** is active in the Heck reaction in [bmim][Br] but much less so in [bmim][BF$_4$] due to the transformation by the latter into less active species.[34]



SCHEME 4.6a *N*-Heterocyclic Carbene Formation

4.7 Further Analysis

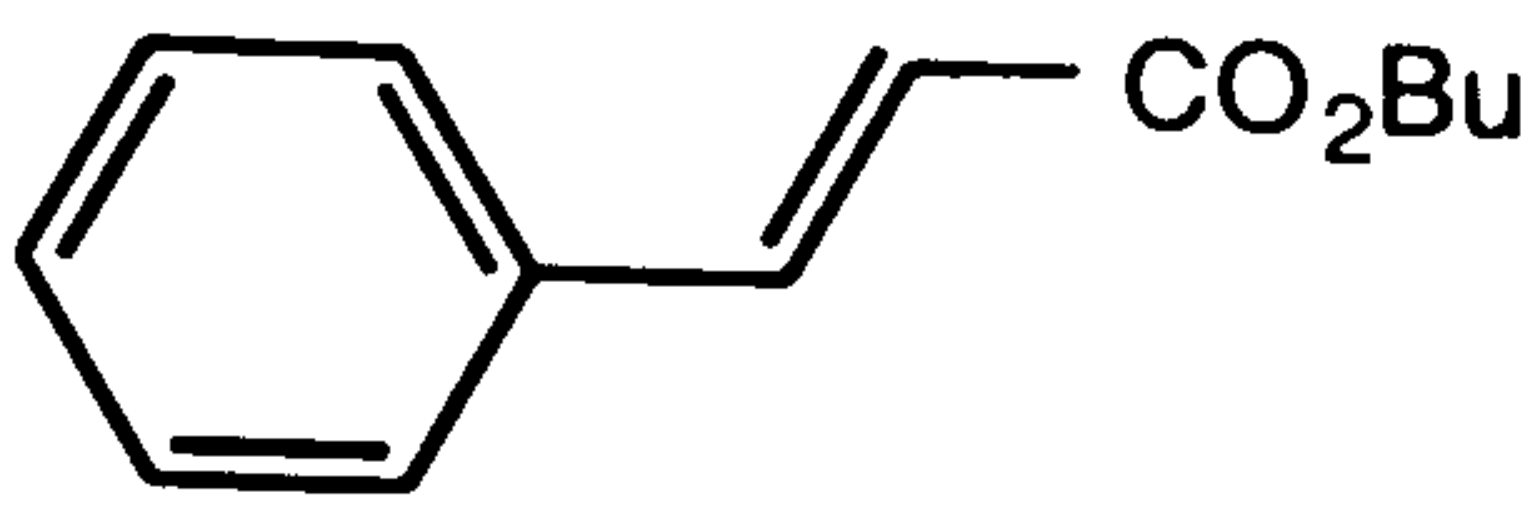
The reason for the lack of activity in the [omim][BF_4] and [omim][PF_6] ionic liquids is due to the fact that they cannot form any of the species outlined in scheme 4.6a. Simply replacing the halide ions with either [BF_4] or [PF_6] is not possible. The lack of activity in the hexafluorophosphate [PF_6^-] ionic liquid can be assumed to be for the same reasons as those outlined for the [BF_4] ionic liquids. As these are highly active catalytic species it is essential that they are produced during the course of the reaction if high conversion Heck reactions are to occur. Herrman *et al.*[17] has demonstrated the high efficiency of palladium carbene complexes involved in the coupling of 4-bromoacetophenone and *n*-butylacrylate. White *et al.* suggest a possible catalytic mechanism involving analogous species where the carbenes play an integral role in the catalysis also. The whole system operates as if it were a Palladium-phosphine catalysed Heck reaction, although there is no phosphine present.[35] (See scheme 4.7a)



SCHEME 4.7a Proposed mechanism for Heck coupling with dicarbene-Pd complexes.

By simply looking at Schemes 4.6a and 4.7a it could be suggested that the reason for the lack of activity in [omim] - based ionic liquids would be because of steric reasons, as both of these schemes appear to be quite clustered. The imidazolium side-chains are significantly more bulky than their [bmim] analogues and hence the formation of the active catalytic species outlined in scheme 4.6a would appear unlikely. This is not true as the side-chains would simply re-arrange themselves into a suitable configuration and hence remove any significant steric problems. Comparing the results obtained using [omim][BF_4] and [bmim][BF_4] show there to be very little difference in the observed Heck reaction conversion values obtained.

4.8. ^{1}H NMR Conversion Calculation



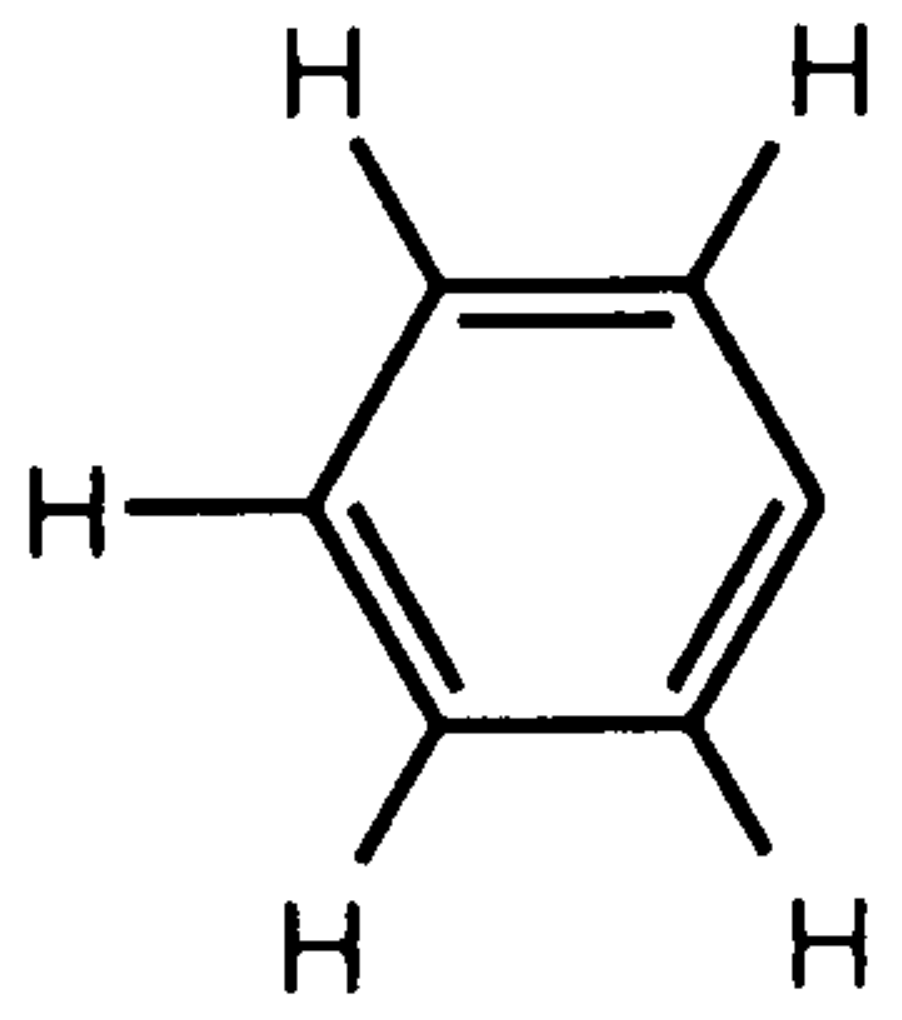
is present in the product sample analysed.

The ^{1}H NMR integration values of the relevant (expanded) area of the spectra shows a total integration value of 4.45. (See FIGURE 4.8a) This value represents:-

5 phenyl hydrogens (starting material)
5 phenyl hydrogens (obtained product)
1 olefinic hydrogen (obtained product)

The ^{1}H NMR clearly shows (via the sharp doublet) that the 'obtained product' is totally responsible for peaks with an integration value of 0.36, representative of 1 hydrogen. (olefinic)

Therefore in the product sample analysed, the total contribution of phenyl hydrogens alone is (4.45 - 0.36) = 4.09.



is present in the product sample analysed, from the 'obtained product' via reaction. If 1 hydrogen (obtained product) contribute 0.36, then 5 hydrogens (obtained product) contribute (5 x 0.36) = 1.80.

To calculate the conversion we must compare the amount of phenyl hydrogens in the sample.

Contribution of phenyl hydrogens (obtained product) = (5 x 0.36) = 1.80

Contribution of phenyl hydrogens (starting material) = (4.45 - 0.36) = 4.09

Therefore % conversion = (1.80 / 4.09) x 100

= 44.0 %

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Chapter 5

Concluding Discussion

5.1 Importance Of Ionic Liquids

It is clear that ionic liquids play an important role in catalytic chemistry. Their application as solvents is without doubt one of the huge developments of industrial chemistry in recent years, and it is somewhat surprising that it has taken since the early 1950's[1], (when the first molten salts were reported), until now to establish molten salts (ionic liquids) as 'every-day' solvents.

5.2 Ionic Liquids - Preparation And Properties

The preparation of ionic liquids has changed significantly over the course of time. Purity is paramount in any catalytic system, therefore only pure ionic liquids that can be easily prepared (and handled) are valuable as solvents. During this research we have developed a procedure capable of preparing pure, room temperature ionic liquids in high yield. By modifying the approach used by Bonhote *et al.*[2] we have successfully prepared a variety of ionic liquids based on the imidazolium cation, and thereafter used these liquids as solvents for both hydroformylation and heck reactions.

The ionic liquids containing the BF_4^-, PF_6^- or SbF_6^- anions were liquid at room temperature and were prepared by mixing the halide salts with either $NaBF_4$, HPF_6 or $NaSbF_6$. The experimental procedure for preparing these ionic liquids was continually modified throughout the course of the research until the optimum conditions for ionic liquid synthesis were achieved. As trace quantities of halide in the ionic liquids would have a detrimental effect on catalytic reactions, it was necessary to remove all halide impurity from the ionic liquids. A modification to the technique used in 1996 by Bonhote *et al* was necessary in order to achieve this high purity.

Ion-exchange resin were initially used in an attempt to prepare pure ionic liquids. The resin was initially converted from its original, 'purchased' form to the desired form (from Cl^- to BF_4^-) by stirring it in a flask containing aqueous $NaBF_4$ for several hours. Then, simply mixing the BF_4 resin with the relevant halide salt, in acetone solution for several hours, allowed straightforward ion-exchange to occur, resulting in the production of ionic liquids. The liquids were then thoroughly dried to remove any trace quantities of water. Although this was the first time that ionic liquids had been synthesised free of halides using ion-exchange techniques, it was decided to be an unsuitable method of ionic liquid preparation on a large scale. The ion-exchange resins undoubtedly contained minute traces of impurities such as lanthanides, therefore one could not be sure as to how much 'new', undetectable impurities the ionic liquids would contain as a direct result of their interaction with the resins. A different method of ionic liquid preparation was therefore developed.

The final, chosen methodology involved, in the case of the $[BF_4]$ ionic liquids, adding dichloromethane and water to the acetone solution containing $NaBF_4$ during preparation. Although the $[BF_4]$ ionic liquid is partially water-miscible the overall effect of water addition (the removal of trace quantities of halide) out-weighs the side effect of a small reduction in yield, due to the partial miscibility of the ionic liquid in the water itself. The preparation technique used for the $[PF_6]$ ionic liquids was straightforward as they are completely immiscible in water. Simple mixing of the relevant halide salt with HPF_6 in aqueous solvent, separating the ionic phase from the aqueous phase by decantation, washing with Et_2O and subsequent drying of the ionic phase, resulted in the production of [PF_6] ionic liquids. The synthesised ionic liquids were tested thoroughly for trace quantities of halide using $AgNO_3$. The ^1H NMR spectra provided evidence as to whether or not unreacted 1-methylimidazole was present in the halide salts. If so, they were thoroughly washed prior to use in further preparation.

Both the [emim] and [bmim] halide salts prepared from 1-methylimidazole and the relevant haloalkanes were solid at room temperature. The longer chain [omim] halide salts were liquids at room temperature, showing that an increase in chain length leads to a decrease in the melting point. The melting point of the halide salts was found to cover a small range of temperatures. The reason for this is probably due to slight impurity. A 100 % pure halide salt would have a sharp melting point whereas a halide salt containing a small amount of impurity (in the form of unreacted 1-methylimidazole) would have a melting point over a small range of temperatures.

Although the ionic liquids prepared were air-stable and therefore very easy to handle, care was taken to ensure than they were stored and handled under air-free conditions. The ionic liquids would readily absorb moisture, if exposed to the atmosphere, and although this would not have a detrimental effect on the liquids themselves, it could potentially interfere with the catalytic reactions attempted using the ionic liquids as solvents.

The ionic liquids [bmim][BF_4] and [omim][BF_4], although slightly different in appearance (moving from C_4 to C_8 results in an increase in brown colouration), were very similar regarding their physical properties. The measured densities of [bmim][BF_4] and [omim][BF_4] were 1.3 gcm^{-3} and 1.2 gcm^{-3} respectively. The calculated viscosity of these liquids was also remarkably similar, varying by only 0.04 in 1141 mp (1140.78 and 1140.82 mp). In the case of [bmim][PF_6] and [omim][PF_6], the densities of the ionic liquids were again similar, 1.5 gcm^{-3} and 1.6 gcm^{-3} respectively, however their viscosities were quite different, the shorter-chain [bmim][PF_6] had a measured viscosity of 6229 mp whereas the longer-chain [omim][PF_6] had a measured viscosity of 11780 mp. The reason for this increase in viscosity is probably structure related (see section 2.9.3).

^{1}H NMR spectroscopy was used to analyse the ionic liquids produced. Fundamentally, the C(2)-H observed chemical shift of the ionic liquids indicated whether or not they had been successfully produced. A change in the anion has a direct effect on the acidity of the imidazolium cation, the result of which is altered C(2)-H, C(4)-H and C(5)-H chemical shifts. As the C(2)-H chemical shift is the most affected by this change in acidity, an observed change in the chemical shift of the C(2)-H is a straightforward way of determining whether or not a change of anion has occurred, and therefore an easy way of identifying whether a reaction has occurred. Chemical shifts in the lower field area of the NMR spectra give information confirming the specific, individual structure of the ionic liquids. By analysing the complete NMR spectra it was possible to see if there was any remaining starting material (either 1-methylimidazole in the case of the halide salts, or halide salts in the case of the ionic liquids), therefore providing information regarding the overall purity of the synthesised halide salts and ionic liquids.

The research carried out in this thesis has enabled the facile synthesis of pure ionic liquids, in good yield, to be achieved. These liquids can then be used as solvents for various catalytic reactions. The methodology involved is straightforward and is quite possibly the easiest way of producing pure ionic liquids on either a small or large scale.

5.3 Catalytic Hydroformylation Of Olefins

Hydroformylation is a well known catalytic reaction in which olefins are converted to their corresponding aldehydes. Organic solvents are often used as reaction media in which hydroformylation can occur, however, as with many catalytic reactions there is often the fundamental problem of product separation at the end of the reaction. The product and the organic solvent are often to be found forming a single homogeneous phase.

Ionic liquids have been used as alternative solvents for the rhodium catalysed hydroformylation of alkenes. The ionic liquids were used as they effectively 'heterogenised' a homogeneous system and allowed easy product separation due to the formation of two completely separate phases at the end of the reactions.

In this research we investigated the effect on rhodium catalysed hydroformylation of two separate olefins, 1-decene and 1-pentene, using various ionic liquids as solvents. The research involved investigating how the choice of ionic liquid could potentially effect the outcome of individual hydroformylation reactions. Although Chauvin *et al.*[3] showed it was possible to carry out hydroformylation in these ionic liquids in 1995, no investigation into the effect of the ionic liquids themselves on the hydroformylation was performed. By using the various ionic liquids I prepared, it was possible to see how changes in the ionic liquid anions and also the length of the ionic liquids' 'side-chains' affected overall hydroformylation, including the % conversion, regioselectivity to aldehyde and the TOF.

Initial hydroformylation was attempted using [Rh(acac)(CO)$_2$] in the absence of PPh$_3$. No hydroformylation was observed in any of these reactions and it was concluded that the presence of PPh$_3$ was necessary, under the conditions used here, if hydroformylation was to occur. Although [Rh(acac)(CO)$_2$] itself is active without PPh$_3$, it was hoped that the ionic liquid would replace the phosphine by co-ordinating to the rhodium and forming a Rh-carbene species, as has been discussed by Herrmann and Kocher.[4] As the results obtained from relevant experiments showed that this unfortunately did not happen, an active catalytic species was not formed in the absence of PPh$_3$ and therefore hydroformylation did not occur. (mechanism, see section 3.9.2)

Subsequent hydroformylation of the respective olefins using ionic liquids as solvent with the addition of PPh$_3$, resulted in successful hydroformylation, producing the expected aldehydes in good yield. There was little difference in the results obtained when using either of the BF$_4$ ionic liquids. The [bmim][BF$_4$] and [omim][BF$_4$] ionic liquid solvents allowed good conversion to desired product with both 1-decene and 1-pentene, the results comparing favourably with those presented by Chauvin *et al* in 1995. Results of hydroformylation using the PF$_6$ ionic liquids were quite different. The shorter chain, [bmim][PF$_6$] ionic liquid gave results very similar to the analogous BF$_4$ liquids, however when the longer chain [omim][PF$_6$] ionic liquid was used there was a significant reduction in the % conversion achieved.

The measured viscosity of [omim][PF$_6$] was much larger than all the other ionic liquids used (see section 2.9.2). Suarez *et al.*[5] in 1997 whilst working on two-phase catalytic hydrogenation in ionic liquid solvent, stated that, "a well stirred system was required, since the mass transfer between phases is an important parameter in these systems.[6] Indeed, in the absence of stirring the consumption of hydrogen is completely stopped." It can be assumed that this is a major contributory factor in the lower conversion results obtained here using the extremely viscous [omim][PF_6].

The effect of water on the rate and regioselectivity of hydroformylation was also investigated. As water was found to be extremely difficult to remove from the ionic liquids, the addition of water to specially dried ionic liquids helped clarify whether its presence affected the rate and / or regioselectivity of the hydroformylation. Results obtained from this work indicated that the presence of water had no observed effect on either the rate or regioselectivity of hydroformylation in ionic liquid solvents. The results were almost identical to those obtained in non-aqueous conditions.

Hydroformylation of olefins in ionic liquid solvents results in the formation of a two-phase product. The phases were easily separated and the ionic liquid layer, containing the rhodium catalyst, was used as solvent for further hydroformylation experiments, showing the potential ability of catalyst / solvent recycling in ionic liquids. Unfortunately the subsequent reactions attempted showed little, if any conversion to aldehyde. The reason for this lack of hydroformylation was attributed to leaching of the rhodium catalyst from the ionic liquid layer. However, although analysis of both the ionic liquid layer and the olefin layer of the reaction products showed little trace of rhodium, an error was later found in the analytical equipment used. In reality the active rhodium catalyst remains in the ionic liquid phase making catalyst / solvent recycle possible.

It can be concluded from this research into hydroformylation of olefins in ionic liquid solvent that it is possible to carry out successful rhodium catalysed hydroformylation of olefins (1-decene and 1-pentene) in ionic liquid solvent in the presence of PPh_3, producing two-phase reaction products. The olefins are hydroformylated with good conversion (> 85 %) to the corresponding aldehydes in [bmim][BF_4], [bmim][PF_6] and [omim][BF_4] ionic liquids with a regioselectivity of approximately 3:1 (n:i). The preferred ionic liquids are the BF_4 solvents, showing conversion values > 95 %. This is contrary to the claim made by Chauvin *et al.* who stated that, results of preliminary experiments indicated that the solubility of 1-pentene was two-times higher in the SbF_6 based salts than in the PF_6 salt. In the case of the [bmim][BF_4] salt, which is partly water miscible and which, he claimed, could not be properly purified, the lower activity could be ascribed to the presence of trace amounts of strongly co-ordinating chloride ion in the salt.[3] As we have successfully prepared chloride free ionic liquids, the results obtained for our [bmim][BF_4] salt were much improved on those results obtained by Chauvin *et al.*

It is also possible to carry out hydroformylation in [omim][PF_6] ionic liquid, however the conversion to aldehyde is significantly reduced due to mass transfer problems, directly resulting from the high viscosity of the ionic liquid. The presence of water has no observed effect on hydroformylation.

When hydroformylation 1-pentene, it was possible for isomerisation of the olefin to occur as a result of the high pressure and high temperature conditions in operation, however, the choice of ionic liquid had no observed effect on olefin isomerisation.

5.4 The Heck Reaction In Ionic Liquid Solvent

The Heck reaction is an important part of synthetic chemistry producing, as it does, a new C-C bond. Conventional Heck reactions invariably involve the use of palladium to catalyse the coupling of olefins with aryl and vinyl halides. Generally polar organic solvents such as DMF and MeCN are used, however in this research we have found ionic liquids to be extremely adequate alternatives to these volatile solvents.

A major problem with the Heck reaction is that the conditions required for successful synthesis often include elevated reaction temperatures, a side effect of which is the decomposition of the active palladium catalyst to 'palladium black'. The gradual build up of this palladium precipitate black renders the catalytic system inactive and therefore the reactions cease. It should be noted that in all of the Heck reactions performed in this research, none of the systems showed any signs of palladium black. This can be attributed to the excellent solvent properties of the ionic liquids.

This research concentrated on what effects the ionic liquid solvents had on the Heck reaction. Investigation into how the nature of the ionic liquids affected the reactions was carried out, with close attention paid to the % yield and conversion values obtained. As recent work in this particular field had suggested the involvement of *N*-heterocyclic carbenes,[8,9] - the use of which as active catalysts came from Herrman *et al.* in 1995.[10] The possible involvement of such compounds was therefore considered.

The use of the prepared ionic liquids as solvents for the Heck reaction, allowed the reactions to proceed without additive phosphine ligands, as in accordance with previous publications.[8,9,11]

It was also clear from our results that the Heck reaction proceeded much more efficiently in [bmim][Br] than in the analogous [bmim][BF_4] ionic liquid. In all of the reactions attempted the conversion values obtained for [bmim][Br] were almost three times higher than for the corresponding [BF_4] ionic liquids.

suggesting perhaps that the catalytically active palladium species in the Heck reaction was different in the two ionic liquids.

Detailed investigation into this hypothesis lead to the isolation of the compounds detailed in scheme 4.6a.[12] It was clear that the [bmim][BF_4] ionic liquids, under identical conditions to the [bmim][Br] behaved in a different manner. The catalytically active *N*-heterocyclic carbene species formed when heating [bmim][Br] with $Pd(OAC)_2$ was not formed when replacing [bmim][Br] with [bmim][BF_4]. The easy formation of the carbene species in [bmim][Br] but not in [bmim][BF_4] explains at least partly the different activity and stability of palladium in the Heck reaction in the two liquids.

A proposed catalytic mechanism for the Heck reaction involving *N*-heterocyclic compounds of this kind by White *et al.*[13] is useful in hypothesising why the [BF_4] and [PF_6] salts are less active than the corresponding halides. The formation of the Pd dicarbene catalyst is integral during the Heck reaction. The presence of the carbenes increase the overall stability of the system, the result of which is a catalytical mechanism essentially the same as the Pd-phosphine catalysed Heck reaction, but without the phosphine. As a palladium dicarbene species is not formed in the case of the [BF_4] ionic liquids (because [BF_4] does not attach to the palladium), the result is a significant reduction in conversion in the Heck reactions performed in [bmim][BF_4]. The same explanation can be used in [PF_6] ionic liquids.

5.5. Future Directions

Since this research project began, ionic liquids have become increasingly popular in catalytic chemistry. The use of such liquids as solvents for catalysis has gradually become accepted and hopefully this particular field of research will continue to expand.

During this work a new route for synthesising pure ionic liquids has been developed, which in turn has shown that they are capable of acting as solvents for catalytic reactions which would otherwise, generally be performed in highly volatile organic solvents, resulting in increased environmental pollution. It has been demonstrated how the use of ionic liquids allows clean, easy product separation and also that catalyst recycling is possible. Now that these properties and general criteria have been clearly established it is realistically possible to attempt many more catalytic experiments in these solvents, with the increased knowledge and higher level of general understanding on how they work.

It would be particularly interesting to synthesise enantiomeric ionic liquids and see if they would operate as enantioselective solvents in catalytic systems. The potential here is huge. The possibility of links to the pharmaceutical industry make this a very interesting channel for potential future research.

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FIGURE 2.9.3a ^1H NMR [bmim][BF_4]

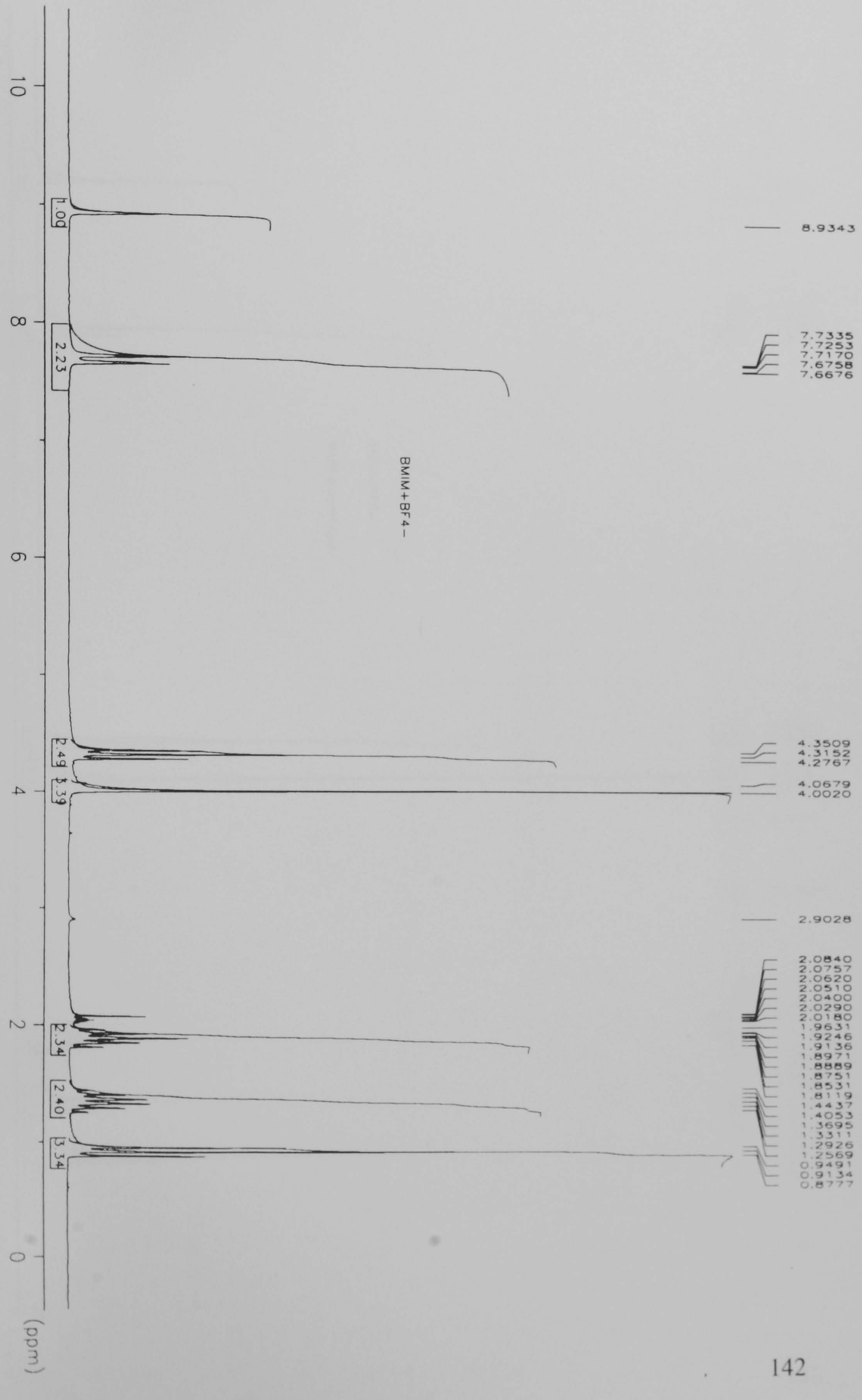


FIGURE 2.9.3b ^{1}H NMR [bmim][PF$_6$]

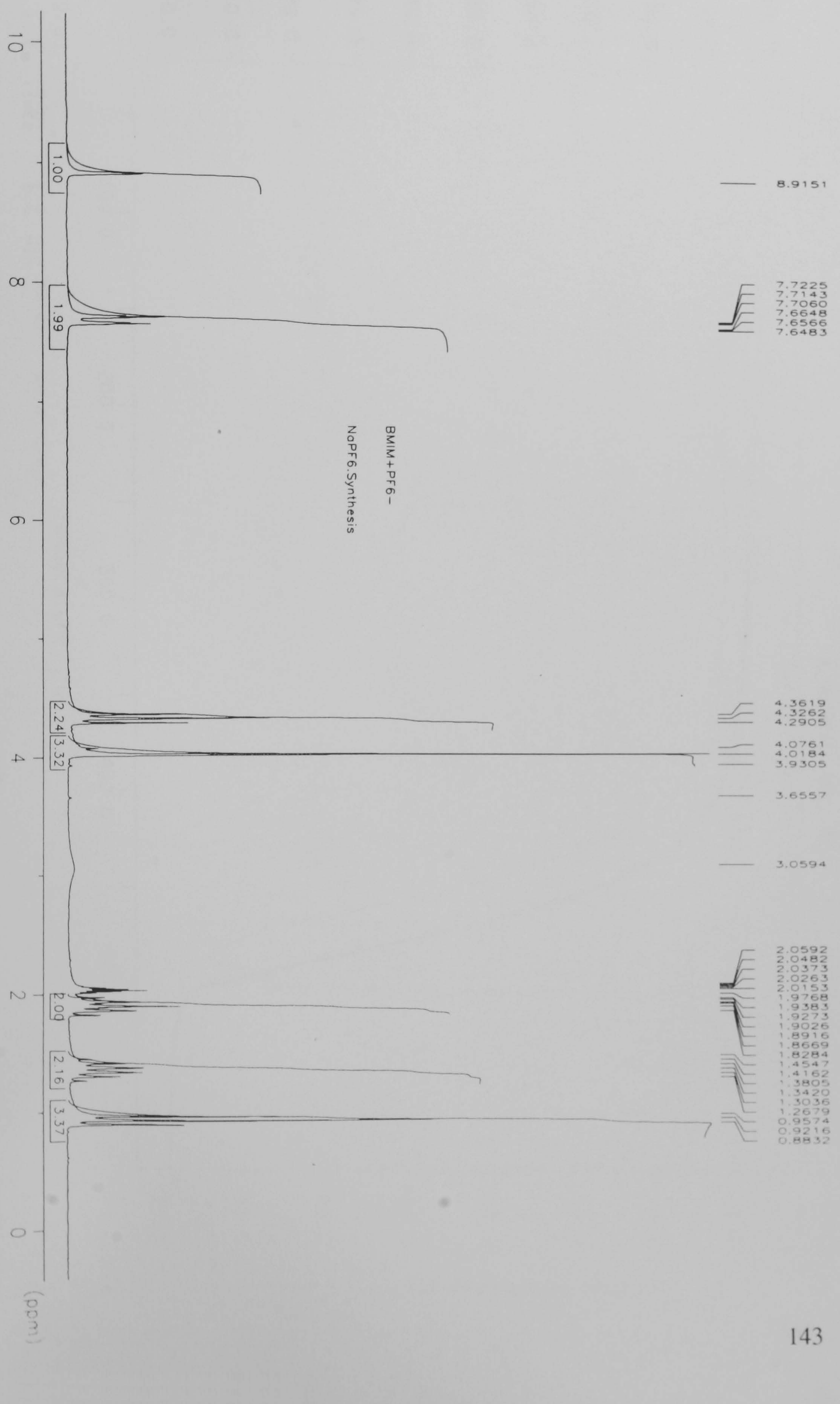


FIGURE 2.9.4a TGA [bmim][BF$_4$]

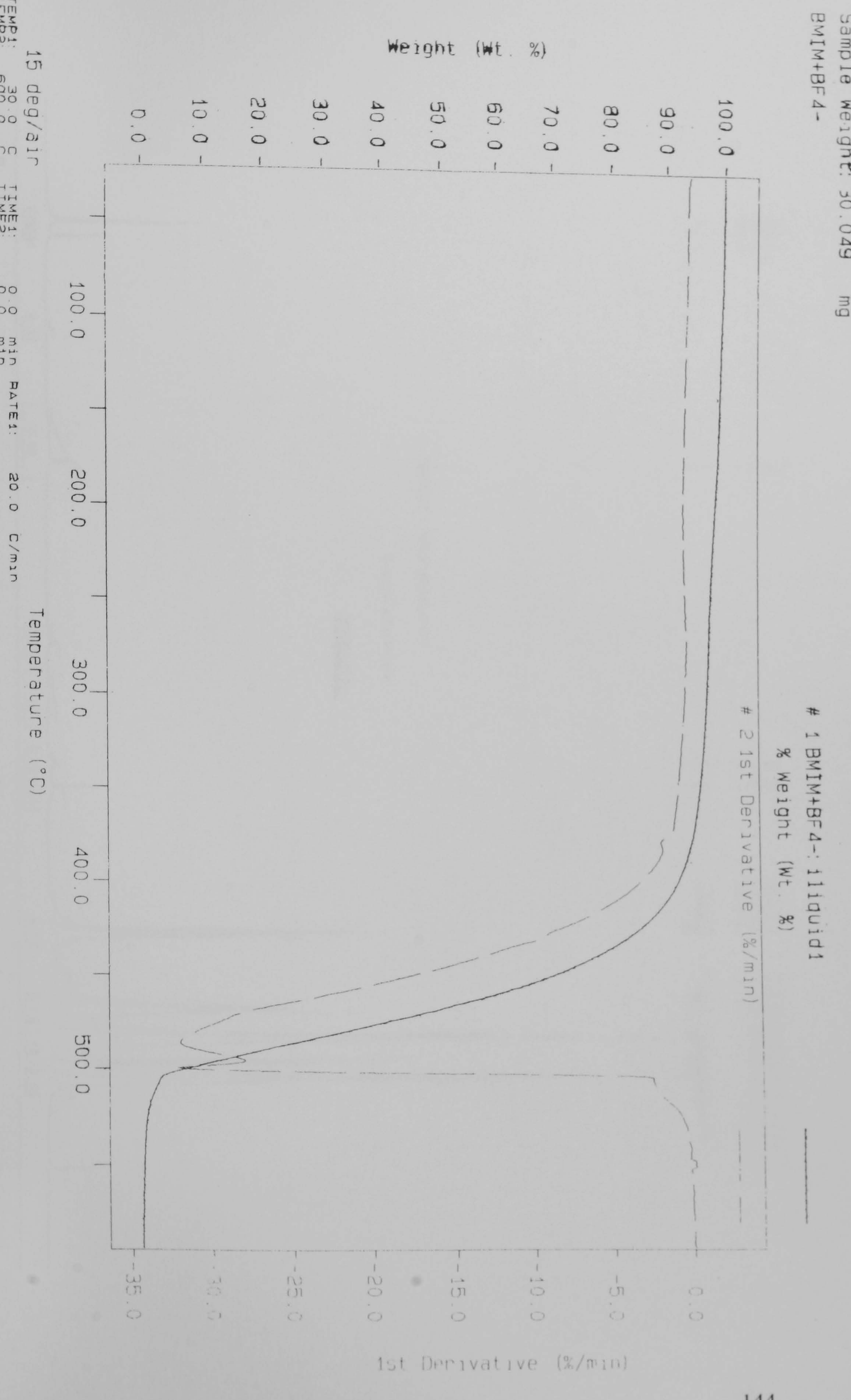


FIGURE 3.4.1a ^{1}H NMR 1-pentene hydroformylation in [bmim][PF_6]

FIGURE 3.5.1a ^1H NMR 1-decene hydroformylation in $[bmim][BF_4]$ - 1hr reaction

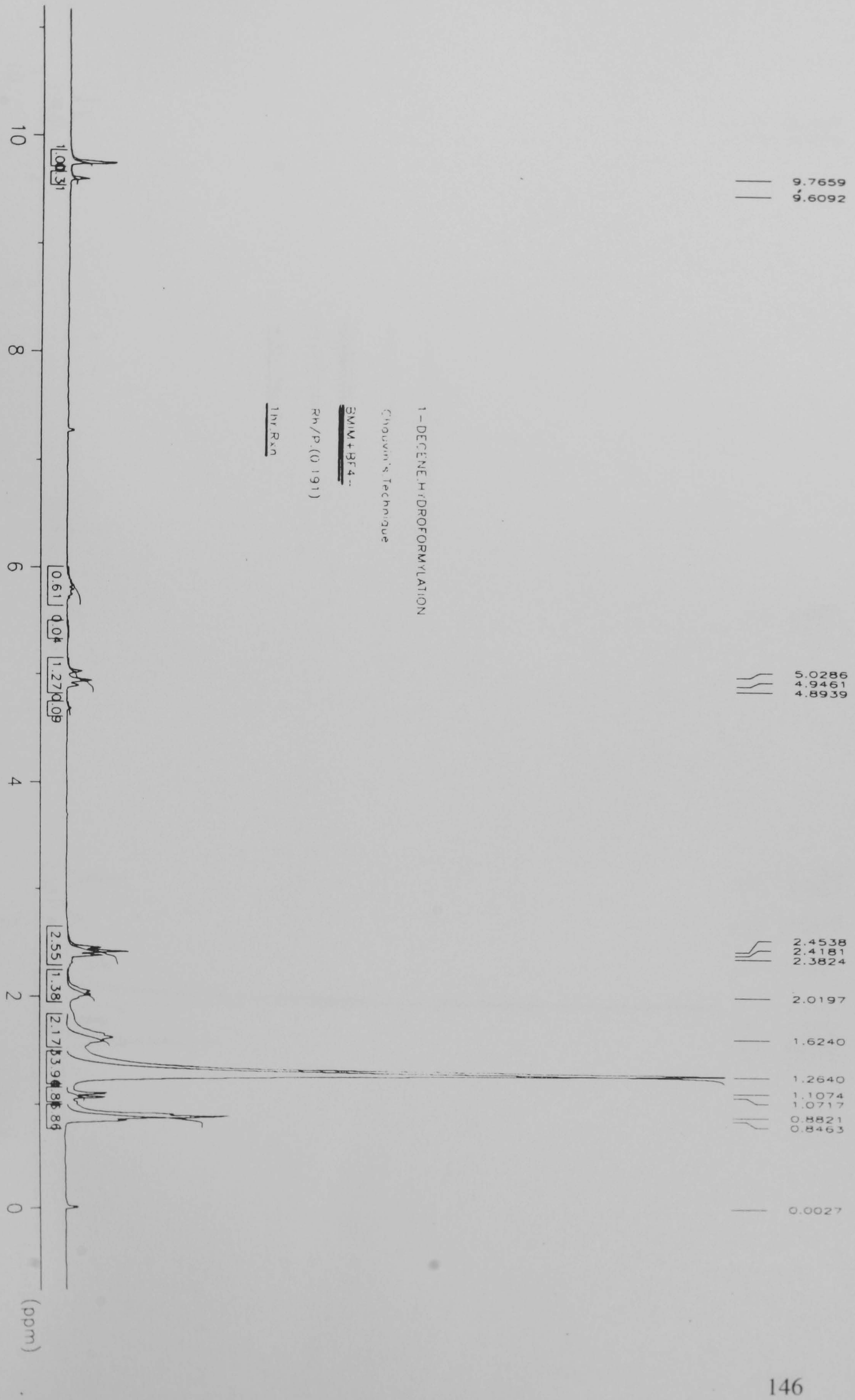


FIGURE 3.6.1a ^1H NMR 1-decene hydroformylation in [bmim][BF_4] - 1hr. H_2O reaction

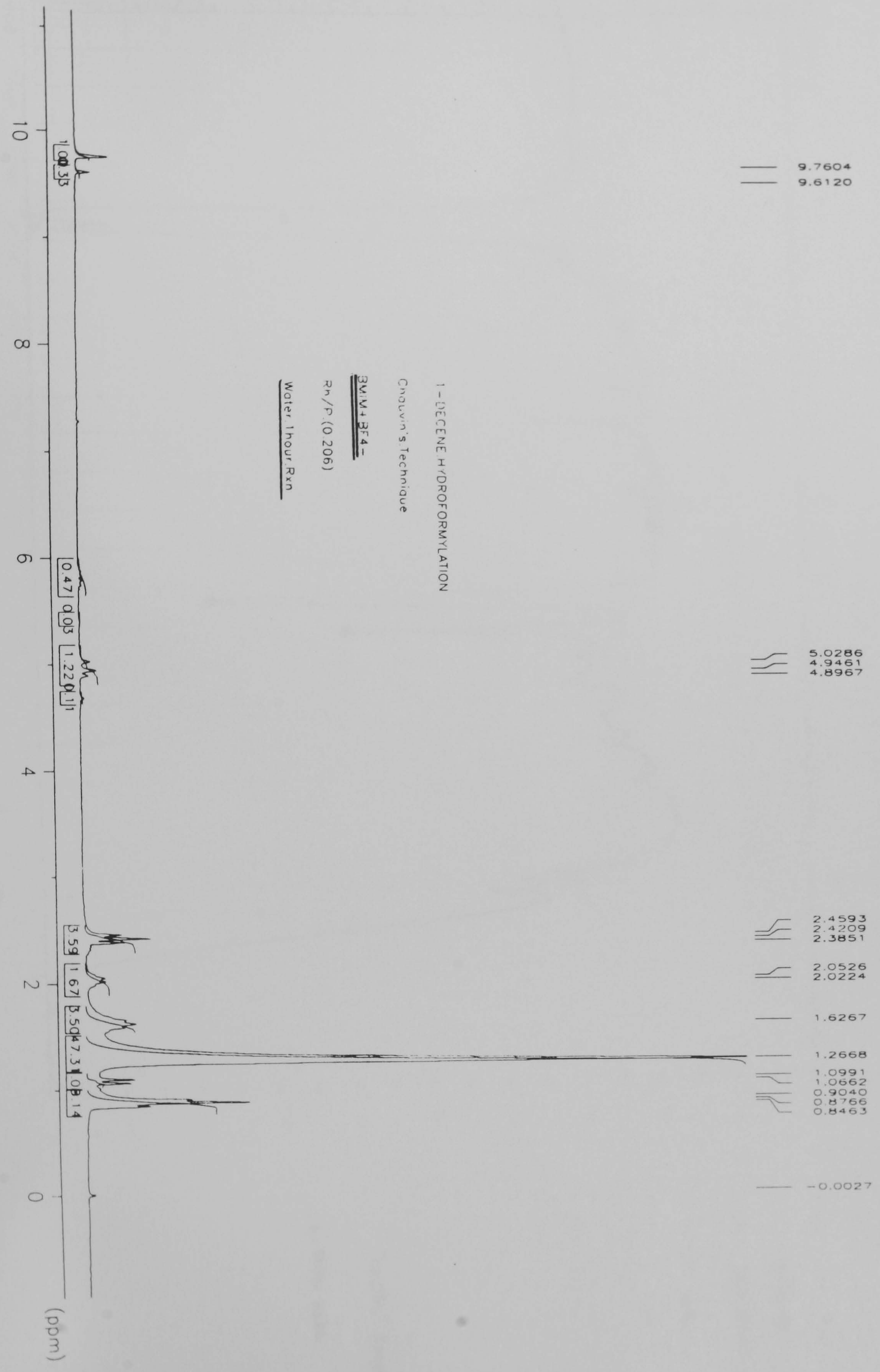
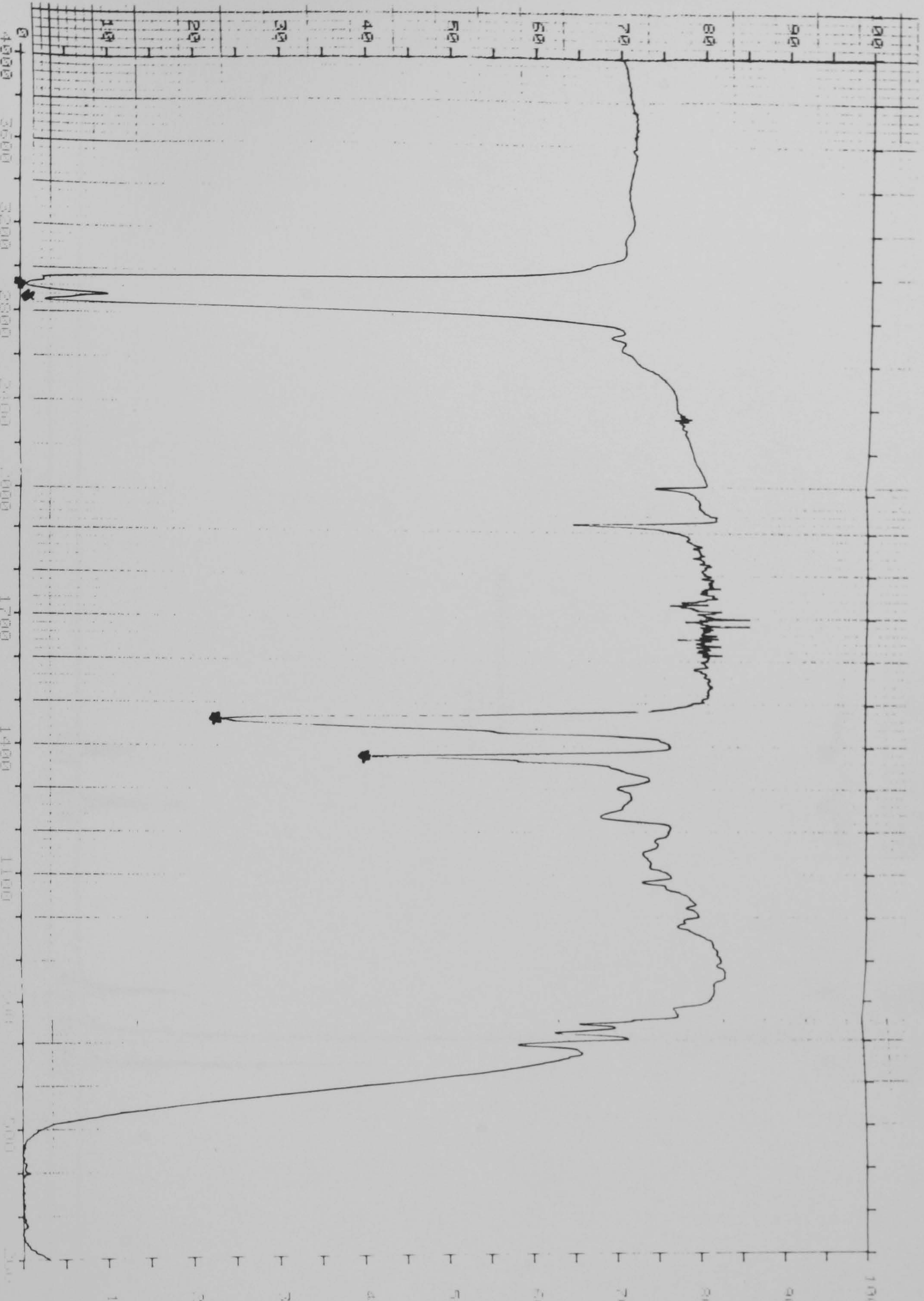


FIGURE 3.8a IR Spectra - Catalyst Investigation



MODEL
DATE 04-05-99.
SAMPLE "CAT. SPECIES - CRYSTALS/NUJOL"
OPERATOR CMC.
RANGE 4000
SLIT PROGRAM
FILTER
ALT GRATING CH
SMOOTH LEVEL
ORD. 0
CHART

"CRYSTAL" Samples :-

★ = Nujol peaks.

FIGURE 3.9.1a ^1H NMR 1-decene hydroformylation

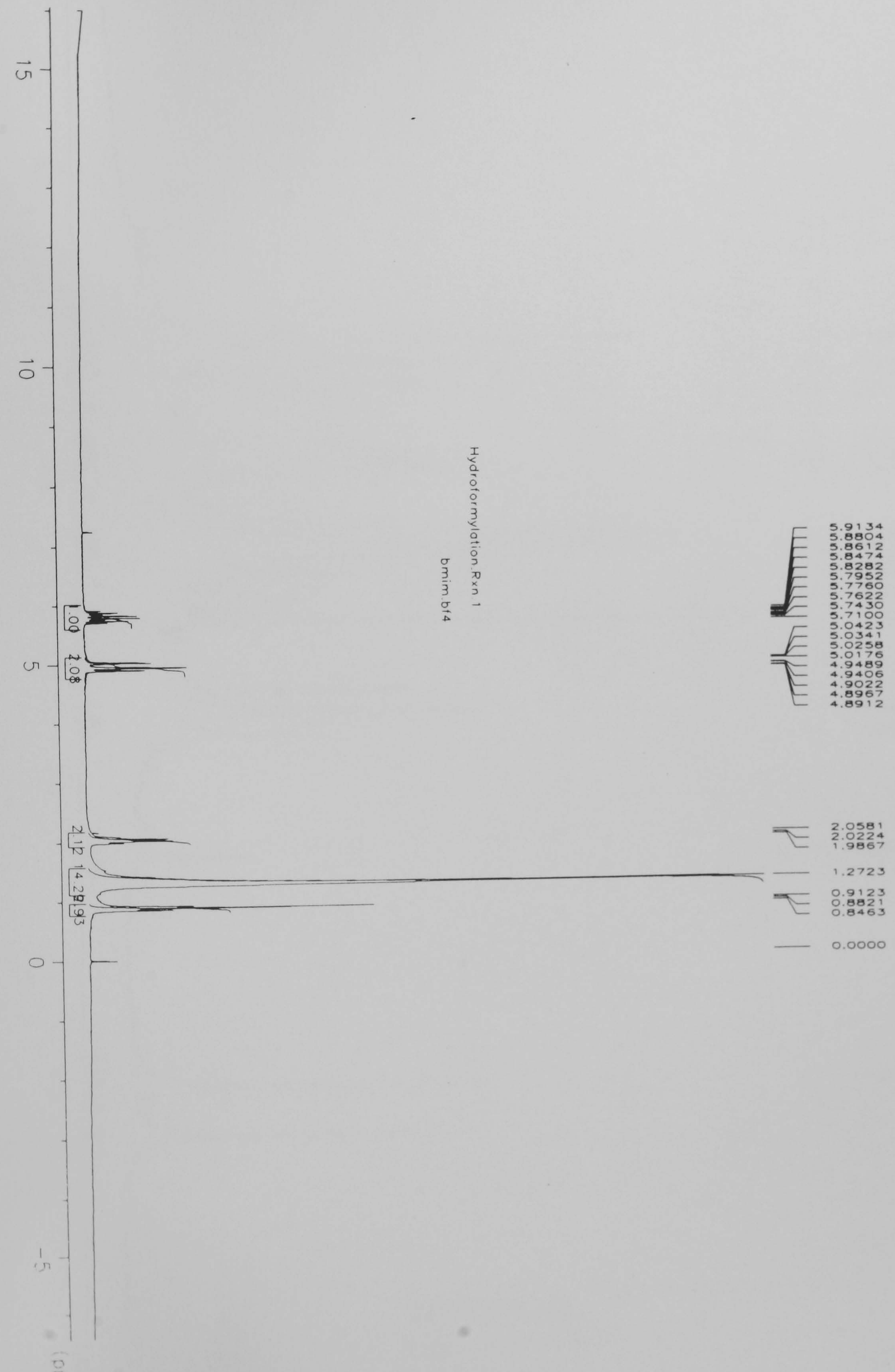


FIGURE 4.8a ^{1}H NMR Heck Reaction, Butyl Acrylate, [bmim][Br]