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## Thiazolium and Benzothiazolium Ionic Liquids

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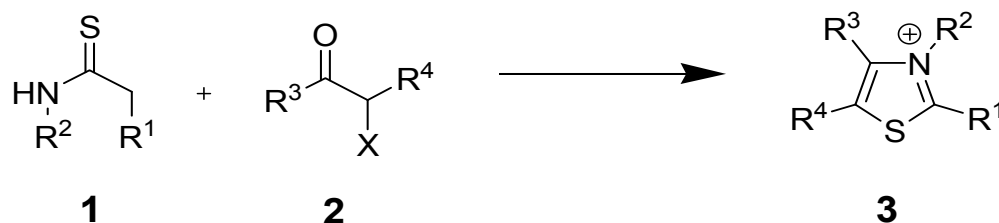
### 1. Introduction

In a general perspective the term "ionic liquid" includes all classical molten salts (Visser 2002), even those which are composed of more thermally stable ions, such as sodium with chloride or potassium with nitrate. Although the term dates back as early as 1943 (Barrer 1943), in the language/field of chemistry an ionic liquid (IL) is specifically a salt having organic cation and organic/inorganic anion, which is liquid at room temperature or reaction temperature. Wasserscheid and Keim (Wasserscheid&Keim 2000) have proposed that an organic salt having a melting point below 100 °C could be called ionic liquid and this is indeed now one of the most widely accepted definitions of ionic liquids. Some scientists consider this set point as 150 °C (Huddleston *et al.* 2001). The low melting behaviour of ionic liquids is due to the poor coordination of the cations and anions. The strength of coordination depends upon the nature and structure of the cation and anion and a little unsymmetry in the structure may lead to decrease the coordination of the ions.

The most common heteroaromatic based ionic liquids include imidazolium, thiazolium, tetrazolium, pyridinium *etc.* However thiazolium and benzothiazolium based ionic liquids are very scarcely studied. This chapter will describe the synthesis and applications of thiazolium and benzothiazolium based ionic liquids.

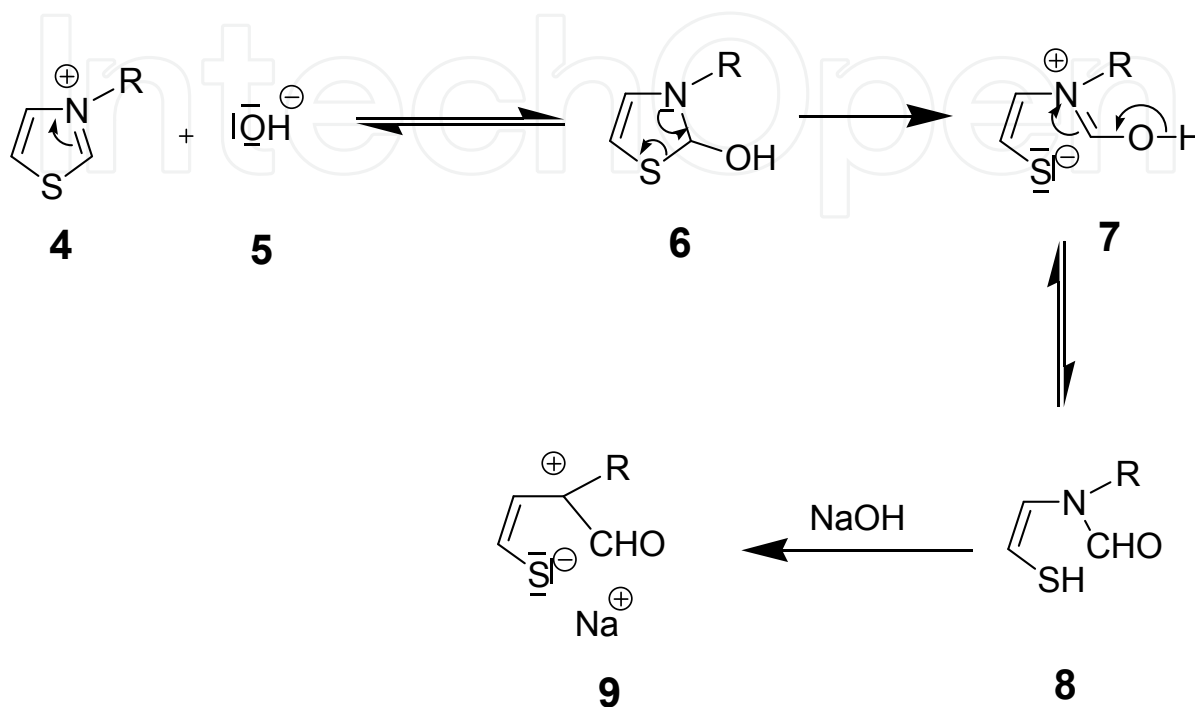
### 2. Thiazolium salts / ionic liquids

The thiazoles are known in chemistry mainly due to their presence in thiamine (Vitamin B<sub>1</sub>) in the form of substituted thiazolium salt (Mcguinness *et al.* 2001). Thiazolium salts can be obtained successfully by a modification of the Hantzsch's thiazole synthesis. This method is particularly valuable for those thiazolium compounds in which the substituent on the ring nitrogen cannot be introduced by direct alkylation, for example, aryl or heteroaryl thiazolium salts.



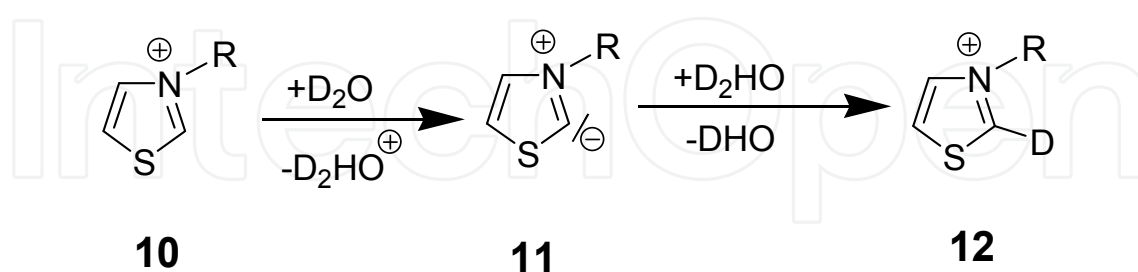
Scheme 1. Preparation of thiazolium salts.

*N*-Monosubstituted thioamides (**1**) can be cyclized with  $\alpha$ -halocarbonyl compounds (**2**) to give thiazolium salts (**3**) in excellent yields. Quaternization of thiazole strongly enhances the reactivity of the thiazole ring towards nucleophiles. The following reactions have been observed. Addition of a nucleophile to the 2-position to give a pseudobase, followed by ring opening, e.g. with sodium hydroxide solution:



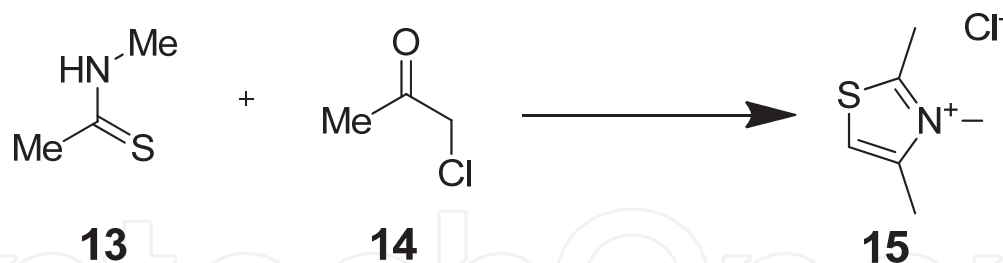
Scheme 2. Reactivity of thiazolium salts

3-Alkyl substituted thiazolium salts react in an analogous way. The deutero-deprotonation of 3-alkylthiazolium salts (e.g. **10**) by  $D_2O$  proceeds via an *N*-ylide (e.g. **11**, scheme-3).



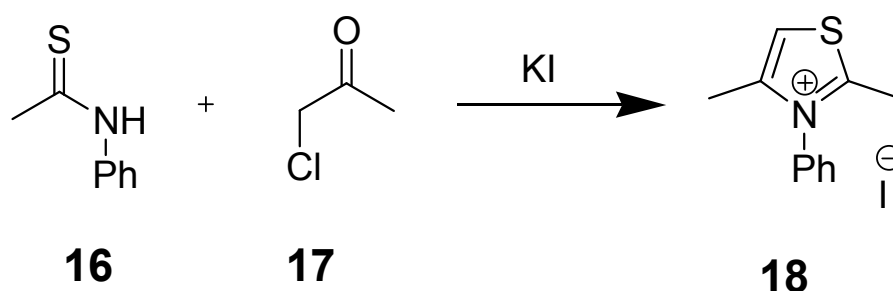
Scheme 3. Deuterium exchange of thiazolium salts.

Todd *et al.* have reported a very convenient method for the preparation of *N*-alkylthiazolium salts. The method of Hantzsch thiazole synthesis was modified to obtain direct formation of thiazolium salts. *N*-substituted thioamides (e.g. **13**) were used instead of the unsubstituted thioamides to obtain the desired thiazolium salts (e.g. **15**) (Todd *et al.* 1936)



Scheme 4. A convenient method for thiazolium salts.

Schöberl and Stock have reported the synthesis of *N*-Benzyl-2,4-dimethylthiazolium chloride followed by the ion exchange with potassium iodide to get *N*-Phenyl-2,4-dimethylthiazolium iodide (18) from *N*-phenylthioacetanilide (16) and chloroacetone (17) (scheme-5) (Schöberl&Stock 1940).

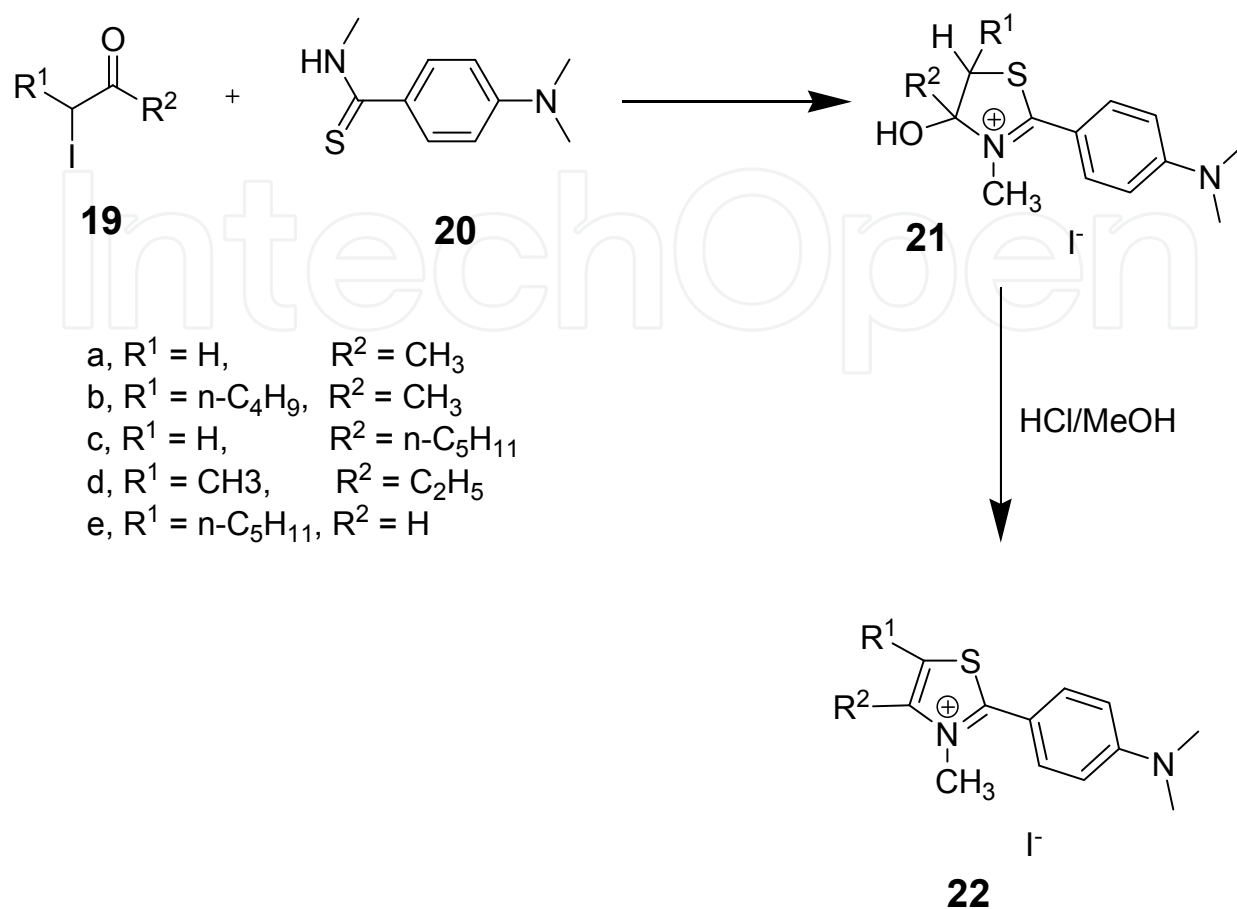


Scheme 5. Preparation of *N*-phenyl-2,4-dimethylthiazolium iodide.

The reaction of *N*-methyl-*p*-dimethylaminothiobenzamide (20) with a number of  $\alpha$ -halo ketones (19a-19d) and one  $\alpha$ -halo aldehyde (19e) have been studied by Egan and his coworkers and they were able to get stable 4-hydroxy-2-thiazolinium derivatives, which were isolated as the iodide salts (21) (scheme-6) (Egan *et al.* 1968). The 4-hydroxy-2-thiazolinium salts (21) were stable in neutral and basic media, but could be dehydrated to the thiazolium salts (22) by treating with methanolic hydrogen chloride. Dehydration could also be accomplished, although less conveniently, by treating with methanesulfonyl chloride containing sulfur dioxide in the presence of collidine (Hazen&Rosenburg 1964).

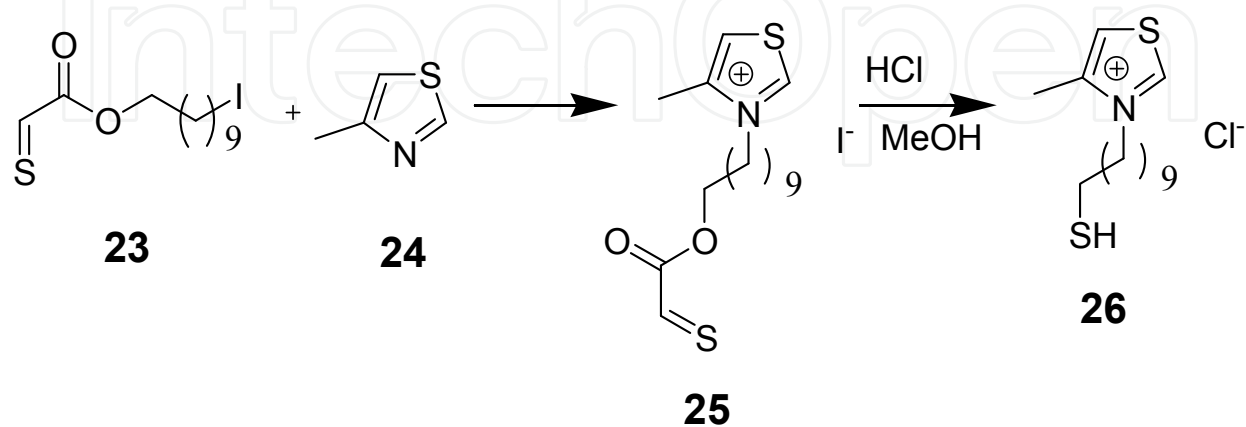
There are many reviews and books regarding the synthesis and applications of thiazolium salts in different fields (Eicher *et al.* 2003). However thiazolium based ionic liquids have not been well documented in the literature. Many researchers have studied the preparation and applications of the thiazole based ionic liquids in different reactions. A brief account of that has been given here.

Chen *et al.* prepared [2-<sup>13</sup>C]-labeled 3-benzyl and 3-methylthiazolium tetrafluoroborate (may be liquids in nature) and studied the reactions of benzaldehyde with thiazolium salts in Me<sub>2</sub>SO. They found that the reactions of thiazolium salts with aromatic aldehydes: *p*-anisaldehyde and cinnamaldehyde, in MeOH/MeONa, led to the formation of significant amounts of the corresponding dimethyl acetals, rather than to the benzoin products (Chen *et al.* 1994).



Scheme 6. Thiazolinium derivatives.

Motesharei and Myles prepared thiazolium salts (e.g. **26**, scheme 7) for the synthesis of self-assembled thiazolium thiolate monolayers on gold (fig-1) which promoted the acyloin condensation. (Motesharei&Myles 1997)



Scheme 7. Thiazolium thiols preparation.

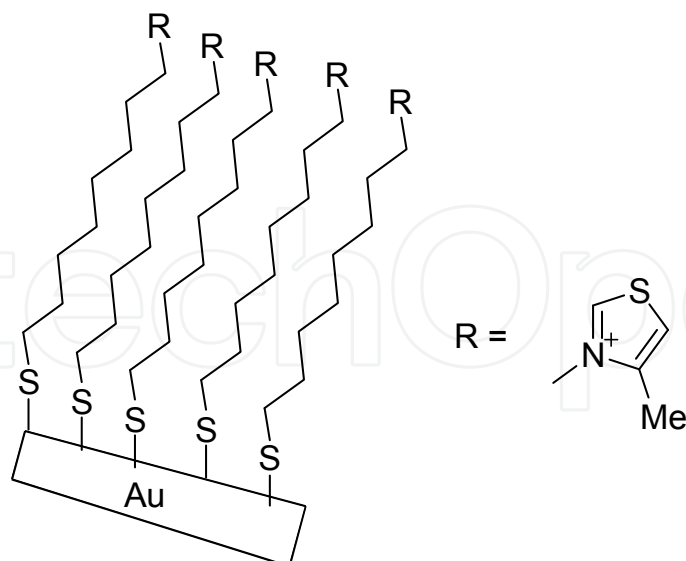
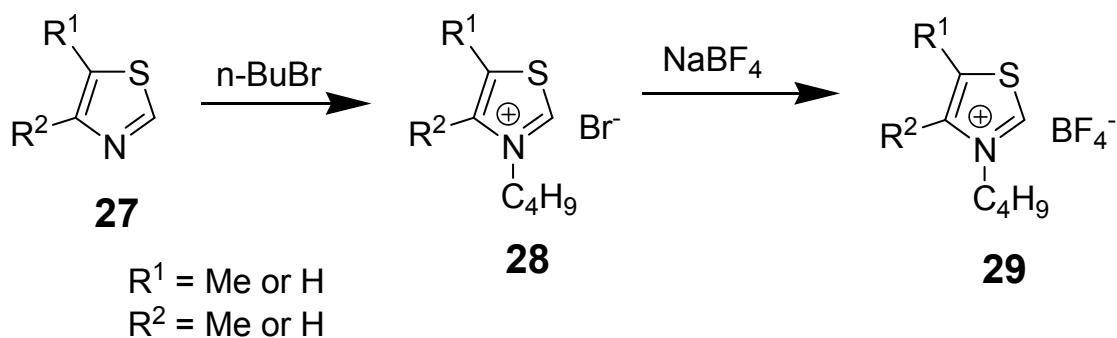


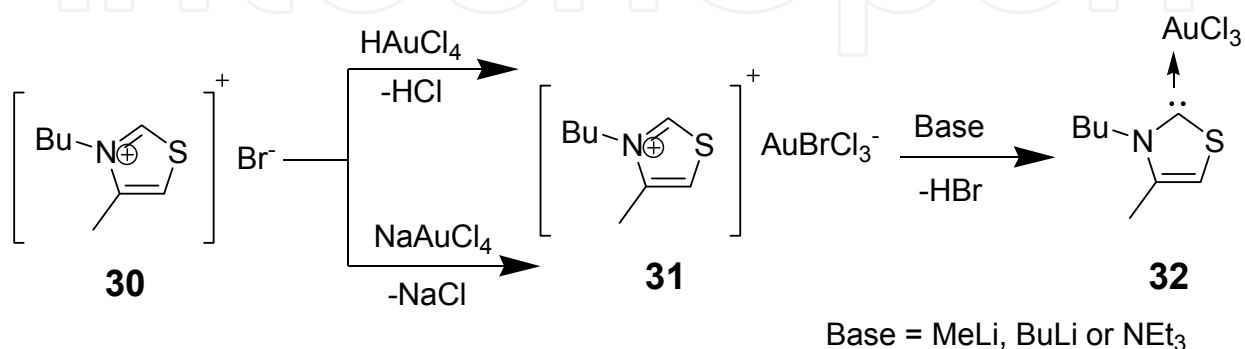
Fig. 1. Thiazolium thiolate monolayers on gold

Davis and Forrester prepared thiazolium based organic ionic liquids (**29**, scheme-8) and used them for catalyzing the benzoin condensation (Davis&Forrester 1999).



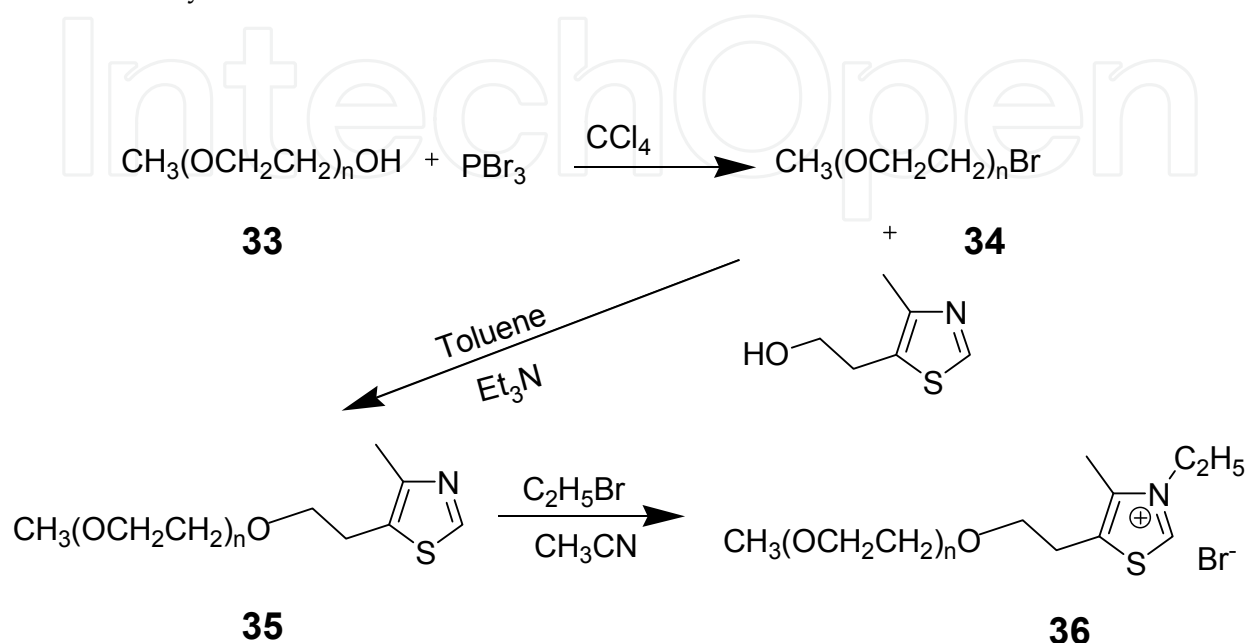
Scheme 8. Tetrafluoroborate thiazolium salts.

The first thiazolium gold (III) compound (**32**) that qualifies as an ionic liquid has been prepared by Deetlefs *et.al.* during the study of stoichiometric and catalytic reactions of gold utilizing ionic liquids (scheme-9) (Deetlefs *et al.* 2002).



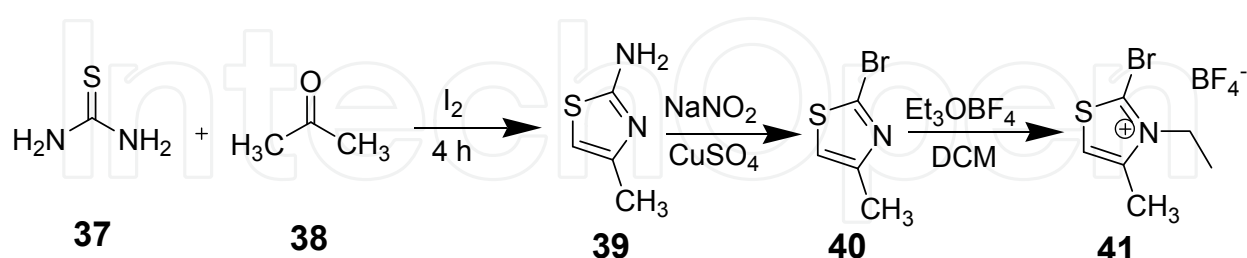
Scheme 9. Thiazolium- gold catalyst.

Yu *et al.* have reported a series of thermoregulated thiazolium based ionic liquids containing polyether moieties attached to thiazolium cation (**36**, scheme-10). These thermoregulated ionic liquids (**36**) were used as catalysts in the Stetter reaction (Yu *et al.* 2010). The ionic liquids were pale yellow, viscous liquids at room temperature. The viscosity was found to increase with the length of the polyether chain. The structures of these ionic liquids were determined by NMR.



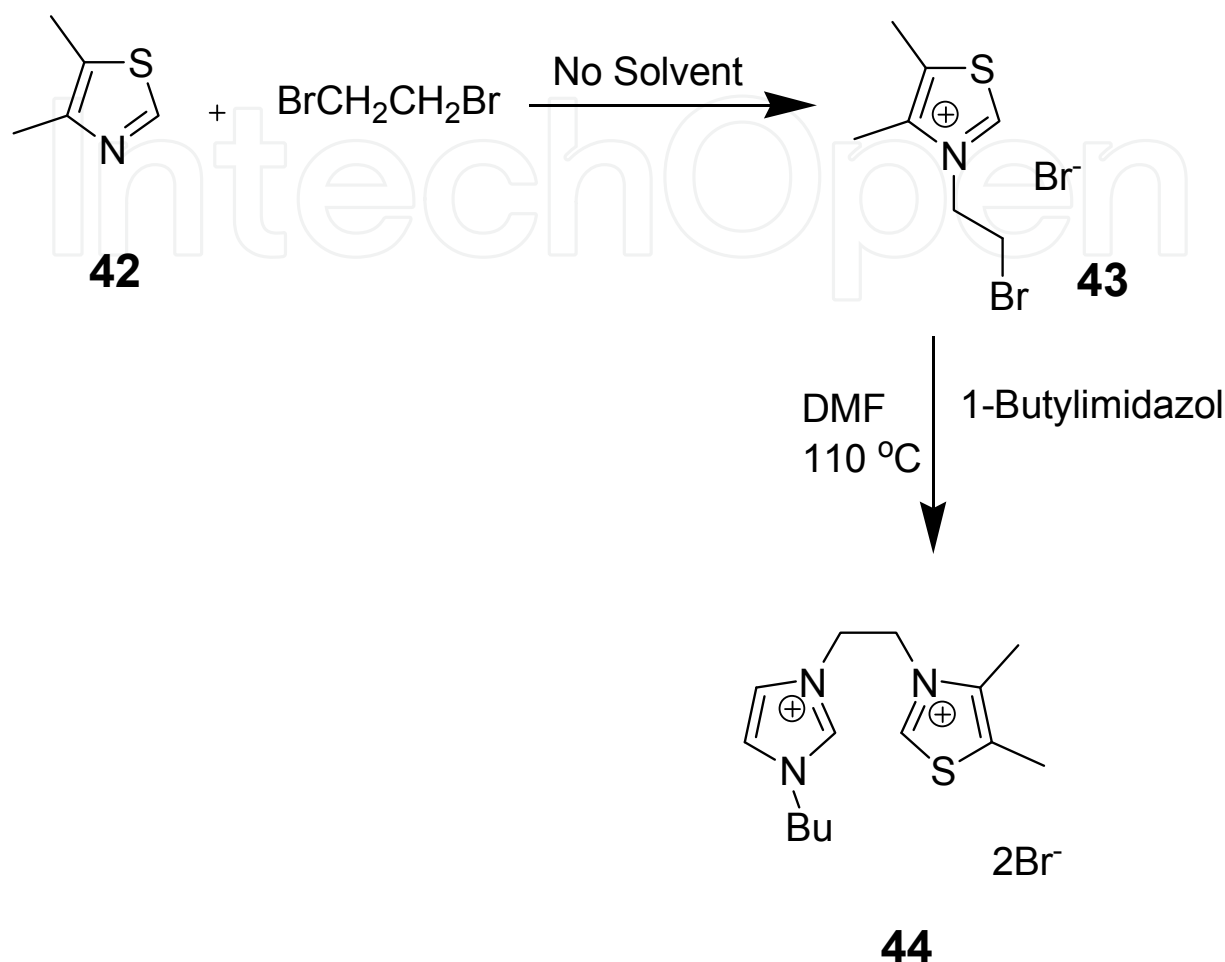
Scheme 10. Thermoregulated thiazolium based ionic liquids.

Li and Xu prepared the 2-bromo-3-ethyl-4-methylthiazolinium tetrafluoroborate (BEMT) (**41**, scheme-11), and found it to be an efficient coupling reagent for hindered amino acids. It was used for the coupling of *N*-alkyl or  $\alpha,\alpha$ -dialkyl amino acids (Li&Xu 1999).



Scheme 11. Preparation of 2-bromo-3-ethyl-4-methylthiazolinium tetrafluoroborate (BEMT).

The dramatic influence of a new tailor-made, task-specific, and stable ionic liquid, 3-[2-(1-butyl-1*H*-imidazol-3-ium-3-yl)ethyl]-4,5-dimethyl-1,3-thiazol-3-ium bromide (**44**, scheme-12), in benzoin condensations have been described by Mohanazadeh and Aghvami (Mohanazadeh&Aghvami 2007).



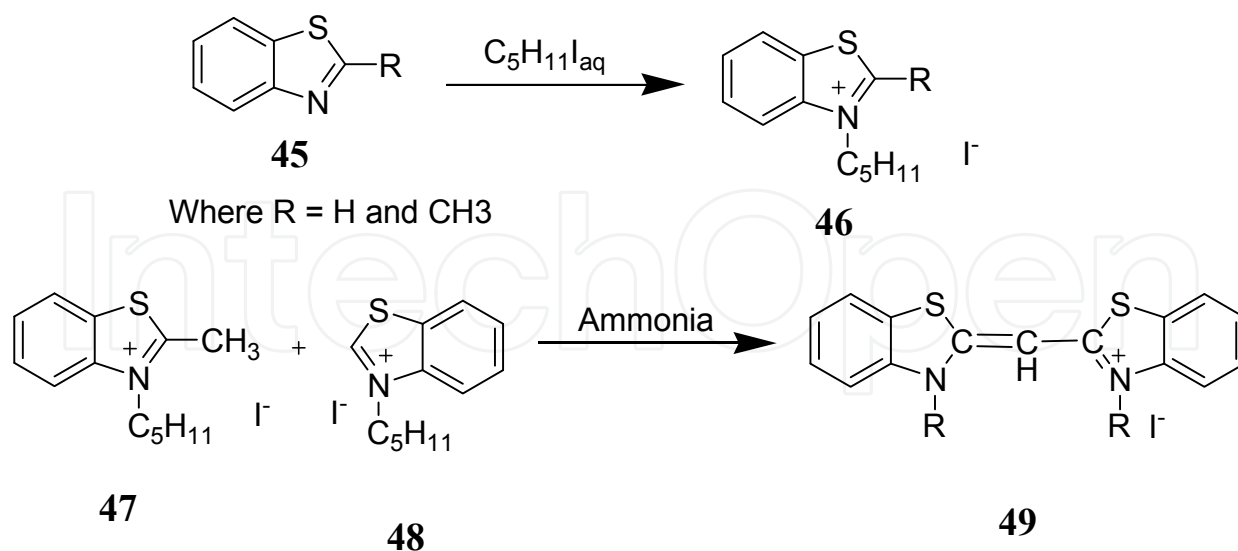
Scheme 12. Preparation of 3-[2-(1-butyl-1H-imidazol-3-ium-3-yl)ethyl]-4,5-dimethyl-1,3-thiazol-3-ium bromide.

### 3. Benzothiazolium salts and ionic liquids

Benzothiazoliums are also a part of many important dyes (Svetlichnyĭ *et al.* 2007) *e.g.* Cyanine Dyes, Thioflavin T & S, (Stsiapura *et al.* 2007) (Sabaté&Saupe 2007) Direct yellow 7, Carnotine, Primuline, *etc.* In medicine the benzothiazolium salts play an important role, for example Riluzole a benzothiazole-based drug is used to treat amyotrophic lateral sclerosis. (Kitzman 2009).

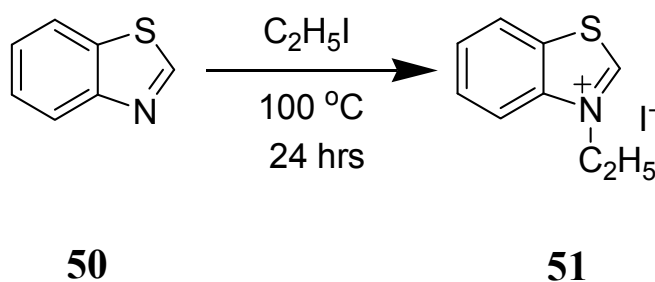
During the attempts to prepare the cyanine dyes (49) in 1887, Hofmann was able to isolate benzothiazolium salts which were produced by reaction of benzothiazole (47) with amyl iodide (Scheme-13) (Hofmann 1887).





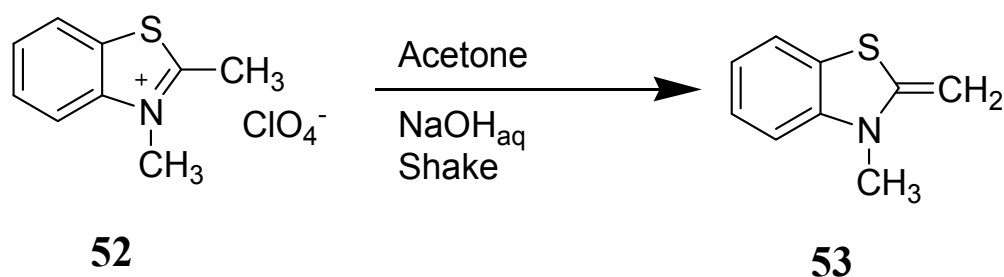
Scheme 13. Hofmann Benzothiazolium synthesis

Mills (1922) prepared N-Ethylbenzothiazolium iodide (**51**), to be used in the synthesis of thiocyanine dyes, by heating the equimolar quantities of ethyl iodide and benzothiazole (**50**) (scheme-14) (Mills 1922).



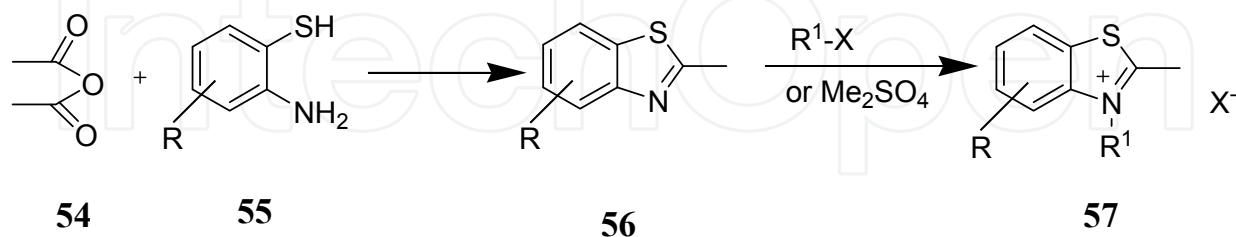
Scheme 14. Mills benzothiazolium synthesis

Then in 1925 Konig used N,2-dimethylbenzothiazolium perchlorate (**52**) for the preparation of methylene base (**53**, scheme-15) which was used in the synthesis of thiocyanine dyes (Konig&Meier 1925). The quaternary salts of benzothiazoles also found recognition in 1928 by Clark (Clark 1928) while studying the absorption sensitivity of the methylene bases from the quaternary salts of 2-methyl benzothiazole.



Scheme 15. Konig preparation of methylene bases from benzothiazolium salts

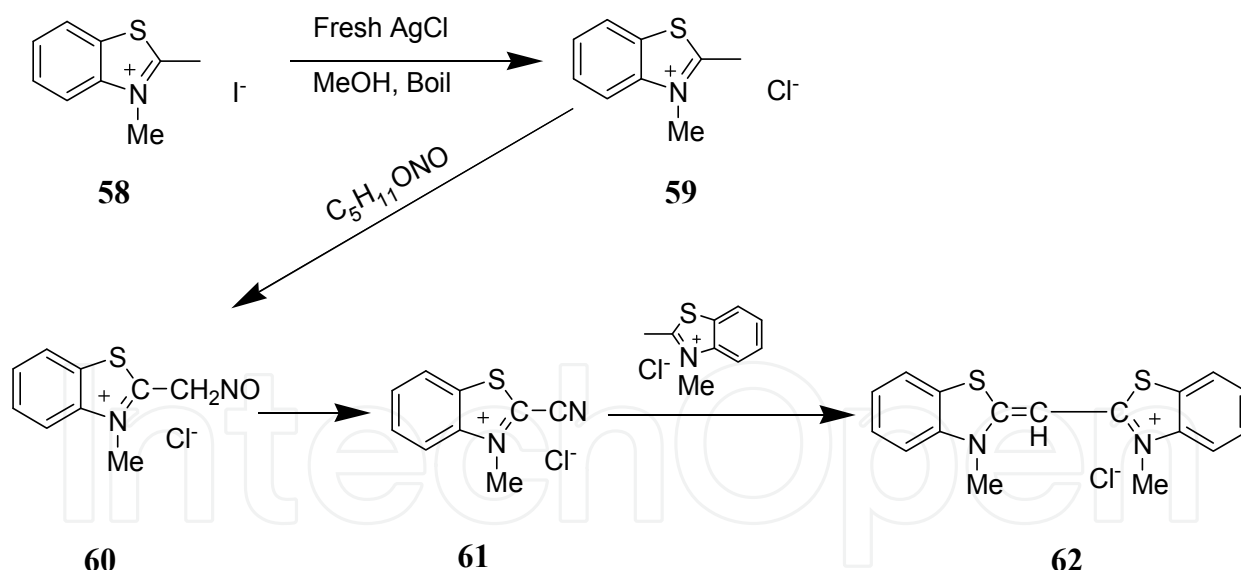
In the same year König (König 1928) used the quaternary salts of benzothiazole for the preparation of the heterocyclopolymethine dyes during investigations on color and constitution. He claimed that a number of 2-methylbenzothiazoles (**56**) can be prepared much more conveniently by heating alkaline solutions of 2-aminobenzenethiol (**55**) with acetic anhydride (**54**). The benzothiazoles (**56**) were converted to quaternary salts (**57**) by reacting with alkyl halides or dimethyl sulfate (scheme-16).



Where X= Halogen or CH<sub>3</sub>SO<sub>4</sub>

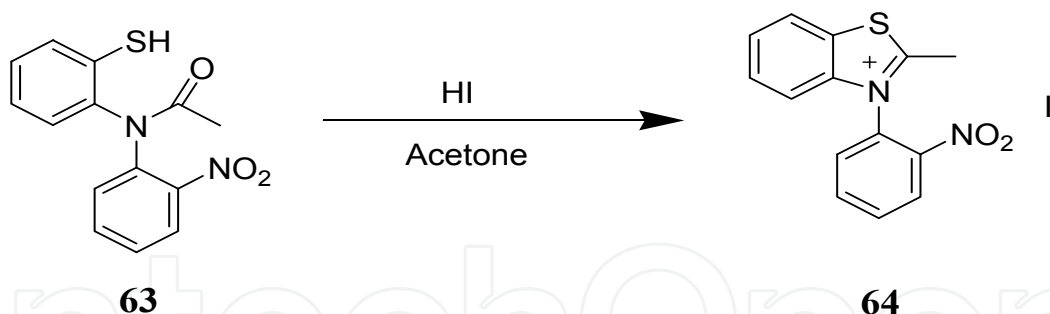
Scheme 16. König benzothiazolium synthesis from 2-aminobenzenethiol

Fisher and Hamer prepared benzothiazolinium chlorides (e.g. **59**) from the corresponding iodides (e.g. **58**), these chlorides (e.g. **59**) were then converted to 2-cyano benzothiazolium chlorides (e.g. **61**) for their onward conversion to thiocyanines (**62**, scheme-17) (Fisher&Hamer 1930).



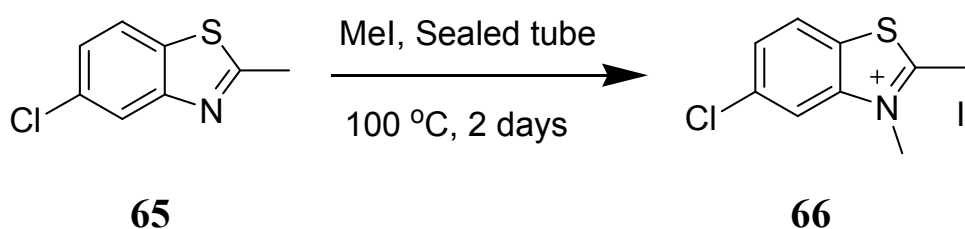
Scheme 17. Fisher and co-workers benzothiazolium synthesis

In 1935 Evans and Smiles obtained 2-methyl-*N*-(2-nitrophenyl)benzothiazolium iodide (**64**) when 2-[*N*-acetyl-*N*-(2-nitrophenylamino)]benzenethiol (**63**) was treated with hydriodic acid in acetone (scheme-18). The same salt was also isolated when 2-[*N*-acetyl-*N*-(2-nitrophenylamino)]benzenesulfinic acid was reduced with hydriodic and sulfurous acids. The corresponding perchlorate was prepared by treating the benzenethiol with perchloric acid (Evans&Smiles 1935).



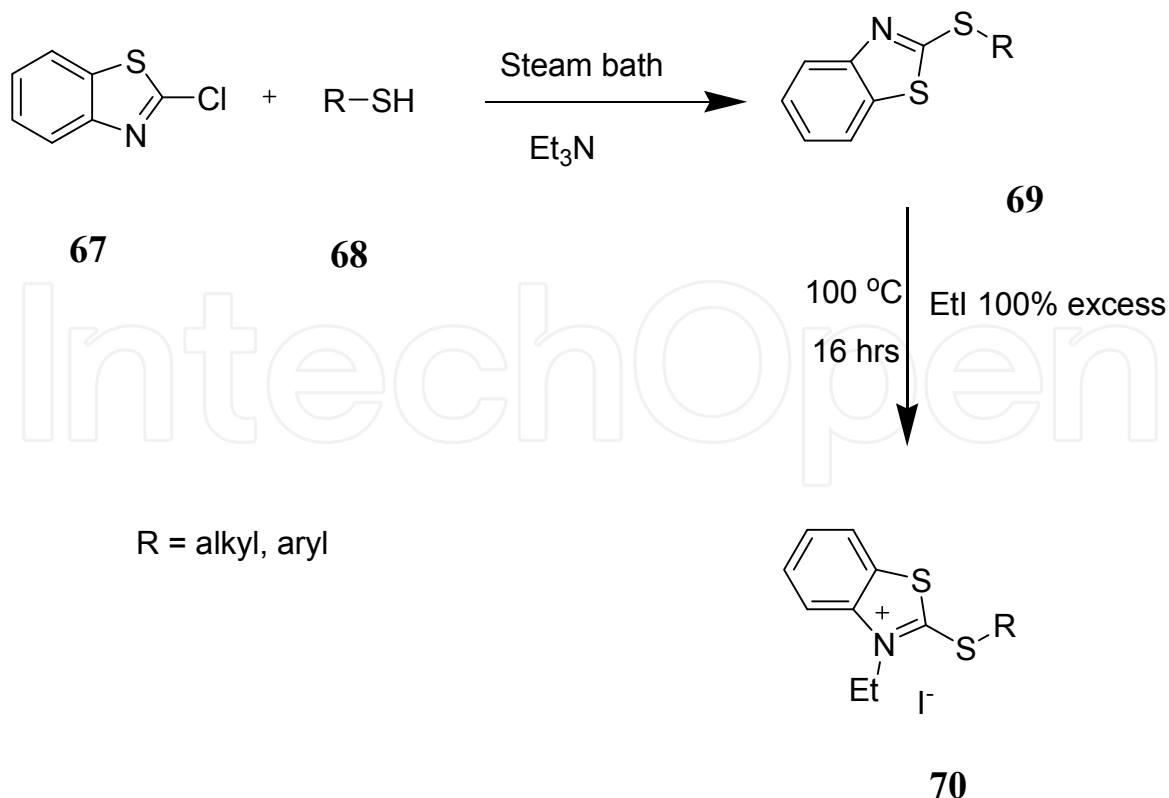
Scheme 18. Evans benzothiazolium synthesis

After one year Beilenson and Hamer prepared the benzothiazoles based quaternary salts (e.g. **66**) by sealed tube reactions of benzothiazoles (e.g. **65**) with methyl iodide at 100 °C (scheme-19) and used them for the preparation of cyanine dyes (Beilenson&Hamer 1936).



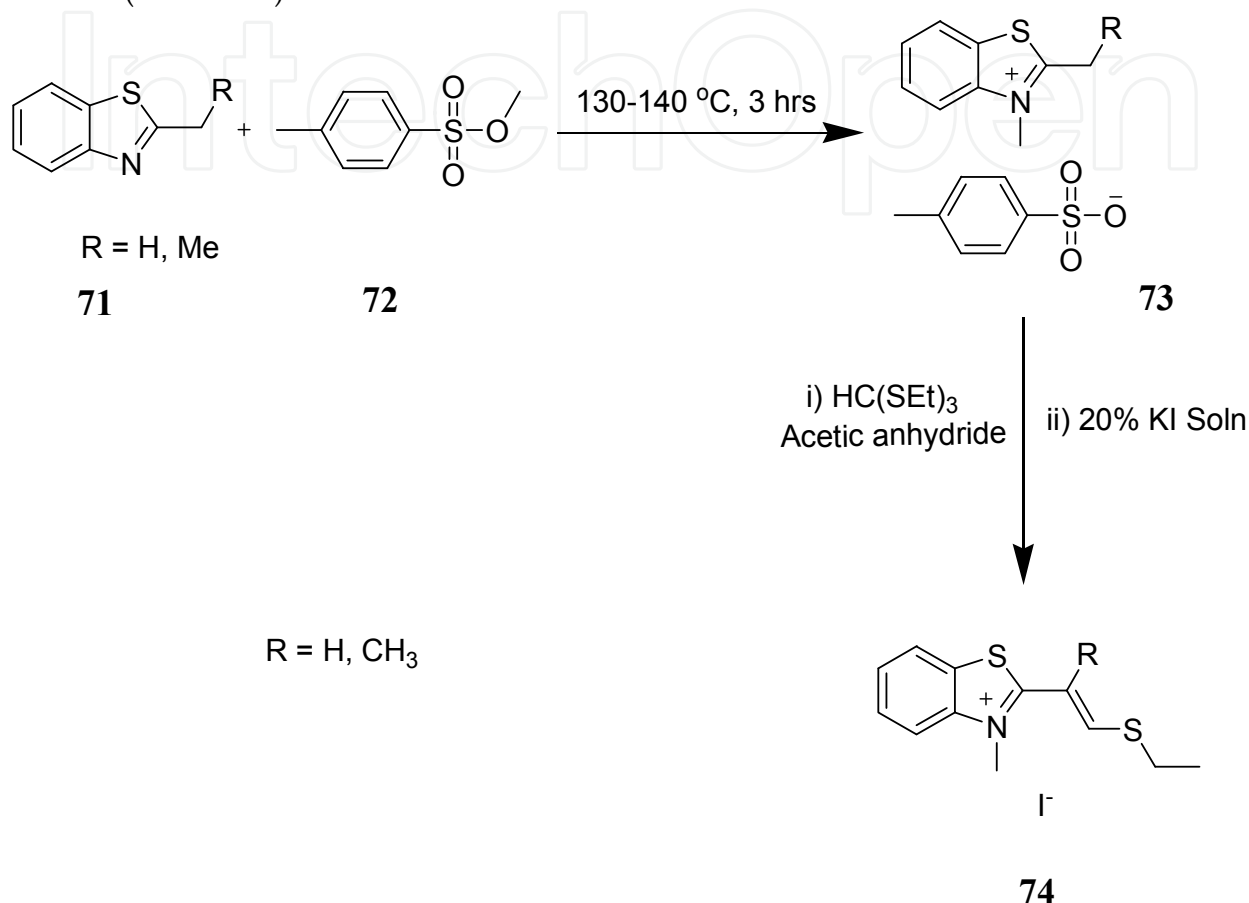
Scheme 19. Beilenson and Hamer benzothiazolium synthesis

In 1941 Brooker and co-workers prepared quaternary salts (**70**) of 2-alkyl/aryl sulfanyl benzothiazoles (**69**) (scheme-20) (Brooker *et al.* 1941).



Scheme 20. Brooker and co-workers benzothiazolium synthesis

In 1948 Kendall and Majer prepared (Kendall&Majer 1948) 2-(2-ethylsulfanylvinyl)-*N*-methylbenzthiazolium iodide (**74**, R = H) and 2-(2-ethylsulfanylvinyl)-1-methyl-*N*-methylbenzthiazolium iodide (**74**, R = Me) by fusing 2-methylbenzothiazole (**71**, R = H) and 2-ethylbenzothiazole (**71**, R = Me) with methyl-*p*-toluene sulphonate respectively followed by treating the resultant quaternary salts with tri(ethylsulfanylmethane and 20% KI solution (scheme-21).

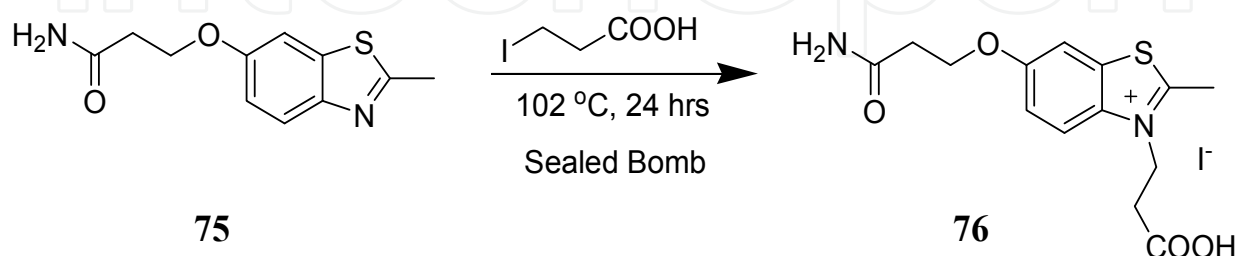


Scheme 21. Kendall and Majer preparation of 2-(2-ethylsulfanylvinyl)-*N*-methylbenzthiazolium iodide

A direct synthesis of quaternary salts (*e.g.* alkylsulfates, iodides, bromides, perchlorates) of benzothiazole from 2-aminobenzenethiol has been narrated in literature by Kiprianov and Pazenko. Fry and Kendall synthesized quaternary salts of 2-alkylsulfanylbzothiazole and used them in the synthesis of thiacyanine dyes (Fry&Kendall 1951). Similar type of synthesis of 2-haloalkylsulfanylbzothiazolium salts was carried out by Knott in 1955 (Knott 1955). Brooker (1951) prepared benzothiazolium salts from substituted benzothiazoline and *p*-toluenesulfonate for further conversion to cyanine dyes (Brooker *et al.* 1951).

Kiprianov (1957) studied the relative rates of formation of quaternary salts of 2-methylbenzothiazole with methyl iodide, methyl sulfate, and methyl esters of sulfonic acids and *p*-nitrosulfonic acids. He found that the reaction with methyl 2-nitrobenzenesulfonate was six times faster than that with  $\text{Me}_2\text{SO}_4$ , while the methyl esters of the 2,3- and 2,4-dinitrobenzenesulfonic acid reacted sixty times more rapidly than did  $\text{Me}_2\text{SO}_4$ . Such esters afford a method for very mild alkylation of very weak bases (Kiprianov&Tolmachev 1957).

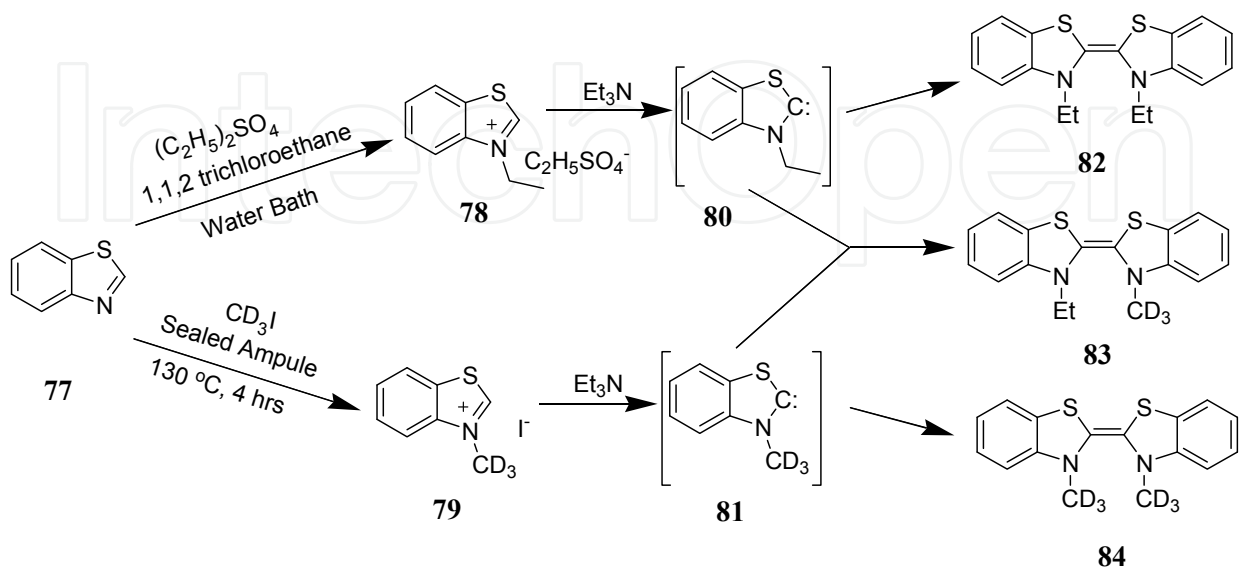
Benzothiazolium salts have great use in the synthesis of different types of cyanine dyes while on the other hand the benzothiazolium salts have also been studied for their activity in different biological systems. In 1959 Pianka and Hall studied the fungi toxicity of 3-ethylbenzothiazolium iodide and 3-ethylbenzoxazolium ethyl sulfate derivatives and activity was found to reside only in the cation (Pianka&Hall 1959). In the same year (1959) Leslie and co-workers patented a method for the preparation of quaternary salts of benzothiazole for making the thiacyanine dyes. In 1961 Horwitz and co-workers prepared a benzothiazolium salt (76) from 6-(2-aminocarbonyl)ethoxy-2-methylbenzothiazole (75, Scheme-22) for the use in preparation of different dyes.



Scheme 22. Horwitz and co-workers preparation of benzothiazolium salts

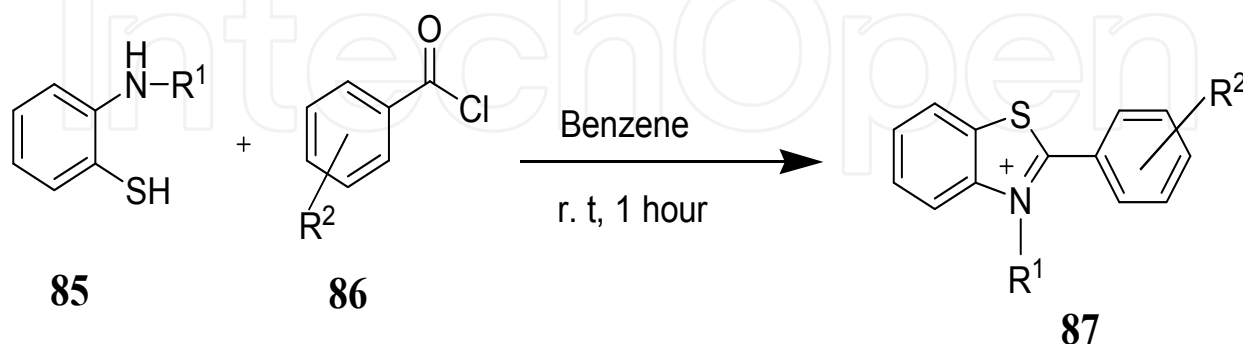
In 1967 Messmer and Gelleri prepared 1,3-diphenyl[1,2,3]triazolo[5,1-*b*]-benzothiazolium and benzimidazolium bromide salts by the action of NBS on benzothiazol-2-yl-phenyl ketone phenyl hydrazone in ethyl acetate at room temperature (Messmer&Gelléri 1967).

Vorsanger (1968) made the spectroscopic studies for the existence of carbenes generated from the heterocyclic bases which were prepared from the quaternary salt (78) of the benzothiazole with diethyl sulphate. Similar studies were made with 3-deuteriomethylbenzothiazolium iodide (79) prepared by heating the  $\text{CD}_3\text{I}$  with benzothiazole in a sealed ampule at 130 °C for 4 hours. He prepared the dimers of (78) and (79) by mixing themselves and also by mixing (80) and (81) separately to get the hybrid dimer (83) (Scheme-23) (Vorsanger 1968).



Scheme 23. Vorsanger's synthesis of 3-deuteriomethylbenzothiazolium iodide

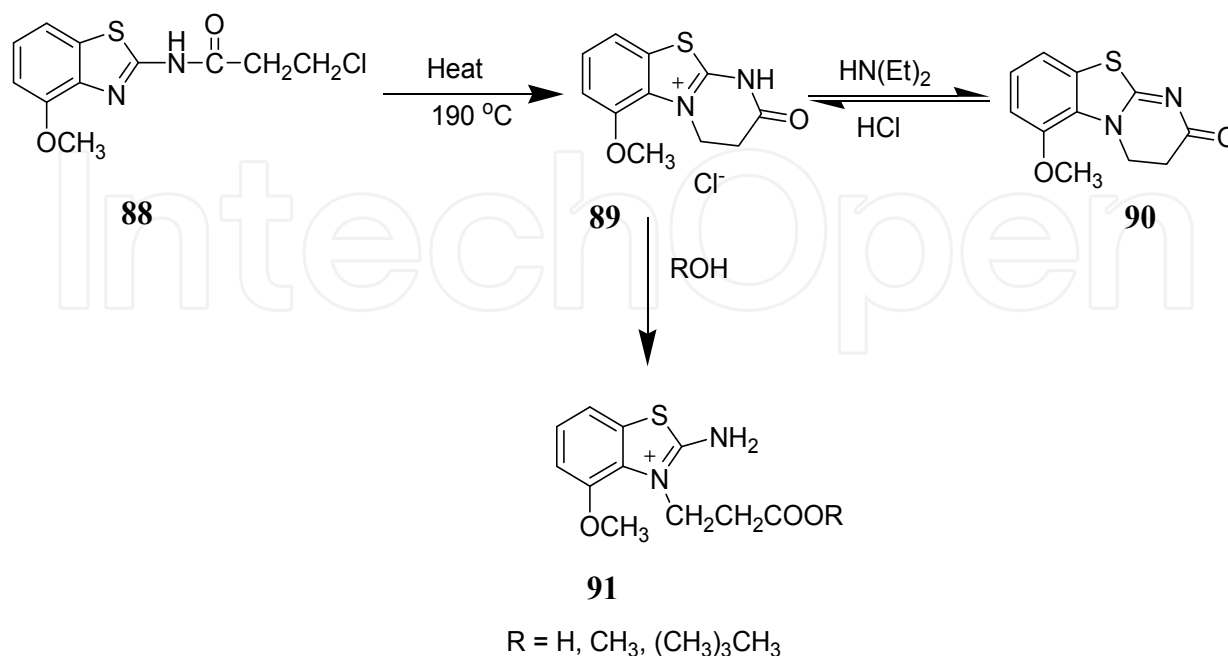
In 1969 Garmaise *et al.* prepared a number of benzothiazolium salts (**87**) from 2-alkylaminobenzenethiol (**85**) (Scheme-24). A study of the anthelmintic activity of the benzothiazolium salts in comparison to the dye thioflavin T was made. Compounds which showed activity were all closely related to thioflavin in that they had a 2-(*p*-dialkylaminophenyl) substituent and were quaternized on the heterocyclic nitrogen atom (Garmaise *et al.* 1969).



Where R<sup>1</sup> = CH<sub>3</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, CH<sub>2</sub>CH=CH<sub>2</sub> and R<sup>2</sup> = 2-Cl, 4-Cl, 4-F *etc.*

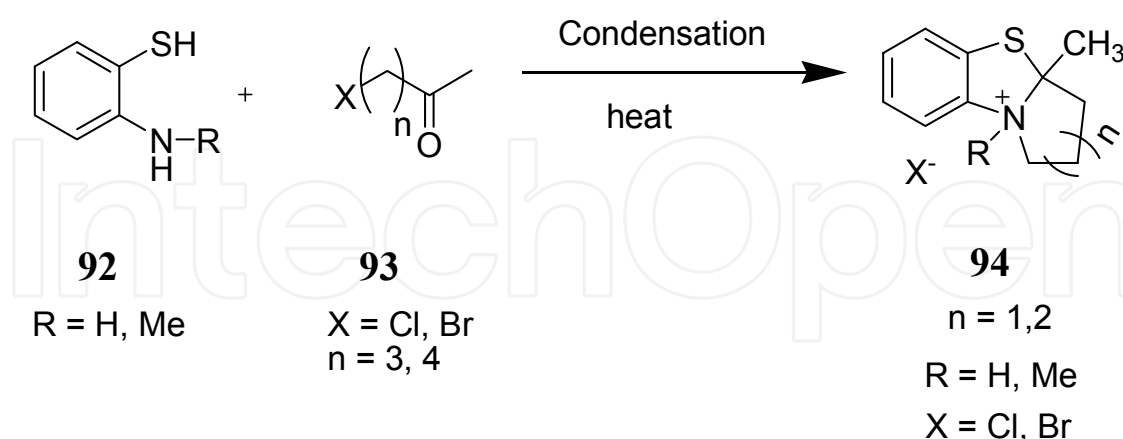
Scheme 24. Benzothiazolium salts from 2-alkylaminobenzenethiol

In 1970 Weinhardt *et al.* prepared 6-methoxy-2-oxo-1,2,3,4-tetrahydropyrimido[2,1-*b*]benzothiazol-5-ium chloride (**89**) by heating 2-(3-chloropropanoylamino)-4-methoxybenzothiazole (**88**) and they observed that the salt with base i.e. diethylamine lead to chloride free product which can be readily converted back to the salt by heating with HCl saturated chloroform. They also claimed that the salt (**88**) can be converted in to (2-amino-6-methoxybenzothiazol-*N*-propanoic acid (**91**, R = H) and their esters (**91**, R = Me or Bu) by reacting with H<sub>2</sub>O and alcohol respectively (scheme-25) (Weinhardt&Neumeyer 1970).



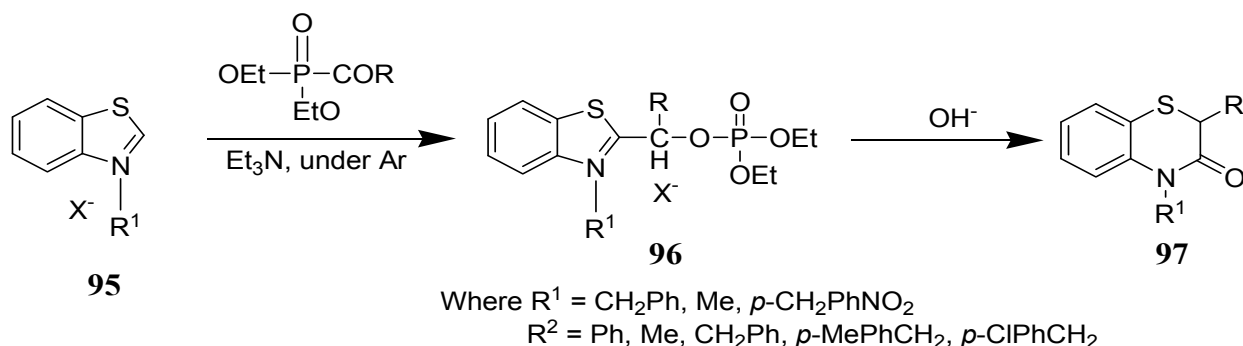
Scheme 25. Weinhardt *et al.* study of substituted benzothiazolium salts

In 1971 Mushkalo *et al.* prepared the benzothiazolium salts (**94**) by the condensation of 2-aminobenzenethiols (**92**) with different  $\alpha$ -haloketones (**93**) (scheme-26) (Mushkalo *et al.* 1971).



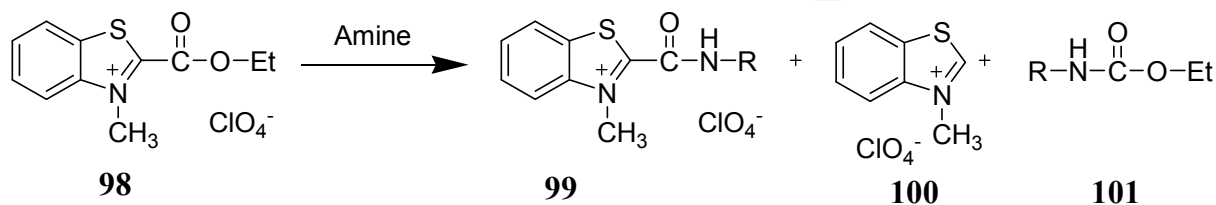
Scheme 26. Synthesis of benzothiazolium salts by the condensation of 2-amino benzenethiol with different  $\alpha$ -haloketones

Takamizawa *et al.* (1972) narrated that benzothiazine derivatives (**97**) could be obtained by treating the benzothiazolium salts (**95**) with diethyl acylphosphonates followed by basic hydrolysis (Scheme-27) (Takamizawa *et al.* 1972).



Scheme 27. Benzothiazine derivatives from benzothiazolium salts

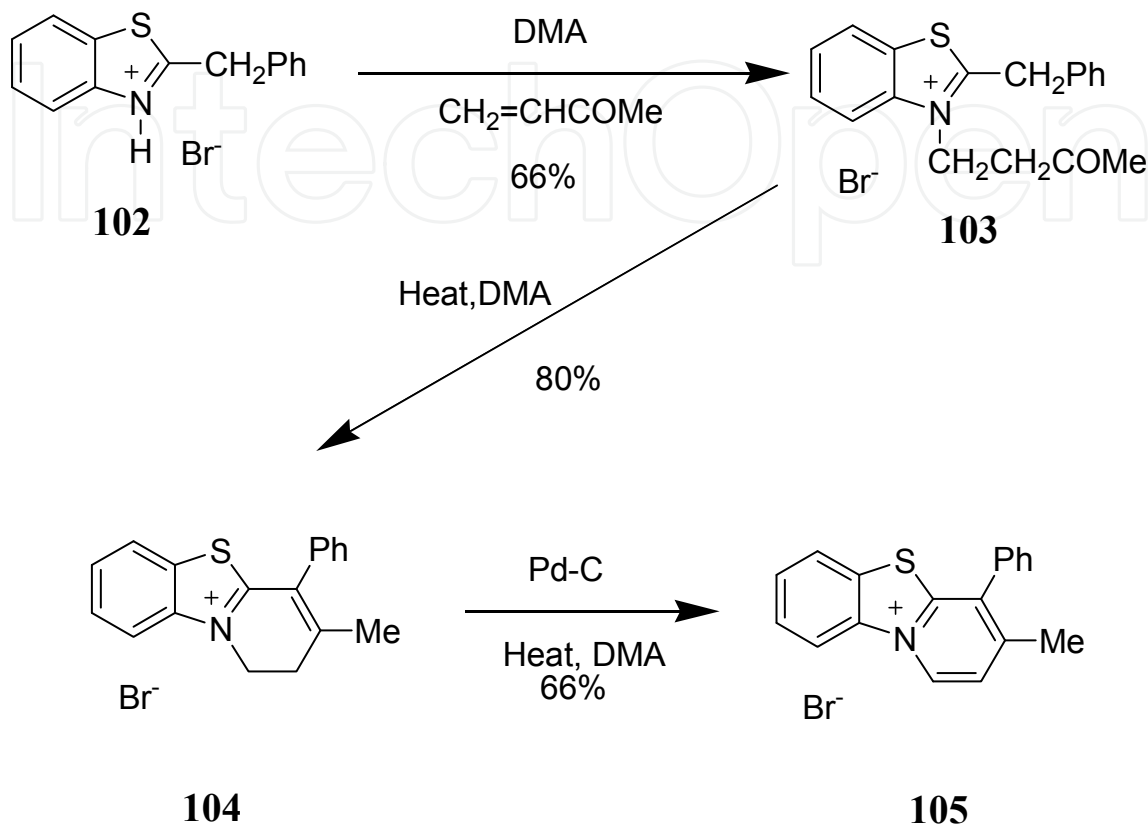
Takahashi *et al.* (1973) studied the aminolysis of the *N*-methyl-2-ethoxycarbonylbenzothiazolium perchlorate (**98**) with a series of amines and obtained *N*-methylbenzothiazolium chlorate (**100**), carbamates (**101**) in addition to the amides (**99**) (scheme-28) (Takahashi *et al.* 1973).



Amine =  $NH_3$ ,  $BuNH_2$ , *iso*- $PrNH_2$ , *tert*- $BuNH_2$ , piperidine

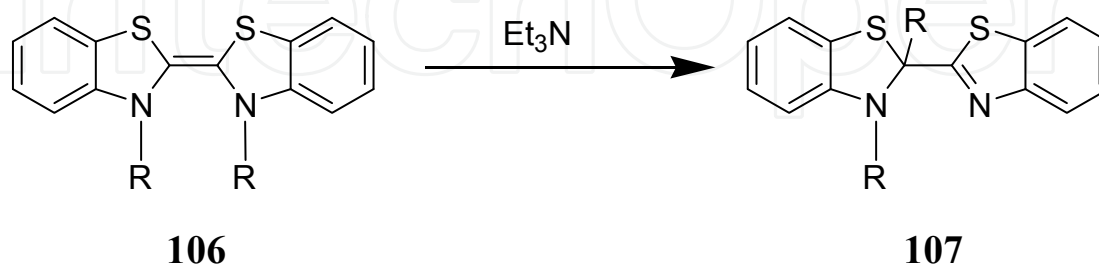
Scheme 28. Reaction of *N*-methyl-2-ethoxycarbonylbenzothiazolium perchlorate with the amine

Chapman *et al.* (1974) found that protonated heterocycles including benzthiazolium bromide (**102**), possessing an alkyl substituent (*e.g.* benzyl) on the carbon adjacent to the positive nitrogen reacted with methylvinylketone to form adduct (**103**) which can be converted into fused pyridinium salts (**104,105**) (Scheme-29) (Chapman *et al.* 1974).



Scheme 29. Benzothiazolium based fused pyridinium salts

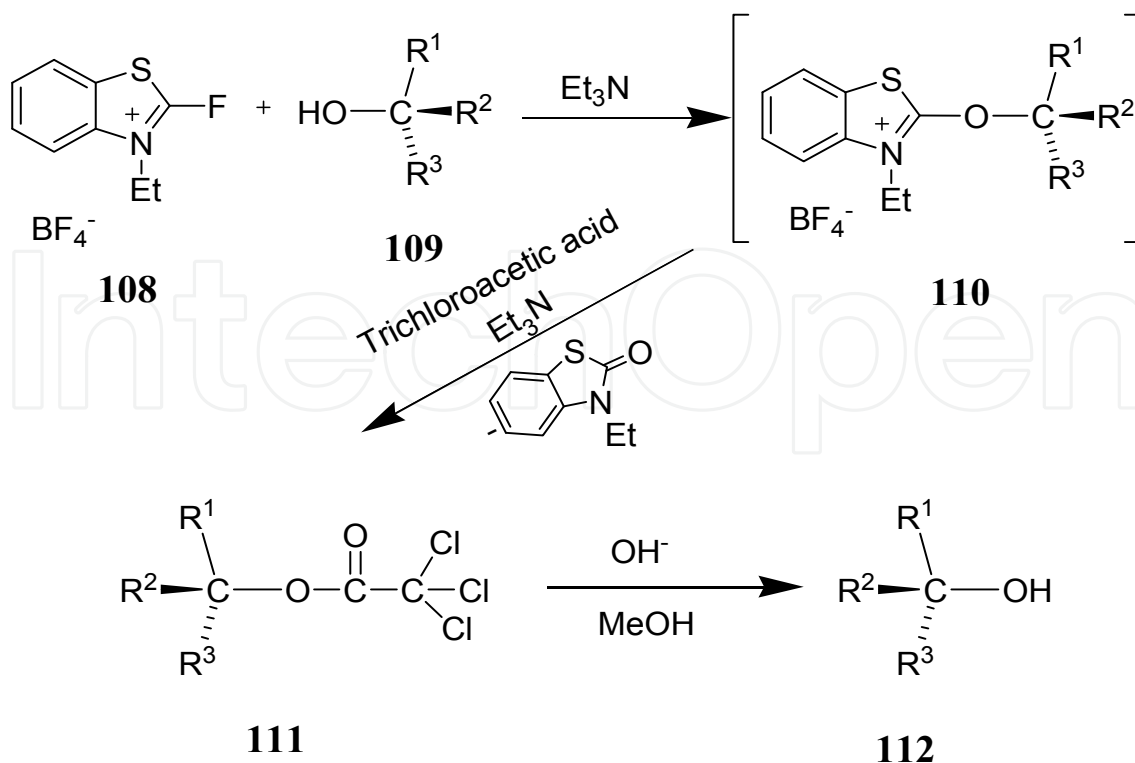
Baldwin and Walker (1974) observed that *N*-benzyl and *N*-allyl benzothiazolium salts form bis benzothiazolidine (**106**) on treatment with triethylamine in DMF at 0 °C. These dimers were found to undergo 1,3 or 3,3 sigmatropic rearrangements (scheme-31) depending upon the reaction conditions and the nature of the *N*-alkyl group to provide the more stable 2,3-dialkyl-2-(benzothiazol-2-yl)benzothiazoline (**107**) (Scheme-30) (Baldwin&Walker 1974).



Scheme 30. Sigmatropic shift in benzothiazolium salts

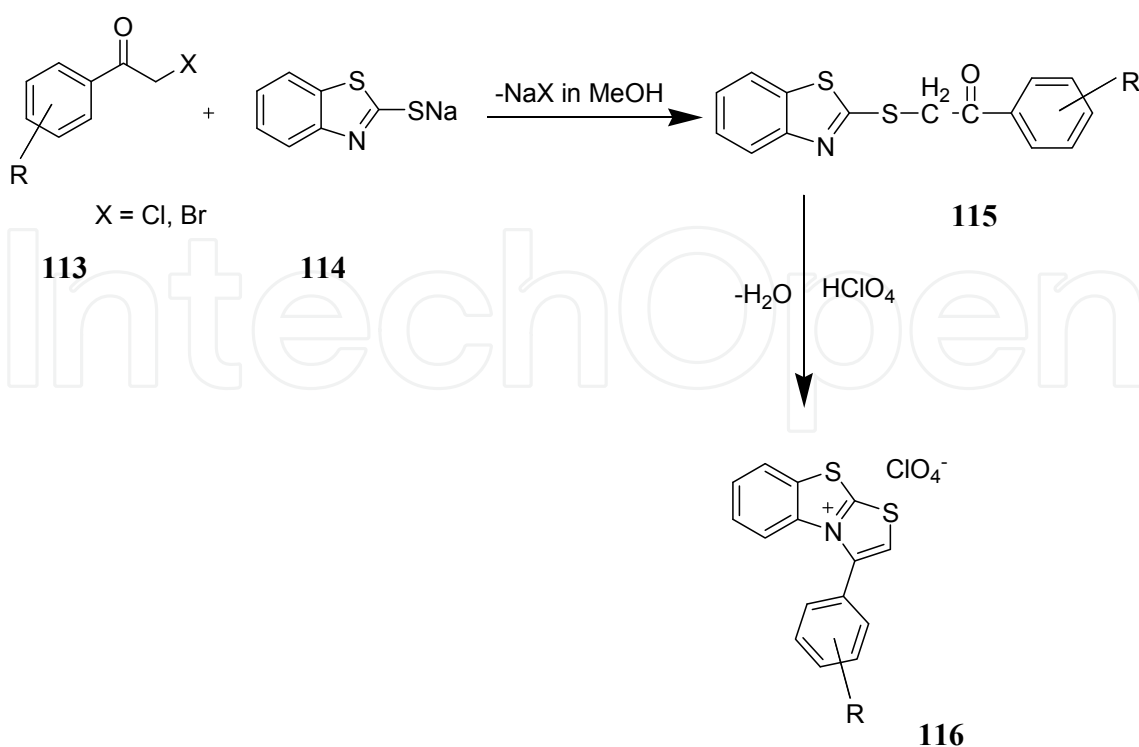
Mukaiyama and Hojo have described the interconversion of enantiomeric secondary alcohols (**112**) by the treatment with an optically active 2-alkoxybenzothiazolium salt (**110**) followed by reaction with trichloroacetic acid and base hydrolysis subsequently (scheme-31) (Mukaiyama&Hojo 1976).





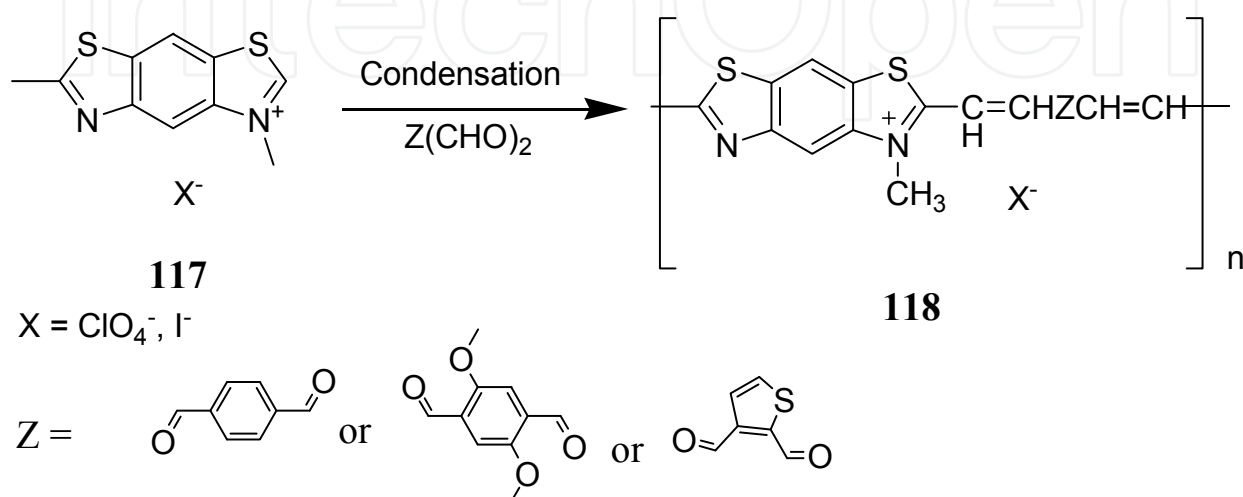
Scheme 31. Interconversion of enantiomeric secondary alcohols with benzothiazolium salts

Sawada *et al.* (1977) synthesized 3-(substituted-phenyl)thiazolo[2,3-*b*]benzothiazolium perchlorates (**116**) by the acid catalysed cyclization of the ketosulfides which were prepared by the alkylation of 2- sulfanylbenzothiazole sodium salt with substituted phenacyl halides (scheme-32).



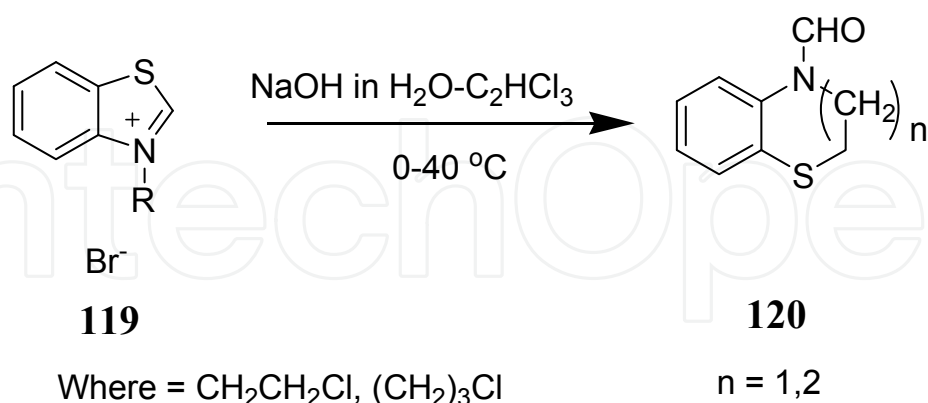
Scheme 32. Acid catalysed cyclization of ketosulfides to benzothiazolium

Kossmehl (1979) *et al.* have described the polymerization of the benzothiazolium salts by the Knoevenagel condensation of 2,3,6-trimethylthiazolo[4,5-*f*]benzothiazolium perchlorate (**117**, X = ClO<sub>4</sub><sup>-</sup>) and iodide (**117**, X = I<sup>-</sup>) with dialdehydes such as *p*-phenylenedicarbaldehyde, 2,5-dimethoxy-*p*-phenylenedicarbaldehyde, thiophene-2,3-dicarbaldehyde (scheme-33) (Kossmehl *et al.* 1979). In the same year Mukaiyama (1979) studied that the benzothiazolium compounds can be used to activate the carboxylic acids or alcohols to give 2-acyloxy or 2-alkoxy intermediates, which can be converted into esters, thioesters, amides, lactones, acid fluorides, isocyanates, *etc* (Mukaiyama 1979).



Scheme 33. Knoevenagel condensation of benzothiazolium salts with dialdehydes

Federsel *et al.* have devised the method for the preparation of 6-, 7- and 8-membered heterocycles (**120**) by base-induced ring expansion of quaternized benzothiazolium salts. The treatment of the quaternized benzothiazolium salt (**119**) with NaOH at 0-40 °C gave benzothiazine and benzothiazepine (Scheme-34) (Federsel&Bergman 1980).



Scheme 34. 6, 7 and 8 membered hetrocycles from benzothiazolium salts

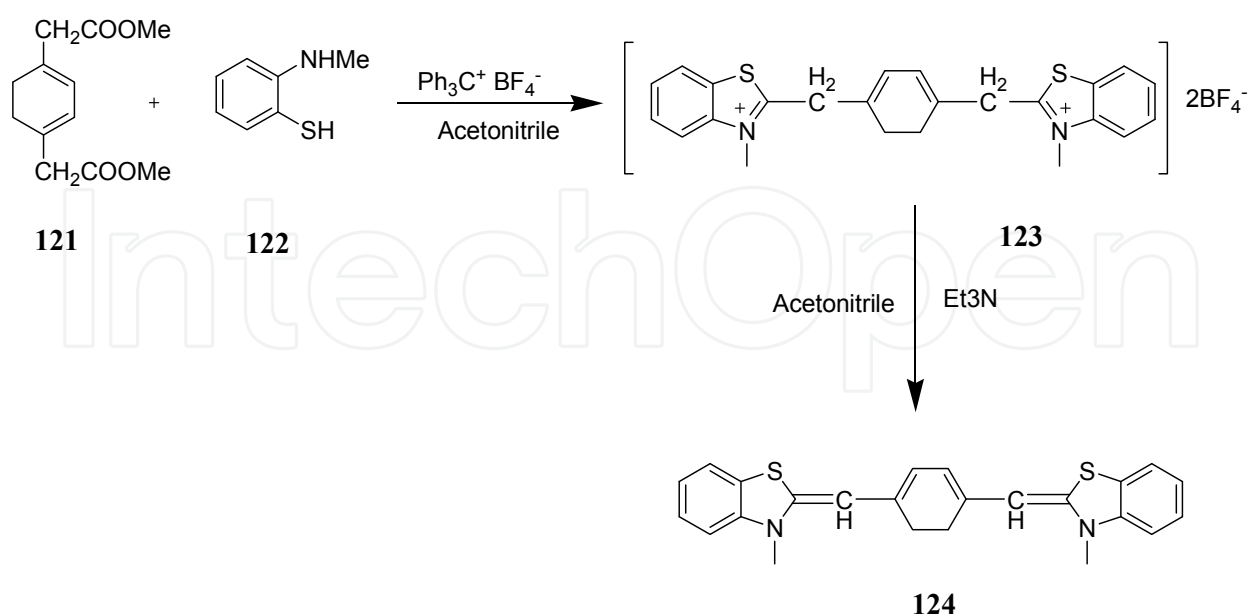
Halgas *et al.* (1983) prepared a series of 3,4,6-substituted benzothiazolium salts and studied their plant growth regulatory and antimicrobial activities. They observed the stimulation and inhibitory effects of the prepared benzothiazolium salts on plants. The highest stimulation activity was found with 6-methyl-3-propoxycarbonylmethylbenzothiazolium bromide and 4-chloro-3-methylbenzothiazolium bromide, and the highest inhibitory effect

was observed with 4-chloro-3-methylbenzothiazolium methyl sulfate, while all these benzothiazolium salts did not show any noticeable antimicrobial activity (Halgas *et al.* 1983). Other reports for the similar studies by the same group can be found in the literature (Sutoris *et al.* 1983).

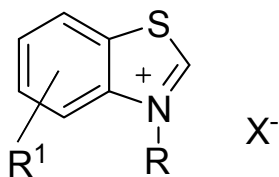
Bryce *et al.* (1984) have reported the preparation of a highly conjugated bisbenzothiazoline (**124**) by the reaction of dimethyl cyclohexa-1,3-diene-1,4-diacetate (**121**) with 2-(methylamino)benzenethiol (**122**) in the presence of triphenylcarbenium tetrafluoroborate and the subsequent treatment of the resultant bisbenzothiazolium tetrafluoroborate (**129**) with triethylamine at 20 °C (Scheme-35) (Bryce *et al.* 1984).

Xu *et al.* (1988) have described a method for the preparation of polystyrene based benzothiazolium salts and their use to study their catalytic activity in the Michael addition reactions of  $\alpha,\beta$ -unsaturated compounds (Xu *et al.* 1988). He also studied the catalytic activity of the benzothiazolium salts for the Michael addition reactions in the presence of triethylamine (Xu *et al.* 1988).

Sutoris *et al.* (1988) studied the effects of benzothiazolium compounds on the growth of sugar beet and vetch (*Vicia sativa*) as well as their sugar and chlorophyll contents. They found that most of the benzothiazolium salts possessed auxin-like activity. *N*-Methylbenzothiazolium bromide was found to stimulate sugar production in vetch at different concentrations and among the *N*-benzyl and substitutedbenzyl benzothiazolium salts, *N*-benzylbenzothiazolium bromide was found to be the most active compound. *N*-(methoxycarbonylmethyl)benzothiazolium bromide was found to be the most active compound for increasing chlorophyll contents in sugar beet leaf after treatment of the seed. Changing the methyl group for ethyl or propyl in benzothiazolium salt decreased chlorophyll contents (Sutoris *et al.* 1988).

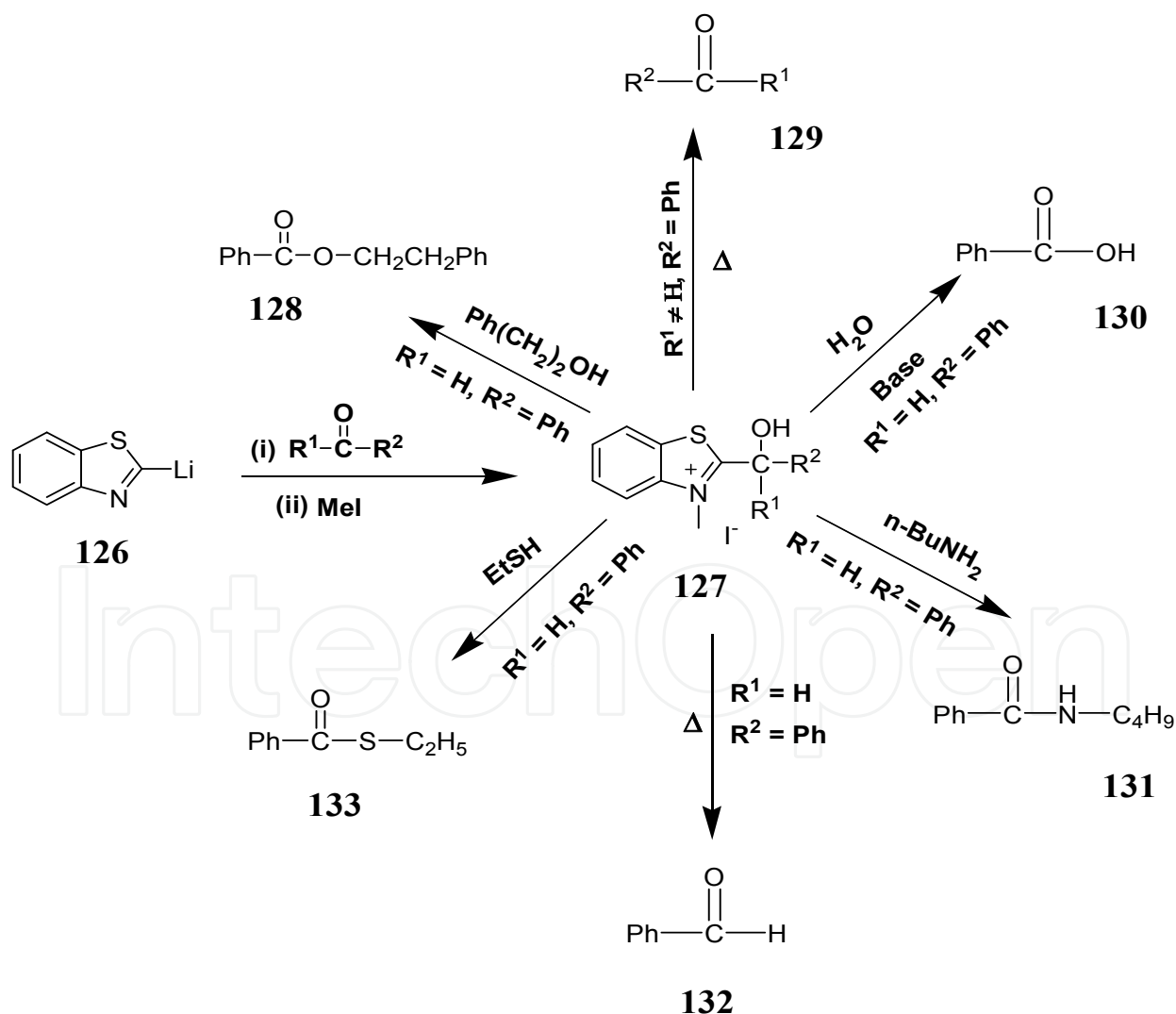


Scheme 35. Preparation of a highly conjugated bisbenzothiazoline



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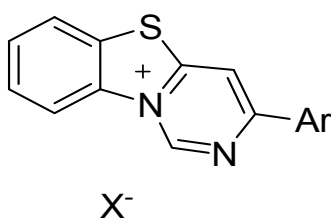
Chikashita *et al.* (1991) have described a synthetic and systematic use of benzothiazole ring system as an "on-off" type of leaving group for the preparation of ketones (**128**) and carboxylic acid derivatives (**129-132**) from a variety of benzothiazoles, *e.g.* ( $R = H, Me, ph$ ;  $R^1 = \text{propyl, ph, cyclohexyl, CH:CHPh}$ ) (off state) via the corresponding benzothiazolium salts (on state) obtained by quaternization (on switch). A variety of such compounds ( $R \neq H$ ) underwent a carbon-carbon bond cleavage at the 2-position to give the corresponding ketones  $RCOR^1$  on simple treatment with a base under mild reaction conditions. The similar reaction ( $R^1 = H$ ) to aldehydes proceeded less efficiently. The oxidative reaction of a variety



Scheme 36. Use of benzothiazole ring system as an "on-off" type of leaving group for the preparation of ketones and carboxylic acid derivatives.

( $R^1 = H$ ) with base and nonactivated  $MnO_2$  in ethanol afforded the corresponding ethyl esters. This type of oxidative reaction could be also achieved in THF with different nucleophiles, such as alcohol, water, thiol, and amine, to give the corresponding ester, carboxylic acid, thioester, and amide, respectively (scheme-36) (Chikashita *et al.* 1991).

Riemer and Liebscher (1993) have described the synthesis of pyrimido[2,1-*b*]benzoxazolium, pyrimido[2,1-*b*]benzothiazolium salt (**134**) by the reaction of 3-isothiocyanato-2-propeniminium salts with 2-aminothiophenol followed by cyclization using methyl iodide by a new condensation reaction (Riemer&Liebscher 1993).



Ar = Ph, 4-MePh, 4-ClPh

X =  $I^-$ ,  $ClO_4^-$

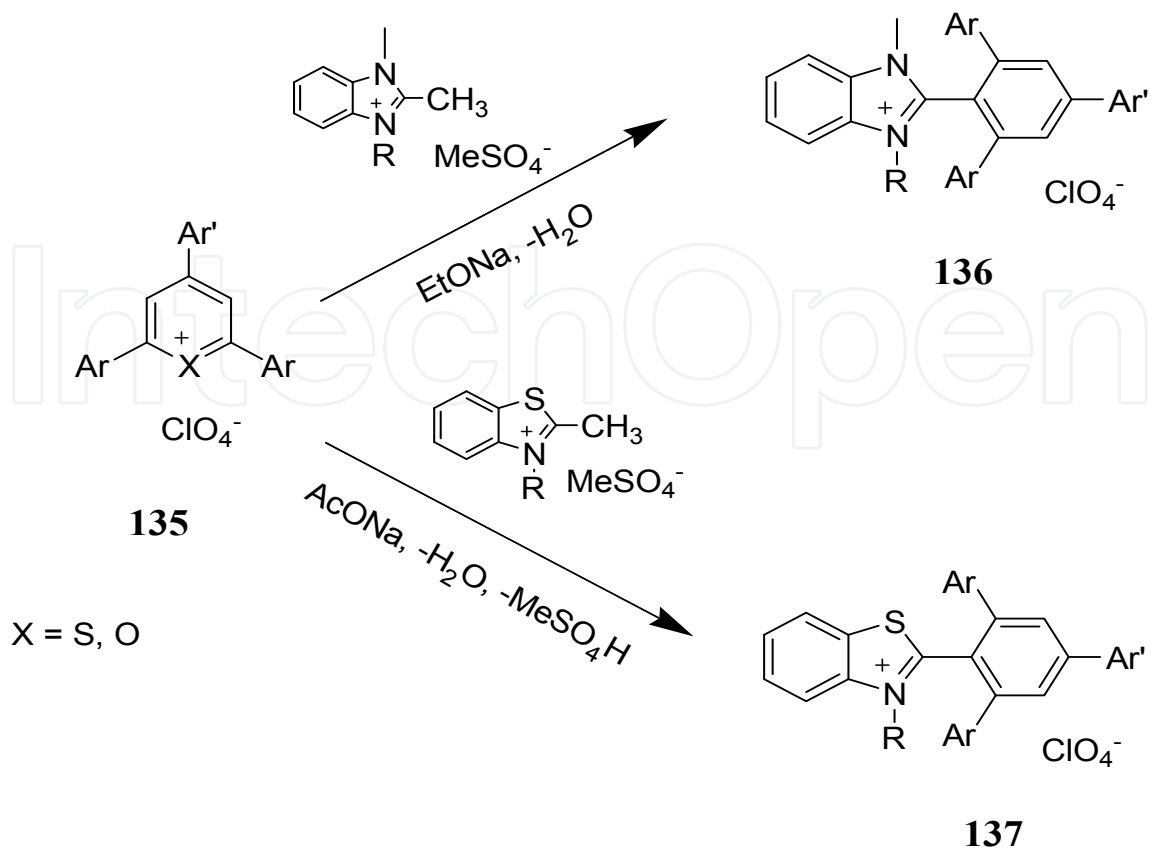
### 134

Lopez-Celahorra *et al.* (1994) have narrated that the 3,3'-polymethylene-bridged benzothiazolium and thiazolium salts could be used as pre-catalysts for the benzoin condensation and that catalytic activity depends strongly on the methylene bridge length. The authors claimed that in aprotic medium, the catalytic activity was due to the bis(thiazolin-2-ylidene)s or bis(benzothiazolin-2-ylidene)s species (Lopez-Celahorra *et al.* 1994).

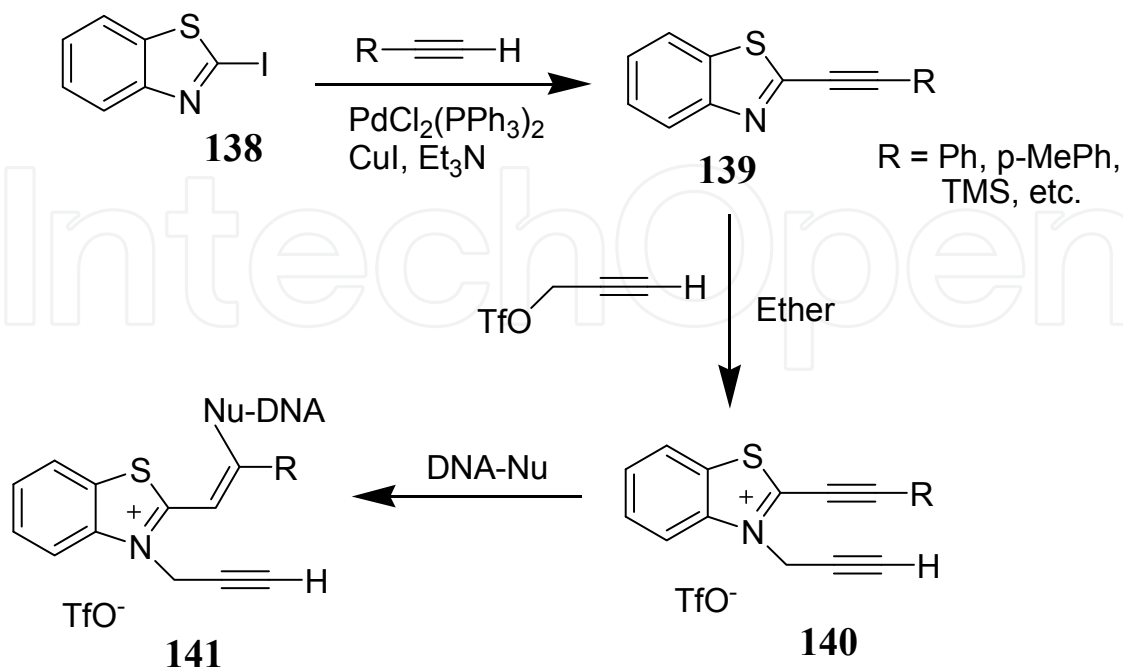
Zimmermann and Klaus (1996) have reported a method in which the ring of the pyrylium and thiopyrylium salts (**135**) have been transformed to substituted benzene ring (**136**, **137**) by treatment with anhydrobases derived from 1*H*-benzimidazolium and benzothioazolium salts (Scheme-37) (Zimmermann&Schmidt 1996).

Hatrik and Zahradnik (1996) have claimed that the toxicity of benzothiazolium salts can be predicted by the neural network (NN) method. Results were found to be in good agreement with the previously used Free-Wilson method. They have used a number of benzothiazolium salts to calculate their toxicity by the NN method (Hatrik&Zahradnik 1996).

Kumar *et al.* prepared aza-enediyne analogues by the incorporation of *N*-propargyl moiety to 2-alkynylbenzothiazolium salts (**139**) and the aza-enediyne (**140**) were proven to be the modest DNA cleavage agents. The mechanism probably involves the formation of an adduct (**141**) prior to cleavage of DNA. They also observed DNA cleavage with the *N*-methyl-2-alkynylbenzothiazolium salt, which lacks the aza-enediyne moiety (scheme-38) (Kumar *et al.* 2001).

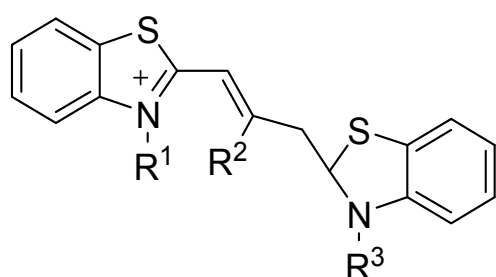
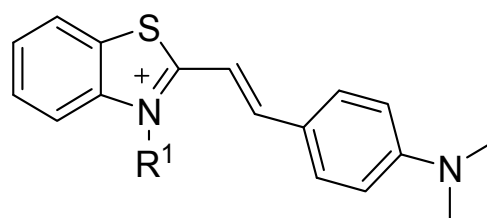


Scheme 37. Conversion of pyrylium and thiopyrylium salts to substituted benzene ring

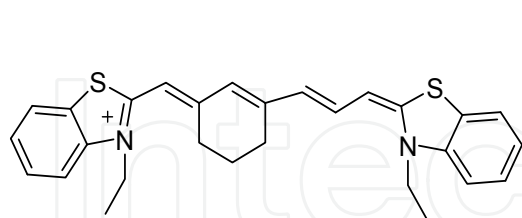
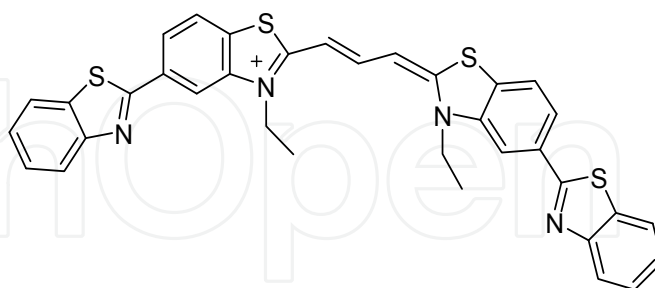
Scheme 38. *N*-propargyl alkynylbenzothiazolium salts as DNA cleavage agents

Puterová *et al.* (2004) have prepared different benzothiazolium compounds by reaction of 5-arylfuran-2-carboxaldehydes and furo[*b*]pyrrole type aldehydes with 2-methyl-3-methyl or ethyl benzothiazolium bromide. The new compounds were based on highly conjugated systems that have potential biological activity. Cyanine dye precursors can also be obtained by the reaction of furo[*b*]pyrrole type aldehydes with benzothiazolium salts (Puterová *et al.* 2004).

Tseng *et al.* (2005) have used different benzothiazolium compounds (**142** & **143**) to study their activity for the inhibition of nitric oxide production in a cell culture system. They found that benzothiazolium salts have been the better inhibitors than *N*-methyl arginine (L-NMMA) a known inhibitor. They have demonstrated these results by the correlation of *in vivo* and *in vitro* activities using mouse paw edema (Tseng *et al.* 2005).

**142****143**

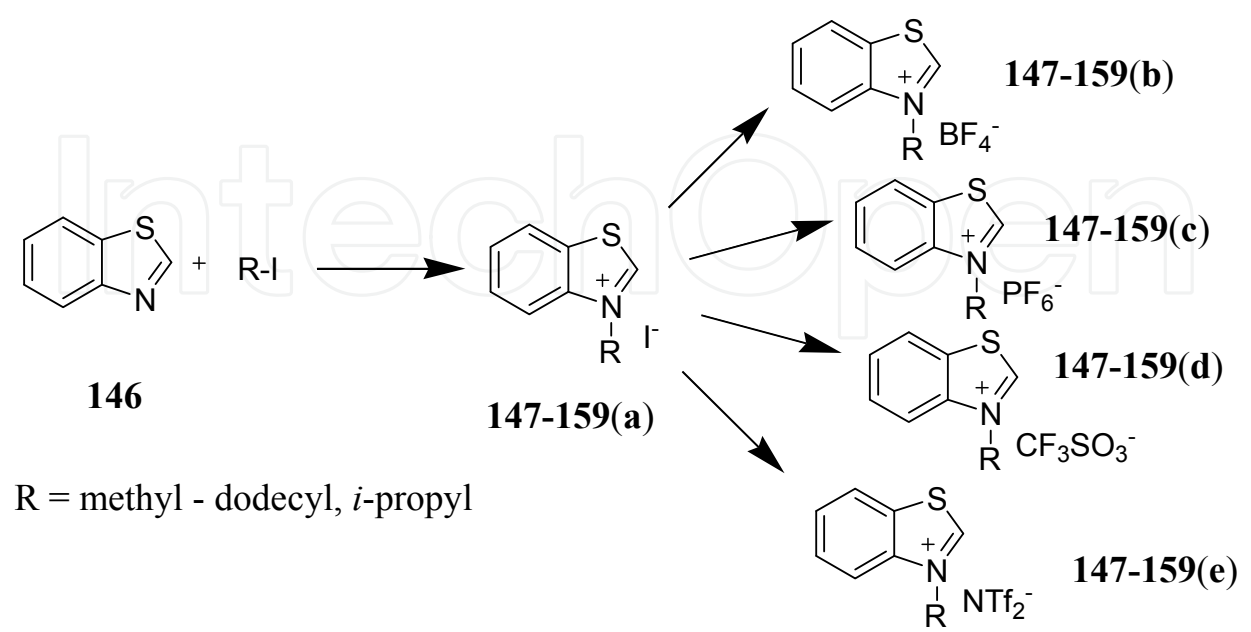
Yang *et al.* (2007) synthesized a series of benzothiazolium compounds (**144** and **145**) which showed inhibitory activity against gastroenteritis virus (TGEV). They used swine testicle (ST) cells infected with transmissible gastroenteritis virus (TGEV) and an indirect immunofluorescent assay with antibodies against TGEV spike and nucleocapsid proteins to screen the benzothiazolium compounds that inhibit TGEV replication. The benzothiazolium compounds were found to have inhibitory activity against TGEV 3CL(pro) (Yang *et al.* 2007).

**144****145**

Wanzlick *et al.* have prepared the Bis(3-methylbenzothiazolin-2-yliden) which was used by Castells *et al.* for the catalysis of benzoin condensation (Castells *et al.* 1988).

Due to the unavailability of data about the liquid range of the above benzothiazolium salts, it is not certain whether the salts should be classified as ionic liquids or not. Recently our group have prepared a series of benzothiazolium iodides in absence of any solvent, studied their physical properties and performed metathesis reactions. The benzothiazolium bistriflimides showed a good liquidity range near ambient temperatures and have wide

stability range of 274-366 °C in comparison to the other benzothiazolium salts having high melting points and low stabilities (Nadeem *et al.* 2010) (scheme-39).



Scheme 39.

No.	R	Yield %	Temperature °C	Time h
147a	CH <sub>3</sub>	82, 99.8*	20-25	9.0
148a	C <sub>2</sub> H <sub>5</sub>	75	50 – 60	4.0
149a	C <sub>3</sub> H <sub>7</sub>	68	80 – 90	6.0
150a	<i>iso</i> C <sub>3</sub> H <sub>7</sub>	62	70 – 80	7.0
151a	C <sub>4</sub> H <sub>9</sub>	80	110 – 120	5.5
152a	C <sub>5</sub> H <sub>11</sub>	79	125 – 135	1.0
153a	C <sub>6</sub> H <sub>13</sub>	77	160 – 170	3.0
154a	C <sub>7</sub> H <sub>15</sub>	75	180 – 190	4.0
155a	C <sub>8</sub> H <sub>17</sub>	80	210 – 220	4.0
156a	C <sub>9</sub> H <sub>19</sub>	73	150 – 160	2.0
157a	C <sub>10</sub> H <sub>21</sub>	70	110 – 120	4.5
158a	C <sub>11</sub> H <sub>23</sub>	75	95 – 105	3.0
159a	C <sub>12</sub> H <sub>25</sub>	72	140 – 150	5.0

\*Sonicated at room temperature.

Table 1. Specific temperatures, reaction times, and yields for compounds 147a-159a (Scheme 39).



4. Thermal studies of benzothiazolium ionic liquids

The benzothiazolium salts/ionic liquids have been comprehensively studied by our group (Nadeem *et al.* 2010). The thermal studies such as TGA and DSC reveal important information about the stability and thermal behavior of these compounds. Decomposition temperatures of benzothiazolium iodide salts were determined by TGA, heating at 10 °C min<sup>-1</sup> under dried air atmosphere and are reported (table-2) as (i) onset to 5 wt% mass loss (T<sub>5%dec</sub>) and (ii) onset to total mass loss (T<sub>dec</sub>) (in parentheses).

Sr No.	R	mp (°C)	T <sub>5% dec</sub> (T <sub>dec</sub> ) (°C)
147a	CH <sub>3</sub>	221-222 <sup>c</sup> (lit 216)	194 (214)
148a	C <sub>2</sub> H <sub>5</sub>	136-137 <sup>c</sup> (lit 140)	177 (205)
149a	C <sub>3</sub> H <sub>7</sub>	158-159 <sup>c</sup> (lit 158)	179 (205)
150a	<i>iso</i> C <sub>3</sub> H <sub>7</sub>	131.1 <sup>a,b</sup> (lit 131)	181 (205)
151a	C <sub>4</sub> H <sub>9</sub>	116.3 (lit 114)	175 (201)
152a	C <sub>5</sub> H <sub>11</sub>	117.8 <sup>a</sup> (lit 119)	172 (199)
153a	C <sub>6</sub> H <sub>13</sub>	126.7	173 (199)
154a	C <sub>7</sub> H <sub>15</sub>	<b>65.1</b> <sup>a,b</sup>	164 (193)
155a	C <sub>8</sub> H <sub>17</sub>	<b>74.5</b> <sup>a,b</sup>	166 (188)
156a	C <sub>9</sub> H <sub>19</sub>	<b>82.1</b> <sup>a,b</sup>	162 (186)
157a	C <sub>10</sub> H <sub>21</sub>	<b>82.4</b> <sup>a,b</sup>	171 (194)
158a	C <sub>11</sub> H <sub>23</sub>	<b>80.4</b> <sup>a,b</sup>	161 (188)
159a	C <sub>12</sub> H <sub>25</sub>	<b>90.5</b> <sup>a,b</sup>	162 (187)

Melting points and thermal stabilities.§

Table 2. [§] Melting (mp) or glass transition (T<sub>g</sub>) points (°C) were measured from the transition onset temperature and determined by DSC from the second heating cycle at 10 °C min<sup>-1</sup>, after initially melting and then cooling samples to -100 °C. Decomposition temperatures shown were determined by TGA, heating at 10 °C min<sup>-1</sup> under dried air atmosphere and are reported as (i) onset to 5 wt% mass loss (T<sub>5%dec</sub>) and (ii) onset to total mass loss (T<sub>dec</sub>) (in parentheses). Salts meeting the definition of ionic liquids (mp < 100 °C) are in **bold**. [a] Sample exhibits additional glass transition temperatures (°C) of supercooled liquids (i) with consecutive crystallization and melting on heating; **148b**, -42.7; **149b**, -48.1; **149c**, -17.3; **150c**, -5.2; **151c**, -4.4;**152a**, 2.3; **152b**, -51.2; **153b**, -47.6; **154b**, -42.8; **155b**, -43.5; **156b**, -49.1; **163b**, -58.2; **164b**, -45.2; **165b**, -48.1; (°C); (ii) with no crystallization and melting under e experimental conditions: **148c**, -5.2; **150a**, 2.4; **152c**, -3.2; **153c**, -6.5; **154a**, -5.6; **154c**, -10.1; **155a**, -2.3; **155c**, -7.2; **156a**, 5.5; **156c**, -9.1;**157a**, -5.6; **163c**, -11.2; **158a**, -5.8; **164c**, -11.1;**158a**, -6.0; **159c**, -10.3 (°C); [b] Irreversible transition, from first heating; [c] melting point measured visually due to close proximity to the decomposition temperature and possibility of contamination of the DSC cell.

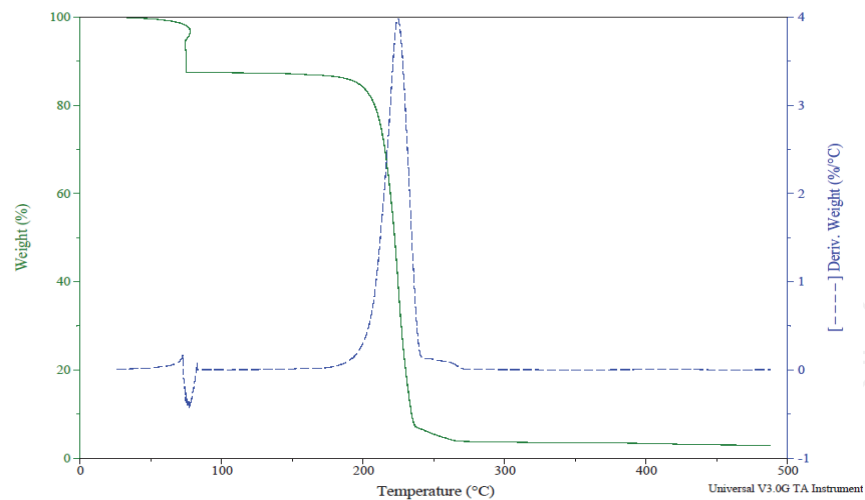


Fig. 2. TGA of *N*-Methyl benzothiazolium iodide

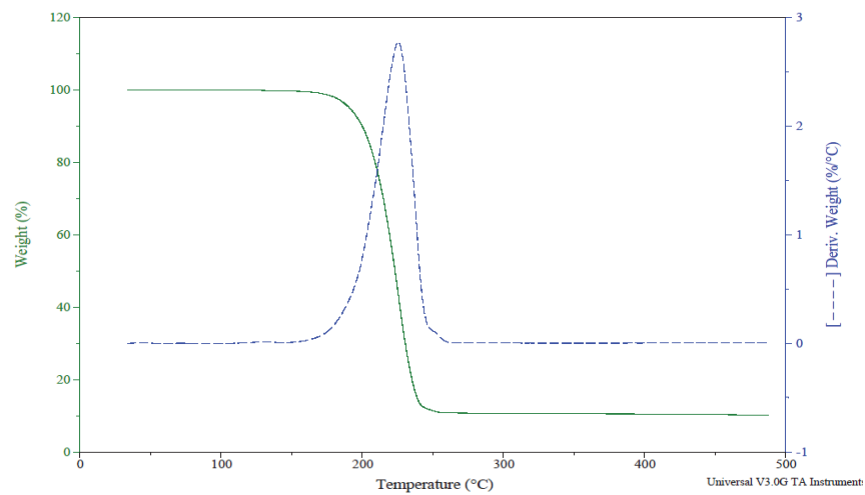


Fig. 3. TGA of *N*-Ethyl benzothiazolium iodide.

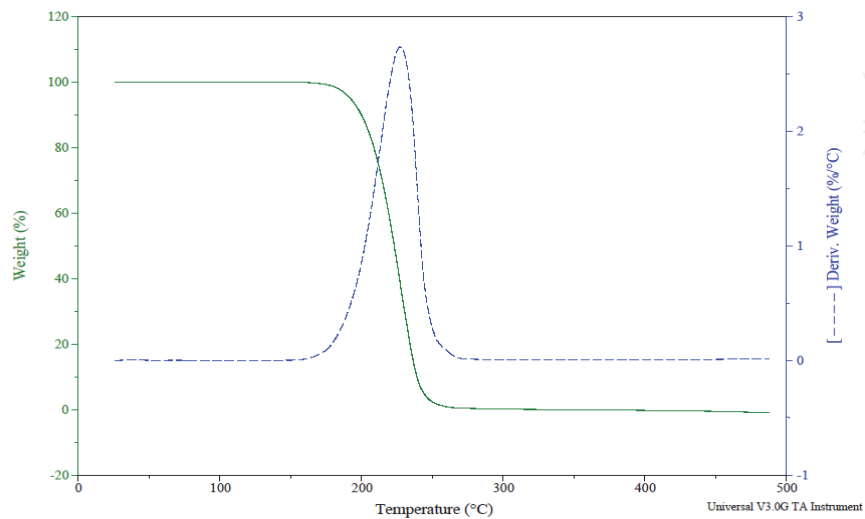


Fig. 4. TGA of *N*-Propyl benzothiazolium iodide.

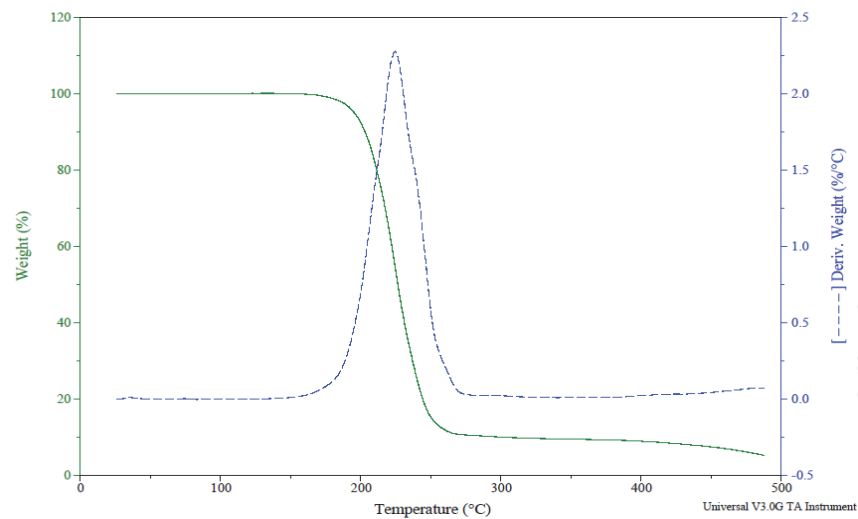


Fig. 5. TGA of N-iso-Propyl benzothiazolium iodide.

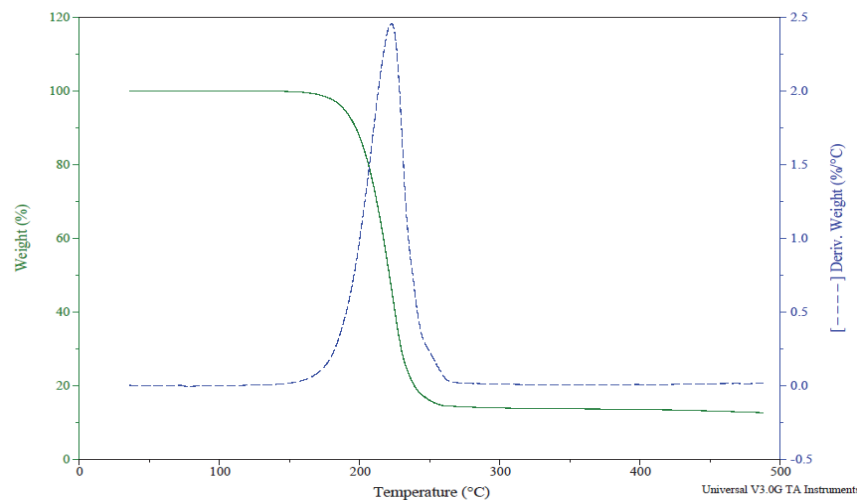


Fig. 6. TGA of N-Butyl benzothiazolium iodide.

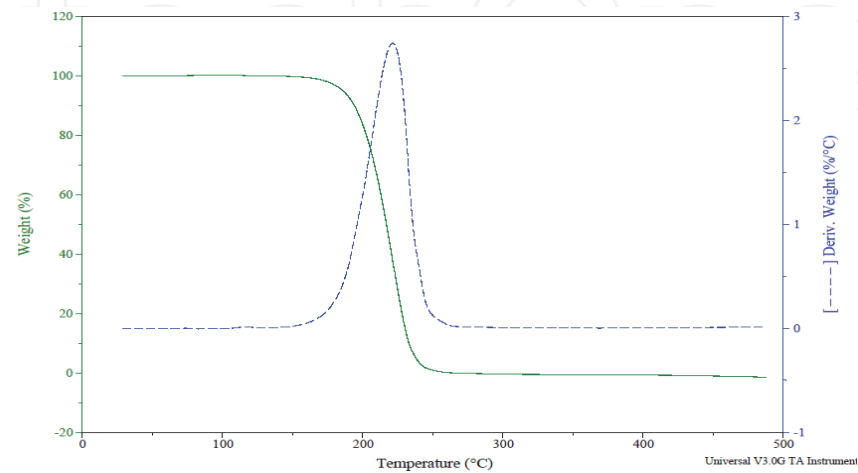


Fig. 7. TGA of N-Pentyl benzothiazolium iodide.

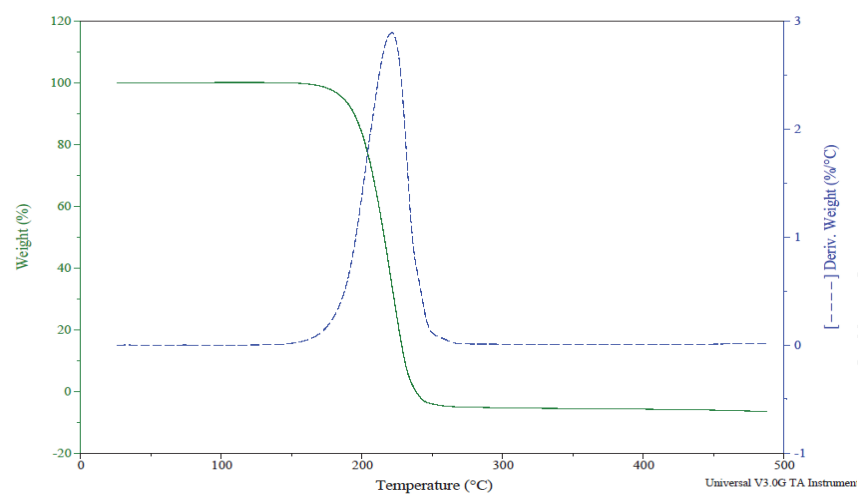


Fig. 8. TGA of N-Hexyl benzothiazolium iodide.

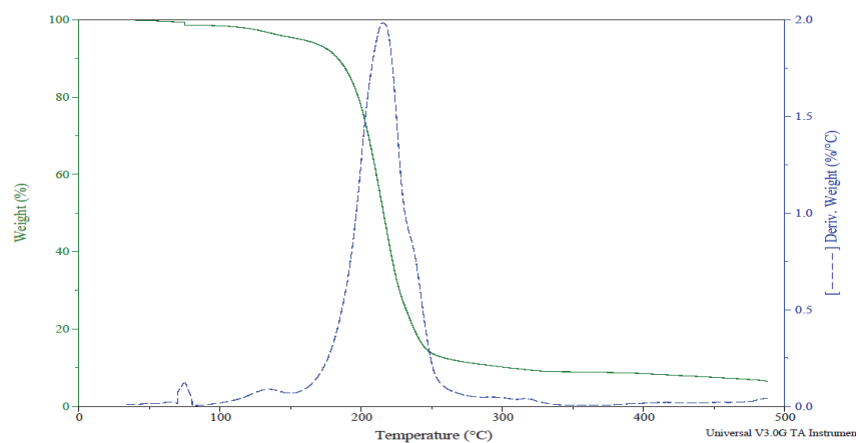


Fig. 9. TGA of N-Heptyl benzothiazolium iodide.

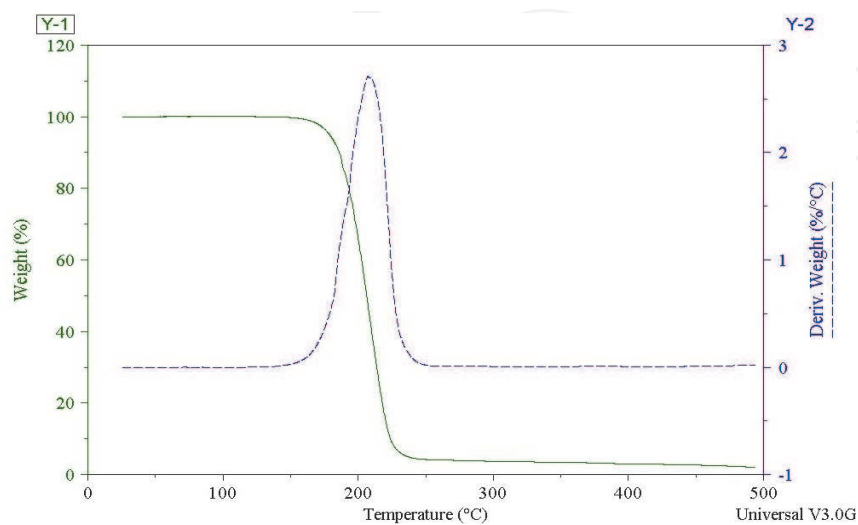


Fig. 10. TGA of N-Octyl benzothiazolium iodide.

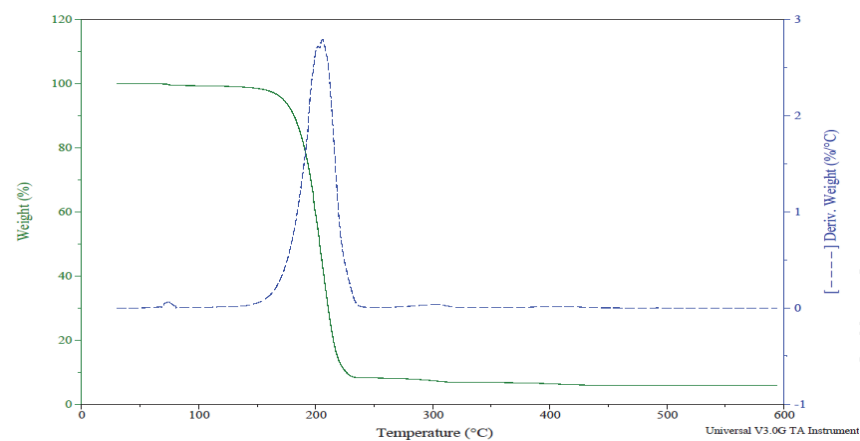


Fig. 11. TGA of N-Nonyl benzothiazolium iodide.

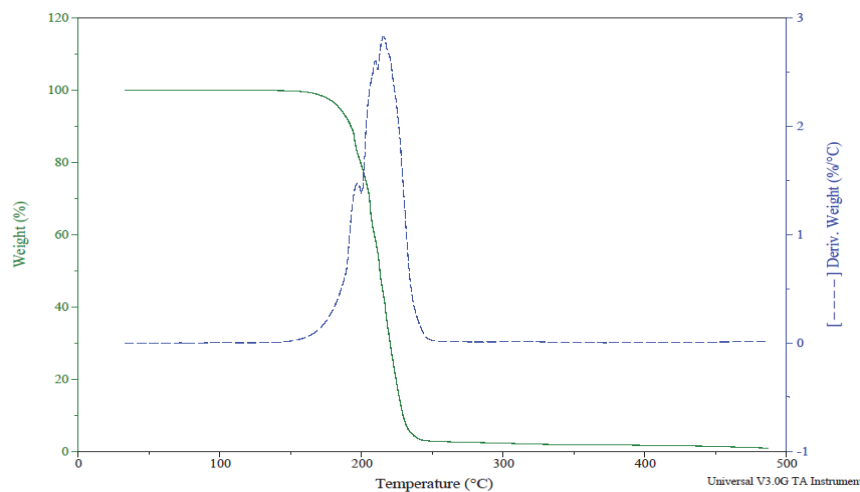


Fig. 12. TGA of N-Decyl benzothiazolium iodide.

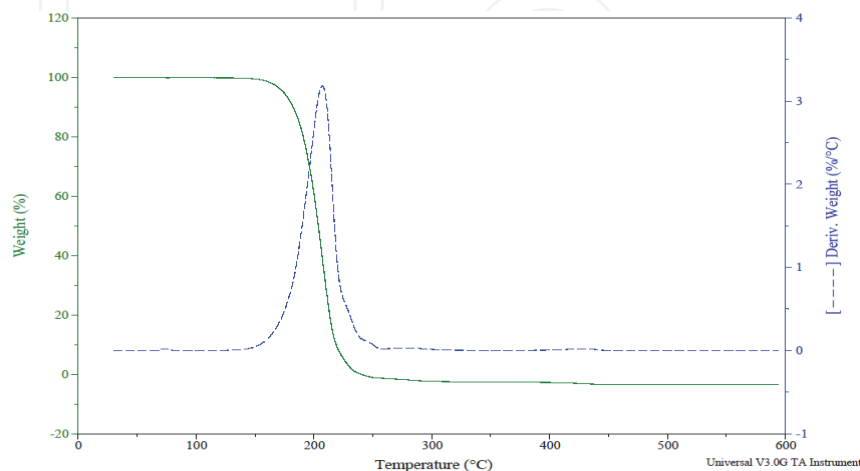


Fig. 13. TGA of N-Undecyl benzothiazolium iodide.

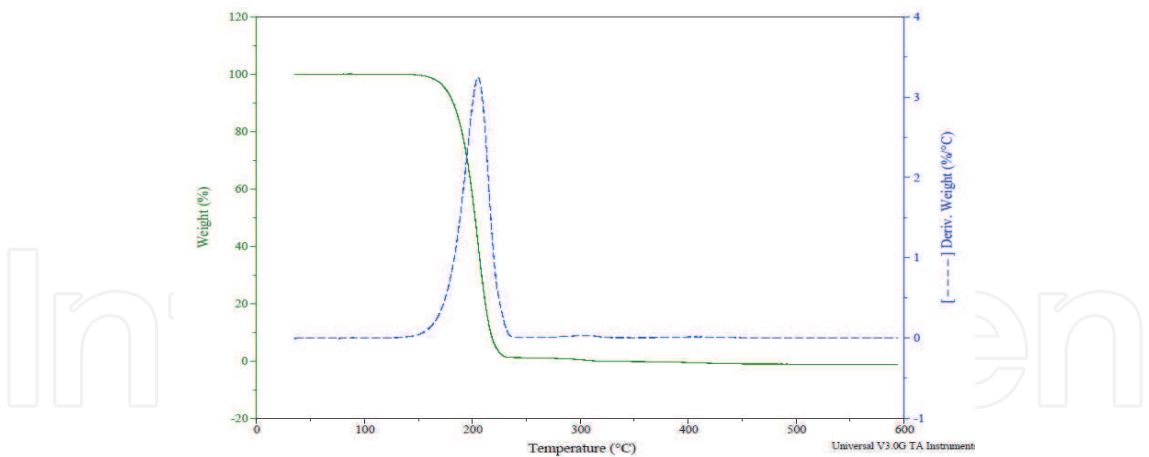


Fig. 14. TGA of N-Dodecyl benzothiazolium iodide.

Melting (mp) or glass transition (Tg) points (°C) were measured from the transition onset temperature and determined by DSC from the second heating cycle at 10 °C min<sup>-1</sup>, after initially melting and then cooling samples to -100 °C. The melting points of *N*-methyl, *N*-ethyl and *N*-propyl were measured visually due to close proximity to the decomposition temperature and possibility of contamination of the DSC cell.

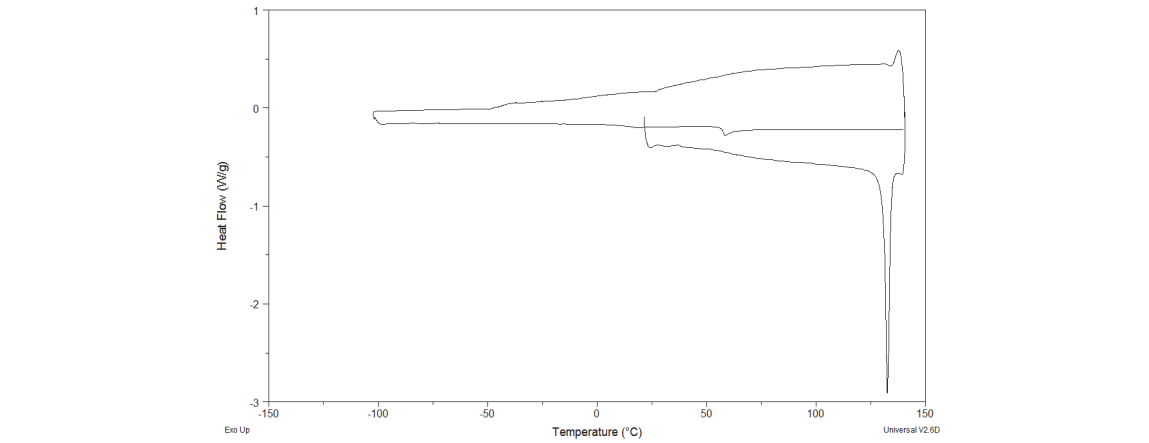


Fig. 15. DSC graph for N-IsopropylBTI

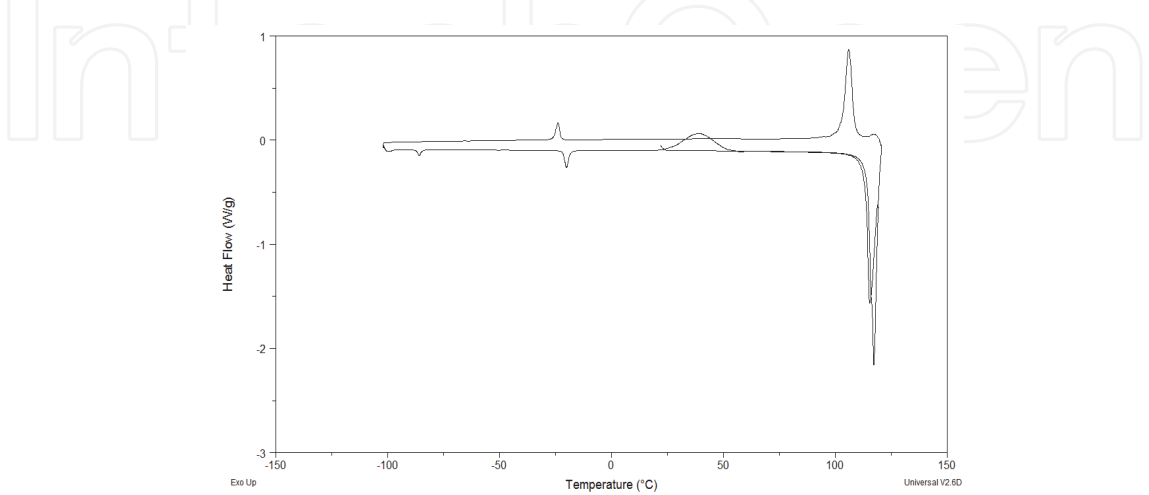


Fig. 16. DSC graph for N-butylBTI

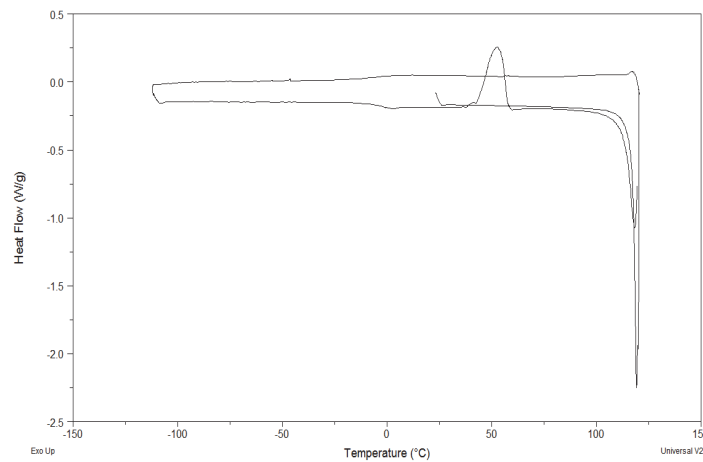


Fig. 17. DSC graph for *N*-pentylBTI

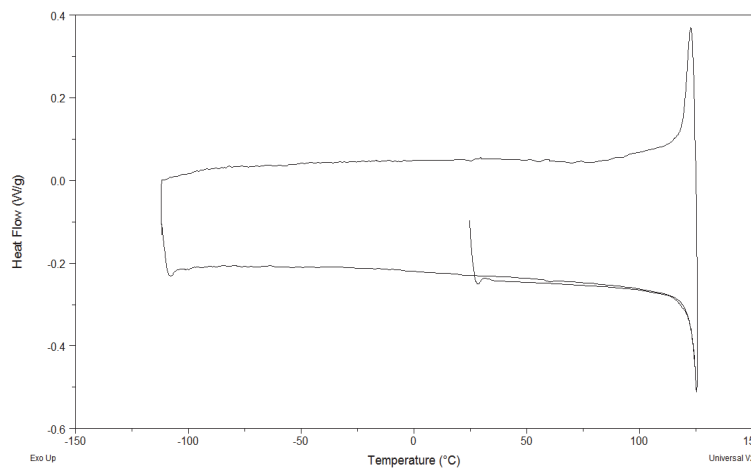


Fig. 18. DSC graph for *N*-hexylBTI

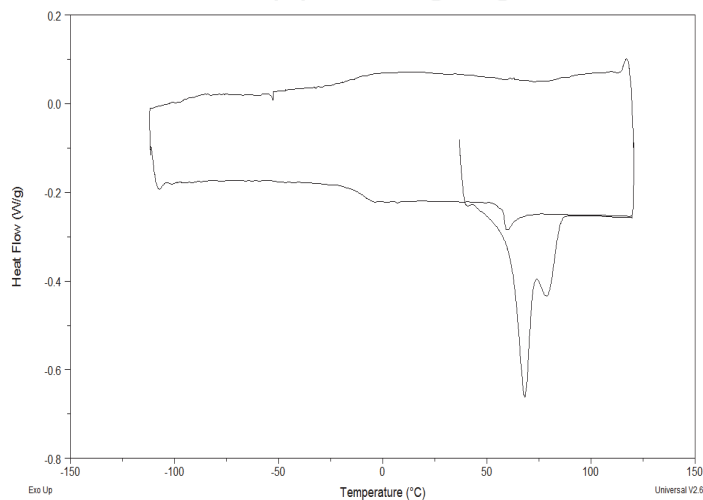


Fig. 19. DSC graph for *N*-heptylBTI

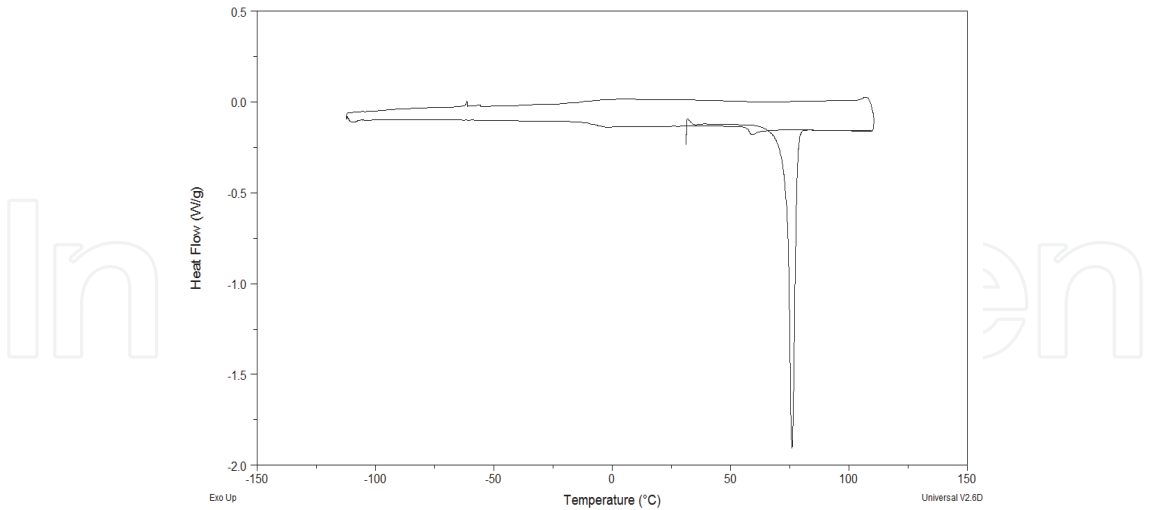


Fig. 20. DSC graph for *N*-octylBTI

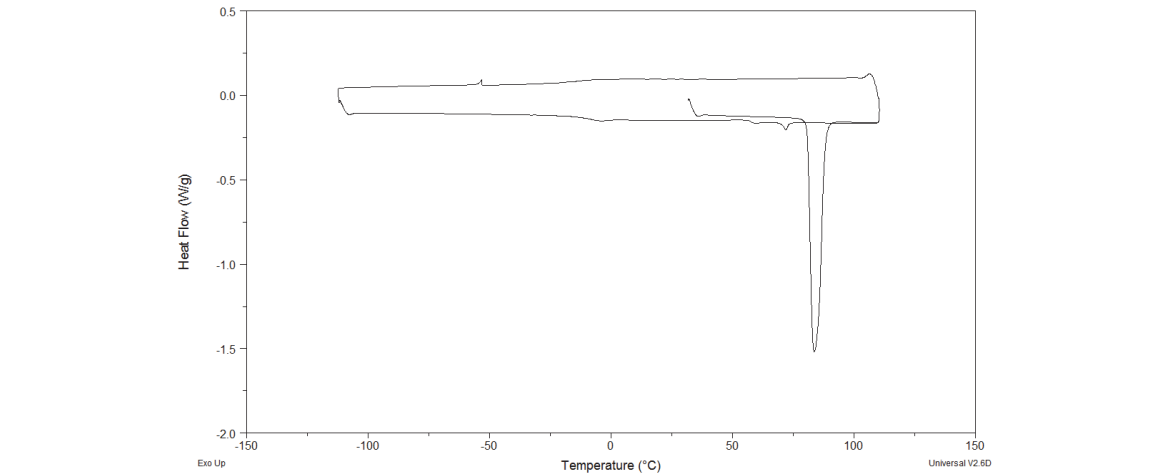


Fig. 21. DSC graph for *N*-nonylBTI

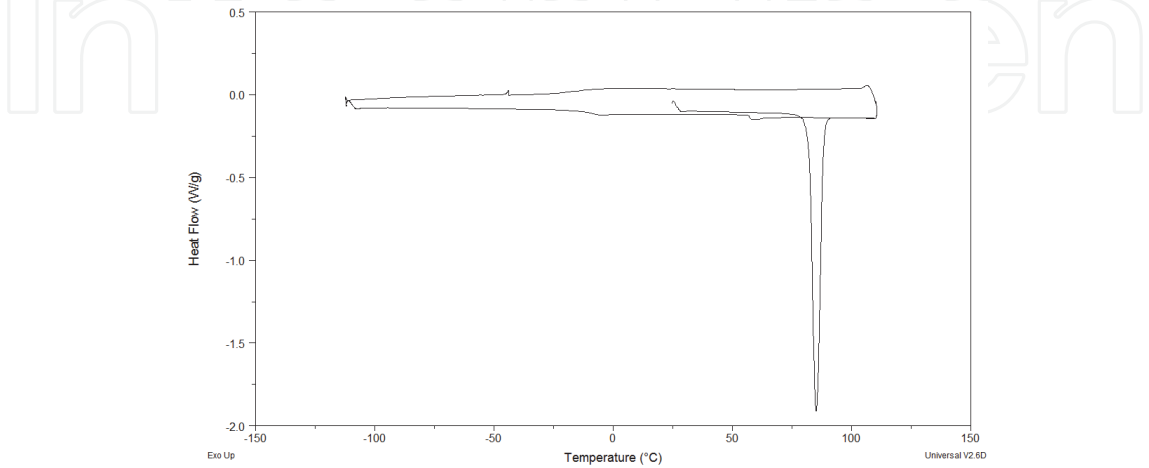
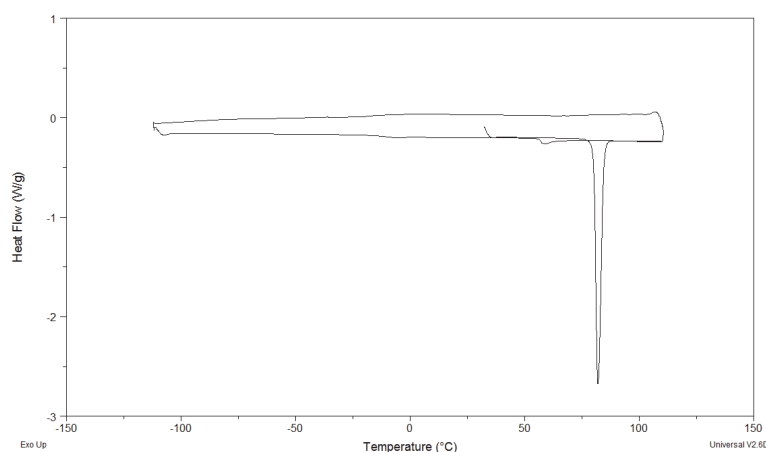
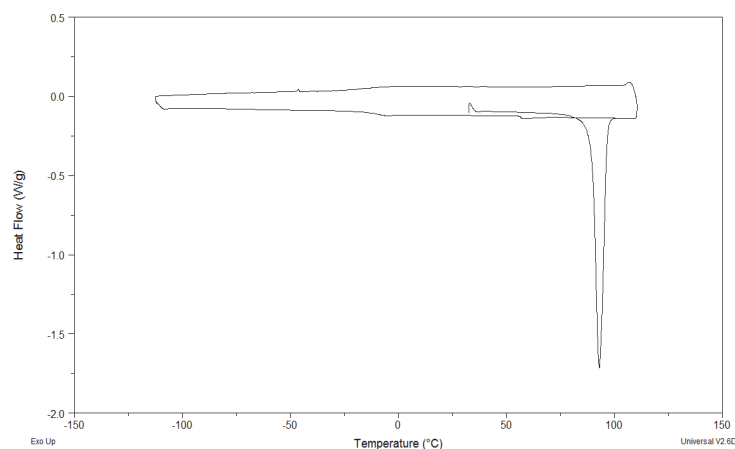


Fig. 22. DSC graph for *N*-decylBTI



Fig. 23. DSC graph for *N*-undecylBTIFig. 24. DSC graph for *N*-dodecylBTI

### 5. Benzothiazolium iodide-chloroaluminate ionic liquid

The phase behaviour study of  $[C_{11}BT]I-AlCl_3$  mixtures have been carried out with the help of DSC to find the appropriate mole ratio of the aluminum chloride to the  $[C_{11}BT]I-AlCl_3$  mixture (Figure-25). From figure-25, it is evident that at mole ratio 0.5% the mixture of  $[C_{11}BT]I-AlCl_3$  gave lowest melting point (22.5 °C) which was checked by DSC. Figure-24 represents the phase diagram of the  $[C_2mim]Cl-AlCl_3$  system as a function of composition,  $X(AlCl_3)$  and figure-25 gives an account of the phase study of the *N*-undecylbenzothiazolium iodide-aluminum chloride system. It is obvious that the most distinctive feature of the chloroaluminate(III) system is its dependence on the apparent mole fraction of aluminium(III) chloride, the ionic liquid is acidic (Visser 2002), basic [ $X(AlCl_3) < 0.5$ ], or neutral [ $X(AlCl_3) = 0.5$ ], referring to the Franklin acidity and basicity (Franklin 1905, 1924). This is frequently assumed to refer to the Lewis acidity and basicity.

From figures 25 and 26, it is immediately clear that the liquid range of both the systems is very different from each other. The  $[C_2mim]Cl-AlCl_3$  system is a low viscosity liquid at room temperature from  $X(AlCl_3) = 0.33$  to  $X(AlCl_3) = 0.67$  (where  $X(AlCl_3)$  is the mole fraction of the nominal aluminium(III) content. While the room temperature liquidity of the

C<sub>11</sub>BTI-AlCl<sub>3</sub> system starts at X(AlCl<sub>3</sub>) = 0.45 and ends up to 0.55. Although the liquidus range of the C<sub>11</sub>BTI-AlCl<sub>3</sub> system is very low as compared to the imidazolium system, there is a eutectic point, which may be useful for different applications.

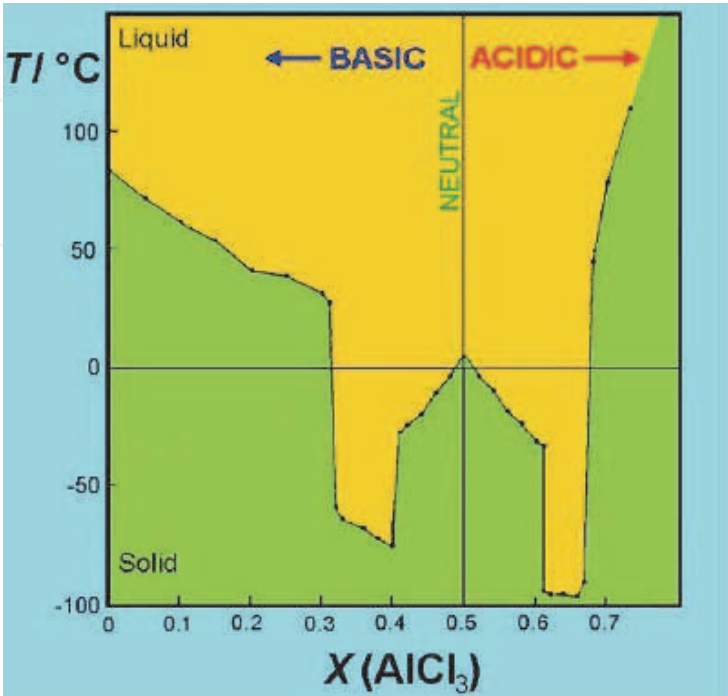


Fig. 25. The phase diagram for the [C<sub>2</sub>mim]Cl-AlCl<sub>3</sub> system a function of composition, X(AlCl<sub>3</sub>)

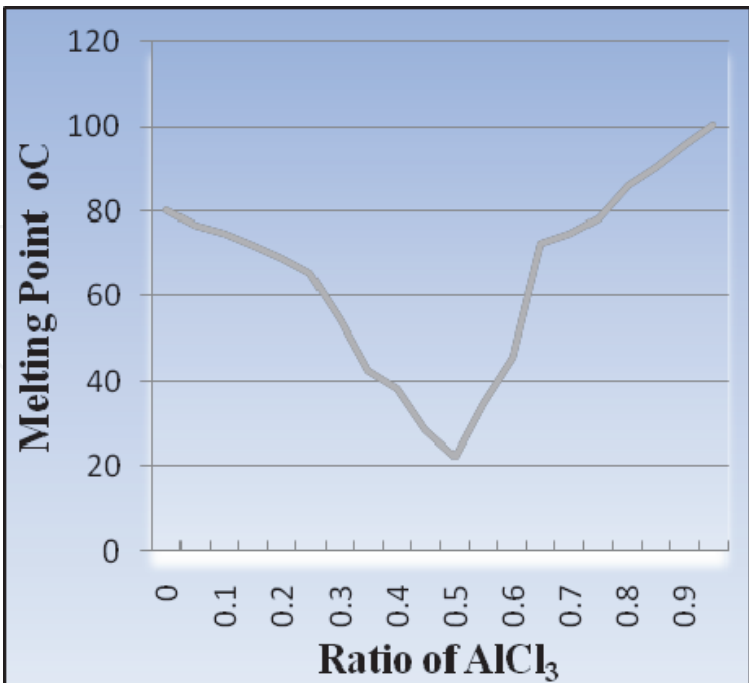


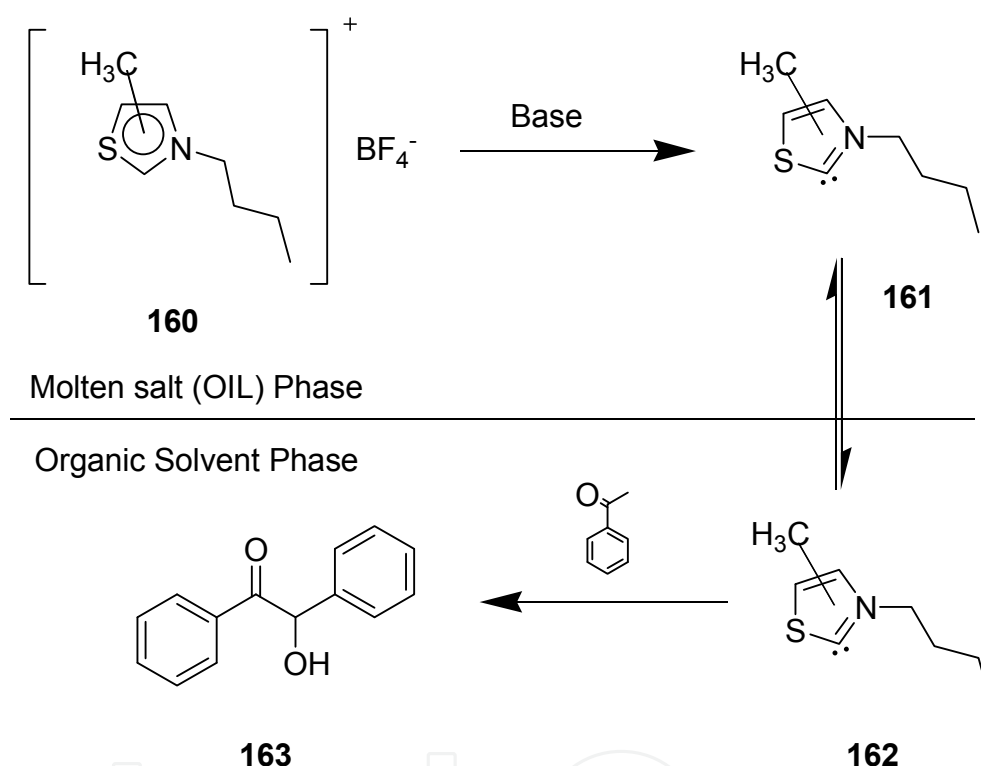
Fig. 26. The phase diagram for the [C<sub>11</sub>BT]I-AlCl<sub>3</sub> system as a function of composition, X(AlCl<sub>3</sub>)

The  $[\text{C}_2\text{mim}]\text{Cl}-\text{AlCl}_3$  system have been considered the first genuine example of an ionic liquid system that was liquid at room-temperature. So the  $\text{C}_{11}\text{BTI}-\text{AlCl}_3$  system would open up a field for electrochemistry specialists, and laid the foundations for the exploration in this field.

## 6. Comparison in catalyzing different organic reactions

### 6.1 Acyloin / benzoin condensation

Davis and Forrester have studied the benzoin condensation promoted with a small ( $\sim 5$  mol %) quantity of triethylamine and thiazolium salts (**160**). The reaction was accomplished when the thiazolium based organic ionic liquid (OIL) was stirred under nitrogen as a clearly heterogeneous mixture with a toluene solution of benzaldehyde. The reaction gave about 80% conversion to benzoin (**163**) (scheme-40) (Davis&Forrester 1999).

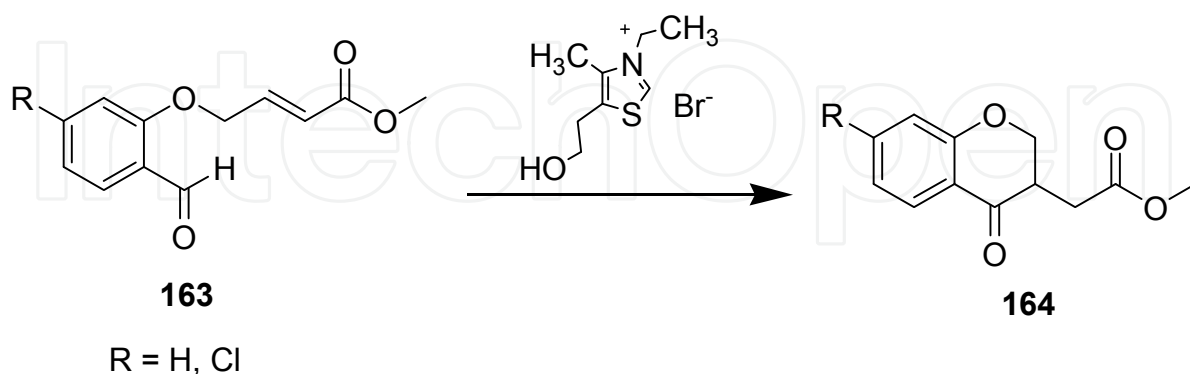


Schem 40.

### 6.2 Stetter reaction

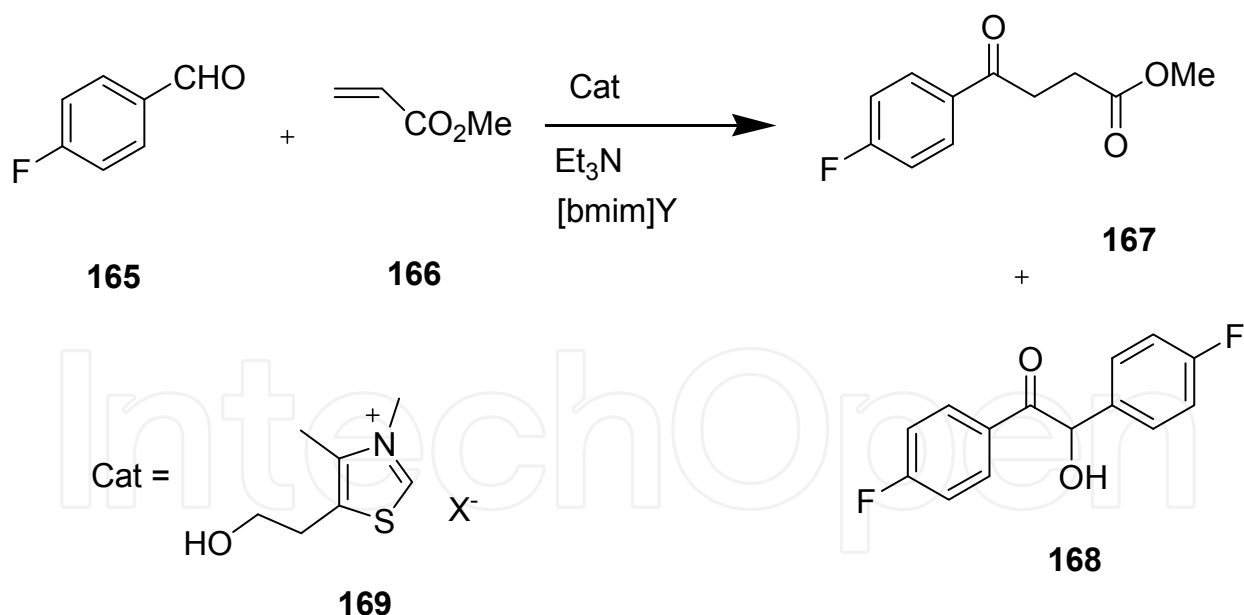
Zhou *et al.* have used the 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide for the microwave-assisted intramolecular Stetter reaction using imidazolium-type room temperature ionic liquids (RTILs) as solvents. The intramolecular Stetter reaction of (*E*)-methyl 4-(2-formylphenoxy) but-2-enoate was selected as a model to optimize the reaction conditions, using butylmethylimidazolium tetrafluoroborate  $[\text{bmim}]^+[\text{BF}_4]^-$  as the solvent. It is known that salts of various heterocycles, including imidazolium salts, can also be used as catalysts. Therefore, the ionic liquids used as solvent is also able to function as a catalyst, even if it is less active than the usual thiazolium salts, and the yields of the desired product in that case are very poor. Subsequently, it was observed that when the quantity of thiazolium salt increased from 5 to 15 mol%, the yield improved accordingly to 96%. Under microwave irradiation, a variety of aromatic substrates undergo the intramolecular Stetter

reaction in imidazolium-type RTILs as solvents, with thiazolium salts and Et<sub>3</sub>N as catalysts. Under these conditions the reactions were finished in 5–20 min and the products could be isolated in good to excellent yields, usually higher than those obtained under conventional heating conditions. Furthermore, it was possible to recycle and reuse the ionic liquid and the catalyst thiazolium salts (Zhou *et al.* 2006).



Scheme 41.

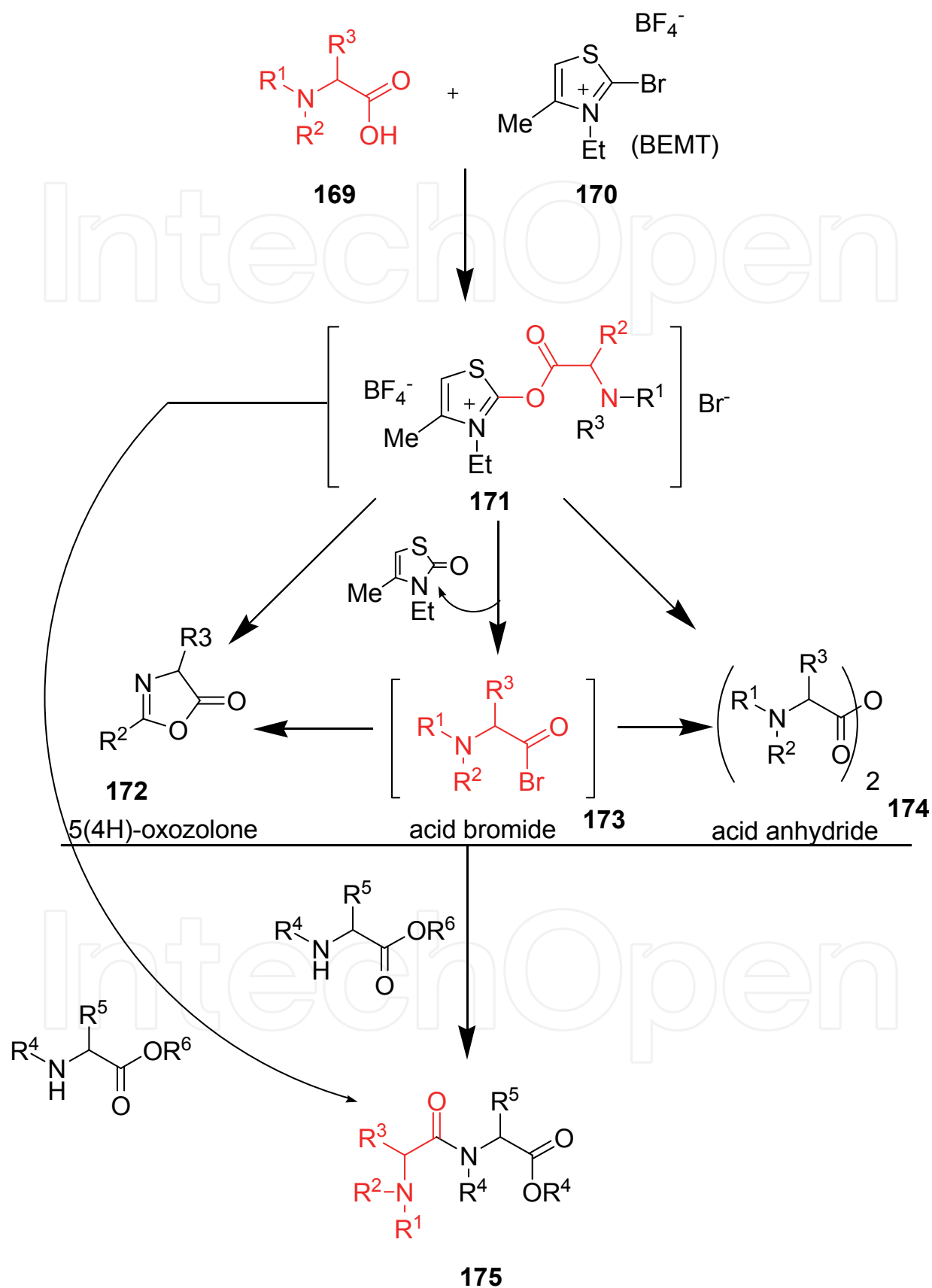
Imidazolium-type room temperature ionic liquids (RTILs) have been used for the Stetter reaction, affording the desired 1,4-dicarbonyl compounds (e.g. **167**) in good yields together with the benzoin (e.g. **168**). Thiazolium salts and Et<sub>3</sub>N are efficient catalysts for this reaction performed in ionic liquid. The possibility to recycle and reuse the solvent has been demonstrated, although it was not possible to recycle the thiazolium catalyst (Anjaiah *et al.* 2004).



Scheme 42.

### 6.3 As coupling reagent

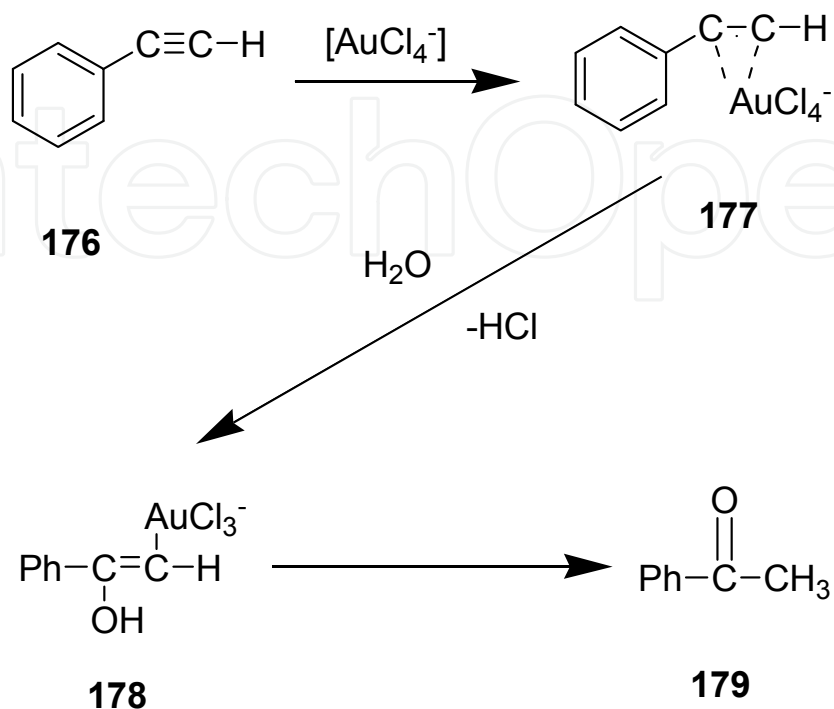
Li and Xu prepared the 2-Bromo-3-ethyl-4-methylthiazolinium tetrafluoroborate (BEMT), which is a crystalline solid, and have been reported to be an efficient coupling reagent for hindered amino acids. It was used for the coupling of *N*-alkyl or  $\alpha,\alpha$ -dialkyl amino acids (Li&Xu 1999). Mechanism of action of BEMT



Scheme 43.

#### 6.4 Use of thiazolium-gold ionic liquid as catalyst for the hydration of phenylacetylene

Deetlefs *et al.* have used the thiazolium-gold ionic liquids for the catalytic hydration of phenylacetylene to acetophenone using imidazolium ionic liquids as the reaction media.



Scheme 44.

## 7. Conclusion

This chapter provides a comprehensive information about the synthesis of thiazolium and benzothiazolium ion based salts and ionic liquids. It is evident that thiazolium and benzothiazolium ionic liquids can be as efficient solvents/catalysts as the other heterocyclic cation based ionic liquids could be (*e.g.* imidazolium). Although the quaternary salts of thiazolium and benzothiazolium have been studied since 18<sup>th</sup> century but their exploitation as ionic liquids remained limited to a few reports in the literature. Based on the Scifinder information the only article on the benzothiazolium ionic liquids has been published by our group. Moreover, the phase behaviour study of  $[\text{C}_{11}\text{BT}]\text{I}-\text{AlCl}_3$  mixtures have been described where the appropriate mole ratio of the aluminum chloride to the  $[\text{C}_{11}\text{BT}]\text{I}-\text{AlCl}_3$  mixture (Figure-25) have been found with the help of DSC. From the figure-25 it is clear that at mole ratio 0.5% the mixture of  $[\text{C}_{11}\text{BT}]\text{I}-\text{AlCl}_3$  gave lowest melting point (22.5 °C) which was checked by DSC. Here the use of thiazolium ionic liquids in different reactions (*e.g.* Acyloin condensation, Stetter reaction) as solvent/catalyst have also been included.

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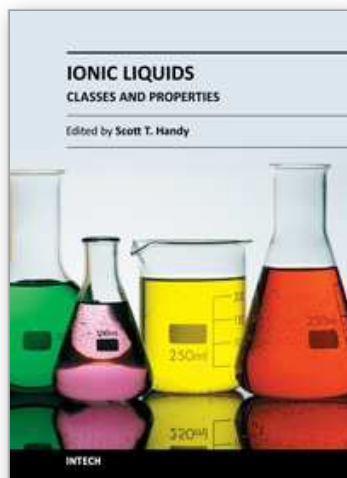
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## **Ionic Liquids - Classes and Properties**

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Room temperature ionic liquids (RTILs) are an interesting and valuable family of compounds. Although they are all salts, their components can vary considerably, including imidazolium, pyridinium, ammonium, phosphonium, thiazolium, and triazolium cations. In general, these cations have been combined with weakly coordinating anions. Common examples include tetrafluoroborate, hexafluorophosphate, triflate, triflimide, and dicyanamide. The list of possible anionic components continues to grow at a rapid rate. Besides exploring new anionic and cation components, another active and important area of research is the determination and prediction of their physical properties, particularly since their unusual and tunable properties are so often mentioned as being one of the key advantages of RTILs over conventional solvents. Despite impressive progress, much work remains before the true power of RTILs as designer solvents (i.e. predictable selection of a particular RTIL for any given application) can be effectively harnessed.

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