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Research Article

Azoniallene Salts: Synthesis and their Utility in Heterocyclic Synthesis

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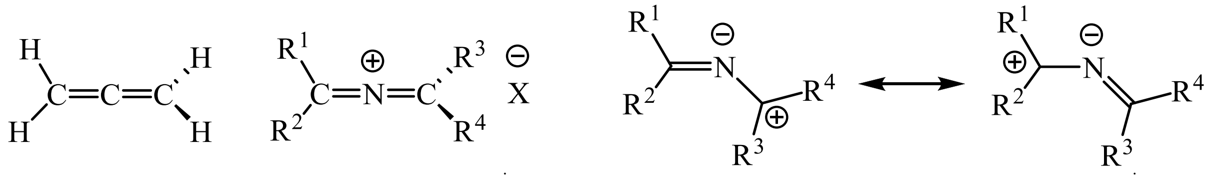
Abstract: Methods for the preparation of different azoniallene salts were reviewed. The utility of azoniallene salts in organic synthesis demonstrates their importance in the synthesis of several heterocycles. The reactions of the title compounds are subdivided into groups that cover reactions yielding mono-heterocycles e.g., pyrimidines, triazines, thiadiazines, pyrazoles, triazoles, thiadiazoles, dithiazoles and even fused heterocyclic e.g., isoindolo-quinazolines, indazoles and benzoxazines.

1. Introduction

Cumulenes, as defined by Richard Kuhn in 1938 [1], are compounds having sp-hyperdized carbon attached to another sp or sp^2 hyperdized-carbon via germinal double bonds. As shown in scheme 1, Allene **1** is the parent compound of cumulenes, where the family of allene-based compounds, broadly known as heterocumulenes, is produced by replacement of one or more carbon atoms by a heteroatom. For instance, the 2-aza analogues of allenes are the 2-azaallenium salts **(2A)**.


1 **2A:** D_{2d}-symmetry for R^i = H, α = 180°, β = 90° **2B** **2B:** C_{2v}-symmetry for R^i = H, α = 120°, β = 0°

α= bond angle C=N=C, β= angle between the planes through N-R^1-C-R^2 and N-R^3-C-R^4

Scheme (1)

Several classes of formal 2-azaallenium compounds can be constructed if the number of unit charges is restricted to one per atom, while the number of electron pairs of the allene unit is restricted to eight. This series of ions that have the general structure **2**, will be referred to as 2-azoniaallene cations throughout, regardless of their symmetry, being local D_{2d}, C_{2v} or an intermediate geometry between these two extremes [2,3]. Interestingly, the C=N=C unit of 2-azoniaallene cations was found to be unexpectedly flexible [4,5], reflecting the intriguing nature of the consecutive two- π bond system of these cations. Crystal structure of compounds **2** with a linear **2A** or bent **2B** C=N=C units are known [6]. For many of these compounds, X-ray structural analyses have shown geometries between those of **2A** and **2B** [6]. Moreover, the molecular geometries of cations **2** are not only determined by the subtle effects of the substituents, but also, they differ in solution from those in the solid state. They even differ from one solvent to another. In most cases the exact geometry of the cations **2** is not known at all [7]. It was suggested that a positive charge is located on the carbon atoms of the C=N=C unit, have lead to the name "2-azapropenylium" being used quite often in the literature, in contrast the widely used name "2-azoniaallene" assumes that the positive charge resides on the nitrogen atom [8]. Actually, in many cases, e.g. in cation **2** with a diamino substituent, the positive charge is located neither on the carbon nor on the nitrogen atom of the C=N=C unit but mainly on the substituent [9]. In order to avoid different naming assumptions for members of such a class of compounds with a continuous range of charge distributions it is recommended to call all types of cations **2** "2-azoniaallene cations", suggesting the relationship of these ions to allenes.

A large number of azoniaallene salts has been synthesized as potential antimalarial drugs [10], hypoglycemic agents [11] and as clinically effective agents for the oral treatment of some types of

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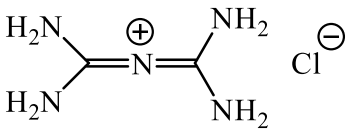
diabetes [12]. Azoniaallene salts are also versatile building blocks for organic synthesis, largely due to their ability to react with heteronucleophilies to produce a series of open-chain and heterocyclic compounds, natural and non-natural products of possible biological interest such as triazol, oxadiazole, triazine, indol, piperazine, ….etc [13]. The main purpose of this review is to present a survey of the literature on the synthesis and reactions of azoniaallene salts.

2. Synthesis of Substituted Azoniaallene Salts

2.1. Synthesis of Substituted 2-Azoniaallene Salts

Certain hetero substituted 2-azoniaallene salts **2** have already been known since the last century. For instance, in 1879 Rathke prepared the monoprotonated biguanide **3**, which regarded as a tetra-amino substituted 2-azoniaallene chloride [14].



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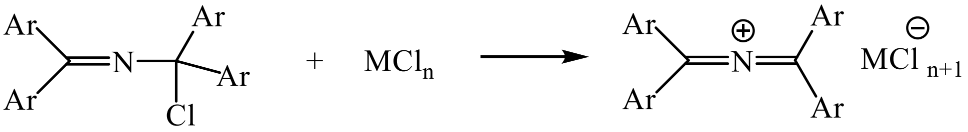
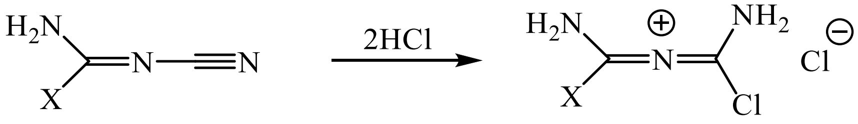
In 1969 the first exclusively carbon substituted 2-azoniaallene salts were prepared by Samuel and Wade, who treated α- chloroimines **4** with Lewis acids to obtain a few tertaaryl substituted 2-azoniaallene salts **5** [15].



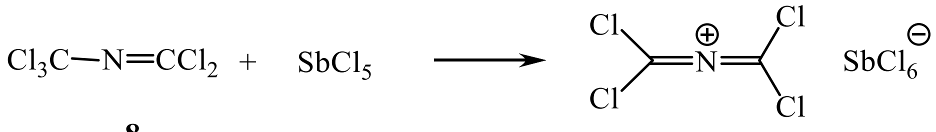
4 **5**

Many methods, mostly starting from imine precursors, have been developed for the preparation of different hetero and exclusively carbon substituted 2-azoniaallene salts **2** [16]. Allenstein et al. added hydrogen chloride to the nitrile group of the cyanamides **6** to obtain the 2-azoniaallene salts **7** [17].



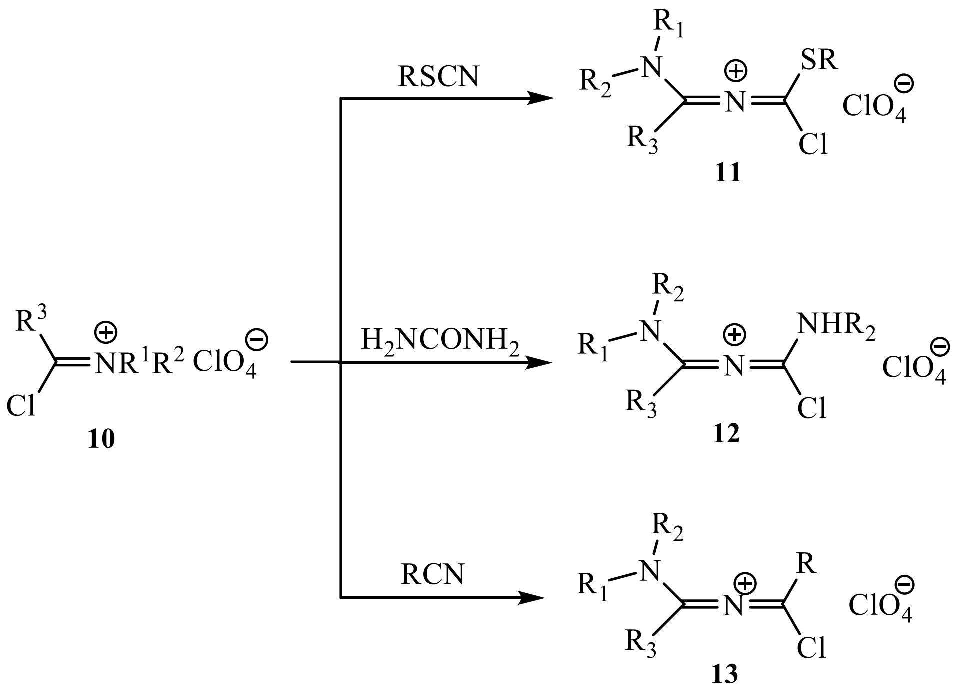
6 **7**

The tetrachloro 2-azoniaallene hexachloroantimonate **9** was first prepared by Schmidt, who reacted trichloromethylisocyanide dichloride **8** with antimony pentachloride [18].



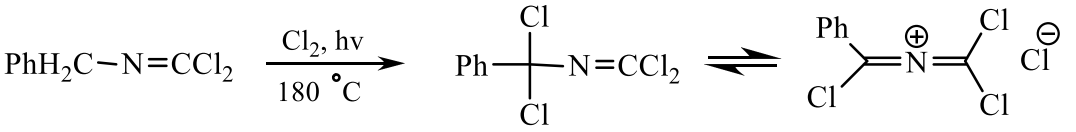
8 **9**

Chlorocarbenium ions of the Vilsmeier-Arnold type **10** (R^1= R^2= substituted phenyl, alkyl; R^3= Ph, 4-ClC_6H_4, Cl) were found to react with thiocyanate, *N*,*N*-dimethylurea, and nitriles under mild conditions, affording the corresponding chlorosubstituted 2-azoniaallene salts **11-13** [19].



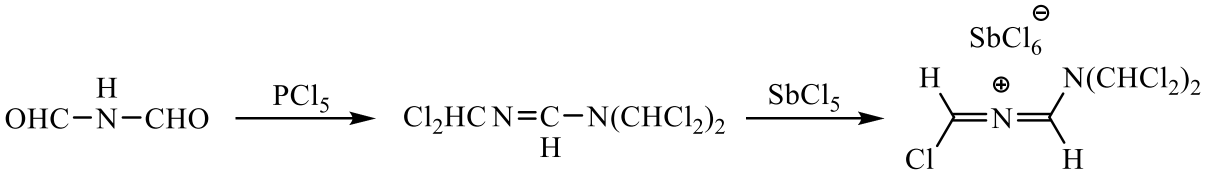
10 **11** **12** **13**

High temperature chlorination of certain alkylimines leads to compounds which can formally be regarded as chloro substituted 2-azoniaallene chlorides, e.g. **14** [20].



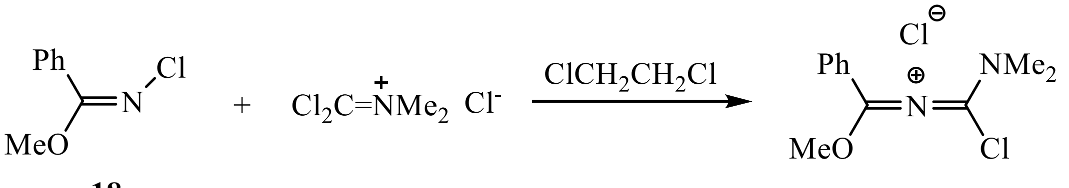
14

Treating diformamide **15** with phosphorous pentachloride gave compound **16** which is transformed upon reaction with $SbCl_5$ into a proposed structural compound **17** [21].



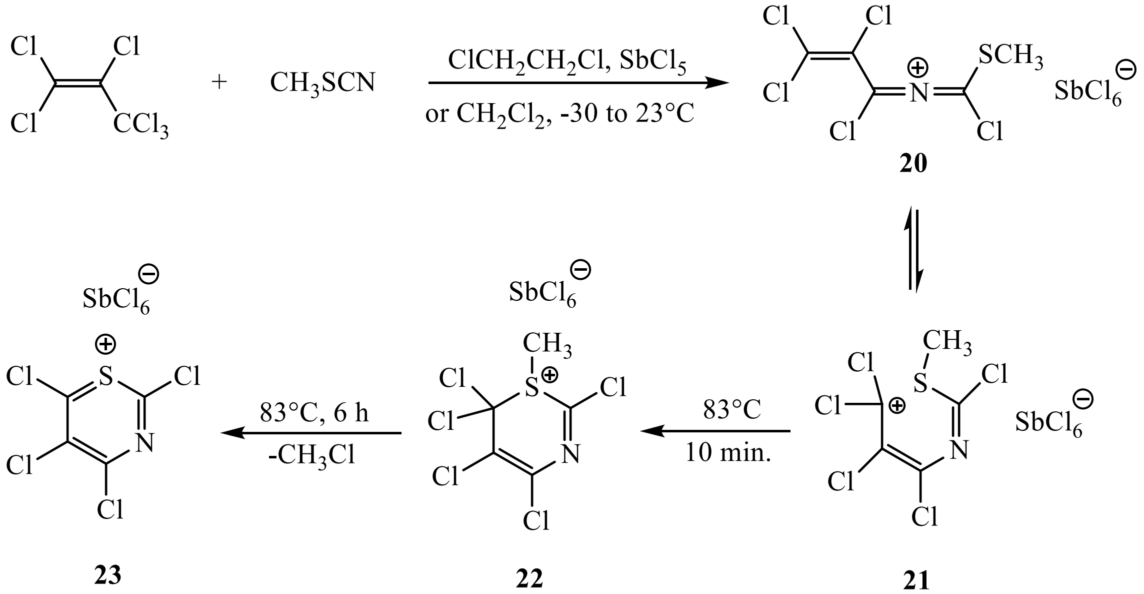
15 **16** **17**

Treatment of the *N*-chloroimidate **18** with iminium chloride leads to the formation of compound **19**, which can be written as a salt [22].

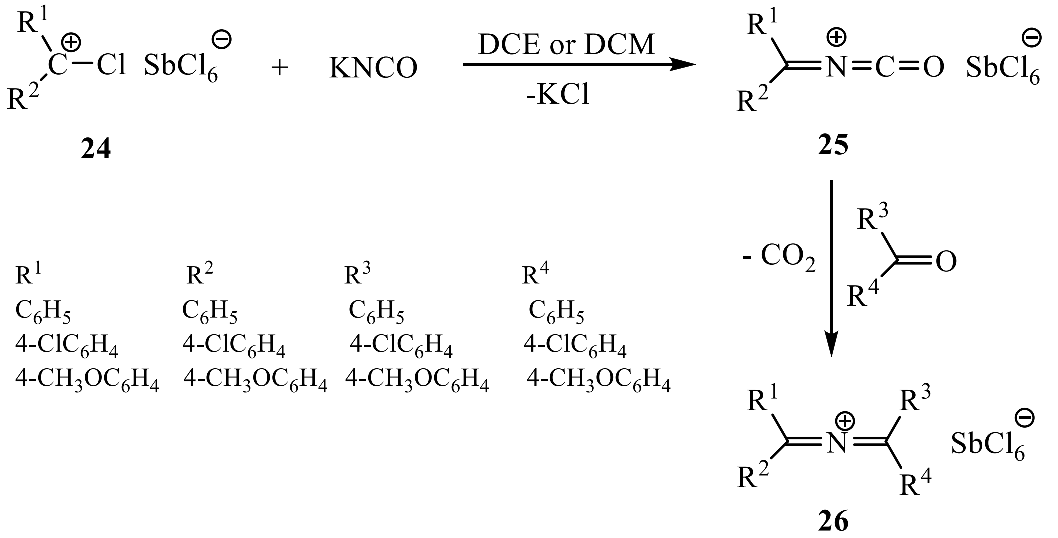


18 **19**

The hexachloropropene undergoes Ritter reaction with methylthiocyanate and subsequent [1,3]-chlorotropic rearrangement, in the presence of $SbCl_5$, furnishing chlorosubstituted 2-azoniaallene hexachloroantimonate **20**. Boiling a solution of **21** in dichloroethane under reflux (83 °C) for few minutes, affects its cyclization to thiazinium salt **22**. Prolonged heating for few hours results the formation of thiazinium salt **23**. The thiazinium salt can also be easily obtained by using isopropyl thiocyanate instead of methyl thiocyanate [23].

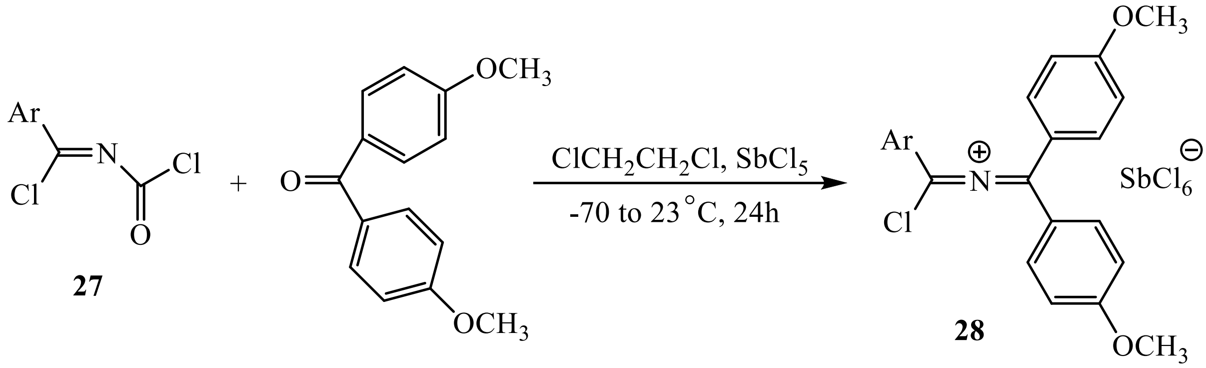


The reaction of diarylchlorocarbenium salts **24** in boiling dichloromethane or dichloroethane with potassium cyanate leads to the formation of the 1-oxo-3-aza-butatrienium cumulene salts **25** which are unstable, and therefore reacting in situ with ketones to give 2-azoniaallene salts **26** [24].

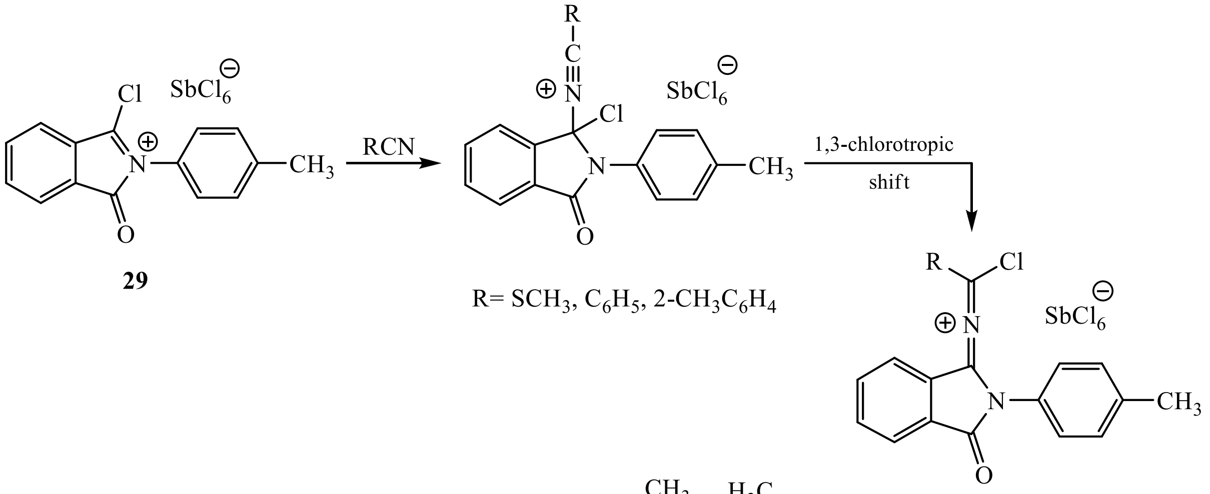


R^1	R^2	R^3	R^4
C_6H_5	C_6H_5	C_6H_5	C_6H_5
$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$

Also, the reaction of ketones with carbamoyl chlorides **27** in presence of antimony pentachloride leads to the corresponding 2-azoniaallene salts **28** [25].



3-Chloro-1-oxoisoindolium salt **29** reacts with nitriles according to Ritter Reaction to give initially an α-chloronitrilium salt, which rearranges *via* a 1,3-chlorotropic shift to the thermodynamically more stable 2-azoniaallene salt. Thus, it reacts with two equivalents of the electron-rich nitriles, dimethylcyanimide to produce 2-azoniallene salts **30** [26].



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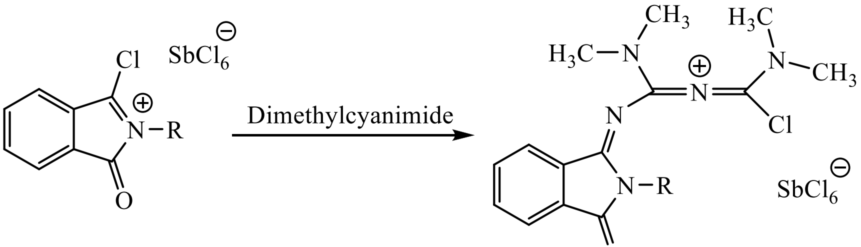
R= SCH_3, C_6H_5, 2-$CH_3C_6H_4$

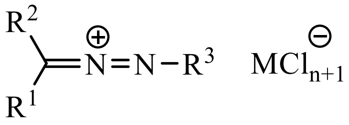


R= 4-CH_3-C_6H_4, $CH_2C_6H_5$, C_6H_{11}

30

2.2. Synthesis of Substituted 1-Aza-2-Azoniaallene Salts

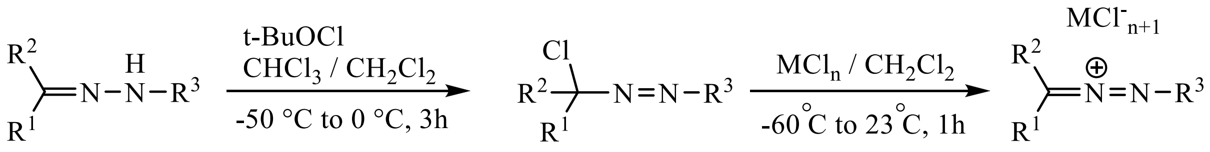
Although many 2-azoniaallene salts are quite stable and form well-crystallized compounds, all attempts to isolate a representative of the related 1-aza-2-azoniaallene salts **33** have failed so far [27].



33

In an attempt to synthesize the first stable 1-aza-2-azoniaalene salt, hydrazones were oxidized with *tert*-butyl hypochlorite to obtain the germinal chloro azo compounds. This method, which was introduced by Moon, seems to be generally applicable to hydrazones of ketones **31**, in contrast to chlorination with chlorine, which sometimes leads to mixtures of compounds [28].

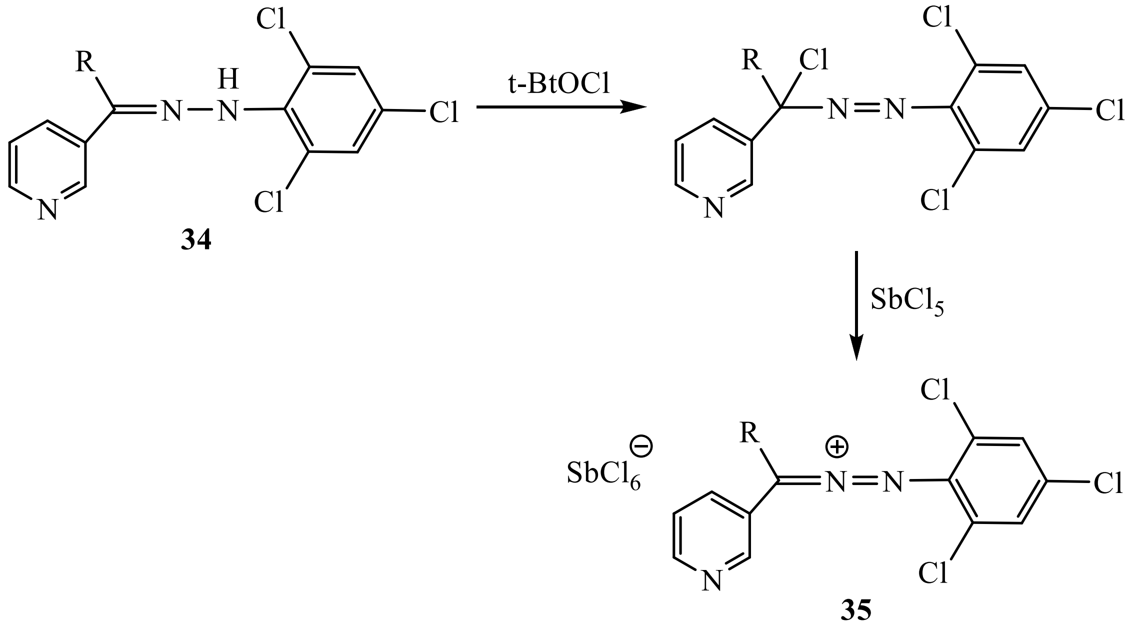
Short lived 1-aza-2-azoniaallene salts **33**, were formed at low temperature from 1-chloroalkyl-azo compounds **32**, *via* treatment with Lewis acids like aluminum chloride ($AlCl_3$) in dichloromethane. A deep yellow solution is formed, which shows a strong broad IR absorption at ν = 1899 cm^{-1}. This band is tentatively assigned to the unsymmetrical valance vibration of a cummulene, with antimony pentachloride ($SbCl_5$) in dichloromethane compound **32** form orange precipitates which easily dissolve in acetonitrile [29,30].



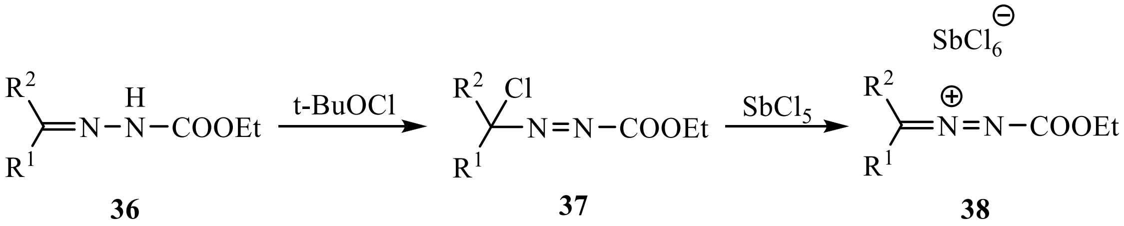
31 **32** **33**

R^1= Me, Et; R_2= Me, Et, i-Pr; R^3= 2,4,6-$Cl_3C_6H_2$, 4-Cl-C_6H_5

A series of highly reactive 1-aza-2-azoniaallene salts derived from pyridine derivatives, prepared by oxidation of pyridyl hydrazones **34** by *tert*-butyl hypochlorite followed by Lewis acid $SbCl_5$ at -60 °C, gave the germinal chloropyridyl-azo compounds **35** in a good yield [31].



The hydrazones **36**, prepared by condensation of ethyl carbazate with ketones in boiling ethanol containing a few drops of acetic acid, were oxidized with *tert*-butyl hypochlorite resulting in the formation of the (chloroalkyl)azo compounds **37**. These were reacted with antimony pentachloride at -60 °C in dry dichloromethane to afford the heterocumullene, *N*-substituted **38** with a leaving ester group [32].



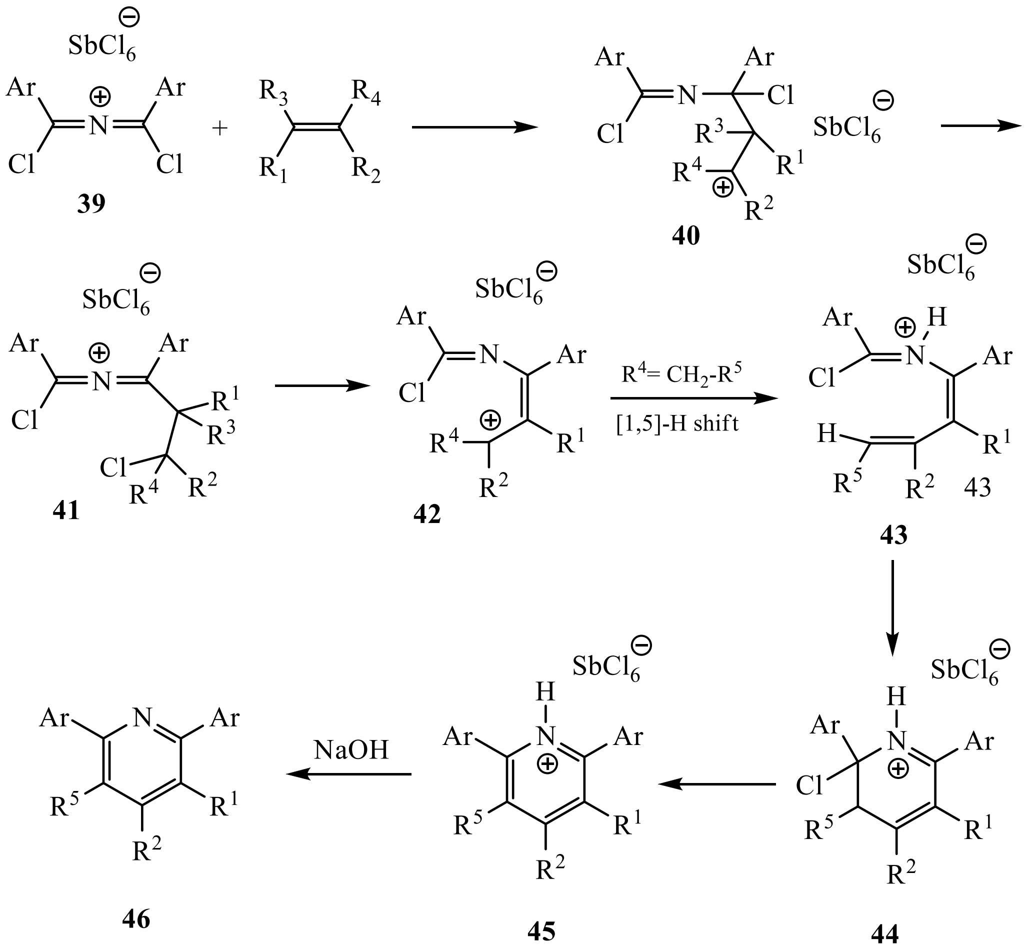
$R^1R^2 = (CH_2)_4$, $R^1R^2 = (CH_2)_5$, $R^1 = Me$; $R^2 = Me, Et, i\text{-}Pr$

3. Utility of Azoniaallene Salts in Heterocyclic Synthesis

Substituted azoniaallene salts are strong electrophiles, which should be versatile reagents for the preparation of heterocyclic and other nitrogen containing compounds. A few transformations with nucleophiles have already been published in the literature.

3.1. Synthesis of six-membered heterocyclic compounds

It was reported that, reactions of 2-azoniaallene salts with olefins and acetylenes depend on the substitution pattern of the olefin. New types of 2-azoniaallene salts **41**, 4-azapentadienyl salt **42**, or pyridinium salt **45**, respectively, were obtained. To account for the results, the reaction sequence shown in scheme (2) was proposed. The olefins added to the electron deficient imidic carbon atom of **39** to give carbenium salts **40** and [1,3]-shift of chloride yielded the 2-azoniaallene salts **41**. For R^3= H, spontaneously even slow elimination of hydrogen chloride, furnished the pentadienyl salt **42**. While appropriately substituted compounds **41** and **42** could be isolated. The intermediates **43** and **44** were only plausible. For R^4= CH_2-R^5, a [1,5]-prototropic rearrangement afforded the hexatrienyl salt **43**. This underwent electrocyclic ring closure to **44**. Elimination of hydrogen chloride provided the pyridinium salts **45** and with aqueous sodium hydroxide or sodium hydrogen carbonate the pyridinium salts **45** were transformed into the free base **46** [33].

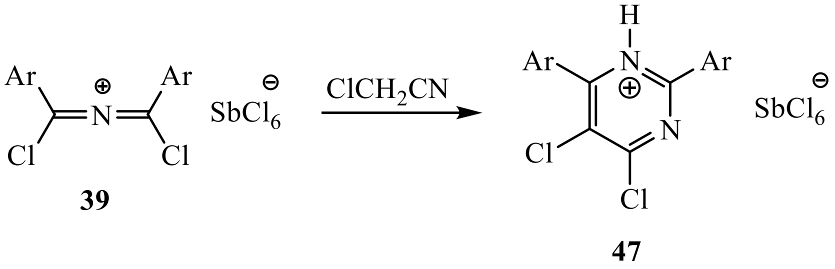


Scheme (2)

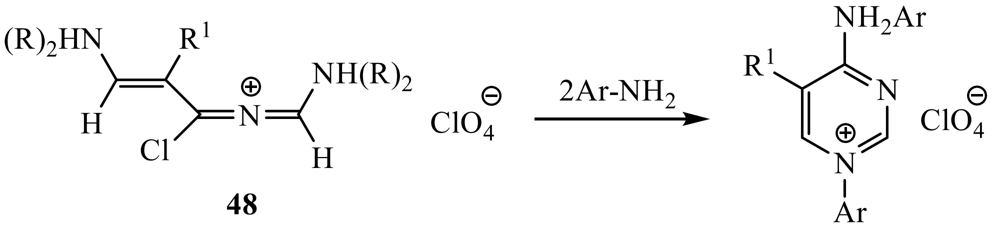
The mechanism of reactions between 1,3-dichloro-1,3-diphenyl-2-azoniaallene cations and 2-methyl-1-propene have been explored at B3LYP/6-31G* level of theory. It was found that the positive charge in 2-azoniaallene made the reaction more complicated. Different reaction paths and products have been rationalized and verified. For the [2+2]-cycloaddition reaction, [2+2]- adduct was not stable due to larger steric hindrance, which accounts for why Hitzler's experiment did not observe the [2+2] product. The rate constants for the main steps were calculated with conventional transition state theory [34].

Density functional theory B3LYP/6-31G* and SCRF//B3LYP studies on the reactions between 1,3-dichloro-1,3-diphyenyl-2-azoniaallene and 2-methyl-1-propene have resulted in the following conclusions: 1- The reaction produced an unstable intermediate first, whose energy is above the reactants, and then two reaction paths could performed, one is to form 4-membered ring adduct; another is to form a new 2-azoniaallene, a carbenium and a 6-membered ring product. 2- Due to its instability, 4-membered ring adduct could go back to the intermediate with a rate constant of 3.58 x 10^{-2} s^{-1}, which accounts the experimental fact that 4-membered ring adduct could not be separated [35,36].

According to work performed by Jochims et al., compound **39** reacted with chloroacetonitrile, where the corresponding primidinium salt **47** is obtained [37].



The azoniaallene salts **48** have been reacted with two moles of primary amines to give the corresponding pyrimidinium salts **49** [38].



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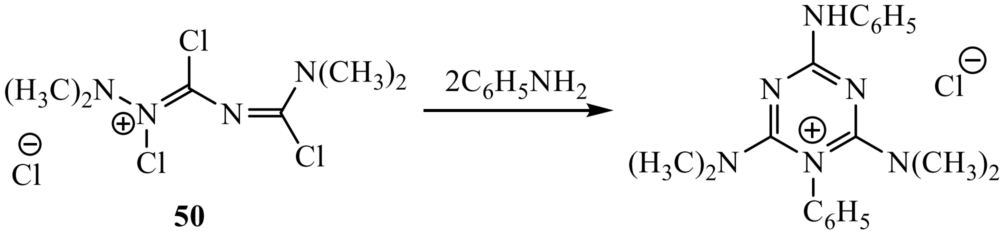
49

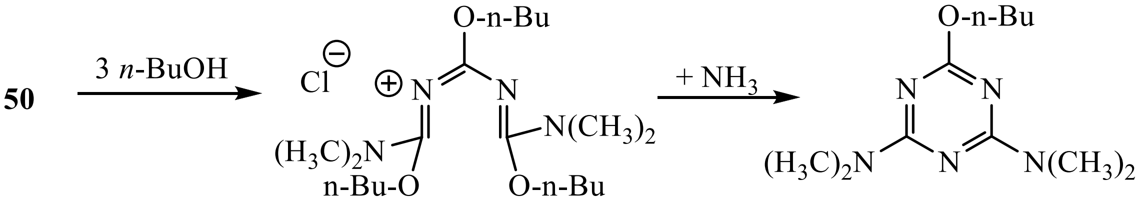
Triazinium salt and trazine derivatives were obtained from azoniaallene salts; the salt **50** reacted with primary amines to give corresponding the triazinium salt **51**.



50

51

The reaction of **50** with an excess of n-butanol at 80 °C led to a mixture of many compounds. With three equivalents of n-butanol, the formation of **52** was postulated, which reacted smoothly with aqueous ammonia to give the triazine derivative **53** [39].



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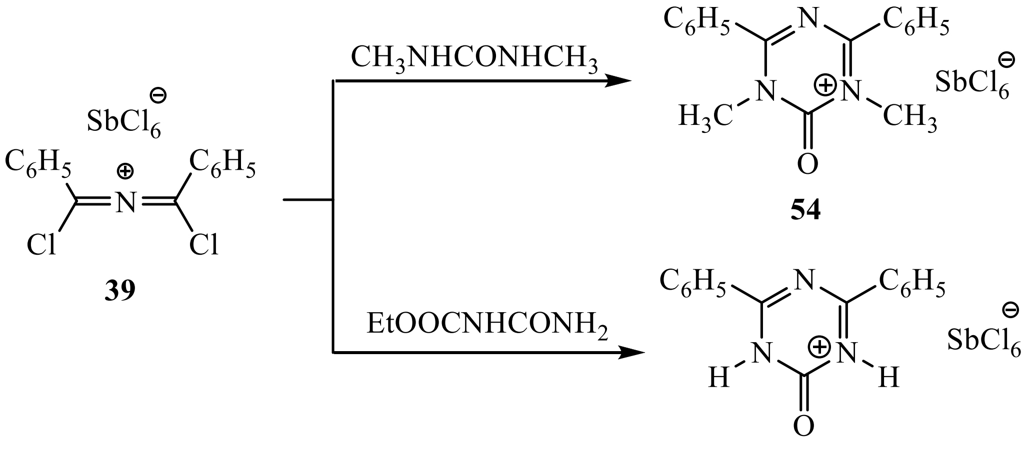
53

1,3-Dichloro-1,3-diphenyl-2-azoniaallene salt **39** reacted with 1,3-dimethylurea to give the triazinium salt **54**. With ethyl allophanate the ester group was lost giving the triazine **55** [40]. The reaction with aminothiazol derivative afforded the bicyclic thiazolo[3,2-a]-[1,3,5]triazinium **56**, Moreover, the reaction of thiosemicarbazone derivatives with symmetric azoniaallene salt afforded the corresponding triazinium salts, which underwent neutralization by Na_2CO_3 solution furnishing the corresponding triazine derivatives **57** [41].



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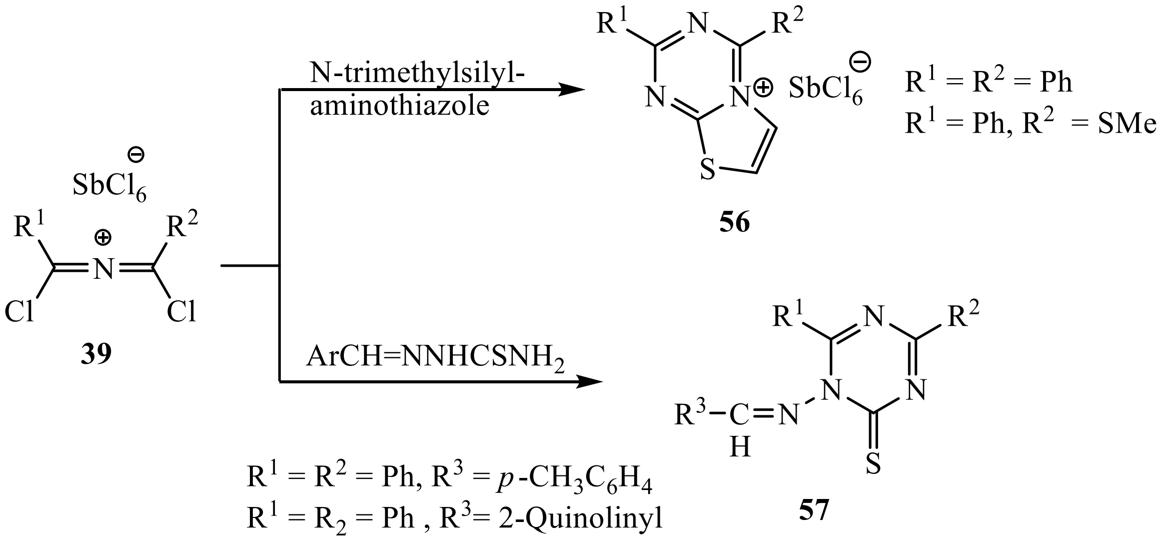
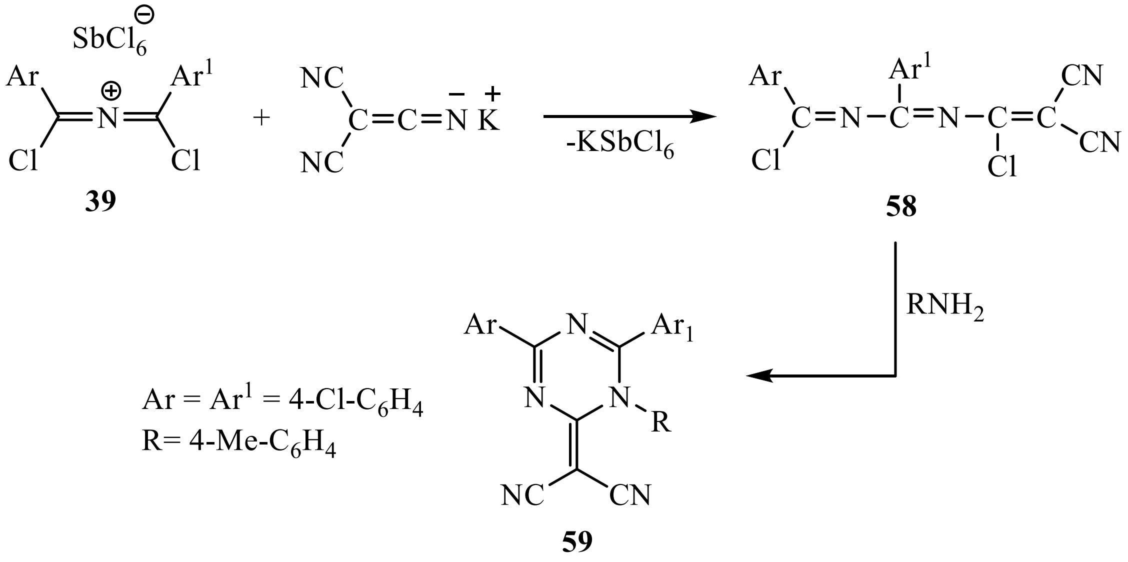
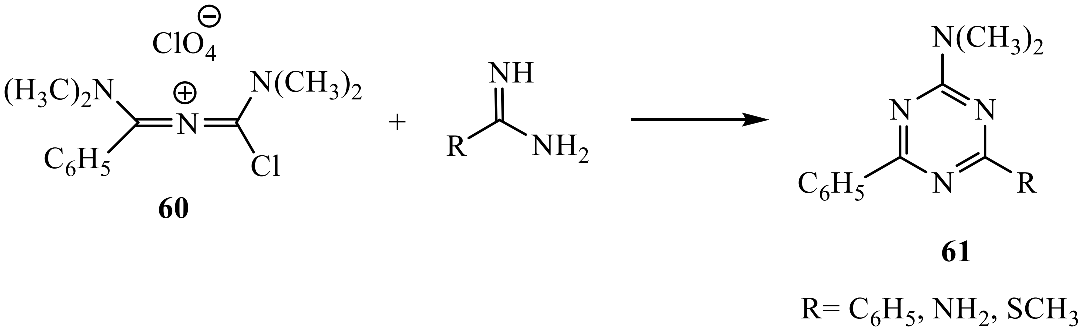


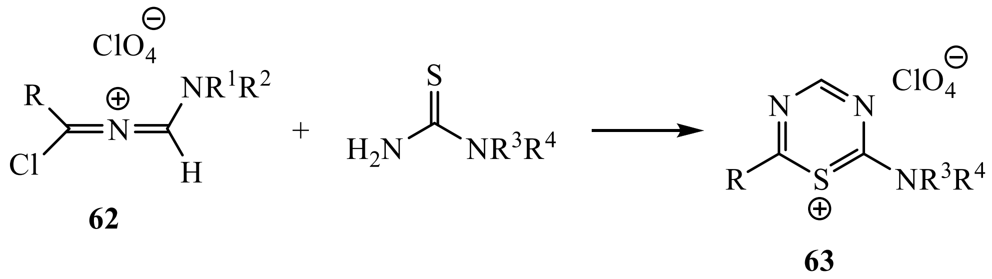
Treating compound **39** (Ar= Ar^1= 4-ClC$_6$H$_4$) with the potassium salt, for which the structure of a dicyano ketenimine had been proven, the electrically neutral compound **58** was formed. Compound **58** reacted as a bifunctional electrophile with p-toluidine to furnish the triazine **59** [42].



Azoniaalene salt of the type **60** had been reacted with simple amidines to furnish the corresponding triazines **61** [43].



It was found also that, thiadiazinium salts **63** were obtained from azoniaallene salts **62** and thioureas. From KSCN and compound **64,** the thiadiazinum salt **65** was obtained [44].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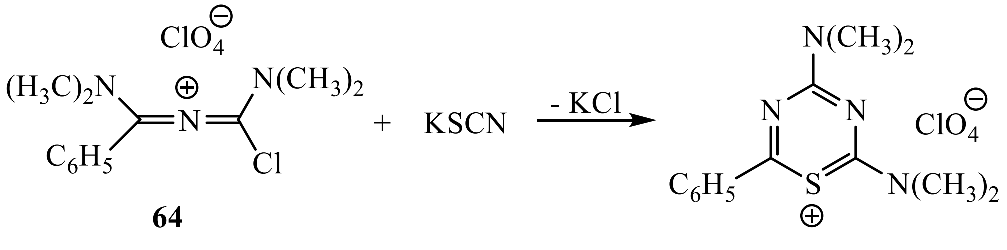
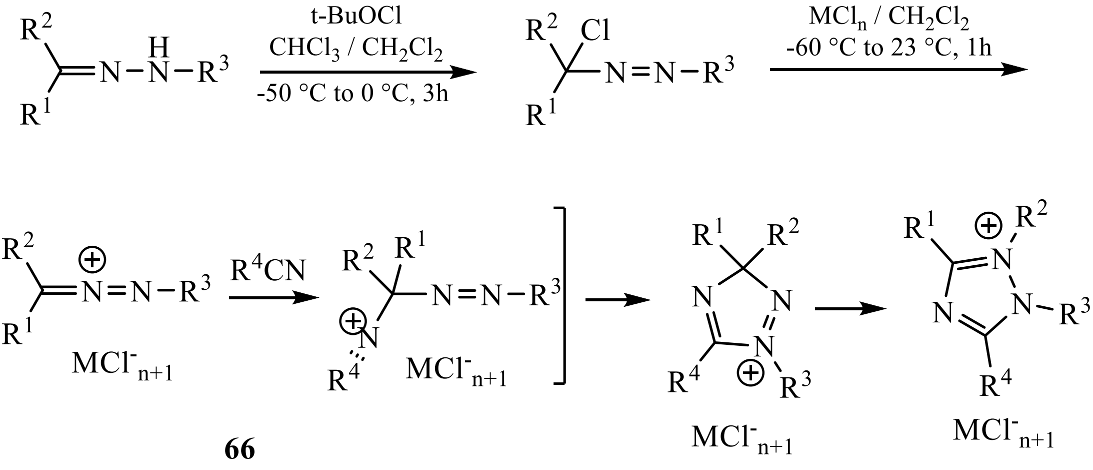

64
65

3.2. Synthesis of five-membered heterocyclic compounds

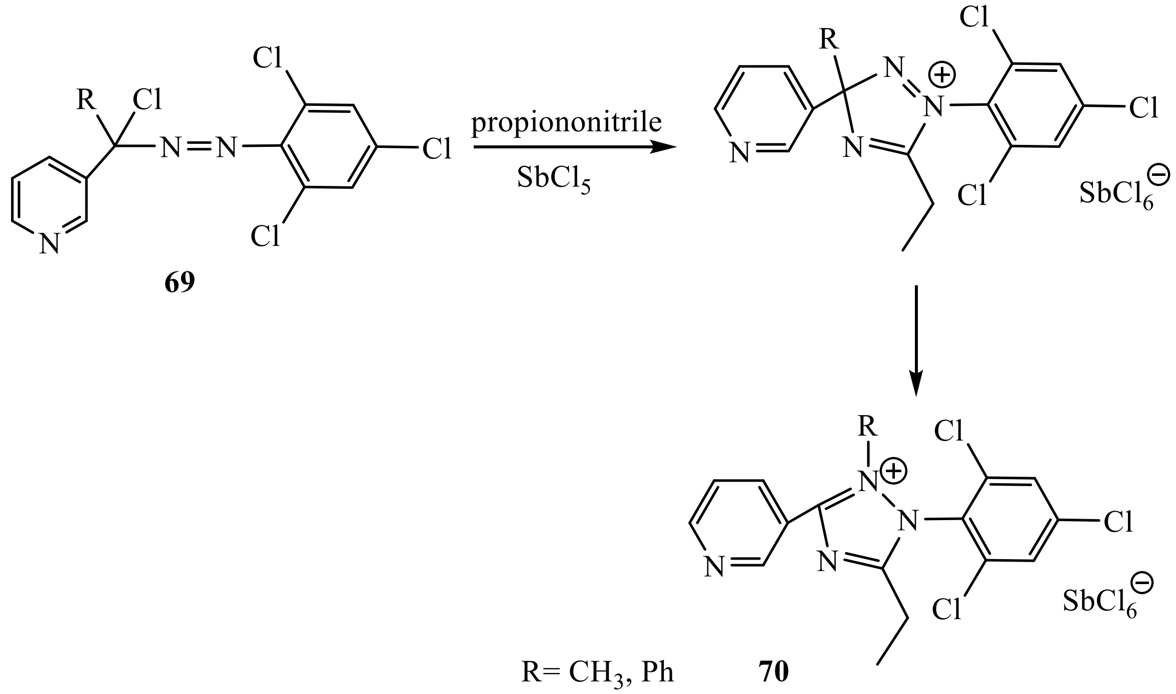
Preparation of azoniaallene salts as reactive intermediates, 2- azoniaallene and 1-aza-2-azoniaallene salts reacted as four electron-three center compounds in cycloaddations with many types of multiple bonds like nitriles.

1-Aza-2-azoniaallene salts reacted with nitriles to give a nitrilium salt **66**. Obviously, nitrilium salts with an azo group in α-position to the nitrilium nitrogen atom cyclized spontaneously to furnish 1,3,3-trisubstituted 3H-1,2,4-triazolium salts **67** and tended to rearrange to 1,2,3-trisubstituted 1H-1,2,4-triazolium salts **68** [45].

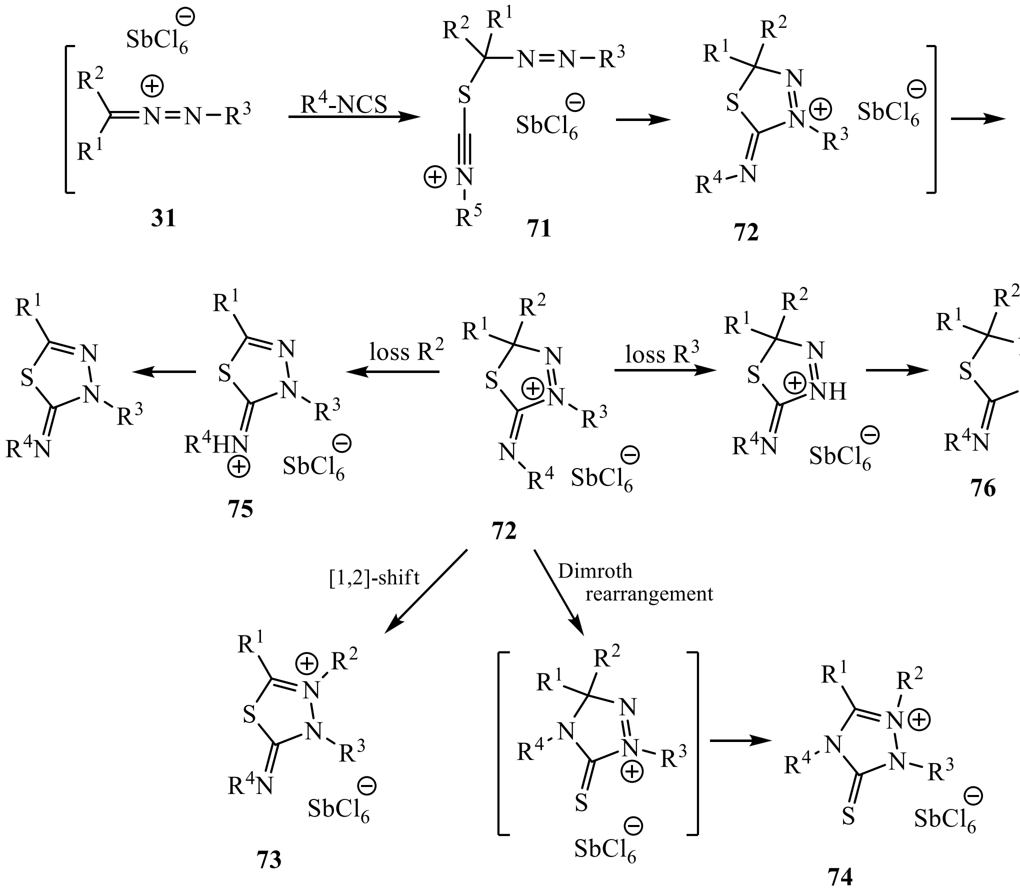

66
67
68

R^1= Me, Et, Ph; R^2= Me, Et, i-Pr; R^3= 2,4,6-$Cl_3C_6H_2$; R^4= Me, Et, i-Pr

It was found that, it is possible to trap the highly reactive 1-aza-2-azoniaallene salts **69** with nucleophiles such as propiononitrile to obtain the triazolium salts **70** [46].

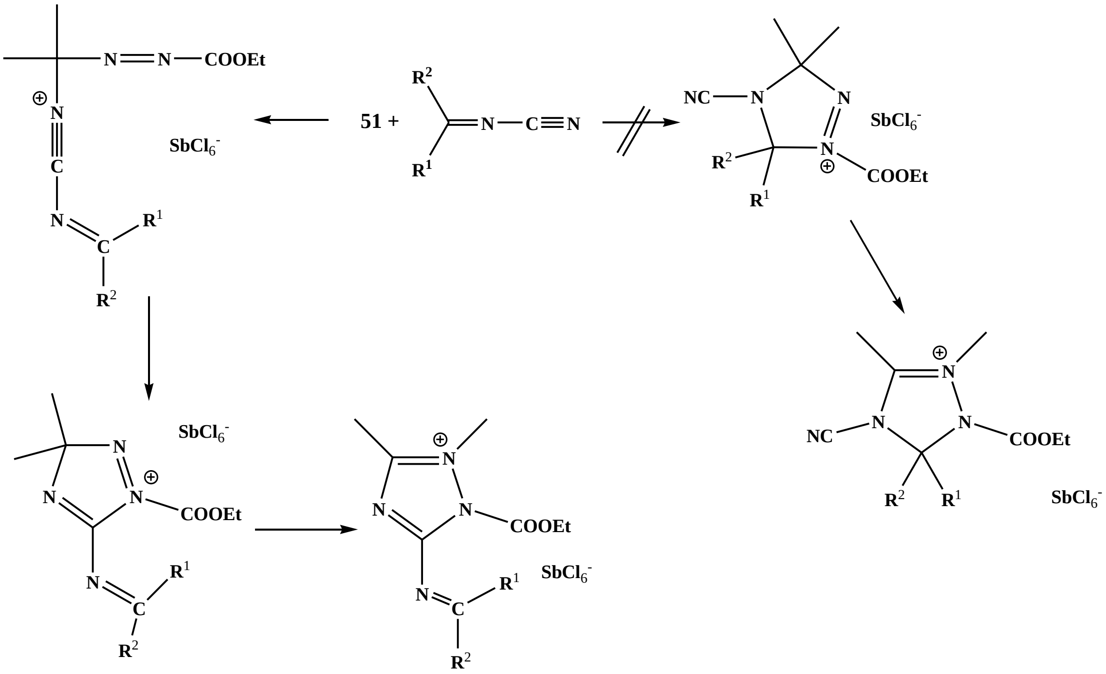


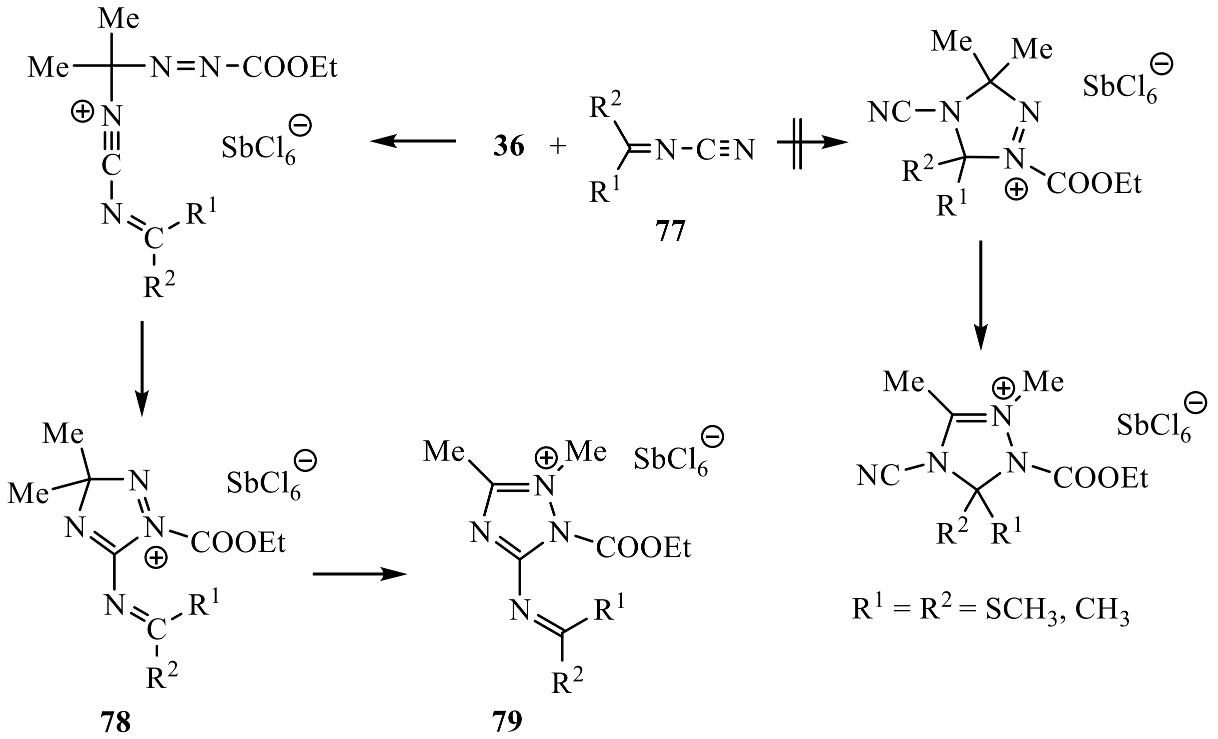
While 1,3-dipolar cycloadditions of neutral 1,3-dipoles are widely used in preparative organic chemistry, where cycloadditions to isothiocyanates are known to occur both on the C=S and the C=N bonds in a competitive manner. Cycloadditions of heteroallenes **31** to isothiocyanates seems to be two step reactions with nitrilium ions **71** as intermediates. While isocyanates act as N-nucleophiles towards heteroallenes **31** furnishing 1,2,4-triazolium salts *via* acylium intermediates, whereas isothiocyanates react as S-nucleophiles affording 1,3,4-thiadiazolium salts **73, 75** and **76** or 1,2,4-triazolium salts **74** [47].



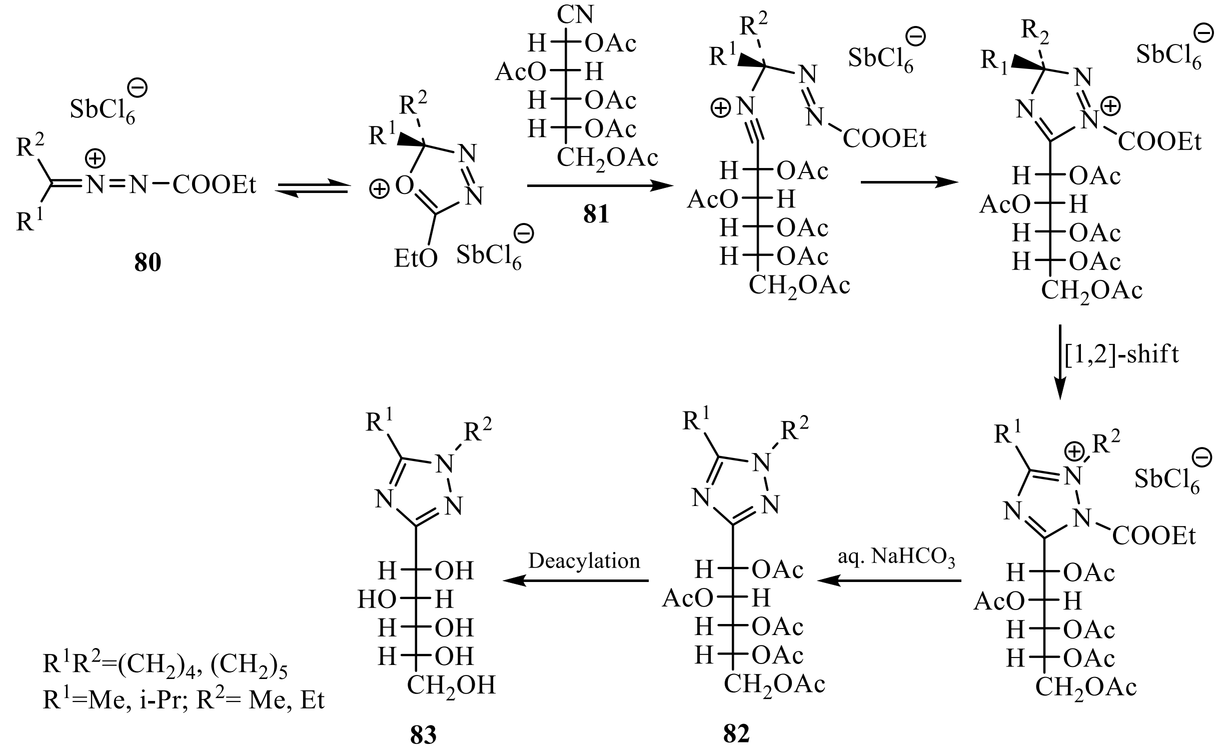
The products obtained from cycloaddition with isothiocyanates depend on; a) ability of a substituent of the heteroallene salts to undergo a [1,2]shift as a cationic charged migrant or to act as a cationic leaving groups (as a stable carbenium ion), b) Dimroth rearrangement of the initially formed thiadiazolium salts to triazolium salts [48].

Also the mechanisms of the cycloaddition reactions between 1-aza-2-azoniaallene salts and isocyanates have been theoretically exprolated by Mei-Ju Wei, et.al. [49]. The applicability of cycloaddition protocol for **36** (R^1= R^2= Me) with another competitive system like α-iminonitrile compounds **77** which contain both C=N and C≡N in a conjugated system. It was found that, the nitrile group of **77** reacted extremely fast with the cation **36** to produce the triazolium salts **79** *via* the intermediate **78** and no reactions were observed with the nucleophilic imino group. On the other hand, the reaction of cumulene **36** with **77** (cyanopyridine) in presence of $SbCl_5$ did not form the expected triazolium salt in contrast to the reaction of cumulene (cyanopyridine) **77** with aromatic nitrile [50].

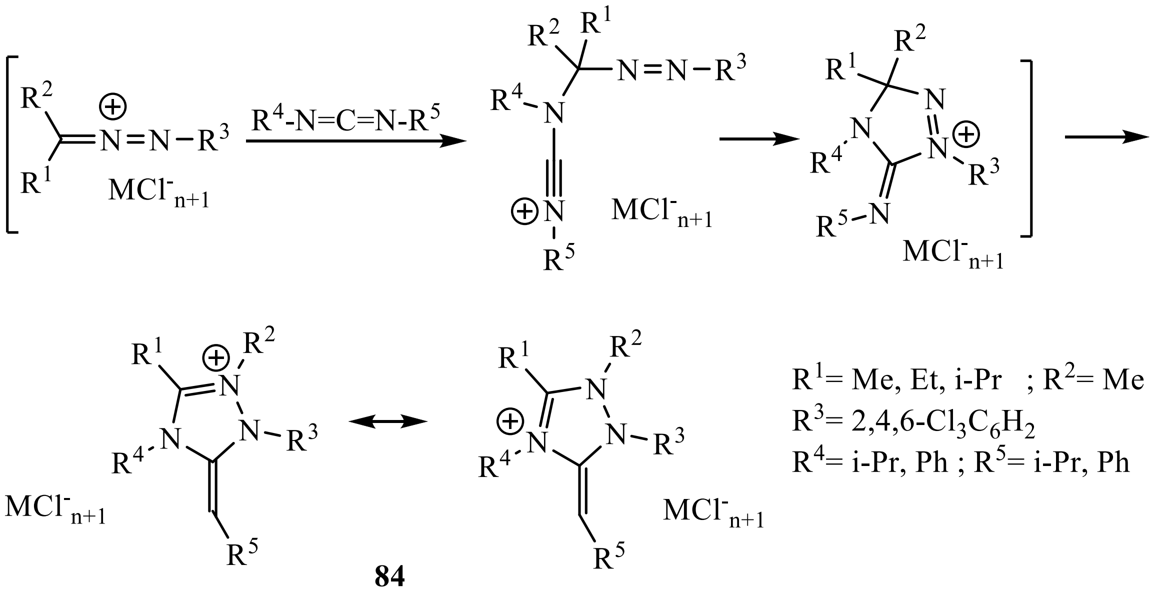




Also, C- and N-glycosides, were prepared by cycloadditions of 1-aza-2-azoniaalene salts to glycosyl nitriles, glycosylalkyne and/or glucopyranosyl isothiocyanates. Reactions of cumulenes **80** with D-gluconitrile-2,3,4,5,6-pentaacetate **81** led to compounds **82** after treatment with aqueous sodium hydrogen carbonate, and to glycosides **83** after deacetylation [32].

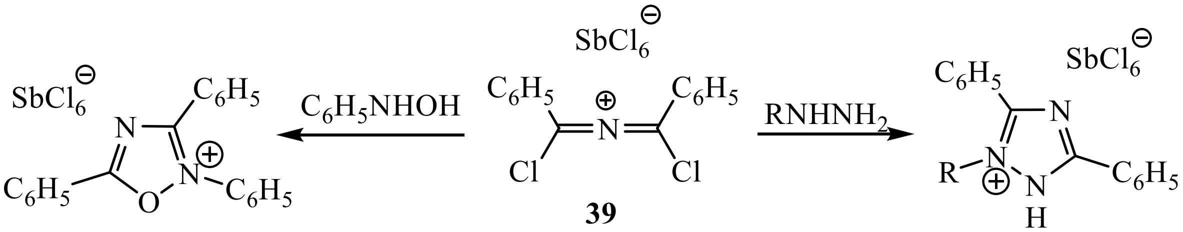


Other triazolium salts **84** were prepared *via* reaction of (chloroalkyl)azo compounds with carbodiimides [27].



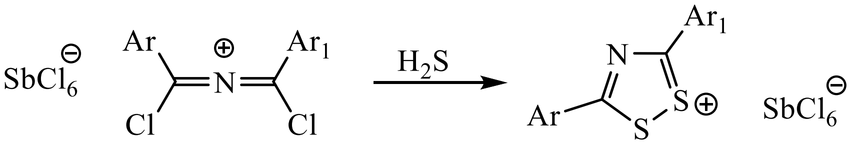
84

Smooth reactions took place with hydrazines leading to 1,2,4- triazolium salts **85**. The oxadiazolium salt **86** was prepared from **39** and *N*-phenyl hydroxylamine [41,51].



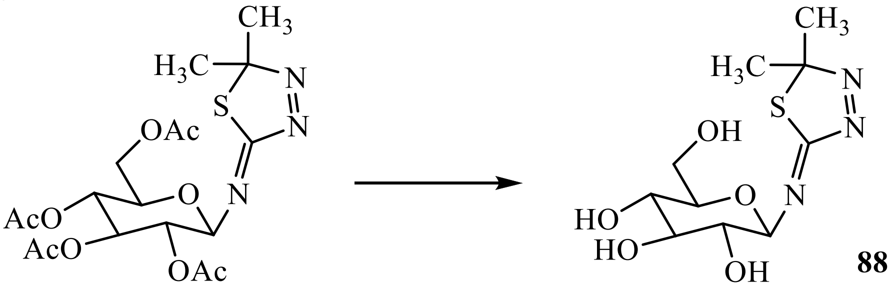
86 **39** **85**

The reaction of **39** (Ar= C_6H_5, Ar^1= 2-Cl-C_6H_4) with H_2S afforded a new access to the synthetically useful dithiazolium salts **87** [52].



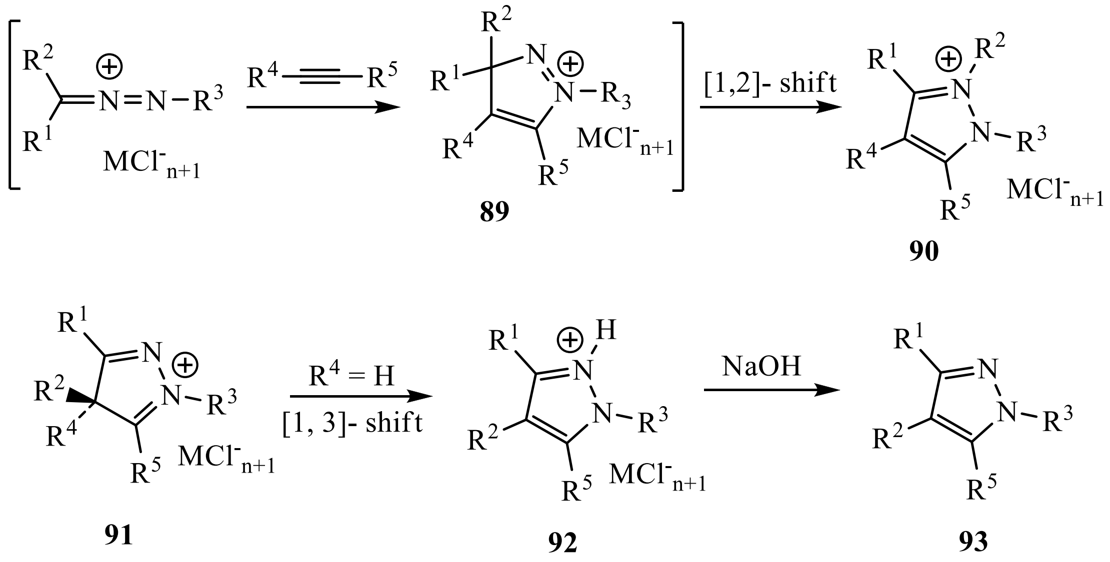
39 **87**

Cycloaddition of the 1-aza-2-azoniaallene salts **31** to the C=S double bond of the glycosyl isothiocyanates furnished glucosylimino-1,3,4-thiadiazole derivatives and de-ethoxy carbonylation with ammonia in methanol afforded the free N-nucleoside **88** [48].



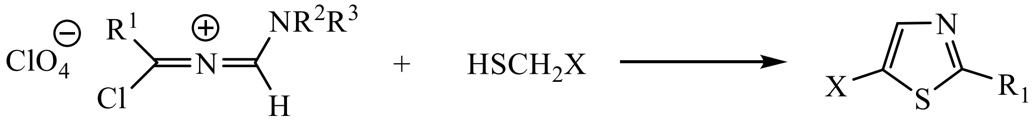
88

1-Aza-2-azoniaallene salts **31** were intercepted with acetylenes to give the pyrazolium salts **90** or **91** *via* 3H-pyrazolium salts **89**. With unsymmetric acetylenes, the cycloadditions occurred with complete regioselecitivity. With monosubstituted acetylenes (R^4= H), the intermediate 4H-pyrazolium salts **89** could not be obtained. Instead, 1H-pyrazolium salts **92** resulting from a [1,3]-portotropic rearrangement of **89** were isolated and characterized as the free bases **93** or as their picrates [53].



R^1= Me ; R^2= Me, Et ; R^3= 2,4-6-$Cl_3C_6H_2$; R^4= Et, H, Me ; R^5= Et, Bu

Azoniaallene salts **94** have been reacted with α-mercaptomethylene compounds to afford the corresponding thiazoles **95** [54].



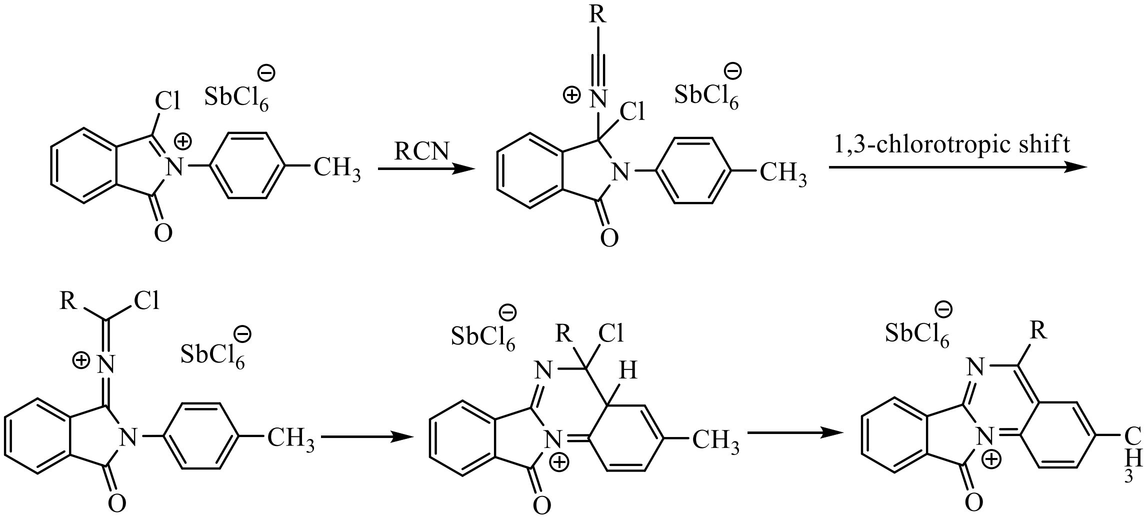
94

95

R^1 = 4-$CH_3OC_6H_4$; X= CH_3OOC, C_2H_5OOC

3.3. Synthesis of Fused Heterocyclic Compounds

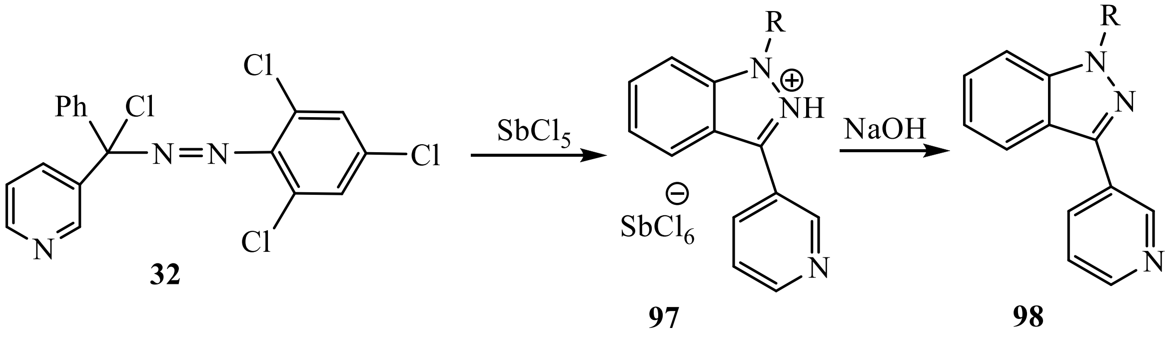
With less reactive nitriles, 2-azoniaallene salts reacted (1:1 ratio) in boiling dichloroethane affording in situ the intermediate 2-azoniaallene salt **5**. Upon prolonged heating, it cyclized to give the tetracyclic compound oxoisoindolo [2,1-a] quinazolinium hexachloroantimonate **96**, which considered as an ellipticine analogue [26,55].



R= SCH_3, C_6H_5

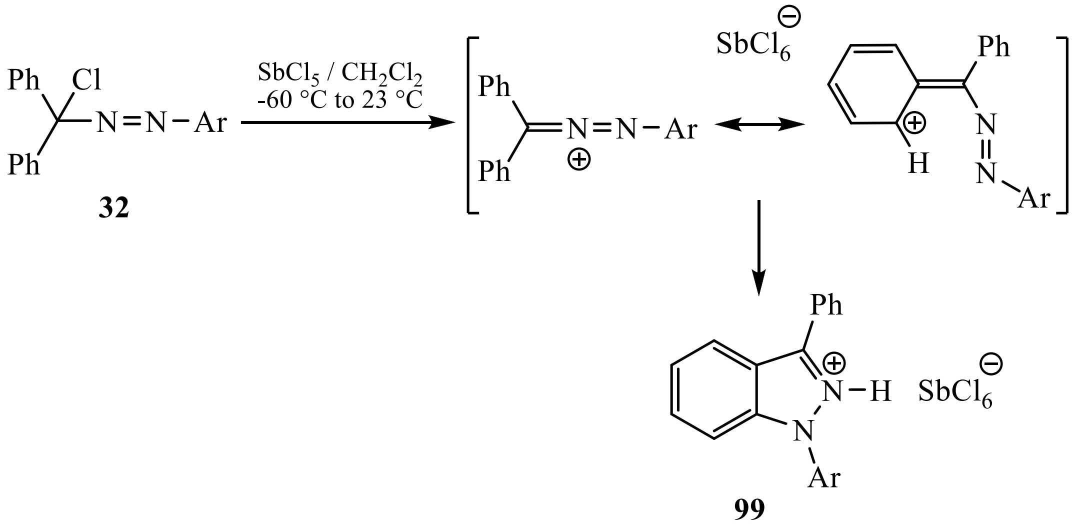
96

The 3-pyridyl-3-yl-1H-indazolium hexachloroantimonates **97** were obtained in a good yield through intramolecular cyclization of **32** in presence of $SbCl_5$ at -50 °C in CH_2Cl_2. Whereas, treatment of 3-pyridyl-indazolium salt **97** with aqueous sodium carbonate yielded the 3-pyridyl-indazol derivatives **98** [31].

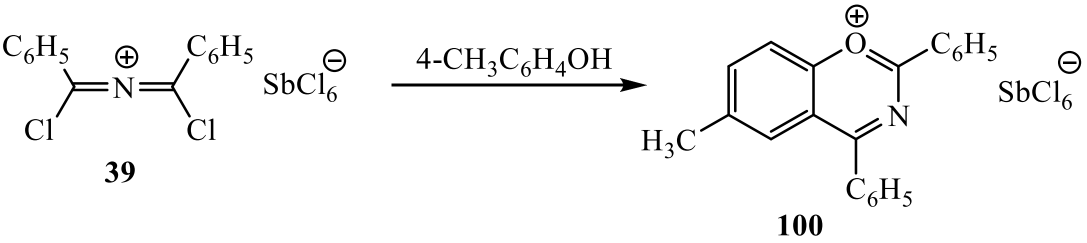


R= 2,4,6-$Cl_3C_6H_2$, $COOC_2H_5$

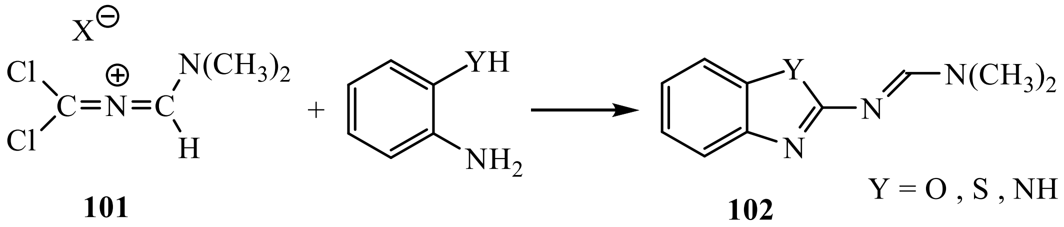
While an intermediate of triazoliuum salts were not able to be observed during the preparation of 1-(1,2,4-trichlorophenyl) substituted salts. However, hydrazones of aryl ketones gave indazolium salts. Thus, the indazolium salt **99** was obtained through an intramolecular nucleophilic aromatic substitution mechanism [56].



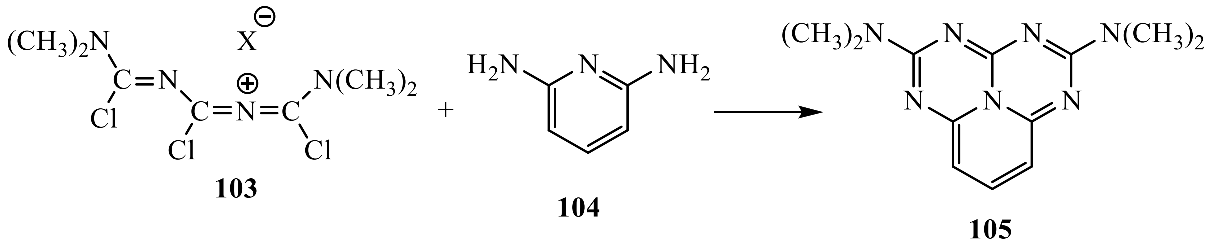
Recently, a few reactions of chloro substituted 2-azoniaallene salts **39**, have no amino substituent, with nucleophiles have already been published by Hamed, while cyclization have occurred with *p*- cresol or its trimethylsilyl ether to yield the benzoxazinium salt **100** [42,57].



From 1,1-dichloro-2-azoniaallene salt **101** and phenylene diamine, *o*-aminophenol as well as aminothiophenol, the corresponding 1,3-benzohetero- azoles **102** were obtained [13].

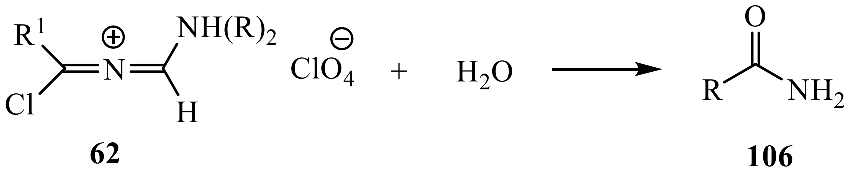


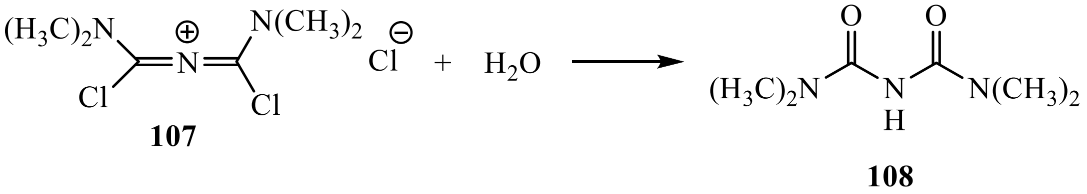
Reaction of trifunctional nucleophiles with chloro substituted 2-azoniaallene salts was reported, where compound **103** of three electrophilic centers reacted with the trifunctional nucleophile **104** yielding the trinuclear heterocycle **105** [13].

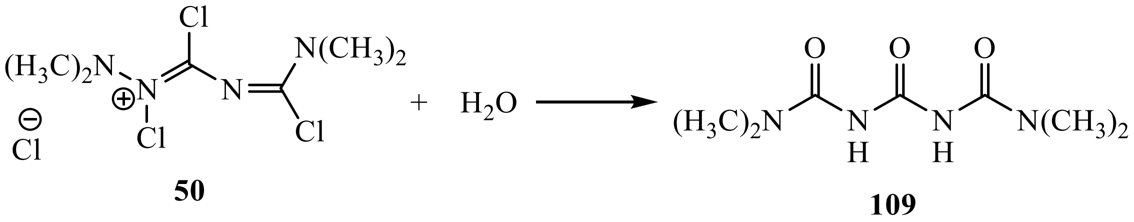


3.4. Miscellaneous Reactions

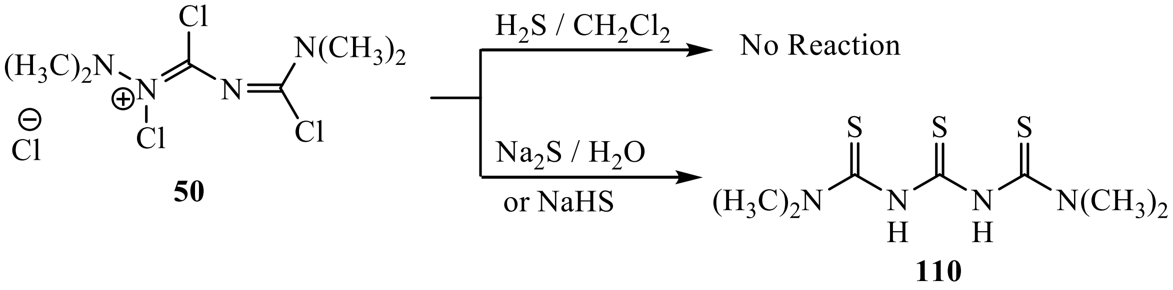
Salts **62, 107** and **50** were hydrolyzed to the corresponding amides **106**, biurets **108** and triurets **109** respectively [58].



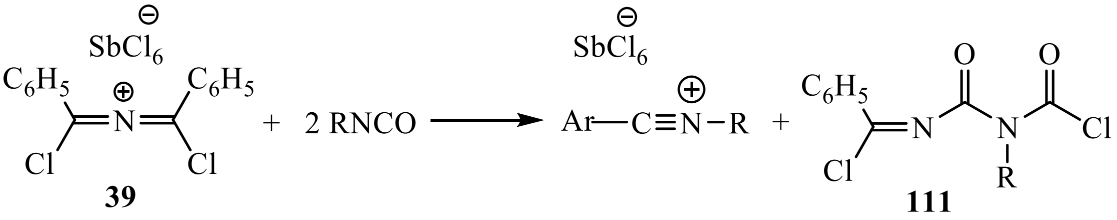




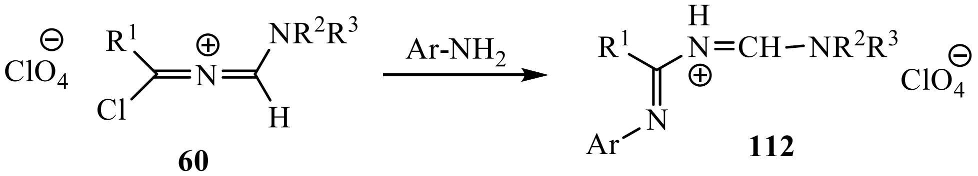
On the other hand, compound **50** was reported to be stable against H_2S, while its reaction with Na_2S or NaHS in aqueous medium, compound **110** was obtained [39].



Reacting of compound **39** with isocyanates afforded the nitrilium salts and the neutral compounds **111**. This reaction is considered as a new route to the synthesis of nitrilium salts [25].



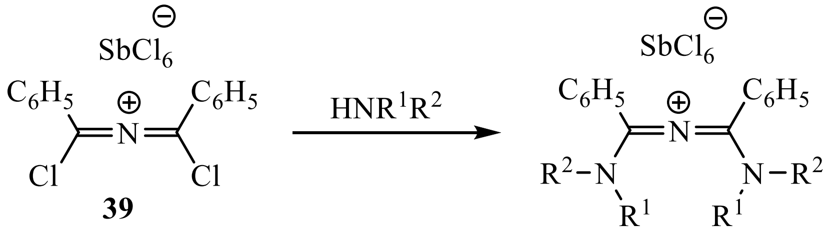
The amidinium salts **112** were prepared from condensation reaction of compound **60** and primary amines [59].



60 **112**

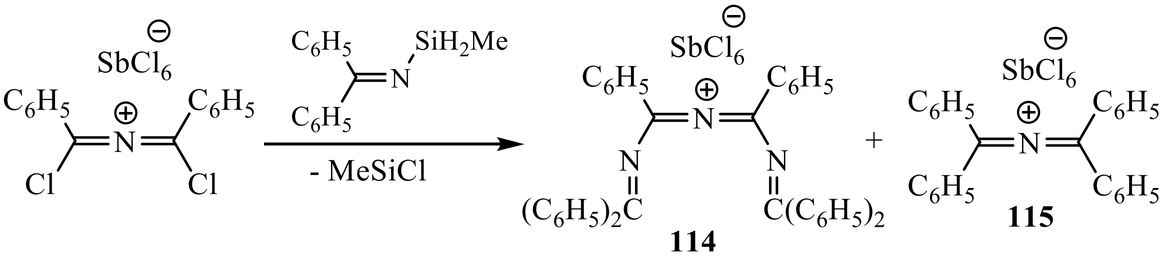
$R^1 = C_6H_5CH_2$; $R^2 = R^3 = CH_3$;
Ar= C_6H_5, 4-$CH_3OC_6H_4$

However, two molecules of *p*-toluidine or diethyl amine reacted readily with one molecule of **39** to give **113** [40].



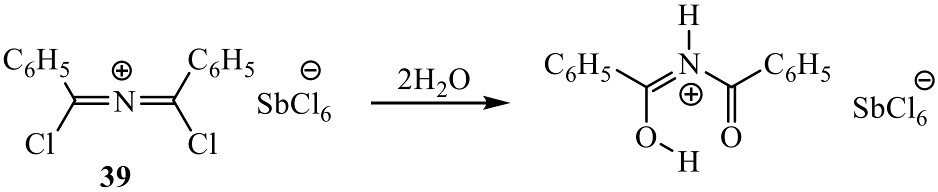
39 **113**

Treatment of compound **39** (Ar= Ar^1= C_6H_5) with N-silylated imine afforded a mixture of two compounds **114** and **115**, in which the well- known tetraphenyl 2-azoniaallene salt **115** predominates [53].



114 **115**

Hydrolysis of compound **39** with calculated amount of H_2O gives dibenzoylammonium salt **116** [60].



39 **116**

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