Addition of Bis (methylthio) acetylene to Nitrilium Salts

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ملخـــص

يتنــاول البحث التالي (فصل ملح ازالينيوم) تحت درجة حرارة منخفضة ، وذلك بإضافة ثنائي
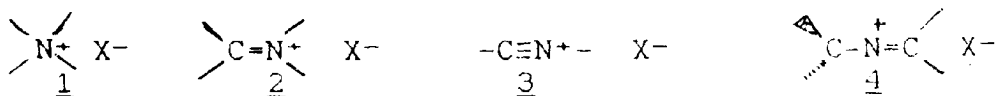(مثيل كبريتو) استيلن الى أملاح النتريليوم .

إن الملح المفصـول قد أعيد ترتيبه تلقائياً لينتج مادة جديدة أخرى ، ولقد نوقشت ميكانيكية
التفاعل بالتفصيل .

Abstract

Azaallenium salt 7 was isolated at low temperature by the addition of bis (methylthio) acetylene to nitrilium salts . The isolated azaallenium salt 7 was rearranged to afford the 1 : 1 heterocyclic adduct 8 . A detailed mechanism is discussed .

Introduction

The preparation of azaallenium salts 4 has recently attracted a great attention [1-7] . 2 – Azaallenium salts like ammonium 1 , alkylideneammonium 3 , and nitrilium salts 4 constitute a class of compounds with a (formally) positively charged " octet " nitrogen atom .

$$\diagdown \overset{+}{\underset{\diagup}{N}}\diagdown \quad X^- \qquad \diagdown C = \overset{+}{N}\diagup \quad X^- \qquad -C \equiv N^+ - \quad X^- \qquad \overset{\diagup}{C} - \overset{+}{N} = C \diagup \quad X^-$$

$$\underline{1} \qquad\qquad \underline{2} \qquad\qquad \underline{3} \qquad\qquad \underline{4}$$

2 – Azaallenium salts have been proposed as intermediates in S_N1 reactions [8] . They are now accessible by several synthetic methods . The structure of some of these derivatives have been determined by X – ray analysis [7,9] .

Recently , we have obtained mono – to tetra – amino substituted azaallenium salts 4 by the addition reaction of imines to nitrilium salts 3 [7] .

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$$R-C\overset{+}{\equiv}N-R \; + \; RRC=NH \; ------> \; \underset{R}{\overset{R}{\diagup}}C=\overset{+}{N}=C\overset{NHR}{\diagdown_R} \qquad X^-$$

$$\underline{3} \qquad\qquad\qquad\qquad\qquad\qquad \underline{4}$$

Nitrilium salts 3 are much more activated for nucleophilic attack at carbon than the parent nitriles . Therefore , they have received a considerable attention for the synthesis of various types of acyclic and cyclic nitrogen containing compounds . Nitrilium salts can be prepared by different methods [7] .

Results and Discussion :

In an attempt to prepare these salts , N-isopropylnitrilium salts 5 have been reacted with bis (methylthio) – acetylene 6 . The isolated product at low temperature was characterized by NMR and IR spectroscopy as azaallenium salt 7 .

$$R-C\overset{+}{\equiv}N-CH(CH_3)_2 \; X^- \; + \; CH_3S-C\equiv C-SCH_3 \; ----> $$

$$\underline{5} \qquad\qquad\qquad\qquad 6$$

7
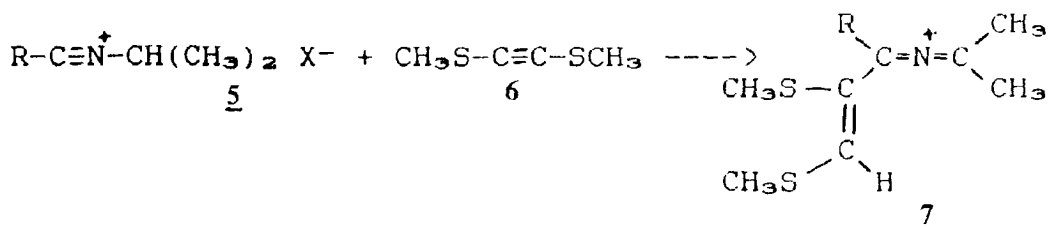
The IR liquid spectra of these salts 7 show a strong band in the range of 1910 to 1880 cm^{-1} . These bands are assigned to asymmetrical C = N = C stretching vibrations . Such absorptions have been reported for azaallenium salts . These bands confirm that these salts have the allene geometry of the form 7A .

7A   7B   7C   7D
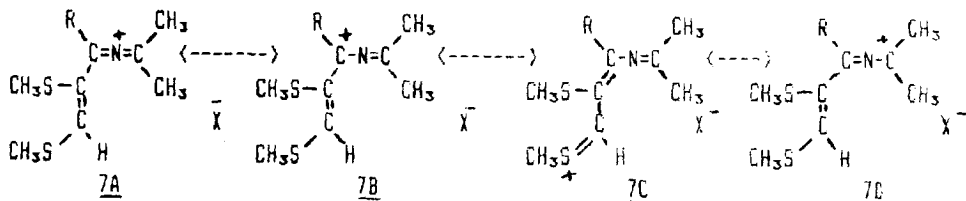
The NMR spectra of these salts 7 at low temperature (263 K) show a singlet at 2.27 ppm for the two methyl groups attached to the sp^2–carbon originating from the N – isopropyl group of the nitrilium salts 5 . The non – equivalent methylthio groups resonate at 2.75 and 2.81 ppm and the C = C–H resonates at 8.19 ppm .
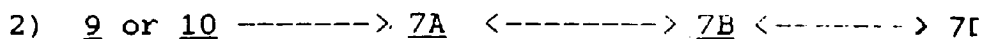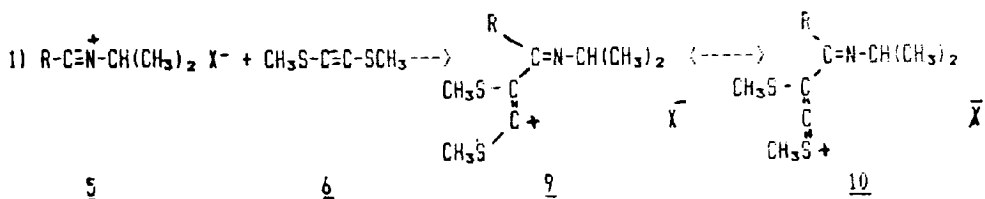
The NMR and IR spectra of these azaallenium salts are temperature – dependant . The spectra , above $0°C$, indicate that these salts are not stable in solution . The interpretation of NMR and IR spectra after a period of time indicates that the heterocyclic product 8 has been formed . The rate of cyclization to 8 depends upon the nature of R – group , the solvent , and the temperature .

The liquid IR spectra of these salts show a decrease in the intensity of $C = N = C$ with time and the gradual appearance of the $C = N$, and $N – H$ bands .

The NMR spectra (CD_2Cl_2) revealed a shift from 2.27 to 1.80 ppm for the C – methyl groups . This indicates that these methyl groups become attached to an sp^3 – carbon . Also, the methylthio groups are shifted from 2.70 and 2.80 to 2.20 and 3.06 ppm . This could be explained by assuming an appreciable contribution of the resonance form 8F .
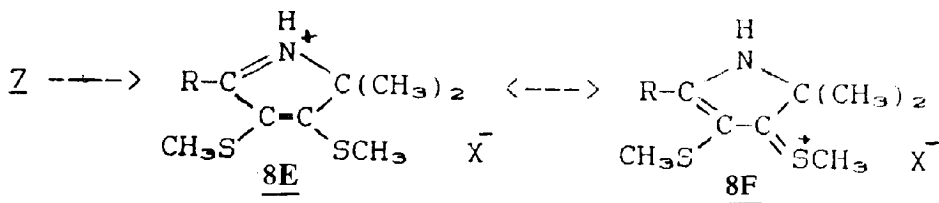
The rate of the cyclization (7 – – → 8) decreases upon changing R from alkyl to phenyl group . Also , it has been found that upon increasing the temperature or dielectric constant of the solvent , the rate increases . This can be explained by the polar cycloaddition , as indicated in the following proposed mechanism :

2)   9 or 10 ———————>· 7A <————————> 7B <— ·——·—— · > 7C

3)   7D ----------> $R-C \overset{\overset{\displaystyle \cdots}{N}}{\underset{\underset{\underset{SCH_3 \quad \bar{X}}{C-C-H}}{+}}{\diagdown}} C(CH_3)_2$

CH_3S

11

4)   11 ----------> 8E <----------> 8F

This mechanism involves , in the first step , a nucleophilic attack of 6 at 5 to give 7 through the intermediate 9 which is stabilized by the resonance structure 10 . This is followed by 1,5 – Hydrogen shift in the second step to give the azaallenium salt 7 . The suggested mechanism as nucleophilic addition can be supported by the effect of the substituents present on the nitrilium salt 5 . Here, the alkyl substituent brings a faster reaction than the aryl group . The addition is stepwise rather than a concerted one . This conclusion is confirmed by the result in which alkyl or unsubstituted acetylene gives no reaction , whereas phenyl and bis (methylthio) acetylene 6 gives a reaction . Apparently , phenyl and methylthio groups do stabilize the carbocation which is formed in 9 .

The third step involves an internal nucleophilic attack of the alkene moiety at the azaallenium moiety of the activated form 7D . This step explains the results of the substituent effect on 7 whereby the phenyl derivative reacts faster than alkyl analogue (in contrast of the first step) in the rearrangement process . This can be explained from step three , in which the reacting species is form 7D , while the presence of phenyl group stabilizes the form 7B through resonance . Further evidence , when $R = R_2N$, a stable azaallenium salt 12 was formed without further rearrangement at all , even unde reflux . This stability is due to the stabilization of form 7B by the amine group to give alkylideneammonium salt 12 .

$5[R=R_2N] + 6$ --------> $\underset{\underset{\underset{CH_3S}{\diagup} \diagdown H}{\overset{\displaystyle \|}{C}}}{\underset{CH_3S-C}{R_2N} \diagdown} C=\overset{+}{N}=C \diagup \overset{CH_3}{\diagdown} CH_3 \quad \bar{X}$ <--------> $\underset{\underset{\underset{CH_3S}{\diagup} \diagdown H}{\overset{\displaystyle \|}{C}}}{\underset{CH_3S-C}{\overset{+}{R_2N}} \diagdown} C-N=C \diagup \overset{CH_3}{\diagdown} CH_3 \quad \bar{X}$

7   12

5   + Ph–C≡C–H ---------> (structure) R C=N–CH(CH₃)₂ ------> (structure) R C=N=C CH₃/CH₃   X⁻

The fourth step involves the migration of the hydrogen to the nitrogen atom . This migration is supported by the appearance of the N–H band in the liquid IR spectra after the decrease of the $C = N = C$ band .

The structures of 7 and 8 have also been confirmed by elemental analysis .

As a solid , the azaallenium salt 7 is stable to storage below room temperature . The kinetic studies of the rearrangement (7 → 8) are under investigtion .

Experimental

IR Spectra : Perkin – Elmer IR 299 . NMR spectra : Jeol JNM – MHz – 100 and Bruker WM – 250 spectrometer , $\mathcal{S}$ - cale , internal reference tetramethylsilane . The melting points are uncorrected .

General Procedure for the preparation of azaallenium salts 7 .

A solution of 14 mmol of bis (methylthio) acetylene 6[10] in 20 ml absolute dichloromethane was added dropwise to a solution of 10 mmol of nitrilium salts 5[7] at – 20 °C . Then the temperature was raised to 0°c and stirred until the band of the nitrilium salts , at $2200 – 2270 \text{ cm}^{-1}$ in IR spectra has disappeared . The reaction solution was cooled to – 40 °C and then absolute ether was added to give precipitate , which was filtered under nitrogen and recrystallized from CH_2Cl_2 / ether .

Preparation of Compounds 8

1. 0 g of the azaallenium salt 7 was dissolved in 20 ml dichloromethane (or acetonitrile , 1,2-dichoroethane , nitromethane) and stirred at room temperature until the disappearance of the $C = N = C$ band . The reaction solution was cooled to – 40 °C then absolute ether was added dropwise giving the precipitate . The product was filtered and recrystallized from dichloromethane /ether

Table . 7 and 8 prepared :

R	m.p°C dec. 7	yield %	m.p°C dec 8	yield %
methyl	65 – 68	84	120 – 125	89
ethyl	98 – 100	75	100 – 106	90
isopropyl	96 – 100	85	100 – 105	94
benzyl	120 – 125	76	130 – 135	89
phenyl	165 – 175	70	170 – 172	66
diisopropyl amino	117 – 120	75		

All of these new compounds show satisfactory microanalyses .

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