Vol.7 No.3
Summer 1996

REACTION OF VINYLENE TRITHIOCARBONATE WITH CHLOROSULFONYL ISOCYANATE

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Abstract

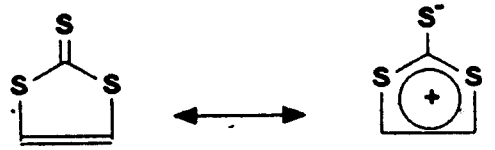
The reaction between vinylene trithiocarbonate and chlorosulfonyl isocyanate proceeds by initial attack of thiocarbonyl on the isocyanate carbon.

Introduction

The cycloaddition reaction of chlorosulfonyl isocyanate (CSI) with olefines has provided the most facile and direct route to β-lactams (2-azetidinones) [1-3]. In connection with the synthetic approach to the sulfur substituted 2-azetidinone [4-6] (found in penicillins and cephalosporins) we investigated the reaction of CSI with vinylene trithiocarbonate (1).

Results and Discussion

Due to the aromatic character of vinylene trithiocarbonate (1) in which the lone pair electron on heteroatoms enters into conjugation with unsaturated bonds forming a stable Huckel-type aromatic system [7], the isolated product from the reaction of (1) with CSI indicates that the reactive site in this molecule is thiocarbonyl group.



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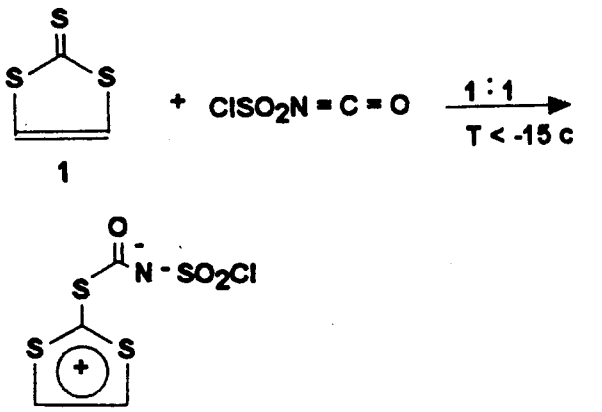
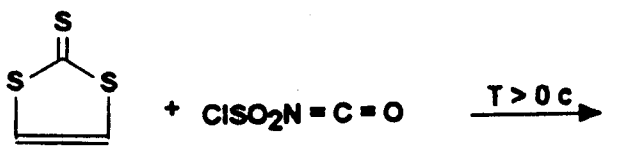
Vinylene trithiocarbonate (1) was prepared according to the published procedure [8]. The reaction of (1) with chlorosulfonyl isocyanate (1:1 M/M) in dry methylene chloride at -15°C under N_2 atmosphere on rapid workup afforded a highly air sensitive compound (2) as crystalline powder in high yield (Scheme 1).



1 2

Scheme 1

However, the long reaction time (1-20 hrs) of (1) with CSI (2-10 fold excess) in dry methylene chloride at subambient temperatures (0 to 25°C) afforded highly air sensitive (3) as crystalline powder in high yield (Scheme 2). No β-lactam product in either reaction was obtained.



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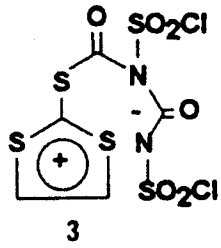
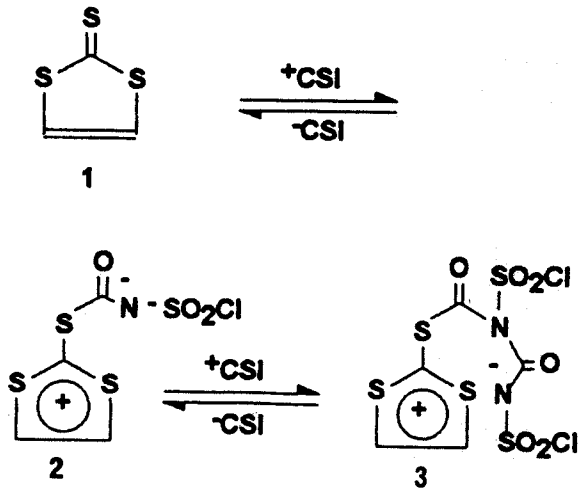
Keywords: Chlorosulfonyl isocyanate: Vinylene trithiocarbonate



3

Scheme 2

The structural assignment of (2) and (3) was based upon their ^{1}H NMR, MS and IR spectral data. Furthermore, their spectroscopic properties suggest that upon dissolving either reaction product in a solvent, equilbrium process occurs readily (Scheme 3).



Scheme 3

In equilibrium, the ratio of compound (1) with compounds (2) and (3) is 45 to 55%, respectively. The ratio was readily ascertained from NMR spectra.

^{1}H NMR (CD_3OD) of (2) and (3) showed similar chemical shifts and each consist of three singlets at $\delta_{7.1}$ ppm for olefinic protons of starting material (1), $\delta_{7.46}$ ppm for olefinic protons of (2) and (3) and a weak broad peak at $\delta_{9.3}$ ppm for N-H (due to absorption of moisture).

Although (3) has two molecules of CSI attached to it, the olefinic shifts of (3) are very similar to (2), possibly as a result of the fast interconversion between two species at room temperature (Scheme 3).

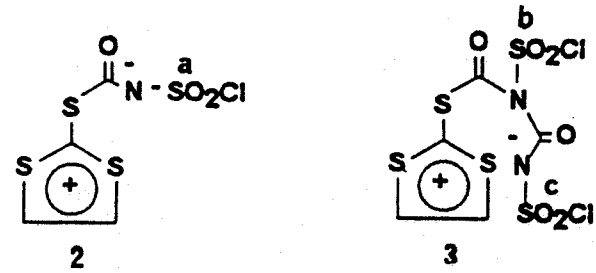
Mass spectrum analysis of (2) revealed a molecular ion peak at m/z 416 (M^+). However, in the absence of solvent, (2) showed a molecular ion peak at m/z 275 (M^+). Although (2) and (3) have a molecular mass of 275 and 416, respectively, these results also suggested the existence of equilibrium between the two.

To verify the existence of equilibrium, the ^{1}H NMR spectrum of either (2) or (3) at -50°C was taken and consisted of four singlets at $\delta_{7.1}$ ppm for olefinic protons of (1), $\delta_{7.52}$ ppm for olefinic protons of (2), $\delta_{7.62}$ ppm for olefinic protons of (3) and a weak broad peak at $\delta_{9.3}$ ppm for N-H.

The striking shift differences for olefinic protons of (2) and (3) is due to slow interconversion between two species. It is important to note that ^{1}H NMR shift at $\delta_{7.46}$ ppm splits into two singlets at $\delta_{7.5}$ ppm and $\delta_{7.62}$ ppm for (2) and (3), respectively.

Chlorosulfonyl amides have been known to undergo rearrangement reaction when treated with dimethyl formamide [9, 10].

Although the rate determining step in these reactions is nucleophilic attack of DMF to chlorosulfonyl group, we consider this rearrangement reaction to be quite informative about the existence of equilibrium between two species.



2 3

Among three chlorosulfonyl groups present in (2) and (3), b site is more electrophilic. When either (2) or (3) was dissolved in deuterated DMF, the ^{1}H NMR spectrum consisted of two singlets at $\delta_{7.5}$ ppm for olefinic protons and $\delta_{11.3}$ ppm for SO_3H. The IR spectrum indicated the lack of carbonyl absorption and the presence of C ≡ N at 2200 cm^{-1}. These features were consistent with the structure of (4).

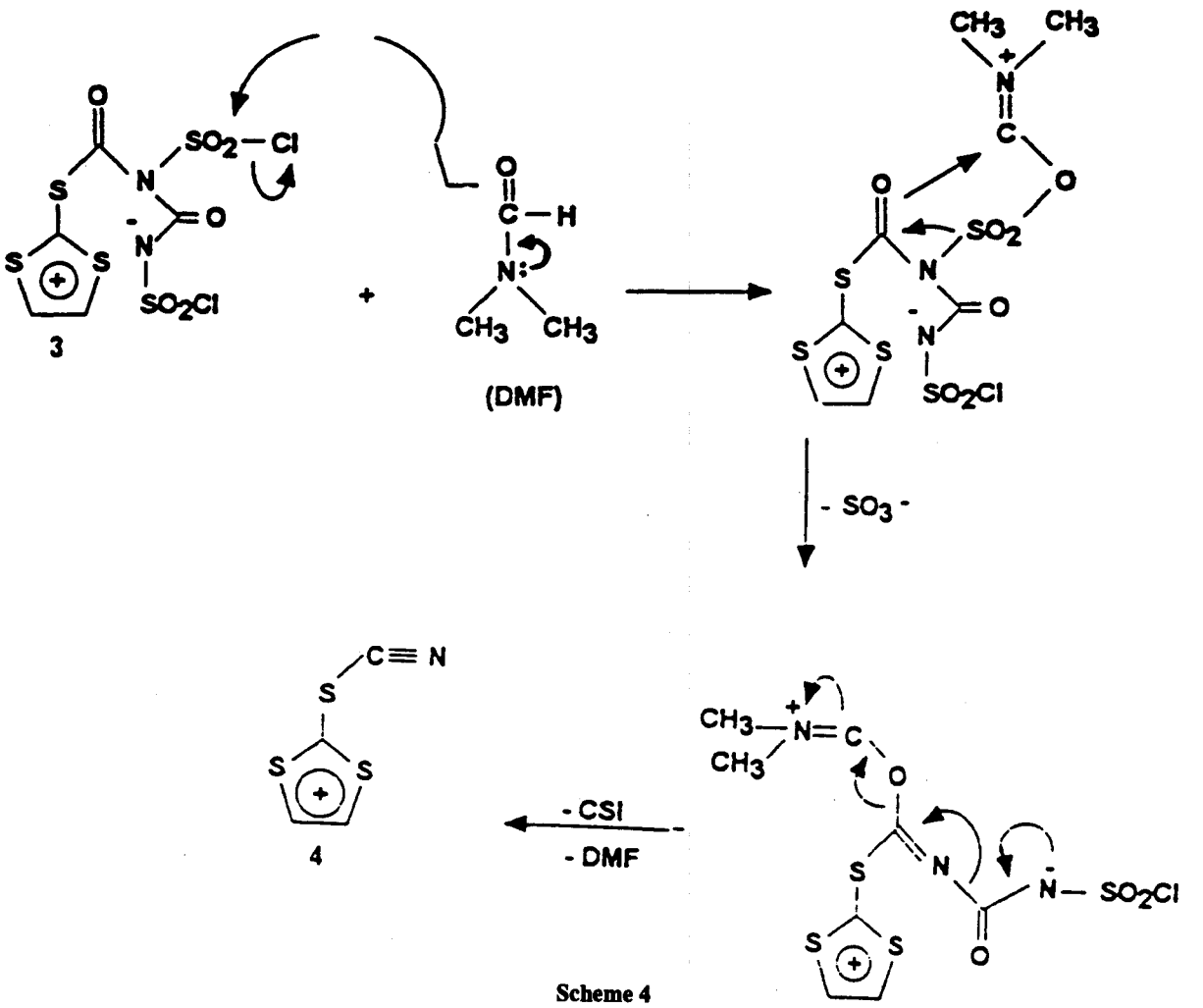
Mechanistically, nucleophilic attack of DMF to more electrophilic chlorosulfonyl group, will cause this equilibrium to be effectively displaced toward the product (4) (Scheme 4).

Experimental Section

IR spectra were recorded on Shimadzu-4300 FTIR spectrophotometers. ^{1}H NMR spectra were recorded on a Bruker AC 80 spectrometer in CD_3OD. MS spectra were recorded on a Shimadzu-14 A spectrometer. Commercial chlorosulfonyl isocyanate (Fluka) was used. Methylene chloride was dried before use.

General Procedure for the Reaction of Vinylene Trithiocarbonate with Chlorosulfonyl Isocyanate

A solution of vinylene trithiocarbonate (1 mmol) in dry methylene chloride was treated dropwise with a solution of chlorosulfonyl isocyanate in dry methylene chloride, main-



Scheme 4

tained at -15°C. After stirring for a few minutes, the precipitated product was filtered, washed with cold dry methylene chloride and stored under nitrogen atmosphere.

1,3-Dithiolium salt (2)

370 mg (90% yield); IR ν_{max} (KBr) 1720, 1751, 1402, 1190 cm^{-1}, ^1H NMR (CD_3OD) $\delta_{7.1}$ ppm (s), 7.46 (s), 9.3 (s); MS m/z 275 (M^+), 134 (M-CSI).

1,3-Dithiolium salt (3)

600 mg (96% yield); IR ν_{max} (KBr) 1720, 1750, 1780, 1398, 1190 cm^{-1}. ^1H NMR (CD_3OD) 7.1 ppm (s) 7.46 (s) 9.3 (s); MS m/z 416 (M^+), 275 (M-CSI), 134 (M-2 CSI).

2- Thiocyanogen-1,3-dithiolium salt (4)

IR ν_{max} 3588, 2230, 2215, 2144 cm^{-1}, ^1H NMR (d-DMF) 7.5 ppm (s, 2H), 11.3 (broad, SO_3H)

Acknowledgements

We are grateful to the University of Tehran for its support of this research.

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