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RESEARCH ARTICLE

Behavior of morpholine and its trimethylsilyl derivative in reactions with trimethylsilyl isocyanate

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Abstract

Objectives. *To study the patterns of behavior of morpholine and its trimethylsilyl derivative in reactions with trimethylsilyl isocyanate.*
Methods. *The study employed infrared and nuclear magnetic resonance spectroscopy, as well as elemental analysis.*
Results. *The formation of mixtures of tautomeric forms of silicon-containing urea—N-(trimethylsilyl)morpholine-4-carboxamide and trimethylsilylmorpholine-4-carboximidoate—was established.*
Conclusions. *It is shown that the composition and structure of the resulting products are determined both by the presence of a morpholine substituent at the nitrogen atom and by the type of isocyanate used. Unlike the trimethylsilyl derivative of morpholine, morpholine itself reacts with trimethylsilyl isocyanate to form a mixture of tautomeric forms.*

Keywords: *morpholine, trimethylsilyl isocyanate, silicon-containing ureas, tautomerism, amide-isoamide tautomerism, N-(trimethylsilyl)morpholine-4-carboxamide, trimethylsilylmorpholine-4-carboxyimidoate*

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НАУЧНАЯ СТАТЬЯ

Поведение морфолина и его триметилсилилпроизводного в реакциях с триметилсилилизоцианатом

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Аннотация

Цели. *Изучить закономерности поведения морфолина и его триметилсилилпроизводного в реакциях с триметилсилилизоцианатом.*
Методы. *В исследовании использовались методы инфракрасной спектроскопии, спектроскопии ядерного магнитного резонанса и элементного анализа.*
Результаты. *Установлено образование смеси таутомерных форм кремнийсодержащей мочевины: N-(триметилсилил)морфолин-4-карбоксамида и триметилсилилморфолин-4-карбоксимидоата.*
Выводы. *Установлено, что состав и строение образующихся продуктов определяется как наличием заместителя при атоме азота морфолина, так и типом используемого изоцианата. Показано, что, в отличие от триметилсилильного производного морфолина, сам морфолин взаимодействует с триметилсилилизоцианатом с образованием смеси таутомерных форм.*

Ключевые слова: *морфолин, триметилсилилизоцианат, кремнийсодержащие мочевины, таутомерия, амид-изоамидная таутомерия, N-(триметилсилил)морфолин-4-карбоксамид, триметилсилилморфолин-4-карбоксимидоат*

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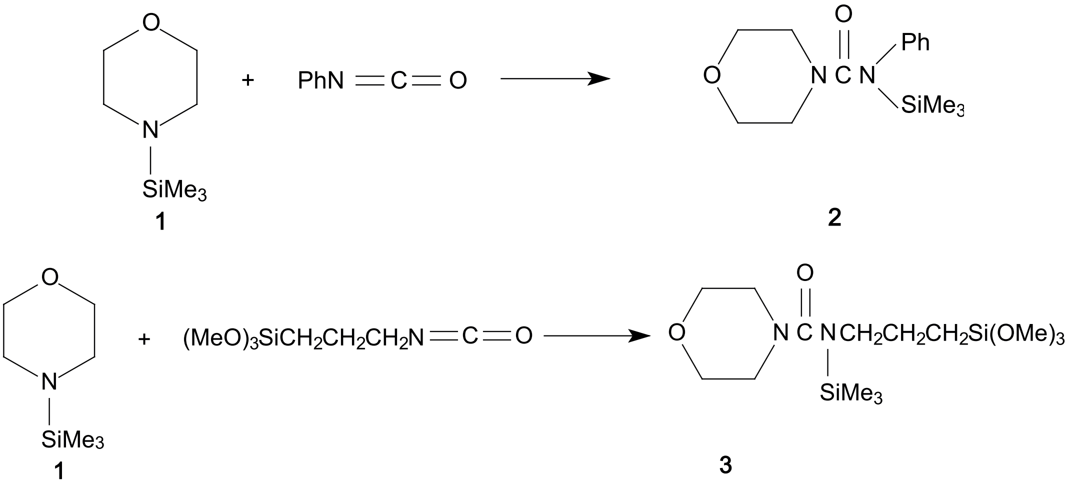
INTRODUCTION

The chemical study of organosilicon derivatives of morpholine began during the second half of the last century. The increase of research interest in this field of chemistry is due to the valuable properties of such compounds both from a practical and a theoretical point of view [1–8]. For example, due to their polarity and high selectivity, organosilicon morpholine derivatives have become widely applied as solvents. They are also used for the synthesis of enamines, which are synthons for the selective alkylation and acylation of carbonyl compounds [8]. It has been shown [7, 9, 10] that 4-(trimethylsilyl)morpholine, like silyl amines, interacts with organic isocyanates: the nature of the initial isocyanate determines the possibility of obtaining organosilicon ureas or organic ureas. Thus, as a result of the reaction with *n*-butyl isocyanate, a stable urea containing a trimethylsilyl group was obtained [7]. Conversely, silicon-containing ureas were also initially obtained when using α-alkoxyalkyl isocyanates in this reaction; these can be easily hydrolyzed in air to form stable organic ureas [9]. However, all these studies were limited to investigated organic isocyanates or their analogs comprising carbofunctional organosilicon isocyanates [10] (Scheme 1).

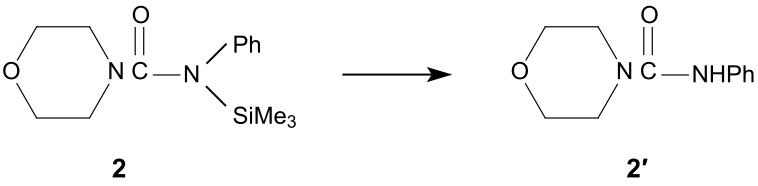
It was also found that 4-phenyl-*N*-(trimethylsilyl)-4-morpholinecarboxamide **2** is a compound hydrolyzed by air moisture to form organic urea **2′** over time (Scheme 2).

Despite the availability of hydrolytically stable *N*-[3-(trimethylsilyl)propyl]-*N*-(trimethylsilyl)-4-morpholinecarboxamide **3** [11], the absence of any publications on the possibility of obtaining silicon-containing ureas using the functional silyl isocyanate trimethylsilyl isocyanatosilane has not yet been the topic of a detailed study. Thus, the continuation of research in this area of chemistry is an urgent task.

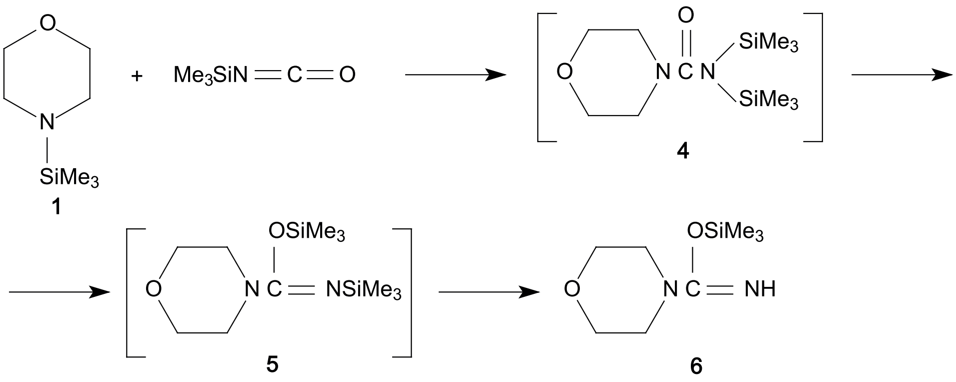
In addition, it should be noted that when using trimethylsilyl isocyanate in the reaction with 4-(trimethylsilyl)morpholine [10], the nature of the process does not change at the first stage: instead unstable (trimethylsilyl)urea **4** is formed. Subsequently, however, it can be easily induced to give up the trimethylsilyl group to transform into trimethylsilylmorpholine-4-carboximidoate **6** (Scheme 3).



Scheme 1. Reactions of 4-(trimethylsilyl)morpholine with isocyanates.



Scheme 2. Scheme of 4-phenyl-*N*-(trimethylsilyl)-4-morpholinecarboxamide **2** conversion to organic urea **2′**.



Scheme 3. Reaction of 4-(trimethylsilyl)morpholine with trimethylsilyl isocyanate.

EXPERIMENTAL

The infrared (IR) spectrum was recorded on a Nicolet 7600 spectrometer (*Thermo Fisher Scientific*, USA) in vaseline oil. The ^{1}H nuclear magnetic resonance (NMR) spectrum was recorded on a DRX400 instrument (*Bruker*, Germany) with an operating frequency of 400.13 MHz in $CDCl_3$. Chemical shifts are given in δ (ppm) scale relative to tetramethylsilane as an internal standard. The ^{29}Si NMR spectrum was recorded on an AVANCE AV-300 instrument (*Bruker*, Germany) with an operating frequency for silicon of 59.64 MHz. Elemental analysis was carried out on a FLASH EA 1112 instrument (*Thermo Finnigan Italia S.p.A.*, Italy). The melting point (m.p.) of the obtained compound was determined on a BUCHI Melting PointB-540 elemental analyzer (*BUCHI*, Switzerland).

All starting compounds were thoroughly dried before use and purified by distillation. Synthesis operations, isolation and sampling for the compounds analysis were carried out under an atmosphere of dry nitrogen.

Trimethylsilylmorpholine-4-carboximidoate (6) and *N*-(trimethylsilyl)-morpholine-4-carboxamide (6′)

Trimethylsilyl isocyanate (6.57 g, 0.057 mol) was added to morpholine (**7**) (4.96 g, 0.057 mol). The reaction mass was kept for 25 min, then evacuated at a pressure of 1 mmHg for 1 h to yield 10.37 g (90%) of compounds (**6** and **6′**), m.p. = 92.5–93.5°C. IR spectrum, $\tilde{\nu}$, cm^{-1}: 3365 (NH), 1666 (C=O), 1609 (C=N). ^{1}H NMR spectrum, ppm: 0.03 s (9H, $SiMe_3$), 0.21 s (9H, $Si(CH_3)_3$), 2.84 t (4H, CH_2NCH_2), 3.34 q (4H, CH_2NCH_2), 3.65 t (8H, CH_2OCH_2). ^{29}Si NMR spectrum, ppm: 5.96 s, 7.34 s. Elemental analysis, found, %: C 47.65; H 8.85; N 13.91. $C_8H_{18}O_2N_2Si$; calculated, %: C 47.49; H 8.97; N 13.85.

RESULTS AND DISCUSSION

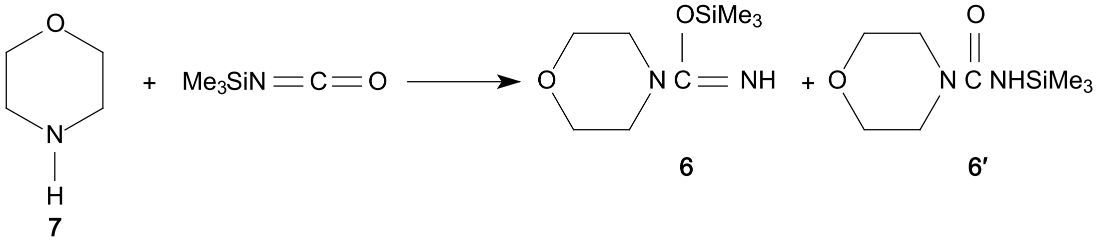
It was found that morpholine **7**, along with its trimethylsilyl derivative **1**, reacts with trimethylsilyl isocyanate without heating. However, the reaction product is a mixture of tautomeric forms of silicon-containing urea: trimethylsilylmorpholine-4-carboximidoate **6** (*O*-form) and *N*-(trimethylsilyl)morpholine-4-carboxamide **6′** (*N*-form) (Scheme 4).

The existence of such isomerism is evidenced by the results of physicochemical studies. In the IR spectrum of compounds **6** and **6′** (Fig. 1), the intense absorption band recorded i n the region of 3365 cm^{-1} corresponds to vibrations of the NH group bond. An intense absorption band in the region of 1666 cm^{-1} corresponds to vibrations of the C=O group bond. An intense absorptionband in the region of 1609 cm^{-1} corresponds to vibrations of the C=N group bond.

In the ^{1}H NMR spectrum (Fig. 2), two signals of the Me_3Si group protons were recorded in the region of 0.03 ppm. and 0.21 ppm. These are characteristic of the protons of the trimethylsilyl group at the nitrogen atom and those of the trimethylsilyl group at the oxygen atom, respectively. The signals of the protons of the CH_2N and CH_2O groups of the morpholine fragment were also recorded in their characteristic regions; here, a doubling of the proton signals of the methylene groups at the nitrogen atom in the region of 2.84 ppm and 3.34 ppm is observed.

The ^{29}Si NMR spectrum (Fig. 3) also contains two silicon signals in the region of 5.96 ppm and 7.34 ppm corresponding to the $NSiMe_3$ and $OSiMe_3$ groups.

Thus, the difference between the interaction of trimethylsilyl isocyanate with 4-(trimethylsilyl) morpholine from its reaction with morpholine



Scheme 4. Reaction of morpholine with trimethylsilyl isocyanate.

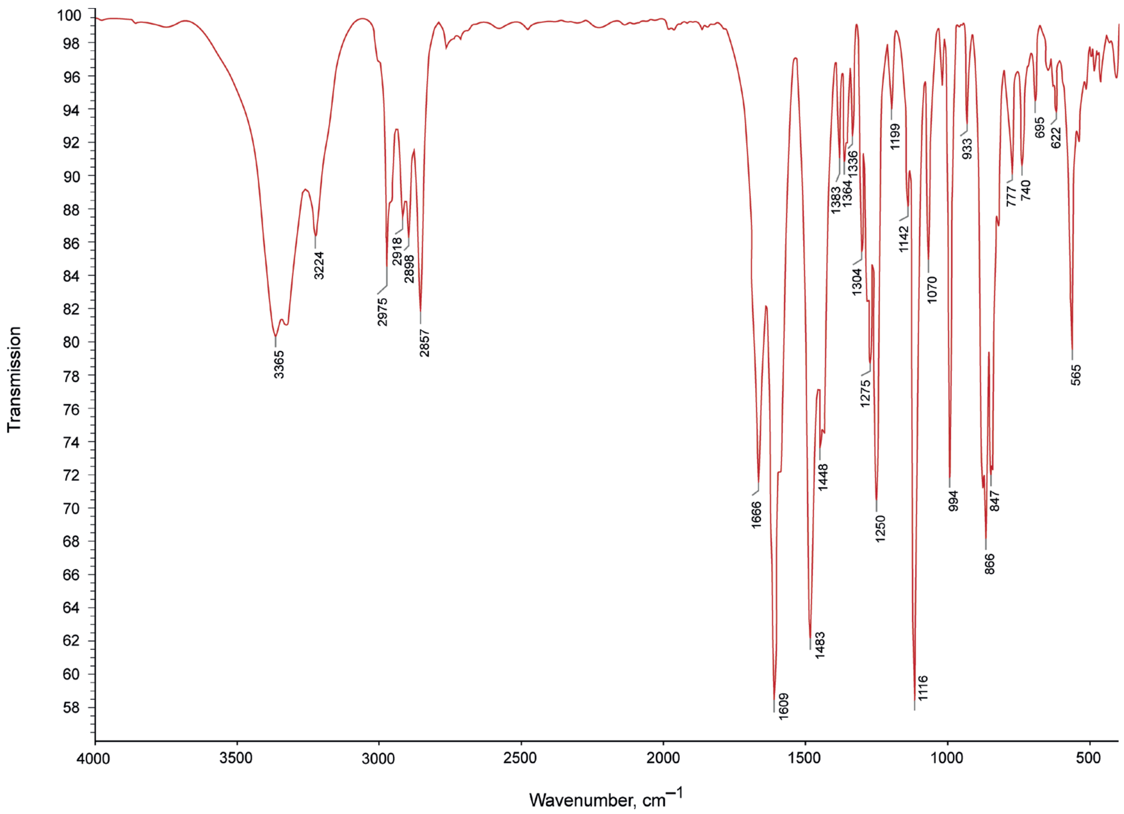


Fig. 1. IR spectrum of trimethylsilylmorpholine-4-carboxyimidoate **6** and *N*-(trimethylsilyl)morpholine-4-carboxamide **6′**.

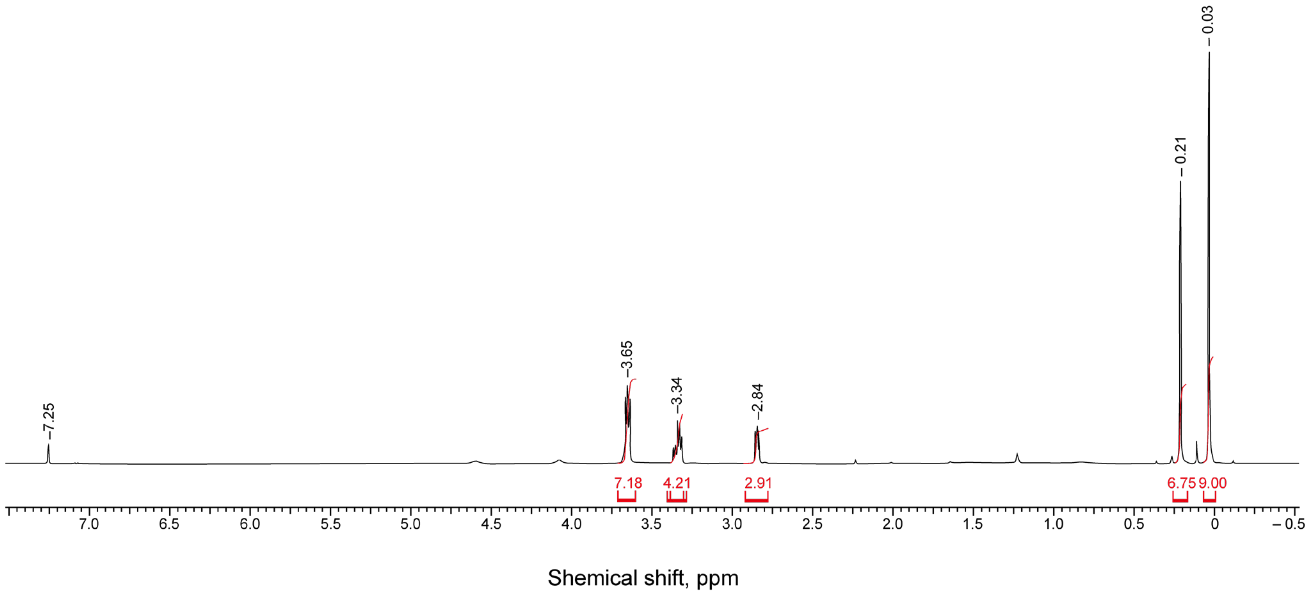


Fig. 2. ^{1}H NMR spectrum of trimethylsilylmorpholine-4-carboxyimidoate **6** and *N*-(trimethylsilyl)morpholine-4-carboxamide **6′**.

is the formation in the second case of *N*-(trimethylsilyl)morpholine-4-carboxamide, i.e., trimethylsilylurea. The formation of a mixture of tautomeric forms (Scheme 5) is known to be typical of the latter compound. The existence of such amide-isoamide tautomerism involving the Me_3Si group in silicon-containing ureas was previously assumed by J.F. Klebe *et al.* [12].

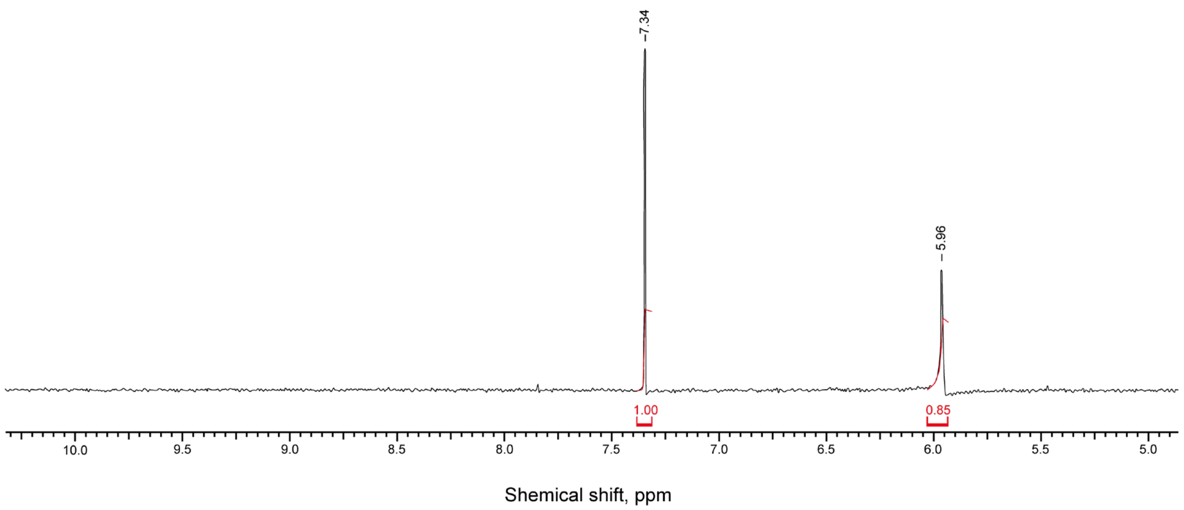
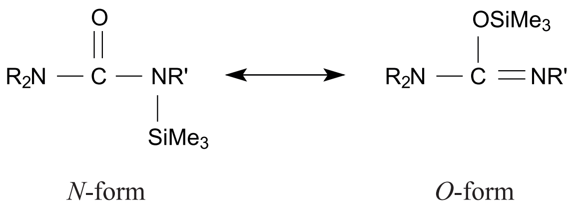


Fig. 3. ^{29}Si NMR spectrum of trimethylsilylmorpholine-4-carboxyimidoate **6** and *N*-(trimethylsilyl)morpholine-4-carboxamide **6′**.



Scheme 5. Amide-isoamide tautomerism involving the Me_3Si group for silicon-containing ureas.

CONCLUSIONS

The study of morpholine derivatives in reactions with isocyanates establishes that the composition and structure of the resulting products are determined both by the presence of a substituent at the nitrogen atom of morpholine and by the type of isocyanate used. It is shown that, unlike the trimethylsilyl derivative of morpholine, morpholine itself reacts with trimethylsilyl isocyanate to form a mixture of tautomeric forms.

Authors' contributions

A.D. Kirilin – idea of the study and general management;

L.O. Belova, N.I. Kirilina – writing the text of the article and the analysis of the obtained results;

N.A. Golub, M.V. Pletneva – conducting the experiments.

The authors declare no conflict of interest.

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