Ph.D. Thesis Summary

Reaction of silyl-carbamates with oxo compounds, as well as preparation and observation of reaction of dithio analogues

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I. Introduction

In the gas phase analytical studies the silylcarbamates has been used silylating for the protic hydrogen containing compounds (alcohols, phenols, carboxylic acids). Besides taking these reactions it is interesting that with acid chlorides or chloroformates acid amide will be created during chlorosilane secession. On the strength of my previous researches I have found out that trimethylsilyl N,N-dimethylcarbamate reacted with ketones enamines were formed, while in the reaction with aldehydes or rather methyl-ketones an aldol condensation side reactions occurred.

The reactions of silyl carbanates thio analogs has not yet been studied against the above-mentioned nucleophilic agents (oxo-compounds, lactons, acid chlorides, chloroformates).

II. Methods, conditions

The silylcarbamates and dithio analogs are sensitive to air humidity, and therefore inert atmosphere were used during the implementation of the experiments. The progress of reactions was followed by gas chromatography. The products are purified by vacuum distillation. For the identification of the structures IR, 1H-NMR and 13C-NMR spectroscopy and GC-MS were used.

III. New results

1. I found that the aldol condensation can not be interfering for the oxo group transformation to oxolane.

2. The reactions of N,O-bis-trimethylsilyl-N-methoxy-carbamate with oxo compounds (trifluoroacetic acid as catalyst was applied), which led to the formation of the corresponding O-methyl oximes, as a mixture of syn and anti isomers, the yields were 50-92%.

\[
R \quad R' + \quad MeO\overset{N}{\underset{O}{\text{Me}}}_3\overset{OSiMe_3}{\text{OSiMe}_3} \quad \overset{-O(SiMe_3)_2}{\longrightarrow} \quad \overset{N}{\underset{OMe}{\text{Me}}} R \quad R' \quad syn + \quad MeO\overset{N}{\underset{R \quad R'}{\text{Me}}} \quad anti
\]

\[
R = \text{alkil} \quad R' = \text{alkil, acil stb.}
\]
In the case of cyclohexanone, methyl isobuthyl ketone and a 3-hydroxy-benzaldehyde gives the corresponding oximes. The oxime formation with ethyl acetoacetate takes place on the ketone moiety.

3. I found that nitrore formation – which is the known side reactions at oxime formation, at this method is not found.

4. In the reaction of 2-chloro-ciklopentanon and 2-chloro-cyclohexanone I did not observe the substitution of halides at the α-position

5. I found that the oxime formation does not takes place through silyl enol ethers moreover these by-product even hold up the oxime formation.

6. In the reaction of \(N,O\)-bis(trimethylsilyl)-\(N\)-methylcarbamates with oxo-compounds I got imines with 20-50% of production

\[
\begin{align*}
&\text{O} \\
&\text{R} \quad \text{R}' \\
&\text{Me} \\
&\text{Me}_3\text{Si} \\
&\text{O} \\
&\text{SiMe}_3 \\
&\text{N} \\
&\text{Me} \\
&\text{R} \quad \text{R}'' \\
&\quad - \text{O(SiMe}_3\text{)}_2 \\
&\quad - \text{CO}_2 \\
\end{align*}
\]

Experiments were carried out by gas chromatography for preparation \(N\)-phenyl imines useing the reaction of phenylcarbamate and oxo-compounds. The transformation in reaction was slight. For the preparation of of imines our method is limited in use.

7. I found that \(S\)-trimethylsilyl-\(N\),\(N\)-dialkyldithiocarbamate in reaction with acid chlorids (acetyl-chloride, benzoyl-chloride, carbamoyl-chloride, thiocarbamoyl chloride, ethyl chloroformate) there is chlorosilane lashing out. The change was effectively effectuated with acetyl-chloride and benzoyl-chloride; together with the lashing out of chlorosilane a certain amount of carbon disulfide and the corresponding amount of acid amide was created.
8. I stated that silylcarbamates and their dithioanalogs get into reaction with N,N-dimethyl-carbamoyl-chloride or with the N,N-dimethyl-thiocarbamoyl-chloride and various carbamic acid anhydrides are created.

\[
\begin{array}{c}
\text{Me} \quad N \quad X \quad + \quad \text{R} \quad N \quad X \quad \text{SiMe}_3 \quad \xrightarrow{-\text{Me}_3\text{SiCl}} \quad \text{R} \quad N \quad X \quad \text{SiMe}_3 \quad \text{Me} \\
\text{Me} \quad \text{Cl} \\
\text{R} = \text{Me}, \text{Et}, \text{szekBu}, \text{Hex} \\
X = \text{O vagy S}
\end{array}
\]

I also stated that the bigger the alkyl group on the dithiocarbamate is, the longer the transformation takes place.

9. The mixed anhydrides that are created are stable on room-temperature. After the elapse of several weeks a slow decomposition has started during the full, with carbon-dioxide and carbon-disulfide splitting out. I did not experience splitting out of COS in any of the cases.

\[
\begin{array}{c}
\text{R}_2\text{N} \quad X \quad \text{Y} \quad \text{NMe}_2 \quad \xrightarrow{} \quad \text{R}_2\text{N} \quad \text{Y} \quad \text{NMe}_2 \quad + \quad \text{CX}_2 \\
\text{R} = \text{Me}, \text{Et}, \text{szekBu}, \text{Hex, (-CH}_2\text{)}_2 \\
X, Y = \text{O vagy S}
\end{array}
\]

It can be stated that the thermic stability of the mixed anhydride is growing in line with the growing of the content of sulphur. A similar experience can be stated in the case when the two parts of the mixed anhydride are connected not by an oxygen atom but by a sulphur atom.

After the reaction of S-trimethylsilyl-N,N-diethylthiocarbamate with N,N-dimethyl-thiocarbamoyl choloride a mixed anhydride was born with an unusual thermic stability. It did not diffuse during vacuum-distillation, and new tests effectuated after several months did not show any diffusion either.

\[
\begin{array}{c}
\text{Me} \quad N \quad S \quad + \quad \text{Et} \quad N \quad S \quad \text{SiMe}_3 \quad \xrightarrow{-\text{Me}_3\text{SiCl}} \quad \text{Et} \quad N \quad S \quad \text{SiMe}_3 \quad \text{Me} \\
\text{Me} \quad \text{Cl} \\
\text{Et}
\end{array}
\]
10. Making reaction between pyrrolidine-$N$-carboxylic acid trimethylsilyl ester and $N,N$-dimethyl thiocarbamoyl chloride on room-temperature, the adequate anhydrid was created. When applying high temperature during the reaction or the application, the mixed anhydrid has lost CO$_2$ and the adequate thiocarbamide was created.

11. I was studying the reaction of ethyl chloroformate on room-temperature with $S$-trimethylsilyl-$N,N$-dihexyldithiocarbamidate and $S$-trimethylsilyl-$N,N$-diethyldithiocarbamate.

$$\text{EtO} - O\text{Cl} + R\text{N} - S\text{SiMe}_3 \rightarrow R\text{N} - S\text{OEt}$$

$$R = \text{Et, Hex}$$

In both cases I experienced decomposition with loss of CS$_2$, which resulted in the creation of $N,N$-dialkyl-$O$-ethyl-carbamate.

12. I have made six anhydride or anhydride-derivatives to react to $O$-trimethylsilyl-$N,N$-dimethylcarbamate. In every case I could see decomposition of the mixed anhydrides, and except for two cases this was the only thing that effectuated. That would have been effectuated independently to the surplus of the reagents, of course. In every case the reaction with $O$-trimethylsilyl-$N,N$-dimethylcarbamate can be double:

$$R\text{N} - X\text{Y} - N\text{Me} + R\text{N} - X\text{SiMe}_3 \rightarrow R\text{N} - X\text{Y} - N\text{Me} + R\text{N} - X\text{SiMe}_3$$

$$X = O \text{ vagy } S \text{ és } Y = O \text{ vagy } S$$

If the mixed anhydrid’s two parts are connected by oxygen, it is presumable that the reaction with $O$-trimethylsilyl-$N,N$-dimethylcarbamate will take place.
13. If the mixed anhydride derivates from dithiocarbamate, that is if the carbamate and the thiocarbamate part are connected by sulphur atom, then reaction will not take place, we can only experience a procedure of diffusion. If the two molecular parts are connected by oxygen, then it silylated and apart from the corresponding carbamate thiocarbamate is created.

14. When I made $O$-trimethylsilyl-$N,N$-dimethylcarbamate and $N,N$-dimethylthio carbamoil chloride react in a 2 to 1 proportion, I got tetrametil-thiocarbamate (productively).
Publications Forming the Basis of the Dissertation

1. Article


2. Poster Presentation


3. Oral Presentation at International Conferences


4. Oral Presentation in Hungarian Conference

1. Kardon Ferenc, Mörtl Mária, Knausz Dezső:
   Reactions of silylcarbamates with oxo compounds
   Meeting of plenary work committee of the Hungarian Academy of Sciences -

2. Kardon Ferenc, Mörtl Mária, Knausz Dezső:
   Application of silylcarbamates for the preparation of imines
   Meeting of plenary work committee of the Hungarian Academy of Sciences -

Other Publication

Article


Poster Presentation


Oral Presentation at International Conferences

1. Mörtl Mária, Knausz Dezső, Kardon Ferenc
   Silyl carbamates as precursors generating nitrenes