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A NEW ROUTE FOR THE SYNTHESIS OF TETRAALKYLUREAS. THE REACTION OF CARBON MONOXIDE WITH SELENIUM AND DIALKYLAMINES

Kiyoshi KONDO, Noboru SONODA, Kokichi YOSHIDA, Masafumi KOISHI, and
Shigeru TSUTSUMI

Department of Petroleum Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka, Japan

The reaction of carbon monoxide with selenium and dialkylamines followed by oxidation with molecular oxygen at 0°C gave bis(N,N-dialkylcarbamoyl) diselenide, pyrolysis of which yielded bis(N,N-dialkylcarbamoyl) selenide and tetraalkylurea.

In the previous paper$^{1)}$ we have shown that carbon monoxide reacts with ammonia or aliphatic amines in the presence of selenium under mild conditions to form selenocarbamate salt which was oxidized with molecular oxygen to give urea or its derivatives in excellent yields.

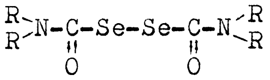
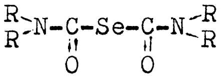
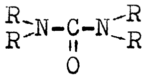
We now found that the process of the formation of ureas from dialkylamines was drastically changed from that previously reported and new selenium compounds, bis(N,N-dialkylcarbamoyl) diselenide and bis(N,N-dialkylcarbamoyl) selenide, were successfully isolated in good yields as the intermediates. For instance, dimethylamine was converted into corresponding amine salt of selenocarbamate (Ia) by the reaction with elemental selenium and carbon monoxide in THF solution at room temperature under atmospheric pressure. The salt was susceptible to molecular oxygen, but it was stable under nitrogen atmosphere at room temperature. Ia gave tetramethylurea by the oxidation at 25°C,$^{1)}$ but upon treatment with oxygen at 0°C yielded a new product melting at 109 - 110°C. The product was assigned to bis(N,N-dimethylcarbamoyl) diselenide (IIa), which was formed by oxidative selenium - selenium coupling. The yields of Ia and IIa were almost quantitative and their structures were established by ir, nmr and mass spectroscopies, and elemental analyses.

It was confirmed that pyrolysis of IIa at 200°C caused the elimination of elemental selenium and carbon monoxide giving tetramethylurea in good yield. This new process for the synthesis of tetraalkylurea was also explored by using diethylamine and di-n-butylamine, and in each case corresponding tetraalkylurea was obtained. When pyrolysis of IIa was carried out under controlled conditions at 150°C, bis(dimethylcarbamoyl) selenide (IIIa) was formed accompanying with deposition of selenium. This clearly showed that IIIa may be an intermediate of the above urea synthesis, and indeed IIIa was pyrolyzed at 200°C giving tetramethylurea accompanying with deposition of selenium and elimination of CO. The results obtained from several amines were shown in Table 1.

Table 1.

Yields of Bis(N,N-dialkylcarbamoyl) Diselenide,

Bis(N,N-dialkylcarbamoyl) Selenide, and Tetraalkylureas

R	 $\mathrm{R_2N{-}\underset{O}{\underset{\|}{C}}{-}Se{-}Se{-}\underset{O}{\underset{\|}{C}}{-}NR_2}$ compd, Yield % a)	 $\mathrm{R_2N{-}\underset{O}{\underset{\|}{C}}{-}Se{-}\underset{O}{\underset{\|}{C}}{-}NR_2}$ compd, Yield % b)	 $\mathrm{R_2N{-}\underset{O}{\underset{\|}{C}}{-}NR_2}$ compd, Yield % c)
Me	IIa, 99	IIIa, 70	IVa, 85
Et	IIb, 99	IIIb, 96	IVb, 74
n-Bu	IIc, 98	IIIc, 43 d)	IVc, 85

a) Yields were based on selenium used.

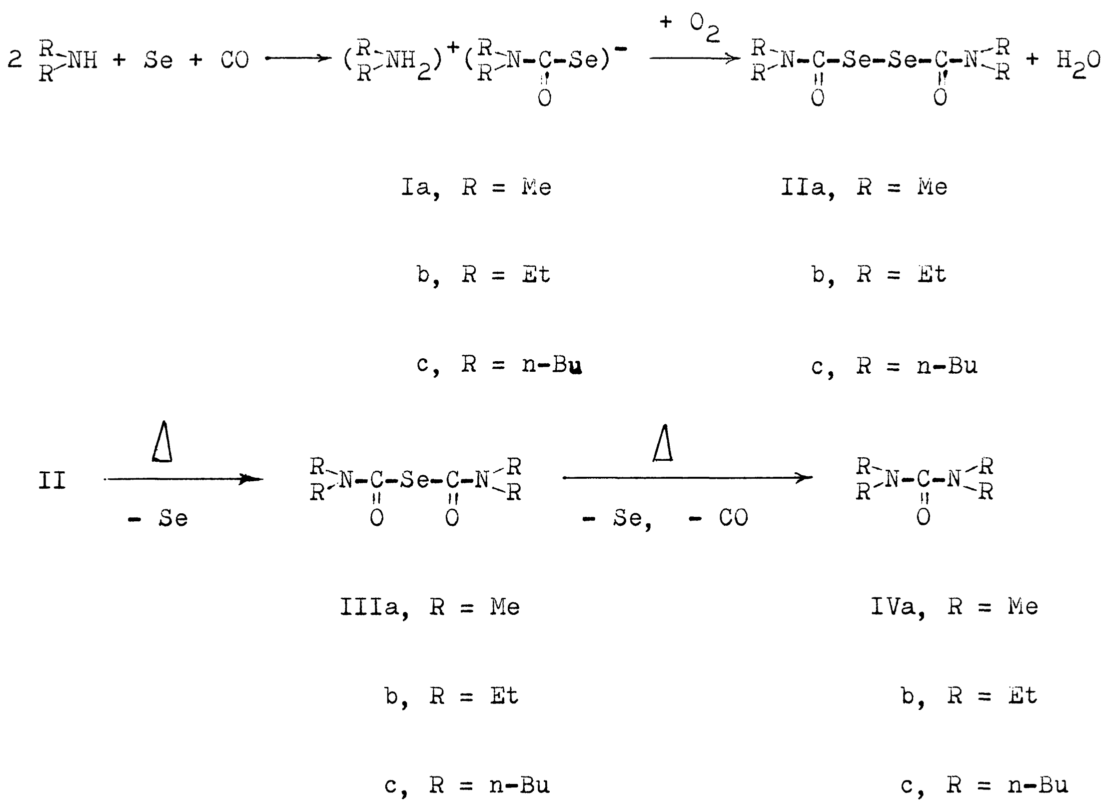
b) Yields were based on II used after pyrolysis at 150°C.

c) Yields were based on II used after pyrolysis at 200°C.

d) Pyrolysis was carried out at 100°C.

The reaction process compatible to present reactions was described by the following Scheme 1.

Scheme 1.



Ia, R = Me   IIa, R = Me

b, R = Et   b, R = Et

c, R = n-Bu   c, R = n-Bu

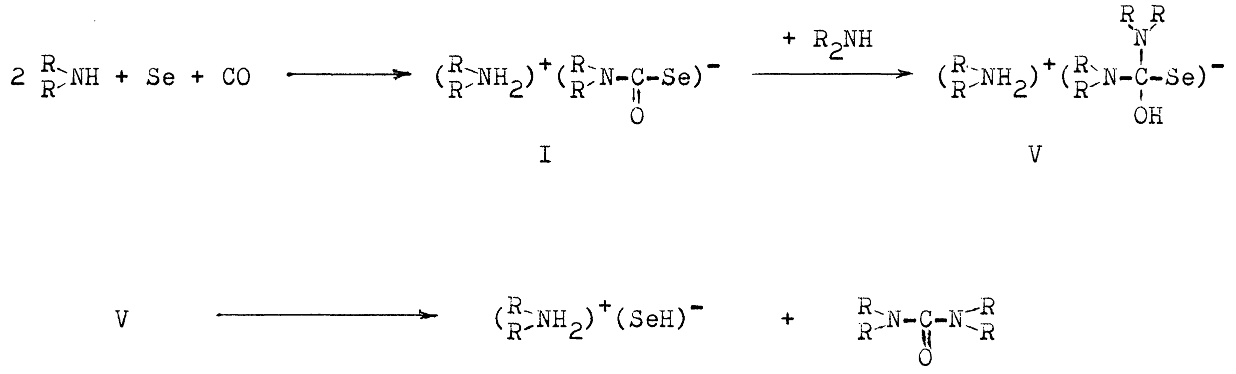
IIIa, R = Me   IVa, R = Me

b, R = Et   b, R = Et

c, R = n-Bu   c, R = n-Bu

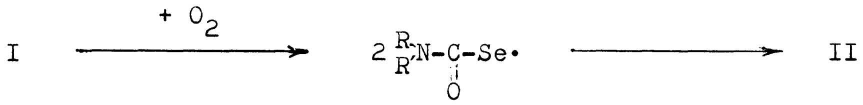
This process was quite different from that of ureas formation already established as shown in Scheme 2.¹⁾

Scheme 2.



I   V

Tetraethylurea was not obtained by the oxidation of Ib at 25°C, but IIb was given selectively. In the case of diethylamine, nucleophilic attack of diethylamine on the carbonyl group of selenocarbamate (I) to give V may be interfered by the steric interaction of alkyl groups, so that the reaction may be stopped at the stage of I. The oxidation of I may, however, occur by the introduction of molecular oxygen into the reaction system and yield selenocarbamoyl radical (VI) which coupled to form diselenide (II).



$$\mathrm{I} \xrightarrow{+\,O_2} 2\,{}^{R}_{R}\!\!>\!N-\underset{\underset{O}{\|}}{C}-Se\cdot \longrightarrow \mathrm{II}$$

VI

The elucidation of the full mechanism of the present reaction is now under investigation, as well as the examination of the reactivities and utilities of I, II, and III with a variety of substrates.

REFERENCE

1) N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, and S. Tsutsumi, J. Amer. Chem. Soc., **93**, 6344 (1971).

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