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STUDIES ON THE ORGANIC REACTIONS BASED ON

THE CHARACTERISTICS OF SELENIUM AND TELLURIUM

（セレンおよびテルルの特性を利用する有機反応に関する研究）

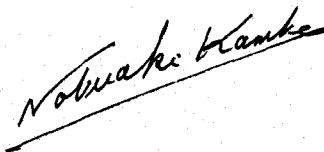NOBUAKI KAMBE

OSAKA UNIVERSITY

1981

Preface

The studies presented in this thesis have been carried out under the direction of Professor Noboru Sonoda at the Department of Petroleum Chemistry, Faculty of Engineering of Osaka University. The thesis is concerned with the organic reactions based on the novel characteristics of selenium and tellurium.

The author wishes to express his sincerest gratitude to Professor Noboru Sonoda for his constant guidance, helpful suggestions and hearty encouradgement throughout this work.   The author is also deeply grateful to Associate Professor Shinji Murai for his continuous advice and stimulating discussions.   The author's grateful thanks are especially due to Assistant Professor Kiyoshi Kondo for his invaluable advices and hearty guidance in both public and private during the course of this study.   The author deeply wishes to acknowledge the constant encouragement of Dr. Noritaka Miyoshi and Dr. Ilhyong Ryu.

Furthermore he wishes to thank Mr. Kiyoyuki Nagano, Mr. Hideo Ishii, Mr. Fumihiko Morimoto, and Mr. Satoru Morita, for their collaborations.   His gratitude is extended to all the members of the research group of Professor Noboru Sonoda for their occasional discussions, helpful assistances, and profound interests.

Finally the author would like to express his thanks to his parents for their perpetual support.

Suita, Osaka

January 1981

Nobuaki Kambe

List of Publications

The contents of this thesis are composed of the following papers.

1 Tellurium-Catalyzed Reaction of Amines with Carbon Monoxide
   Nobuaki Kambe, Kiyoshi Kondo, Hideo Ishii, Shinji Murai,
   and Noboru Sonoda,
   Angew. Chem., 91, 582(1979); Angew. Chem. Int. Ed. Engl., 18,
   547(1979).

2 Carbon Monoxide/Water as a Reducing Agent : Formation of
   Selane from Selenium
   Noboru Sonoda, Kiyoshi Kondo, Kiyoyuki Nagano, Nobuaki Kambe,
   and Fumihiko Morimoto,
   Angew. Chem., 92, 317(1980); Angew. Chem. Int. Ed. Engl., 19,
   308(1980).

3 Water Gas Shift Reaction with the Aid of Selenium/Platinum
   Catalyst
   Nobuaki Kambe, Fumihiko Morimoto, Kiyoshi Kondo,
   and Noboru Sonoda,
   Angew. Chem., 92, xxx(1980); Angew. Chem. Int. Ed. Engl., 19,
   xxx(1980).

4 Reduction of Carbonyl Compounds by Aluminum Telluride and
   H_2O or D_2O
   Nobuaki Kambe, Kiyoshi Kondo, Satoru Morita,
   and Noboru Sonoda,
   Angew. Chem., 92, xxx(1980); Angew. Chem. Int. Ed. Engl., 19,
   xxx(1980).

5   Photoreduction of Ketones and Aldehydes to Alcohols with
    Selane
    Nobuaki Kambe, Kiyoshi Kondo, Shinji Murai, and Noboru Sonoda
    Angew. Chem. 92, xxx(1980); Angew. Chem. Int. Ed. Engl., 19,
    xxx(1980).

6   Reduction of Aromatic Nitro, Nitroso, Hydroxylamino, Azo, and
    Azoxy Compounds with Hydrogen Telluride from Aluminum
    Telluride and Water
    Nobuaki Kambe, Kiyoshi Kondo, and Noboru Sonoda,
    Angew. Chem., 92, xxx(1980); Angew. Chem. Int. Ed. Engl., 19,
    xxx(1980).

7   Photoreduction of Carbonyls with Hydrogen Selenide.
    An Estimation of the High Hydrogen Donating Ability of
    Hydrogen Selenide by Kinetic Study and Chemical Trapping
    Nobuaki Kambe, Kiyoshi Kondo, and Noboru Sonoda,
    Chem. Lett., 1980, 1629.

8   Tellurium-Catalyzed Carbonylation of Amines with Carbon
    Monoxide
    Nobuaki Kambe, Kiyoshi Kondo, and Noboru Sonoda,
    Bull. Chem. Soc. Jpn., submitted for publication.

9   Chemical Trapping of 1,4-Biradical with Hydrogen Selenide
    Nobuaki Kambe, Kiyoshi Kondo, and Noboru Sonoda,
    Angew. Chem., submitted for publication.

Contents

General Introduction

Selenium and Tellurium belong to VIa group in the periodic table, as oxygen and sulfur. For the chemical utilization of sulfur, a lot of studies have been made in organic chemistry and have provided many useful synthetic reactions. In contrast to sulfur, application of selenium and tellurium in organic reactions are under way.

Selenium was discovered in 1817 and named from the Greek 'δελην', the moon. With respect to its application in organic chemistry, only dehydrogenation[1] of aliphatics with elemental selenium and oxidation[2] with selenium dioxide were available until comparatively lately. During a last few decades, however, utilization of elemental selenium[3] and organic selenium compounds[4] in synthetic reactions have been investigated resulting in the discovery of new organic reactions using selenium or its compounds as a new catalyst or novel organic reagents. Most of these reactions are formally similar to those by sulfur, but proceed under much milder conditions with high selectivity.

Tellurium was recognized as an element in 1782, which mane was derived from the Latin ' *tellus* ', the earth. Until quite recently, there was no remarkable use of the element in organic reactions. Nevertheless striking progress in sulfur and selenium chemistry stimulated the investigation of tellurium, and some fascinating pursuits have been reported lately.[5]

With these background it contains great interest in making
investigations on the chemical behavior of selenium and tellurium.
Moreover, on progressing down the chalcogen group, metallic
character of the elements gradually increases.   Therefore
unique reactivity could be expected for these two elements.

This thesis deals with the results obtained from the research
on the chemical characteristics of selenium and tellurium and its
application to the organic reactions.

Chapter 1 is concerned with the new tellurium-catalyzed
carbonylation reaction of amines with carbon monoxide.
Effects of the temperature, the pressure of carbon monoxide,
and additives on this reaction are mentioned.   A plausible
reaction path is also proposed.

In Chapter 2 is dealt novel reduction with hydrogen
telluride.   Aromatic nitro compounds and their related
compounds, carbonyl compounds, imines, and enamines are examined.
This chapter also involves the selective reduction of carbon-
carbon double bond of α,β-unsaturated carbonyl compounds as well
as a facile reductive deuteration of carbonyls.

Chapter 3 refers to the photoreduction of carbonyls to
carbinols with hydrogen selenide.   The high hydrogen donating
ability of hydrogen selenide is revealed and chemical trapping
of photochemically generated 1,4-biradicals is stated.

Chapter 4 deals new synthesis of hydrogen selenide from selenium, carbon monoxide, and water. As an application of this reaction, a novel water gas shift reaction by use of selenium/platinum catalyst is described.

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4   K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patric

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    Tetrahedron Lett., 1979, 1509;   N. Kambe, K. Kondo, H.

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Chapter 1   Tellurium-Catalyzed Carbonylation of Amines with

   Carbon Monoxide

1-1   Introduction

   Carbonylation of amines with carbon monoxide to produce urea

derivatives by use of S,[1] Se,[2] Fe(CO)$_5$,[3] AgOAc,[4] and inorganic

oxidizing agents,[5] have been known to proceed as stoichiometric

reaction.   On the other hand, in order to carry out this

carbonylation catalytically many studies have been done to show

the effectiveness of Se,[2] transition metals and their complexes

of Hg,[6] Mn,[7] Fe,[8] Co,[9] Ni,[10] Rh,[11] Pd,[12] W,[13] and Pt.[14]

   Carbonylation of amines with carbon monoxide in the presence

of sulphur proceeds to give hydrogen sulfide[1] and corresponding

urea derivatives(eq. 1).

   $$S + 2 RNH_2 + CO \longrightarrow H_2S + (RNH)_2CO \qquad (1)$$

This reaction requires high temperature and high pressure of

carbon monoxide.   In the carbonylation of ammonia in gas phase,

isocyanate is proposed as the intermediate.

   On the other hand, selenium reacts with various amines and

carbon monoxide at room temperature under atmospheric pressure

to yield selenol carbamate which reacts with amines and gives

quantitative amounts of hydrogen selenide and urea derivatives

(eq. 2).[2]

$$\text{Se} + 2\ RNH_2 + CO \longrightarrow H_2Se + (RNH)_2CO \qquad (\ 2\ )$$
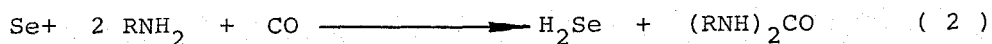
Thus formed hydrogen selenide is easily reduced with oxygen to regenarate selenium, so that the co-presence of oxygen in this carbonylation system enables the reaction to proceed catalytically (eq. 3).

$$2\ RNH_2 + CO + \tfrac{1}{2}O_2 \xrightarrow{\ \text{Se}\ } (RNH)_2CO + H_2O \qquad (\ 3\ )$$
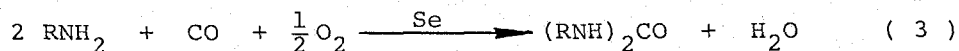
This reaction is considered to proceed via selenol carbamic acid as the key intermediate. Its intermediacy was supported by the successful isolation of selenol carbamate from the reaction system by the evaporation of the solvent. Furthermore carbonyl selenide was obtained by acidifying the reaction system. From these evidences, the following scheme is proposed for this carbonylation reaction.
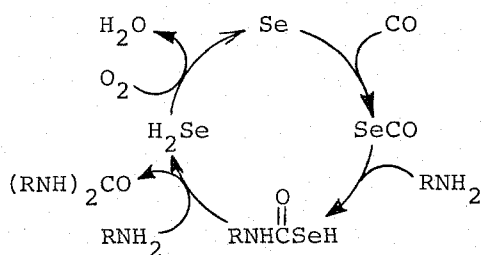
Scheme 1

Whereas, there has been no report dealing with such kind of carbonylation catalyzed by tellurium. It should be important

to clarify the chemical behavior of tellurium in the reaction of amines with carbon monoxide in order to open up its new applications for the organic chemistry.

This chapter describes the novel carbonylation of amines with carbon monoxide catalyzed by elemental tellurium.[15]

1-2 General Reaction
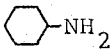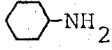
In the presence of tellurium, reaction of n-butylamine with carbon monoxide under atmospheric pressure of carbon monoxide at 25°C, the similar conditions as selenium-catalyzed carbonylation, failed resulting in the recovery of the materials.   But under more severe conditions tellurium-catalyzed carbonylation of amines with carbon monoxide took place to yield urea derivatives, hydrogen, and formamide derivatives (eq. 4, Table 1).

$$RNH_2 + CO \xrightarrow{\quad Te \quad} (RNH)_2CO + H_2 + RNHCHO \qquad (4)$$
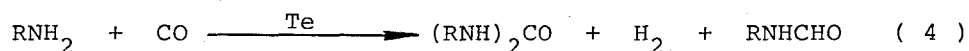
n-Butylamine, n-octylamine, cyclohexylamine, and benzylamine were examined for this carbonylation reaction.   The equimolar amounts of ureas and molecular hydrogen were obtained in any experiments.   This point is the chracteristics of the urea formation in this carbonylation catalyzed by tellurium, and also is a important aspect since there has been no report dealing with the exact stoichiometry between the amounts of formed ureas and

that of molecular hydrogen.　　Unless otherwise noted, 1 mmol of
tellurium was always used, and thus the values of yields of
products (in mmol) corresponded to the turnover number.
For any kinds of amines, the carbonylation reaction proceeded
catalytically.　　The turn over number for the urea formation
in Run 5 in Table 1, for example, corresponded to 5.8 per hour.

Table 1.　Tellurium-Catalyzed Carbonylation[a] of Amines with CO

Run	Amine (100 mmol)	Te (mmol)	Time (h)	Urea (mmol)	H_2 (mmol)	Formamide (mmol)
1	n-BuNH$_2$	1	10	7.6	7.1	10.0
2	n-BuNH$_2$	1	10	7.7	7.4	15.3
3	n-BuNH$_2$	1	10	7.4	7.0	12.5
4	n-BuNH$_2$	1	10	7.8	7.2	17.3
5	n-BuNH$_2$	0.05	10	2.9	2.9	1.3
6	n-BuNH$_2$	1	72	22.0	21.0	51.8
7	n-BuNH$_2$	0	10	0.01	0.04	0.3
8	⬡-NH$_2$	1	10	4.1	3.3	7.2
9	⬡-NH$_2$[b]	1	72	12.1	12.2	37.1
10	n-OctNH$_2$	1	10	2.3	1.9	1.0
11	n-OctNH$_2$[c]	1	72	10.0	d)	24.8
12	PhCH$_2$NH$_2$	1	10	4.7	5.0	1.1

a) Temp.: 140°C,　CO : 30 kg/cm^2.

b) Cyclohexylamine : 85.1 mmol (10 ml).

c) n-Octylamine : 60.2 mmol (10 ml).　After the reaction
    13.0 mmol of n-octylamine was recovered.

d) Not determined.

The reaction of n-butylamine with carbon monoxide in the presence of tellurium catalyst was carried out four times under the identical reaction conditions. The reproducibility of the formation of 1,3-di-n-butylurea and hydrogen was satisfactory (Run 1-4). The reproducibilyty using n-octylamine and cyclohexylamine was also confirmed fairly good by duplicated experiments. In regard to the reproducibility of formamide derivatives, the yields varied much more than those of the urea derivatives and hydrogen.

In the reaction performed for 72 h, almost all n-butylamine was consumed to give urea and formamide derivatives (Run 6). The material balance in the carbonylation of n-octylamine was confirmed nearly 100 % (Run 11).

From these results, it could be supposed that the present carbonylation consists of two reactions, urea formation to produce equimolar amounts of ureas and hydrogen (eq. 5) and formylation (eq. 6).

$$2 \ RNH_2 \ + \ CO \longrightarrow (RNH)_2CO \ + \ H_2 \qquad\qquad (\ 5 \ )$$

$$RNH_2 \ + \ CO \longrightarrow RNHCHO \qquad\qquad\qquad (\ 6 \ )$$

1-3 Effect of Temperature and CO Pressure

The temperature higher than 100°C was required for the
effective performance of the catalytic reaction.   The yields
of 1,3-di-n-butylurea increased as the temperature was elevated,
whereas plots of the yields of hydrogen and n-butylformamide
showed the maxima around at 160°C (Table 2, Fig. 1).
At temperatures below 160°C, the amounts of ureas formed were
equal to those of hydrogen.

Table 2.   Effect of Temperature and CO Pressure

Run	Temp. (°C)	CO (kg/cm^2)	Urea (mmol)	H_2 (mmol)	Formamide (mmol)
1	100	30	1.2	0.5	0.9
2	120	30	3.1	2.1	10.5
3	140	30	7.7	7.4	15.3
4	160	30	11.8	9.9	20.1
5	180	30	12.2	9.6	12.7
6	200	30	17.3	5.1	10.4
7	140	10	2.6	2.8	0.7
8	140	50	8.5	8.6	29.2
9	140	70	10.7	10.0	32.4
10	140	90	12.0	10.2	45.4

Te : 1 mmol, n-BuNH$_2$: 100 mmol, time : 10 h.
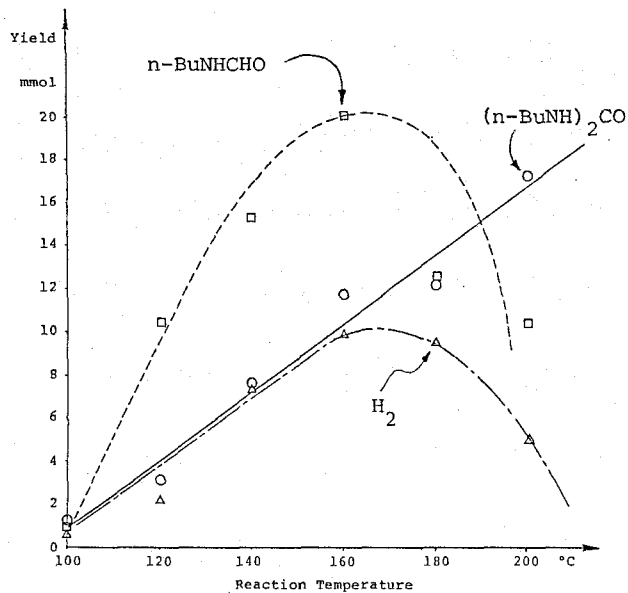
Fig. 1.   Effect of temperature on tellurium-
catalyzed carbonylation.   Te:1 mmol, n-BuNH$_2$:
100 mmol, CO:30 kg/cm^2, time:10 h.
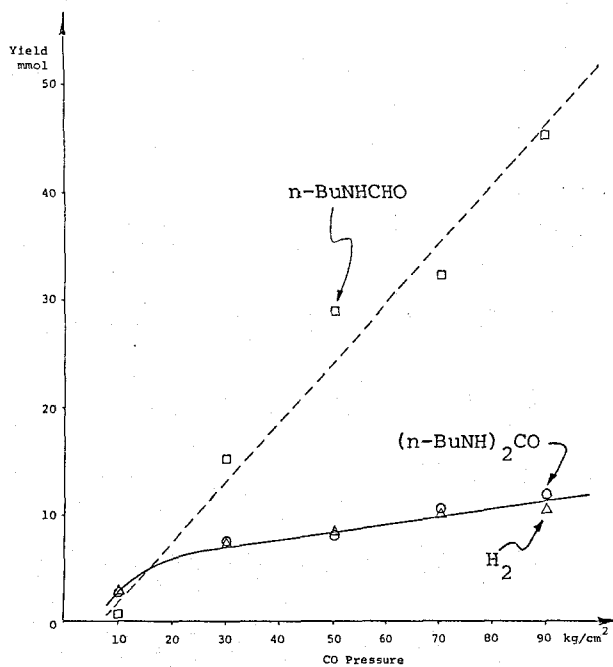
Fig. 1.   Effect of CO pressure on tellurium-
catalyzed carbonylation.   Te:1 mmol, n-BuNH$_2$:
100 mmol, temp.:140°C, time:10 h.

Although no relevant explanation has been made for the decrease of formations of hydrogen and formamide, some postulations could be proposed. First, in both reactions the same species, which is tentatively considered to be hydrogen telluride, plays important roles, and some reaction path for the consumption of hydrogen telluride takes place at temperatures higher than 160°C. Secondly, formamide might react with the precursor of hydrogen, which would be hydrogen telluride. Neither decomposition of formed formamide nor consumption of molecular hydrogen generated in the carbonylation reaction is likely.

Higher pressures of carbon monoxide were advantageous for all the formations of 1,3-di-n-butylurea, hydrogen, and n-butyl-formamide (Talle 3, Fig. 2). But it should be noted that the formamide formation was more sensitive to the pressure than the others.

1-4   Effect of Aditives

As will be discussed in Chapter 2, aromatic nitro compounds were found to be reduced with hydrogen telluride to give corresponding amino compounds.[16]   Evidently, the addition of nitrobenzene to the present tellurium-catalyzed carbonylation system gave aniline in good yield, resulting in the drastic suppression of the formation of hydrogen and n-butylformamide (Run 2 in Table 3).

Table 3. Effect of Additives

Run	Additive (10 mmol)	Temp. (°C)	$(n\text{-}BuNH)_2CO$ (mmol)	H_2 (mmol)	n-BuNHCHO (mmol)	Reduced Prod. (mmol)
1	-	72	22.0	21.0	51.8	-
2 [a]	$PhNO_2$	72	15.9	1.3	2.0	$PhNH_2$:9.0
3	-	40	19.9	16.7	33.5	-
4 [b]	$PhNO_2$	40	5.2	0.0	0.9	$PhNH_2$:4.5
5	$PhCHCH_2$	20	16.1	6.8	31.2	PhEt:1.3
6	⬡	72	c)	11.5	28.7	⬡:3.6
7 [d]	PhMeC=O	22	19.9	c)	29.2	PhEt:0.8
8	O_2	24	15.8	2.8	13.9	-
9	O_2	10	9.0	trace	5.0	-
10	-	10	7.6	7.1	10.1	-
11	Se [e]	10	19.1	14.5	28.7	-

Te : 1 mmol, n-BuNH$_2$: 100 mmol, CO : 30 kg/cm^2, temp.: 140°C.
a) Unreacted nitrobenzene was not detected after the reaction.
b) After the reaction 3.5 mmol of nitrobenzene remained.
c) Not determined.
d) α-Phenethyl alcohol was not formed.
e) In this reaction 1.0 mmol of selenium was used.

The value of the reaction constant, ρ, of the Hammett equation of the concurrent reduction of nitrobenzenes in the tellurium catalyzed carbonylation system was obtained as +0.8 (see Experimental). These results do not contradict the assumption that hydrogen telluride is the key intermediate both in formylation and in hydrogen formation. In the presence of nitrobenzene tellurium-catalyzed carbonylation may be expressed by Scheme 2.

$$PhNH_2 \quad\rightleftarrows\quad Te \quad\rightleftarrows\quad RNH_2 + CO$$
$$PhNO_2 \quad\rightleftarrows\quad H_2Te \quad\rightleftarrows\quad (RNH)_2CO$$
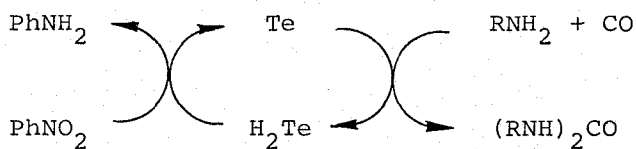
Scheme 2.

For the purpose of performing the concurrent reduction of organic compounds, styrene was added in the carbonylation system. In this case only a small amount of ethylbenzene was produced, and reductive dimerization of styrene predominated. In order to prevent the dimerization, cyclohexene was used and cyclohexane was produced in good yield (Run 7 in Table 3). But olefins were not effective to suppress the formations of hydrogen and formamide in comparison with nitrobenzene. When the carbonylation was carried out in the co-presence of acetophenone, no suppression of the formation of formamide was observed and condensed product of acetophenone with n-butylamine ($PhMeC=NC_4H_9$) was obtained. In this reaction α-phenethyl alcohol was not formed but a small

amount of ethylbenzene.   This result might suggest the unique

reduting ability of hydrogen telluride or some compounds with

hydrogen-tellurium bond toward carbonyl compounds.

From the analogy of selenium-catalyzed urea formation

(eq. 3), the carbonylation by tellurium was carried out in

the presence of oxygen (Table 3).   The suppression of the

formations of hydrogen and formamide was not drastic.   In a

reaction caried out for 5 h, carbonylation did not occur. Glpc

analysis of the reaction mixture showed the complex pattern on

the chart.   In the reaction performed for 10 h without tellurium,

similar chromatogram was obtained.   These results may indicate

that tellurium-catalyzed carbonylation did not start until all

of the oxygen was consumed by some reactions with n-butylamine.

The oxidized products were considered to act as mild oxidizing

agents.   This assumption accounts for the evidence that the

formations of hydrogen and formamide were suppressed to some

extent in the presence of oxygen.   Addition of 5 mmol of water

into the carbonylation system showed a little suppression on the

whole reaction to some extent.   Formamide formation was not

enhanced by water.   It is not likely that water reacted with

tellurium and carbon monoxide under this condition to give

hydrogen telluride and carbon dioxide which was not detected

after the reaction.

The addition of selenium accelerated the carbonylation

effectively.   The following equations might be one of the

$$2 \text{ RNH}_2 \quad + \quad \text{CO} \quad + \quad \text{Se} \longrightarrow (\text{RNH})_2\text{CO} \quad + \quad \text{H}_2\text{Se} \qquad (7)$$

$$\text{H}_2\text{Se} \quad + \quad \text{Te} \longrightarrow \text{Se} \quad + \quad \text{H}_2\text{Te} \qquad (8)$$
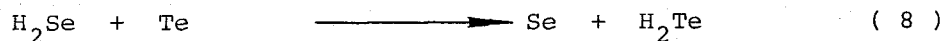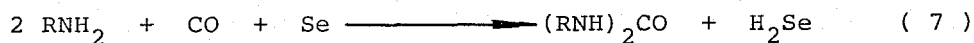
plausible explanations for the selenium participation in this reaction.   This assumption would be supported by the following evidences.   Selenium-catalyzed urea synthesis much favorably than tellurium.   In the selenium-catalyzed carbonylation reaction, molecular hydrogen was not produced and hydrogen selenide was the final product of the catalyst.   It does not seem unreasonable to assume the presence of the equilibrium between hydrogen selenide and hydrogen telluride (eq. 8) in this carbonylation system.

Tellurium was found to react with hydrazine under mild conditions to give hydrogen telluride and hydrogen ditelluride.[17] In order to facilitate the reaction, tellurium-catalyzed carbonylation was carried out in the co-presence of hydrazine. Under severe conditions, no effect was caused by the addition of hydrazine.   But in the reaction at 80°C using hydrazine, the initiation of the carbonylation was accelerated.   At low temperature the reaction was very slow, and it is one of the subjects to be solved in order to carry out this carbonylation under milder conditions.

Table 4.   Effect of Hydrazine

Run	N_2H_4 (mmol)	n-BuNH$_2$ (mmol)	Solv. (10ml)	Temp. (°C)	Time (h)	Urea (mmol)	Formamide (mmol)
1	0	50	THF	100	20	0.09	0.01
2	2	50	THF	100	20	0.34	0.20
3	0	100	–	140	72	22.9	13.9
4	28	100	–	140	72	22.9	13.3

Tellurium : 1 mmol, carbon monoxide : 30 kg/cm^2.
a) Amorphous tellurium was used.

1-5 Carbonylation Using Tellurium Dioxide Instead of Tellurium

Reaction of n-butylamine with carbon monoxide was carried out in the presence of tellurium dioxide (Table 5).   In the reaction for 20 h at 200°C, tellurium dioxide (white solid) was reduced to tellurium and a small amount of urea was formed with a trace of formamide, indicating that tellurium dioxide was reduced in the reaction system.   In the reaction for the prolonged period, the product distribution was similar to that in tellurium-catalyzed reaction.   Therefore, once tellurium dioxide was reduced to tellurium, the same tellurium-catalyzed carbonylation would proceed.

Table 5.   Carbonylation Using Tellurium Dioxide

Time (h)	$(n-BuNH)_2CO$ (mmol)	n-BuNHCHO (mmol)	H_2 (mmol)
20	1.0	trace	trace
52	18.8	15.3	16.7

TeO_2 : 1 mol, $n-BuNH_2$: 100 mmol (10 ml),
CO : 30 kg/cm^2, temp.: 140°C.

1-6 Comparison of Catalyses by Selenium and Tellurium in
     the Urea Formation Reaction

     Carbonylation reaction of amines in the presence of selenium
afforded stoichiometric amounts of urea derivatives and hydrogen
selenide.   By use of selenium under the typical reaction
condition, at 140°C for 10 h, the carbonylation was carried out
in an autoclave.   This reaction gave the stoichiometric amount
of 1,3-di-n-butylurea to the used selenium with little formation
of hydrogen.   When this inserted glass tube was not used, more
than equimolar amount of urea to selenium catalyst was produced
with a small amount of hydrogen.   This result would be attributed
to the wall effect of the autoclave.   These results show the
similarity and the difference in the catalyses by selenium and
tellurium; both non-transition metal elements, selenium and

tellurium, catalyzed the carbonylation of amines with carbon
monoxide, where the former requires suitable oxidizing agents such
as oxygen to give water, while the latter does not with the
production of hydrogen. With regard to the reaction conditions,
the selenium-catalyzed urea synthesis was achieved under much
milder conditions than the other. At present selective formations
of urea derivatives (eq. 5) by tellurium catalyst are not
succeeded in contrast with the selenium-catalyzed reaction which
provided only urea derivatives (eq. 3).

1-7 A Plausible Reaction Path

There is not enough evidence to propose the precise reaction
path for this tellurium-catalyzed carbonylation. But from a
close analogy to the selenium chemistry,[2] tellurium-catalyzed
urea formation (eq. 5), would be best explained by the assump-
tion that it consists of two reactions: one, the stoichiometric
reaction of amines, carbon monoxide, and tellurium to produce
ureas and hydrogen telluride (eq. 9); the other, the dehydro-
genative decomposition of hydrogen telluride to molecular hydrogen
and tellurium (eq. 10).

$$2 \ RNH_2 \ + \ CO \ + \ Te \longrightarrow (RNH)_2CO \ + \ H_2Te \qquad (\ 9 \ )$$

$$H_2Te \longrightarrow H_2 \ + \ Te \qquad (\ 10 \ )$$
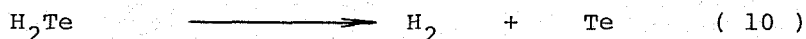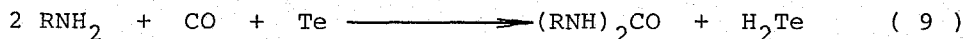
The assumption of the intermediacy of hydrogen telluride in this reaction does not contradict the following evidences.   i) Pure hydrogen telluride was prepared by the reaction of aluminum telluride and water.   Thus prepared hydrogen telluride was found to decompose quite readily to its components, molecular hydrogen and tellurium (eq. 9).   This may be due to the weak bond energy between hydrogen and tellurium reported as 64 kcal/mol.[18] Therefore hydrogen telluride may well be the precursor of molecular hydrogen and tellurium catalyst.   ii) The equimolar formation of ureas and hydrogen should be well accounted for by eqs. 9 and 10.   iii) The formylation of nitrogen-hydrogen bond with carbon monoxide was also mentioned in the catalysis by the trietylammonium salt of hydrogen selenide at elevated temperature under CO pressure similar to the present reaction conditions.[19]   The formation of formamides was observed in the tellurium catalyst system (Table 1 and eq. 4). The results might be also due to the catalysis of hydrogen telluride.   iv) There was found a similar tendency in the temperature effects in the yields of hydrogen and formamides (Fig. 1).   The same species, which is supposed to be hydrogen telluride, might be responsible for it.   v) The addition of nitrobenzene into the tellurium-catalyzed carbonylation system gave important results as mentioned already; a) no effect on the urea formation, b) the drastic suppression on the formation of molecular hydrogen and formamides, c) the production of aniline

as the reduced form of nitrobenzene.

In conclusion, a plausible reaction path could be represented as shown in Scheme 2.

$$H_2 \longrightarrow Te \longrightarrow CO + RNH_2$$

RNHCHO $\longrightarrow$ H_2Te $\longrightarrow$ $(RNH)_2CO$

CO

RNH_2 $\longrightarrow$ $\left[H\overset{O}{\underset{||}{C}}TeH \right]$
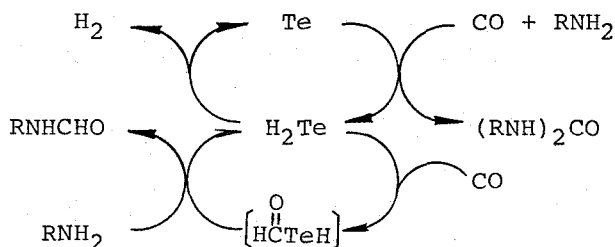
Scheme 2.

The intermediacy of tellurol formic acid, $H\overset{O}{\underset{||}{C}}TeH$,[20] in the formamide formation reaction is still a subject to be solved.

1-8 Experimental

Instrument

Melting points were measured with a Yanagimoto Micro Melting Point apparatus.   IR spectra were taken with a Shimadzu IR-400. NMR spectra were recorded on a Hitachi Mass Spectrometor, Model RMU-6E.   Analitical gas chromatography were performed with a Shimadzu 3BT with thermal conductivity detector, Shimadzu 3BF and GC-6A both with flame ionization detector.

Apparatus

All carbonylations were carried out using 50 ml stainless steel autoclaves (SUS-304) manufactured by Taiatsu Glass Kogyo. In order to eliminate the wall effect, some reactions were carried out in a glass tube inserted in the autoclave.

Materials

n-Butylamine, cyclohexylamine, n-octylamine, and benzylamine were purchased from Nakarai Kagaku, and were purified by distillation from KOH just before use. Tellurium lump (99.999%) was obtained from Wako Junyaku. Tellurium was powdered by use of agate mortar and pestle, and stored under dry nitrogen in the absence of light. The reactive gray tellurium had to be used within a few weeks, since it gradually turned black becoming inactive for the carbonylation under similar conditions. Amorphous tellurium was prepared by the reduction of tellurium dioxide with sulfur dioxide.[21] Carbon monoxide (99.99 %) was purchased from Neriki Gas in a syrinder and was used without any purification. CO pressure values mentioned in this paper refer to those at room temperature.

Product Analyses

The analysis of the gas phase after the reaction was performed with a Shimadzu 3BT gas chromatography using a 3.3 m x 3 mm stainless steel column packed with 30-60 mesh Molecular Sieves 5A

and nitrogen effluent gas at 150°C of the oven temperature.   The
analytical error of hydrogen was less than 2 %.   1,3-Di-n-butyl-
urea was analyzed on a Shimadzu GC-6A using a 70 cm x 3 mm glass
column packed with 3 % DEGS on acid-washed, base-treated, DMCS-
treated, 80-100 mesh Shimalite W at 150°C of the oven temperature,
and diethyl phthalate was used as an internal standard.
Formamides, nitrobenzenes, and anilines were analyzed on a
Shimazdu 3BF using a 3.3 m x 3 mm stainless steel column packed
with 25 % PEG-20M on acid-washed, 60-80 mesh Shimalite W at 200°C
of the oven temperature, and n-dodecane was used as an internal
standard.   1,3-Di-cyclohexylurea, 1,3-di-n-octylurea, and
1,3-dibenzylurea were obtained after the removal of unreacted
amines and formed formamides from the reaction mixtures under
reduced pressure.   Recrystallization from ethanol gave corre-
sponding ureas.   Identification was made based on spectroscopic
data (IR, NMR, and Mass measurements).   Melting points were
in good agreement with those[22] of authentic samples.

Carbonylation of n-Butylamine (Run 1 in Table 1)

     In a 50 ml stainless steel autoclave were placed tellurium
(1 mmol, 128 mg),   n-butylamine (100 mmol, 10 ml), and a
magnetic stirring bar.   The autoclave was flushed with carbon
monoxide three times and charged at 30 kg/cm^2.   The autoclave
was sunk in an oil bath maintained at 140°C, and the reaction was
conducted for 10 h with magnetic stirring.   After the reaction,

the autoclave was immediately cooled to room temperature with cold

water.   Then the resulting gas was collected in a gas sampler.

From vpc analysis the gas was found to contain 7.1 mmol of

molecular hydrogen.   The reaction mixture was transferred into

a 100 ml flask and was allowed to contact with air for 30 minutes

with magnetic stirring in order to precipitate tellurium.

Products were obtained after the removal of deposited tellurium

followed by the evaporation of the unreactd n-butylamine.

From glpc analyses, 1,3-di-n-butylurea and n-butylformamide were

found to be produced in the yields of 7.6 mmol and 10.1 mmol,

respectively.   1,3-Di-n-butylurea was purified by recrystal-

lization from n-hexane and was identified by comparison with IR,

NMR, Mass spectroscopy, and mp of the authentic sample (71°C).[22]

Carbonylation of n-Octylamine (Run 11 in Table 1)

In a 50 ml stainless steel autoclave were placed telurium

(1 mmol, 128 mg),   n-octylamine (60.2 mmol, 10 ml), and a

magnetic stirring bar.   The apparatus was flushed with carbon

monoxide three times and charged at 30 kg/cm^2.   After the

reaction at 140°C for 10h, the autoclave was allowed to cool to

room temperature, and the pressure was released.   Several

portions of hot ethanol were poured into the autoclave and the

resulting mixture was transferred into a 200 ml flask.   Tellurium

was precipitated by air oxidation, and was filtered off.   1,3-

Di-n-octylurea was obtained as crystals in the yield of 2.48 g

(10.0 mmol) after the evaporation of ethanol.   Then the filtrate
was fractionated, and n-octylformamide (114-120°C/4 mmHg, 3.90 g,
24.8 mmol) and unreacted n-octylamine (54-57°C/10 mmHg, 1.68 g,
13.0 mmol) were obtained.

Carbonylation of n-Butylamine by Tellurium in the Presence of Nitrobenzen

In a 50 ml stainless steel autoclave, tellurium (1 mmol,
128 mg), n-butylamine (100 mmol, 10 ml), and nitrobenzene
(10 mmol, 123 mg) were placed with a magnetic stirring bar. The
autoclave was then flushed with carbon monoxide three times and
charged at 30 kg/cm^2.   The reaction was conducted at 140°C
for 72 h with vigorous stirring.   After the reaction, resulting
gas was analyzed by vpc, and 1.3 mmol of hydrogen was found to
be formed.   Glpc analyses of the reaction mixture, after the
removal of tellurium as mentioned above, showed the formation
of 15.9 mmol of 1,3-di-n-butylurea and 2.0 mmol of n-butyl-
formamide.   Neither 1-n-butyl-3-phenylurea nor 1,3-diphenylurea
was detected.   Reactions using other additives except oxygen
were performed in the similar way.

Tellurium-Catalyzed Carbonylation in the Presence of Oxygen

In a 50 ml stainless steel autoclave were placed tellurium
(1 mmol, 128 mg), n-butylamine (100 mmol, 10 ml), and a
magnetic stirring bar under nitrogen.   The apparatus was

charged with oxygen at 4 kg/cm^2 (ca. 10 mmol) and additionally
with carbon monoxide to the total pressure of 34 kg/cm^2.
The reaction was conducted at 140°C for desired periods, and
products were analyzed by glpc similarly.

Competitive Reduction of Nitrobenzene and p-Nitrotoluene in
This Carbonylation System

In a 50 ml stainless steel autoclave were placed tellurium
(1 mmol, 128 mg), n-butylamine (100 mmol, 10 ml), nitrobenzene
(5 mmol, 615 mg), and p-nitrotoluene (5 mmol, 685 mg).   The
apparatus was flushed with carbon monoxide three times and charged
at 30 kg/cm^2.   After the reaction for 72 h at 140°C, deposited
tellurium was removed by filtration.   Glpc analyses of the
filtrate revealed that 2.48 mmol of aniline and 1.81 mmol of
p-toluidine were formed.

Carbonylation of n-Butylamine by Selenium using a Glass Tube

Into a glass tube in the autoclave were placed tellurium
(1 mmol, 128 mg), n-butylamine (100 mmol, 10 ml), and a
magnetic stirring bar.   The apparatus was flushed with carbon
monoxide three times and charged at 30 kg/cm^2.   After the
reaction at 140°C for 10 h, the autoclave was allowed to cool to
room temperature.   The resulting gas was collected in a gas
sampler, and little amount of hydrogen was detected by vpc anal-
ysis.   The resulting mixture was transferred into a 100 ml

flask and the oxidation with air at room temperature for 1 h precipitated selenium. Products were obtained by the removal of selenium followed by the evaporation of the solvent. Glpc analyses of the products showed the formation of 1.0 mmol of 1,3-di-n-butylurea and 1.5 mmol of n-butylformamide.

Generation of Hydrogen Telluride

In a 100 ml three necked glass vessel equipped with a 10 ml dropping funnel, a stopper, and a connection tube to a trapping vessel maintained at -196°C, was placed powdered aluminum telluride (29 g, 66 mmol) under nitrogen atmosphere. All the apparatus was covered with aluminum foil to eliminate the effect of light. Then, 10 ml of water was dropped very slowly into the reaction vessel over a period of 1 h. The reaction was exothermic and the reaction vessel should be cooled with ice. Hydrogen telluride was trapped at -196°C as a white solid. When warmed to -78°C, hydrogen telluride began to decompose. As the temperature was slowly elevated, hydrogen telluride completely decomposed below its melting point of -4°C and gray tellurium remained.

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17 In n-butylamine (20 ml), recation of tellurium (2 mmol,

    0.256 g) with hydrazine (20 mmol, 0.64 ml) was carried out

    at reflux temperature.   The solution turned to pale purple,

    but most of tellurium remained at the bottom of the flask.

    As soon as n-butyl iodide (4 mmol, 0.462 ml) was introduced

    at 0°C into the resulting mixture, the color turned to green.

    n-Bu_2Te (0.1 mmol) and n-Bu_2Te_2 (0.3 mmol) were obtained

    by column chromatography (Kieselgel 60, 70-230 mesh, hexane).

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20 In the triethylammonium salt of hydrogen selenide ($Et_3N·H_2Se$)

    catalyzed formylation of aromatic amines under similar

    reaction conditions as present ones, the intermediacy of

    selenol formic acid, $H\overset{O}{\overset{\|}{C}}SeH$, was considered; see ref. 19.

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Chapter 2 New Reduction with Hydrogen Telluride

2-1 Introduction

In the course of the study on tellurium-catalyzed dehydro-
genative carbonylation[1] as shown in Chapter 1, the recognition of
the importance of tellurium-hydrogen bond led one to investigate
the chemical behavior of hydrogen telluride and its application
in organic reactions.

Reduction of aromatic nitro compounds to corresponding amino
compounds with a variety of reducing agents has been investigated;
catalytic hydrogenations,[2] Clemmensen type reductions,[3] Birch
reduction,[4] reductions with hydrogen sulfide and its sodium salt,[5]
with selenophenol,[6] and transition metal hydride reductions.[7]
On the other hand, typical hydride reagents such as LiAlH$_4$,[8]
LiAl(OR)$_3$H,[8] NaBH$_4$,[9] are usually known to be sluggish.
Reaction of hydrogen telluride with aromatic nitro compounds and
their related compounds were tried and hydrogen telluride was
found to have a high reducing ability.[10]

Application of this reduction for carbonyl compounds[11]
revealed that aromatic aldehydes were reduced to correspondig
alcohols quantitatively with hydrogen telluride under mild reac-
tion conditions.   A new method for reductive deuteration was
developed by use of deuterium telluride from aluminum telluride
and deuterium oxide.   Furthermore selective reduction of
carbon-carbon double bond of α,β-unsaturated carbonyls was
successfully achieved.

2-2　Reduction of Aromatic Nitro, Nitroso, Hydroxylamino, Azo, and

　　　Azoxy Compounds with Hydrogen Telluride from Aluminum

　　　Telluride and Water

　　　Reaction of nitrobenzene with hydrogen telluride was carried

out at room temperature by introducing gaseous hydrogen telluride

into the THF solution of nitrobenzene.　After the filtration of

deposited tellurium, glpc analysis of the reaction mixture showed

that nitrobenzene was completely consumed and aniline was formed.

In order to facilitate the reaction　procedure, hydrogen telluride

was generated in situ by the reaction of aluminum telluride and

water.　Some results obtained from the reaction of nitrobenzene

and its derivatives are shown in Table 6.

　　THF and benzene were good as the solvent.　Higher the

temperature, higher the yields.　But in all cases, nitrobenzene

did not remain.　From glpc analysis, nitrosobenzene and/or

phenylhydroxylamine were found to be formed especially in the

reaction conducted at low temperature.　Amounts of the products

seemed to correspond to the difference between that of used

nitrobenzene and that of formed aniline.　In addition to these

products a small amounts of azobenzene and azoxybenzene were

formed.

Table 6. Reduction[a] of Some Aromatic Nitro
Compounds with Aluminum Telluride and Water

Run	ArNO$_2$	Temp. (°C)	Solvent	ArNH$_2$ (%)[b]
1	C$_6$H$_5$NO$_2$	66	THF	90
2	C$_6$H$_5$NO$_2$	66	Benzene	88
3	C$_6$H$_5$NO$_2$	66	n-Hexane	63
4	C$_6$H$_5$NO$_2$	66	DMF	63
5	C$_6$H$_5$NO$_2$	40	THF	73
6	C$_6$H$_5$NO$_2$	20	THF	63
7	C$_6$H$_5$NO$_2$	0	THF	48
8	C$_6$H$_5$NO$_2$	-15	THF	45
9	p-MeC$_6$H$_4$NO$_2$	66	THF	92
10	m-MeC$_6$H$_4$NO$_2$	66	THF	94
11	p-ClC$_6$H$_4$NO$_2$	66	THF	60
12	p-BrC$_6$H$_4$NO$_2$	66	THF	47
13	p-MeOC$_6$H$_4$NO$_2$	66	THF	60

a) ArNO$_2$: 1 mmol, Al$_2$Te$_3$: 2 mmol, H$_2$O : 24 mmol,
   solvent : 10 ml, time : 1 h.
b) Yield % : based on reactant used.

Under the same reaction condition, nitrosobenzene, phenylhydroxylamine, azobenzene, and azoxybenzene are examined. Products are shown in the following equations.

$$PhNO_2 \longrightarrow PhNH_2 \qquad 90\ \%$$

$$PhNHOH \longrightarrow PhNH_2 \qquad 96\ \%$$

$$PhNO \longrightarrow PhNHNHPh \qquad 63\ \%$$

$$PhN=NPh \longrightarrow PhNHNHPh \qquad 97\ \%$$

$$\underset{\overset{\downarrow}{O}}{PhN=NPh} \longrightarrow PhNHNHPh \qquad 86\ \%$$
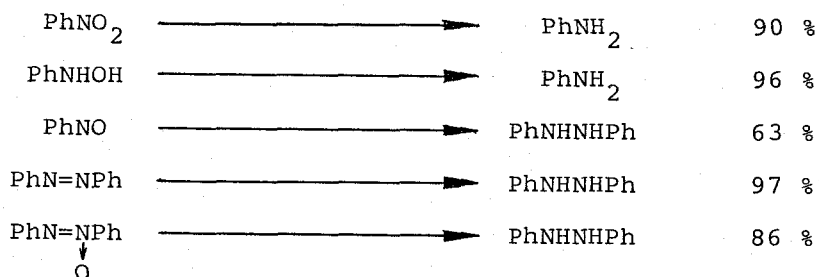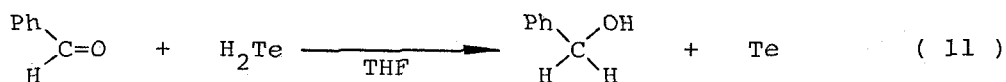
It is noteworthy that nitrosobenzene gave hydrazobenzene as a major product while phenylhydroxylamine yields aniline quantitatively.   This result might be taken to suggest that nitrosobenzene is not the intermediate in the reduction of nitrobenzene to aniline.   But alternatively, the intermediacy of nitrosobenzene in the reduction of nitrobenzene is accommodated if transiently formed nitrosobenzene undergoes rapid further reduction to give phenylhydroxylamine before the condensation[12] with phenylhydroxylamine.   The reductions of both azoxybenzene and azobenzene afford good yields of hydrazobenzene, indicating that neither azo nor azoxy compounds is the probable intermediate in the reduction of nitrobenzene.

2-3 A Novel Reduction of Carbonyl Compounds by the Aid of
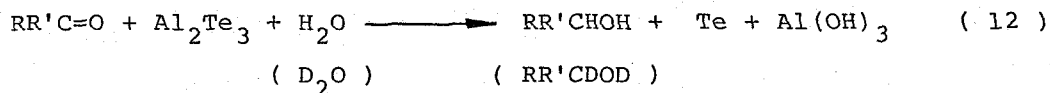
     Aluminum Telluride and Water

2-3-1 Reduction of Carbonyl Compounds

    The typical example is shown in the reduction of benzaldehyde
with hydrogen telluride.   The reduction proceeded at 0°C under
nitrogen to produce benzyl alcohol according to the stoichiometry
shown in eq. 11.

$$\underset{H}{\overset{Ph}{>}}C=O \quad + \quad H_2Te \xrightarrow[\text{THF}]{} \quad \underset{H}{\overset{Ph}{>}}C\underset{H}{\overset{OH}{<}} \quad + \quad Te \qquad (\ 11\ )$$
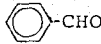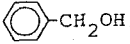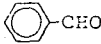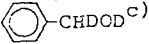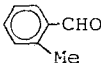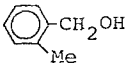
The amount (0.33 mmol) of benzyl alcohol formed was in good
agreement with that (0.29 mmol) of tellurium deposited.
The reaction was not affected by room light.
    Since the use of thermally unstable, air and light sensitive,
gaseous hydrogen telluride requires troublesome experimental
procedures, principally similar and practically more convenient
method has been developed by the combined use of aluminum
telluride and water (eq. 12).

$$RR'C=O + Al_2Te_3 + H_2O \xrightarrow{\hspace{1cm}} RR'CHOH + Te + Al(OH)_3 \qquad (\ 12\ )$$
$$\qquad\qquad\quad (\ D_2O\ ) \qquad\qquad (\ RR'CDOD\ )$$

The representative results are shown in Table 7.

Table 7.   Reduction of Carbonyl Compounds

Run	Substrate (1 mmol)	Al_2Te_3 (mmol)	Temp. (°C)	Time (h)	Product	Yield (%)[a)
1	⟨benzene⟩-CHO	2	0	2.5	⟨benzene⟩-CH₂OH	100
2	⟨benzene⟩-CHO	2	0	2.5	⟨benzene⟩-CHDOD[c)	100
3	⟨benzene⟩-CHO, Me	1	0	2.5	⟨benzene⟩-CH₂OH, Me	86
4	n-C₇H₁₅-CHO	2	0	2.5	n-C₇H₁₅-CH₂OH	50
5	⟨cyclohexyl⟩=O	6	66	5	⟨cyclohexyl⟩⟨OH, H⟩	51

a) Isolated yield.   b) D_2O was used.

Benzaldehyde and its derivatives were reduced in excellent yields.
Octanal and cyclohexanone were also reduced and gave corresponding
alcohols, but their yields were not fair.

It should be important that water acts as the hydrogen source
in the present reduction.   Therefore the use of the deuterium
oxide instead of water enables the reductive deuteration of the
carbonyl compounds.

In the reduction of aromatic aldehydes, reaction constant
of Hammett equation was +1.6, suggesting that the transition state
of this reaction have nucleophilic factor, that is, hydride or
electron transfer (Table 8).

Table 8.   Competitive Reduction of Benzaldehyde

$X-C_6H_4CHO$ X	$X-C_6H_4CH_2OH$ k_X/k_H
m-Cl	5.5
p-Cl	1.95
m-Me	0.83
p-Me	0.41

Aldehydes : 1 mmol, Al_2Te_3 : 2 mmol, H_2O : 24 mmol
THF : 10 ml, temp.: 0°C, time : 1 h.

Aromatic ketons such as acetophenone and benzophenone were unreactive for this reduction.   Both cycloheptanone and cycloctanone were sluggish, and the yields of the corresponding alcohols were 4 % and 5 %, respectively.

2-3-2 Selective Reduction of α,β-Unsaturated Carbonyl Compounds

This reduction system was applied for α,β-unsaturated carbonyl compounds.   The reaction proceeded with high selective manner to reduce carbon-carbon double bond (eq. 13, Table 9).[13] In the reduction for prolonged period using a large excess of the reagent, further reduced alcohol was formed (Run 3).
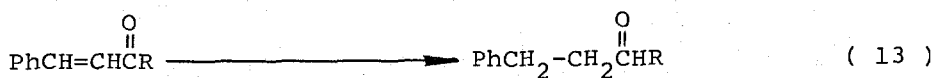
$$PhCH=CHCR \xrightarrow{\quad\quad\quad} PhCH_2-CH_2\overset{O}{\overset{\|}{C}}HR \qquad (13)$$

Table 9.   Selective Reduction of α,β-Unsaturated Carbonyls

Run	Substrate (1 mmol)	Al$_2$Te$_3$ (mmol)	Temp. (°C)	Time (h)	Product	Yield (%) [a]
	Ph-CH=CH-CHO	2	-15	0.3	Ph-CH$_2$CH$_2$-CHO	89(96)
	Ph-CH=CH-$\overset{\overset{\text{O}}{\|}}{\text{C}}$-Me	2	0	1	Ph-CH$_2$CH$_2$-$\overset{\overset{\text{O}}{\|}}{\text{C}}$-Me	75(90) [b]
	Ph-CH=CH-$\overset{\overset{\text{O}}{\|}}{\text{C}}$-Me	6	0	5	Ph-CH$_2$CH$_2$-$\overset{\overset{\text{O}}{\|}}{\text{C}}$-Me	54
					Ph-CH$_2$CH$_2$-$\overset{\overset{\text{OH}}{\|}}{\text{CH}}$Me	21
	Ph-CH=CH-$\overset{\overset{\text{O}}{\|}}{\text{C}}$-Ph	4	0	6	Ph-CH$_2$CH$_2$-$\overset{\overset{\text{O}}{\|}}{\text{C}}$-Ph	84

a) Isolated yield. Numbers in parentheses are glpc yield.

b) 4-Phenyl-2-butanol(Ph-CH$_2$CH$_2$-$\overset{\overset{\text{OH}}{\|}}{\text{CH}}$Me, 2 %) is also found by glpc.

2-4 Application for Other Compounds

In addition to carbonyl compounds, imines and enamines were reduced in good yields as shown below.   Epoxides did not give the corresponding alcohols.   Glpc analysis of the reaction mixture showed the formations of corresponding olefins.
For example, styrene oxide and cyclohexene oxide gave styrene (63 %) and cyclohexene (16 %), respectively.   Simple olefins were recovered unreacted.

$$\text{PhCH=NPh} \xrightarrow{\text{Al}_2\text{Te}_3/\text{H}_2\text{O}} \text{PhCH}_2\text{NH-Ph} \qquad 71\ \%$$

$$\text{PhCH=NEt} \xrightarrow{\text{Al}_2\text{Te}_3/\text{H}_2\text{O}} \text{PhCH}_2\text{NHEt} \qquad 60\ \%$$

 $\xrightarrow{\text{Al}_2\text{Te}_3/\text{H}_2\text{O}}$ ~100 %
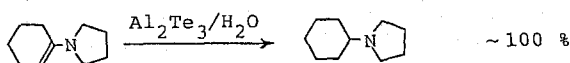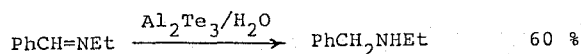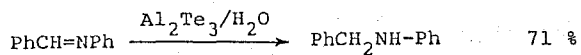
2-5 Experimental

Reduction of Nitrobenzene

Reduction of aluminum telluride (2 mmol, 674 mg), stored under nitrogen in the dark, was added into the tetrahydrofuran (THF, 10 ml) solution of nitrobenzene (1 mmol, 123 mg) under nitrogen at room temperature. Then the temperature was elevated to 66°C. Into the reaction mixture was slowly introduced an excess amount of water (24 mmol, 0.43 ml) dropwise by a syringe over a period of 40 minutes with vigorous stirring. The reducti on was conducted at reflux for another 20 minutes. After a usual work-up, glpc, ^{1}H-NMR, and IR analyses of the product mixture showed the formation of aniline (90 %) with a trace of hydrazobenzene. Experiments in section 2-2 are carried out in the same way. In all cases, no unreacted material was detected.

Reduction of Benzaldehyde with Hydrogen Telluride

Hydrogen telluride[14] was generated in a separate flask by the addition of a large excess of water (2 ml) to aluminum telluride (5 mmol, 2.19 g) at 25°C. Thus formed hydrogen telluride was introduced by a gentle flow of nitrogen into the reaction flask containing benzaldehyde (1 mmol, 106 mg) and tetrahydrofuran (THF, 10 ml) at 0°C. Tellurium began to deposit immediately. After 5 minutes, tellurium (0.29 mmol) was recovered by filtra- tion, and the filtrate was shown by glpc (Shimadzu 3BF with flame

ionization detector using a 2.2 m x 1.5 mm glass column packed with 5 % PEG-HT on 80-100 mesh Uniport HP, 140°C) to contain benzyl alcohol (0.33 mmol) and benzaldehyde (0.67 mmol).

Reduction of Carbonyl Compounds by Use of Deuterium Oxide

Deuterium oxide (12 mmol, 0.22ml) was added at -78°C to the suspension of aluminum Telluride (2 mmol, 876 mg) in THF (10 ml) containing benzaldehyde (1 mmol, 106 mg) with vigorous stirring.　　Then, the temperature was raised up to 0°C in 30 minutes and maintained for another 2 h.　　Filtration of the precipitates followed by evaporation of the solvent leaves essentially pure PhCHDOD (110 mg, 1.0 mmol) quantitatively. The reduction of other carbonyl compounds were carried out under the similar reaction conditions.　　When necessary, isolation of the products was made by column chromatography.

Selective Reduction of α,β-Unsaturated Carbonyl Compounds

Water (12 mmol, 0.22 ml) was added into the suspension of benzalacetone ($PhCH=CHCOMe$, 1 mmol, 149 mg), aluminum telluride (2 mmol, 876 mg) and n-$C_{17}H_{36}$ (internal standard) in THF (10 ml) at -78°C.　　The temperature was raised up to 0°C in 30 minutes with stirring and maintained.　　The consumption of benzalacetone was monitored by glpc (PEG-HT, 5 %, mesh 80-100, 2.2 m, 160°C).　　When the starting material was almost consumed, the reaction was quenched by the filtration of mixtures

of precipitates which consisted of tellurium, aluminum hydroxide,
and excess aluminum telluride.   Quantitative analysis by
glpc revealed that benzylacetone ($PhCH_2CH_2COMe$) was formed
selectively in the yield of 90 %.   In addition to the
main product, further reduced product, 4-phenyl-2-butanol
($PhCH_2CH_2CHOHMe$), was formed as a minor product (2 %).
Unreacted benzalacetone (2 %) was also detected.   Almost
identical procedures were applied for the selective reduction
of cinnamaldehyde ($PhCH=CHCHO$) and benzalacetophenone
($PhCH=CHCOPh$).

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Chapter 3 Photoreaction of Carbonyls with Hydrogen Selenide

3-1 Photoreduction of Carbonyl Compounds with Hydrogen Selenide

3-1-1 Introduction

Among various photoreactions [1] of carbonyl compounds, photoreduction of aldehydes and ketones is very commonly encountered and one of the best understood of all photoreactions. In this reaction, corresponding pinacol derivative[2] is usually[3] obtained as a single product.
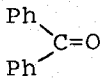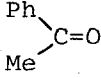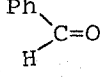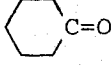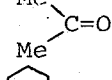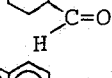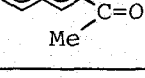
The photoreaction of carbonyl compounds and hydrogen selenide was investigated and it was found that hydrogen selenide had a high reducing ability toward photoexcited carbonyl compounds to give corresponding carbinols instead of pinacols.[4] The rate constant for the photoreduction of acetophenone in THF was estimated as 4.7×10^8 M^{-1}s^{-1}.[5]

3-1-2 Photoreduction of Ketones and Aldehydes

The reduction was achieved by irradiation of the substrates in tetrahydrofuran (THF) by use of pyrex reaction tube at 15°C under nitrogen atmosphere. The results of the photoreduction of carbonyl compounds are listed in Table 10. The reduction of aryl substituted carbonyl compounds proceeded more rapidly than

that of alkyl substituted carbonyl compounds.   The following two

experiments are important in relation to the mechanism of the

early stage of this reaction.   First, hydrogen selenide in THF

has very weak absorption band in the region $\lambda > 300$ nm ($\lambda_{max} =$

~213 nm), and irradiation of hydrogen selenide in the absence of

carbonyl compounds in the same reaction apparatus used for the

photoreduction caused no apparent change.[6]

Table 10.   Photoreduction of Carbonyls with H_2Se

Run	Substrate	Time	Alcohol (%)[a]
1	Ph₂C=O (Ph, Ph)	2 h	78 [b]
2	Ph, Me C=O	20 min	98
3	Ph, H C=O	30 min	92
4	(cyclohexyl) C=O	18 h	93
5	Me, Me C=O	27 h	81
6	(cyclohexyl)CH C=O, H	13 h	80
7	(naphthyl) C=O, Me	3 h	70

Substrate : 0.25 mmol, H_2Se : 0.45 mmol, THF : 3 ml,
15 °C, pyrex filter, high pressure Hg lamp.
a) Based on substrate used.
b) Benzpinacol (7 %) was formed.

Secondly, in the reaction of acetophenone, the addition of diphenyl as a triplet quencher resulted in retarding the rate of the reduction.   It should be noted that 2-acetonaphthone, which is known to give $\pi-\pi^*$triplet on photoexcitation,[3,7] is reduced to form methyl-2-naphthylcarbinol in the yield of 70 %.

The success of the reduction may be attributed to high hydrogen donating ability of hydrogen selenide.   Carbinol formation should result from the rapid reaction of kethyl radical with hydrogen selenide than its coupling.

3-1-3 An Estimation of the Rate Constant for the Photoreduction
       of Acetophenone

The rate constant k_r for the reduction of acetophenone (eq. 14) was estimated by a Stern-Volmer treatment.

$$\underset{\text{PhCCH}}{\overset{\overset{\textstyle O}{\|}}{\text{PhCCH}}} \quad + \quad H_2Se \quad \longrightarrow \quad \underset{\text{PhCHCH}_3}{\overset{\overset{\textstyle OH}{|}}{\text{PhCHCH}_3}} \quad + \quad Se \quad (14)$$

A relevant reaction mechanism for the photoreduction of acetophenone with hydrogen selenide is shown in Scheme 3, where K represents acetophenone, the superscripts 1 and 3 correspond to excited singlet and triplet states, respectively, and Q represents biphenyl as a triplet quencher.   The rate constant for the deactivation of ^3K with hydrogen selenide by some interaction is represented by $K_q^{H_2Se}$.

$$K \quad + \quad h\nu \quad \xrightarrow{\sim100\%} \quad {}^1K$$

$${}^1K \quad \xrightarrow{\sim100\%} \quad {}^3K$$

$${}^3K \quad \xrightarrow{k_d} \quad K$$

$${}^3K \quad + \quad Q \quad \xrightarrow{k_q} \quad \text{quenching}$$

$${}^3K \quad + \quad H_2Se \quad \xrightarrow{k_q^{H_2Se}} \quad \text{quenching}$$

$${}^3K \quad + \quad H_2Se \quad \xrightarrow{k_r} \quad \text{carbinol}$$
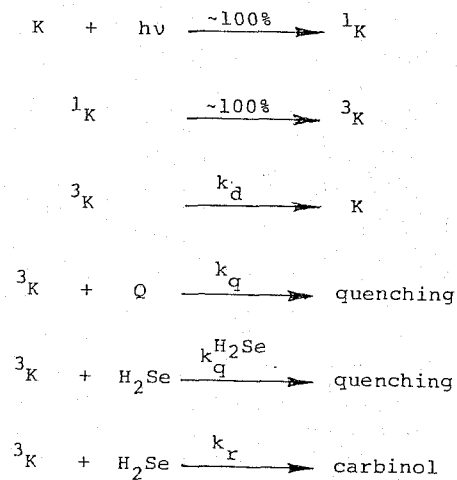
Scheme 3.
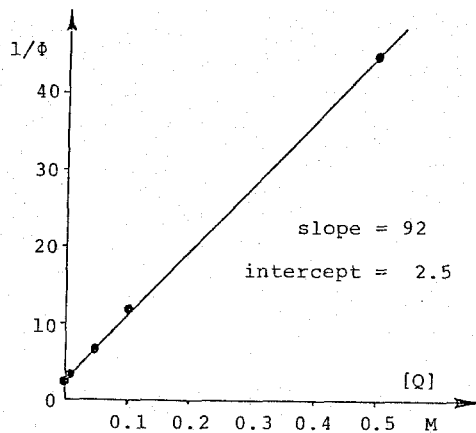
Figure 3. Stern-Volmer plot for the reduction of acetophenone (0.1 M) with hydrogen selenide (0.21 M) at 313 nm employing biphenyl as a triplet quencher,Q, at 20°C in THF.
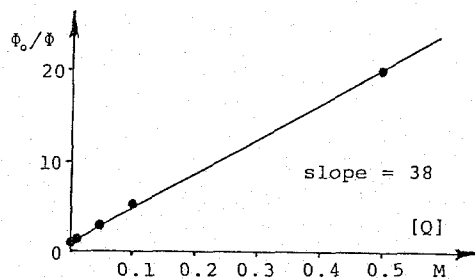
Figure 4. Stern-Volmer plot. Conditions are the same as in Figure 1.

Thus the quantum yield, Φ, for α-phenethyl alcohol formation is given as

$$\Phi = \frac{k_r [H_2 Se]}{k_d + k_q [Q] + (k_q^{H_2 Se} + k_r) [H_2 Se]} \qquad (15)$$

Stern-Volmer plots fell on strait lines as shown in Figs. 3 and 4. The quenching rate constant k_q is estimated to be 9.1×10^9 $M^{-1}s^{-1}$,[8] and k_d is much smaller[9] than ($k_q^{H_2 Se} + k_r$) [$H_2 Se$], therefore k_d is neglected.   With these assumptions and data from Figs. 3 and 2, where [$H_2 Se$] = 0.21 M, we obtain

$$k_r = 4.7 \times 10^8 \ M^{-1}s^{-1} \qquad (16)$$
$$k_q^{H_2 Se} = 6.7 \times 10^8 \ M^{-1}s^{-1} \qquad (17)$$

These values lead to $\Phi = 0.41$ from eq. 15, which is in good agreement with the quantum yield (0.40) estimated from the value of the intercept in Fig. 3.   The rate constant thus obtained is much larger than those[10] reported for the photoreduction of aceto-phenone with 2-propanol, which were in the order of 10^6 $M^{-1}s^{-1}$.

This result is one of the supporting evidence for the high hydrogen donating ability of hydrogen selenide which might be due to the weak hydrogen-selenium bond.[11]

3-1-4   Selective Photoreduction of α,β-Unsaturated

        Carbonyl Compounds

      Photoreduction of α,β-unsaturated carbonyl compounds with

hydrogen selenide gave saturated carbonyl compounds **2** and further

reduced carbinols **3** as minor products (eq. 18).

$$\text{RR'C=CH-CO-R''} + H_2Se \xrightarrow[\text{THF}]{h\nu > 300nm} \text{RR'CHCH}_2\text{-CO-R''} + \text{RR'CHCH}_2\text{-CHOH-R''} + Se \quad (18)$$
     1   **2**   **3**
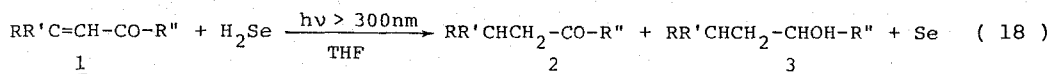
The selective reduction of 4-phenyl-3-buten-2-one (**1b**, 0.17 M)

in THF with hydrogen selenide (0.2 M) shows the typical example.

Irradiation of this mixture with high pressure mercury lamp

(300-W) for 2 h in pyrex tube produce almost quantitative amount

of saturated ketone **2b**.   Metallic selenium came to deposit at

the bottom of the pyrex reaction tube.   Results obtained from

several enones under the similar conditions are shown in Table 11.

Table 11. Photoreduction of α,β-Unsaturated Carbonyls with Hydrogen Selenide.

RR'C=CH-CO-R''					H_2Se	Time	RR'CHCH$_2$-CO-R''		RR'CHCH$_2$-CHOH-R''		**1**[a]	
R	R'	R''	**1**	(Conc.)	(Conc.)		**2**	Yield	**3**	Yield		
Ph	H	H	**1a**	0.17 M	0.2 M	2 h	**2a**	49 %	**3a**	12 %	**1a**	10 %
Ph	H	Me	**1b**	0.17 M	0.2 M	2 h	**2b**	92 %	**3b**	2 %	**1b**	6 %
Ph	H	Ph	**1c**	0.17 M	0.2 M	2 h	**2c**	70 %	**3c**	24 %	**1c**	-[b]
Me	Me	Me	**1d**	0.07 M	0.5 M	10 min	**2d**	73 %	**3d**	5 %	**1d**	0 %

a) Unreacted enones.   b) Not determined.

In each case no selenium incorporated adducts[12] nor THF incorporated products were found. Irradiation of benzilideneacetophenone 1c in the presence of hydrogen selenide for 1.5 h gave almost quantitative amounts of ketone 2c, which then underwent further reduction to 3c. The photoreduction of 4-methyl-3-penten-2-one 1d with hydrogen selenide for 10 min was found to afford 22 % yield of acetone as a by-product. This result may suggest that the formed saturated ketone 2d, which has γ-hydrogen to the carbonyl group, would suffer Norrish type II reaction. But at present it is still in question whether the production of carbinol 3d is through the direct reduction of 2d and/or through 1,4-biradical intermediate.

3-2 Reaction of Hydrogen Selenide with Photogenerated Radicals

3-2-1 Introduction

Since the photolysis of dibenzyl ketone has been well known to undergo rapid Norrish type I reaction, the photoreaction of the ketone with hydroen selenide was investigated[5] in order to examine the chemical behavior of hydrogen selenide in this photoreaction system. The product analysis showed that hydrogen selenide reacted with an acyl radical resulting in effective trapping of it. Furthermore, chemical trapping of photoinduced 1,4-biradicals was successfully achieved.[13]

3-2-2 Photoreaction of Dibenzyl Ketone with Hydrogen Selenide

The photoreaction of dibenzyl ketone (0.041 M) with hydrogen selenide (0.21 M) was carried out in THF using pyrex reaction tube.   The products and their amounts are shown in the following equation.

$$PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ph \xrightarrow[\text{THF}]{\overset{H_2Se\,(\,0.21\,M)}{h\nu > 300\,nm}} PhCH_2\overset{OH}{\overset{|}{C}H}CH_2Ph + PhCH_2\overset{O}{\overset{\|}{C}}H + PhCH_2\overset{OH}{\overset{|}{C}}H_2 + PhCH_3 \quad (\ 19\ )$$

100 μmol
(0.041 M)   11 μmol   8 μmol   54 μmol   107 μmol
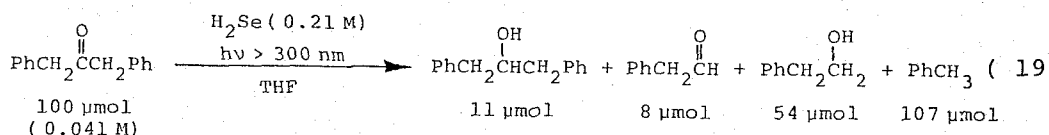
The formation of dibenzylcarbinol suggests that the reduction of photoexited dibenzyl ketone[14] in singlet and/or triplet states with hydrogen selenide competed with α-cleavage.   Therefore the rate constant for the photoreduction of dibenzyl ketone with hydrogen selenide might be estimated at least in the order of $1.6 \times 10^8 \ M^{-1}s^{-1}$.   α-Phenethyl alcohol is considered to be formed by the reduction of phenylacetaldehyde produced by the trapping of the acyl radical ($PhCH_2\overset{O}{\overset{\|}{C}}\cdot$) generated by Norrish type I reaction.   1,2-Diphenylethane was not detected and toluene was formed.   These results suggest that benzyl radical was trapped much faster than its coupling.   The photoreduction of phenylacetaldehyde was successfully carried out under the similar reaction conditions, (eq. 20).

$$PhCH_2\overset{O}{\overset{\|}{C}}H \xrightarrow[\text{THF}]{\overset{H_2Se\,(\,0.21\,M)}{h\nu > 300\,nm}} PhCH_2\overset{OH}{\overset{|}{C}}H_2 + PhCH_3 \quad (\ 20\ )$$

100 μmol
(0.045 M)   67 μmol   20 μmol
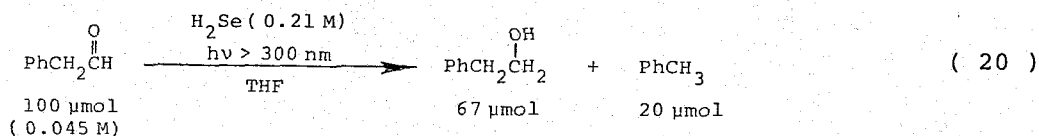
3-2-3 Chemical Trapping of 1,4-Bidadicals

Photoreaction of butyrophenone 4a, valerophenone 4b, and
γ-methylvalerophenone 4c with hydrogen selenide gave corresponding
alcohols 5 in good yields (eq. 21).

$$\underset{\substack{\| \\ \text{O}}}{\text{PhCCH}_2\text{CH}_2\text{CHRR'}} \xrightarrow{\text{H}_2\text{Se}} \underset{\substack{| \\ \text{OH}}}{\text{PhCHCH}_2\text{CH}_2\text{CHRR'}} \quad (\, 21 \,)$$

	R	R'	Yield %
5a	H	H	82
5b	H	Me	66
5c	Me	Me	81
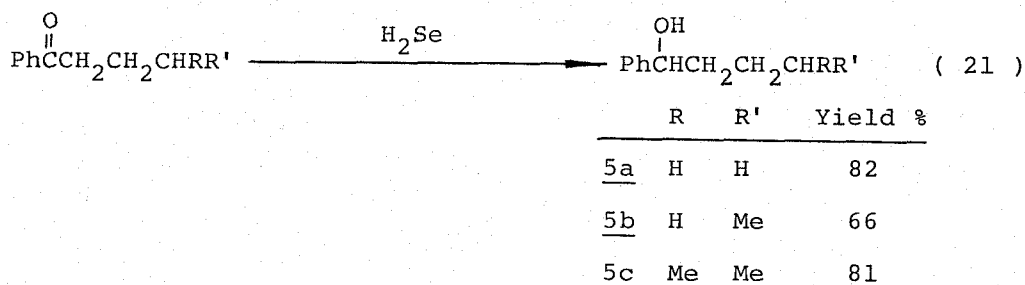
We can postulate two plausible reaction paths, such as, by direct
photoreduction of excited carbonyls and by chemical trapping of
1,4-biradicals derived from intramolecular γ-hydrogen abstraction
of photoexcited triplet carbonyls.   In order to elucidate the
reaction path, photolysis of γ-methylvalerophenone was carried
out using deuterium selenide in methanol-OD (eq. 22).

$$\underset{\substack{\| \\ \text{O}}}{\text{PhCCH}_2\text{CH}_2\text{CHMe}_2} \xrightarrow[\text{MeOD}]{\text{D}_2\text{Se, } h\nu > 300 \text{ nm}} \underset{\substack{| \\ \text{OD}}}{\text{PhCDCH}_2\text{CH}_2\text{CDMe}_2} \quad (\, 22 \,)$$

4c   5d
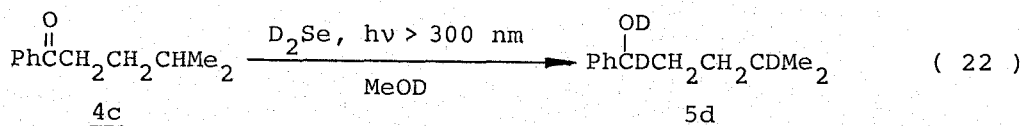
The corresponding alcohol, $\underline{5d}$, was obtained in the yield of 53 %, and NMR analysis showed that deuterium incorporation at original carbonyl carbon was 98 % and that at γ-carbon to the original carbonyl group was 83 %. This result indicates that the reaction of 1,4-biradicals with deuterium selenide was predominant in this system. At high concentration of deuterium selenide as in this reaction, Type II reaction was almost completely suppressed.

A kinetic study was performed by monitoring the formations of corresponding carbinols $\underline{5}$, acetophenone and α-phenethyl alcohol in the photoreduction of three ketones $\underline{4}$ with hydrogen selenide in methanol. The latter two products are formed by Type II reaction and further reduction of formed acetophenone, respectively. The ratios of the amounts of corresponding carbinols $\underline{5}$ to those of acetophenone and α-phenethyl alcohol were constant for each ketone at any stages of conversion, and correspond to ratios of quantum yields, Φ_r/Φ_{II}, where Φ_r represent quantum yields for formations of corresponding alcohols $\underline{5}$ and Φ_{II} for Type II reaction (Table 12). The values of Φ_r/Φ_{II} are similar for different ketones. And the tendency of the variation of the values was similar to that of lifetimes of 1,4-biradicals, but was different to that of lifetimes of the triplet ketones. This result suggests that alcohol formation competes with Type II reaction via a 1,4-biradical as the common intermediate. In the case of butyrophenone, the reaction of the triplet ketone with hydrogen selenide : the direct reduction of the photoexited carbonyl : can

not be ruled out because of its long lifetime. Indeed, the deuterium incorporation at the terminal carbon in 1-phenylbutanol obtained by the photoreduction of butyrophenone with deuterium selenide in methanol-OD was 36 %.

In the absence of hydrogen selenide quantum yield for Type II reaction of valerophenone was reported as 0.70 in alcohols.[15] Therefore the rate constant for trapping of the 1,4-biradical from valerophenone with hydrogen selenide is calculated as 1.3 X 10^8 $M^{-1}s^{-1}$.[16] This value would correspond to the rate constant for the reaction of alkyl radicals with hydrogen selenide and is much larger than those with mercaptans[17] or trialkylstannanes.[18]

Successful trapping of 1,4-biradical is attributed to high hydrogen donating ability of hydrogen selenide.

Table 12. Chemical Trapping of 1,4-Biradicals with H_2Se

$$K \xrightarrow{h\nu} K^* \longrightarrow BR \overset{k_r}{\underset{k_{II}}{\longleftarrow}} \begin{array}{l} \text{Alcohol} \\ \text{Type II Product} \end{array}$$

Substrate	τ_K (n sec.)	τ_{BR} (n sec.)	$\dfrac{\Phi_r}{\Phi_{II}}$	k_r [b)] ($M^{-1}s^{-1}$)
Butyrophenone	279	157 ± 79	5.47	2.44 X 10^8
Valerophenone	16 [a)]	102 [a)]	2.27	1.56 X 10^8
γ-Methylvalerophenone	4.7 [a)]	97 [a)]	2.51	1.81 X 10^8

Substrate : 0.05 M, H_2Se : 0.10 M, solv. : MeOH, hν>300 nm, 20°C.
a) R. D. Small, Jr. and J. C. Scaiano, J. Phys. Chem.,
   81, 2126(1977).
b) Φ_{II} was estimated to be 0.70 for all ketones;
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3-3 Experimental

Photoreduction of Acetophenone with Hydrogen Selenide

Well degassed THF solution (3 ml) of acetophenone (0.25 mmol, 30 mg) in a pyrex reaction tube was irradiated by high pressure mercury lamp (300-W) in the presence of hydrogen selenide (0.45 mmol).   Metallic selenium started to deposit immediately.   After irradiation for 20 minutes followed by oxidation of remaining hydrogen selenide by introducing air into the reaction mixtures, metallic selenium was filtered off.   The glpc and ^{1}H-NMR analyses of the reaction products showed that α-phenethyl alcohol was formed in the yield of 98 % with 2 % of unreacted acetophenone.   No dimerized product, (PhMeCOH $\rightarrow_2$, was found.   Reduction of the other carbonyl compounds was carried out similarly.

Estimation of the Rate Constant

The quantum yield for the formation of α-phenethyl alcohol was determined at 313 nm.   Absolute light intensity was determined by detecting the formation of acetone from 2-pentanone. The light source was 300 watt high pressure mercury lamp using potassium permanganate solution as the filter.   Pyrex reaction tubes (9 mm in diameter) containing THF solution (2.5 ml) of acetophenone (0.10 M), hydrogen selenide (0.21 M), and biphenyl (0, 0.010, 0.50, 0.10, 0.50 M) were mounted on a

rotating turntable, about 8 cm from the lamp.   During the
irradiation for 20 minutes (5.33 x 10^{-7} einsteins/min), the
reaction solutions were maintained at 20°C by cooling with water.
After the reaction, remaining hydrogen selenide was oxidized
with air and deposited selenium was filtered off.
α-Phenethyl alcohol was analyzed by glpc using a 4 m x 3 mm glass
column packed with 5 % PEG-HT on 80-100 mesh Uniport HP at 180°C
of the oven temperature.   Coversions of acetophenone were 0.094
t0 1.88 %.

Selective Reduction of Benzalacetone

     THF solution (3 ml) of benzalacetone (0.17 M) and
hydrogen selenide (0.20 M) was irradiated in pyrex reaction
tube (10 mm in diameter).   The formation of benzylacetone and
the consumption of benzalacetone were monitored by glpc (OV-17,
5 %, 2m, 140°C).   In 2 h, benzalacetone was almost converted to
benzylacetone and a small amount of 4-phenyl-2-butanol was formed.
After the reaction, remaining hydrogen selenide was oxidized by
air oxidation and deposited selenium was filtered off.   Products
were analyzed by glpc with diphenylmethane as the internal
standard.

Labeling Experiment with Deuterium Selenide

     In a pyrex reaction tube, γ-methylvalerophenone (0.30 M)
and deuterium selenide (D_2Se, 0.50 M) in MeOD were irradiated

for 24 h with the high pressure mercury lamp (300-W).   After the air oxidation of remaining D_2Se, deposited selenium was filtered off.   Evaporation of the solvent followed by column chromatography gave practically pure alcohol 5d (isolated yield, 53 %).   ^{1}H-NMR analysis of the product showed that deuterium incorporation at original carbonyl carbon is 98 % and that at γ-carbon to original carbonyl group was 83 %.   In this reaction little of acetophenone or α-phenethylalcohol was formed.

Kinetic Experiment for the Chemical Trapping of 1,4-Biradicals

Methanol solution (3 ml) of butyrophenone (0.050 M) and hydrogen selenide (H_2Se, 0.10 M) was irradiated in a pyrex reaction tube with the high pressure mercury lamp.   The formation of 1-phenylbutanol, acetophenone, and α-phenethyl alcohol were traced by glpc (PEG-HT, 5 %, 4 m, 180°C).   The ratio of the formation of 1-phenylbutanol to those of acetophenone and α-phenethyl alcohol, which was formed by the photoreduction of acetophenone with H_2Se, showed the constant value at any stages of the conversion.   Reactions were carried out in the identical way using valerophenone and γ-methylvalerophenone.

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Chapter 4   Synthesis of Hydrogen Selenide and New Water Gas

         Shift Reaction

4-1 Introduction

     One of the striking applications of carbon monoxide in both

organic and inorganic chemistry is its use as an reducing agent.

There has been increasing interest in developing catalysts active

at low temperature for the water gas shift reaction, and in

establishing a convenient homogeneous hydrogenation system using

carbon monoxide and water.[1]   During the course of studies on the

selenium-catalyzed carbonylation of various compounds with carbon

monoxide,[2] metallic selenium was found to be reduced to hydrogen

selenide by carbon monoxide and water in the presence of base

under mild conditions.   Furthermore the co-presence of platinum

black in this reaction enabled the establishment of the effective

hydrogen formation system from carbon monoxide and water, this is
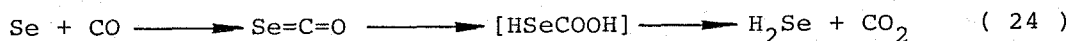
new water gas shift reaction.

4-2   New Synthesis of Hydrogen Selenide from Carbon Monoxide and

     Water

     The reaction of selenium, carbon monoxide, and water

proceeded at 25°C under atmospheric pressure of carbon monoxide,

but was accelerated at high temperature and high pressure (eq. 23

$$Se \ + \ CO \ + \ H_2O \xrightarrow{\text{Base}} H_2Se \ + \ CO_2 \qquad (\ 23 \ )$$
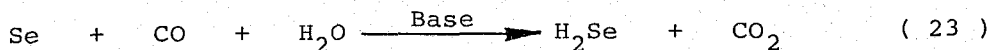
To obtain solvent-free hydrogen selenide, water could be used as reaction solvent.[3] In this case, 60°C and 5 kg/cm^{2} of carbon monoxide were required.   Acidification of the reaction mixture with sulfuric acid liberated hydrogen selenide,[4] which was trapped in a receiver cooled to -196°C.

This reaction was considered to proceed via carbonyl selenide (eq. 24).[5]

$$Se + CO \longrightarrow Se=C=O \longrightarrow [HSeCOOH] \longrightarrow H_2Se + CO_2 \qquad (\ 24 \ )$$

4-3   New Water Gas Shift Reaction Catalyzed by Selenium and Platinum

The success of new hydrogen selenide synthesis[6] from carbon monoxide and water led one to investigate the catalytic decomposition of hydrogen selenide for the purpose of the development of new water gas shift reaction system.[7] Among the various catalysts, platinum black was effective for the reaction (eq. 25).

$$H_2Se \xrightarrow{\text{Pt}} H_2 \ + \ Se \qquad (\ 25 \ )$$

The reaction of carbon monoxide and water was carried out in the co-presence of selenium and platinum black at 200°C.
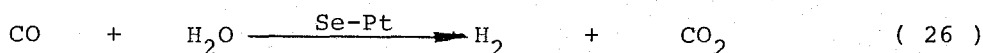
The representative results are shown in Table 13.

Table 13. Water Gas Shift Reaction[a] Catalyzed by Se/Pt

Run	Se	Pt	H_2	CO_2
1	1	0	0.1	1.0
2	1	0.01	1.6	2.3
3	1	0.1	5.7	5.9
4	1	1	21.1	20.8
5	0.1	0.1	2.1	2.0
6	0.1	1	12.1	12.0
7	0	1	0.9	0.9

a) CO : 30 kg/cm^2, H_2O : 10 ml, 200°C, 20 h.
   Data are shown in mmol.

This reactin could be expressed by the folowing equation.

$$CO \ + \ H_2O \xrightarrow{\text{Se-Pt}} H_2 \ + \ CO_2 \qquad\qquad (\ 26\ )$$

As shown in the table, the controlled experiments using selenium
or platinum black alone (Run 1, 7) could not catalyze this
reaction (eq. 26).   The experiment in Run 1 is represented by
eq. 23, which is substantially the stoichiometric reaction of
selenium with carbon monoxide and water.   The conversion[8] of
carbon monoxide in Run 4 is 43 %.

4-4 Experimental

New Synthesis of Hydrogen Selenide

Metallic selenium (0.40 g, 5 mmol), water (10 g), and N-methylpyrrolidine (1.04 ml, 10 mmol) are placed with a magnetic stirring bar in a 50 ml stainless steel autoclave, and the apparatus was flushed several times with carbon monoxide and finally charged at 5 kg/cm^2. The reaction was carried out at 60°C for 7 h with vigorous stirring.   On completion of the reaction the resulting gas was collected in a gas sampler and analyzed by vpc (Porapak Q, mesh 80/100, 2.9 m, He 1 kg/cm^2, 150°C). Carbon dioxide was found to be formed in the yield of 4.5 mmol. Causious addition of well degassed aqueous sulfuric acid (10 N, 10 ml, ca. 50 mmol) to the solidified reaction mixture at -78°C followed by distillation from the autoclave at -5°C under 10 mm Hg directly into a trap maintained at -196°C gave hydrogen selenide containing carbon dioxide.   Trap-to-trap distillation at -41 to -39°C under atmospheric pressure afforded pure hydrogen selenide (bp = -41.3 °C).   The yield (82 %) was by gravimetry after the oxidation of hydrogen selenide with oxygen at room temperature in the presence of triethylamine (2.02 g, 20 mmol) in THF (10 ml) to give selenium (0.320 g, 4.1 mmol) and water.

Decomposition of Hydrogen Selenide on Platinum Black

Hydrogen selenide (0.162 g, 2 mmol), platinum black (0.195

g, 1 mmol), and water (10 ml) were placed in the 50 ml autoclave at room temperature under nitrogen. The reaction was carried out under 30 kg/cm^2 of nitrogen at 200°C for 20 h. Vpc analysis of the gas phase revealed that almost quantitative amount of molecular hydrogen based on hydrogen selenide was formed (Molecular Sieves 5 A, mesh 30/60, 3.3 m, N_2 1 kg/cm^2, 150°C).

Water Gas Shift Reaction Catalyzed by Selenium

Metallic selenium (0.079 g, 1 mmol), platinum black (0.195 g, 1 mmol), and water (10 ml) were placed with a magnetic stirring bar in a glass tube mounted in the stainless steel autoclave, and the apparatus is then flashed several times with carbon monoxide and finally charged at 30 kg/cm^2 at 25°C. After the reaction at 200°C for 20 h, the resulting gas was collected in a gas sampler. Analysis of the resulting gas by vpc revealed that it consisted of carbon monoxide (27.7 mmol), carbon dioxide (20.8 mmol), and molecular hydrogen (21.1 mmol).

Water Gas Shift Reaction Using Hydrogen Selenide

In the same apparatus hydrogen selenide (0.162 g, 2 mmol) and platinum black (0.195 g, 1 mmol), and water (10 ml) were placed with magnetic stirring bar. The apparatus was charged with carbon monoxide at 30 kg/cm^2. The reaction was carried out at 200°C for 20 h with vigorous stirring. After the reaction the amounts of hydrogen and carbon monoxide were 32.4 mmol and 31.6 mmol, respectively.

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