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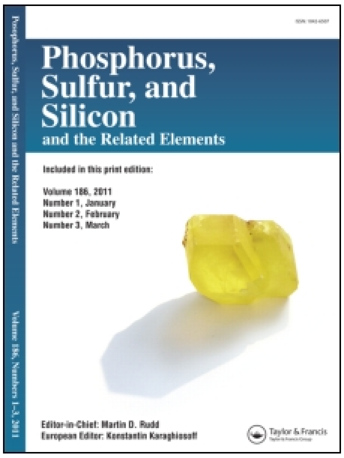

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Masahito Segi; Hiroaki Yamamoto; Takeyoshi Hori; Tadashi Nakajima

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REACTION OF SELENOCARBONYL COMPOUNDS WITH OXYGEN-FUNCTIONALIZED CONJUGATED DIENES

MASAHITO SEGI,* HIROAKI YAMAMOTO, TAKEYOSHI HORI,
and TADASHI NAKAJIMA
Department of Chemistry and Chemical Engineering,
Faculty of Engineering, Kanazawa University,
2-40-20 Kodatsuno, Kanazawa 920, JAPAN

Selenoaldehydes and selenoketones, generated by thermal retro-Diels-Alder reaction of their cycloadducts with cyclopentadiene, reacted with oxygen-functionalized conjugated dienes such as 1-acetoxy-1,3-butadiene, Danishefsky's diene, and 1,4-diacetoxy-1,3-butadiene to give the corresponding cycloadducts in good yields regioselectively.

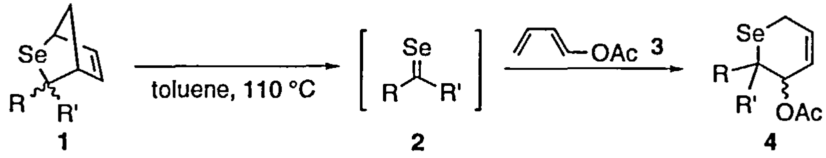
Keywords: selenoaldehyde; selenoketone; Diels-Alder reaction

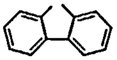
INTRODUCTION

In recent years, chemistry of selenocarbonyl compounds which are key intermediates in the synthesis of selenium heterocycles has been actively studied, and generally the carbon-selenium double bond serves as the 2π dienophile component of the [4+2] cycloaddition with cyclopentadiene[1]. However, Diels-Alder addition reaction with other reactive dienes substituted by heteroatom groups has been little reported[2]. We have reported an efficient method to directly convert a carbonyl group into a selenocarbonyl group using bis(dimethylaluminum) selenide, $(Me_2Al)_2Se$, as a selenating reagent[3]. Selenoaldehydes or selenoketones generated by this method were *in situ* effectively trapped by cyclopentadiene to give [4+2] cycloadducts. However, when 1,3-dienes substituted by functional groups with oxygen atoms were used as a conjugated diene in this reaction, the desired Diels-Alder reaction did not proceed because of the coordination of the aluminum atom in the selenating reagent to the oxygen atom of the dienes. On the other hand, the resulting cycloadducts with cyclopentadiene also serve as convenient, ancillary precursors of selenocarbonyl compounds by thermal retro-Diels-Alder cleavage. In this paper we report the reaction of selenoaldehydes or selenoketones with oxygen-functionalized dienes under the neutral conditions by the method of retro-Diels-Alder reaction and discuss about the stereo- and regiochemistry.

RESULTS AND DISCUSSION

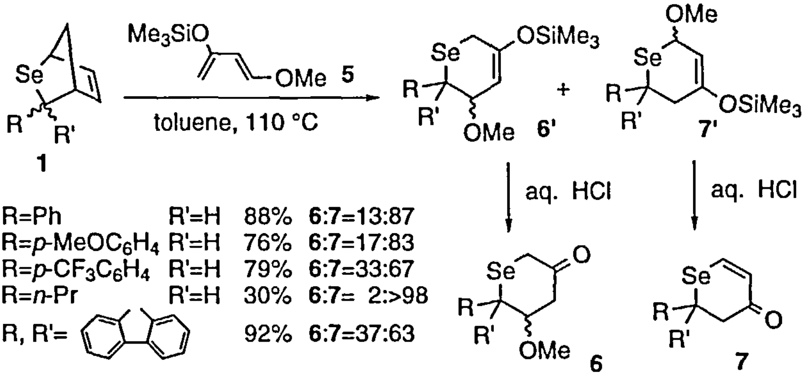
The cycloadducts (**1**) of selenoaldehydes or selenoketones with cyclopentadiene were prepared in good yields by our previous reported methods[3,4]. The treatment of **1** and *trans*-1-acetoxy-1,3-butadiene (**3**) at 110 °C for 12-19 h in toluene gave the Diels-Alder adducts (**4**) of the corresponding selenocarbonyl compounds (**2**) with **3** with a complete regioselectivity (OAc substituted at the β position toward selenium atom) as a mixture of diastereomers in excellent yields (Scheme 1). The structure of **4** was fully characterized by NMR, IR, and MS data.



	R	R'		
a	R=Ph	R'=H	90%	*cis:trans*=85:15
b	R=*p*-MeOC$_6$H$_4$	R'=H	97%	*cis:trans*=90:10
c	R=*p*-CF$_3$C$_6$H$_4$	R'=H	80%	*cis:trans*=89:11
d	R=MeOCO	R'=H	35%	*cis:trans*=44:56
e	R,R'= 		87%	*cis:trans*= —

Scheme 1

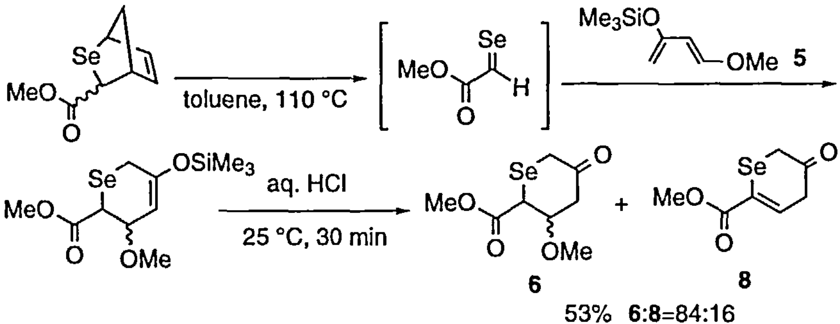
Generation of selenocarbonyl compounds by thermolysis of **1** in toluene in the presence of *trans*-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (**5**, Danishefsky's diene) followed by hydrolysis with diluted hydrochloric acid resulted in the formation of selenacyclohexanone derivatives **6**, **7**, which were presumably formed from the primary regioisomeric products **6 '**, **7 '** in the Diels-Alder cycloaddition, respectively (Scheme 2).



Scheme 2

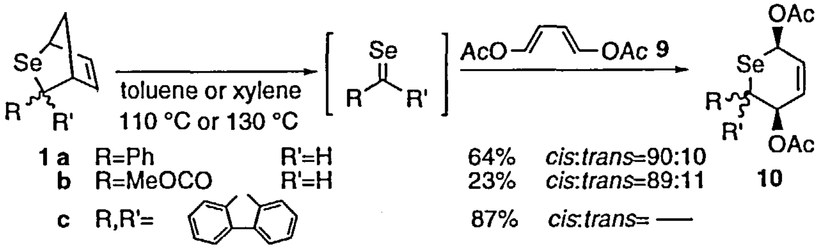
Whereas an acidic hydrolysis of **6 '** underwent at the silyl enol ester moiety to give 3-selenacyclohexanone **6** remaining a methoxy group, **7 '** under the same conditions afforded 4-selena-2-cyclohexenone **7** with the elimination of the methoxy group. In the cases of aromatic and aliphatic substituents, the primary cycloaddition reaction proceeded regioselectively to yield the isomer **7 '** in moderate to high preference. In contrast, the reaction of **1** substituted by a methoxycarbonyl group with **5** at 110 °C for 8 h in toluene and the subsequent acidic hydrolysis gave **6** (R=MeOCO, R'=H) as a major product together with **8** (Scheme 3). This means that the above Diels-Alder cycloaddition proceeded with a complete regioselectivity, but opposite regiochemistry exhibited in reactions of aromatic or aliphatic substituted derivatives.

trans,trans-1,4-Diacetoxy-1,3-butadiene (**9**)[5] is a reactive diene in the Diels-Alder reaction. It has been used as the starting material in stereo-



Scheme 3

specific syntheses of carbohydrate and thiosugar derivatives[6]. The reaction of thermally generated selenobenzaldehyde with **9** at 130 °C for 26 h in xylene gave the cycloadduct **10a** as a 9:1 mixture of two isomers in 64% yield. Two acetoxy groups must be necessarily oriented in a *cis* relationship in this concerted cycloaddition. The ^{1}H NMR spectrum of the major isomer showed a benzylic methyne proton at δ 4.43 as a doublet having a relatively small vicinal coupling (J = 4.1 Hz), which indicates *cis* configuration. The coupling constant of the corresponding proton of the minor isomer was 10.0 Hz. Several examples of the Diels-Alder reaction with **9** are summarized in Scheme 4.



Scheme 4

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