Tetrahedron Letters, Vol. 33, No. 24, pp. 3515-3518, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

α,β-Unsaturated Selenoaldehydes and Selenoketones. The Reaction Behavior as a Heterodiene and/or a Dienophile

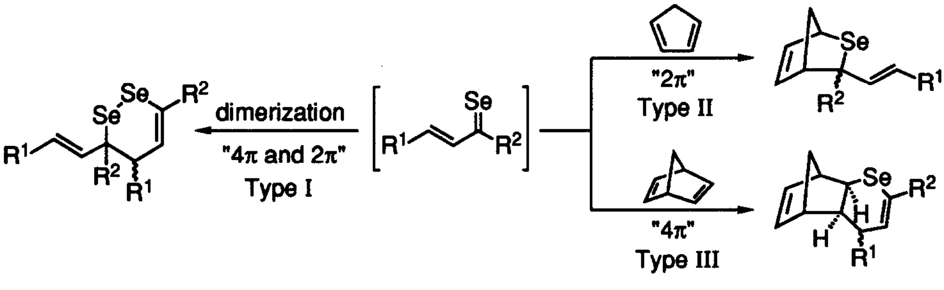
Guang Ming Li, Masahito Segi,* and Tadashi Nakajima*

Department of Chemistry and Chemical Engineering, Faculty of Technology,
Kanazawa University, Kodatsuno, Kanazawa 920, Japan

Key Words: α,β-unsaturated selenoaldehyde; α,β-unsaturated selenoketone; cycloaddition; heterodiene; dienophile

Abstract: *α,β-Unsaturated selenoaldehydes and selenoketones, generated in situ by selenation of the corresponding carbonyl compounds with bis(dimethylaluminum) selenide, underwent regioselective self-condensation to yield cyclic diselenide derivatives. On the other hand, in the presence of a trapping agent, they underwent intermolecular Diels-Alder cycloadditions in two different modes depending on the trapping agent, that is, as a heterodiene toward norbornadiene or a dienophile toward cyclopentadiene.*

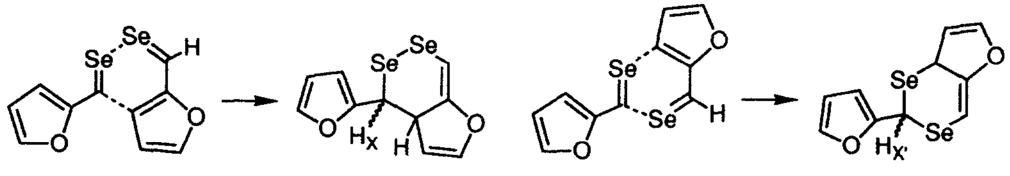
In recent years, chemistry of selenoaldehydes and selenoketones which are key intermediates in the synthesis of selenium heterocycles has been actively studied,[1] and generally the carbon-selenium double bond serves as the 2π dienophile component of the [4+2] cycloaddition with conjugated dienes.[2] In this letter, we describe an interesting and unique face in hetero Diels-Alder reactions of α,β-unsaturated selenoaldehydes and selenoketones, in which the selenocarbonyl group participates as the 2π dienophile or comprises a component of the 4π diene system (Types I ~ III, eq. 1).



(eq. 1)

α,β-Unsaturated selenocarbonyl compounds were generated by the reaction of the corresponding α,β-unsaturated carbonyl compounds with bis(dimethylaluminum) selenide (1)[3] and simultaneously *in situ* subjected to Diels-Alder cycloaddition reactions. A general experimental procedure is illustrated as follows: trimethylaluminum (1.0 M solution in hexane, 1.1 mmol) was added using a syringe technique to a toluene (10 ml) solution of bis(tributyltin) selenide (0.5 mmol) under an argon atmosphere and the mixture was stirred for 3 h at 80°C. After the addition of THF or dioxane (10 ml) as a co-solvent, α,β-unsaturated carbonyl compound (0.75 mmol) was added to that solution. If necessary, trapping agent was added concurrently. The mixture was subsequently heated at 65°C or 100°C for 4~5 h and poured into water. Extraction with ether, drying over MgSO$_4$, and evaporation of the solvent followed by flash column chromatography on silica gel (hexane: dichloromethane=4:1) yielded the cycloaddition product.

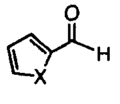
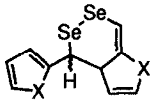
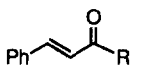
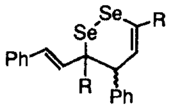
In the absence of trapping agents, the reaction of 2-furfural with **1** resulted in the formation of the dimer (A) of the corresponding selenoaldehyde in 91% yield as a mixture of *trans*:*cis*=85:15. The structure of this dimer was determined by ^{1}H, ^{13}C NMR, and MS spectra. In the ^{1}H NMR spectrum of the stereoisomeric mixture, the two doublets at δ 4.52 (J=10.37 Hz) and 5.81 (J=6.71 Hz) were assigned to the H_X proton of *trans* and *cis* isomers, respectively. The other regioisomer A', in which the signal of $H_{X'}$ proton should appear without such large coupling constants as the above because of the absence of *vicinal* protons, was not obtained in this [4+2] dimerization reaction. The reaction of other α,β-unsaturated aldehydes or ketones with **1**, similarly, gave



"head-to-head" A "head-to-tail" A'

the dimer of the corresponding selenocarbonyl compounds. The results are shown in Table 1.[4] Only one regioisomer having a cyclic diselenide structure was obtained in all cases. The dimerization of 2-selenofurfural or 2-selenothiophenaldehyde yielded predominantly *trans* isomer (entries 1 and 2), but the unambiguous structural evidence for *trans* and *cis* isomers in dimers of selenocinnamoyl derivatives did not come from NMR spectral analysis (entries 3~5). In any event, the formation of dimeric [4+2] cycloadducts implies that α,β-unsaturated selenocarbonyl compounds serve as both a 4π selenadiene (C=C-C=Se) and a 2π dienophile (C=Se) in the regioselective Diels-Alder reaction *via* the transition state with a head-to-head orientation.

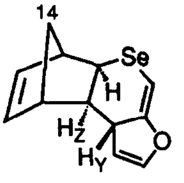
Table 1 [4+2] Dimerization of α,β-Unsaturated Selenoaldehydes or Selenoketones

entry	substrate	dimer	yield(%)$^{a)}$		*trans* : *cis*$^{b)}$
1			X=O	91	85 : 15
2			S	80	82 : 18
3			R=H	60	(82 : 18)$^{c)}$
4			Me	45	(57 : 43)$^{c)}$
5			Ph	42	(62 : 38)$^{c)}$

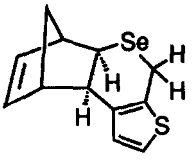
a) Isolated yield. b) Determined by ^{1}H NMR. c) It was not determined whether the major isomer was *trans* or *cis*.

The above results prompted us to investigate the cycloaddition reaction of α,β-unsaturated selenocarbonyl compounds with dienophiles having C=C bond. In the presence of excess norbornadiene, the reaction of 2-furfural with **1** at 100°C gave the Diels-Alder adduct of 2-selenofurfural and norbornadiene as the sole isomeric product in 45% yield.[5,6] The ^{1}H NMR spectrum of this compound showed the signal of H_Y proton at δ 3.22 as a doublet-quartet having a large coupling (J_{YZ}=10.07 Hz) with the adjacent H_Z proton. The large J value indicates H_Y-H_Z *trans* relationship as represented by the structure **B** (or its enantiomer). In the ^{13}C NMR spectrum, the signal of C14 carbon appeared at higher field (δ 40.0 ppm) than similar carbon of norbornene (δ 48.8 ppm) because of steric compression shift,[7] which suggests that this compound has probably *exo* configuration.

The reaction of 2-thiophenaldehyde with **1** in the presence of excess norbornadiene at 100°C gave one isomeric product which showed a different signal pattern in the ^{1}H NMR spectrum,[8] compared with that of the above furyl derivative. The product isolated was actually aromatized adduct as shown by the structure **C**. The results on the cycloaddition of several α,β-unsaturated selenocarbonyl compounds with norbornadiene are summarized in Table 2.[4] When cinnamoyl derivatives were used as a substrate, the dimerization of the corresponding selenocarbonyl compounds preferentially took place to give the mixture of Type I and Type III cycloadducts (entries 5 and 6).

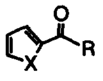
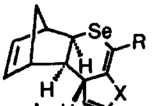
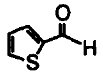
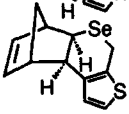
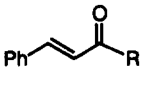
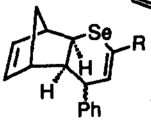
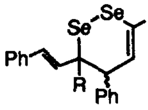


B



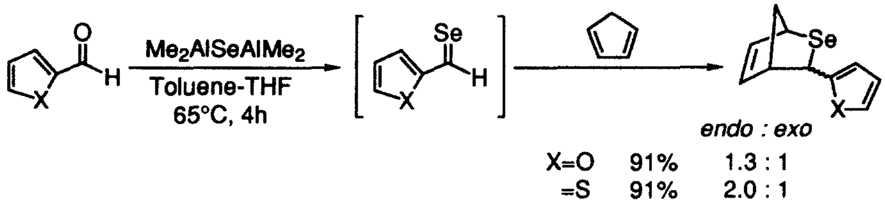
C

Table 2 Diels-Alder Reaction of α,β-Unsaturated Selenoaldehydes or Selenoketones with Norbornadiene[a)]

entry	substrate			product	yield(%)[b)]
1		X=O	R=H		45
2		O	Me		52
3		S	Me		56
4					44
5		R=H		 18[c)] + 	50[d)]
6		Me		27[c)]	36[d)]

a) The reaction was carried out at 100°C in the presence of 5 equiv of norbornadiene in a toluene-dioxane mixture. b) Isolated yield. c) *Trans* : *cis* = 85 : 15 (R=H), 82 : 18 (R=Me). d) Diastereoisomer ratio = 80 : 20 (R=H), 55 : 45 (R=Me).

On the other hand, when cyclopentadiene was used as a trapping agent, the reaction of furfural or thiophenaldehyde with **1** at 65°C afforded the Diels-Alder adducts of the corresponding selenoaldehydes and cyclopentadiene, with the preferential *endo* adduct, in excellent yields as shown in eq. 2. In these reactions, the selenocarbonyl moiety (C=Se) completely participated as a 2π dienophile.



(eq. 2)

In summary, α,β-unsaturated selenocarbonyl compounds derived readily from the selenation of the corresponding carbonyl compounds with **1** acted as not only a C=Se 2π dienophile but also a C=C-C=Se 4π selenadiene, depending on the kind of trapping agent. Further studies on the chemistry of heterodienes involving selenium or tellurium atom are in progress in our laboratory.

Acknowledgements: Financial support from Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan and the Asahi Glass Foundation is greatly acknowledged. We also thank Nitto Kasei Co. Ltd. for the gift of tributyltin chloride.

References and Notes

1. For reviews on selenocarbonyl compounds, see the following. Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Baldwin, J. E., Ed.; Pergamon Press: **1986**; pp. 58-83. Guziec, Jr., F. S. *Organoselenium Chemistry*; Liotta, D., Ed.; John Wiley & Sons: **1987**; pp. 277-324. Guziec, Jr., F. S. *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; John Wiley & Sons: **1987**; Vol. 2; pp. 215-273. Okazaki, R. *Yuki Gosei Kagaku Kyokai Shi* **1988**, *46*, 1149-1163.
2. For reviews on hetero Diels-Alder reaction, see the following. Boger, D. L.; Weinreb, S. M. *Hetero Diels-Alder Methodology in Organic Synthesis*; Academic Press: **1987**; pp. 120-145. Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: **1990**.
3. We have reported the selenation of carbonyl compounds using this reagent **1**. a) Segi, M.; Koyama, T.; Nakajima, T.; Suga, S.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1989**, *30*, 2095-2098. b) Segi, M.; Koyama, T.; Takata, Y.; Nakajima, T.; Suga, S. *J. Am. Chem. Soc.* **1989**, *111*, 8749-8751. c) Segi, M.; Kojima, A.; Nakajima, T.; Suga, S. *Synlett* **1991**, 105-106.
4. All new compounds prepared by the present study exhibited satisfactory spectra (^{1}H, ^{13}C NMR, IR, and Mass).
5. The products obtained in this reaction depended on the reaction temperature. When the reaction was carried out at 65°C in the presence of norbornadiene, only the dimer (**A**) of 2-selenofurfural was obtained in 85% yield.
6. The analogous cycloadducts from aryl 2-furyl or 2-thienyl thioketones and norbornene also have been reported. Ohmura, H.; Motoki, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1131-1137.
7. Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd Ed.; John Wiley & Sons: **1980**, p. 80.
8. In the ^{1}H NMR spectrum, the two doublets at δ 3.69 and 3.81 with J=14.16 Hz each other were assigned to the methylene protons adjacent to selenium atom in the structure **C**, as a AB pattern.

(Received in Japan 9 March 1992)