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CYCLOPENTENONE ANNULATION REACTION USING (E)-1-(PHENYLSELENO)-2-(TRIMETHYLSILYL)ETHENE

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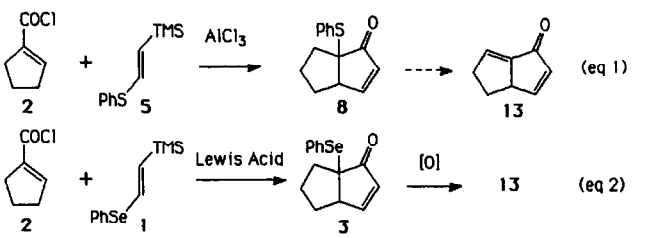
Summary: Reaction of (E)-1-(phenylseleno)-2-(trimethylsilyl)ethene (**1**) with 1-cyclopentenoyl chloride (**2**) in the presence of Lewis acid gave 1-phenylselenobicyclo[3.3.0]oct-3-en-2-one (**3**). When the reaction was carried out at low temperature, Z-1-(1'-cyclopentenyl)-3-phenylseleno-2-propen-1-one (**4**) was obtained, as the intermediate of this cyclization. The merit for using the cycloannulation reagent **1** is postulated, and the reaction mechanism of each synthetic step is elucidated.

Introduction.

The development of new methods of the five-membered-ring formation is important for synthesis of natural and nonnatural products.[1] Magnus reported that the reaction of (E)-1-(phenylthio)-2-(trimethylsilyl)ethene (**5**) and cyclopentenoyl chlorides in the presence of $AlCl_3$ results in thiophenyl migration to give rearranged cyclopentenones (eq 1).[2] However, the elimination of the thiophenyl group (from **8** to **13**, not reported) requires a severe condition and is a difficult process. Instead of sulfur, use of selenium is expected to give selenium functionalized cyclopentenone **3**, which allows to introduce a double bond in ring under the mild condition[3] to give **13** (eq 2). This cycloannulation would bring a potentially highly unsaturated cyclopentanoid.[4]

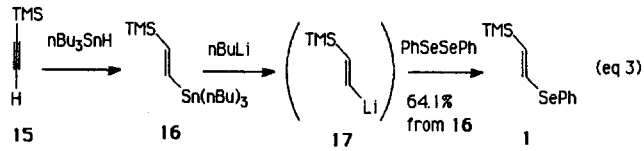


We have examined the synthesis of the reagent, (E)-1-(phenylseleno)-2-(trimethylsilyl)ethene (**1**), and the reaction of **1** and unsaturated chloride **2** in the presence of Lewis acid. Here, we describe that reactions of **1** and **2** in the presence of $AgBF_4$ or $TiCl_4$ gave 1-phenylselenobicyclo[3.3.0]oct-3-en-2-one (**3**), and that when the reaction was carried out at low temperature under the similar condition, Z-1-(1'-cyclopentenyl)-3-phenylseleno-2-propen-1-one (**4**) was obtained, as the intermediate of this cyclization. **3** was converted to the desired product, bicyclo[3.3.0]octa-3,8-dien-2-one (**13**) by oxidation and treatment with pyridine.

Synthesis of (E)-1-phenylseleno-2-trimethylsilylethene (1)

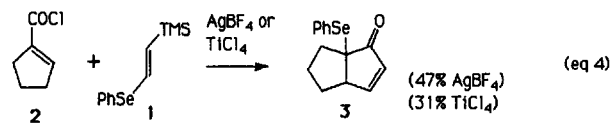
1 was prepared by two steps from commercially available trimethylsilylacetylene (**15**) (eq 3). Treatment of (E)-trimethylsilylvinyllithium (**17**), which is prepared in situ from (E)-1-

trimethylsilyl-2-tri-n-butylstannylethene (**16**) and n-butyllithium,[5] with diphenyldiselenide in THF (-78 °C → r.t., overnight) gave **1**[6] in 64.1% yield. NMR analysis of **1** indicated the absence of detectable amounts of the corresponding Z-isomer.

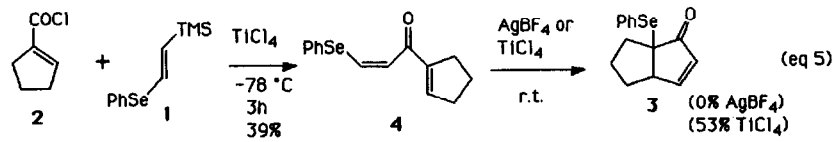


Reactions of 1 and 2.

To a solution of $AgBF_4$ in CH_2Cl_2/CH_2ClCH_2Cl, cooled to -50 °C, was added **1** and subsequently 1-cyclopentenoyl chloride (**2**). After warming the mixture to room temperature, 1-phenylselenobicyclo[3.3.0]oct-3-ene-2-one (**3**)[7] was obtained in 47% yield (eq 4). Treatment of **1** with **2** in the presence of $TiCl_4$ in CH_2Cl_2 gave **3** in 31% yield. Use of other Lewis acids such as BF_3OEt_2, $FeCl_3$ and $AlCl_3$ gave none of cyclized products. Using $SnCl_4$ as a Lewis acid gave cis-bicyclo[3.3.0]oct-3-ene-2-one (**6**) as a main cyclized product. Attempts to isolate pure **6** were not successful.[8] Treatment of **2** with phenyl vinyl selenide (**7**)[9] instead of **1**, in the presence of $TiCl_4$ (r. t., 4 h), gave only trace amount of **3** (7%).

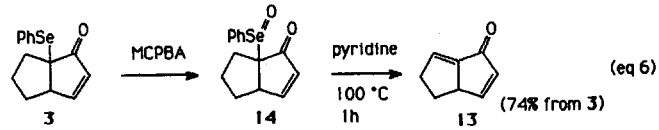


In order to determine the intermediate of this cyclization reaction and examine Friedel-Crafts acylation of **1**, the reaction was carried out at low temperature. When **1** was treated with **2** in the presence of $TiCl_4$ at -78 °C for 3 h, **4**[10] was obtained as a major product in 39% yield (eq 5). The Z-geometry of the selenophenyl-substituted double bond was assured by 9.0 Hz vicinal coupling constant in ^1H NMR spectrum. E-isomer was not isolated. **4** was converted to **3** by treatment with $TiCl_4$ at room temperature (4 h) in 53% yield, but **4** remains unchanged by treatment with $AgBF_4$. Possibly, one pot cycloannulation using $AgBF_4$ was effected by the TMS^+ and Cl^- generated in situ.



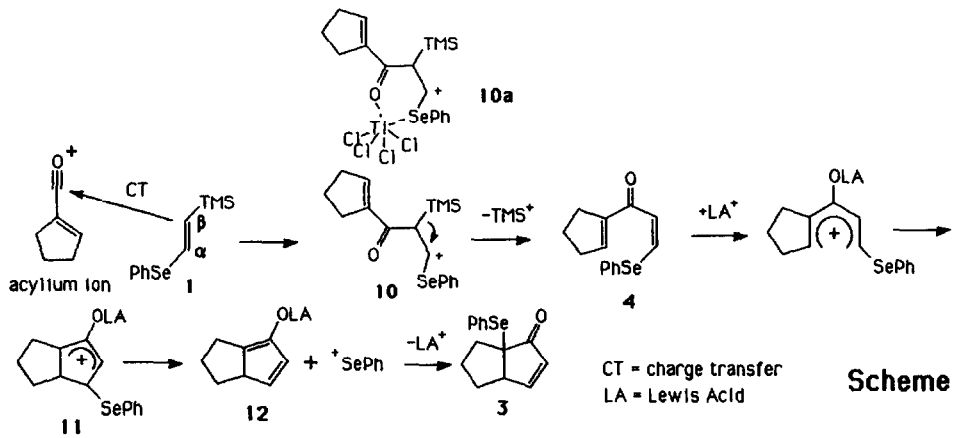
Synthesis of 13

3 was converted to the selenoxide **14** by m-chloroperbenzoic acid (MCPBA) in dichloromethane (eq 6). **14** was heated in pyridine at 100 °C for 1h to give **13**[11] in 74% yield (from **3**). The double bond was introduced regioselectively.



Mechanistic Interpretation of Cyclopentenone Annulation

A plausible mechanism of cyclopentenone annulation is outlined in Scheme 1. In the first step of the reaction, the olefinic C_β of **1** is linked to the carbon of the acylium ion. This selectivity is supported by the STO-3G frontier electron density calculation for electrophilic reactions, $f_\alpha^{(E)} = 0.074 < f_\beta^{(E)} = 0.220$. The silicon and selenium atoms are working together to stabilize the resultant carbonium ion **10**. Since the $SiMe_3$ group (TMS) is β to a carbonium ion, it can be eliminated to give **4**. The result that the reaction using **7** gave the low yield (7%) suggests the Me_3Si group assists the electrophilic substitution reaction of **1** with the acylium ion derived from **2**. The Z-olefin formation at low temperature is possibly explained by the chelete model **10a**. Nazarov cyclization[12] of **4** leads to the oxyallyl cation **11**, which can lose $PhSe^+$ to give the kinetic enolate **12**. Selenenylation of **12** with the $PhSe^+$ generated in situ gives **3**. This pathway is consistent with the observation in the reaction between the thiophenyl analogue **5** and **2** in the presence of $AlCl_3$ (eq 1).[2]



Scheme 1

New results obtained in the present work are summarized in two respects, i) synthetic merit and ii) mechanistic finding.

i) Reaction of (E)-1-(phenylseleno)-2-(trimethylsilyl)ethene (**1**) with 1-cyclopentenoyl acid chloride (**2**) in the presence of Lewis acid gave the selenophenyl functionalized bicyclo[3.3.0]octenone **3** in one pot reaction in modest yield (47% $AgBF_4$, 31% $TiCl_4$). **3** is converted to **13** by oxidation and treatment with pyridine. The advantage of use of the phenylseleno group instead of the thiophenyl group is that another double bond is easily introduced to the bicyclo[3.3.0]octenone **3**. Because double-bond introduction process seems to be usually difficult in the synthesis of polyquinenes, this cyclization could become a general method of their synthesis.

ii) When the reaction in the presence of $TiCl_4$ was carried out at low temperature, Z-1-(1'-cyclopentenyl)-3-phenylseleno-2-propen-1-one (**4**) was obtained, as the intermediate of this cyclization. Friedel-Crafts acylation of **1** results in the inversion of configuration of the double bond, although the acylation of vinyltrimethylsilanes takes place with retention of configuration of the double bond in general.[13] In the case of sulfur reported by Magnus,[2] the intermediate was not isolated and only suggested as an E-isomer of thiophenyl analogue of **4**. Friedel-Crafts

acylation of 1-thio-2-silylalkene ($MeS(CH_2)_3SCH{=}CHSiMe_3$) was reported, but E or Z stereochemistry of the product was not mentioned.[14]

This work has demonstrated that **1** is a new and efficient reagent for cycloannulation and introduction of the phenylseleno group. We are currently investigating applications of the present methods to the synthesis of cyclopentanoid products.

Acknowledgment: We are grateful to Prof. I. Murata and Dr. K. Yamamoto (Osaka Univ.) for measurement of mass spectra and elemental analysis. Thanks are also due to the Institute for Molecular Science for the ab initio (STO-3G) calculation of **1**.

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6) **1**: colorless oil; bp 80-82 °C/1 mmHg; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.072 (s, 9H), 6.18 (d, J = 18.1 Hz, 1H), 7.02 (d, J = 18.1 Hz, 1H), 7.31-7.35 (m, 3H), 7.51-7.56 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) -1.18 (CH_3), 127.8(CH), 129.4(CH), 129.5(C), 133.9(CH), 134.3(CH), 134.5(CH).

7) **3**: pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.19-1.31 (m, 1H), 1.58-1.69 (m, 2H), 1.73-1.89 (m, 2H), 2.19 (dd, J = 6.2, 12.8 Hz, 1H). 3.35 (bd, J = 9.7 Hz, 1H), 7.23-7.28 (m, 2H), 7.31-7.36 (m, 2H), 7.60-7.63 (m, 2H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 24.31(CH_2), 29.04(CH_2), 37.10(CH_2), 55.06(CH), 57,62(C), 126.8(C), 128.9(CH), 129.0(CH), 133.4(CH), 137.1(CH), 164.7(CH), 209.3(C); IR (neat) 1700 cm^{-1}. **3** is a single diastereomer by NMR, and is assigned to cis ring junction stereochemistry on the basis of thermodynamic expectations about [3.3.0] ring system.

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10) **4**: pale yellow crystals; mp 128.5 °C (from hexane-$CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 1.88-2.08 (m, 2H), 2.52-2.74 (m, 4H), 6.78-6.82 (m, 1H), 7.30 (d, J = 9.0 Hz, 1H), 7.34-7.38 (m, 3H), 7.58-7.66 (m, 2H), 7.91 (d, J = 9.0 Hz, 1H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 22.96, 30.91, 34.18, 120.67, 128.11, 129.31, 133.10, 134.48, 142.65, 146.42, 150.01, 187.91; IR (KBr) 1624, 1528 cm^{-1}.

11) **13**: colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 1.60-1.81 (m, 1H), 2.26-2.38 (m, 1H), 2.69 (ddd, J = 17.3, 8.3, 3.9 Hz, 1H), 2.88 (dddd, J = 17.3, 11.4, 2.0, 2.0 Hz, 1H), 3.89 (dddd, J = 11.1, 7.2, 2.0, 2.0 Hz, 1H), 6.22 (dd, J = 2.0, 6.0 Hz, 1H), 6.54 (bd, J = 2.0 Hz, 1H), 7.47 (d, J = 6.0, 1H); ^{13}C NMR (50.1 MHz, $CDCl_3$) δ (ppm) 31.17(CH_2), 36.98(CH_2), 52.28(CH), 132.8(CH), 138.3(CH), 148.4(C), 158.7(CH), 191.4(C); IR ($CHCl_3$) 1688, 1638 cm^{-1}.

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