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NOVEL ROUTE TO SELENOKETONES FROM KETONES BY THE USE OF BIS(DIMETHYLALUMINUM) SELENIDE

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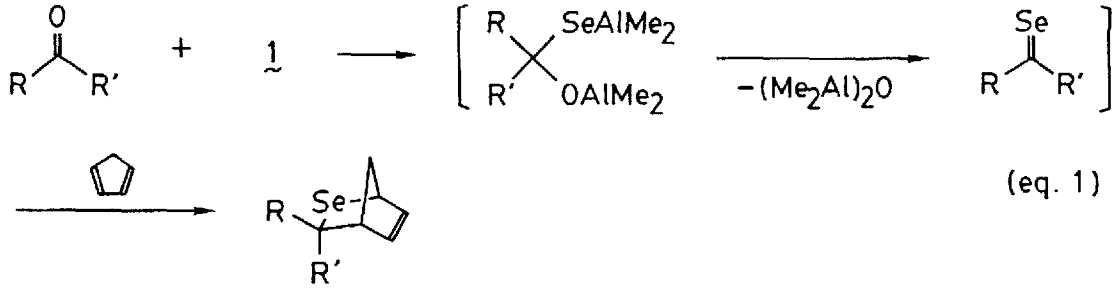
Summary: Bis(dimethylaluminum) selenide, prepared in situ via transmetallation reaction of bis(trimethylsilyl) selenide with dimethylaluminum chloride, reacted with ketones in the presence of a diene to give Diels-Alder adducts of the corresponding selenoketones and the diene.

The chemistry of reactive compounds having carbon-selenium double bond has been actively studied for some years past.[1)] Recently, we have described a simple and convenient synthesis of selenoaldehydes via base-catalyzed reaction of aldehydes with bis(trimethylsilyl) selenide **2**, which takes advantage of the large affinity of silicon to oxygen atom.[2)] Our attempts, however, for the application of this method to the preparation of selenoketones have been unsuccessful. Now we have found that bis(dimethylaluminum) selenide **1**[3)] can serve as an efficient selenating reagent for this purpose. In this letter we

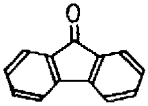
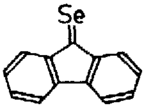
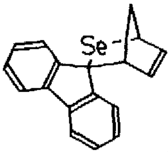
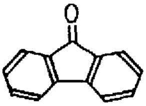
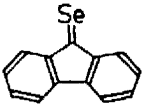
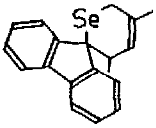
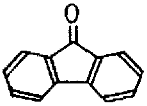
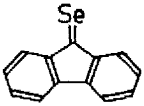
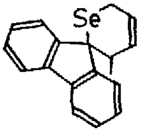
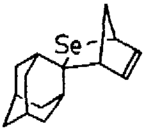
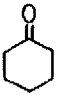
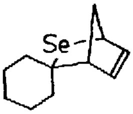
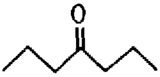
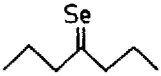
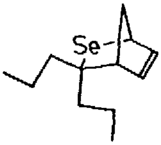
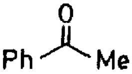
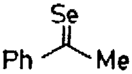
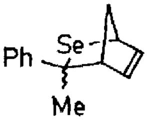
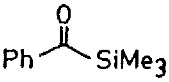
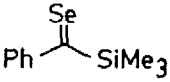
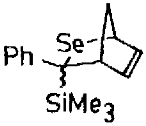
$Me_2AlSeAlMe_2$ **1** $Me_3SiSeSiMe_3$ **2**

report a new method for the direct conversion of ketones to selenoketones, which can be trapped as Diels-Alder adducts (eq. 1). Although some sterically hindered selenoketones have been prepared so far,[4)] synthesis of simple selenoketones has been unsuccessful. Diels-Alder reaction of selenoketones with a diene has been reported only for selenofluorenone.[5)]



(eq. 1)

Table 1. Generation and Trapping of Selenoketones.

Run	Ketone	Selenoketone	Diene	Cycloadduct	Yield (%)[a]
1					77
2				 b)	58
3				 b)	65
4					63
5					53
6					55
7	 $PhC(=O)Me$	 $PhC(=Se)Me$		 (endo : exo = 1 : 1)[c]	44
8	 $PhC(=O)SiMe_3$	 $PhC(=Se)SiMe_3$		 (endo : exo = 1 : 1)[c]	72

[a] Isolated yields. b) Regioisomer was not detected. c) Isomer ratio was determined by ^{1}H-NMR integration, but the isomers could not be separated by column chromatography.

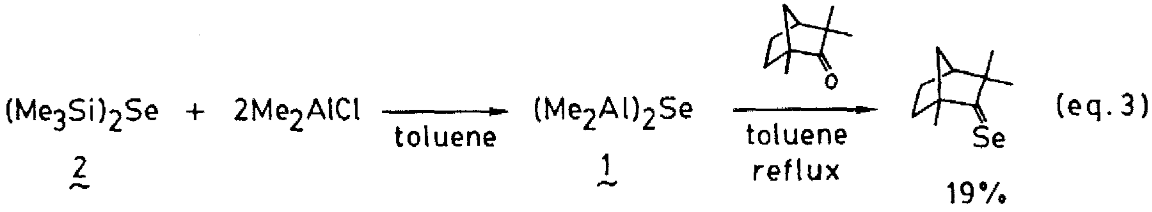
The synthesis of the new reagent 1 could not be accomplished via the Li_2Se route that was used for the synthesis of 2.[6)] However, the transmetallation of 2 with two equivalents of Me_2AlCl in toluene provided an effective alternative route, as shown in eq. 2. In fact, the quantitative formation of chlorotrimethylsilane was confirmed by ^{1}H-NMR measurement. After

$$\underset{\textbf{2}}{(Me_3Si)_2Se} + 2Me_2AlCl \xrightarrow[\text{toluene}]{} \underset{\textbf{1}}{(Me_2Al)_2Se} + \underset{\text{quant.}}{2Me_3SiCl} \qquad \text{(eq. 2)}$$

the removal of toluene, the reaction of 1 with a ketone in refluxing THF[7)] in the presence of a diene in excess gave a cycloadduct of the corresponding selenoketones in moderate to good yields.[8)] The results of these Diels-Alder reactions are summarized in Table 1.[9)]

Diels-Alder reaction of selenofluorenone with 2-methyl-1,3-pentadiene or 1,3-pentadiene gave only one isomer with a complete cycloaddition regioselectivity (runs 2 and 3).[10)] These regiochemical results are consistent with Krafft's results.[5)] It is especially noteworthy that even simple ketones can react with 1 in the presence of cyclopentadiene to afford cycloadducts of simple selenoketones in moderate yields (runs 5-7). Moreover, when benzoylsilane was used as a starting ketone, the Diels-Alder reaction of selenobenzoylsilane,[11)] an interesting new class of compounds which have not been reported because of the difficulty of preparation, proceeded efficiently to give the cycloadduct, although less stereoselectively (run 8).

After various attempts for isolation of a selenoketone by the present new procedures, we have succeeded in the isolation of a sterically hindered selenoketone. Thus, selenofenchone[4)] which showed the characteristic blue color was prepared in 19 % yield directly from fenchone using refluxing toluene as the solvent (eq. 3).



The described method using bis(dimethylaluminum) selenide 1 opens a new and general route to selenoketones. The application to the other selenocarbonyl compounds, as well as the use of 1 as a novel selenating reagent, is under investigation.

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2) Segi, M.; Nakajima, T.; Suga, S.; Murai, S.; Ryu, I.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* 1988, *110*, 1976-1978.
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6) Detty, M. R.; Seidler, M. D. *J. Org. Chem.* 1982, *47*, 1354-1356.
7) When the generation of selenoketones was conducted in toluene, the reaction proceeded very slowly probably because of a heterogeneous nature of the aggregated state of **1**.
8) A typical experimental procedure is described as follows. Dimethylaluminum chloride (1.0 M solution in hexane, 2.2 mL, 2.2 mmol) was added to a solution of bis(trimethylsilyl) selenide (225 mg, 1.0 mmol) in toluene (15 mL) under argon and the mixture was stirred for 15 h at 100°C. After the removal of toluene carefully under reduced pressure, THF (20 mL) as solvent, cyclopentadiene (660 mg, 10 mmol), and fluorenone (216 mg, 1.2 mmol) were added in that order to the residue. The mixture was subsequently heated under reflux for 16 h and then worked up with water. After extraction with ether, the combined extracts were dried, concentrated, and purified by flash column chromatography on silica gel (hexane: dichloromethane=2:1 as eluent) to give the selenofluorenone cycloadduct (238 mg, 77 % yield).
9) All new compounds prepared by the present study exhibited satisfactory spectral data (^{1}H-NMR, IR, and mass spectra).
10) Unusually high field signal at δ 0.45 or 0.40 in the ^{1}H-NMR spectrum of cycloadduct of selenofluorenone and 2-methyl-1,3-pentadiene or 1,3-pentadiene, respectively, would be due to shielding of the methyl protons by the surrounding aromatic ring. Therefore, the methyl group must be adjacent to fluorenyl group as shown in Table 1.
11) Recently, Diels-Alder reaction of sulfur analogue, thiobenzoylsilane, with dienes was reported. Bonini, B. F.; Lenzi, A.; Maccagnani, G. *J. Chem. Soc., Perkin Trans. 1* 1987, 2643-2646.

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