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A Regioselective Aluminum Chloride-catalyzed Acylation of Allylic Selenides via α-Silyl Intermediates. A Facile Route to Dihydrojasmone

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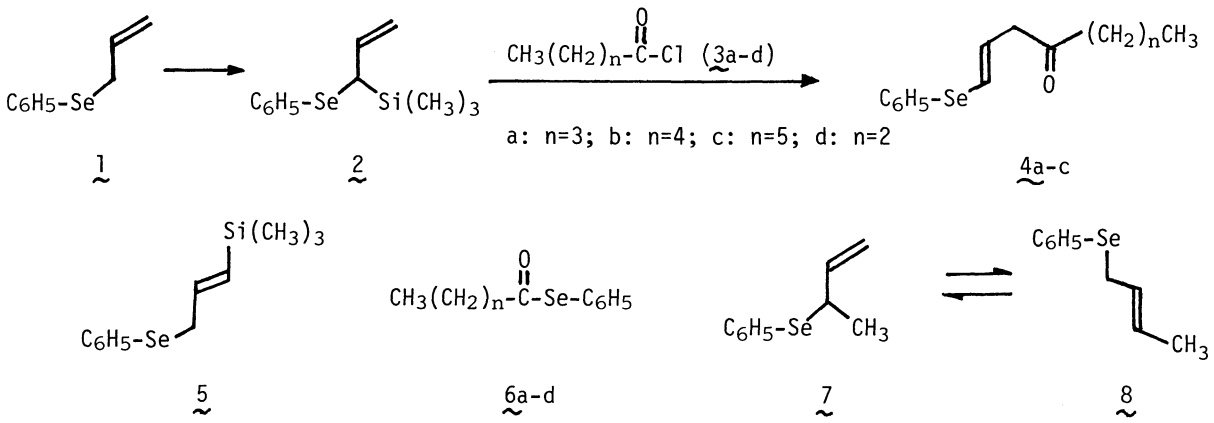
The aluminum chloride-catalyzed acylation of α-silylallylic selenides with acid chlorides at -78 °C produced γ-acylated vinylic selenides regioselectively. α-Silylallylic selenides in some cases underwent [1,3] shifts of the selenenyl groups by the catalysis with aluminum chloride, affording γ-silylallylic selenides. This regioselective acylation of allylic selenides provides a new route to dihydrojasmone.

Many efforts have been made to develop a new methodology for the efficient regioselective alkylation of the carbanions of allylic sulfides using alkylboranes[1] and alkylaluminums,[2] or introducing functionalities at the α'-positions of the sulfenyl groups of allylic sulfides such as thioamides,[3] 2-pyridyl,[4] 2-thiazolinyl,[5] and 2-imidazolyl,[6] for stabilization of the α-carbanions of the allylic systems by chelation with the functionalities.

We have already reported a highly regioselective acylation of allylic sulfides via α-silyl intermediates[7] and further developed a novel method for cyclopentannelation[8] and furan annelation[9] using this acylation of allylic sulfides. We have applied this technique to allylic selenides, in order to develop its use further in organic synthesis, utilizing the chemical characteristics of vinylic selenides. We wish to communicate herein a regioselective acylation of allylic selenides via α-silyl intermediates and its use in the synthesis of a 2-cyclopentenone such as dihydrojasmone.[10]

α-Silylation of allyl selenide 1 was performed highly regioselectively by treating 1 with lithium diisopropylamide in tetrahydrofuran at -78 °C followed



1 2 4a-c 5 6a-d 7 8

by addition of trimethylsilyl chloride to produce α-trimethylsilylallyl selenide 2 in 96% yield.[11]

Reactions of the α-silylallyl selenide 2 with acid chlorides 3a-c in the presence of aluminum chloride in dichloromethane at -78 °C gave γ-acylated selenides 4a-c, besides with recovery (11-35%) of 3-trimethylsilylallyl selenide 5 instead of the starting material 2 and with formation of a small amount of phenylseleno esters 6a-c. The yields of these products are listed in Table 1.

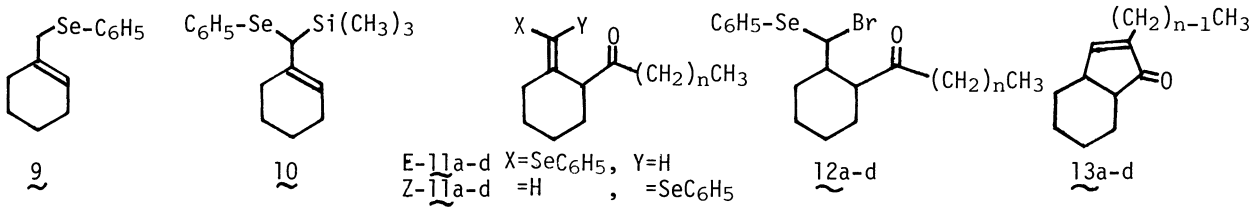
This γ-silylallyl selenide 5 was easily formed quantitatively from 2 upon treatment with aluminum chloride at -78 °C for 1 h. This transformation can be rationalized by acid-catalyzed [1,3] selenoallylic rearrangements. This rationalization was confirmed by the following acid-catalyzed conversion of 7 into 8; treatment of 7 with 0.5 equiv. of aluminum chloride, titanium(IV) chloride, or tin(IV) chloride in dichloromethane at -78 °C for 1 h afforded the

Table 1. The Aluminum Chloride-catalyzed Acylation of α-Silylallyl Selenide 2[a]

	Acid chlorides 3a-c	Reaction temp / °C	Reaction time / h	Yields of Products / % [b] 4a-c	5	6a-c
a	3a	-78	6	26 (35)	26	12
		-20	6	36 (43)	16	30
b	3b	-78	6	22 (34)	35	17
		-20	6	35 (43)	17	32
c	3c	-78	6	27 (38)	29	13
		-78	8	38 (48)	20	12
		-78	10	32 (41)	23	15
		-20	6	43 (51)	15	28
		-20	8	34 (38)	11	23
		0	6	42	36	-

a) The reactions of 2 with 3a-c (1.2 equiv.) were carried out in dichloromethane in the presence of aluminum chloride (1.0 equiv.).

b) Corrected yields based on the recovered material 5 are listed in parentheses.



9 10 E-11a-d X=SeC_6H_5, Y=H; Z-11a-d =H, =SeC_6H_5 12a-d 13a-d

product 8 in extremely high yields (97-100%), by the [1,3] shift of the selenenyl group. [1,3] Shifts in selenoallylic systems have not been studied in detail and only a paper on the thermal [1,3] shifts has appeared.[12] It should be noted that [1,3] shifts in selenoallylic systems were accomplished under extremely mild reaction conditions in the acid catalysis, as mentioned above.

The aluminum chloride-catalyzed acylation of vinylic silane 5[13] with acid chlorides 3a-c produced also γ-acylated vinylic selenides 4a-c exclusively. Therefore the aforementioned aluminum chloride-catalyzed acylation of α-silylallylic selenide 2 with acid chlorides would presumably be accomplished competitively via α- or γ-silylallylic selenides 2 or 5.

Reactions of α-silylallylic selenide 10, prepared from 9 quantitatively, with acid chlorides 3a-d were carried out in dichloromethane at -78 °C for 8 h in the presence of aluminum chloride to provide exclusively γ-acylated products 11a-d and phenylseleno esters 6a-d, without any product by [1,3] selenoallylic rearrangements. The yields of the products are listed in Table 2. The stereochemistry of the olefins in the products 11a-d was assigned by the NMR spectral analysis[8] and the ratios of E-11a-d to Z-11a-d were calculated to be 4:1 - 5:2. The ratios were reversed in contrast to those obtained from allylic sulfides,[8] as not expected.

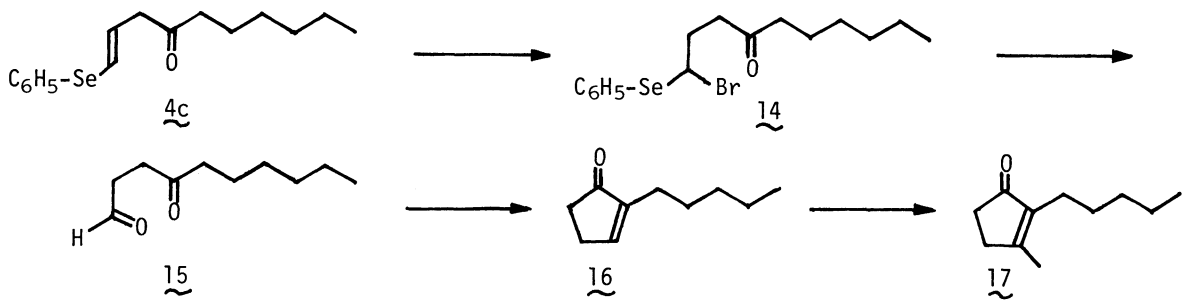
This regioselective acylation of allylic selenides provides a new route to dihydrojasmone, utilizing the chemical properties of vinylic selenides as follows. The vinylic selenide 4c obtained above was reacted with hydrogen bromide (a 30% acetic acid solution) in benzene at room temperature for 2 h to give an adduct 14

Table 2. The Aluminum Chloride-catalyzed Acylation of Cyclic α-Silylallylic Selenide 10[a]

	Acid chlorides 3a-d	n	Yields of products / %[b] 11a-d	6a-d
a	3a	3	60 (73)	13
b	3b	4	56 (60)	12
c	3c	5	61 (89)	10
d	3d	2	57 (79)	6

a) The reactions of 10 with 3a-d (1.2 equiv.) were carried out in dichloromethane at -78 °C for 8 h in the presence of aluminum chloride (1.2 equiv.).

b) Corrected yields based on the recovered starting material 10 are listed in parentheses.



in 94% yield.[14] Treatment of 14 with dimethyl sulfoxide[14] at room temperature for 2 h afforded an aldehyde 15[10b] in 82% yield. An intramolecular aldol condensation of 15 with sodium hydroxide and addition of methyllithium to the resulting 2-cyclopentenone 16 followed by oxidation with chromic acid led to a smooth conversion into dihydrojasmone (17) in the same way as reported previously.[10b]

The same synthetic sequences were applicable to the cyclic vinylic selenides 11; hydrobromination of the vinylic selenide 11a and the subsequent treatment of the resulting bromide 12a with dimethyl sulfoxide followed by the aldol condensation afforded a 2-cyclopentenone derivative 13a in 69% yield from 11a. The stereochemistry of the fused ring system would be deduced as the more stable cis configuration.

Thus these procedures provide a new and facile entry to synthetically valuable 2-cyclopentenone derivatives.

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