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REGIOREVERSED REACTIONS OF TRIMETHYLSILYL OR PHENYLSELENYL ALLYLIC CARBANION WITH CARBONYL COMPOUNDS VIA ALLYLIC ALUMINUM "ATE" COMPLEXES

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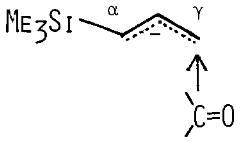
Summary Triethylaluminum "ate" complexes of trimethylsilyl and phenylselenyl allylic carbanion react with carbonyl compounds at the α-position either exclusively or predominantly.

The lithio-anion of allyltrimethylsilane[1] or allyl phenyl selenide[2] usually reacts with carbonyl compounds at the γ-position predominantly (**1** and **2**).



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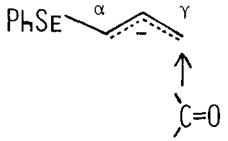
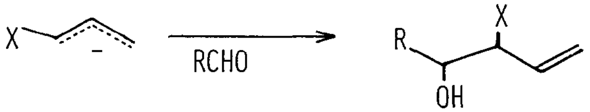


2

The γ-selectivity of **1** can be converted to the α-selectivity by changing the counterion to magnesium (II).[1] We have been seeking a general method for creating the α-selectivity regardless of the substituent, X, of allylic carbanions (eq 1), and previously reported that the regiochemistry of oxygen and sulfur substituted allylic carbanions (X = O and S) can be controlled to the α-selectivity via allylic aluminum ate complexes.[3]



X = RS, RS(O), RS(O_2), RO, RSe, R_2N, R_3Si, R_2B.... (1)

We now wish to report that this aluminum ate complex method is also applicable to silyl and selenyl substituted allylic carbanions (eq 2).

The results are summarized in Table 1. Evidently, the aluminum ate

Table 1. Regioreversed reactions via allylic aluminum "ate" complexes[a]

Allyl Carbanion	Carbonyl Compound	Additive	α-Attack (%)	γ-Attack (%)
1	CH_3CH_2CHO	Et_3Al	94	6
		None	10	90
	$(CH_3)_2CHCHO$	Et_3Al	85	15
		None	10	90
	C_6H_5CHO	Et_3Al	71	29
		None	17	83
	$C_6H_5-\underset{\underset{O}{\|}}{C}-CH_3$	Et_3Al	24	76
		None	-	~100
2	CH_3CH_2CHO	Et_3Al	~100	-
		None	12	88
	$(CH_3)_2CHCHO$	Et_3Al	~100	-
		None	-	~100
	C_6H_5CHO	Et_3Al	78	22
		None	18	82
	$C_6H_5-\underset{\underset{O}{\|}}{C}-CH_3$	Et_3Al	64	36
		None	15[b]	85[b]

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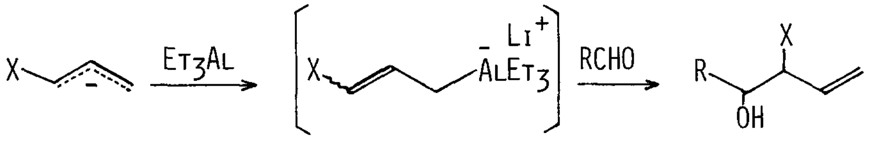
[a] All reactions were carried out on a 1-mmol scale with the same procedure in the text. The products were identified by NMR, IR, and mass spectroscopy, or comparison with authentic materials. "None" indicates the normal reaction without additives. The α/γ ratio was determined by NMR spectra or GLPC analysis. The total yields of ate complex reactions and normal reactions were high, around 75 ~ 85 %. [b] The data from H. J. Reich, <u>J. Org. Chem.</u>, 40, 2570 (1975).



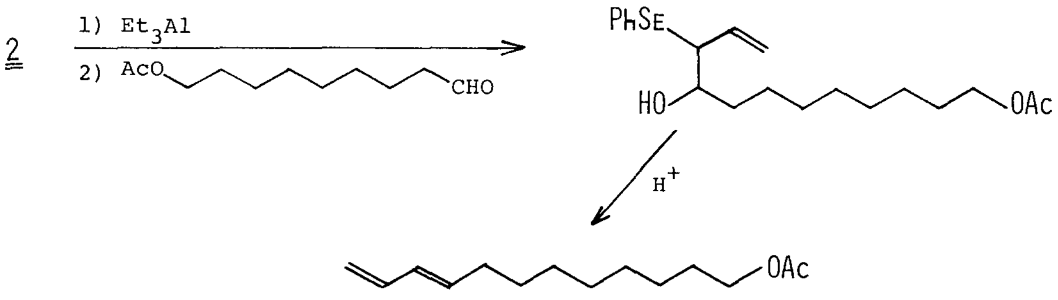
X = Me3Si, PhSe

(2)

complex method works well for aldehydes, such as propionaldehyde, iso-butyraldehyde, and benzaldehyde. Unfortunately, however, acetophenone reacts predominantly at the γ-position of **1** even when triethylaluminum is used. Although "reversed" regioselectivity is achieved by using ate complex in the reaction of **2** with acetophenone, the degree of the selectivity is not so high. These results indicate that the reversal of regioselectivity depends upon the steric bulkiness of both carbonyl compounds and heterosubstituents (X).

The general procedure is as follows. To a solution of allyl trimethylsilane (0.14 ml, 1 mmol) and NNN'N'-tetramethylethylenediamine (0.15 ml, 1 mmol) in dry THF (1 ml) was added sec-butyllithium in hexane (0.7 M, 1 mmol) at -78°C under N_2. The reaction temperature was kept at -30°C for 30 min. Et_3Al in hexane (15 % in hexane, 1 mmol) was added, and an electrophile was added after a few minutes. The mixture was allowed to warm to room temperature, and then quenched with aqueous NH_4Cl solution at 0°C. Similar procedure was used for **2**. To a solution of diisopropylamine (0.2 ml, 1.4 mmol) in dry THF (1 ml) was added n-butyllithium in hexane (1.4 M, 1.4 mmol) at 0°C under N_2. Allyl phenyl selenide (0.14 ml, 1 mmol) was added at -78°C. After 30 min, Et_3Al in hexane (1.4 mmol) was added at this temperature, and then an electrophile was added. The mixture was allowed to warm to room temperature and then quenched with aqueous NH_4Cl solution at 0°C. The usual work-up afforded the desired product.

We next turned our attention to an application of the present method to the stereoselective synthesis of 9.11-dodecadiene-1-yl acetate, a pheromone of Diparopsis castanea[4] (eq 3).



(3)

Treatment of triethylaluminum ate complex of **2** with 9-oxonon-1-yl acetate produced 12-acetoxy-4-hydroxy-3-phenylseleno-1-dodecene[5] in 70 % yield. Elimination[6] via p-toluenesulfonic acid gave the desired diene[7] in 77 % yield. The ratio of E/Z was 84/16.[8]

References and Notes

1) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London 1981, p. 118 and references cited therein.
2) D. L. J. Clive, Tetrahedron, 34, 1049 (1978) and references cited therein.
3) Y. Yamamoto, H. Yatagai, K. Maruyama, J. Org. Chem., 45, 195 (1980).
4) B. F. Nesbitt, P. S. Beever, R. A. Cole, R. Lester, R. G. Poppi, Tetrahedron Lett., 4669 (1973).
5) ^{1}H NMR (CCl_4, TMS) δ 1.10-1.76 (bm, 14H), 1.96 (s, 3H), 2.00-2.44 (m, 2H), 3.54 (t-d, J=8 and 2 Hz, 1H), 3.98 (t, J=6 Hz, 2H), 4.92 (d-d, J=10 and 2 Hz, 2H), 5.76 (t-d, J=10 and 16 Hz, 1H), 7.20 (m, 3H), 7.48 (m, 2H). Although there may be two diastereoisomers (erythro and threo) in this adduct, the exact ratio is not determined at this stage.
6) J. Remion, W. Dumont, A. Krief, Tetrahedron Lett., 1385 (1976).
7) ^{1}H NMR (CCl_4, TMS) δ 1.20-1.90 (bm, 12H), 2.00 (s, 3H), 2.00-2.24 (m, 2H), 4.02 (t, J=6 Hz, 2H), 4.80-6.54 (m, 5H); mass spectrum, m/e 225 (M^+).
8) The ratio of E/Z was determined by GLPC analysis of the corresponding epoxide of 9.11-dodecadiene-1-yl acetate which was prepared with m-chloroperbenzoic acid; L. M. McDonough, D. A. George, J. Chromat. Sci., 8, 158 (1970). Interestingly, the maximum sex attraction occurs at the level of 88 to 93 % E isomer, and not at 100 % E isomer; C. A. Henrick, Tetrahedron, 33, 1845 (1977). Since the acid mediated β-elimination of β-hydroxy-phenylselenyl compounds proceeds in a trans fashion,[6] the threo/erythro ratio of the precursor is 84/16. The stereochemical control based on heterosubstituted carbanions will be published in due course.

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