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[3,3]Claisen *vs*. [2,3]Wittig Shift in Thermal and Fluolide Ion-Promoted Rearrangements of the *O*- and *C*-Silylated Forms of α-Allyloxy Esters[1)]

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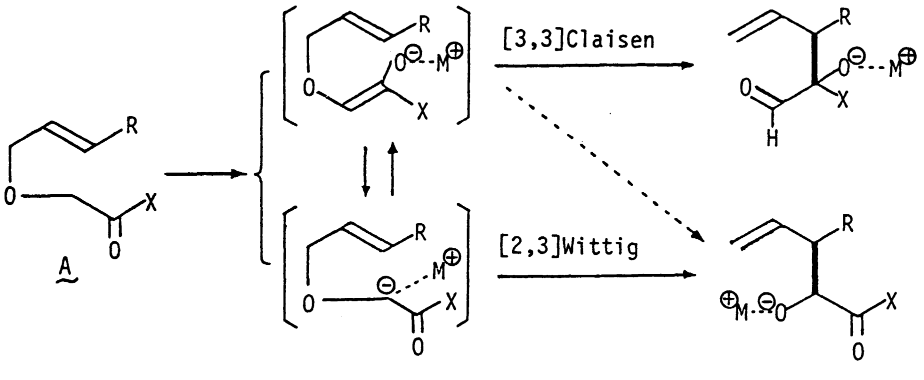
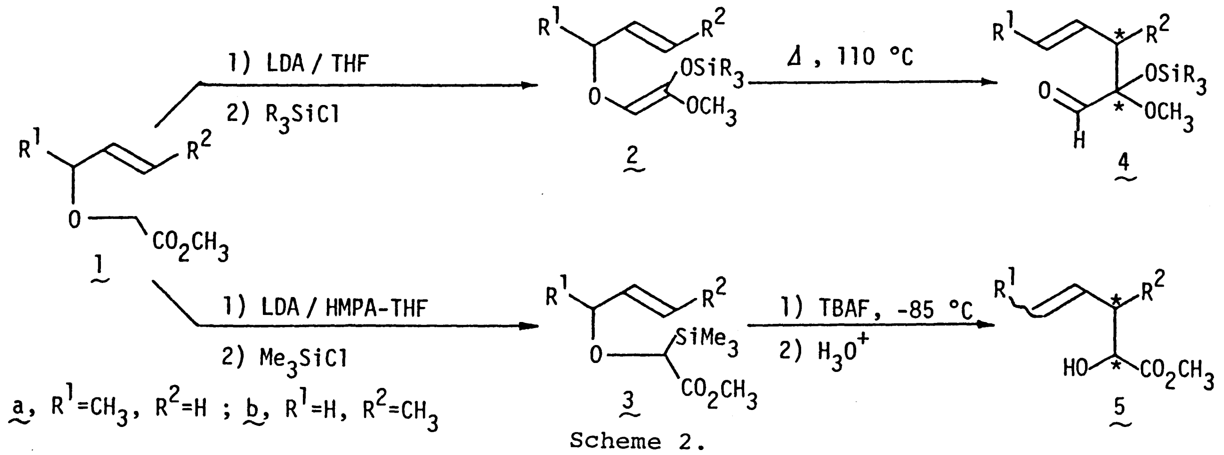
Thermolysis of the *O*-silylated forms of α-allyloxy esters is shown to afford exclusively the [3,3]Claisen products with high stereocontrol. In direct contrast, the fluoride ion-promoted rearrangement of the α-silylated esters gives exclusively the [2,3]Wittig products with moderate stereocontrol.

The sigmatropic rearrangement of metal enolates of α-allyloxy carbonyls (**A**) has been the controversial subject of current studies since the two competing modes of sigmatropic shifts are conceivable as depicted in Scheme 1. While conflicting observations have been reported for ketone enolate rearrangements,[2)] we have reported that the lithium enolates generated from acid **A** (X=OH)[3)] and amide **A** (X=NR$'_2$)[4)] with LDA[5)] in THF undergo exclusively the [2,3]Wittig shift at *ca*. -80 °C, whereas the lithium enolate of ester **A** (X=OR) generated in the same way does not undergo the [2,3]Wittig nor the [3,3]Claisen shift under similar conditions.[1)]



Scheme 1.

In order to obtain an insight into the rather unexpected behavior of the ester enolate terminus, we have now investigated the thermal and fluoride ion-promoted rearrangement of the *O*- and *C*-silylated forms of methyl (α-allyloxy)-acetates (**1**) which may be considered as structurally well-defined "ester enolates". This report discloses that the *O*-silylated forms (**2**) on thermolysis undergo exclusively the [3,3]Claisen shift,[6)] whereas the *C*-silylated forms (**3**) on treatment with tetrabutylammonium fluoride (TBAF), by contrast, undergo exclusively the [2,3]Wittig shift (Scheme 2).



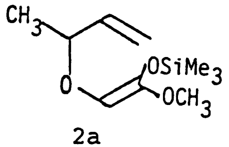
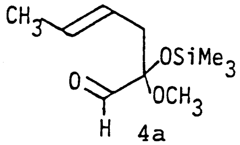
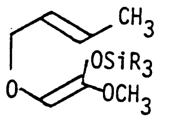
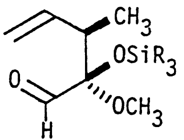
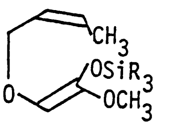
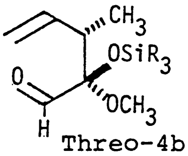
Scheme 2.

The *O*- (**2**) and *C*-silylated forms (**3**) were selectively prepared according to the procedure of Wissner[7)] and Rathke,[8)] respectively. Thus, **1** was treated with LDA in THF at -78 °C and trapped with either trimethylsilyl or *t*-butyldimethylsilyl chloride to afford a nearly quantitative yield of the corresponding acetal **2** with the (*Z*)-geometry (>95%). The exclusive formation of the (*Z*)-isomer is explicable in terms of the well-known chelation control by the α-alkoxy in the lithiation step.[9)] When the lithiation-silylation sequence was performed in HMPA-THF (1 : 4), on the other hand, the *C*-silylated esters (**3**) were obtained, along with a small amount of the [2,3]Wittig products **5** (10–15%).[10),11)]

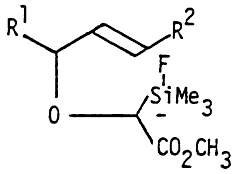
With the two silylated forms in hand, we first carried out thermolysis of the *O*-silylated forms (**2**) under various conditions. Thus, a $CDCl_3$ solution of **2** was heated in a sealed tube at 110 °C to afford an essentially quantitative yield of the corresponding [3,3]Claisen product (**4**) with no evidence of the [2,3]Wittig shift (monitored by ^1H NMR). Table 1 shows representative examples, which reveal the high (*E*)-selectivity with respect to the newly formed double bond and the high diastereoselectivity over the newly created chiral centers.[12)] The high degree of stereocontrol is best explained by essentially the same arguments used to rationalize the comparable stereoselectivity observed for the Ireland-Claisen rearrangement.[13)] Thus, this novel Claisen variant permits the otherwise difficult preparations of a variety of the protected α-keto aldehydes (**4**).

Next, we studied the fluoride ion-promoted rearrangement of **2** and **3** using TBAF as the F^- source. Thus, **3a**[10)] was treated with TBAF (1.0 equiv.) in THF at -85 °C to afford a quantitative yield of the [2,3]Wittig product (**5a**) in a modest (*E*)-selectivity (*E*/*Z* = 78 : 22). A similar reaction of **3b**[10)] provided **5b** in a relatively low diastereoselectivity (erythro/threo = 70 : 30). In contrast, however, similar treatments of **2** with TBAF did not give the [2,3]Wittig nor the [3,3]Claisen product and, after hydrolytic workups, resulted in the complete recovery of **1**.[14)] These observations suggest that the anionic hypervalent *C*-silicon species (**6**) *can* undergo the [2,3]Wittig shift by virtue of its carbanionic character, whereas the *O*-silicon counterpart (**7**) *cannot*. It thus appears very unlikely that the free enolate anion (**8**) would be formed to an appreciable extent from **2** via the O-Si bond cleavage with fluoride ion.[14)]

Table 1. The [3,3]Claisen Rearrangement of 2[a]

Substrate (2) (E / Z)[b]		Time / h[c]	Product (4)[d]	Diastereo-selectivity[e]
 2a		3	 4a	97 : 3[f]
 (E)-2b (93 : 7)	SiR$_3$ = SiMe$_3$	3 (72)[g]	 Erythro-4b	85 : 15 (93 : 7)[g]
	SiR$_3$ = SiMe$_2$Bu-t	3		80 : 20
 (Z)-2b (7 : 93)	SiR$_3$ = SiMe$_3$	5	 Threo-4b	80 : 20
	SiR$_3$ = SiMe$_2$Bu-t	5		80 : 20

a) Unless otherwise noted, the reaction was run at 110 °C in a sealed tube to provide 4 in an essentially quantitative yield (by ^{1}H NMR assay). b) Refers to the geometric ratio of crotyl alcohol used. c) Refers to the time required for the completion. d) The ^{1}H and ^{13}C NMR data were in accord with the assigned structure. For the stereochemical assignment of 4b, see : Ref. 12. e) Determined by ^{13}C NMR analysis. f) Refers to the E/Z-selectivity. g) The reaction was run at 28 °C. In this case 4b was isolated in 78% yield.



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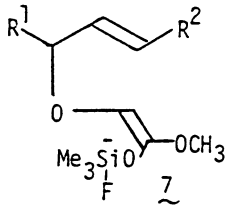

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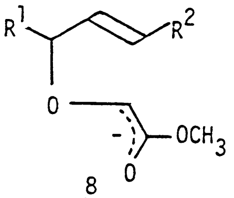

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In summary, this work has demonstrated that the O-silylated forms of α-allyloxy esters undergo the [3,3]Claisen rearrangement at 110 °C, whereas the C-silylated forms on treatment with fluoride ion undergo the [2,3]Wittig rearrangement at -85 °C. The results of this work not only reveal the stereochemical features of the two sigmatropic processes, but also point out the great importance of the "enolate" structure in dictating the operating mode of sigmatropic shift. We are further investigating sigmatropic rearrangements involving different (transition) metal enolates as the migrating termini.

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References

1) Presented at the 50th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1985, Abstr. No. 3036 and 3037 and also at the 3rd IUPAC Symposium on Organometallic Chemistry Directed toward Organic Synthesis, Kyoto, July 1985, Abstr. III-09.

2) a) M. Koreeda and J. I. Luengo, J. Am. Chem. Soc., 107, 5572 (1985); b) J. L. C. Kachinsky and R. G. Salomon, J. Org. Chem., 51, 1393 (1986); c) A. F. Thomas and R. Dubini, Helv. Chim. Acta, 57, 2084 (1974). The three groups have reported that the silyl enol ethers of α-allyloxy ketones undergo the [3,3]-Claisen shift. However, the K-enolates were reported to undergo exclusively the [2,3]Wittig shift by Thomas[2c)] and the [3,3]Claisen shift by Koreeda.[2a)] The reasons for this discrepancy remain unclear. Koreeda also reported that the Li-enolate underwent preferentially the [3,3]Claisen shift, along with 20% of the [2,3]Wittig shift.[2a)]

3) T. Nakai, K. Mikami, S. Taya, Y. Kimura, and T. Mimura, Tetrahedron Lett., 22, 69 (1981).

4) K. Mikami, O. Takahashi, T. Kasuga, and T. Nakai, Chem. Lett., 1985, 1729.

5) Abbreviations: LDA = lithium diisopropylamide; THF = tetrahydrofuran, HMPA = hexamethylphosphoramide.

6) After completion of this work,[1)] S. Raucher and L. M. Gustavson [Tetrahedron Lett., 27, 1557 (1986)] have independently reported a similar [3,3]Claisen rearrangement of 2 (R_3Si = t-$BuMe_2Si$) which was carried out in refluxing toluene; however, no detailed information concerning the stereoselectivity has been reported. They also recorded one example where a Li-enolate, when warmed to 0 °C, underwent the [2,3]Wittig shift.

7) A. Wissner, J. Org. Chem., 44, 4617 (1979).

8) M. W. Rathke and D. F. Sullivan, Synth. Commun., 3, 67 (1973).

9) S. D. Burke, W. F. Fobare, and G. J. Pacofsky, J. Org. Chem., 48, 5221 (1983).

10) The crude samples were employed for the subsequent rearrangements, since all attempts to separate 3 from 5 were unsuccessful.

11) Separate experiments clearly showed that the Li-enolates generated in HMPA-THF underwent rapidly the [2,3]Wittig shift even at -78 °C. The unusual Li-enolate [2,3]Wittig process will be the subject of our subsequent publication.

12) Although no attempt was made to assign the relative stereochemistry of 4b, the well-established chair-like transition state for the Claisen process,[9,13)] coupled with the defined geometries of both double bonds, allows us to make the stereochemical assignments as depicted in Table 1.

13) R. E. Ireland, R. H. Mueller, and A. K. Willard, J. Am. Chem. Soc., 98, 2868 (1976).

14) However, a separate experiment showed that, in the presence of a catalytic amount of TBAF, 2a did undergo an aldol reaction with benzaldehyde at -78 °C in a reasonable yield (41%) as previously reported: cf. I. Kuwajima and E. Nakamura, Acc. Chem. Res., 18, 181 (1985).

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