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NOVEL SILYL TRIFLATE-MEDIATED "[2,3]WITTIG" SIGMATROPIC REARRANGEMENT. THE POSSIBLE INTERVENTION OF AN OXYGEN YLIDE

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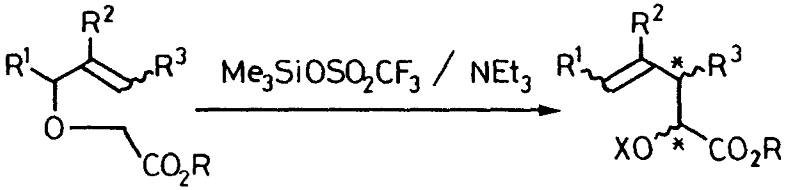
SUMMARY: A novel silyl triflate-mediated [2,3]sigmatropic rearrangement of (allyloxy)acetates and their ketene silyl acetals is described, which is proposed to proceed via rarely precedented oxygen ylides. The formal [2,3]Wittig shift is characterized by the unique stereoselectivity, *i.e.*, the rarely precedented *Z*-selectivity and the high erythro-selectivity.

In the course of studies on enolate [2,3]Wittig rearrangements,[1] we made the unanticipated observation that treatment of (allyloxy)acetates 1 with trimethylsilyl triflate (TMSOTf)[2] under usual silylation conditions gave rise to the [2,3]sigmatropic product 2 (eq 1). The mechanistic and stereochemical features of this novel formal [2,3]Wittig rearrangement are the subject of this communication.



1

2, X= H or SiMe3

(1)

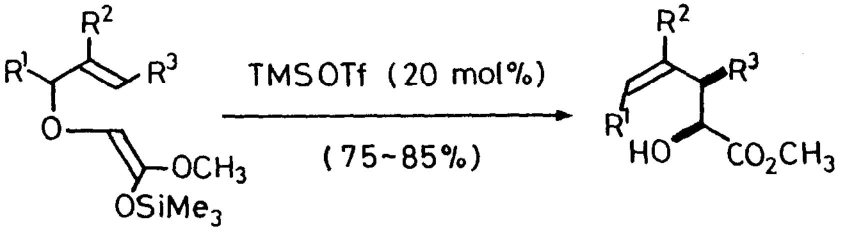
The rearrangement was carried out by simply adding TMSOTf (1.2 equiv) to a mixture of ester 1 and triethylamine (1.1 equiv) in dichloromethane at 0 °C and stirring the mixture at 25 °C for 5-10 h. Hydrolytic workup afforded the hydroxy ester 2 in high yields (Table 1). A similar rearrangement of acids 1 (R=H) was effected with 2.2 equiv of TMSOTf. The TMSOTf-mediated rearrangement is characterized by exclusive [2,3]regioselectivity and unique stereoselectivity. Particularly revealing is the *Z* stereoselectivity observed in the rearrangements creating a di- or trisubstituted olefin; this is in direct contrast to the high *E* selectivity widely observed for [2,3]sigmatropic processes[3] including the dianionic [2,3]Wittig process of 1 (R=H).[1a] In the rearrangements creating vicinal chiral centers the (*E*)-substrate provides a high-to-moderate erythro selectivity (depending on the R group), while the (*Z*)-substrate does not show an appreciable selection. Both the sense and degree of diastereoselection are consistent with those reported for the dianionic [2,3]Wittig process of 1 (R=H),[1a] suggesting that the mechanism of the rearrangement concerned may resemble the carbanionic concerted path.

Table I. Rearrangements of **1** with TMSOTf/NEt_3

substrate	product **2** (X=H)	
	%yield[a]	stereoselectivity[b]
1a: R=CH_3, R^1=CH_3, R^2,R^3=H	93	*E*/*Z* = 31 : 69
1a': R=H[c]	85	43 : 57
1b: R=CH_3, R^1,R^2=CH_3, R^3=H	98	31 : 69
(*E*)-**1c**: R=CH_3, R^1,R^2=H, R^3=CH_3[d]	83	*E*/*T*[e] = 92 : 8
(*E*)-**1c'**: R=H[c,d]	92	88 : 12
(*Z*)-**1c** : R=CH_3[d]	86	53 : 47
(*E*)-**1d**: R=*i*-Pr, R^1,R^2=H, R^3=CH_3[d]	86	95 : 5
(*E*)-**1e**: R=*t*-Bu, R^1,R^2=H, R^3=CH_3[d]	56[f]	88 : 12[f]

[a] Isolated yields (not optimized yet). [b] Determined by ^{13}C NMR and/or GLC analysis after conversion of the product to the corresponding methyl ester **2** (R=CH_3). For the stereochemical assignments, see: ref 1a. [c] The actual substrate should be the silyl ester **1** (R=$SiMe_3$). [d] The geometric purity was of 93%. [e] *E*/*T* = erythro : threo. [f] The product obtained was the hydroxy acid which arises obviously from the rearrangement of the silyl ester **1c** (R=$SiMe_3$) once formed via the known elimination of *t*-Bu with TMSOTf (ref 4a).

Any mechanisms advanced for the novel rearrangement must be initiated by the *O*- (and *C*-)silylation of **1** with TMSOTf.[2,4] In fact, we found that the ketene silyl acetal (**3**) independently derived from **1**[5] underwent the [2,3]-shift *even with a catalytic amount of TMSOTf at -72 °C to provide a higher degree of either Z or erythro selectivity* (eq 2). Taken as a whole these observations, coupled with the known reactivity of TMSOTf,[6] lead us to suggest a rarely precedented oxygen ylide[7] such as **5** as a reasonable rearranging species which would be generated from the silyloxonium salt **4** (Scheme 1).[8]



(2)

3a; R^1=CH_3, R^2, R^3= H

3b; R^1, R^2= CH_3, R^3= H

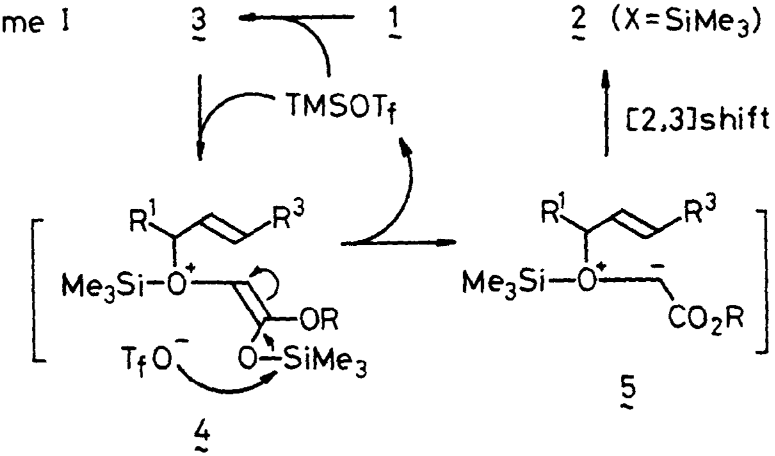
3c; R^1,R^2= H, R^3= CH_3 (93% *E*)

2a, 81% *Z*

2b, 75% *Z*

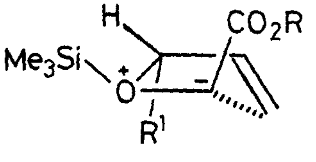
2c, 97% erythro

Scheme I

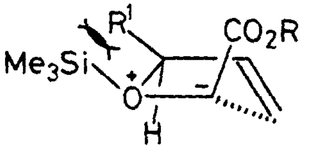


In order to confirm the ylide mechanism we explored the rearrangement of the silyl acetal (3) with *t*-$BuMe_2SiOTf$ (1.5 equiv) at -95 °C for 30 min and then at -65 °C for 3 h (monitored by GLC). We found that the γ-methylallyl derivative (3c) afforded the [2,3]-rearranged product 2c (X=$SiMe_2Bu$-*t*) as the *sole* product, whereas the α-methylallyl derivative (3a) *did not* definitely due to a large steric interaction between the α-methyl in 3a and entering bulky silyl group. These finding strongly suggest that the formation of the oxonium salt 4 is essential for the rearrangement.

Finally, it should be emphasized that the proposed mechanism nicely accomodates the stereochemical outcomes described above, especially the unusual Z stereoselectivity. Of the two possible conformations A and B[9] where $SiMe_3$ occupies the sterically favorable exo orientation, the former should be sterically *less* constrained, since the latter suffers the large eclipsing interaction of $R^1 \leftrightarrow SiMe_3$.



A → (Z)-olefin



B → (E)-olefin

In summary, we have established an entirely new type of "enolate [2,3]Wittig" rearrangement that is promoted by silyl triflates. We believe that this involves the unprecedented silyloxonium ylide as the key species. Compared with the conventional carbanionic methodology, the TMSOTf-mediated methodology has the advantage of avoiding strongly basic conditions. We are continuing to explore the synthetic and mechanistic aspects of the present sigmatropic methodology.

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References and Notes

(1) (a) Nakai, T.; Mikami, K.; Taya, S.; Kimura, Y.; Mimura, T. *Tetrahedron Lett.*, **22**, 69 (1981). (b) Mikami, K.; Fujimoto, K.; Nakai, T. *ibid.*, **24**, 513 (1983). (c) Mikami, K.; Fujimoto, K.; Kasuga, T.; Nakai, T. *ibid.*, **25**, 6011 (1984). (d) Mikami, K.; Takahashi, O.; Kasuga, T.; Nakai, T. *Chem. Lett.*, **1985**, 1729.

(2) For reviews on the synthetic utility of TMSOTf, see: Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron*, **37**, 3899 (1981). Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Götz, A.; Hergott, H. H.; Hofmann, K.; Kober, W.; Krageloh, K.; Oesterle, T.; Steppan, W.; West, W.; Simchen, G. *Synthesis*, **1982**, 1.

(3) (a) For a review on [2,3]Wittig sigmatropic rearrangements, Nakai, T.; Mikami, K. *Chem. Rev.*, in press. (b) For reviews on stereochemistry of [2,3]sigmatropic variants, see: Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.*, **18**, 563 (1979); Nakai, T.; Mikami, K.; Sayo, N. *J. Synth. Org. Chem., Jpn.*, **41**, 100 (1983). For one exception exhibiting a high *Z* stereoselectivity, see: Still, W. C.; Mitra, A. *J. Am. Chem. Soc.*, **100**, 1927 (1978).

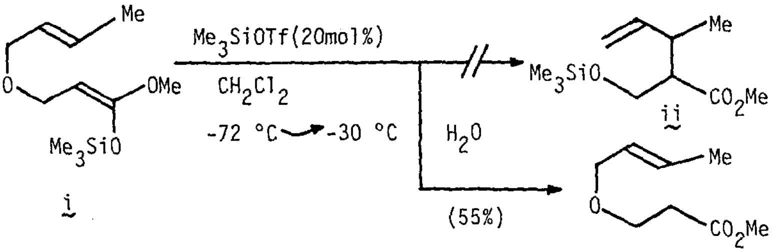
(4) Silylation of α-alkoxy esters with TMSOTf/NEt_3 has been reported to give a mixture of the ketene silyl acetal and the α-silylated ester which are interconvertible via TMSOTf catalysis: (a) Wissner, A. *J. Org. Chem.*, **44**, 4617 (1979). (b) Bergulya, J.; Bernauer, K. *Synthesis*, **1980**, 545.

(5) The (*Z*)-silyl acetal **3** was prepared from **1** according to the standard lithiation/silylation procedure (LiN(*i*-Pr)$_2$, THF, -72 °C/Me_3SiCl). Particularly notable is that the lithium enolate thus generated is not capable of undergoing the [2,3]sigmatropic shift under the lithiation condition, in sharp contrast to the fact that the dilithium enediolate generated from **1** (R=H) *does* undergo rapid [2,3]shift under the same condition.[1a]

(6) The ability of TMSOTf to silylate an ether-oxygen is amply precedented (ref 2).

(7) For [2,3]sigmatropic shifts involving oxygen ylides generated via carbene addition to allylic ethers, see: (a) Doyle, M. P.; Griffin, J. H.; Chinn, M. S.; Leusen, D. *J. Org. Chem.*, **49**, 1917 (1984). (b) Ando, W.; Kondo, S.; Nakayama, K.; Ichibori, K.; Kohoda, H.; Yamato, H.; Imai, I.; Nakaido, S.; Migita, T. *J. Am. Chem. Soc.*, **94**, 3870 (1972). (c) Kirmse, W.; Kapps, M. *Chem.Ber.*, **101**, 994 (1968).

(8) Alternatively, **2** (X=$SiMe_3$) might be formed directly via an intramolecular S_N2' reaction of **4**. The possibility can be excluded by our separate observation that a similar reaction of the homologous ketene silyl acetal **i** totally failed to produce the substitution product **ii**, instead resulting in the recovery of the ester after hydrolytic workup.



(9) For a general discussion of the transition state model for the [2,3]-sigmatropic rearrangement, see: Mikami, K.; Kimura, Y.; Kishi, N.; Nakai, T. *J. Org. Chem.*, **48**, 279 (1983), and references cited therein.

(10) On the basis of this type of transition state geometries, the high erythro selectivity described above is also explicable by essentially the same argument used to rationalize the erythro selectivity previously observed for related enolate [2,3]Wittig processes (ref 1).

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