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THERMAL 1,5-REARRANGEMENT OF A SILYL GROUP FROM OXYGEN TO CARBON

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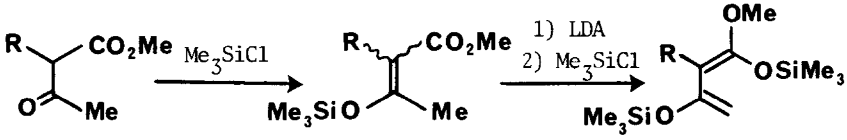
Abstract. Trialkylsilyl ethers of 1,1-dioxygenated butadienes, substituted at position 3 by electron releasing substituents, undergo thermal rearrangement with 1,5-migration of the silyl group from oxygen to carbon.

This communication reports the 1,5-migration of silicon from oxygen to carbon, a process without literature precedent. The reaction appears to be general for trialkylsilyl ethers of 1,1-dioxygenated butadienes containing electron donating substituents in the 3-position.

As part of our work on the synthesis of natural polycyclic quinones[1,2] we are exploring the involvement of 1,1,3-trioxygenated butadienes in Diels-Alder reactions. Following recent studies on β-keto esters [3-7] such dienes are accessible by silylation of the dienolate ions of 3-oxy-2-butenoates. We and others[6] have noted the thermal instability of such dienes, which in some cases has precluded their purification by distillation.



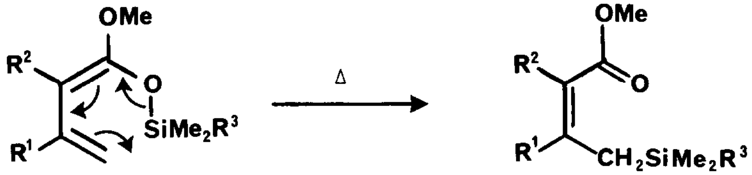
Scheme 1

Preparation of the parent diene (1)[3] according to Scheme 1 gave only one isomer detectable by n.m.r. spectroscopy ($CDCl_3$). This could be distilled safely below 80°, the vinyl methylene group showing characteristic ^{13}C and ^{1}H resonances (δ 89.22; 4.14, 3.94 respectively).

On being heated at 120°C for 1 h this diene smoothly rearranged to a new αβ-unsaturated ester (6) (Table 1) [ν_{max} 1710, 1600 cm^{-1}; λ_{max}(cyclohexane) 243 nm (ε 11,340)]. Its silyl-substituted methylene group showed appropriate ^{13}C and ^{1}H resonances (δ 26.62; 2.42 respectively), there was only one vinyl methine (95.12; 4.95) and the remaining resonances were consistent with structure. It was assigned (E)-stereochemistry following consideration of the mixture of (E)- and (Z)-(6) obtained by direct C,O-bis-silylation of the dianion of methyl acetoacetate.[3] [For the (Z)-isomer δ_{CH_2} 30.65; 1.64.]

The efficiency of the rearrangement (1 → 6) and its apparent stereospecificity require intramolecular 1,5-migration of silicon from oxygen to carbon. This rearrangement, whose closest analogy is in 1,5-silyl migration from oxygen to oxygen[8], requires the stereochemistry of the rearranging diene to be as shown in Table 1. Unlike the literature analogy, however, the process involves replacement of a strong O-Si bond by a weaker C-Si bond.[9] Thermodynamic compensation presumably arises from concomitant formation of the conjugated ester group.

Table 1: Thermal 1,5-Rearrangements



Diene	R^1	R^2	R^3	Product	Yield (%)
(1)[3]	Me_3SiO	H	Me	(6)	70
(2)[A]	Me_3SiO	Me	Me	(7)	90
(3)[1,A]	Me_3SiO	MeO	Me	(8)	86
(4)[B]	Me_3SiO	H	Bu^t	(9)	75
(5)[7]	Me	H	Me	(10)	14

[A] Presence of minor geometrical isomer (up to 10%) from ^{13}C and ^1H n.m.r. spectra.
[B] Hexamethylphosphoramide (1.2 eq) cosolvent used in preparation of this diene.

In order to determine the scope of this novel reaction dienes (2)-(5) were prepared by adaptation of Scheme 1 and were satisfactorily distilled at temperatures below 60^o. Thus purified, all underwent similar rearrangement to esters (7)-(10) respectively when heated at $150\text{-}165^o$ for 30 min (Table 1). The 2-methyl and 2-methoxy dienes (2), (3) reacted the most readily, whilst for the 3-methyl diene (5) slow rearrangement was complicated by competitive decomposition. Dienes which lacked an electron donating substituent at C-3 $[CH_2{=}CHCH{=}C(OMe)\text{-}OSiMe_2Bu^t]$ or lacked dioxygenation at C-1 $[CH_2{=}C(OSiMe_3)CH{=}CHOSiMe_3]^{10}$ could not be rearranged, prolonged heating leading to intractable gums.

Satisfactory elemental analysis and spectroscopic data have been obtained for all new compounds reported in this work. We acknowledge financial assistance from the Australian Research Grants Committee.

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