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REVERSIBLE 1,4 MIGRATION OF A SILYL GROUP FROM OXYGEN TO CARBON: AN UNEXPECTED ROUTE TO α-TRIALKYLSILYL KETOXIMES

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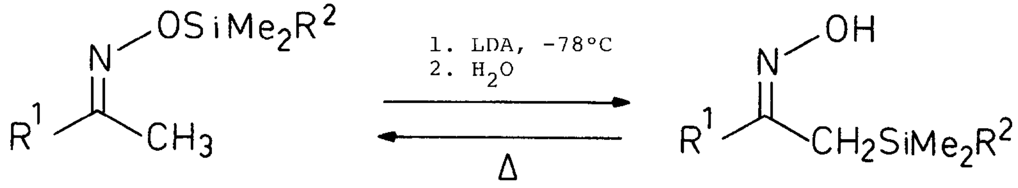
Summary: Anions generated from trialkylsilyl ethers of methyl ketoximes (1) undergo anionic rearrangement with 1,4 migration of the silyl group. After protonation, the resulting α-trialkylsilyl ketoximes (2), suffer thermal rearrangement with 1,4 migration of the silyl group from carbon to oxygen.

As a part of a wider project related to Beckmann rearrangement and fragmentation we needed several ketoximes O-silyl ethers as starting materials. To this end we decided to investigate the direct alkylation of the enolate-like anions of the corresponding methyl ketoxime-O-silyl ethers[1] which we expected to occur regioselectively as proven for oximes and derivatives.

Once the initial experiments were carried out it inmediately became evident that extensive rearrangements were taking place under our working conditions (vide infra)



(1) (2)

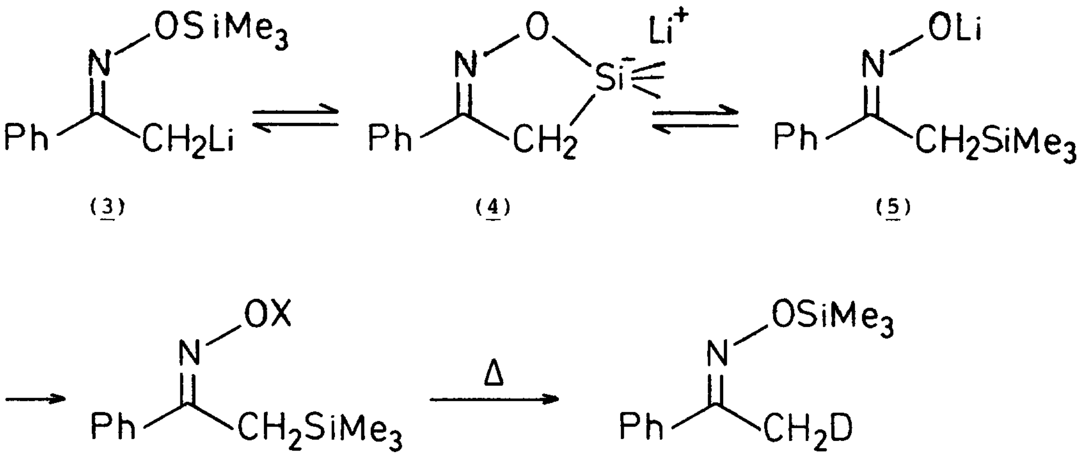
a, R^1= Ph, R^2= Me; b, R^1= t-Bu, R^2= Me; c, R^1= Ph, R^2= t-Bu

In fact, 1,n anionic migrations of silyl groupings are a class of well-known processes prone to occur with decreasing ease in the order 1,2 >1,3≫1,4 or 1,5[2]. However, to our knowledge, only one intramolecular 1,4 anionic shift of a silyl group from oxygen to carbon has been previously reported[3].

In this communication we would like to report that the silyl group of methyl ketoxime-O-silylethers (1) suffers a 1,4 intramolecular anionic shift from oxygen to the syn α-carbon with extreme ease. This provides a unique and very simple entrance to the otherwise difficult-to-obtain α-trialkylsilyl ketoximes (2).

Thus treatment of methyl ketoxime-O-silylethers (1a,b) with LDA at -78°C for one hour, followed by quenching with water, drying and final evaporation under vacuum, yielded (2a,b)[4,5] in excellent yield (up to 98%). (1c) rearranges more slowly and after 12 hr at room temperature a mixture of (1c) and (2c)(30:70)[6] is obtained. In this case free oxime could not be detected in the reaction mixture in accordance with the known resistance of t-butyldimethylsilylethers towards hydrolysis[7].

The reaction appears to be limited to the silylethers of methyl ketoximes having anti configuration, failing completely with oxime silylethers not having these characteristics[8,9].



(3) (4) (5)

(6a-c) (7a)

a, X= D; b, X= SiMe$_3$; c, X= SiMe$_2{}^t$Bu

(scheme 1)

Presumably the rearrangement occurs through the intermediate formation of a pentavalent silicon anion (4)[2,10], thus establishing an effective equilibrium between the starting carbanion (3) and the oximate anion (5). Undoubtely the replacement of a strong O-Si bond by a weaker C-Si bond finds the necesary driven force on the formation of a strongly covalent O-Li bond (hard-hard) from the C-Li bond (soft-hard). Accordingly, quenching the reaction mixture at -78°C with D_2O, Me_3SiCl or *t*-$BuMe_2SiCl$, afforded the corresponding oxime derivatives (6a-c)^{11}(scheme 1). On the other hand, as expected, quenching (Me_3SiCl) at -78°C of the reaction mixture resulting after treatment of (1c) with LDA, lead only to (6c).

Thus the assumed intramolecularity of the 1,n anionic rearrangement could not be demonstrated by the appropiate crossover experiments being the rate constants so highly dependent of steric volume of the silicon substituents^{3}.

Furthermore, we have also found that the reverse process (2 ⟶ 1) can be driven quantitatively to the O-trialkylsilyl ketoximes (1) upon heating at 100°C for several minutes or upon attempted distillation of (2).

This 1,4 carbon-to-oxygen silyl shift can be succesively monitored by ^{1}H n.m.r. spectroscopy at room temperature (probe temperature 35°C), thus allowing the relative stability of (2) to be determined^{12} .

As expected, (6b) and (6c) were found not to rearrange upon heating for an extended period of time.

To test for the intramolecularity of this thermal rearrangement (2 ⟶ 1) we have performed two different experiments. Firstly, an equimolar mixture of (6b) and acetophenone oxime kept at 35°C for ten hours which did not show observable change. Secondly, an equimolar mixture of (2b) and acetophenone oxime under the above conditions which lead to the unambiguous formation of (1b), no crossover products (2a) or (1a) being detected.

Further investigations to underline the synthetic utility of α-trialkylsilyl oximes is underway.

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4.- n.m.r. analysis of these crude materials proved them to be, at least, 95% pure (2a,b). Ketoxime O-silyl ethers (1a,b) and the corresponding free ketoximes, presumably products of hydrolysis, account for the remaining 5%

5.- (2a,b) show typical ^{13}C and ^{1}H n.m.r. resonances in comparison with (1a,b). Spectral data in $CDCl_3$ (TMS) are given below. (1a) (δ 12,31; 2,25 ppm,

respectively) CH_3; (-0,56; 0,26) $OSiMe_3$; (2a) (18,85; 2,39) CH_2Si; (-0,58; 0,02) $Si(CH_3)_3$; (1b) (10,18; 1,82) CH_3; (-0,70; 0,17) $OSi(CH_3)_3$; (2b) (17,15; 1,82) CH_2Si; (0,17; 0,07) $Si(CH_3)_3$

6.- The percentage of (2c) was found to be only 5% after treatment of (1c) with LDA at -78°C for one hour. An aproximate (1:1) mixture of (1c:2c) was shown to be present (^{1}H n.m.r.) after standing at room temperature for 3 hours (anion generated at -78°C)

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8.- Both acetophenone and pinacolone oximes exist almost exclusively in a single anti form; see for example: G.E. Hawkes, K. Hervig, J.D. Roberts, J. Org. Chem., 39, 1017(1974)

9.- Ketoxime O-silyl ethers arising from cyclohexanone, 2-methyl cyclohexanone, 4-*t*-butyl cyclohexanone and 5-nonanone did not rearrange under our working conditions

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11.- All new compounds had satisfactory microanalytical data and|or spectroscopic properties

12.- (2a) $t_{1|2}$ = 7 hr; (2b) $t_{1|2}$ = 1,5 hr; (2c) $t_{1|2}$ = 150 hr at 35°C. $t_{1|2}$ refers to the time required to achieve a 50% transformation of (2) to (1) as determined by integration of the proper signals in their ^{1}H n.m.r. spectra. Interestingly, C-silyl ketoximes (2) are stable for periods up to a month without observable change, on storage at -40°C

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