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ANIONIC 1,4 O→C SILYL REARRANGEMENTS

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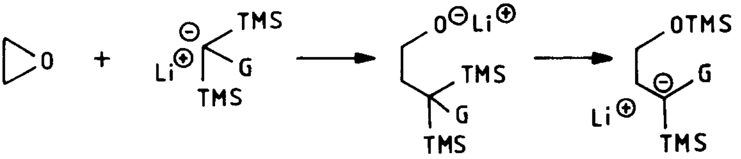
Summary: γ-Silyloxy-alkyl phenyl thioethers are transformed into γ-silylalcohols by treatment with lithium di-tert-butylbiphenyl.

In the preceding communication[1] the 1,3 O→C migration of silyl groups in carbanions made by deprotonation of ketone silyl enol ethers was described. In the present note similar anionic 1,4 O→C silyl migrations are reported.

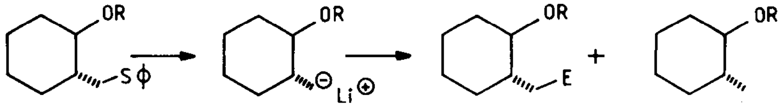
Anionic 1,4 C→O silyl shifts are known to occur when epoxides are opened by methyllithiums substituted by a TMS and at least one other strongly anion stabilizing group[2,3].



G = TMS[2)]
= $S\phi$[3)] (eq. 1)

Relief of steric crowding may contribute to the driving force of this reaction. The reverse reaction, though postulated[2], was not observed.

Lithium di-tert-butylbiphenyl (LiDBB)[4] enabled us routinely to produce nonstabilized primary carbanions 2 containing a γ-alkoxy or γ-silyloxy substituent.



(eq. 2)

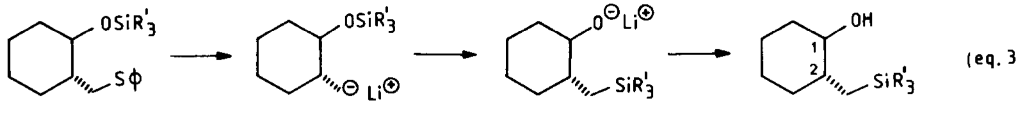
1 2 3 4

	a	b	c	d
R	H	Me	TMS	TIPS

E = D, CO_2H, CO_2Me, TMS, OH

Thus when 1b[5] is treated at -78° in THF with LiDBB, within seconds the C_{alkyl}-S bond is cleaved, and the organolithium 2b formed in high yield can be converted to products 3 by addition of an electrophile, e.g. D_2O, CO_2, $ClCO_2Me$, TMS-OTf, O_2 and appropriate workup[6] (yield e.g. 80 % for 3b, E = CO_2H), 4b being a minor byproduct (~10 %).
With 1c rapid reaction with LiDBB is observed as before. Addition of an electrophile, however, does not produce 3c, 6a is isolated instead in 73 % yield, 4a is a minor component.

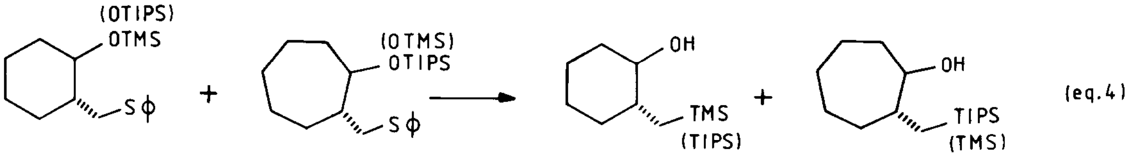
This SiR'_3 migration is very fast: 6a and 4a were isolated as the sole products when it was tried to quench 2c by excess CO_2 5 sec after addition of LiDBB to 1c, all at -78°. Even when TMS was replaced by the sterically demanding TIPS group7), monitoring the appearance of 9a by GC showed that of all 9a formed (85 % isolated) 88 % appeared within the first 5 min after addition of LiDBB to 1d at -78°. This is in marked contrast to the only known case of an anionic 1,4 O→C Si rearrangement8), where the $SiMe_3$, but not the $SiEt_3$ group was found to migrate.



1c 2c 5 6a R' = Me

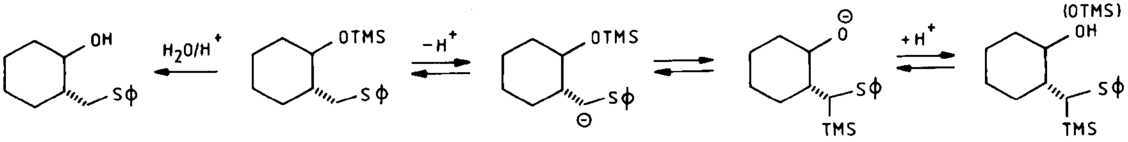
d d 9a = iPr

The Si migration probably occurs via intramolecular nucleophilic substitution at Si (e,e-conformation), as demonstrated by crossover experiments. Thus an equimolar mixture of 1c and 7d (1d and 7c) yielded 6a and 8a (9a and 10a) only (GC, NMR). Analogous mechanisms involving pentacoordinate Si were proposed recently for 1,4 O→O9a), 1,5 O→O9b) and 1,4 C→C silyl migrations9c).



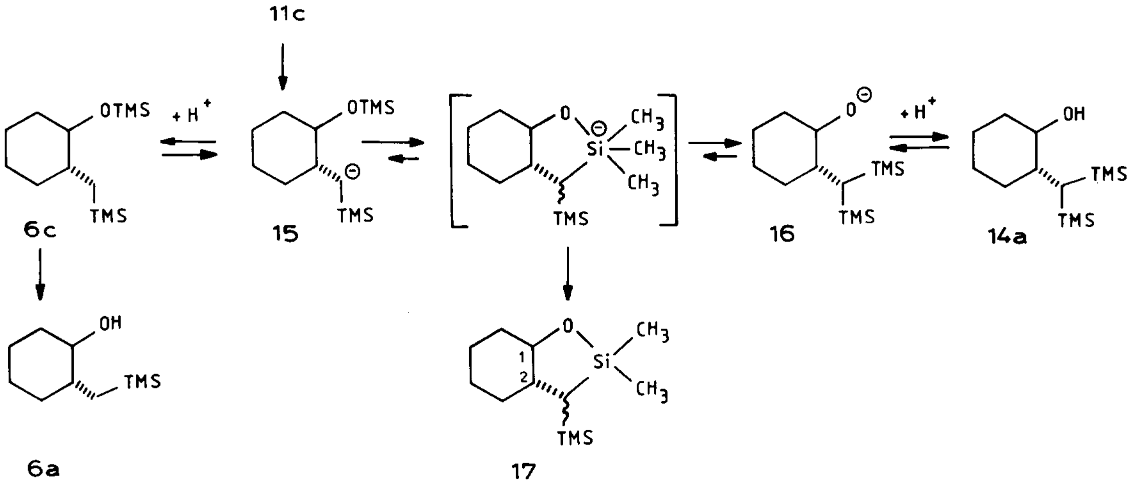
1c(d) 7d(c) 6a(9a) 8a(10a)

This 1,4 O→C silyl shift is not restricted to a primary carbanion migration terminus. Thus 11a10) was obtained when 1c was treated with tBuLi/HMPA11). In this case the carbanion (12) and the alkoxide (13) seem to be in equilibrium: When 11a was deprotonated by 1 eq nBuLi at -15° in THF and then stored at the same temperature for up to 15 hr, 11a was completely recovered after aqueous workup. When, on the other hand, 10 % HMPA were added to the THF solution of 13, treatment with aqueous acid after 2 or 18 hr yielded a 1.2 : 1 mixture of 11a and 1a12). Thus if the ratio 11a : 1a is taken as a measure of the ratio 13 : 12 (i.e. if protonation is much faster than equilibration13)), the anion stabilizing influence of -Sϕ

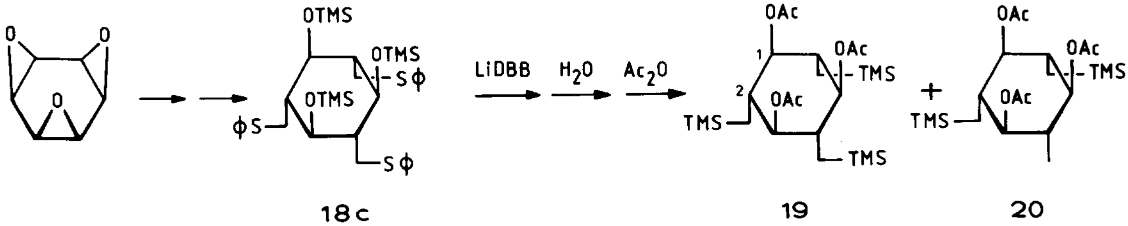


1a 1c 12 13 (eq.5) 11a(c)

is clearly seen by comparing eq. 5 and eq. 3 . Similarly 11c on treatment with LiDBB furnished 14a cleanly (91 %). When this alcohol, however, was deprotonated with 1 eq nBuLi in THF/HMPA, no trace of 6c or 6a could be detected. Obviously the equilibrium 15⇌16 lies far on the right side due to the poor stabilization of carbanion 15 by only one TMS group2). That the alkoxide oxygen in 16 does attack the Si is seen in the slow formation of 17 (mixture of diastereomers, ~ 15 % conversion after 2 d at -15°).



The 1,4 O→C Si migration may be of preparative interest. Thus the all-trans substituted cyclohexane derivative 19, which is not obtainable from cis-benzene trioxide directly, was formed from 18c14) in 36 % yield (not optimized) along with 8 % 20 and other minor products.



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4. P.K.Freeman and L.L.Hutchinson, J.Org.Chem. 45 (1980), 1924. We found that this reagent readily forms organolithiums from phenylthioalkanes (within fractions of seconds at -78°), for which purpose Li metal, Na naphthalene or its dimethylamino derivative were used hitherto, requiring longer reaction times and/or higher temperatures [C.G.Screttas and M.Micha-Screttas, J.Org.Chem. 43 (1978), 1064; T.Cohen and J.R.Matz, J.Am.Chem.Soc. 102 (1980), 6900; D.J.Ager, J.Org.Chem. 49 (1984), 168].
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6. The structures of all new compounds are confirmed by spectral data (^{1}H-NMR, MS and IR) as well as by derivatization of product alcohols to acetates. E.g. ^{1}H-NMR ($CDCl_3$, 250 MHz): 6a: 3.06 dt (1-H), 1.92-0.8 m (10H), 1.06 dd (A) and 0.25 dd (B)(α-CH_2), -0.01 s ($SiMe_3$), $J_{1,2}$= 9.6, $J_{1,6}$= 9.6, $J_{1,6'}$= 4, $J_{2,A}$= 3.5, $J_{2,B}$= 10.5, $J_{A,B}$= 14; 17 (major diastereomer): 3.12 td (1-H), 2.15-2.08 m (9H), 0.20 s (Me), 0.18 s (Me), 0.02 s ($SiMe_3$), -0.02 d (α-CH), $J_{1,2}$= 10.5, $J_{1,6}$= 10.5, $J_{1,6'}$= 4, $J_{2,\alpha\text{-CH}}$= 12.8; 19: 4.71 t (1(3,5)-H), 2.06 s (3 OAc), 1.78 tt (2(4,6)-H), 0.42 d (3 CH_2), -0.04 s (3 $SiMe_3$), $J_{1,2}$= 10.5, J_{2,CH_2}= 4.2 [δ, ppm, Hz]
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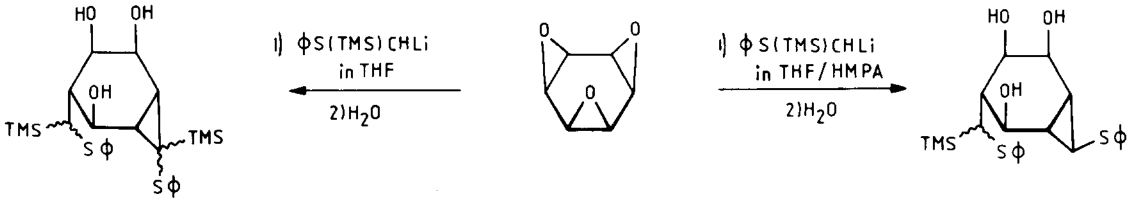

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