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Preliminary communication

STABILIZATION OF A CARBANION BY α-Me_3Si GROUPS. THE KINETIC ACIDITY OF TRIS(TRIMETHYLSILYL)METHANE

COLIN EABORN*, RUDOLF EIDENSCHINK, PATRICIA M. JACKSON and DAVID R.M. WALTON
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

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Summary

In $Me_2SO/H_2O/KOH$ at 50°C, $(Me_3Si)_3C^3H$ undergoes detritiation about 5-7 times as rapidly as Ph_3C^3H, indicating that α-Me_3Si groups substantially stabilize carbanions.

The metallation which occurs at C—H bonds α to Me_3Si groups [1,2] can reasonably be attributed to some stabilization of the carbanions by $(p\rightarrow d)_\pi$ interaction with the silicon atom. Such stabilization was considered to contribute to the low reactivity of $(Me_3Si)_3CLi$ [2], but steric effects probably dominate in this case. Steric effects also account for the fact that additional α-Me_3Si groups hinder the base cleavage of a C—$SiMe_3$ bond [e.g. $PhCH(SiMe_3)_2$ is less reactive than $PhCH_2SiMe_3$] in spite of the expected additional stabilization of the separating carbanion [3].

Recently ab initio calculations in this School indicated that the α-H_3Si group should substantially stabilize a carbanion, possibly more so than an α-Ph group [4], and there is recent indirect evidence from preparative studies that an α-Me_3Si does stabilize more than an α-Ph group [5]. To obtain direct information we have now compared the kinetic acidities of $(Me_3Si)_3CH$ and Ph_3CH.

With Ph_3C^3H, detritiation in a mixture of Me_2SO(6 vol) and 1.0 *M* aqueous KOH (1 vol) at 50°C gave a good first-order plot to more than 75% completion of reaction, with a residual count of <5% of the initial count; the first order constant is 3.6×10^{-5} s^{-1}. With $(Me_3Si)_3C^3H$, in a period equal to 25 times that for loss of the first 25% count the count fell by only 75%, i.e. there was an unexpected residual activity of ca. 25%, though this "residual" count continued to fall slowly. The residual count of ca. 25% could in principle be due to contamination of the $(Me_3Si)_3C^3H$ by material tritiated in a Me_3Si group, and effectively inert. A first order plot based on this extreme assumption is linear to about

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*To whom correspondence should be addressed.

70% reaction and corresponds with a rate constant of 2.3×10^{-4} s^{-1}. However, GLC analysis showed that $(Me_3Si)_2CH_2$ was formed, and the residual count is probably mainly due to conversion of $(Me_3Si)_3C^3H$ into $(Me_3Si)_2CH^3H$ at a rate equal to about one-quarter of that of the exchange. On this assumption and the further simplifying assumption that the $(Me_3Si)_2CH^3H$ is effectively inert to exchange, the first order plot is linear to about 65% of reaction and corresponds to a rate constant of 1.9×10^{-4} s^{-1}. If the residual count is ignored, and the assumption made that the count is tending to zero, the first order plot is linear over only about 35% of reaction, and the corresponding rate constant is ca. 1.8×10^{-4} s^{-1}. Probably the $(Me_3Si)_3C^3H$ both contained inert tritiated material and gave $(Me_3Si)_2CH^3H$, with the latter undergoing detritiation at a significant rate, but further analyses seems unprofitable, since the uncertainties do not cast doubt on the conclusion that $(Me_3Si)_3C^3H$ undergoes exchange about 5-7 times as fast as Ph_3C^3H.

This evidence that the kinetic acidity of $(Me_3Si)_3CH$ is greater than that of Ph_3CH does not necessarily mean that the equilibrium acidities would be in this order, though this is likely. Furthermore, since for steric reasons the 3 phenyl groups in the Ph_3C^- ion are thought to be unable to exert their maximum delocalizing potential, the acidity of Me_3SiCH_3 would not necessarily be greater than that of $PhCH_3$. It is clear, however, that α-Me_3Si groups can substantially stabilize carbanions.

The fairly ready cleavage of $(Me_3Si)_3CH$ to $(Me_3Si)_2CH_2$ is itself a reflection of the influence of the Me_3Si groups in stabilizing the $(Me_3Si)_2HC^-$ anion.

Experimental

Materials

The sample of Ph_3C^3H was made by adding tritiated water to Ph_3CLi obtained by treating Ph_3CH with n-BuLi in ether/THF. The product was recrystallized from methanol to constant activity (1580 c.p.s./mg).

The $(Me_3Si)_3C^3H$ (activity 8680 c.p.s./mg) was made analogously from $(Me_3Si)_3CLi$ obtained by metallation of $(Me_3Si)_3CH$ with MeLi in THF/Et_2O [2]. It had b.p. 216°C and GLC revealed no impurity.

Rate measurements

A solution of the tritiated material (ca. 5 mg) in Me_2SO (30 ml) at 50°C was mixed with 1.0 *M* aqueous KOH (5 ml) and the mixture was placed in a thermostat at 50.0°C. At appropriate intervals 1 ml aliquots were withdrawn and added to a mixture of water (20 ml) with toluene (10 ml) containing a scintillator [6]. The toluene layer was washed with water (3 × 20 ml) and dried, and a 5 ml sample taken for counting.

For $(Me_3Si)_3C^3H$, a typical pattern of the variation with time (min. unless otherwise indicated) of the percentage count (in parentheses) was as follows: 0 (100); 10(90); 20(80); 30(72.5); 50(60); 60(55); 70(51); 80(48); 100(44); 130(41); 6 h(27); 24 h(25); 48 h(23). If the residual activity is due to formation of $(Me_3Si)_2CH^3H$ at a rate 0.25 that of the exchange, when the count has fallen to $(100-x)$%, the proportion, P, of $(Me_3Si)_3C^3H$ which has lost its tritium is given by $(100-x)/(100-0.25x)$; a plot of log $(1-P)$ against time is linear down to $P = 0.35$ (i.e. 65% exchange).

Products

GLC analyses (5% Carbowax M) of the mixture obtained from $(Me_3Si)_3CH$ after about 15 h revealed that in addition to $(Me_3Si)_3CH$ some $(Me_3Si)_2CH_2$ was present, this was identified by its retention time and mass spectrum in a linked GLC-mass spectrometer system. [The peak of highest mass was at 145 ($M - 15$) (strong), just as that from $(Me_3Si)_3CH$ was at 217 ($M - 15$)].

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