Configurational Stability of the Silyl Anion

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Summary The nonequivalence of the diastereotopic isopropyl methyl groups in di-isopropylphenylsilyl-lithium up to 185 °C indicates that the barrier to inversion about silicon in the silyl anion is > 24 kcal mol^{-1}.

No experimental barrier or limits to the barrier to inversion about silicon in the silyl anion have been reported.[1] The entire literature consists of an LCAO–MO–SCF calculation on SiH_3^-.[2] We report the first experimental studies on the silyl anion, leading to the calculation of a lower limit to the barrier. We utilize the n.m.r. method rather than the optical activity method, since decay of optical activity of the anion cannot be measured directly. Any attempt to observe loss of optical activity in materials formed from the silyl anion suffers from the threefold problems of racemization during formation of the anion, lack of knowledge of the exact stereochemistry of the product-forming reactions, and lack of accurate knowledge of the optical purity of the products.[3] None of these difficulties exists in the equilibrium n.m.r. method, which utilizes groups whose diastereotopic nature relies on the configurational stability of the silyl anion. Diastereotopic groups have previously been observed in the presence of chiral tetraco-ordinate silicon,[4] but the experiments described below provide the first example of diastereotopic groups caused by trico-ordinate, negatively charged silicon.

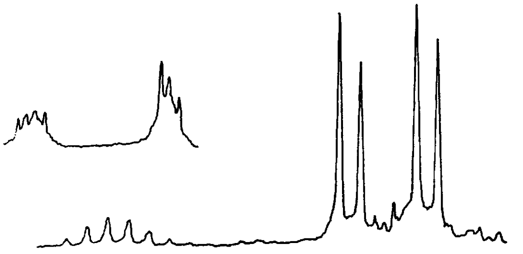

FIGURE. The 270 MHz ^1H n.m.r. spectrum of di-isopropylphenyl-lithium (0·32 M) in $[^2H_8]$-tetrahydrofuran at 40 °C. The phenyl resonances are given as an inset. The splitting of each methyl resonance is 7·2 Hz.

The system we chose for study was di-isopropylphenylsilyl-lithium, $Ph(Me_2CH)_2SiLi$. The phenyl group is necessary to convey enough stability to the anion that reaction with common solvents is slow; the phenyl group may also lower the silicon inversion barrier slightly. The isopropyl groups offer a pair of methyl groups that are diastereotopic and potentially anisochronous when inversion about silicon is slow. At fast inversion, however, the methyl groups would be enantiotopic and isochronous on the average. The anion was generated by cleavage of 1,1,2,2-tetraisopropyl-1,2-diphenyldisilane with lithium.[5] This reaction, in preference to treatment of di-isopropylphenylchlorosilane with lithium, provides a halogen-free solution.

N.m.r. spectra were observed at 35 °C in hexamethylphosphoramide, diglyme, $[^2H_8]$-tetrahydrofuran, 1,2-dimethoxyethane, C_6D_6, and 1,4-dioxan. In all solvents the isopropyl methyl groups were anisochronous, indicative of slow inversion about silicon in the anion. The 270 MHz spectrum in $[^2H_8]$-tetrahydrofuran is given in the Figure. The methyl groups are clearly anisochronous (two doublets); the methinyl proton gives rise to a well resolved septet. The identical behaviour in all solvents (dielectric constant varying from 2·2 to 37) suggests that aggregation and ion pairing of the silyl-lithium reagent are not contributing factors to the spectral nonequivalence. In the chemistry of carbon lithium reagents, exchange out of the aggregate is fast on the n.m.r. time scale.[1] To eliminate the possibility that anion radicals were present and affecting the spectrum, the e.s.r. spectrum was examined. Unpaired electron spins were present in $< 1{\cdot}2 \times 10^{-2}\%$. Hydrolysis of the silyl-lithium reagent in D_2O gave $[^2H]$-di-isopropylphenylsilane in excellent yield.

The n.m.r. spectrum of di-isopropylphenyl-lithium in diglyme was examined up to 185 °C without discernible change in the diastereotopic nature of the methyl groups. Thus inversion about silicon is slow on the n.m.r. time-scale throughout the observable temperature range. Assumption of a coalescence temperature > 200 °C leads to a lower limit to the barrier to inversion about silicon of *ca.* 24 kcal mol^{-1}.

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[5] For details, see M. Urdaneta-Perez, Ph. D. Dissertation, Northwestern University, 1976; all new compounds gave correct elemental analyses.