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THE DYNAMIC STEREOCHEMISTRY OF DI-ISOPROPYLAMINOTRICHLOROSILANE

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Much of the recent interest in the detailed dynamic stereochemistry of nitrogen compounds has been focussed on the relative merits of torsion around C-N bonds and inversion at nitrogen as the rate determining processes in temperature variable n.m.r. spectra of simple amines and their derivatives[1,2,3]. For comparison with the published work on t-butylbenzylmethylamine[3] $(CH_3)_3CN(Me)CH_2Ph$, we first prepared methylbenzylaminotrimethylsilane $(CH_3)_3SiN(Me)CH_2Ph$. The ^1H spectra of this compound and the corresponding trichlorosilylamine $Cl_3SiN(Me)CH_2Ph$ for solutions in vinylbromide were invariant in the temperature range 0 to -150°. In the absence of accidental equivalence this temperature invariance means that the benzylic protons do not become diastereotopic in contrast to those in the carbon compounds suggesting that the inversion barrier at nitrogen is lower in the silylamines. This result is not unexpected in view of the known effect of silicon on inversion barriers at nitrogen[4]. The barrier to nitrogen inversion in the chloro compound could be lowered even further if the $SiCl_3$ group shows similar effects to those demonstrated for the $Si(OMe)_3$ group.[5] Indeed, the nitrogen atom in these silylamines may be close to planar in the ground state[4,6].

A spectrum of di-isopropylaminotrichlorosilane (1) in vinylbromide at -150° showed two isopropyl doublets ($\Delta\nu$ 8.0 Hz) which broadened and coalesced at

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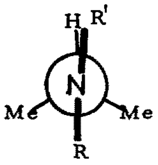
$-135\pm5^{\circ}$ corresponding to a rate process with $\Delta G^{\ddagger}$ 30 ± 2 kJ mol^{-1} at -135°[7]. In the temperature region -130 to -160° di-isopropylaminotrimethylsilane (2) showed broadening of both the isopropyl and silylmethyl signals whereas the TMS reference signal remained sharp. In view of the previous discussion it seems unlikely that the observed coalescence phenomena could be due solely to restricted inversion at nitrogen especially as the barrier is higher for the di-isopropyl than the benzylmethyl compounds (see ref. 4 for a discussion of steric effects on inversion barriers). A more plausible explanation is that at low temperature, rotation round the $(CH_3)_2C\text{-}\dot{N}$ bond has become slow in (1) and the molecule is unable to pass through a conformation of type (3) that renders the isopropyl groups enantiotopic and isochronous. The line broadening observed in the spectra of (2) could arise from similar effects, but could also arise from more facile relaxation at low temperatures[8].

(3)



$R = SiC\ell_3$ or $CHMe_2$

$R' = CHMe_2$ or $SiC\ell_3$

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