The Vicinal Methyl–Methyl Eclipsing Interaction across a Carbon–Nitrogen Single Bond. Activation Parameters for *tert*-Butyl Rotation in *tert*-Butyldimethylaminoborane and *tert*-Butyldimethylaminotrideuterioborane

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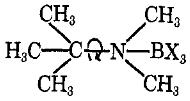
Nonequivalence in the *tert*-butyl group of *tert*-butyldimethylaminoborane (I) and *tert*-butyldimethylaminotrideuterioborane (II) made possible the determination of activation parameters for *tert*-butyl rotation in I (E_a = 11.6 ± 0.3 kcal/mol, $\Delta H^{\ddagger}$ = 11.2 ± 0.3 kcal/mol, $\Delta G^{\ddagger}$ = 10.0 ± 0.1 kcal/mol at −79°, $\Delta S^{\ddagger}$ = 6 ± 2 eu) and II (E_a = 11.5 ± 0.3 kcal/mol, ΔH^* = 11.1 ± 0.3 kcal/mol, $\Delta G^{\ddagger}$ = 10.1 ± 0.1 kcal/mol, $\Delta S^{\ddagger}$ = 5 ± 2 eu) using total nuclear magnetic resonance line-shape analysis. Available data from other systems indicating little difference in the steric requirements of CH_3 and BH_3 made possible the calculation of the methyl-methyl eclipsed repulsion (3.7 ± 0.3 kcal/mol) across the carbon–nitrogen single bond in I or II.

The availability of barriers to rotation about single bonds in simple acyclic systems is important for understanding the conformational dynamics of more complex structures[2] and for the development of a consistent theory for predicting such barriers.[3] Although a respectable amount of data is available regarding rotation about carbon–carbon and other single bonds,[3b,4] there is relatively little information concerning rotation about legitimate carbon–nitrogen single bonds, *e.g.*, CH_3NH_2 ($\Delta H^{\ddagger}$ = 2.0 kcal/mol),[5] $(CH_3)_3N$ ($\Delta H^{\ddagger}$ = 4.4 kcal/mol),[6] CH_3NO_2 ($\Delta H^{\ddagger}$ = 0.006 kcal/mol),[7] and (*tert*-C_4H_9)$(CH_3)_2N$ ($\Delta H^{\ddagger}$ = 6.2 kcal/mol).[8] However, many reports have been forthcoming concerning the detection of substantial rotational barriers about carbon–nitrogen bonds across which there is significant π bonding in the ground-state conformation[9] (*e.g.*, amides) or in which π bonding plays a role in the rotational process.[10]

There have been several reports of the detection of slowed rate processes in acyclic trialkylamines using dynamic nuclear magnetic resonance (dnmr) spectroscopy,[8,11] although the nature of the rate process observed, *i.e.*, rotation, inversion, or rotation–inversion, is controversial.[11] Some evidence is available supporting a common transition state for rotation and inversion in acyclic trialkylamines.[12]

This report concerns the determination of activation parameters for *rotation* about the central *tert*-butyl carbon–nitrogen single bond in *tert*-butyldimethylaminoborane (I)[13] and *tert*-butyldimethylaminotrideuterioborane (II) using the dnmr method and involves one of relatively few examples of the observation of nonequivalence in *tert*-butyl.[8,14]



I, X = H
II, X = D

Results and Discussion

Examination of the pmr spectrum (60 MHz) of I in CH_2CHCl at −15° reveals two sharp singlet resonances due to *tert*-butyl (δ 1.32, 9 H) and $N(CH_3)_2$ (δ 2.56, 6H). The BH_3 resonance is not visible at amplitudes convenient for observing the *tert*-butyl and $N(CH_3)_2$ resonances due to large boron–hydrogen coupling constants[15] and broadening due to quadrupole-induced ^{10}B and ^{11}B spin relaxation.[16] Upon lowering the temperature, the $N(CH_3)_2$ peak remained unchanged to −110°, but the *tert*-butyl resonance broadened and separated into two sharp singlets at δ 1.34 and 1.16 with a respective area ratio of 2:1 (Figure 1). The width at half height ($W_{1/2}$) of the upfield *tert*-butyl peak (2.3 Hz) is slightly greater than the $W_{1/2}$ of the low field resonance (2.0 Hz) under slow exchange conditions (−100°, Figure 1). Over the temperature range from −95 to −125°, the chemical shift *difference* between the two *tert*-butyl resonances (10.9 ± 0.3 Hz) is independent of temperature, although the same slight downfield shift of both resonances is observed with increasing temperature (0.03 Hz/deg). From −95 to −125°, the $W_{1/2}$ of both *tert*-butyl resonances is independent of temperature.[8]

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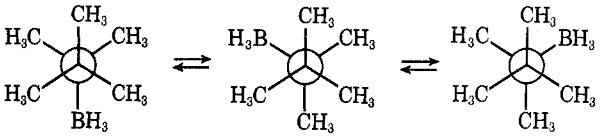
The temperature dependence of the *tert*-butyl resonance in I is best rationalized by a slowing of *tert*-butyl rotation on the pmr time scale at low temperatures (eq 1). Since, as shown in eq 1, the N–CH_3 groups always experience equivalent environments, the shape of the $N(CH_3)_2$ resonance should be independent of any rate process except CH_3–N rotation. However, for the *tert*-butyl group in any of the three rotamers (eq 1), there are two equivalent methyls bisected by the BH_3 group and one other different methyl which bisects the $N(CH_3)_2$ group. Under conditions of slow rotation, the *tert*-butyl resonance should consist of two singlets of relative intensity 2:1 as observed.



(1)

Other possible rationalizations of the temperature dependence of the *tert*-butyl peak in I or II involve an inherently high barrier (>11 kcal/mol) to *tert*-butyl rotation with a rate-determining dissociation (eq 2) to free amine in which rotation is very rapid[8] or bimolecular displacement of one amine by another (eq 3) with both

$$\text{amine-BH}_3 \rightleftarrows \text{amine} + \text{BH}_3 \qquad (2)$$

$$\text{amine-BH}_3 + \text{amine*} \rightleftarrows \text{amine} + \text{amine*-BH}_3 \qquad (3)$$

processes effectively causing an exchange of the BH_3 moiety among the various amine molecules. If such processes were important on the time scale for the experiments reported above, such intermolecular exchange of BH_3 at higher temperatures should cause a coalescence of the respective *tert*-butyl and $N(CH_3)_2$ peaks of the complex and any added free amine. Addition of 1 molar equiv of *tert*-butyldimethylamine to a sample of I did not cause any change in the spectral behavior of I from room temperature to low temperatures. The *tert*-butyl resonance of the free amine (δ 1.00) remained sharp from room temperature to −110°, providing strong evidence against a dissociation or S_N2 process. Thus, complexation by BH_3 has effectively stopped nitrogen inversion.

Because of the current interest in the relative steric size of hydrogen *vs.* deuterium, a dnmr study of *tert*-butyldimethylaminotrideuterioborane (II) was performed. The *tert*-butyl resonance of II displayed spectral changes at low temperature essentially the same as in I, although, under conditions of slow exchange, the chemical shifts of the two *tert*-butyl resonances (δ 1.32, 1.14) and the $N(CH_3)_2$ peak (δ 2.47) are slightly but consistently at higher field than in I.

A total nmr line shape analysis[17] of the *tert*-butyl resonances of I (Figure I) and II gave a series of rate constants as a function of temperature for *tert*-butyl rotation in I and II (Table I). A least-squares treatment of ln k_H (Table I) *vs.* $1/T$ (correlation coefficient 0.995) and ln k_D (Table I) *vs.* $1/T$ (correlation coefficient 0.998) gave activation parameters for *tert*-butyl rotation in I and II (Table II). The error assigned to E_a (Table II) is a maximum error obtained by drawing another line through the Arrhenius plot which gave a reasonable though worse fit than the line used.

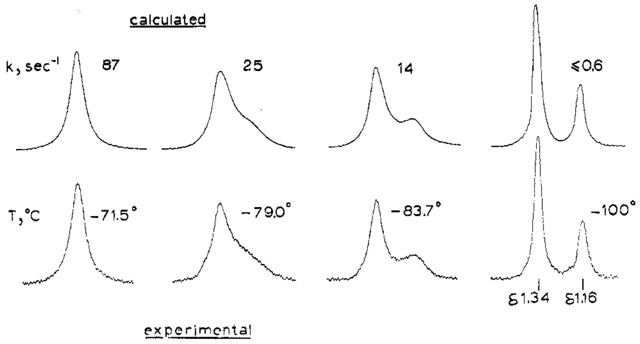


Figure 1.—The temperature dependence of the pmr spectrum (60 MHz) of the *tert*-butyl resonance of *tert*-butyldimethylaminoborane (I) and calculated spectra as a function of the rate of *tert*-butyl rotation.

TABLE I

RATE CONSTANTS FOR *tert*-BUTYL ROTATION IN I AND II AS A FUNCTION OF TEMPERATURE

I		II	
Temp, °C	k_H,[a] sec^{-1}	Temp, °C	k_D,[b] sec^{-1}
−67.9	140	−65.2	166
−71.5	87	−69.0	98
−75.8	45	−72.6	56
−79.0	25	−75.8	34
−83.7	14	−79.0	20
−87.0	7.0	−84.0	10
−90.0	5.0	−88.6	5.0

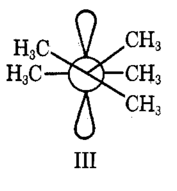
[a] k_H = first-order rate constant for disappearance of any methyl from any of the three sites on *tert*-butyl in I. [b] k_D = same for II.

TABLE II

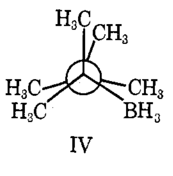
ACTIVATION PARAMETERS FOR *tert*-BUTYL ROTATION IN I AND II

	I	II
E_a, kcal/mol	11.6 ± 0.3	11.5 ± 0.3
$\Delta H^{\ddagger}$, kcal/mol	11.2 ± 0.3	11.1 ± 0.3
$\Delta G^{\ddagger}$, kcal/mol	10.0 ± 0.1	10.1 ± 0.1
$\Delta S^{\ddagger}$, eu	6 ± 2	5 ± 2

The barriers to rotation of *tert*-butyl about a carbon–nitrogen single bond in I and II (Table II) are substantially higher than in the free *tert*-butyldimethylamine (E_a = 6.4 ± 0.3 kcal/mol, $\Delta H^{\ddagger}$ = 6.2 ± 0.3 kcal/mol, $\Delta G^{\ddagger}$ = 6.0 ± 0.1 kcal/mol, $\Delta S^{\ddagger}$ = 1.3 ± 2.0 eu)[8] and attest to significantly increased vicinal nonbonded repulsions in the transition state for I or II as compared to the free amine. Since nitrogen inversion is effectively locked *via* complexation by BH_3 in I and II and there exists in free *tert*-butyldimethylamine the definite possibility of nitrogen inversion, it would be naive to extract any trends regarding the relative magnitude of vicinal eclipsing interactions in these two systems. In the case of the free *tert*-butyldimethylamine, rotation and inversion most likely share a common transition state involving a planar (sp^2) configuration at nitrogen (III).[8,12] However, in I and II, complexation by BH_3 prevents any inversion process at nitrogen and the most



III



IV

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reasonable transition state is the eclipsed form (IV) analogous to ethane. The positive $\Delta S^{\ddagger}$ for rotation in I and II may reflect in part a stretching of the nitrogen-boron bond in the transition state for rotation (IV) and slight concomitant rehybridization of nitrogen toward sp^2.

It is interesting to note that within experimental error the substitution of deuterium (II) for hydrogen (I) does not change the barrier to *tert*-butyl rotation (Table II) and that hydrogen and deuterium possess essentially the same conformational requirements in systems of this type.

The barrier to *tert*-butyl rotation in I and II is comparable to that for *tert*-butyl rotation in a series of halogenated methylbutanes (E_a = 10–12 kcal/mol).[18]

Recent evidence obtained for the 4-*tert*-butyl-1-methylpiperidine boranes indicates little preference for BH_3 axial (~53%) or equatorial (~47%);[19] *i.e.*, BH_3 has approximately the same conformational requirements as CH_3. Thus, the three vicinal eclipsing interactions in the transition state (IV) for *tert*-butyl rotation in I may be assumed to be approximately equal. The magnitude of one methyl–methyl eclipsed repulsion may be calculated to be one third of $\Delta H^{\ddagger}$ (Table II) for *tert*-butyl rotation or 3.7 ± 0.4 kcal/mol. The potential maximum for *n*-butane involving eclipsing of two methyl groups is estimated to be 4.4–6.1 kcal/mol.[20] Subtracting the two H–H eclipsing interactions (~2 kcal/mol), the methyl–methyl eclipsed repulsion in *n*-butane is estimated to be 2.4–4.1 kcal/mol.

Experimental Section

The nmr spectra were obtained using a Varian HR-60A spectrometer equipped with a custom-built variable-temperature probe. Spectral calibrations were performed by the audiomodulation technique using a Hewlett-Packard 651-A audiooscillator and 5221B electronic counter.

Temperature measurement was performed using a calibrated copper–constantan thermocouple permanently in place in the probe and is done simultaneously with the recording of the spectrum. Temperature measurement is accurate to ±0.3° at the sample.

The error (±5%) associated with the rate constants (Table I) obtained by matching theoretical to experimental spectra by superposition is a maximum error established by obviously poor fits at higher and lower values of the rate constant giving the best fit.

***tert*-Butyldimethylaminoborane (I) and *tert*-butyldimethylaminotrideuterioborane (II)** were prepared by the method of Shore and Parry[21] using $LiBH_4$ and $LiBD_4$, respectively. The nmr, ir, and mass spectral data for I and II are entirely consistent with their respective structures.

Registry No.—I, 31121-07-0; II, 31819-36-0.

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The Thermal Decomposition of Bissilyl Peroxides and Triphenylsilyl Triphenylgermyl Peroxide[1]

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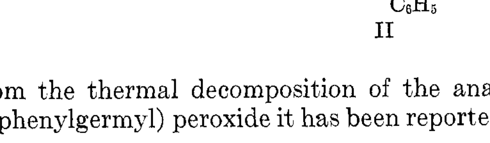
The thermal decomposition of bis(triphenylsilyl) peroxide gave an essentially quantitative yield of pentaphenylphenoxydisiloxane. Bis(*p*-tolyldiphenylsilyl) peroxide and bis(*p*-anisyldiphenylsilyl) peroxide were synthesized and analysis of the products of their thermal rearrangements gave a migratory aptitude series: *p*-anisyl, 6.0; *p*-tolyl, 1.1; phenyl, 1.0. These figures are consistent with a free-radical mechanism for the rearrangement. Triphenylsilyl triphenylgermyl peroxide was synthesized and its thermal decomposition occurs exclusively by phenyl–silicon bond cleavage to yield, ultimately, phenol, 0.62, triphenylgermyl moiety, 0.98, and polymeric diphenylsilyl oxide. Reproducible first-order kinetics were obtained with difficulty for 1 half-life for the thermal decomposition of the silylgermyl peroxide: k_{180}, 0.4; k_{190}, 1.0; k_{200}, 6.0 × 10^{-5} sec^{-1}.

In a previous paper the synthesis of several bissilyl peroxides was described. The present work was planned to study the decomposition of these bis peroxides and to attempt the synthesis of an unsymmetrical organometallic peroxide in which silicon and germanium would be joined by a peroxide link.

Results and Discussion

Bissilyl Peroxides.—Heating bis(triphenylsilyl) peroxide (I)[2] above its melting point (140–141°) gave an essentially quantitative yield (96%) of the rearrangement product II. The isolation of II was unexpected,



$$\underset{\text{I}}{(C_6H_5)_3SiOOSi(C_6H_5)_3} \xrightarrow{\text{heat}} \underset{\text{II}}{(C_6H_5)_3SiO\underset{\underset{C_6H_5}{|}}{\underset{O}{\underset{|}{Si}}}(C_6H_5)_2}$$

for from the thermal decomposition of the analogous bis(triphenylgermyl) peroxide it has been reported[3] that

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[1] (a) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, ORGN 131. Taken in part from the Ph.D. thesis of A. K. Shubber, Case Western Reserve University, 1970. (b) Supported in part by the National Science Foundation through Grant GP-19018.

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