Stereodynamics of *N-tert*-Butyl-*N*-haloamines. Experimental and Theoretical Investigations of Nitrogen Inversion and *tert*-Butyl Rotation. A Dynamical Model for the Rotation–Inversion Dichotomy in All Alkylamines

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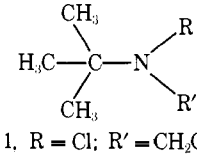
Abstract: Examination of the ^1H DNMR spectra of *N-tert*-butyl-*N,N*-dichloroamine, *N-tert*-butyl-*N*-(ethyl-*2,2,2-d*$_3$)-*N*-chloroamine, *N-tert*-butyl-*N*-benzyl-*N*-chloroamine, *N-tert*-butyl-*N*-methyl-*N*-chloroamine, and *N-tert*-butyl-*N*-methyl-*N*-bromoamine revealed changes as a function of temperature consistent with slowing isolated *tert*-butyl rotation and/or nitrogen inversion on the DNMR time scale. For those compounds above in which both *tert*-butyl rotation and nitrogen inversion could be detected by the DNMR method, the potential barrier for inversion is higher than that for *tert*-butyl rotation. Theoretical calculations (INDO) for a series of *N*-alkyl-*N*-haloamines are consistent with a dynamical model incorporating barriers to inversion invariably higher than simple isolated rotation about the carbon–nitrogen bond. The above data and previous results for several trialkylamines reveal a general picture of the rotation–inversion dichotomy in all alkylamines. If the barrier to nitrogen inversion is greater than that for isolated rotation about the carbon–nitrogen R_3C–N bond, then the lowest barrier process available for equilibrating the environments of the three R groups is simple *rotation with no inversion*. If the barrier to nitrogen inversion is lower than that for isolated R_3C–N rotation, the lowest barrier process available for equilibrating the environments of the three R groups involves *concomitant* R_3C–N rotation and inversion at nitrogen.

In attempting to elucidate the stereodynamics of acyclic amines, one must be cognizant of two rate processes associated with the nitrogen atom. One of these processes is atomic *inversion* about nitrogen, and the other is *rotation* about bonds to the nitrogen atom. In simple alkylamines, it is generally observed that the potential barrier to nitrogen inversion is significantly higher than that for rotation about carbon–nitrogen bonds. For example, the barrier to nitrogen inversion in methylamine is 4.8 kcal/mol,[2a] while the barrier to threefold methyl rotation is only 2.0 kcal/mol.[2b] In acyclic trialkyl*phosphines*, the difference in the potential barriers to inversion at phosphorus ($\Delta H^{\ddagger} \sim 30$ kcal/mol)[3] and rotation about carbon–phosphorus bonds even in the hindered tri-*tert*-butylphosphine ($\Delta H^{\ddagger} = 9.0 \pm 0.4$ kcal/mol)[4] is significant. However, in more hindered trialkylamines, the rate of inversion at nitrogen determined using the dynamic nuclear magnetic resonance (DNMR)[5] method for molecules such as dibenzylmethylamine reveals a barrier ($\Delta H^{\ddagger} = 7.2 \pm 0.4$ kcal/mol)[6] which is very similar in magnitude to that for the process which equilibrates the environments of the *N-tert*-butyl methyl groups of *N-tert*-butyl-*N,N*-dimethylamine ($\Delta H^{\ddagger} = 6.2 \pm 0.4$ kcal/mol).[7] In fact, an examination of the ^1H DNMR spectra of a series of *N-tert*-butyl-*N,N*-dialkylamines revealed that the rate of inversion is equal to the rate of exchange of the environments of the *N-tert*-butyl methyl groups.[8] These observations and complementary theoretical calculations support a dynamical model incorporating *coupled* nitrogen inversion and *tert*-butyl rotation.[8] In contrast, complexation of the nitrogen in *N-tert*-butyl-*N,N*-dimethylamine borane, thus preventing nitrogen inversion, leads to a relatively high barrier to simple threefold *tert*-butyl rotation ($\Delta H^{\ddagger} = 11.1 \pm 0.3$ kcal/mol).[9]

In light of other studies which have shown that increasing the electronegativity of substituents bonded directly to nitrogen leads to an increase in the barrier to nitrogen inversion[3,10] and our observation of coupled inversion and *tert*-butyl rotation in *N-tert*-butyl-*N,N*-dialkylamines, it was intriguing to contemplate what effect *N*-halogen substitution would have on the relative rates of *tert*-butyl rotation and nitrogen inversion in a series of *N-tert*-butyl-*N*-haloamines. Indeed, this report concerns the observation of distinctly different rates of *tert*-butyl rotation and nitrogen inversion in a series of *N-tert*-butyl-*N*-haloamines[11] measured using the DNMR method and theoretical calculations[8] which provide a description of changes in molecular geometry along the potential surfaces associated with nitrogen inversion and *tert*-butyl rotation.

Results and Discussion

Examination of the ^1H DNMR spectrum (60 MHz) of **1** (12% v/v in $CBrF_3$) at −60° with irradiation at the ^2H resonance frequency (9.2 MHz) revealed two singlet resonances for the methylene (δ 2.83) and *tert*-butyl (δ 1.21) groups consistent with rapid conformational exchange on the DNMR time scale. At lower temperatures (Figure 1), the methylene resonance broadens and separates into one AB spectrum (δ 3.06, 2.64; $J_{AB} = -13.2$ Hz) which remains symmetrical to about −130°. In addition, the *tert*-butyl signal broadens and separates at lower temperatures into three peaks of equal area (Figure 1) at δ 1.27 (3 H), 1.19 (3 H), and 1.13 (3 H).



1, R = Cl; R′ = CH_2CD_3
2, R = Cl; R′ = $CH_2C_6H_5$
3, R = Cl; R′ = CH_3
4, R = Br; R′ = CH_3
5, R = R′ = Cl

Changes in the methylene proton resonance of **1** with temperature (Figure 1) may be understood with the aid of eq 1 in which the various stable staggered conformations of the ethyl group are represented by a Newman projection

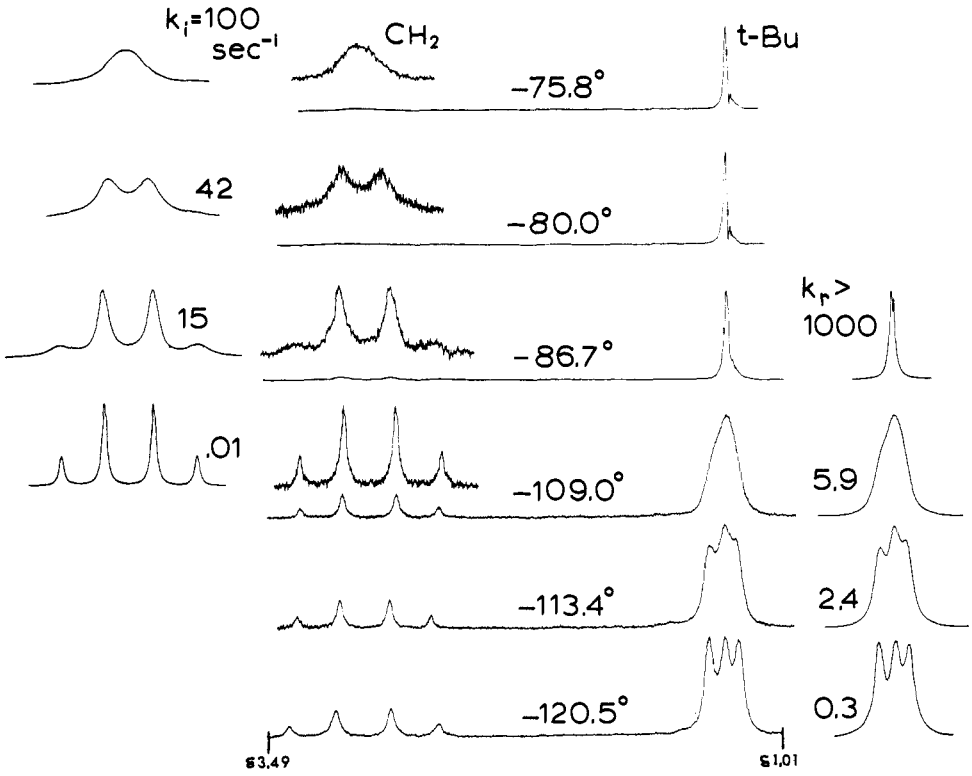
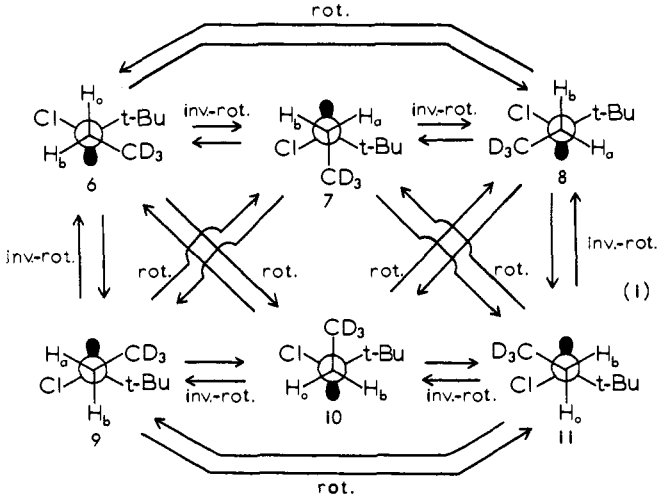
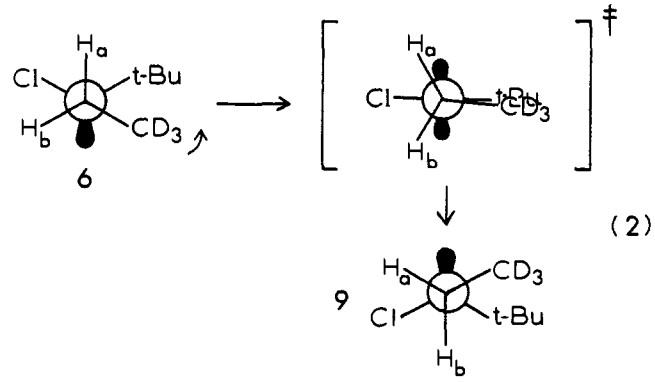


Figure 1. The experimental ^{1}H DNMR spectra (60 MHz) of *N-tert*-butyl-*N*-[ethyl-*2,2,2-d*$_3$]-*N*-chloroamine (**1**; 12% v/v in $CBrF_3$) with irradiation at the ^{2}H resonance frequency (9.2 MHz) and theoretical spectra calculated as a function of the rate of nitrogen inversion (k_i) and the rate of conversion of one *tert*-butyl rotamer to one other rotamer (k_r).



down the CH_2–N bond. The conversion of **6** to **9** involves both inversion at nitrogen and rotation about the CH_2–N bond. The process may be visualized as nitrogen rehybridizing to a planar (sp^2) transition state with a concomitant 30° counterclockwise rotation about the CH_2–N bond[8] (eq 2)



and then completion of the inversion process to **9** along with an additional 30° counterclockwise rotation of ethyl (eq 2). All of the processes labeled *inv.-rot.* in eq 1 may be viewed in this way. The conversions **6** → **10** → **8** → **6** and **9** → **7** → **11** → **9** are complete simple threefold rotations about the CH_2–N bond *with no inversion* and are labeled *rot.* in eq 1. However, it is clear from a perusal of eq 1 that just simple threefold rotation is not sufficient to swap the environments of H_a and H_b leading to acumination of the CH_2 resonance at temperatures above −60° and that inversion-rotation (e.g., **6** → **9**; etc.) is a prime requisite for exactly exchanging the environments of H_a and H_b to give a singlet under conditions of rapid exchange on the DNMR time scale. Thus, it is possible under conditions of slow inversion-rotation *and* slow CH_2–N threefold rotation (eq 1) that three separate AB spectra for three separate pairs of enantiomers (**6** and **9**; **7** and **10**; **8** and **11**) would be observed. Rapid threefold rotation with slow inversion-rotation will lead to an averaging of the respectively different environments of H_a and H_b resulting in *one* AB spectrum. Thus, the observation of *one* AB spectrum for **1** at −109.0° (Figure 1) is consistent with this latter dynamical situation. It is also quite possible that a strong conformational preference (e.g., for **8** and **11**) exists because of significantly different nonbonded repulsions in the various invertomers in which case rapid *or* slow threefold rotation would also lead to one AB spectrum. However, the conversion of the methylene resonance of **1** from a singlet at high temperatures to an AB spectrum at low temperatures is clearly consistent with slowing the inversion-rotation process at nitrogen. A complete DNMR line shape analysis performed using the computer program DNMR3[12] in a substantially modified version[13] gave the theoretical spectra (Figure 1) as a function of the rate of inversion.

The observation of three singlets of equal area for the *tert*-butyl group of **1** at −120.5° (Figure 1) is consistent with the symmetry experienced by a static *tert*-butyl in **1**, i.e., three methyl groups in three different environments.

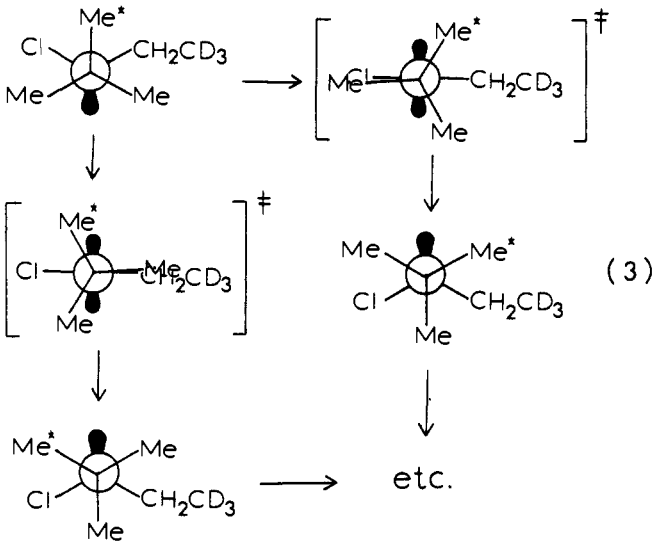
Table I. NMR Chemical Shifts at Slow Exchange and Activation Parameters for *tert*-Butyl Rotation and Nitrogen Inversion in *N*-*tert*-Butyl-*N*-haloamines

Compd	R	R'	Dynamic resonance	^{1}H chemical shifts, ppm from Me_4Si	Rate process[a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, gibbs	$\Delta G^{\ddagger}$, kcal/mol (T, °C)
1[b]	Cl	CH_2CD_3	t-C_4H_9	1.27 (3 H); 1.19 (3 H); 1.13 (3 H);	Rot.	9.6 ± 0.4	4 ± 3	8.9 ± 0.1 (−109)
			CH_2	3.06 (1 H); 2.64 (1 H); J_{AB} = −13.2 Hz	Inv.	10.8 ± 0.3	5 ± 3	9.7 ± 0.1 (−80)
2[c]	Cl	$CH_2C_6H_5$	t-C_4H_9	1.26 (3 H); 1.18 (3 H); 1.15 (3 H)	Rot.	9.8 ± 0.8	9 ± 7	8.3 ± 0.3 (−122)
			CH_2	3.96 (1 H); 3.26 (1 H); J_{AB} = −13.8 Hz	Inv.	10.0 ± 0.3	5 ± 3	9.0 ± 0.1 (−84)
3[d]	Cl	CH_3	t-C_4H_9	1.26 (3 H); 1.19 (3 H); 1.18 (3 H)	Rot.	8.8 ± 0.4	0 ± 4	8.8 ± 0.1 (−115)
4[d]	Br	CH_3	t-C_4H_9	1.24 (3 H); 1.20 (3 H); 1.19 (3 H)	Rot.	8.8 ± 0.4	2 ± 4	8.5 ± 0.1 (−121)
5[e]	Cl	Cl	t-C_4H_9	1.38 (3 H); 1.21 (6 H)	Rot.	10.5 ± 0.4	4 ± 3	9.7 ± 0.1 (−89)

[a] Rot. ≡ *tert*-butyl isolated rotation; inv. ≡ nitrogen inversion. [b] 12% v/v in $CBrF_3$. [c] 15% v/v in 50% CD_2Cl_2–50% $ClFC{=}CF_2$. [d] 7% v/v in $ClFC{=}CF_2$. [e] 5% v/v in $CH_2{=}CHCl$.

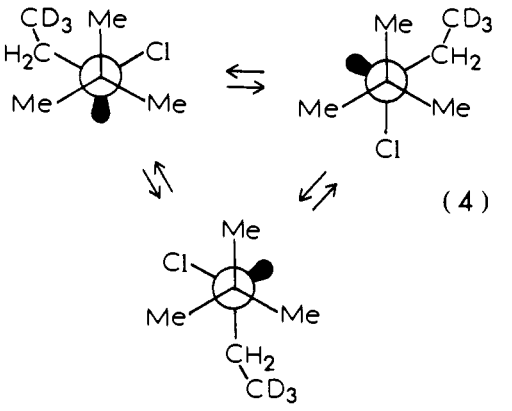
However, one important observation may be made concerning the DNMR spectra of the methylene and *tert*-butyl groups. At −86.7° in Figure 1, the methylene AB spectrum has already split out, while the *tert*-butyl resonance is a relatively sharp singlet. At −109.0°, the methylene spectrum represents a system essentially static on the DNMR time scale, while the *tert*-butyl spectrum is significantly exchange broadened. *It is apparent that nitrogen inversion is proceeding more slowly than the rate process which exchanges the environments of the methyl groups of tert-butyl.* In fact, a total DNMR line shape analysis for the *tert*-butyl resonance[12,13] reveals the rates of the two processes to be quite different at the same temperature (Figure 1). Activation parameters for both processes are compiled in Table I.

One can envision two fundamentally different dynamical itineraries for exchanging the environments of the *tert*-butyl methyl groups of **1**. Analogous to a series of *N*-*tert*-butyl-*N*,*N*-dialkylamines,[8] *concerted tert*-butyl rotation and nitrogen inversion would effect the exchange (eq 3)



(3)

with the requirement of course that the rate of inversion be equal to the rate of equilibration of the *tert*-butyl methyl groups.[8] Indeed, theoretical calculations to be described below are completely consistent with the geometry of the transition states for *inversion* shown in eq 3 which requires *concomitant tert*-butyl rotation and nitrogen inversion. However, it is clear from the DNMR spectra of **1** (Figure 1) that equilibration of the *tert*-butyl methyl groups proceeds at a rate significantly *faster* than inversion, and that some other rate process with a barrier lower than that for inversion is exchanging the *tert*-butyl methyl groups. Obviously, this rate process is *simple isolated rotation with no inversion* (e.g., eq 4). Since the DNMR method is capable



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of measuring only the lowest potential barrier of a number of rate processes which effect the same net conformational exchange, the DNMR spectra of **1** (Figure 1) are sensitive only to slowing simple isolated rotation of *tert*-butyl from −100 to −120°. The DNMR spectrum of **1** at −109.0° (Figure 1) reveals the first-order rate constant for inversion (1×10^{-2} sec^{-1}) to be significantly smaller than that for isolated *tert*-butyl rotation (5.9 sec^{-1}).

Thus, the lowest barrier process for conformational exchange of the tert-butyl group of **1** *involves rotation of tert-butyl against what is to a good first approximation a fixed pyramidal nitrogen.* This is in contrast to a series of *N*-*tert*-butyl-*N*,*N*-dialkylamines in which the minimum potential-energy surface for equilibrating the *tert*-butyl methyls involves *concerted tert*-butyl rotation and nitrogen inversion.[8] These observations for **1** attest again to the effectiveness of *N*-chlorine in raising the barrier to inversion at nitrogen.[3,10]

DNMR spectral changes similar to **1** were observed for *N*-*tert*-butyl-*N*-benzyl-*N*-chloroamine (**2**; 5% v/v in 50% CD_2Cl_2–50% $ClFCCF_2$) with the methylene protons separating at low temperatures into one cleanly defined AB spectrum and the *tert*-butyl resonance splitting at even lower temperatures.[11b] Small chemical shift differences between the *tert*-butyl methyl resonances and broad lines precluded determination of accurate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for *tert*-butyl rotation (Table I). However, more accurate activation parameters could be determined for inversion from clearly defined changes in the methylene resonance (Table I). It is observed again in **2** as in **1** that isolated *tert*-butyl rotation proceeds at a rate faster than inversion.

With this dynamical model in mind for *N*-*tert*-butyl-*N*-alkyl-*N*-haloamines, i.e., that the lowest barrier process for *tert*-butyl equilibration is the isolated rotation process (e.g., eq 4), we examined the ^{1}H DNMR spectra of other more symmetrical haloamines (**3**–**5**) having no diastereotopic groups. In light of the results obtained for **1** and **2**, changes in the *tert*-butyl resonance for **3**–**5** may be assigned to slowing isolated *tert*-butyl rotation.

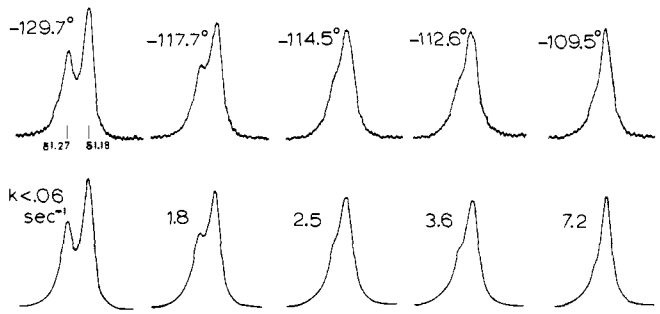


Figure 2. The experimental ^1H DNMR spectra (60 MHz) of the *tert*-butyl group of *N-tert*-butyl-*N*-methyl-*N*-chloroamine (**3**; 7% v/v in $ClFCCF_2$) and theoretical spectra calculated as a function of the rate of conversion of one *tert*-butyl rotamer to one other rotamer.

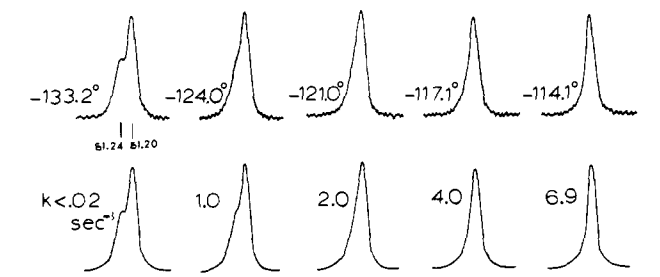


Figure 3. The experimental ^1H DNMR spectra (60 MHz) of the *tert*-butyl group of *N-tert*-butyl-*N*-methyl-*N*-bromoamine (**4**; 7% v/v in $CFClCF_2$) and theoretical spectra calculated as a function of the rate of conversion of one *tert*-butyl rotamer to one other rotamer.

Examination of the ^1H DNMR spectrum of *N-tert*-butyl-*N*-methyl-*N*-chloroamine (**3**; 7% v/v in $ClFCCF_2$) at −60° reveals two sharp singlet resonances due to the *tert*-butyl (δ 1.21) and *N*-methyl (δ 2.81) groups. At lower temperatures, no changes occur for the *N*-methyl resonance, consistent with the threefold symmetry of *tert*-butyl. However, with decreasing temperature, the *tert*-butyl resonance of **3** broadens and separates into two resolved signals (Figure 2), consistent with slowing *tert*-butyl rotation. In fact, the best fit of a total theoretical DNMR line shape at −129.7° (Figure 2) required the use of *three* separate methyl signals for *tert*-butyl at δ 1.26, 1.19, and 1.18, consistent with the symmetry felt by static *tert*-butyl. The peaks at δ 1.19 and 1.18 are of course not resolved (Figure 2). Activation parameters for *tert*-butyl rotation in **3** are compiled in Table I. Similar results were obtained for *N-tert*-butyl-*N*-methyl-*N*-bromoamine (**4**; 7% v/v in $CFClCF_2$) as illustrated in Figure 3. DNMR and activation parameters for *tert*-butyl rotation are compiled in Table I. The *tert*-butyl resonance of *N-tert*-butyl-*N,N*-dichloroamine (**5**; 5% v/v in CH_2CHCl) separates into two singlets of 1:2 relative area ratio completely consistent with slow *tert*-butyl rotation (Figure 4) and the requirement of two equivalent methyl groups under conditions of slow *tert*-butyl rotation. It is noteworthy that the DNMR spectral changes for **5** occur at significantly higher temperatures than for the tert-butyl resonances of **1–4**, revealing an appreciably higher barrier to rotation (Table I).

Since the DNMR method (Figures 1–4) reveals only the rate of a given conformational equilibration (i.e., the enthalpy, entropy, and free energy differences between ground and transition states) and is incapable of providing a description of changes in molecular geometry along the potential surface associated with the specific equilibration, theoretical calculations were performed in this laboratory to provide at least a qualitative picture of inversion and rotation itineraries in *N-tert*-butyl-*N*-haloamines. Such studies were revealing in the case of a series of *N-tert*-butyl-*N,N*-dialkylamines.[8]

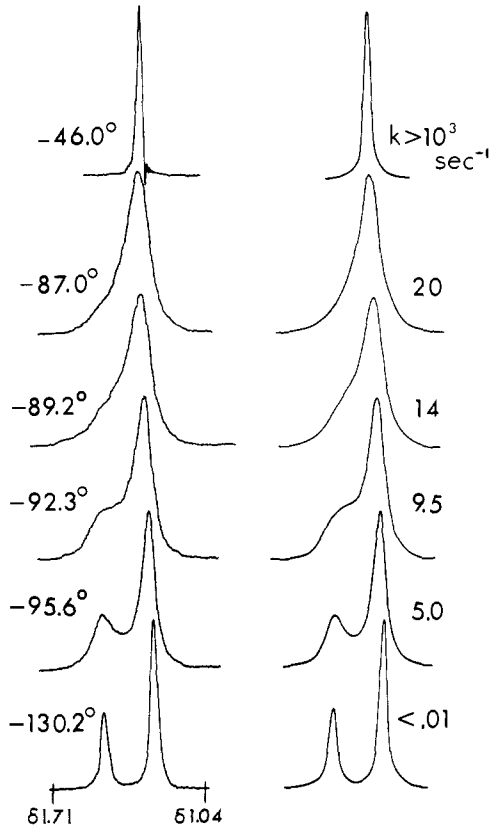
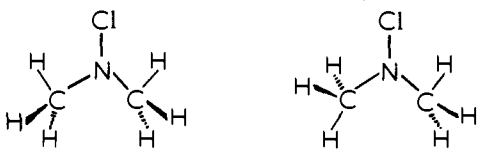


Figure 4. The experimental ^1H DNMR spectra (60 MHz) of *N-tert*-butyl-*N,N*-dichloroamine (**5**; 5% v/v in CH_2CHCl) and theoretical spectra calculated as a function of the rate of conversion of one *tert*-butyl rotamer to one other rotamer.

For the *N-tert*-butyl-*N*-haloamines of interest in this report, the INDO-A method parameterized for second row elements by Stevenson and Burkey[14a] was selected for the theoretical calculations. Cartesian coordinates used for these calculations were obtained using the computer program COORD (time-sharing version).[14b] The computations were performed using a modified version of CNINDO.[15] Standard values of bond lengths (C–C, 1.54 Å; C–H, 1.09 Å; C–N, 1.47 Å; N–Cl, 1.75 Å) have been employed.[16] The rationale for selecting the INDO-A method has been presented elsewhere.[14] Assuming all bond angles in *N,N*-dimethyl-*N*-chloroamine (**12**) to be 109.5°, rotation of one methyl by 60° to a perfectly eclipsed conformation, while keeping the other methyl fixed, gives a calculated (INDO-A) increase in energy of 2.29 kcal/mol which is of course the barrier to threefold rotation with *no* nitrogen inversion. Using a *geometry optimization* approach to calculating the energy of the transition state for nitrogen inversion, the minimum energy geometry having planar (sp^2) nitrogen (∠CNC = ∠CNCl = 120°) has C_{2v} symmetry with two CH bonds and the NCl bond in the same plane (**13**). Conformation **13** is calculated to be 12.89 kcal/mol higher in energy



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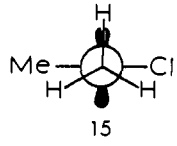
than the pyramidal ground state. This calculated barrier to inversion is in good agreement with an experimental value ($\Delta G^{\ddagger}$) of 10.2 kcal/mol for *N,N*-diethyl-*N*-chloroamine[17] which would be expected to have a lower inversion barrier than **12** due to increased crowding in the ground state conformation.

The less symmetrical **14** is calculated to be 0.2 kcal/mol higher in energy than **13**, i.e., the major contribution to the increased energy of **13** over the ground state results from rehybridization of nitrogen. In order to proceed from the staggered ground state of **12** to **13**, nitrogen must rehybridize to sp,[2] and a 30° *rotation* of each methyl must also occur. Direct inversion with no rotation gives **15** which is



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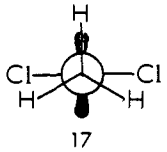
less stable than **13**. At this point, it is important to note that the difference between the barriers to threefold rotation, and inversion in **12** is much larger than in trimethylamine [$\Delta H^{\ddagger}$(rot) = 4.4 kcal/mol; $\Delta H^{\ddagger}$(inv.) $\simeq$ 5.2 kcal/mol],[8] attesting to the established effectiveness of *N*-halogen to retard nitrogen inversion.

Assuming all bond angles to be 109.5° in *N*-methyl-*N*,*N*-dichloroamine (**16**), rotation to the eclipsed conformation with no nitrogen hydridization gives a calculated barrier to rotation of 3.00 kcal/mol. The minimum energy geometry having a planar nitrogen is **17** which is calculated to be 23.06 kcal/mol above the ground state energy, revealing a substantial increase in the inversion barrier over **12**. Rotation of methyl in **17** to **18** increases the energy by only



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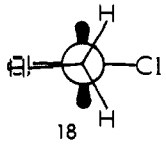

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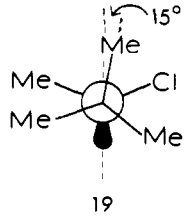
0.006 kcal/mol; i.e., methyl is essentially freely rotating in the planar nitrogen geometry. This situation is highly analogous to that for the planar nitrogen forms of methylamine[8] and for nitromethane [$\Delta H^{\ddagger}$(rotation) = 0.006 kcal/mol].[18]

The calculated barrier to inversion in trichloroamine is, not unexpectedly, 33.54 kcal/mol. All of these theoretical results are summarized in Table II. Experimentally accessible barriers are compiled in Table I of this paper and in Table I of a previous paper.[8]

Since the *N*-*tert*-butyl-*N*-alkyl-*N*-chloroamines are of central interest in this report, we performed extensive geometry optimization calculations using the INDO-A method on *N*-*tert*-butyl-*N*-methyl-*N*-chloroamine (**3**). The geometry-optimized ground state has CNC and CNCl bond angles equal at 111.8°. This is a somewhat more pyramidal geometry than that in *N*-*tert*-butyl-*N*,*N*-dimethylamine (all ∠CNC = 114.3°),[8] consistent with the idea that electronegative *N*-chlorine will increase the s character of the nitrogen lone pair as compared with *N*-methyl. In addition, the dihedral angle between the nitrogen lone pair in **3** and the *tert*-butyl methyl trans to the lone pair is 165° (**19**), and the corresponding dihedral angle for *N*-methyl is 173° (**20**). This situation is analogous to but not as extreme as



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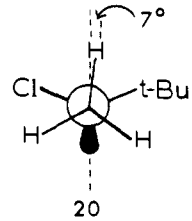

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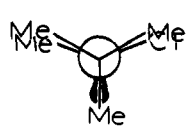
that in *N*-*tert*-butyl-*N*,*N*-dimethylamine.[8] Rotation of *tert*-butyl from **19** keeping the geometry at nitrogen fixed gave a transition state (**21**) calculated to be 4.62 kcal/mol higher in energy than **19**. The geometry-optimized transition state for nitrogen inversion is **22** analogous to **13** for *N*,*N*-di-

Table II. Barriers to Rotation and Inversion in *N*-*tert*-Butyl-*N*-haloamines Calculated by the INDO-A Method[14]

Compd	Rate process[a]	Calculated barrier, kcal/mol
$(CH_3)_3N$	Rotation	2.38[b]
	Inversion	5.15[b]
$(CH_3)_2NCl$	Rotation	2.29
	Inversion	12.89
CH_3NCl_2	Rotation	3.00
	Inversion	23.06
NCl_3	Inversion	33.54
t-$C_4H_9N(CH_3)_2$	t-C_4H_9 rotation	4.02[b]
	Inversion	3.01[b]
$(t$-$C_4H_9)(CH_3)NCl$	t-C_4H_9 rotation	4.62
	Inversion	9.62
t-$C_4H_9NCl_2$	t-C_4H_9 rotation	7.81
	Inversion	22.17

[a] Rotation = isolated rotation; inversion = nitrogen inversion. [b] INDO method used; See ref 8.



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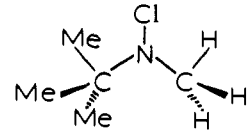

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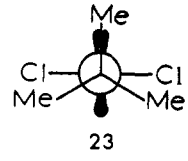
methyl-*N*-chloroamine discussed above. Conformation **22** is 9.62 kcal/mol higher than the ground state **19**. This calculated barrier to inversion is in good agreement with the experimental value of 10.8 kcal/mol for *N*-*tert*-butyl-*N*-(ethyl-2,2,2-d_3)-*N*-chloroamine (**1**). Again, it is clear that *both* inversion and rotation have occurred in going to the planar nitrogen transition state **22**.

Similar calculations for *N*-*tert*-butyl-*N*,*N*-dichloroamine (**5**) revealed a geometry-optimized ground state having CNCl and ClNCl bond angles near 109.5° and a perfectly staggered *tert*-butyl. The barrier to threefold *tert*-butyl rotation is calculated to be 7.81 kcal/mol (experimental $\Delta H^{\ddagger}$ = 10.5 kcal/mol; Table I). A direct inversion of the staggered pyramidal geometry of **5** to **23** having sp^2 hybridized nitrogen raises the calculated energy by 22.35 kcal/mol. Rotation of *tert*-butyl in **23** to **24** *lowers* the energy by



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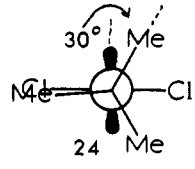

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0.180 kcal/mol. Although the energy difference between **23** and **24** is very small, the lower calculated energy for **24** speaks again for *tert*-butyl rotation occurring in a *concomitant* fashion with inversion.[8] *However*, the barrier to inversion in **5** via a transition state such as **24** is much higher than simple threefold rotation which is indeed the rate process detected by the DNMR method (Figure 4). Thus, a free-energy profile for *tert*-butyl rotation and nitrogen inversion in **5** (Figure 5) may be constructed which is significantly different from that describing *concerted tert*-butyl rotation and nitrogen inversion in *N*-*tert*-butyl-*N*,*N*-dialkylamines.[8]

It is clear from a perusal of the data summarized in Tables I and II that replacement of one *N*-methyl of *N*-*tert*-butyl-*N*,*N*-dimethylamine by an *N*-chlorine is sufficient to raise the barrier to inversion in *N*-*tert*-butyl-*N*-methyl-*N*-chloroamine (**3**) above that for isolated *tert*-butyl rotation. Indeed, two *N*-chlorines further accentuate the barrier dif-

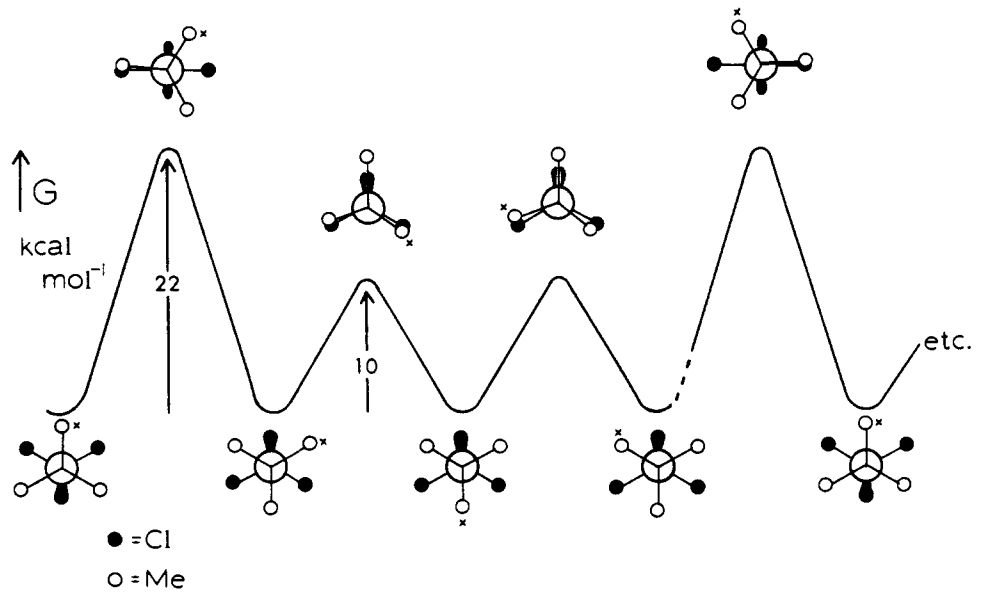


Figure 5. A portion of the free-energy profile for *tert*-butyl rotation and nitrogen inversion in *N-tert*-butyl-*N,N*-dichloroamine (**5**).

ference. Also, it is apparent that, while the barriers to isolated *tert*-butyl rotation in **3** and **5** are higher than that for the concerted *tert*-butyl rotation–nitrogen inversion process in *N-tert*-butyl-*N,N*-dimethylamine, the barrier to isolated rotation does not increase with additional *N*-chlorines anywhere near as dramatically as the barrier to inversion. The trends are presented graphically in Figure 6.

Thus, for compounds **1–5,** both the experimental (DNMR) and theoretical (INDO-A) results support the concept that the lowest barrier process for averaging the environments of the *tert*-butyl methyls is isolated rotation against an essentially noninverting pyramidal nitrogen. The *tert*-butyl methyl groups may of course exchange environments via an inversion–rotation itinerary (eq 3) but, for compounds **1–5,** this is a higher barrier process than simple isolated *tert*-butyl rotation, and it is not reflected in changes in the *tert*-butyl DNMR spectra. This situation is in contrast to *N-tert*-butyl-*N,N*-dialkylamines in which the lowest barrier process for equilibrating *tert*-butyl methyl environments involves *concerted* nitrogen inversion and *tert*-butyl rotation[8] with the implication that simple isolated *tert*-butyl rotation has a *higher* barrier than nitrogen inversion.[8] In addition, the higher barrier to *tert*-butyl rotation in **5** compared with **1, 2,** or **3** may indicate that chlorine is more hindering to rotation than alkyl,[19] or that the increasing pyramidality at nitrogen with increasing numbers of *N*-chlorines renders eclipsing in the transition state for isolated rotation more perfect, leading to increased pairwise nonbonded repulsions. It is also apparent from a comparison of the activation parameters for **3** and **4** (Table I) that *N*-bromine is very comparable to the smaller *N*-chlorine in restricting *tert*-butyl rotation. Although the van der Waals radius of bromine is clearly larger than that for chlorine, the longer N–Br bond and more polarizable bromine may serve to attenuate van der Waals repulsions. In addition, it is interesting to note that, while chlorine and nitrogen have identical electronegativities (3.0), chlorine is *more* electronegative than bromine (2.8). This could result in a slightly decreased pyramidality at nitrogen in the *N*-bromoamine as compared with the *N*-chloroamine.[3,8,10] The net result would be less perfect eclipsing in the transition state for isolated rotation in **4** as compared with **3** and a less effective hindering potential in **4** than one might expect for the large *N*-bromine.

Finally, it is interesting to compare the rates of site exchange of *tert*-butyl methyl groups in the series of related

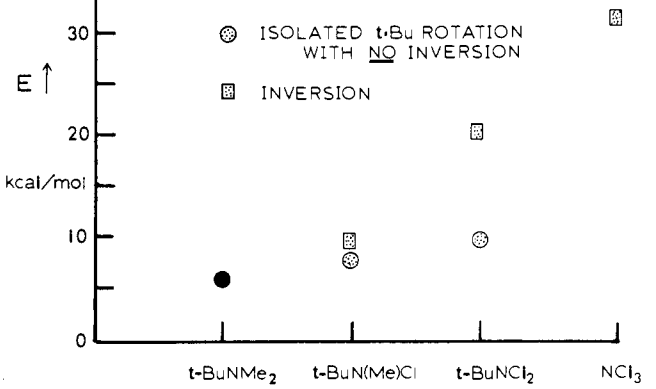


Figure 6. Trends in the barriers to *tert*-butyl group stereomutation and nitrogen inversion. The barriers to inversion for the *N*-chloroamines are derived from theoretical calculations (INDO-A), and all other barriers are experimentally determined.

compounds in Table III. The concerted inversion–rotation itinerary in t-$C_4H_9N(CH_3)_2$ provides a very low barrier process for exchanging the environments of *tert*-butyl methyl groups. The significant increase in the rotational barrier in t-$C_4H_9(CH_3)_2NBH_3$ reflects three pairwise nonbonded repulsions in the transition state for threefold *tert*-butyl rotation with nitrogen fixed in a tetrahedral geometry *via* complexation to borane. It is interesting to note that only two chlorines in t-$C_4H_9NCl_2$ are almost as effective as two methyl groups *and* a borane in t-$C_4H_9(CH_3)_2NBH_3$ with regard to hindering *tert*-butyl rotation. The much lower barrier in t-$C_4H_9PCl_2$ as compared with t-$C_4H_9NCl_2$ reflects the longer C–P bond length (1.84 Å) as compared with the C–N (1.47 Å) value.

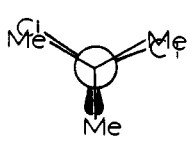
One of the goals of research of this type is to assess the magnitude of vicinal eclipsed pairwise contributions to rotational barrier heights. While it may be valid to compare the threefold *tert*-butyl rotational barriers in t-$C_4H_9(CH_3)_2NBH_3$ and t-$C_4H_9NCl_2$ for such a purpose, it is incorrect to derive any relative magnitudes of vicinal pairwise nonbonded repulsions from a comparison of t-$C_4H_9NCl_2$ or t-$C_4H_9(CH_3)_2NBH_3$ with t-$C_4H_9N(CH_3)_2$. The respective transition states of minimum potential energy for equilibration of *tert*-butyl methyl groups in t-$C_4H_9NCl_2$ (**25**) and t-$C_4H_9N(CH_3)_2$ (**26**) have very differ-

Table III. Free Energies of Activation for *tert*-Butyl Stereomutation

Compd	Rate process	$\Delta G^{\ddagger}$, kcal/mol
t-$C_4H_9N(CH_3)_2$	Concerted inversion–rotation	6.2 ± 0.1 (−153°)[a]
t-$C_4H_9(CH_3)_2NBH_3$	Threefold rotation	10.0 ± 0.1 (−79°)[b]
t-$C_4H_9NCl_2$	Threefold rotation	9.7 ± 0.1 (−89°)[c]
t-$C_4H_9PCl_2$	Threefold rotation	6.4 ± 0.1 (−148°)[d]

[a] See ref 8. [b] See ref 9. [c] This work. [d] See ref 4.

ent symmetries and very different energy components. In **25**, the principal contribution to the barrier is *vicinal eclipsed nonbonded repulsions* while, in **26**, the principle con-



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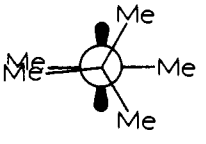

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tribution to the barrier arises from *rehybridization of nitrogen.*

From the data available for very simple amines,[2] more hindered *N-tert*-butyl-*N,N*-dialkylamines,[8] and the *N-tert*-butyl-*N*-haloamines discussed in this report, a general picture of the rotation-inversion dichotomy in all alkylamines emerges. *If the barrier to nitrogen inversion is greater than that for isolated rotation about the R_3C–N bond, then the lowest barrier process available for equilibrating the environments of the three R groups is simple isolated rotation.* This situation applies obviously to the very simple amines (e.g., CH_3NH_2)[2] and the *N-tert*-butyl-*N*-haloamines herein. *However, if the barrier to nitrogen inversion is lower than that for isolated R_3C–N rotation as in the case of tert-butyl rotation in the N-tert-butyl-N,N-dialkylamines,[8] the lowest barrier process for equilibrating the environments of the three R groups involves concomitant R_3C–N bond rotation and inversion at nitrogen.*

Experimental Section

The 60-MHz ^1H DNMR spectra were obtained using a Varian HR-60A NMR spectrometer equipped with a custom-built variable-temperature probe.[20] Irradiation at the ^2H resonance frequency was performed using an NMR Specialties SD-60B heteronuclear spin decoupler.

The theoretical DNMR spectra were calculated using DEC PDP-10 and RCA Spectra 70/46 computers and plotted using a Calcomp plotter.

All DNMR samples were freshly prepared within hours of compound isolation and purification, and all solvents were degassed.

***N-tert*-Butyl-*N,N*-dichloroamine (5).** To 100 ml of cooled (−8°) 5% aqueous sodium hypochlorite (Clorox) was added 2.0 g of *tert*-butylamine in one portion. The mixture was stirred at −8° for 24 hr, after which time an oily top layer formed. The top layer was separated, washed quickly with three 10-ml portions of ice-cold 0.2 *M* sulfuric acid, one 10-ml portion of cold water, and one 10-ml portion of ice-cold 5% sodium hydroxide. The oil was then dried (Na_2SO_4 followed by molecular sieves) and was characterized as *N-tert*-butyl-*N,N*-dichloroamine: ^1H NMR peak at δ 1.34 (singlet, *tert*-butyl protons).

Anal. Calcd for $C_4H_9Cl_2N$: C, 33.82; H, 6.39; Cl, 49.92; N, 9.86. Found: C, 33.67; H, 6.18; Cl, 50.58; N, 9.27.

***N-tert*-Butyl-*N*-ethyl-*N*-chloroamine** was prepared in a manner exactly analogous to that for *N-tert*-butyl-*N,N*-dichloroamine above.

Anal. Calcd for $C_6H_{14}ClN$: C, 53.13; H, 10.40; Cl, 26.13; N, 10.33. Found: C, 52.80; H, 10.09; Cl, 26.53; N, 10.58.

***N-tert*-Butyl-*N*-(ethyl-2,2,2-d_3)-*N*-chloroamine (1)** was prepared by the procedure immediately above except that *N-tert*-butyl-*N*-(ethyl-2,2,2-d_3)amine as prepared previously[8] was employed.

***N-tert*-Butyl-*N*-methyl-*N*-chloroamine (3) and *N-tert*-butyl-*N*-benzyl-*N*-chloroamine (2)** were prepared using the procedure described above for *N-tert*-butyl-*N*-ethyl-*N*-chloroamine.

***N-tert*-Butyl-*N*-methyl-*N*-bromoamine (4).** A sodium hypobromite solution was prepared by the dropwise addition with stirring over 45 min of 0.3 mol of bromine into a 0.93 *M* aqueous solution of sodium hydroxide cooled to −16° with an ice-salt-water bath. After addition of the bromine was complete, the solution was stirred at −16° for 30 min and then warmed to −5°. A 0.1-mol sample of *N-tert*-butyl-*N*-methylamine was added slowly (15 min) with vigorous stirring at −5° and allowed to stir for 2 hr at −5°. Then, the solution was allowed to warm to 0° and allowed to stir for another 30 min. The reaction mixture was extracted with three 75-ml portions of ether. The ether solution was washed quickly with two 25-ml portions of ice-cold 4% sulfuric acid, one 50-ml portion of cold water, and one 25-ml portion of ice-cold 5% aqueous sodium hydroxide. The ether solution was dried (Na_2SO_4; molecular sieves) and filtered. The ether was removed under vacuum to leave *N-tert*-butyl-*N*-methyl-*N*-bromoamine: NMR peaks at δ 3.01 (3 H singlet; N-CH_3) and 1.21 (9 H singlet; t-C_4H_9). This sample was used immediately to prepare the DNMR sample. The bromoamine **4** decomposes on standing.

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