Stereodynamics of *N*-*tert*-Butyl-*N*,*N*-dialkylamines. Experimental and Theoretical Evidence for a Common Potential Surface for *tert*-Butyl Rotation and Nitrogen Inversion

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Abstract: Examination of the ^{1}H dnmr spectra of a series of *N*-*tert*-butyl-*N*,*N*-dialkylamines revealed spectral changes consistent with slowing *tert*-butyl rotation and in appropriate compounds changes corresponding to slowing the nitrogen inversion–rotation process. In each compound where *tert*-butyl rotation and nitrogen inversion could be observed simultaneously, the activation parameters for the two processes are identical within experimental error. The experimental results are rationalized on the basis of a common potential surface for *tert*-butyl rotation and nitrogen inversion and are consistent with intermediate neglect of differential overlap (INDO) calculations.

One of the important aspects of conformational analysis is an assessment of the rates of various types of stereomutation (*e.g.*, bond rotation, pyramidal inversion, ring reversal) possible in a molecular system. Particularly in the case of simple systems, microwave,[2] infrared,[3] and Raman[3] spectroscopy as well as thermodynamic measurements[4] have been useful in determining barriers to simple intramolecular rate processes.

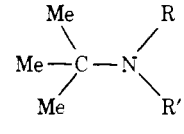
Recently, dynamic nuclear magnetic resonance (dnmr)[5] spectroscopy has been applied very successfully to the study of rotation about carbon–carbon single bonds,[6] carbon–nitrogen single bonds,[7] carbon–phosphorus single bonds,[8] and inversion about nitrogen.[9]

Although extensive experimental and theoretical studies indicate a substantial barrier (~30 kcal/mol) to pyramidal inversion about phosphorus in acyclic trialkylphosphines,[9b] nitrogen inversion in acyclic trialkylamines is a much more facile process ($\Delta H^{\pm} < 9$ kcal/mol).[10] Indeed, the occurrence of comparable barriers to C–N rotation[7d] and nitrogen inversion[10] in acyclic trialkylamines presents interesting dynamical possibilities. In fact, preliminary results indicated that in a series of *N*-*tert*-butyl-*N*,*N*-dialkylamines, *tert*-butyl rotation and nitrogen inversion occur at the same rate, *i.e.*, the *tert*-butyl rotation and nitrogen inversion itineraries may share the same potential surface.[11]

This report concerns dnmr investigations of a series of *N*-*tert*-butyl-*N*,*N*-dialkylamines which provide additional evidence supporting a common potential surface for *tert*-butyl rotation and nitrogen inversion.

Results and Discussion

Examination of the ^{1}H dnmr spectrum (60 MHz) of *N*-*tert*-butyl-*N*-methyl-*N*-(methyl-d_3)amine (**2**; 7% v/v in CH_2CHCl) at −44° reveals two sharp singlet resonances at δ 2.14 (3 H; NCH_3) and 1.00 (9 H; t-C_4H_9). In the temperature range from −130° to −165°, the *N*-methyl resonance of **2** remains a singlet albeit broadened at lower temperatures by increasing viscosity while the *tert*-butyl peak undergoes exchange broadening and then separation into two singlet resonances at δ 1.09 (6 H) and 0.84 (3 H). Such spectral behavior is best



1, R = R′ = CH_3
2, R = CH_3; R′ = CD_3
3, R = R′ = CD_3
4, R = CH_3; R′ = $C_6H_5CH_2$
5, R = CH_3; R′ = CD_2CD_3
6, R = CD_3; R′ = CH_2CD_3
7, R = R′ = CH_2CD_3
8, R = CH_3; R′ = $CD(CD_3)_2$
9, R = CH_2CD_3; R′ = $CD(CD_3)_2$

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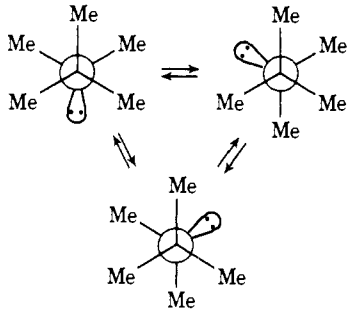
Table I. Dnmr Chemical Shifts at Slow Exchange and Activation Parameters for *tert*-Butyl Rotation and Nitrogen Inversion in *N*-*tert*-Butyl-*N*,*N*-dialkylamines

Compd	Resonance	^{1}H chemical shifts, ppm from TMS	Rate process[a]	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, gibbs	$\Delta G^{\pm}$, kcal/mol (T, °C)
1[b]	*t*-C_4H_9	0.84 (3 H); 1.08 (6 H)	Rot	6.2 ± 0.4	0 ± 3	6.2 ± 0.1 (−153)
2[c]	*t*-C_4H_9	0.84 (3 H); 1.09 (6 H)	Rot	6.2 ± 0.4	0 ± 3	6.2 ± 0.1 (−153)
3[c]	*t*-C_4H_9	0.84 (3 H); 1.07 (6 H)	Rot	6.2 ± 0.4	0 ± 3	6.2 ± 0.1 (−153)
4[d]	*t*-C_4H_9	1.00 (3 H); 1.11 (3 H); 1.28 (3 H)	Rot			6.4 ± 0.2 (−142)
	CH_2	3.89 (1 H); 2.72 (1 H); J_{AB} = −13 Hz	Inv			6.3 ± 0.2 (−142)
5[e]	*t*-C_4H_9	1.15 (6 H); 0.87 (3 H)	Rot	8.5 ± 0.4	9 ± 3	7.1 ± 0.1 (−128)
6[e]	*t*-C_4H_9	1.12 (6 H); 0.84 (3 H)	Rot	8.6 ± 0.4	8 ± 3	7.3 ± 0.1 (−128)
	CH_2	2.80 (1 H); 1.87 (1 H); J_{AB} = −12.0 Hz	Inv	8.5 ± 0.4	8 ± 3	7.2 ± 0.2 (−128)
7[f]	*t*-C_4H_9	1.17 (6 H); 0.94 (3 H)	Rot	6.4 ± 0.4	4 ± 3	6.0 ± 0.1 (−157)
	CH_2	Two superimposed AB spectra: 2.73, 2.11 (J_{AB} = −12.5 Hz; 68%); 2.74, 1.77 (J_{AB} = −12.5 Hz; 32%)	Inv	6.2 ± 0.4	3 ± 3	6.0 ± 0.1 (−157)
8[g]	*t*-C_4H_9	1.20 (3 H); 1.12 (3 H); 0.98 (3 H)	Rot	5.3 ± 0.5	−2 ± 4	5.5 ± 0.2 (−166)

[a] Rot = rotation; inv = nitrogen inversion–rotation. [b] 15% v/v CH_2CHCl. [c] 7% v/v CH_2CHCl. [d] 7% v/v CD_2CDCl. [e] 14% v/v $CBrF_3$. [f] 7% v/v $CBrF_3$. [g] 4% v/v $CBrF_3$.

rationalized in terms of slowing *apparent threefold rotation* of *tert*-butyl in **2** (eq 1) and is essentially identical with that already reported for *N*-*tert*-butyl-*N*,*N*-dimethylamine (**1**).[7cd] A complete dnmr line-shape analysis (see Experimental Section) was performed for the *tert*-butyl resonance in **2** taking into account the variation in T_2 with temperature as described previously.[7cd] The derived activation and dnmr parameters are compiled in Table I. *N*-*tert*-Butyl-*N*,*N*-di(methyl-d_3)amine (**3**; 7% v/v in CH_2CHCl) displayed essentially the same *tert*-butyl dnmr spectra as for **1** and **2** with T_2 values used in the total dnmr line-shape analysis for **3** taken from the dnmr spectra of **2**. Activation and dnmr parameters for **3** are found in Table I.



(1)

A perusal of the activation parameters for **1**, **2**, and **3** (Table I) indicates that deuteriation has essentially no effect on the dynamics of *tert*-butyl rotation and we will assume this to be valid in subsequent discussion of other deuteriated amines. The higher barriers to *tert*-butyl rotation in **1**, **2**, and **3** as compared to threefold C–N rotation in CH_3NH_2 ($\Delta H^{\pm}$ = 2.0 kcal/mol)[12] and $(CH_3)_3N$ ($\Delta H^{\pm}$ = 4.4 kcal/mol)[13] and sixfold C–N rotation in CH_3NO_2 ($\Delta H^{\pm}$ = 0.006 kcal/mol)[14] attest to the not unexpected increased nonbonded repulsions in the transition state for *tert*-butyl rotation in **1**, **2**, and **3**. The barriers to *tert*-butyl rotation in the BH_3 or BD_3 complexes of **1** in which nitrogen inversion is locked and an additional substituent is bonded to nitrogen are understandably higher ($\Delta H^{\pm}$ = 11.2 ± 0.3 kcal/mol).[7a]

The comparable barriers to the inversion–rotation process in dibenzylmethylamine ($\Delta H^{\pm}$ = 7.2 ± 0.4 kcal/mol, $\Delta S^{\pm}$ = 4 ± 3 gibbs, $\Delta G^{\pm}$ = 6.6 ± 0.1 kcal/mol at −141°)[10a] and *tert*-butyl rotation in **1** (Table I) present some intriguing dynamical possibilities. Indeed, a dnmr investigation of *N*-benzyl-*N*-*tert*-butyl-*N*-methylamine (**4**) indicated *equal* free energies of activation at −142° for *tert*-butyl rotation and nitrogen inversion (Table I)[11a] suggesting the possibility of a common potential surface for *tert*-butyl rotation and nitrogen inversion in **4**. Unfortunately, significantly shortened T_2 values for **4** broadened the low-temperature dnmr spectra substantially resulting in poor resolution and the inability to obtain reliable $\Delta H^{\pm}$ and $\Delta S^{\pm}$ values from a complete dnmr line-shape analysis.[5] Unusually small T_2 values at low temperatures seem to be general for a host of phenyl-containing compounds investigated in this laboratory. The phenomenon may be due to a large molecular volume or more effective solvation of the phenyl moiety at low temperatures leading to an effectively larger molecular volume, a longer molecular rotational correlation time or slower rate of molecular tumbling, and a shorter T_2.[15]

Dnmr studies of a series of other *N*-*tert*-butyl-*N*,*N*-dialkylamines (**5**–**8**) have provided more definitive results regarding the existence of a common potential surface for *tert*-butyl rotation and nitrogen inversion.

The ^{1}H dnmr spectrum (60 MHz) of *N*-*tert*-butyl-*N*-methyl-*N*-(ethyl-d_5)amine (**5**; 14% v/v in $CBrF_3$) at −58° consists of two sharp singlet resonances at δ 2.11 (NCH_3) and 1.03 (*t*-C_4H_9). At lower temperatures, the *tert*-butyl peak undergoes exchange broadening and separates into two broad singlet resonances at δ 1.15 (6 H) and 0.87 (3 H) at −148° again consistent with slowing *tert*-butyl rotation. It is apparent from the *tert*-butyl spectrum under conditions of slow exchange that the two *tert*-butyl methyl groups gauche to the nitrogen lone pair (**10**) have identical chemical shifts indicating the same effective diamagnetic anisotropic effects of CH_3 and CD_2CD_3. A complete ^{1}H dnmr line-shape analysis was performed for the *tert*-butyl resonance of **5** using the T_2 of the NCH_3 resonance as a measure of the T_2 for *tert*-butyl throughout the region

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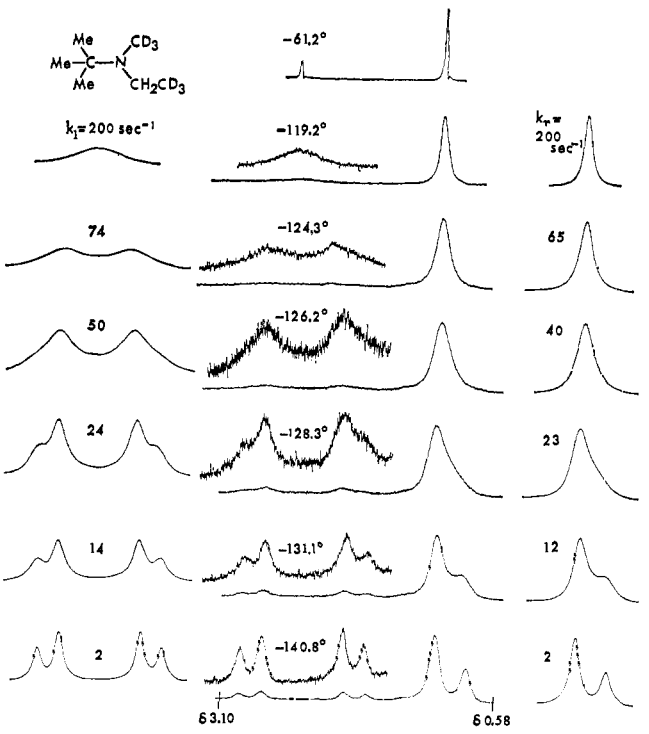
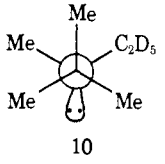


Figure 1. The ^1H dnmr spectra (60 MHz; ^2H decoupled) of *N-tert*-butyl-*N*-(methyl-d_3)-*N*-(ethyl-2,2,2-d_3)amine (**6**; 14% v/v in $CBrF_3$) and theoretical spectra calculated as a function of the rate of *tert*-butyl rotation (k_r = first-order rate constant for conversion of one *tert*-butyl rotamer to *one* other rotamer) and nitrogen inversion (k_i).



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of exchange broadening. The derived activation parameters (Table I) reveal an expected increase in the barrier to *tert*-butyl rotation in **5** as compared to **1–3** in accord with simple steric repulsion arguments.

Subsequent examination of the ^1H dnmr spectrum (with ^2H irradiation) of *N-tert*-butyl-*N*-(methyl-d_3)-*N*-(ethyl-2,2,2-d_3)amine (**6**; 14% v/v in $CBrF_3$) revealed changes in the *tert*-butyl *and* CH_2 resonances at low temperatures consistent with slowing both *tert*-butyl rotation and nitrogen inversion in a manner similar to *N-tert*-butyl-*N*-benzyl-*N*-methylamine (**4**).[11a] However, contrary to **4**, well-defined spectra under conditions of slow exchange are observed for **6**. The ^1H dnmr spectrum of **6** at −61.2° (Figure 1) consists of sharp singlets at δ 2.37 (CH_2) and 1.05 (t-C_4H_9). At lower temperatures, the CH_2 resonance separates into a single AB spectrum having chemical shifts at δ 2.80 (1 H) and 1.87 (1 H) with J_{AB} = −12.0 Hz consistent with slowing *nitrogen inversion*.[9,10] The AB spectrum remained *symmetrical* to −160°. In a manner exactly analogous to **5**, the *tert*-butyl resonance of **6** separates at low temperatures into two singlets at δ 1.12 (6 H) and 0.84 (3 H) consistent with slowing *tert-butyl rotation*. It is important to note (Figure 1) that the *tert*-butyl and methylene resonances of **6** undergo exchange broadening over approximately the same temperature range. *Indeed, complete dnmr line-shape analyses for both the methylene and tert-butyl resonances gave activation parameters for nitrogen inversion and tert-butyl rotation which are equal within experimental error* (Table I). Thus, the rate process which averages the environments of the two diastereotopic methylene protons of **6** travels an energy surface which has an identical transition state energy and entropy as the rate process which averages the environments of the *tert*-butyl methyl groups. This speaks strongly for a *common potential surface for tert-butyl rotation and nitrogen inversion.*

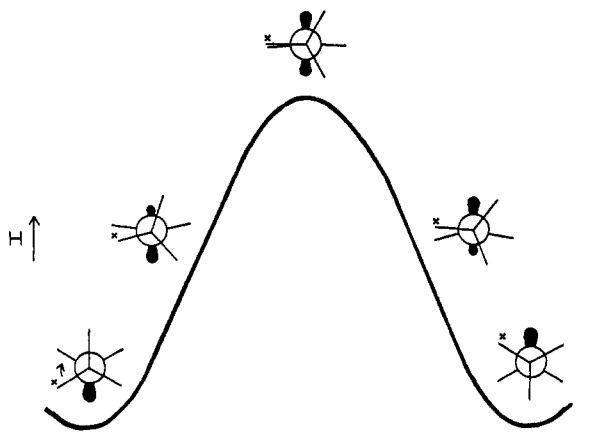
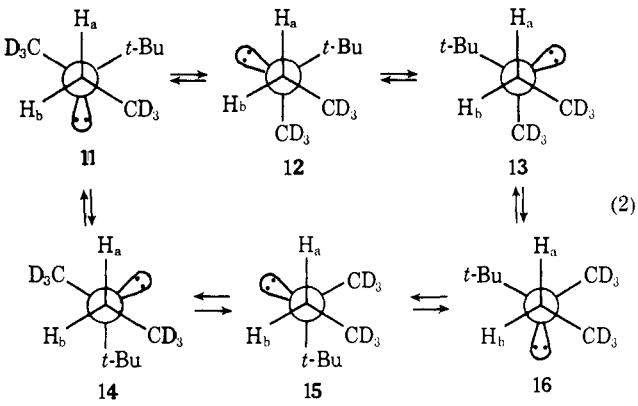


Figure 2. A proposed itinerary for *tert*-butyl rotation and nitrogen inversion proceeding *via* a common potential surface.

In considering possible models for concerted *tert*-butyl rotation and nitrogen inversion, one dynamical itinerary seems most plausible and that is illustrated for the case of *one inversion* in Figure 2. As the *tert*-butyl group begins to rotate, vicinal nonbonded repulsions across the carbon–nitrogen bond will increase. However, these repulsions may be minimized by a concomitant rehybridization of nitrogen toward sp^2. If the energy associated with nitrogen rehybridization is less than that due to vicinal nonbonded repulsions, this route would clearly be the preferred dynamical itinerary for *tert*-butyl rotation. As the *tert*-butyl group continues to rotate, a potential maximum might be expected at the point where nitrogen is sp^2 hybridized and one methyl of *tert*-butyl is eclipsed with one other N substituent (Figure 2). The implication in this dynamical model is that the barrier to *tert*-butyl rotation in the absence of nitrogen inversion is greater than that associated with the concerted process (Figure 2). Perusal of Figure 2 indicates also that as a result of *one* inversion–rotation, the *tert*-butyl group rotates only 60° as compared to 120° in passing over one potential maximum in a threefold rotation (eq 1). Thus, a complete rotation of *tert*-butyl *via* the common potential surface model (Figure 2) requires passing over *six* potential maxima, *i.e.*, a sixfold rotation.

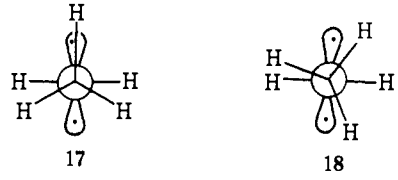
A similar rationale can be applied to the CH_2CD_3 group of **6** (eq 2; Newman projection down the CH_2N bond). Equation 2 represents the six possible potential minima involved in a complete rotation about the CH_2–N bond *via* the concerted rotation–inversion itinerary (Figure 2). For example, the **11** → **15** → **13** → **11** process represents a complete *threefold* rotation of CH_2 as does **14** → **12** → **16** → **14**. However, it is clear from eq 2 that these two subsets of threefold rotation are not sufficient to exchange the environments of H_a and H_b leading to a singlet resonance (−61.2°, Figure 1) and that inversion–rotation (*e.g.*, **11** ⇄ **14**, **11** ⇄ **12**,



(2)

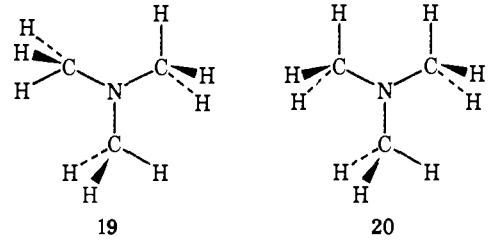
etc.) must occur to effect time averaging of H_a and H_b environments. Rapid threefold CH_2–N rotation and slow nitrogen inversion will result in one time-averaged AB spectrum for CH_2CD_3 as observed at −140.8° (Figure 1). Thus, the dnmr spectra of **6** (Figure 1) are best rationalized at low temperatures in terms of *slow* *tert*-butyl rotation, *slow* nitrogen inversion, and *fast* CH_2–N rotation with *tert*-butyl rotation and nitrogen inversion proceeding probably *via* a common potential surface.

Intermediate neglect of differential overlap (INDO) calculations[16] performed in this laboratory support the concept of a common potential surface for rotation and inversion in *hindered* amines[17] such as **1–9**. Assuming a tetrahedral geometry about nitrogen in methylamine and the perfectly staggered form as the most stable pyramidal conformation, the INDO calculations indicate the perfectly eclipsed rotamer (*no* nitrogen rehybridization) is 1.56 kcal/mol higher in enthalpy than the staggered geometry. The experimental barrier ($\Delta H^{\pm}$) to rotation in methylamine is 2.0 kcal/mol[12] in excellent agreement with our theoretical calculations. In considering nitrogen inversion in methylamine, proceeding from the staggered ground state conformation to a geometry having planar (sp^2 hybridized) nitrogen ($\angle CNH = \angle HNH = 120°$) with maximum staggering of methyl (**17**) requires an increase of 4.67 kcal/mol. Once the nitrogen is sp^2 hybridized, methyl rotation to the eclipsed form (**18**) increases the potential energy



by only 0.003 kcal/mol, *i.e.*, methyl is essentially freely rotating in the planar nitrogen geometry. This situation is analogous to the very low barrier to sixfold rotation in nitromethane ($\Delta H^{\pm} = 0.006$ kcal/mol).[14] Since **17** or **18** is very likely the transition state for nitrogen inversion in methylamine, the calculated barrier ($\Delta H^{\pm} = 4.67$ kcal/mol) is at least consistent with the experimental value of 7.2 ± 0.4 kcal/mol for the more hindered dibenzylmethylamine.[10a] However, it is clear from the INDO calculations that rotation and inversion in methylamine proceed *via* different potential surfaces, *i.e.*, different barriers, and there is no justification for invoking a common potential surface for the two processes.

However, INDO calculations on more hindered amines reveal interesting trends. Assuming a tetrahedral geometry for nitrogen in trimethylamine, rotation of *one* methyl group into an eclipsed conformation (*no* nitrogen rehybridization) increases the energy by 2.38 kcal/mol (experimental $\Delta H^{\pm} = 4.4$ kcal/mol for methyl rotation in trimethylamine[13]). The geometry having two methyl groups in eclipsed configurations and one staggered is calculated to be 6.20 kcal/mol higher in energy than the completely staggered form. It is apparent that methyl rotation in trimethylamine proceeds *via* one methyl rotation at a time. With regard to nitrogen inversion in trimethylamine, the minimum energy geometry having an sp^2 hybridized planar nitrogen ($\angle CNC = 120°$) is a structure having C_{3h} symmetry with one C–H bond of each methyl in the plane defined by the three carbons and nitrogen (**19**).



This structure (**19**) is 5.15 kcal/mol higher in energy than the all staggered pyramidal ground state. Rotation to the less symmetrical **20** or a concerted 30° rotation of all methyls in **19** increases the energy above **19** by 0.24 and 0.28 kcal/mol, respectively. It is interesting to note that in order to go from the all staggered pyramidal geometry of trimethylamine to **19**, both nitrogen rehybridization and a concomitant 30° rotation of all three methyls must occur which is consistent with our previously proposed itinerary for *tert*-butyl rotation and nitrogen inversion in **6** (Figure 2). One other important difference between the planar nitrogen forms of methylamine (**17** and **18**) and trimethylamine (**19**) is a significantly larger barrier to rotation (~0.2 kcal/mol) in the trimethylamine case although nitrogen rehybridization still accounts for better than 95% of the energy increase in **19** above the ground state conformation. However, there still exist in trimethylamine different barriers to threefold rotation in the pyramidal form and to nitrogen inversion. A common potential surface for the two processes does not pertain.

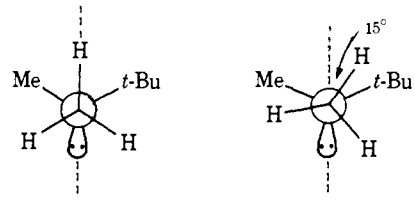
Similar calculations indicate a barrier to *tert*-butyl rotation in pyramidal *tert*-butylamine of 1.66 kcal/mol and essentially free rotation of *tert*-butyl in the planar (sp^2 hybridized nitrogen) form which is calculated to be 4.41 kcal/mol higher in energy than the completely staggered pyramidal ground state geometry.

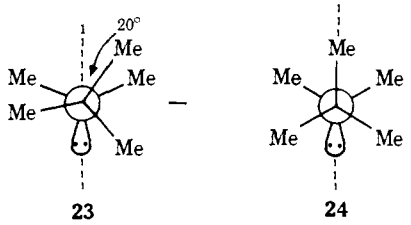
More extensive INDO calculations were performed for the hindered *N*-*tert*-butyl-*N*,*N*-dimethylamine (**1**).

(16) The computer program used for the INDO calculations is by D. L. Beveridge and P. A. Dobosh, Program No. 141, Quantum Chemistry Program Exchange, Indiana University, and is based on the report of J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967). The rationale for selecting INDO has been given elsewhere: P. E. Stevenson and D. L. Burkey, *J. Amer. Chem. Soc.*, **96**, 3061 (1974). Standard values of bond lengths (C–C, 1.54 Å; C–H, 1.09 Å; C–N, 1.47 Å; N–H, 1.01 Å) have been used throughout. Angular geometries are tetrahedral and staggered unless stated otherwise.

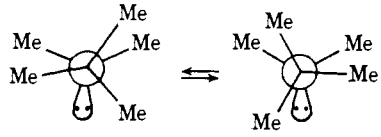
(17) Cartesian coordinates for these calculations were obtained using the computer program "COORD (time sharing version)," P. E. Stevenson and J. E. Merrill, Quantum Chemistry Program Exchange, Program No. 186, Indiana University.

Because **1** is a significantly more hindered amine than methyl-, trimethyl-, or *tert*-butylamine, we searched carefully for the geometry of minimum potential energy for both ground state and transition state conformations. With regard to the most stable ground state conformation, the energy minimum occurs at CNC bond angles of 114.3° which is essentially half-way between tetrahedral (sp^3) and planar (sp^2) nitrogen configurations. The minimum energy rotamer conformation for each N-methyl group is not the perfectly staggered conformer (**21**) but one in which the dihedral angle





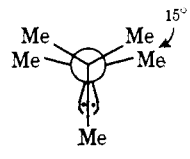
between the lone pair and the hydrogen trans to the lone pair is 165° (**22**). A similar energy minimum is calculated for the *tert*-butyl group with each methyl of *tert*-butyl kept in a staggered form in which the dihedral angle between the methyl group trans to the lone pair and the lone pair is 160° (**23**). Conformation **24** is calculated to be 1.55 kcal/mol higher in energy than **23** indicating a small barrier to torsional motion of *tert*-butyl (eq 3). The calculations indicate that in the



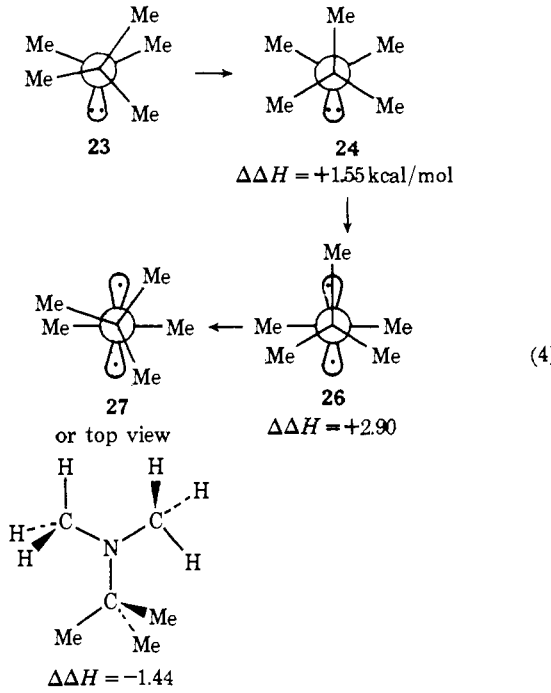
(3)

ground state conformation of **1**, all groups have rotated in part and nitrogen has rehybridized in part toward the transition state geometries associated with simple rotation or inversion. *It is apparent that the increased steric repulsions in hindered amines will tend to alter the ground state geometry toward less staggering of vicinal substituents and decreased pyramidality at nitrogen.*

In searching for the dynamical itinerary of minimum potential energy for *tert*-butyl rotation, the first calculation we performed involved pure *tert*-butyl rotation (no nitrogen rehybridization) starting from **23**. Keeping all methyl hydrogens fixed and rotating *tert*-butyl gave a transition state of minimum energy in which one methyl of *tert*-butyl eclipses the lone pair exactly and the other two methyls form dihedral angles of 15° with the N-methyl groups (**25**). Conformation **25** is calculated



to be 4.02 kcal/mol higher in energy than **23**. It then became necessary to test our proposed common potential surface for *tert*-butyl rotation and nitrogen inversion in **1** (Figure 2). For purposes of a systematic summary, consider the first step in the concerted dynamical process to be the start of *tert*-butyl rotation (eq 4). In eq 4,



(4)

the $\Delta\Delta H$ values represent the change in potential energy as compared to the immediately previous species. Indeed, **27** (eq 4) is calculated to be the transition state of minimum potential energy and is calculated to be only 3.01 kcal/mol higher in energy than **23**. In order to go from **23** to **27**, nitrogen rehybridization to sp^2 and approximately a 15° rotation of N-methyl and a 10° rotation of *tert*-butyl must occur in good qualitative agreement with the itinerary proposed in Figure 2. As the nitrogen of **27** completes its inversion to the invertomer of **23**, another 10° rotation of *tert*-butyl occurs. An additional torsional movement *via* **24** (see eq 3) adds another 40° giving a net 60° rotation of *tert*-butyl with one complete inversion. At this juncture, one important comparison needs to be made. Rotation of *tert*-butyl with no nitrogen inversion *via* **25** involves a significantly higher potential maximum (4.02 kcal/mol) than the concerted *tert*-butyl rotation/nitrogen inversion process *via* **27** (3.01 kcal/mol; eq 4). Since *tert*-butyl will obviously prefer to rotate *via* the route of lowest activation energy, it seems clear that it will rotate *via* a potential surface common with nitrogen inversion. *Thus, if the barrier to tert-butyl rotation with a fixed pyramidal nitrogen is greater than that for nitrogen inversion, nitrogen inversion provides a lower energy pathway for rotation.* It must be noted that *tert*-butyl rotation *via* the common potential surface model proceeds *via six* principal maxima for a complete 360° rotation, *i.e.*, a *sixfold process.* A free energy profile for *tert*-butyl rotation in **1** is illustrated in Figure 3.

Examination of the ^1H dnmr spectra (60 MHz) of *N-tert*-butyl-*N*,*N*-di(ethyl-2,2,2-d_3)amine (**7**; 7% v/v in $CBrF_3$ with ^2H irradiation) also revealed changes in the *tert*-butyl resonance consistent with slowing *tert*-butyl rotation giving at slow exchange two broad singlet

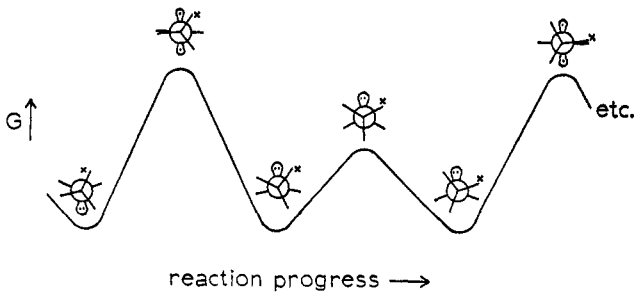
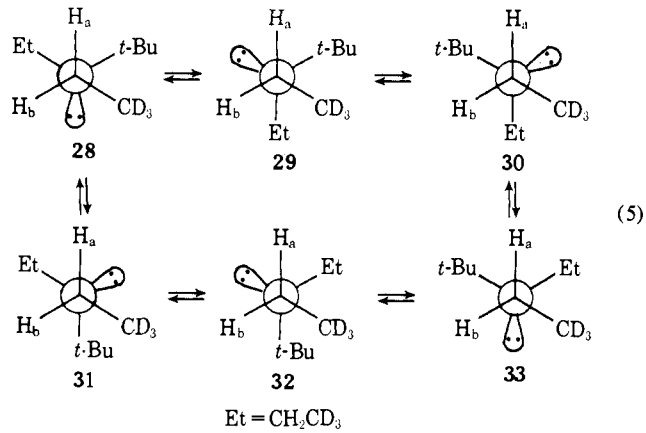


Figure 3. A free energy profile for concerted *tert*-butyl rotation and nitrogen inversion in *N*-*tert*-butyl-*N*,*N*-dimethylamine.

resonances at δ 1.17 (6 H) and 0.94 (3 H). A complete dnmr line-shape analysis gave the activation parameters for *tert*-butyl rotation compiled in Table I.

Simultaneous observation of the ^{1}H dnmr spectra of the CH_2 groups of **7** gave an interesting series of spectral changes at low temperatures (Figure 4). At $-120.2°$, the singlet CH_2 peak is entirely consistent with rapid CH_2–N rotation *and* nitrogen inversion on the dnmr time scale. However, at lower temperatures, the CH_2 resonance broadens in a definitely asymmetric fashion (Figure 4) and then sharpens into the spectrum at $-167.3°$ displaying definite AB characteristics albeit asymmetric. An iterative procedure established that the CH_2 spectrum at $-167.3°$ is best analyzed as *two* superimposed AB spectra with chemical shifts of δ 2.73 and 2.11 ($J_{AB} = -12.5$ Hz) and δ 2.74 and 1.77 ($J_{AB} = -12.5$ Hz) with respective intensities of 68:32. Such an observation implies a unique dynamical situation and can be rationalized in terms of eq 5 (Newman projection down the CH_2N bond of **7**). Equation 5 is analogous to eq 2 and a conversion from one conformation to an adjacent form (*e.g.*, **28** → **29**, **28** → **31**, etc.) is achieved *via* the concerted rotation–inversion mechanism described above. The processes **28** → **32** → **30** → **28** and **33** → **29** → **31** → **33** involve a simple threefold rotation about the CH_2–N bond with *no* inversion. However, this threefold rotation is not sufficient to average the environments of H_a and H_b (eq 5). Inversion must also



(5)

occur (*e.g.*, **28** ⇄ **31**, **28** ⇄ **29**, etc.). In the event of rapid threefold rotation about the CH_2–N bond and slow inversion, the CH_2 spectrum would be comprised of *one* time-averaged AB spectrum as observed for **6** (Figure 1). In the case of **7**, the observation of two separate AB spectra reveals a dynamical situation different from **6** and is consistent with *slow ethyl or CH_2N rotation*. For a given invertomer in eq 5, it is clear

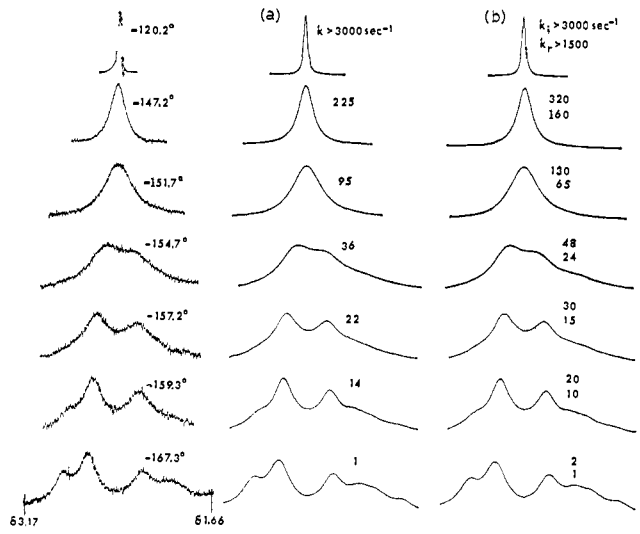


Figure 4. The ^{1}H dnmr spectra (60 MHz) of the CH_2 groups of *N*-*tert*-butyl *N*,*N*-di(ethyl-*2,2,2-d*$_3$)amine (**7**; 7% v/v in $CBrF_3$ with ^{2}H irradiation) and theoretical spectra calculated as a function of the rate of nitrogen inversion. Column a: k = first-order rate constant for the processes (eq 5) **30** → **28**, **33** → **31**, **28** → **31**, **30** → **33**. Column b: k_i = rate constant for processes (eq 5) **28** → **31** and **30** → **33** which is twice k_r for processes **30** → **28** and **33** → **31**.

that H_a and H_b are nonequivalent. In **28** and **31**, H_a and H_b have exchanged environments, but **28** and **31** will obviously give the same CH_2 dnmr spectrum under static conformational conditions. The same reasoning may be applied to **29** and **32** as well as **30** and **33**. Thus, under conditions of slow inversion and slow CH_2–N rotation, one might expect to observe a series of three superimposed AB spectra due to CH_2 resonances in the various invertomers of **7** (eq 5). However, an excellent fit of the slow exchange CH_2 spectrum ($-167.3°$, Figure 4) indicates only *two* AB spectra, *i.e.*, two pairs of invertomers. This observation seems quite reasonable in light of the substantial vicinal nonbonded repulsions in **29** and **32** (eq 5). It is probable that very little of **29** or **32** is present. The invertomers present to the extent of 68% may be assigned to **30** and **33** in which the methyl/ethyl vicinal repulsion would be expected to be less than the methyl/*tert*-butyl vicinal repulsion in **28** and **31** (32%). In subsequent dnmr line-shape calculations, this conformational situation was assumed to prevail.

In assigning the chemical shifts for H_a and H_b, it would be reasonable to assign the upfield AB chemical shifts at δ 2.11 to H_b of **30** (eq 5) and at 1.77 to H_a of **28** by analogy with much other data revealing a significant upfield shift for protons trans to a nitrogen lone pair.[18] The essentially identical low-field chemical shifts at δ 2.73 and 2.74 may be assigned to H_a in **30** and H_b in **28**, respectively. Of course, the various assignments are reversed in invertomers **31** and **33**.

In selecting a dynamical model in order to generate theoretical dnmr spectra for the CH_2 resonance in **7**, several possibilities exist. However, in light of the itinerary suggested by the previously described theoretical calculations, a model based on eq 5 was tested initially. Using this model, the total rates of inter-

(18) J. B. Lambert, F. G. Keske, R. E. Carhart, and A. P. Ivanovich, *J. Amer. Chem. Soc.*, **89**, 3761 (1967); M. J. T. Robinson, *Tetrahedron Lett.*, 1153 (1968); P. J. Halls, R. A. Y. Jones, A. R. Katritsky, M. Snarey, and D. L. Trepanier, *J. Chem. Soc. B*, 1320 (1971).

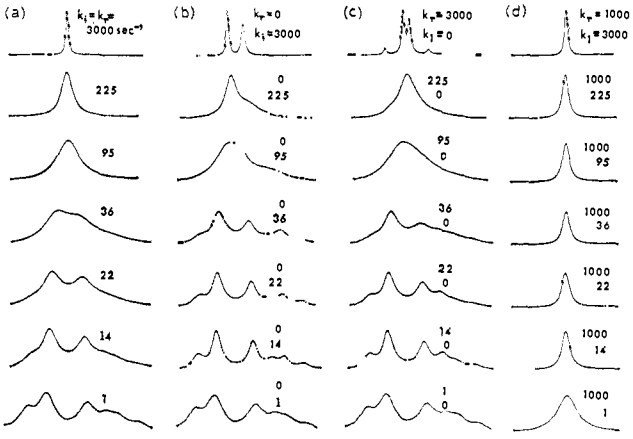


Figure 5. Theoretical ^{1}H dnmr spectra for the CH_2 resonance of *N-tert*-butyl-*N*,*N*-di(ethyl-2,2,2-d_3)amine (**7**) using different dynamical models: (a) rate of apparent threefold CH_2N rotation or a double inversion (k_r; **30** → **28**, **33** → **31**, eq 5) equals the rate of a single nitrogen inversion (k_i, **28** → **31**, **30** → **33**; eq 5; see Figure 4a); (b) $k_r = 0$; k_i is variable; (c) $k_i = 0$; k_r is variable; (d) $k_r = 1000$, k_i is variable.

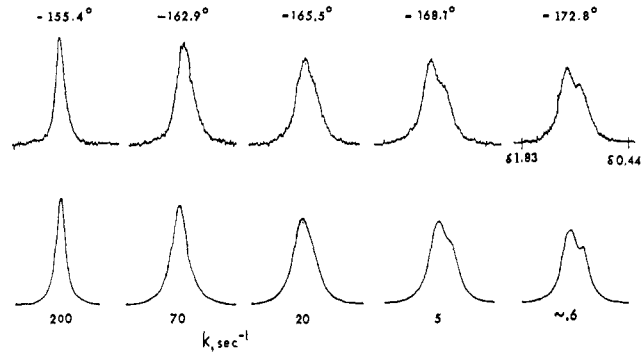


Figure 6. The ^{1}H dnmr spectra (60 MHz) of the *tert*-butyl group in *N-tert*-butyl-*N*-methyl-*N*-(isopropyl-d_7)amine (**8**; 4% v/v in $CBrF_3$) and theoretical spectra calculated as a function of the rate of *tert*-butyl rotation.

conversion among all four species (**28**, **30**, **31**, **33**) were set equal with the rate constants adjusted simply to reflect the different populations of the various rotamers (*i.e.*, equilibrium conditions). Perusal of Figure 4a indicates an excellent fit of the theoretical to experimental spectra. This result is consistent with at least two kinetic models: (1) the itinerary described in eq 5 in which the rates of single inversion processes **30** ⇄ **33** and **28** ⇄ **31** and double inversion processes **30** ⇄ **28** and **33** ⇄ **31** are all equal; (2) rates of direct threefold CH_2N rotation (no inversion) (**28** ⇄ **30**; **31** ⇄ **33**) equal to that for nitrogen inversion (**28** ⇄ **31**; **30** ⇄ **33**). If eq 5 is an accurate portrayal of the dynamical situation in **7** with **29** and **32** as unstable intermediates, then a statistical factor of 2 may be introduced in the processes **28** ⇄ **30** or **31** ⇄ **33** as compared to **28** ⇄ **31** and **30** ⇄ **33**. If **28** goes to **29**, **29** has an equal probability of going back to **28** or on to **30**. Thus, the *observed* rate constants for the **28** ⇄ **30** and **31** ⇄ **33** processes may be about one-half those for the **28** ⇄ **31** and **30** ⇄ **33** processes. A series of theoretical dnmr spectra was generated based on this model (Figure 4b) giving essentially the same "fit" as the previous model. Unfortunately, any subtle line-shape differences in the two models were effectively obscured by short T_2 values at these low temperatures. Very similar activation parameters were calculated using the two models and the values are compiled in Table I. However, the theroetical spectra are entirely consistent with slowing *both* ethyl (CH_2N) and *tert*-butyl rotation as well as nitrogen inversion. In light of the theoretical calculations described previously and the essentially identical barriers to *tert*-butyl rotation, ethyl rotation, and nitrogen inversion, an intuitive choice of dynamical mechanism favors the common potential surface route for ethyl and *tert*-butyl rotation as well as nitrogen inversion.

Although the broad lines observed for **7** at low temperatures obscured a rigorous mechanism selection, some mechanistic extremes can be ruled out based on theoretical dnmr line shapes. In column a of Figure 5 is compiled a series of theoretical spectra for the CH_2 resonance in **7** using the previously described model involving equal total rates of conversion between **28**, **30**, **31**, and **33** which gave a good fit to the experimental spectra (Figure 4a). In column b, the rate of threefold CH_2N rotation (**28** ⇄ **30**; **31** ⇄ **33**) is set equal to zero and the rate of inversion (**28** ⇄ **31**; **30** ⇄ **33**) varied. Although the slow exchange spectrum fits as it must, the spectra in the intermediate and fast exchange regions clearly do not. In column c, the rate of inversion was set equal to zero and the rate of CH_2N threefold rotation varied. It is clear that this model does not fit the experimental data. In column d, the rate constant for threefold CH_2N rotation is kept at 1000 sec^{-1} and the rate of inversion varied giving a series of spectra which deviate very seriously from experimental. Thus, it is evident that both CH_2–N rotation and nitrogen inversion must be retarded at low temperatures at least consistent with the common potential surface model (Figure 2).

The ^{1}H dnmr spectra of the *tert*-butyl group of *N-tert*-butyl-*N*-methyl-*N*-(isopropyl-d_7)amine (**8**; 4% v/v in $CBrF_3$) also revealed changes consistent with slowing *tert*-butyl rotation (Figure 6). For the best fits of the slow and intermediate exchange spectra, it was necessary to employ three chemical shifts at δ 1.20 (3 H), 1.12 (3H), and 0.98 (3 H) using the NCH_3 T_2 as a measure of T_2 for *tert*-butyl throughout the region of collapse. Activation parameters are compiled in Table I. While significant viscosity broadening occurred for the *tert*-butyl dnmr signals of *N-tert*-butyl-*N*-(ethyl-2,2,2-d_3)-*N*-(isopropyl-d_7)amine (**9**; 3% v/v in $CBrF_3$), *N-tert*-butylaziridine (5% v/v in $CBrF_3$), and *N-tert*-butyl-*N*-methylacetamide (**34**; 5% v/v in $CBrF_3$), no peak separation was observed to −180°. A very low barrier to *tert*-butyl rotation in **34** would be consistent with an essentially planar geometry at nitrogen and sixfold *tert*-butyl rotation.

In perusing the data in Table I, some interesting trends emerge which can be rationalized in terms of a common potential surface for *tert*-butyl rotation and nitrogen inversion proceeding *via* a transition state similar to **27** (eq 4). There are two contributions to the potential energy of **27**: (1) the energy associated with rehybridizing nitrogen and (2) nonbonded repulsions involving proximate substituents. As indicated in the above INDO calculations, the energy of rehybridization is usually significantly larger than that associated with the nonbonded repulsions. Thus, any changes in pyramidality about nitrogen might be expected to change the intramolecular dynamics.

In proceeding from *N-tert*-butyl-*N*,*N*-dimethylamine (**1–3**) to *N-tert*-butyl-*N*-methyl-*N*-ethylamine (**5–6**), two significant differences are observed (Table I). The $\Delta H^{\pm}$ values for *tert*-butyl rotation and nitrogen inversion in **5–6** are larger than in **1–3** and the $\Delta S^{\pm}$ values are more positive for **5–6** as compared to **1–3**. An examination of models indicates very similar nonbonded repulsions in the pyramidal ground states of **1–3** and **5–6**, although the ethyl group in **5** or **6** is much less free to rotate than methyl in **1–3**. Thus, one might conclude that the respective energies associated with nitrogen rehybridizing to sp^2 in **1–6** are very similar. However, by analogy with the INDO calculations, substituting a methyl group for a methyl hydrogen in the transition state **27** can do nothing but increase nonbonded repulsions and lead to a higher barrier in **5** or **6** as compared to **1–3**. The more positive $\Delta S^{\pm}$ for **5** and **6** may be rationalized on the basis of significantly increased freedom of rotation about C–N and C–C bonds in proceeding to the transition state as compared to **1**.

In comparing **5** and **6** with *N-tert*-butyl-*N*,*N*-di(ethyl-*2,2,2-d*$_3$)amine (**7**), an examination of models reveals significantly increased crowding in the pyramidal form of **7** due to a buttressing effect of two ethyl groups. This should decrease the pyramidality at nitrogen, decrease the energy necessary to rehybridize nitrogen, and decrease the barrier associated with a transition state common to rotation and inversion as observed (Table I). *N-tert*-Butyl-*N*-methyl-*N*-(isopropyl-*d*$_7$)amine (**8**) also follows this trend.

The experimental and theoretical results reported herein indicate the interesting observation in *hindered amines* that rotation and inversion may proceed *via* a common potential surface and that increasing N-substituent steric bulk may serve to *lower* the barrier to C–N rotation.

Experimental Section

The *60 MHz ^{1}H dnmr spectra* were obtained using a Varian HR-60A nmr spectrometer equipped with a custom-built variable-temperature probe.[19]

The theoretical ^{1}H dnmr spectra were calculated using a locally expanded version of DNMR3[20] in order to accommodate the dynamical model for **7**, *i.e.*, four molecular configurations with two nuclei in each configuration. The original program allowed for a maximum of three configurations and three nuclei in each *or* two configurations with four nuclei in each and was limited by the size of the major complex matrices to 48 by 48. In order to allow for the six rate constants necessary for a four configurations and two nuclei problem, the appropriate arrays were redimensioned and I/O statements changed accordingly. The theoretical spectra were calculated using DEC PDP-10 and RCA Spectra 70/46 computers and plotted using a Calcomp plotter.

***N-tert*-Butyl-*N*,*N*-di(methyl-*d*$_3$)amine (3).** To a cooled (0°) stirred mixture of 30 g (0.41 mol) of *tert*-butylamine in 100 ml of ether was added dropwise a solution of 20 g (0.14 mol) of methyl-*d*$_3$ iodide in 50 ml ether. After addition the solution was heated to reflux for 4 hr and then cooled to 0° while 10 g (0.17 mol) of KOH in 100 ml of H_2O was added slowly with stirring. Distillation of this mixture yielded fractions at 67–68° (1 atm) and 88–90° (1 atm). Based on a comparison of glpc retention times, boiling points, and nmr spectra with the nondeuterated analogs prepared in the same fashion as well as a commercial sample of *N-tert*-butyl-*N*,*N*-dimethylamine, these two samples proved to be *N-tert*-butyl-*N*-methyl-*d*$_3$-amine and *N-tert*-butyl-*N*,*N*-di(methyl-*d*$_3$)amine (**3**), respectively.

***N-tert*-Butyl-*N*-methyl-*N*-(methyl-*d*$_3$)amine (2).** To a stirred and cooled (0°) solution of 9 g (0.10 mol) of *N-tert*-butyl-*N*-methyl-*d*$_3$-amine (obtained as a by-product in synthesis of **3**) in 200 ml of ether was added dropwise a mixture of 5 g (0.04 mol) of methyl iodide in 50 ml of ether. After refluxing for 2 hr, it was cooled and dry HCl was bubbled slowly through the solution. The solid amine salt formed was removed by filtration and dissolved in 20 ml of H_2O to which was then added solid KOH to saturate the solution. The top liquid layer was separated and dried over sodium sulfate. Characterization was made by the same procedure as the preceding compound. A 10 ft. 20% SE-30 column was used for the glpc purification of **2**: nmr peaks at δ 2.14 (3 H singlet, methyl protons) and 1.00 (9 H singlet, *tert*-butyl protons); bp 88–90° (1 atm).

***N-tert*-Butyl-*N*-methyl-*N*-ethylamine.** A mixture of 2.2 g (0.3 mol) of acetyl chloride in 50 ml of chloroform was added dropwise to a stirred and cooled (0°) solution of 4.3 g (0.05 mol) of *N-tert*-butyl-*N*-methylamine in 50 ml of chloroform. The mixture was allowed to reflux after which it was heated and refluxed for 4 hr more. After cooling, 5 g (0.12 mol) of solid anhydrous NaOH was added and the mixture was allowed to stir at room temperature for 12 hr. After drying (sodium sulfate) and filtering, the chloroform and excess amine were removed under vacuum to give crystalline *N-tert*-butyl-*N*-methylacetamide, mp 32–34°. A solution of 2.5 g (0.02 mol) of the acetamide in 30 ml of ether was added dropwise with stirring to a cooled mixture of 0.8 g (0.02 mol) of lithium aluminum hydride in 30 ml of ether. This was allowed to reflux after which it was heated to maintain refluxing for 12 hr more. After cooling, 3 g of H_2O was added and the mixture again refluxed for 4 hr. Following filtration, the solution was fractionally distilled on an 18 in. × $^5/_{16}$ in. vacuum-jacketed, packed column to remove the ether. The remaining liquid was dried (sodium sulfate) and filtered and the title compound was collected by glpc on a 10 ft. 20% SE-30 column: nmr peaks at δ 2.11 (3 H singlet, N-methyl), 1.03 (9 H singlet, *tert*-butyl), 2.37 (2 H, quartet, J = 7 Hz, methylene), and 1.01 (3 H, triplet, J = 7 Hz, methyl).

Anal. Calcd for $C_7H_{17}N$: C, 72.97; H, 14.86; N, 12.16. Found: C, 72.96; H, 14.66; N, 12.21.

***N-tert*-Butyl-*N*-methyl-*N*-(ethyl-*d*$_3$)amine (5)** was prepared in exactly the same manner as *N-tert*-butyl-*N*-methyl-*N*-ethylamine above except that acetyl-*d*$_3$ chloride and lithium aluminum deuteride were employed: ^{1}H nmr peaks (CCl_4) at δ 1.03 (9 H singlet, *tert*-butyl) and 2.11 (3 H singlet with ^{2}H irradiation, N-methyl).

***N-tert*-Butyl-*N*-(methyl-*d*$_3$)-*N*-(ethyl-*2,2,2-d*$_3$)amine (6)** was prepared by adding dropwise 10.0 g (0.06 mol) of ethyl-*2,2,2-d*$_3$ iodide in 25 ml of ether to a solution of 5 g (0.06 mol) of *N-tert*-butyl-*N*-trideuteriomethylamine in 25 ml of ether. The reaction mixture was refluxed for 6 hr after which dry HCl was bubbled through the cooled solution. The ether was removed under vacuum and the salt residue was dissolved in 25 ml of H_2O. Finally the cooled solution was saturated by careful addition of solid KOH and the top liquid layer removed and dried (sodium sulfate). Characterization was made by comparison of glpc and nmr results of the nondeuterated material prepared in the above fashion. The product (**6**) was collected using a 20% SE-30 glpc column: nmr peaks at δ 2.37 (2 H singlet, methylene) and 1.05 (9 H singlet, *tert*-butyl).

***N-tert*-Butyl-*N*,*N*-diethylamine.** A solution of 1.25 ml (0.011 mol) of *N-tert*-butylamine and 2.10 ml (0.24 mol) of ethyl iodide were refluxed for 24 hr. A cooled solution (0°) of the product mixture in 20 ml of H_2O was saturated with KOH and the top amine layer separated. This was shown to contain the unreacted *N-tert*-butylamine and *N-tert*-butyl-*N*-ethylamine together with *N-tert*-butyl-*N*,*N*-diethylamine which was collected by glpc using a 20% SE-30 column: nmr peaks at δ 2.50 (4 H quartet, J = 7.2 Hz, methylene), 1.03 (9 H singlet, *tert*-butyl), and 0.99 (6 H triplet, J = 7.2 Hz, methyl).

Anal. Calcd for $C_8H_{19}N$: C, 74.34; H, 14.82; N, 10.84. Found: C, 74.34; H, 14.55; N, 10.95.

***N-tert*-Butyl-*N*,*N*-di(ethyl-*2,2,2-d*$_3$)amine (7)** was prepared by exactly the same procedure as *N-tert*-butyl-*N*,*N*-diethylamine above except that ethyl-*2,2,2-d*$_5$ iodide was employed: ^{1}H nmr peaks (CCl_4) at δ 2.47 (4 H singlet with ^{2}H irradiation, methylene) and 1.05 (9 H singlet, tert-butyl).

***N-tert*-Butyl-*N*-methyl-*N*-isopropylamine.** To a cooled (0°) stirred solution of 4 g (0.10 mol) of lithium aluminum hydride in 50 ml of anhydrous ether was added dropwise 15 g (0.23 mol) of acetone in 40 ml of anhydrous ether. The solution was refluxed for 24 hr after which it was cooled and 1 ml of H_2O added. It was then refluxed for 6 hr more. The solid salt was filtered and refluxed in 30 ml of ether for 2 hr and this procedure was again repeated. The combined filtrates were fractionally distilled and yielded 10 ml of an isopropyl alcohol/water azeotrope.

(19) F. R. Jensen, L. A. Smith, C. H. Bushweller, and B. H. Beck, *Rev. Sci. Instrum.*, **43**, 894 (1972).

(20) D. A. Kleier and G. Binsch, *J. Magn. Resonance*, **3**, 146 (1970).

To 12 ml of a cooled stirred solution of 48% HBr in H_2O was added first about 10 g of concentrated H_2SO_4 and then 7.3 ml (~0.1 mol) of the isopropyl alcohol/water azeotrope. The solution was heated to reflux for 6 hr and then distilled to give a fraction with a bp 59–62° (shown to be isopropyl bromide by comparison of nmr and glpc retention time with a commercial sample). Conversion of the bromide to the iodide was accomplished by refluxing a mixture of 10 g of isopropyl bromide in 200 ml of acetone with 30 g of sodium iodide. After 72 hr the solution was filtered and again 30 g of sodium iodide added. An additional 24 hours of refluxing yielded a mixture in which about 95% of the bromide had been converted to the iodide.

A solution of 20 g (0.27 mol) of *N-tert*-butylamine and 10 g (0.06 mol) of isopropyl iodide was refluxed for 24 hr after which the mixture was cooled and 50 ml of 2 *M* NaOH was added dropwise. The solution was then saturated wih sodium chloride and the top amine layer separated and distilled. An impure fraction (bp 75–83°) was shown to contain the *N-tert*-butyl-*N*-isopropylamine and final purification of this compound was achieved by collection on a 20% SE-30 glpc column.

A solution of 2 g (0.014 mol) of methyl iodide and 1.8 g (0.024 mol) of *N-tert*-butyl-*N*-isopropylamine was sealed in a glass reaction bomb and heated to 60° for 12 hr. The product mixture was added to 10 ml of H_2O and this cooled solution (0°C) was then saturated with KOH. The top amine layer was analyzed on a 20% SE-30 column and *N-tert*-butyl-*N*-methyl-*N*-isopropylamine collected: nmr peaks at δ 2.10 (3 H singlet, methyl), 1.04 (9 H singlet, *tert*-butyl), 0.95 (6 H, doublet, J = 7.0 Hz, methyl) and 3.23 (1 H, septet, J = 7.0 Hz, methine hydrogen).

Anal. Calcd for $C_8H_{19}N$: C, 74.34; H, 14.82; N, 10.84. Found: C, 74.28; H, 14.55; N, 10.97.

***N-tert*-Butyl-*N*-methyl-*N*-(isopropyl-d_7)amine (8)** was prepared in exactly the same fashion as *N-tert*-butyl-*N*-methyl-*N*-isopropylamine above except that acetone-d_6 and lithium aluminum deuteride were employed. For **8**: ^{1}H nmr peaks (CCl_4) at δ 2.10 (3 H singlet, N-methyl) and 1.07 (9H singlet, *tert*-butyl).

***N-tert*-Butyl-*N*-(2,2,2-trideuterioethyl)-*N*-(isopropyl-d_7)amine (9)** was prepared in the same manner as *N-tert*-butyl-*N*-methyl-*N*-isopropylamine using 2 g (0.016 mol) of the *N-tert*-butyl-*N*-(isopropyl-d_7)amine and 1 g (0.006 mol) of ethyl-d_5 iodide: nmr peaks at 2.51 (2 H singlet, methylene protons) and 1.10 (9 H singlet, *tert*-butyl protons).

***N-tert*-Butylaziridine** was prepared by the method of Bottini and Roberts.[21]

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Effect of α Substitution on the Solvolysis of Bicyclo[3.1.1]heptyl-6 and Bicyclo[3.2.0]heptyl-6 Derivatives[1]

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Abstract: The effects of α-methyl, α-phenyl, and α-*p*-anisyl substitution on the rates and products of solvolysis of bicyclo[3.1.1]heptyl-6 and bicyclo[3.2.0]heptyl-6 3,5-dinitrobenzoates have been determined. Methyl substitution led to a marked rate increase for the less reactive isomers and only a small increase for the more reactive isomers. It did not have a major effect on the products of the solvolysis of the latter compounds. Phenyl and *p*-anisyl substitution was far more effective in localizing charge and led in part to unrearranged solvolysis products. The nature of the cyclobutyl cation is considered in the light of these results.

We have previously reported on the solvolyses of bicyclo[3.1.1]heptyl-6 and bicyclo[2.1.1]hexyl-5 derivatives.[3,4] In each case the endo derivative was much more reactive (10^6–10^7) than the exo isomer and rearranged products were formed. It appeared that rearrangement occurred during the ionization step and that the high rate acceleration resulted from the driving force for rearrangement.

It seemed possible to confirm this conclusion and to obtain an estimate of the driving force for rearrangement by examining the effect of α substitution. The introduction of a charge stabilizing substituent should result in localization of charge and a decreased tendency for rearrangement. The endo/exo rate ratio should correspondingly be reduced.

The preparation of the 6-methylbicyclo[3.1.1]heptan-6-ols as well as the related 6-methylbicyclo[3.2.0]heptan-6-ols has been reported in another connection.[5] The alcohols were converted to dinitrobenzoates, and the rates of solvolysis were determined in 80% acetone. The kinetic data are summarized in Table I and the product distribution is recorded in Table II. Relative rate factors are summarized in Table III.

Methyl substitution at a secondary center usually leads to a rate increase on the order 2×10^4.[6] The k_{CH_3}/k_H ratio observed with the less reactive *exo*-bicyclo[3.1.1]heptyl-6 dinitrobenzoate (5×10^5) is larger by a factor of 10. On the other hand, the endo isomer gave a k_{CH_3}/k_H ratio of only 20. Thus, the exo compound appears normal in its behavior leading to an unrearranged classical ion in the rate-determining step. The higher than normal k_{CH_3}/k_H ratio is probably a reflection of the difficulty of forming the cyclobutyl cation in the absence of a means of stabilization. Thus, the k_{CH_3}/k_H ratio has been found to increase to 5×10^7 for the acetolysis of 7-norbornyl tosylates.[7] In the case of

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