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RATE PROCESSES IN N-TERT-BUTYL-N-HALOAMINES

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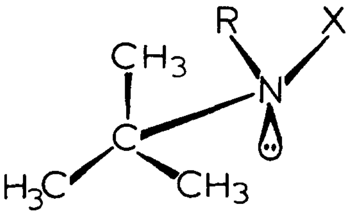
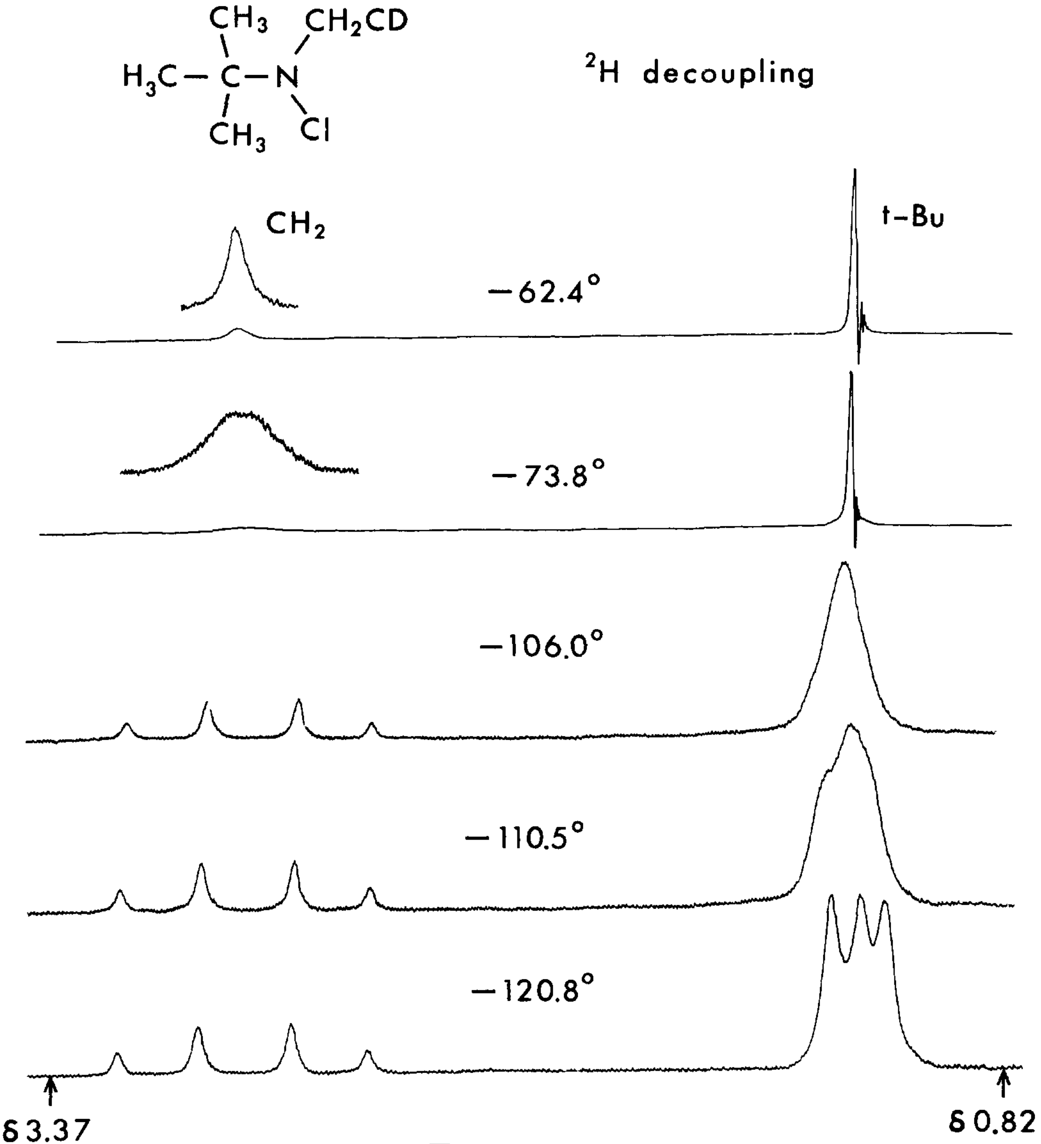
Although significant experimental and theoretical efforts have been expended in order to provide an incisive depiction of pyramidal inversion about nitrogen,[2] relatively little information is available regarding substituent effects on the rate of C–N bond rotation.[3] This paper concerns the observation of significant substituent effects on the rate of tert-butyl rotation in a series of N-tert-butyl-N-haloamines (**1**). Examination of the ^{1}H DNMR spectrum (60 MHz; ^{2}H decoupled) of **1d** (Table; 12% v/v in CBrF$_3$) at -62° (Figure) revealed a kinetically broadened CH$_2$ resonance (δ2.86) and a sharp tert-butyl peak (δ1.21). Upon lowering the temperature, the CH$_2$ resonance separated cleanly into an AB spectrum ($\Delta\nu_{AB}$ = 25.7 Hz; J_{AB} = 13.2 Hz) consistent with slowing nitrogen inversion on the DNMR time scale and giving a barrier ($\Delta G^{\ddagger}$) to inversion of 9.7 ± 0.2 kcal/mole at -76° (total line shape method). Further lowering of the temperature resulted in the separation of the tert-butyl resonance into three resolved



1

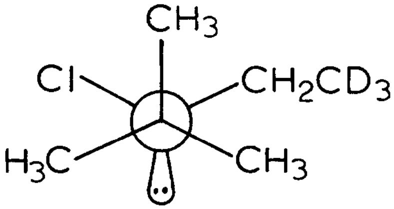

CH3
CH2CD
H3C—C—N
CH3
Cl
2H decoupling
CH2
t-Bu
−62.4°
−73.8°
−106.0°
−110.5°
−120.8°
δ3.37
δ0.82

Figure

TABLE. Barriers ($\Delta G^{\ddagger}$) to tert-Butyl Rotation in N-tert-Butyl-N-haloamines

compound	X	R	$\Delta G^{\ddagger}$, kcal/mole
1a	Cl	Cl	9.4 ± 0.2 (-92°)
1b	Cl	CH_3	8.6 ± 0.2 (-114°)
1c	Br	CH_3	8.3 ± 0.2 (-121°)
1d	Cl	CH_2CD_3	8.6 ± 0.2 (-109°)
1e	Cl	$CH_2C_6H_5$	8.3 ± 0.2 (-122°)
1f	Cl	$CH(CD_3)_2$	7.0 ± 0.4 (-143°)
1g	CH_3	CH_3	6.0 ± 0.1 (-153°)

singlets of equal intensity (3H) at δ1.14, δ1.20, and δ1.28 consistent with slowing tert-butyl rotation on the DNMR time scale and also consistent with the symmetry experienced by tert-butyl in the static form of 1d below. A complete line shape analysis of these spectral changes gave $\Delta G^{\ddagger} = 8.6 \pm 0.2$ kcal/mole (-109°) for tert-butyl rotation.



1d

The ^1H DNMR spectra of the tert-butyl resonance of other members of the series 1 also revealed changes at low temperatures consistent with slowing tert-butyl rotation (Table). Using the total line shape method, barriers ($\Delta G^{\ddagger}$) to tert-butyl rotation in 1a-e were calculated and are compiled in the Table.

Perusal of the Table reveals some trends with regard to the rate of tert-butyl rotation. Substitution of one halogen for an N-methyl results in a significantly increased hindering (ca. 2.5 kcal/mole) of tert-butyl rotation, e.g, compare 1g to 1b-e (Table). Substitution of two chlorines increases the barrier by ca. 3.4 kcal/mole in 1a as compared to 1g.[4] The increased effectiveness of halogen as compared to methyl in hindering tert-butyl rotation attests to the idea that vicinal eclipsed CH_3/halogen repulsions are greater than vicinal eclipsed CH_3/CH_3 repulsions across a C–N bond. The significantly higher barrier to inversion as compared to tert-butyl rotation in 1d and 1e ($\Delta G^{\ddagger}_{inv} = 9.0$

± 0.2 kcal/mole at -84°) suggests that to a first approximation at low temperatures, tert-butyl is rotating against a noninverting, pyramidal nitrogen. This is in apparent contrast to a series of N-tert-butyl-N,N-dialkylamines in which tert-butyl rotation and nitrogen inversion proceed at the same rate.[4]

A comparison of **1b** and **1c** (Table) reveals no effective difference between N-chlorine and N-bromine in hindering tert-butyl rotation. The lower barrier to tert-butyl rotation in **1f** as compared to **1b** or **1d** is consistent with significantly increased crowding in the ground state (decreased pyramidality about nitrogen) and an increased six-fold character to tert-butyl rotation.[4] It is also interesting to note that the rate of tert-butyl rotation in **1a** is substantially slower than in tert-butyldichlorophosphine ($\Delta G^{\dagger}$ = 6.4 ± 0.3 kcal/mole at -148°)[5ab] or di-(tert-butyl)-chlorophosphine ($\Delta G^{\ddagger}$ = 6.0 ± 0.3 kcal/mole at -158°)[5b] presumably the result of changes in bond length.

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