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STEREOCHEMISTRY AT TRIVALENT NITROGEN. IV. A STERIC EFFECT ON CONFORMATIONAL INTERCHANGE IN TRIALKYLHYDROXYLAMINES (1)

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Substantial torsional barriers about formal single bonds have attracted considerable attention recently. Of especial interest are those between atoms bearing pairs of nonbonding electrons which can be measured using n. m. r. spectroscopy. These systems have included sulfenamides (1, 2), aminophosphines (3) and α- sulfinyl carbanions (4, 5). It was of importance to extend these studies to bonds between atoms in the first row of the periodic table to determine whether the presence of d-orbitals is a necessary prerequisite for the existence of an appreciable torsional barrier. We report here a steric effect on the hindered conformational interchange in trialkylhydroxyl amines.

The observation of chemical shift nonequivalence of diastereotopic nuclei has been noted in the n. m. r. spectra of cyclic (6) and acyclic (7) trialkylhydroxylamines. The coalescence of signals from diastereotopic protons in these systems is associated with a conformational interchange which may be described as degenerate racemization. This degenerate racemization has been equated to inversion of the nitrogen pyramid in both the acyclic and cyclic examples (6, 7). Although in the cyclic examples slow nitrogen inversion must almost certainly be involved, in the acyclic examples two steps are necessary to effect degenerate racemization (Figure 1). One (step a) involves pyramidal inversion at nitrogen while the second, (step b) could be either rotation of the nitrogen-oxygen bond or inversion at oxygen. Two different transition states are encountered in transversing the reaction coordinate from the ground state conformation to its enantiomer. The higher of these two transition states, representing the slower of step a and step b, is associated with the activation free energy of the overall reaction. Consequently, slow rotation about the N-O bond must also be considered as a possible origin of the observed chemical shift nonequivalence and the barrier to conformational interchange. (1, 2, 8)

The origin of chemical shift nonequivalence in the sulfur analogs, N, N-dialkylsulfenamides, has been investigated and evidence presented that a substantial torsional barrier is the source of the activation free energy for degenerate racemization (1, 2). The

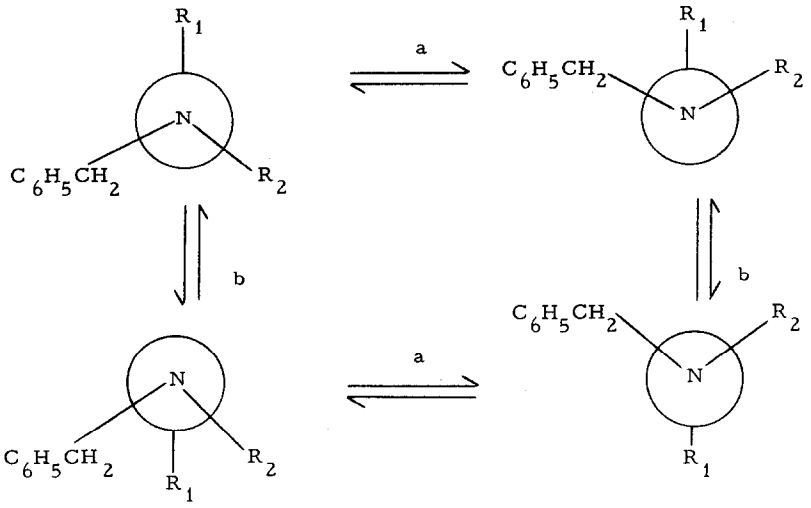


Fig. 1

Degenerate racemization of an N-benzyl-N, O-dialkylhydroxlamine.
(a) Pyramidal inversion at nitrogen
(b) N-O torsion or inversion at oxygen

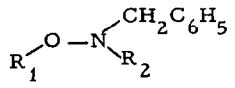
steric effect on the barrier has provided a diagnostic for the assignment of the slow step to torsion or pyramidal inversion: Steric acceleration signifies inversion (9) and steric deceleration signifies torsion (1, 2, 3).

The trialkylhydroxylamines 1-3 were prepared and their n. m. r. spectra examined. Compound 1 was prepared by alkylation of N, O-dimethylhydroxylamine with benzyl chloride as previously reported (7b). Compounds 2 and 3 were synthesized from hydroxyurethane by successive alkylation.

The n. m. r. spectra of 1-3 in deuterochloroform at low temperatures, all exhibited chemical shift nonequivalence of diastereotopic benzyl methylene protons. In addition 3 also exhibited nonequivalent isopropyl methyl groups. By contrast, Compound 2 exhibits an observable chemical shift difference only for the methylene protons, the diastereotopic methyl groups exhibit apparent chemical shift equivalence. It is noteworthy that the n. m. r. spectrum of the sulfur analog N-benzyl-N-isopropyltrichloromethanesulfenamide (1) in the same solvent also exhibits nonequivalence of benzyl methylene protons and apparent equivalence of methyl groups, attesting to the conformational similarity of the two systems. Coalescence temperatures of the nonequivalent benzyl and isopropyl signals were measured and the free energies of activation were calculated. The results (see table) clearly indicate that the replacement of either methyl group of 1 by an isopropyl

group leads to an increase in the free energy of activation for conformational interchange. The steric effect on the barrier in this system is comparable to those observed in the sulfenamide (1, 2) and aminophosphine systems (3).

The observation of steric deceleration points to the presence of a substantial torsional barrier in these compounds as well as in their sulfur analogs and indicates that the presence of d-orbitals is not a necessary condition for the existence of torsional barriers around nitrogen-heteroatom bonds. A theoretical calculation of the C-S torsional barrier in the α - sulfinyl carbanion system has likewise indicated that resonance involving d-orbitals is unimportant as a contributor to that barrier (4). Although a dependence between bond order and dihedral angle was indicated in that study, it seems likely that repulsion between lone pairs of electrons on neighboring atoms play an important, if not preponderant, role in the hindering of rotation about bonds connecting atoms which have pairs of nonbonded electrons.



1 $R_1 = R_2 = CH_3$
2 $R_1 = CH_3 R_2 = CH(CH_3)_2$
3 $R_1 = CH(CH_3)_2$ $R_2 = CH_3$

TABLE I

Compound	$\Delta\nu$ [a]	J_{AB} [b]	Tc [c]	$\Delta G^{\ddagger}$ [d]
1 [e]	6.8	12.9	-25°C.	12.3
2	16.0	12.6	-15°C.	12.8
3 [f]	10.5	12.6	-15.5°C.	12.8
3 [g]	11.4	12.1	-23.5°C.	12.9

a. Hz at 60 MHz.
b. Absolute values.
c. Calibrated with methanol spectra.
d. Kilocalories per mole.
e. Reported (7b): $\Delta\nu$ = 9.3 Hz, J_{AB} = 12.9, Tc = -26°C.
f. Methylene protons.
g. Methyl groups.

A second important conclusion may be drawn from these experimental results, namely that step b takes place by O-N torsion rather than oxygen inversion. Thus we may conclude that the free energy of activation for inversion at the divalent oxygen atom must be greater than 12 kcal/mole. This is in sharp contrast to the far lower barriers for inversion at trivalent oxygen in oxonium ions (11). The order of difficulty of the three processes must be nitrogen inversion < N-O torsion < oxygen inversion.

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