bath for 15 min. The volume of the mixture was reduced by ½ by distillation. Water was added to the boiling solution to the point of saturation; on cooling the diol precipitated as a mixture of stereoisomers: 7.5 g (80%); mp 104–168° (lit. mp[8] 94°, 129° for each racemic pair of enantiomers, respectively); ir ($CHCl_3$) 3590 cm^{-1} (OH), no C=O.

Reaction of 1-(*p*-Tolyl)-2-phenyl-1,2-ethanediol with Acid. General Procedure. A stirred mixture of the diol (1.0 g) and acid (50 ml) was refluxed (see Table I for acids and reaction times). After cooling to room temperature and pouring into water, the reaction mixture was extracted with ether four times. The combined ether extracts were washed with water, dried ($MgSO_4$), evaporated under reduced pressure, and weighed. The crude product mixture was then subjected to glc analysis using authentic samples of *p*-tolylphenylacetaldehyde,[8] and ketones **1a** and **1b**[15] for comparison. The results of the reactions are shown in Table I.

Reaction of Amino Alcohols 1a and 1b with Acid. General Procedure. A stirred mixture of the amino alcohol (0.2–1.3 g) and acid (15–50 ml) was refluxed for the periods indicated in Table I. After cooling and dilution with water the reaction mixture was extracted with ether. The combined ether extracts were washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. The crude products were subjected to glc analysis. In every reaction of **1a** only ketone **4a** could be detected; likewise **1b** furnished only **4b**. The crude solid products were purified[16] by recrystallization and their identities were further confirmed by melting point and mixture melting point and by their infrared spectra, which were identical with those of authentic samples of the ketones. In the reactions with 85% H_3PO_4 the crude products were reddish pastes from which the pure products were extracted by trituration with hot petroleum ether, followed by filtration and cooling.

In the reaction of **1b** with 12 *M* HCl, the reaction mixture contained solid material which was filtered off prior to extraction with ether. This material was then remixed with the aqueous layer and the mixture was neutralized with excess 3 *M* NaOH. Extraction of the alkaline mixture with $CHCl_3$ followed by workup gave unreacted amino alcohol (80%).

Registry No.—**1a**, 50600-27-6; **1b**, 50600-28-7; **2a**, 50600-29-8; **4a**, 2430-99-1; **4b**, 2001-28-7; *p*-$CH_3C_6H_4(C_6H_5)CHCH{=}O$, 50600-30-1; amino ketone, 50600-31-2.

References and Notes

(1) The receipt of an NSF and a Lafayette summer fellowship in support of this research is gratefully acknowledged.

(2) F. Kröhnke and A. Schulze, *Chem. Ber.*, **75**, 1154 (1942).

(3) H. Auterhoff and H. J. Roth, *Arch. Pharm. (Weinheim)*, **289**, 470 (1956).

(4) P. T. Sou, *Bull. Fac. Sci. Univ. Fr-Chin. Peiping*, **5**, 1 (1935); *Chem. Abstr.*, **30**, 4463 (1936).

(5) S. A. Fine and R. L. Stern, *J. Org. Chem.*, **35**, 1857 (1970).

(6) S. A. Fine, R. F. Freese, and M. G. Greene, *J. Org. Chem.*, **38**, 2089 (1973).

(7) An exception is an amino alcohol with Ar = R′ = phenyl (ref 2), but this compound would be expected to yield α-phenylacetophenone regardless of mechanism.

(8) M. Tiffeneau and J. Levy, *Bull. Soc. Chim. Fr.*, **49**, 1742 (1931).

(9) Reference 5 and references cited therein.

(10) Melting points were taken on a Fisher-Johns block and are uncorrected. Infrared spectra were taken on a Beckman IR-10 instrument and were calibrated against the 1601-cm^{-1} peak of polystyrene. Nmr spectra were recorded in $CDCl_3$ on a JEOL MH-60 spectrometer. Glc analyses were performed on a Carle Model 8000 gas chromatograph using a 6 ft × 0.125 in. 8% G.E. SF-96 on 90–100 mesh Anakrom ABS column. Elemental microanalyses were performed by Dr. G. I. Robertson, Jr., Florham Park, N. J.

(11) F. Brown and F. G. Mann, *J. Chem. Soc.*, 858 (1948).

(12) G. Drefahl and H. Crahmer, *Chem. Ber.*, **91**, 750 (1958).

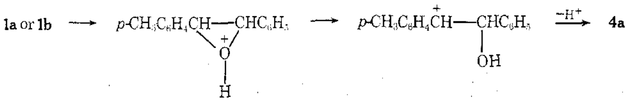
(13) S. S. Jenkins, *J. Amer. Chem. Soc.*, **56**, 682, 1137 (1934).

(14) A. McKenzie, G. Martin, and H. G. Rule, *J. Chem. Soc.*, **105**, 1583 (1914).

(15) M. S. Newman and R. Gaertner, *J. Amer. Chem. Soc.*, **72**, 264 (1950).

(16) Melting points of the crude products were only slightly lower than those of the pure ketones, except for the 85% H_3PO_4 reaction products.

(17) The results also rule out the possibility of an epoxide intermediate, since amino alcohols **1a** and **1b** would both furnish the same epoxide, hence the same product.



$$\mathbf{1a}\text{ or }\mathbf{1b} \longrightarrow p\text{-}CH_3C_6H_4CH{-}\underset{\overset{+}{O}H}{}{-}CHC_6H_5 \longrightarrow p\text{-}CH_3C_6H_4\overset{+}{C}H{-}\underset{OH}{CH}C_6H_5 \xrightarrow{-H^+} \mathbf{4a}$$

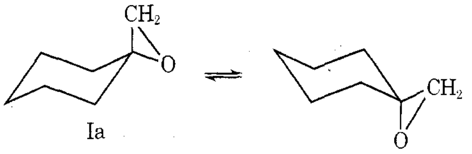
Conformational Preference of Cyclohexanespiroaziridine As Determined by Low Temperature Carbon-13 Magnetic Resonance

Gerald W. Buchanan* and Robert Kohler

Department of Chemistry, Carleton University, Ottawa, Ontario, Canada K1S 5B6

Received September 12, 1973

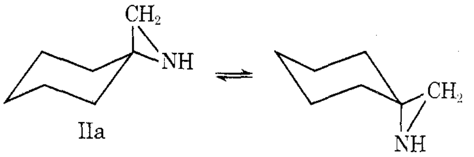
Considerable effort has been recently directed toward the elucidation of conformational preferences of spirocyclohexane derivatives. Cyclohexanespirooxirane (I) has been studied *via* kinetic,[1] low-temperature ^1H nmr,[2] and electric dipole moment[3] methods. The preference of *ca.* 0.27 kcal/mol for the conformation in which the oxygen is quasi-axial (Ib) is evident.



Ia

Ib

By contrast, attempts to study the analogous spiroaziridine II by electric dipole moments have not permitted definitive conformational conclusions.[3]



IIa

IIb

The low-temperature ^1H nmr peak area procedure cannot be applied to the problem owing to the accidental overlap of the aziridine methylene resonance (δ 1.45) with the cyclohexane ring methylene protons (δ 1.25–1.75). It is expected, however, that ^{13}C nmr should afford a solution, since it is now well established that carbon shieldings are an order of magnitude more sensitive to steric factors than proton shifts in favorable cases.[4,5] Furthermore, the likelihood of peak overlap in carbon spectra is considerably reduced. Accordingly, a sample of II 61% ^{13}C enriched at the aziridine methylene carbon was prepared and examined.

At room temperature under conditions of complete proton noise decoupling the aziridine methylene carbon of II appears as a sharp singlet at δ 31.84 downfield from internal TMS. When a 0.5 *M* solution of II in CD_2Cl_2 is cooled the absorption for this carbon gradually broadens and at −80 ± 2° the coalescence temperature is reached. Further cooling leads to the separation of the signal into completely resolved components separated by 6.4 Hz.

The resonance of higher integrated intensity appearing at lower field is assigned to conformer IIb. This is consistent with the observations for methylcyclohexane at low temperature,[6] where the equatorial methyl group is at considerably lower field than its axial counterpart. The peak areas were determined by a cutting and weighing procedure and the conformational energy of the spiroaziridine function was calculated from the equation $-\Delta G° = RT \ln K$. Results are shown in Table I, which indicate that conformer IIb is the more stable by 0.16 kcal/mol.

It is apparent that the preference for conformer IIb is much less than that predicted on the basis of the difference between the conformational free energy of the Me (1.7 kcal/mol) and the NHMe (1.0 kcal/mol) groups.[7] No doubt the small angle of the aziridine ring causes appreciable reduction in the nonbonded interactions between the quasi-axial CH_2 group and the syn-axial ring hydrogens. Notably the preference of the spiroaziridine group is appreciably smaller (by 0.1 kcal/mol) than that of the spirooxirane. This is consistent with the fact that $-\Delta G°$ for the NHMe function is 0.2–0.4 kcal/mol higher than for the OMe moiety in the monosubstituted cyclohexanes.[7]

Under conditions of complete proton noise decoupling, nuclear Overhauser effects (NOE's) are operative and thus may affect the observed integrated intensity ratios. In order to verify that no differential NOE has occurred in these experiments the coupled spectrum was recorded. $J(^{13}CH)$ is 166 Hz and no detectable change in the *relative* intensities of the resonances at low temperature was found compared to the decoupled spectra. This is consistent with expectation, since the directly bonded methylene protons will be essentially the only contributors to dipole–dipole relaxation and we have found that these protons have nearly identical chemical shifts below −80°.

Attempts to evaluate the effect of medium on the equilibrium IIa $\rightleftarrows$ IIb were unsuccessful. In toluene-d_8 below −80° no resolvable chemical shift difference between the two conformers was found. Choice of solvents in this study was severely limited owing to the necessity for a deuterium lock signal when an XL-100 nmr spectrometer is used for ^{13}C investigations.

Experimental Section

Spectra. Carbon-13 spectra were recorded at 25.2 MHz on a Varian XL-100-12 spectrometer using 5-mm sample tubes. Temperatures were calibrated using a copper–constantan thermocouple (in a dummy nmr tube) and are judged accurate to ±2°. Conditions of complete proton noise decoupling were used.

To ensure that nonsaturating radiofrequency (rf) conditions were employed, spectra were initially recorded at widely different rf powers, and the relative peak areas were measured. Final conditions were then chosen where the slope of the relative peak area *vs.* rf power graph was zero. Integration of the areas under the peaks was done by the cutting and weighing procedure. Each value represents an average of five determinations at a given temperature. Error limits quoted (±0.01 kcal/mol) represent the standard deviation.

Table I
$-\Delta G°$ Values for the Equilibrium IIa $\rightleftarrows$ IIb (±0.01 kcal/mol)

Temp, ±2°C	$-\Delta G°$, kcal/mol
−88	0.16
−92	0.17
−96	0.16

Materials. ^{13}C enriched (61%) methyltriphenylphosphonium bromide was prepared from triphenylphosphine and methyl bromide-^{13}C (61%, obtained from Stohler Isotope Chemicals, Montreal) according to the procedure of Trippett.[8] A Wittig reaction[9] between cyclohexanone and the ^{13}C-enriched phosphonium salt yielded labeled methylenecyclohexane in 65% yield. This material was converted to the spiroaziridine II in 68% yield according to the procedure of Fowler, Hassner, and Levy.[10]

Acknowledgment. We thank the National Research Council of Canada for financial support.

Registry No.—II, 185-69-3.

References and Notes

(1) J. J. Uebel, *Tetrahedron Lett.*, 4751 (1967).
(2) R. G. Carlson and N. S. Behn, *Chem. Commun.*, 339 (1968).
(3) R. A. Y. Jones, A. R. Katritzky, P. G. Lehman, A. C. Richards, and R. Scattergood, *J. Chem. Soc., Perkin Trans. 2*, 41 (1972).
(4) G. W. Buchanan, D. A. Ross, and J. B. Stothers, *J. Amer. Chem. Soc.*, **88**, 4301 (1966).
(5) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972.
(6) F. A. L. Anet, C. H. Bradley, and G. W. Buchanan, *J. Amer. Chem. Soc.*, **93**, 258 (1971).
(7) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).
(8) S. Trippett, *Advan. Org. Chem.*, **1**, 83 (1960).
(9) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962).
(10) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967).