

with the increasing availability of pulsed multinuclear spectrometers chemists should turn their attention to high resolution ^2H nmr for conformational and mechanistic problems. In studies of very complex biological systems such as cell membranes this technique provides a powerful and inexpensive alternative¹² to ^{13}C enrichment.

(12) H. Saitô, S. Schreier-Muccillo, and I. C. P. Smith, *FEBS (Fed. Eur. Biochem. Soc.) Lett.*, **33**, 281 (1973).

(13) Visiting professor from the University of Cluj, str. Donath 65, Cluj, Romania.

(14) Visiting scientist from Basic Research Laboratories, Toray Industries, Inc., Kamakura, Japan 248.

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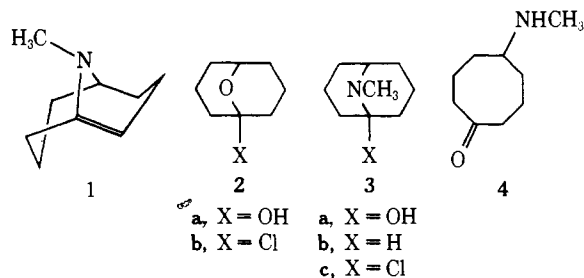
Henry H. Mantsch,¹³ Hazime Saitô¹⁴
L. C. Leitch, Ian C. P. Smith*
Division of Biological Sciences,
National Research Council of Canada¹⁵
Ottawa, Ontario, Canada K1A 0R6
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9-Methyl-9-azabicyclo[3.3.1]non-1-ene¹

Sir:

We have previously reported on the synthesis and chemistry of bridgehead alkenes of the bicyclo[3.3.1]nonyl system in which the 9 position is occupied by a heteroatom.^{2,3} Such substrates are attractive for the investigation of inductive and resonance effects of heteroatoms on the properties of double bonds because the $n-\pi, \pi^*$ resonance effects are severely inhibited by the geometry of the system.

In this report we describe the synthesis and interesting chemistry of 9-methyl-9-azabicyclo[3.3.1]non-1-ene (**1**).⁴⁻⁶ Hemiketal **2a**² was converted in 97% yield to amino alcohol **3a** upon treatment with 20% aqueous methylamine containing some *p*-toluenesulfonic acid.^{7,8} Amino alcohol **3a** totally predominates over the tauto-



(1) Bredt's Rule. IX. For previous paper see ref 3b.

(2) C. B. Quinn and J. R. Wiseman, *J. Amer. Chem. Soc.*, **95**, 1432 (1973).

(3) (a) C. B. Quinn and J. R. Wiseman, *J. Amer. Chem. Soc.*, **95**, 6120 (1973); (b) C. B. Quinn, J. R. Wiseman, and J. C. Calabrese, *ibid.*, **95**, 6121 (1973).

(4) For the synthesis of 11-azabicyclo[4.4.1]undec-1-ene see (a) A. C. Cope, R. J. Cotter, and G. C. Roller, *J. Amer. Chem. Soc.*, **77**, 3590 (1955); (b) K. Biemann, G. Büchi, and B. H. Walker, *ibid.*, **79**, 5558 (1957).

(5) For examples of isolable compounds containing bridgehead double bonds involving nitrogen see (a) for an imine, M. Toda, and Y. Hirata, *Chem. Commun.*, 1597 (1970); (b) for iminium salts and enamines, H. Newman and T. L. Fields, *Tetrahedron*, **28**, 4051 (1972); (c) for trans azo linkages in medium-sized rings, C. G. Overberger, M. S. Chi, D. G. Pucci, and J. A. Barry, *Tetrahedron Lett.*, 4564 (1972).

(6) For examples of intermediate amines containing bridgehead saturation see (a) P. Kovacic, J.-H. Liu, P. D. Roskos, and E. M. Levi, *Chem. Commun.*, 1034 (1970); (b) J. O. Reed and W. Lwowski, *J. Org. Chem.*, **36**, 2864 (1971); (c) P. Kovacic, J.-H. Liu, E. M. Levi, and P. D. Roskos, *J. Amer. Chem. Soc.*, **93**, 5801 (1971).

(7) C. B. Quinn, Ph.D. Thesis, University of Michigan, 1973.

(8) Reported yields refer to isolated yields of pure materials.

meric amino ketone **4** since the infrared spectrum shows no carbonyl absorption.

A substrate suitable for elimination was prepared by converting amino alcohol **3a** into the bridgehead chloride **3c** (bp 59°, 0.45 Torr) in 62% yield using thionyl chloride. Bridgehead olefin **1** was produced in 90% yield (bp 48°, 0.9 Torr) by heating **3c** with sodium *tert*-amylate in benzene at reflux.

The spectral data for **1** are collected in Table I along

Table I. Spectral Data of Bridgehead Alkenes in the Bicyclo[3.3.1]nonyl System

Compound	ν_{max} (C=C), cm^{-1}	δ (vinyl H)	J	λ_{max} (ϵ) ^d	Ref
1	1620 m ^a	5.86, t	(6 Hz) ^c	240 (1667) End absorption 184	
	1640 w ^b	5.74, t	(6 Hz) ^b	190 (6200)	2
	1600 w ^b	6.25, t	(7 Hz) ^b	196 (4560) 210 (1780)	3a
	1620 w ^a	5.62, t	(7 Hz) ^b	206 (7500)	e

^a Neat. ^b CCl_4 solution. ^c CDCl_3 solution. ^d Pentane solution. ^e J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 5966 (1967); J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970).

with the other known isolable heterobicyclic and carbocyclic bridgehead olefins of the [3.3.1] series. The infrared spectra of 1,2-dialkyl substituted enamines usually display a *strong* band between 1646 and 1652 cm^{-1} .^{9,10} Enamines in which the double bond is endocyclic in a six-membered ring normally show a chemical shift between δ 4.1 and 4.6 for the vinyl proton on the β -carbon atom.¹¹ Enamines wherein resonance interaction between the lone pair of electrons on nitrogen and the double bond is possible show absorption at 230 ± 10 nm (ϵ 5000–9000).¹¹

The ir and nmr spectra indicate a lack of interaction of the nitrogen lone pair with the bridgehead double bond in **1**. The interpretation of the uv spectrum is less certain since the absorption band at 240 nm could be taken as evidence for some residual conjugation. However, this band probably corresponds to the $n \rightarrow \sigma^*$ band of amines, bathochromically shifted due to flattening of the bridging nitrogen atom.^{12,13}

The chemistry of **1** also indicates a lack of conjugation. Thus treatment of **1** with methyl iodide in acetonitrile afforded quaternary ammonium bridgehead alkene **5a** in a quantitative yield while reaction of **1** with cyanogen bromide in dioxane gave cyanamide **6** along with some quaternary ammonium bromide **5b**.

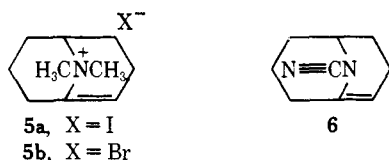
(9) N. J. Leonard and V. W. Gash, *J. Amer. Chem. Soc.*, **76**, 2781 (1954).

(10) N. J. Leonard and F. P. Hauck, *J. Amer. Chem. Soc.*, **79**, 5279 (1957).

(11) (a) S. K. Malhotra in "Enamines: Synthesis, Structure, and Reactions," A. G. Cook, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 1; (b) K. Nagarajan and S. Rajappa, *Tetrahedron Lett.*, 2293 (1969).

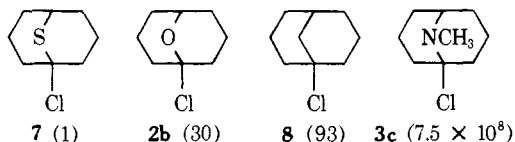
(12) 9-Azabicyclo[3.3.3]undecane, with a flattened bridgehead nitrogen atom, shows λ_{max} 240 nm, ϵ 2935; J. C. Coll, D. R. Crist, M. del C. G. Barrio, and N. J. Leonard, *J. Amer. Chem. Soc.*, **94**, 7092 (1972). *N*-Methylgranatinine (**3b**) shows λ_{max} 208 nm (ϵ 1220) in pentane.

(13) For examples in which molecular geometry precludes mesomerism involving polarized and nonpolarized forms of enamines see O. Cervinka, ref 11a, p 269.



With normal enamines alkylation occurs primarily at carbon, and cyanogen bromide adds across the double bond¹⁴ rather than promoting a von Braun type reaction. Upon treatment of **1** with methyl acrylate in refluxing benzene only starting material was recovered. When olefin **1** was allowed to react with 1,3-diphenylisobenzofuran, the expected Diels–Alder adduct was obtained. Catalytic hydrogenation of **1** gave *N*-methylgranatinine (**3b**)¹⁵ which was also obtained by lithium aluminum hydride reduction of bridgehead chloride **3c**. The pK_a 's in 40% aqueous ethanol for the conjugate acids of **1** and **3b** are 9.09 and 10.19, respectively. The difference, 1.10 pK_a units, is in substantial agreement with the 1.13 unit difference found for quinuclidine and dehydroquinuclidine in water.¹⁶ Other reactions of **1** will be reported at another time.

Evidence relating to the geometric inhibition of resonance of nitrogen in satisfying electron demand by a bridgehead cation in the bicyclo[3.3.1]nonyl system has been gained by determining the kinetics of solvolysis of bridgehead chloride **3c** in 96% ethanol at 29°. The first-order rate constant calculated for **3c** under these conditions is $1.72 \pm 0.12 \text{ min}^{-1}$.¹⁷ The relative rates for a series of bridgehead chlorides are shown below in parentheses.¹⁷ In each case the products of solvolysis



are unrearranged alcohols and ethers. The tremendous rate enhancement of **3c** compared to **8** (nearly ten million times faster) is astounding and indicates that participation by nitrogen is much more effective than is the case for sulfur or oxygen. It should be noted that the majority of α -amino halides are ionic, existing as immonium halides.¹⁸ Indeed only five molecular α -amino chlorides have been reported previously,^{19–21} and these, like **3c**, owe their existence as covalent species to the fact that the immonium ion would introduce trans double bond character in a six-membered ring.^{22–24}

(14) O. Mumm, H. Hinz, and J. Diederichsen, *Ber.*, **72**, 2107 (1939).

(15) A. C. Cope and C. G. Overberger, *J. Amer. Chem. Soc.*, **70**, 1433 (1948).

(16) C. A. Grob, A. Kaiser, and E. Renk, *Chem. Ind. (London)*, 598 (1957).

(17) The rate constant was determined by measuring the half-life of **3c**. The values cited for **2b**, **7**, and **8** were adjusted from the previously reported values^{2,3a,7} for temperature differences and solvent composition using the Grunwald–Winstein equation: (a) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(18) H. Bohme and K. Osmer, *Chem. Ber.*, **105**, 2237 (1972), and previous papers.

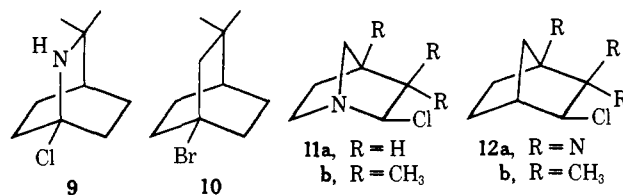
(19) H. Stetter, P. Tacke, and J. Gartner, *Chem. Ber.*, **97**, 3480 (1967).

(20) R. D. Fisher, T. D. Bogard, and P. Kovacic, *J. Amer. Chem. Soc.*, **94**, 7599 (1972); **95**, 3646 (1973).

(21) (a) P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **90**, 1355 (1968); **91**, 2047 (1969); (b) P. G. Gassman, R. L. Cryberg, and K. Shudo, *ibid.*, **94**, 7600 (1972).

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However, in spite of this restriction, nitrogen must participate in the ionization of **3c** in order to account for the dramatic rate increase observed. Fisher, Bogard, and Kovacic have reported that bridgehead chloride **9** exhibits enhanced solvolytic reactivity compared to **10**,²⁰ and Gassman, Cryberg, and Shudo have presented evidence for participation by nitrogen in the 1-azabicyclo[2.2.1]heptyl chlorides (**11**).^{21b} The Gassman group found that the rates of solvolysis of **11** and **12** in anhydrous methanol are within 1 order of mag-



nitude of one another²⁵ and proposed that the bridgehead nitrogen provides an apparent rate acceleration of at least 10^3 and possibly 10^8 . In the bicyclo[3.3.1]nonyl system there is considerably less rigidity compared to the norbornyl framework, which might explain the real 10^7 increase in rate of **3c** over **8**.

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(25) For an example in the quinuclidine system see C. A. Grob and A. Sieber, *Helv. Chim. Acta*, **50**, 2531 (1967).

Herman O. Krabbenhoft, John R. Wiseman,* Clayton B. Quinn

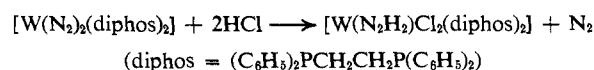
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

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Reduction of Coordinated Dinitrogen to the Coordinated Hydrazido Dianion. The Structural Characterization of the 1- η -Hydrazido(2-)-chlorobis-[1,2-bis(diphenylphosphino)ethane]tungsten(IV) Cation

Sir:

The reduction, under mild conditions, of dinitrogen complexes of molybdenum(0) and tungsten(0) by hydrogen chloride and hydrogen bromide has been described by Chatt, *et al.*¹ If, for example, the reaction



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