mp 91–93°; mass spectrum m/e 160 (100), 116 (M − CS), 30; ir (KBr) 2950, 2400, 1460, 1420, 1310, 1120, 1050, 985, 950, 940, 780, 745 cm^{-1}; nmr (CCl$_4$) τ 3.2, 3.6 (11:1), *ca.* 20% undeuterated material.

If the reaction time is extended, complete deuteration of the thiophene ring occurs, but this is accompanied, however, by more extensive decomposition. Increasing the acidity of the medium in an attempt to deuterate the benzene ring led only to decomposition.

Bicyclo[3.3.3]undecane and 1-Azabicyclo[3.3.3]undecane. Geometry, Strain, and Spectroscopic Behavior of These Systems

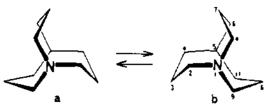
John C. Coll, DeLanson R. Crist, Maria del Carmen G. Barrio, and Nelson J. Leonard*

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. *Received January 25, 1972*

Abstract: Syntheses of bicyclo[3.3.3]undecane (manxane) (**1**) and 1-azabicyclo[3.3.3]undecane (manxine) (**2**) are reported: a multistep synthesis, involving double-ring expansion of the short bridge of bicyclo[3.3.1]non-2-en-9-one (**3**), to give manxane (**1**) and a one-step reductive fission of the short bridge of 1-azoniatricyclo[3.3.3.0]undecane bromide (**16**) with sodium in liquid ammonia to give manxine (**2**). Interesting spectroscopic properties are reported for compounds **1** and **2** and derivatives thereof. The ^{13}C and ^{1}H nmr spectra for manxane and manxine showed chemical shifts for the bridgehead carbon and hydrogen atoms at lower field than normal, and decoupling studies were used to confirm assignment of signals and structures. A "frozen" nmr spectrum was obtained (at 100 MHz) for the free base manxine (**2**) at $\sim -80°$ in keeping with the reported value for manxane (**1**). The uv spectrum of manxine (**2**) in ether had λ_{max} at 240 nm (ϵ 2935), an exceptionally long wavelength for a saturated tertiary amine, and the vapor-phase uv promised additional interest. The conjugate base of manxine (**2**) had a lower pK_a' value than related saturated tertiary amines. Most properties were rationalized on the basis of a flattening of the bridgehead regions of the molecule, affecting the hybridization of the atoms at the bridgehead; this flattening was confirmed by the X-ray study carried out in conjunction with these investigations.

Just as the quest for a compound with the diamond lattice structure led to the isolation, identification, and synthesis of adamantane,[1] so interest in eight-membered rings[2] and in conjoined arrays of eight-membered rings[3,4] has led to the synthesis of the hydrocarbon, bicyclo[3.3.3]undecane[3,4] ("manxane").[5,6] This compound has C_{3h} molecular symmetry[3] and at room temperature is in a state of rapid conformational equilibrium between two degenerate forms (**1**). Possibly

1



2

even more interesting is the related amine, 1-azabicyclo[3.3.3]undecane ("manxine"), since the two corresponding forms, **2a** and **2b**, will be dissymetric (chiral) with a C_3 axis.[7,8] We now provide details of the syntheses of "manxane" and "manxine" and some of their unusual properties.

Syntheses

Our first synthesis of manxane was accomplished by lengthening the short bridge of bicyclo[3.3.1]nonan-9-

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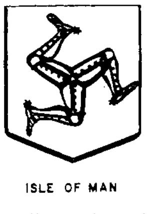
(1) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(2) (a) Sj. Kaarsemaker and J. Coops, *Recl. Trav. Chim. Pays-Bas*, 71, 261 (1952); (b) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Amer. Chem. Soc.*, 74, 5884 (1952); (c) N. J. Leonard, R. C. Fox, M. Ōki, and S. Chiavarelli, *ibid.*, 76, 630 (1954); (d) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, Chapter 4; (e) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **86**, 4854 (1964); (f) *ibid.*, **89**, 7036 (1967); (g) K. B. Wiberg, *ibid.*, **87**, 1070 (1965); (h) N. L. Allinger and S.-E. Hu, *ibid.*, **83**, 1664 (1961); (i) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, **90**, 1199 (1968); (j) F. A. L. Anet and M. St. Jacques, *ibid.*, **88**, 2585, 2586 (1966); (k) A. Peake, J. A. Wyer, and L. F. Thomas, *Chem. Commun.*, 95 (1966); (l) J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 1386 (1969); (m) P. Groth, *Acta Chem. Scand.*, **19**, 1497 (1965); (n) P. Groth, *ibid.*, **21**, 2695 (1967).

(3) M. Doyle, W. Parker, P. A. Gunn, J. Martin, and D. D. MacNicol, *Tetrahedron Lett.*, 3619 (1970).

(4) N. J. Leonard and J. C. Coll, *J. Amer. Chem. Soc.*, **92**, 6685 (1970); **93**, 287 (1971).

(5) The name suggested for this compound class was inspired by the coat of arms of the Isle of Man,[3] whose triskelion is reproduced here.



ISLE OF MAN

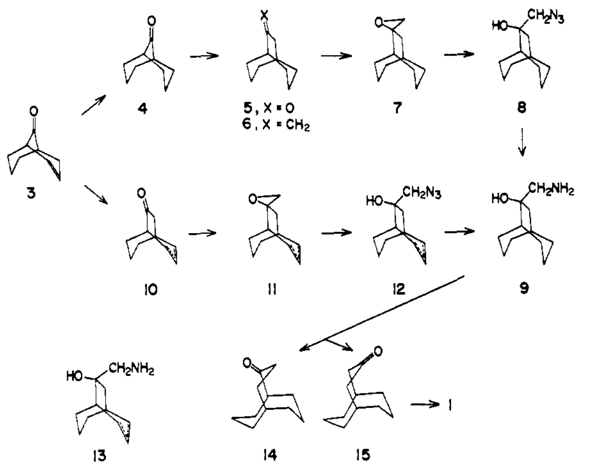
(6) Or, in further imagery, "propellanes" without the hub: see D. Ginsburg, *Accounts Chem. Res.*, 121 (1969).

(7) N. J. Leonard, J. C. Coll, A. H.-J. Wang, R. J. Missavage, and I. C. Paul, *J. Amer. Chem. Soc.*, **93**, 4628 (1971). For specification of molecular chirality, see R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966). Professor Prelog has very kindly pointed out to us that our system can be treated as case (78), p 408. Accordingly, **2a** receives the descriptor 1(P)$_3$ or N(P)$_3$ and **2b**, 1(M)$_3$ or N(M)$_3$, where, as designated by the helicity rule (p 391), P is plus and M is minus. For the case of substitution on one or both bridgehead carbons of **1**, specification would depend on that carbon which is higher by sequence rule.

(8) Accompanying article: A. H.-J. Wang, R. J. Missavage, S. R. Byrn, and I. C. Paul, *J. Amer. Chem. Soc.*, **94**, 7100 (1972).

one (**4**),[9] which, although less convenient than bicyclo[3.3.1]non-2-en-9-one (**3**),[3] seemed to offer the possibility of fewer complications due to transannular bridging or rearrangements than if the double bond remained present during the ring-enlargement sequences. The work in Parker's laboratory[3] shows that this concern was unnecessary, and, in fact, the presence of the double bond in the eight-membered ring makes a number of steps, impossible in the saturated series, quite facile. The original sequence in the saturated series[4] and a shorter, more convenient route *via* the unsaturated ketone **3** more recently developed are presented.

Ring expansion of both bicyclo[3.3.1]non-2-en-9-one (**3**) and bicyclo [3.3.1]nonan-9-one (**4**) gave the related bicyclo[3.3.2] ketones **10** and **5** when treated with methanolic diazomethane in strongly basic solution,[10] while further treatment under the same conditions, or with diazomethane and boron trifluoride etherate in ether,[11] gave no new products. The saturated bicyclo[3.3.2] ketone **5** was unreactive to hydrocyanic acid under many different conditions,[12] nor did it react with nitromethane[13] or the Corey epoxidation reagents in dimethyl sulfoxide.[14] The epoxide **7** was prepared *via* the methylene derivative **6** formed from the action of methyl sulfinyl carbanion on methyltriphenylphosphonium bromide in dimethyl sulfoxide.[15] Epoxidation was achieved by the action of *m*-chloroperbenzoic acid in chloroform[16] or monoperphthalic acid[17] in ether. The epoxide **7** was unreactive to sodium azide in dioxane[18] and sodamide in liquid amonia,[14] and treatment with boron trifluoride etherate in benzene[19] yielded an aldehyde as shown by nmr and ir spectroscopy. The epoxide **7** was converted to the hydroxy azide **8** using Kirk and Wilson's combination of sodium azide and boric acid in refluxing dimethylformamide.[20] Reduction of the hydroxy azide **8** with hydrogen over Adams catalyst[21] afforded the related hydroxyamine **9** which was also available from the bicyclo[3.3.2]dec-2-(3)-en-9-one mixture (**10**) by similar steps of epoxide formation (**11**), ring opening with azide (**12**), and reduction.



Treatment of the unsaturated ketone mixture **10** with trimethyloxosulfonium iodide, sodium hydride in dimethylformamide,[20] or with dimethyl sulfoxide, sodium hydride, and dimethylsulfonium methylide[14] afforded the epoxide mixture **11**, which was converted[20] to the related hydroxy azide **12** as in the saturated series. Hydrogenation at 3 atm gave the saturated hydroxyamine **9**.

The difference in reactivity between the saturated ketone **5** and the unsaturated bicyclo[3.3.2] ketone mixture **10** may be ascribed to the difference in transannular H–H interactions which are so important in the cyclooctanes, resulting in a more favorable energy profile of the transition state for the addition of various reagents to the carbonyl carbon of **10**. Most reactions involved were reversible and subject to steric retardation.

Demjanov–Tiffeneau ring expansion[22] of the hydrochloride salt of **9** afforded a mixture of bicyclo[3.3.3]-undecan-9- and -10-ones, **14** and **15**, that was not readily separated. The presence of both ketones was shown by the nmr spectrum in which the methine proton α to the carbonyl in the 9-ketone **14** was at lower field (δ 2.9) than the methylene protons α to the carbonyl in the 9- and 10-ketones (**14**, **15**) (δ 2.69). Since the ratio of the integrated areas for these protons was 1:4, a 2:1 mixture of the 9- and 10-ketones was indicated. Mass spectrometry of the ketone mixture after exhaustive treatment with sodium deuterioxide in dioxane[3] showed peaks at 169 and 170 corresponding to replacement of 3 *and* 4 hydrogens. The unsaturated hydroxyamine **13** provided an alternative route to manxane (**1**).[3] The ketone mixture **14** and **15** on modified Wolff–Kishner treatment[23] afforded the volatile, high-melting hydrocarbon, manxane (**1**). With the publication of the synthesis of manxane in Parker's laboratory and subsequent private communications with him, we have concentrated our researches on the properties of the related amine, 1-azabicyclo[3.3.3]undecane, or manxine (**2**).

The convenient synthesis of Šorm and Beránek provided us with fairly easy access to 1-azoniatricyclo-[3.3.3.0]undecane bromide (**16**).[24] Compound **16** is an early member of the class of compounds recently categorized as propellanes.[6] A number of early attempts

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[9] (a) D. M. Bailey, J. E. Bowers, and C. D. Gutsche, *J. Org. Chem.*, **28**, 610 (1963); (b) A. C. Cope and D. M. Gale, *J. Amer. Chem. Soc.*, **85**, 3743 (1963); (c) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964); (d) B. Fell, W. Seide, and F. Asinger, *Tetrahedron Lett.*, 1003 (1968).

[10] P. v. R. Schleyer, E. Funke, and S. H. Liggero, *J. Amer. Chem. Soc.*, **91**, 3965 (1969). Thanks are due especially to S. H. Liggero for providing experimental details prior to the publication of this paper.

[11] G. D. Gutsche and D. Redmore, *Advan. Alicycl. Chem.*, **2**, 81 (1968).

[12] (a) F. F. Blicke, J. Azuara, N. J. Doorenbos, and E. B. Hotelling, *J. Amer. Chem. Soc.*, **75**, 5418 (1953); (b) N. L. Wendler, D. Taub, and H. L. Slates, *ibid.*, **77**, 3559 (1955); (c) J. J. Lumm and G. H. Whitham, *Tetrahedron*, **21**, 499 (1965).

[13] D. V. Nightingale, F. B. Erickson, and J. M. Shackelford, *J. Org. Chem.*, **17**, 1005 (1952).

[14] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

[15] (a) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962); (b) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

[16] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1967, p 135.

[17] M. A. Stahmann and M. Bergmann, *J. Org. Chem.*, **11**, 589 (1946).

[18] C. A. VanderWerf, R. Y. Heisler, and W. E. McEwen, *J. Amer. Chem. Soc.*, **76**, 1231 (1954).

[19] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 122.

[20] D. N. Kirk and M. S. Wilson, *Chem. Commun.*, **64** (1970); *J. Chem. Soc. C*, 414 (1971).

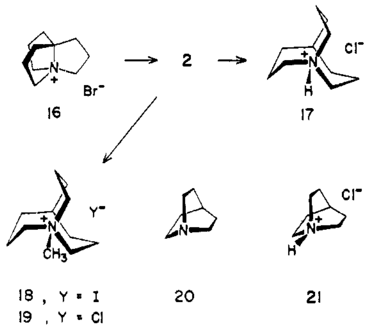
[21] R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York, N. Y., 1965, p 95.

[22] K. Alder, S. Hartung, and G. Hausmann, *Chem. Ber.*, **89**, 1972 (1956).

[23] W. Nagata and H. Itazaki, *Chem. Ind. (London)*, 1194 (1964).

[24] F. Šorm and J. Beránek, *Collect. Czech. Chem. Commun.*, **19**, 298 (1954).

to cleave the short bridge by means of potassium cyanide[25] and hydrogenation were unsuccessful. We then benefitted from Grovenstein and Stevenson's finding[26] that sodium in dioxane or in liquid ammonia cleaved methyl and the higher alkyl groups from quaternary ammonium salts as carbanions but secondary and tertiary alkyl groups predominantly as free radicals and at a faster rate. Application of the cleavage with sodium and liquid ammonia to 1-azoniatricyclo[3.3.3.0]undecane bromide (**16**) afforded manxine (**2**) in 60% yield. The hydrochloride salt of manxine **17** crystallized in the triclinic system, conducive to single-crystal X-ray analysis.[7,8] The methiodide **18** and, after Dowex treatment, the methochloride **19** were also prepared for comparison of physical and spectroscopic properties within this and related series of compounds.



16 17

18, Y = I
19, Y = Cl
20 21

Physical and Chemical Properties

Calculations by Hendrickson[2e,f] and Bixon and Lifson[27] suggest that the minimum energy conformation for cyclooctane is the boat–chair (BC) conformation. The theoretical considerations are in agreement with the nmr work of Anet[2j] on perdeuterated cyclooctanes which indicates that the BC conformation or twist forms thereof predominate in solution. However, substituents and the mode of substitution do affect the preferred conformation,[28] for while Anet[2j] found that some monosubstituted cyclooctanes also seem to prefer the boat–chair conformation, Roberts[21] found that the di- and tetrafluorocyclooctanes take up a twist–boat or boat–chair conformation and cautions against the transposition of conformer percentages found at low temperatures to room temperature. A similar proviso applies to the extrapolation of the findings of crystal studies to solution phenomena. X-Ray crystal data for *cis*- and *trans*-cyclooctane-1,2-dicarboxylic acid indicate boat–chair conformations[29] and for *trans*,-*syn*,*trans*-1,2,5,6-tetrabromocyclooctane, a twisted–crown (D_2).[30] Further crystal studies of cyclooctanes with one[31] or more carbons[32] replaced by heteroatoms established the BC conformation in the crystal lattice.

When the cyclooctane ring is constrained by charge interaction, as in 5-methyl-1-thia-5-azacyclooctane 1-oxide perchlorate,[33a] X-ray study has shown the boat–chair conformation to be present,[33b,c] but in general when the eight-membered ring is constrained with a one carbon methylene bridge it has been shown that the eight ring is in the boat–boat (BB) conformation, six-membered rings in modified twin–chair conformation.[34] Bicyclo[3.3.2]decane, with an ethylene bridge, also appears to take up the BB conformation of the eight ring in solution.[35]

The intraannular 1,5 hydrogen–hydrogen distance for the boat–boat conformation of the eight ring decreases markedly in going from the [3.3.1] to the [3.3.2] system, and a model of the [3.3.3] system in the boat–boat conformation has the 1,5 hydrogens in contact.[4] Calculations based on the strain energy of the boat–chair, crown, and boat–boat conformations of cyclooctanes[2e] suggest that the all-BC conformation for the bicyclo-[3.3.3]undecane system is *at least* 6 kcal/mol more stable than the alternative conformations. On these grounds, in solution, it is expected that manxane (**1**) and manxine (**2**) will be present in all-BC conformation with rapid equilibrium between the degenerate conformational forms[3] in manxane and the mirror image forms of manxine.[4] These forms were shown to be present in the crystals of manxine hydrochloride (**17**) by X-ray diffraction.[7,8]

Because of its volatility and reactivity (peroxidation) we only report the physical and spectroscopic properties of manxane and did not carry out an X-ray analysis or conformational study. It has been shown in Parker's laboratory that manxane is in rapid conformational equilibrium at room temperature (**1**) in which the rings undergo practically simultaneous flipping, a "frozen" spectrum being obtained at −80° at 100 MHz. The nmr spectrum of manxane is of interest when compared with the spectra of adamantane[1,36] and bicyclo[2.2.2]octane.[37] In the manxane spectrum, the methine (bridgehead) protons appear at δ 2.3 while the methylene peak is sharp and located at δ 1.55; in the spectra of adamantane and bicyclo[2.2.2]octane, the methylene and methine protons are together under the same sharp peak, a doublet at δ 1.78 and a narrow multiplet at δ 1.88, respectively. The natural abundance ^{13}C nmr, with proton decoupling,[38] showed a similar shift. The

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(25) G. H. Foster, J. Harley-Mason, and N. R. Waterfield, *Chem. Commun.*, 21 (1967); J. Harley-Mason and Attar-ur-Rahman, *ibid.*, 209 (1967).

(26) E. Grovenstein, Jr., and R. W. Stevenson, *J. Amer. Chem. Soc.*, 81, 4850 (1959).

(27) M. Bixon and S. Lifson, *Tetrahedron*, 23, 769 (1967).

(28) J. D. Dunitz in "Perspectives in Structural Chemistry," Vol. 2, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1968, pp 35–39.

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(30) G. Ferguson, D. D. MacNicol, W. Oberhansli, R. A. Raphael, and J. A. Zabkiewicz, *Chem. Commun.*, 103 (1968).

(31) J. D. Dunitz and V. Prelog, *Angew. Chem.*, 72, 896 (1960).

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(33) (a) A. E. Yethon, Ph.D. Thesis, University of Illinois, 1963; (b) K.-T. Go and I. C. Paul, *Tetrahedron Lett.*, 4265 (1965); (c) I. C. Paul and K.-T. Go, *J. Chem. Soc. B*, 33 (1969). This system is suggestive of a bicyclo[3.3.2]decane type.

(34) (a) W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 57 (1964); (b) W. A. C. Brown, J. Martin, and G. A. Sim, *ibid.*, 1844 (1965); (c) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 47, 695 (1964); (d) I. Laszlo, *Recl. Trav. Chim. Pays-Bas*, **84**, 251 (1965); (e) N. C. Webb and M. R. Becker, *J. Chem. Soc. B*, 1317 (1967). Molecules with bulky endo substituents at the 3 or 7 position may adopt the boat–chair conformation: (f) C. Tamura and G. A. Sim, *ibid.*, 1241 (1968); (g) P. D. Cradwick and G. A. Sim, *ibid.*, 2218 (1971); and references cited therein.

(35) (a) M. P. Doyle and W. Parker, *Chem. Commun.*, 319 (1969); (b) *ibid.*, 755 (1970).

(36) R. C. Fort, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, 30, 789 (1965).

(37) Sample kindly provided by Professor D. E. Applequist, University of Illinois.

(38) ^{13}C nmr spectra courtesy of Brucker Scientific Inc., Elmsford, N. Y. G. E. Maciel and H. C. Dorn, *J. Amer. Chem. Soc.*, **93**, 1268 (1971), have reported ^{13}C chemical shifts for 1-substituted bicyclo-[2.2.2]octanes.

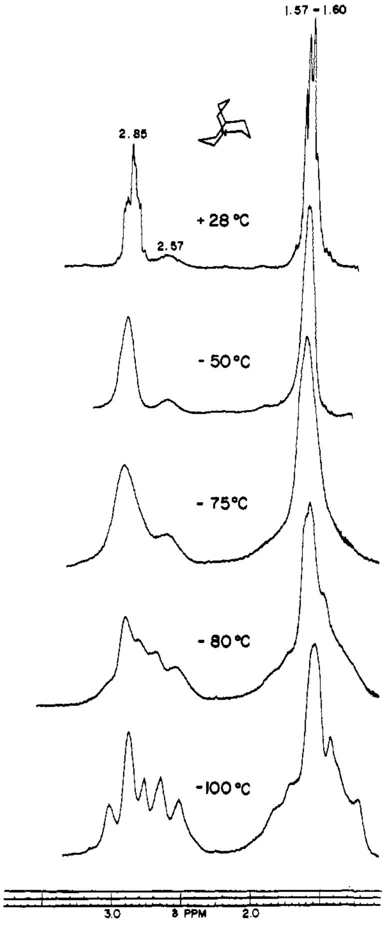

Figure 1. Temperature dependence of the nmr spectrum of 1-azabicyclo[3.3.3]undecane (**2**) at 100 MHz in 1:1 CD_2Cl_2–$CDCl_3$.

bridgehead carbon signal was located *downfield* from the methylene carbon signal in manxane but at a similar shift *upfield* from the methylene carbons in bicyclo[2.2.2]octane, where the 1-CH may be experiencing a through-space shielding from C-4 constrained to proximity. These facts point to a difference in hybridization between the bridgehead carbons and hydrogens in manxane *vs.* the other hydrocarbons that we have compared with it and is reflected in the extreme reactivity of the bridgehead position to radical reactions.[39]

1-Azabicyclo[3.3.3]undecane (manxine) (**2**) was subjected to nmr analysis, and, in methylene chloride–chloroform (1:1) at 100 MHz, a "frozen spectrum" was obtained near −80° (Figure 1), a temperature in close agreement with that found for manxane.[3] It is of interest that the methine protons in manxane (δ 2.3, $W_H \sim$ 20 Hz) and the methine proton in manxine (δ 2.57, $W_H \sim$ 16 Hz) are broad multiplets with no discernible couplings; we suggest that this is a "virtual coupling" phenomenon,[40] due to the near equivalence of the β and γ methylenes (β and γ with respect to the bridgehead nitrogen in **2** or the other bridgehead carbon in **1**). The broad signal became a septet on addition of the dipivaloylmethanatoeuropium(III) complex[41] to a sample of manxine, suggesting that once the β and γ protons become nonequivalent, the six γ-methylene protons, which appear to be equivalent due to rapid conformational "flipping" of the three bridges, are coupled equally to the methine proton (J = 5 Hz). Further structure proof comes from decoupling experiments on the free base. The nmr spectrum of manxine (**2**) at 100 MHz (Figure 1, 28°) shows a multiplet at δ 2.85 (6 H, $W_H \sim$ 9–10 Hz, α CH_2's), a multiplet at δ 2.57 (1 H, $W_H \sim$ 16 Hz, CH), and a multiplet at δ 1.57–1.60 (12 H, $W_H \sim$ 7–8 Hz, β and γ CH_2's). Irradiation of the sample with the frequency corresponding to δ 1.57–1.60 (β and γ CH_2's) resulted in the signal at δ 2.85 (α CH_2's) collapsing to a singlet, while the broad multiplet at δ 2.57 (CH, $W_H \sim$ 16 Hz) sharpened greatly. Irradiation at δ 2.85 resulted in a narrowing of the band at δ 1.60 and irradiation at δ 2.50 produced a collapse of the δ 1.6 signal.

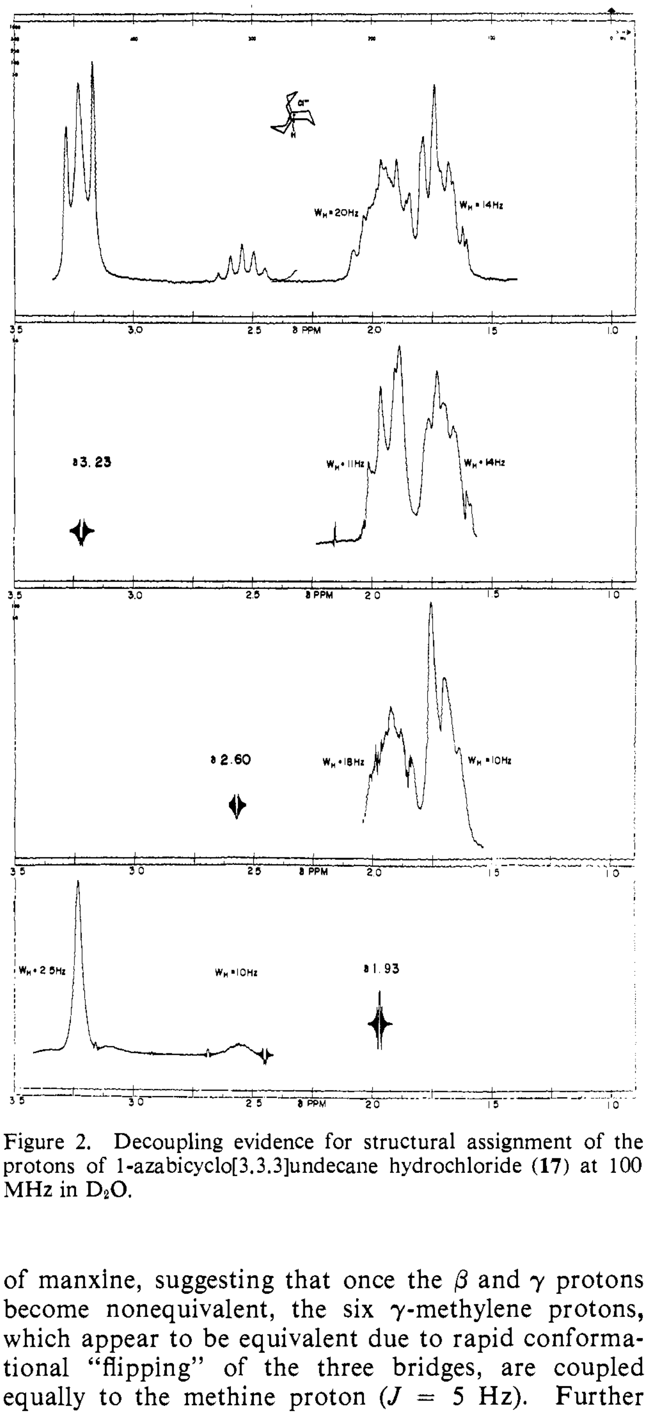

Figure 2. Decoupling evidence for structural assignment of the protons of 1-azabicyclo[3.3.3]undecane hydrochloride (**17**) at 100 MHz in D_2O.

Comparable decoupling studies at 100 MHz with manxine hydrochloride (**17**) are shown in Figure 2. In this case it is possible to differentiate between the β- and γ-methylene protons and to confirm the assign-

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[39] W. Parker, private communication.

[40] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 147.

[41] J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

ments of all protons. Irradiation at δ 3.23 (α CH_2's) resulted in a simplification of the multiplet at δ 1.93 as apparent in Figure 2, while the signal for the γ CH_2's was not greatly affected. Irradiation at δ 2.60 (CH) resulted in a reduction of coupling in the multiplet at δ 1.93. Irradiation at δ 1.93 (β CH_2's) produced narrowing of the signal at δ 3.23 (α CH_2's, $W_H \sim 15$ Hz became $W_H \sim 2.5$ Hz), while the methine proton became a poorly resolved multiplet but was not appreciably sharpened. The methine proton, at 60, 100, and 220 MHz, in manxine hydrochloride, was a well-resolved septet ($J = 5$ Hz) (*cf.* manxine and the europium shift reagent[41]), suggesting that the α methylenes are equivalent due to rapid (on the nmr time scale) equilibration of the conformations.

The pmr spectral values of manxine (**2**) and manxine hydrochloride (**17**) are shown in Table I, together with equivalent values for quinuclidine (**20**) and quinuclidine hydrochloride (**22**) for comparison and contrast. In each case the chemical shift of the methine proton in the [3.3.3] system is (a) downfield with respect to the equivalent chemical shift of the methine proton in the [2.2.2] system and (b) much further downfield compared (Δδ) to the position of its vicinal methylenes than the methine of the [2.2.2] system compared to its vicinal methylenes. This is not due to interaction with the nitrogen lone pair "through space,"[42] since the methine proton in the free base and its hydrochloride salt are at very similar chemical shifts (δ 2.57 *vs.* 2.60). It would seem to be a hydridization factor (*i.e.*, the angles and electron density around the methine carbon in the [3.3.3] system are dissimilar to those in the related [2.2.2] system) and to be a property of the bicyclo[3.3.3]undecane system (*cf.* manxane nmr).

Table I. Pmr Chemical Shifts for [3.3.3] *vs.* [2.2.2] Series

	δ values, ppm				
	α CH_2	β CH_2	γ CH_2	Methine	Δδ[c]
[3.3.3]N:[a] (**2**)	2.85	1.60	*1.57*	*2.57*	1.0
[3.3.3]NH^+Cl^-[b] (**17**)	3.23	1.93	*1.75*	*2.60*	0.85
[2.2.2]N:[a] (**20**)	2.81	1.50		1.3–1.8	(±0.3)
[2.2.2]NH^+Cl^-[b] (**21**)	3.35	1.95		2.07	0.12

[a] $CHCl_3$–TMS. [b] D_2O–DSS. [c] δ proceeding downfield from CH_2 vicinal to $CH_{methine}$.

Table II. ^{13}C Nmr Chemical Shifts for [3.3.3] *vs.* [2.2.2] Series

		^{13}C nmr				
		α C	β C	γ C	Bridgehead	Δδ[b]
[3.3.3]$\overset{+}{N}H$ Cl^- (**17**)	Chemical shift, Hz[a]	400.2	915.0	*1095.6*	868.7	226.9
	$J_{^{13}C-H}$, Hz	142 ± 4	126 ± 4	129 ± 4	~125[c]	
[2.2.2]$\overset{+}{N}H$ Cl^- (**21**)	Chemical shift, Hz[a]	453.8	*1000.4*		1083.4	−83.0
	$J_{^{13}C-H}$, Hz	144 ± 4	133 ± 4		≥140[c]	

[a] Upfield from dioxane. [b] Shift proceeding downfield from $C_{vicinal}$ to $C_{bridgehead}$. [c] Approximate values.

The ^{13}C nmr[38] of manxine hydrochloride and quinuclidine hydrochloride, which are given in Table II, also reflect the unusual nature of the hybridization around the methine carbon in the bicyclo[3.3.3]undecane system. As in the ^{13}C nmr spectrum of manxane, the bridgehead carbon of manxine hydrochloride appears at lower field than the β and γ carbons, whereas in the spectrum of quinuclidine hydrochloride the bridgehead carbon is at higher field than the β carbons. The approximate value for $J_{^{13}C-H}$ of the bridgehead carbon–hydrogen in manxine hydrochloride (~125 Hz) as compared with the value for quinuclidine hydrochloride (≥140 Hz) speaks for the difference in C–H hybridization between the two systems.[43] It is quite usual for a tertiary carbon to have a ^{13}C–H coupling constant about 10–20 Hz *greater than* secondary carbons,[44] and this in in fact what is found in quinuclidine hydrochloride. Manxine hydrochloride, by contrast, has a ^{13}C–H coupling constant for the tertiary carbon at a *lower* value than the secondary carbons and this trend is in the direction of increased p character in the C–H bond.[45] These findings are in agreement with the X-ray crystal data for manxine hydrochloride[7,8] which show the CH_2CHCH_2 angles to be in the range 113.5–114.8 (3)° for **17**, making a comparison with the [2.2.2] system especially interesting because the angles in this system are all close to the tetrahedral value.[46]

The increased p character in the bridgehead carbon–hydrogen bond and the corresponding flattening of the bridgehead region with an increase in the s character of the carbon–carbon bonds in that region are also indicated by the detailed X-ray study of **17**, which includes the determination that the bridgehead carbon is only 0.387 Å above the plane of the three adjacent carbon atoms (75% of normal). A similar effect is observed at the nitrogen end, where the nitrogen atom lies only 0.326 Å above the plane of the α_N carbons (64% of normal). Presumed similar flattening results in very interesting electronic absorbance for the corresponding base (**2**). The uv spectrum of manxine in ether shows a distinct maximum at 240 nm (ε 2935) in ether (Figure 3), probably the highest wavelength maximum recorded for a saturated tertiary amine.[47] By contrast, quinucli-

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(42) (a) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *Chem. Commun.*, 1535 (1970).

(43) The $J_{^{13}C-H}$ values for the bridgehead carbon–hydrogen are subject to some extrapolation; in the spectrum of manxine hydrochloride, the doublet for the bridgehead carbon appeared under the triplet for the β_N carbons and its position was estimated from symmetry considerations and from where it was not. The value in the quinuclidine hydrochloride spectrum was obtained from the visible half of the bridgehead carbon doublet, the other half being under one of the peaks of the β_N-carbon's triplet.

(44) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 121 (1965).

(45) (a) C. S. Foote, *Tetrahedron Lett.*, 579 (1963); (b) K. Mislow, *ibid.*, 1415 (1964).

(46) (a) O. Ermer and J. D. Dunitz, *Chem. Commun.*, 567 (1968); (b) *Helv. Chim. Acta*, **52**, 1861 (1969); (c) A. F. Cameron, G. Ferguson, and D. G. Morris, *J. Chem. Soc. B*, 1249 (1968); (d) A. Meyerhöffer and D. Carlstrom, *Acta Crystallogr., Sect. B*, **25**, 1119 (1969).

(47) N. J. Leonard and D. M. Locke, *J. Amer. Chem. Soc.*, 77, 437 (1955).

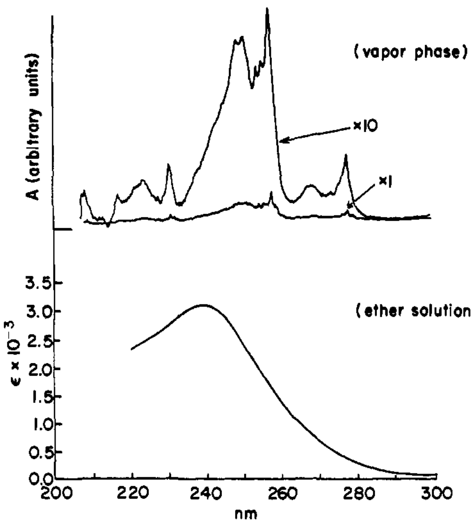

Figure 3. Ultraviolet spectra of 1-azabicyclo[3.3.3]undecane in ether solution and (qualitative) in the vapor phase.

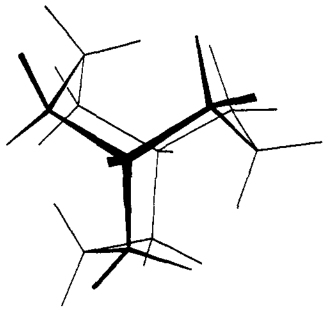

Figure 4. Projection of the Dreiding model of 1-azabicyclo[3.3.3]-undecane hydrochloride.

dine in ether shows only end adsorption. An even more interesting spectrum was obtained when a few milligrams of solid amine were placed in the bottom of the cuvette and a qualitative "vapor" spectrum was taken. The spectrum of manxine, taken in the presence of air (Figure 3), is impressive when compared with the qualitative spectrum of quinuclidine (**20**) taken under the same conditions.[48] The shift to longer wavelength for the n → p transition, for example,[48] is compatible with the flattening of the nitrogen region, because the excited state, by comparison with quinuclidine[48] and ammonia,[49] would be expected to approach planar bonding; thus, any flattening of the ground-state geometry, as observed for manxine hydrochloride[7,8] and presumed for the base, would be expected to lower the energy required for such a transition.

This flattening of the bridgehead regions of the bicyclo[3.3.3]undecane system, as suggested by the nmr and uv (liquid phase) studies and confirmed by the X-ray crystallographic study of manxine hydrochloride, helps to explain the susceptibility of manxane to undergo radical (and carbonium ion?) reactions,[39] for with this flattening, the ground-state geometry of the system comes closer to the presumed planar transition state geometry for radical (and carbonium ion) reactions.[50]

Flattening of the bridgehead region of the bicyclo-[3.3.3]undecane system is accompanied by widening of the angles in the bridges and by a torsional twisting of the bridges (C-3 *vs.* C-2 and C-4), according to the X-ray determination of the manxine hydrochloride crystal structure. A comparison of the Dreiding model (Figure 4) and the X-ray structure (Figure 1 in ref 8) shows that the $\geq 90°$ value for the torsion angles in the trimethylene bridges in the model is reduced to an observed 66.5–68.7° in **17**.[7,8] It has been pointed out that potential energy balancing may occur by valency-angle *vs.* dihedral-angle deviations.[51] The twisting of the trimethylene bridges results in one set of three vicinal trans–trans hydrogens lying in anti conformation and the other set lying in gauche configuration in the X-ray structure, instead of, for the latter set, partially eclipsing each other as in the Dreiding model (Figure 4). A further result of this twisting is to relieve the intraannular hydrogen–hydrogen interaction by pushing apart the endo hydrogen on C-7 from the buttressing intraannular hydrogen atoms on C-2 and C-4.

Another property of manxine which may be attributed to the flattening of the bridgehead region is the low pK_a' value of its conjugate acid. In 66% aqueous dimethylformamide, manxine has a pK_a' value of 8.8 as compared with 10.05 for quinuclidine, and in water the corresponding values are 9.9 and ~10.9.[52] In addition, and from models of manxine hydrochloride, one of the hydrogens on each of the carbons adjacent to nitrogen is syn periplanar with the proton on nitrogen, causing steric crowding (F strain)[53] in comparison with quinuclidine hydrochloride, which has all six hydrogens on the adjacent carbons well below the proton on nitrogen and directed equatorially away.

In summary, the work here reported shows that the unusual properties of the bicyclo[3.3.3] system are a consequence of geometric properties and the strain inherent in a bicyclic array made up entirely of eight-membered rings. The reactivity of the bridgehead positions suggests further experimental and theoretical interest in the bicyclo[3.3.3]undecane system.

Experimental Section[54]

Bicyclo[3.3.1]non-2-en-9-one (3). The morpholine enamine of cyclohexanone was prepared by the method of Stork[55] and was

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[48] For the quantitative spectrum of quinuclidine, see A. M. Halpern, J. L. Roebber, and K. Weiss, *J. Chem. Phys.*, **49**, 1348 (1968). A quantitative spectrum of 1-azabicyclo[3.3.3]undecane (2), also abbreviated "ABCU," in the vapor state will be reported separately by Professor A. M. Halpern, New York University, along with other, more detailed spectroscopic studies on samples of this model compound.

[49] G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 515.

[50] J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, p 155. Professor P. v. R. Schleyer, Princeton University, on the basis of molecular mechanics calculations on the manxane system, has concluded that strain will be relieved in going to the bridgehead carbonium ion [private communication; see also R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971)].

[51] J. Dale, *Angew. Chem., Int. Ed. Engl.*, **5**, 1000 (1966).

[52] We are grateful to the Lilly Research Laboratories, Eli Lilly and Co., Indianapolis, Ind., for the pK_a determinations.

[53] H. C. Brown, D. H. McDaniel, and O. Häfliger in "Determination of Organic Structures by Physical Methods," Vol. 1, E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, Chapter 14.

[54] All melting points are uncorrected. Nuclear magnetic resonance spectra were determined on Varian Associates A-60A, HA-100, and HR-220 spectrometers. Electronic absorption spectra (uv) were recorded on a Cary Model 15 spectrophotometer while infrared spectra were recorded on a Perkin-Elmer 421 or 337 spectrophotometer.

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condensed and cyclized with acrolein in dry dioxane[56] to give 2-*N*-morpholinobicyclo[3.3.1]nonan-9-one. Oxidation to the *N*-oxide with hydrogen peroxide in refluxing methanol followed by pyrolysis[9c] gave bicyclo[3.3.1]non-2-en-9-one (**3**): mp 93–97° (lit.[9c] 98–99°); ir ($CHCl_3$) 3010, 1720, 1400 cm^{-1}; nmr ($CDCl_3$) δ 6.2–5.4 (m, 2), 3.0–2.2 (m, 4), 1.95 (m, 6).

Bicyclo[3.3.1]nonan-9-one (4). Bicyclo[3.3.1]non-2-en-9-one (**3**) (16 g, 0.12 mol) was hydrogenated over 5% palladium on charcoal (200 mg) in methanol (200 ml) at room temperature and pressure.[9c] The unsaturated ketone **3** and the saturated compound **4** could be differentiated by glpc on 20% XE-60 on Ankrom ABS at 175°. When reaction was complete, the catalyst was removed by filtration and the solvent by concentration *in vacuo*. The waxy solid was sublimed at 80° (12 mm) to give the ketone **4** (15 g, 93% conversion): mp 153–155° (lit.[9c] 155–158°); ir ($CHCl_3$) 1710 cm^{-1}; nmr ($CDCl_3$) δ 2.4 (m, 2), 2.1 (m, 12).

Bicyclo[3.3.2]decan-9-one (5). A solution of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ["Diazald") (49 g, 0.23 mol) in 350 ml of methanol was added dropwise to a stirred solution containing bicyclo[3.3.1]nonan-9-one (**4**) (15 g, 0.11 mol), potassium hydroxide (67 g), water (27 ml), and methanol (15 ml) at 0° over a period of 4 hr.[10] The mixture was allowed to warm gradually to 20° and was stirred overnight. The suspension was filtered, and the filtrate was concentrated *in vacuo*. The filtered salt was washed with ether (200 ml), the ether washes were combined with the concentrate, more ether was added, the whole organic phase was washed with water and dried, and the ether was removed. The residue in ether–hexane (1:19) was placed on a silica column (500 g) in the same solvent and eluted to give, in first recovery, bicyclo[3.3.2]decan-9-one (**5**) (10 g) (60% conversion), which, after vacuum sublimation at 60° (10 mm), had mp 177–179° (lit.[57] 182–186°): ir ($CHCl_3$) 1680 cm^{-1}; nmr ($CDCl_3$) δ 2.85 (m, 1, CHCO), 2.50 (d, 2, J = 6 Hz), 1.7 (m, 13); mass spectrum (8 eV) *m/e* (rel intensity), 152 (100).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.61; H, 10.85.

Elution with ether–hexane (1:4) afforded 3 g of bicyclo[3.3.1]-nonan-9-one (**4**).

9-Methylenebicyclo[3.3.2]decane (6). By the method of Corey, *et al.*,[15] the methyl sulfinyl carbanion, generated from sodium hydride (5 g of a 56% mineral oil dispersion) in dimethyl sulfoxide (50 ml) under nitrogen at 70°, was used to make methylenetriphenylphosphorane from methyltriphenylphosphonium bromide (35.7 g). The ylide was allowed to react with the ketone **5** (12 g) added in dimethyl sulfoxide (20 ml) at room temperature and heated at 56° for 16 hr. The mixture was poured into ice–water (200 ml), and the layers were separated. The upper and lower layers were extracted separately with pentane (2 × 20 ml) and filtered as necessary to remove precipitated solid, and the combined pentane layers were washed with water–dimethyl sulfoxide (1:1) and saturated sodium chloride solution and dried (Na_2SO_4). After removal of the solvent, the residue was placed on a silica column (150 g) in ether–hexane (1:39) and eluted with the same solvent. The early fractions contained 9-methylenebicyclo[3.3.2]decane (**6**) (6 g, 50% conversion): mp 67–69° (2.5 mm); $n^{23}D$ 1.5022; ir (film) 3040, 1610 cm^{-1}; nmr ($CDCl_3$) δ 4.70 (dd, 1, J_{AB} = 2.7 Hz, J_{AX} = 2 Hz), 4.57 (dd, 1, J_{BA} = 2.7 Hz, J_{BX} = 2 Hz), 2.85 (m, 1), 2.56 (m, 2, $J_{AX} = J_{BX}$ = 2 Hz, J_{XZ} = 4 Hz), 2.20 (m, 1, J_{XZ} = 4 Hz), 1.65 (m, 12). Each doublet of doublets collapsed to a doublet (J_{AB} = 2.7 Hz) on irradiation with the frequency of the signal for the H_X protons at δ 2.56, while irradiation with the frequency of the H_A and H_B protons (δ 4.70, 4.57) separately resulted in the multiplet δ 2.56 collapsing to a doublet of doublets ($J_{AX} = 2 = J_{BX}$), and irradiation with the frequency of H_A and H_B simultaneously (δ 2.63) resulted in further collapse to a doublet (J_{XZ} = 4 Hz).

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.78; H, 11.98.

Epoxidation of 9-Methylenebicyclo[3.3.2]decane (6). To a stirred solution of *m*-chloroperbenzoic acid (1.5 g) in chloroform (40 ml) at 0° was added 9-methylenebicyclo[3.3.2]decane (**6**) (1 g), and the resulting mixture was stirred at 0° for 30 min. The chloroform solution was filtered, diluted with ether (200 ml), washed with water, ice-cold 5% sodium bicarbonate solution (3 × 50 ml), and water, and then dried (Na_2SO_4) before removal of the solvent. The residue was a sweet-smelling oil that solidified on standing and was sublimed at 60° (5 mm) to give the epoxide **7** (850 mg): mp 97–98° (77% conversion); nmr ($CDCl_3$) δ 2.62 (s, 2, epoxide CH_2), 2.0 (m, 3, α CH, α CH_2), 1.65 (m, 13).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.69; H, 10.72.

A similar product yield was obtained when the olefin 6 in ether was treated with ethereal monoperphthalic acid at 0° for 48 hr, followed by filtration and identical work-up as above.

Hydrochloride Salt of 9-Aminomethylbicyclo[3.3.2]decan-9-ol (9). The epoxide **7** (1.5 g) in dimethylformamide (50 ml) was treated with sodium azide (2 g) and boric acid (2.0 g) at reflux for 3 hr.[20] The solvent was removed, and the residue was partitioned between ether and water. The ether extracts were washed with water and saturated sodium chloride and dried (Na_2SO_4). The residue **8**, an oil, showed: ir (film) 3570, 3530, 3420 (OH), 2100 cm^{-1} (N_3); nmr ($CDCl_3$) δ_A 3.39, δ_B 3.61, J_{AB} = 13 Hz (CH_2N_3). The hydroxy azide **8** in ethanol (25 ml) was shaken with hydrogen over Adams catalyst at 3 atm for 2 hr at room temperature, and the catalyst was removed by filtration. The ethanol was evaporated, and the residue was treated with hydrochloric acid (20 ml of 1 *N*) and extracted with ether. The aqueous layer was basified with 2 *N* sodium hydroxide, and the resulting precipitate was extracted with ether, washed with saturated aqueous sodium chloride solution, and dried (Na_2SO_4). The dried ether solution was saturated with hydrogen chloride gas. The filtered solid was recrystallized from ethanol: 1 g (50% from epoxide); mp 241–242°; ir (Nujol) 3225, 3195 (NH, OH), 1615 cm^{-1}; nmr (D_2O) δ_A 3.04, δ_B, 3.22, J_{AB} = 13 Hz ($CH_2NH_3^+$).

Anal. Calcd for $C_{11}H_{22}ClNO$: C, 60.11; H, 10.09; N, 6.37. Found: C, 60.34; H, 9.96; N, 6.31.

Bicyclo[3.3.2]dec-2(3)-en-9-one (10). By the same method used to prepare the saturated ketone **4**, bicyclo[3.3.1]non-2-en-9-one (**3**) was treated with diazomethane and isolated with ether. The residue was purified by chromatography on a silica column in ether–hexane (1:19) and eluted with the same solvent, affording the bicyclo-[3.3.2]dec-2(3)-en-9-one mixture (**10**), which was sublimed at 70° (0.1 mm): yield, 60%; ir ($CHCl_3$) 1690 cm^{-1}; nmr ($CDCl_3$) δ 5.8 (m, 2), 3.0–2.2 (m, 6), 2.0–1.6 (m, 6); mass spectrum (9.5 eV) *m/e* (rel intensity) 150 (100); semicarbazone, mp 204°; mass spectrum (9.0 eV) *m/e* (rel intensity) 207 (100).

Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.76; H, 8.21; N, 20.28. Found: C, 63.96; H, 8.38; N, 19.81.

9-Epoxymethylenebicyclo[3.3.2]dec-2(3)-ene (11). After Corey and Chaykovsky,[14] a solution of methyl sulfinyl carbanion (Na^+) was prepared under nitrogen from sodium hydride (2 g, suspension in mineral oil) and dimethyl sulfoxide (50 ml). The solution was cooled to room temperature; dry tetrahydrofuran (50 ml) was added, followed by further cooling at ice–salt temperature. With stirring, a solution of trimethylsulfonium iodide (12.2 g) in dimethyl sulfoxide (50 ml) was added over a period of 3 min and the mixture was stirred for 1 min before the addition of 2.5 g of bicyclo[3.3.2]dec-2(3)-en-9-one (**10**) in dimethyl sulfoxide (20 ml). Stirring was continued briefly at ice–salt temperatures and then for 2 hr at room temperature. The reaction mixture was diluted with water (600 ml) and extracted with pentane (3 × 100 ml). The pentane solution was washed with water and dried (Na_2SO_4), and the solvent was removed to give an oil, **11** (700 mg, 26%), which was passed through a silica gel column in ether–hexane (1:19), and elution with the same solvent afforded the epoxide **11**: selected nmr signals ($CDCl_3$) δ 5.63 (m, 2), 3.32 (s, 2); mass spectrum (9.0 eV) *m/e* (rel intensity) 164 (100).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.48; H, 9.75. Found: C, 80.10; H, 9.55.

The Hydrochloride Salt of 9-Aminoethylbicyclo[3.3.2]decan-9-ol (9). The unsaturated epoxide **11** (700 mg) in dimethylformamide (20 ml) was treated with sodium azide (1 g) and boric acid (1 g) at reflux for 3 hr.[20] The solvent was removed *in vacuo*, water was added, and the mixture was extracted with ether. The ether extracts were washed with water, followed by saturated sodium chloride solution, and dried (Na_2SO_4). The residue **12** was an oil: yield, 470 mg (53%); ir (film) 3600–3100 (OH), 2100 cm^{-1} (N_3).

The hydroxy azide **12** in ethanol (10 ml) was shaken with hydrogen over Adams catalyst at 3 atm for 2 hr at room temperature, and the catalyst was removed by filtration. The ethanol was evaporated, and the residue was acidified with concentrated hydro-

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Microanalyses were performed by Mr. Josef Nemeth and staff, who also weighed samples for quantitative ultraviolet spectral studies. Mass spectra were recorded on a Varian-MAT CH-5 mass spectrometer. Chromatography was carried out using Grace Davison silica gel, Grade 950, and glp chromatography on an F & M 300 or Varian Aerograph Series 1700 apparatus.

(55) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(56) G. Stork and H. K. Landesman, *ibid.*, **78**, 5129 (1956).

(57) R. C. Bingham and P. v. R. Schleyer, *J. Org. Chem.*, **36**, 1198 (1971).

chloric acid (10 ml) and partitioned between ether and water. The aqueous phase was basified with sodium hydroxide pellets and ether extracted. The dried ether extracts were saturated with dry hydrogen chloride gas and the amine hydrochloride **9** was collected by filtration. Ethanol recrystallization afforded a sample identical with that obtained *via* the saturated route (**4** → **8** → **9**); yield, 329 mg (66%).

Bicyclo[3.3.3]undecan-9- and -10-ones (14, 15). The amine hydrochloride **9** (1 g) in water (20 ml) containing acetic acid (1 ml) was treated with sodium nitrite (1 g) in water (10 ml) dropwise at room temperature and warmed on a steam bath for 1 hr after the addition. The mixture was cooled, ether extracted, washed with water, sodium bicarbonate solution, water, and saturated sodium chloride, and dried and the solvent was removed. The semicrystalline solid was homogeneous by tlc and glpc on a variety of different phases: mp 196–205°; ir (Nujol) 1690 cm^{-1}; nmr ($CDCl_3$) δ 2.9 (m, 0.62, CHC=O in **14**), 2.69 (m, $2 \times 0.62 + 4 \times 0.38$); mass spectrum (10 eV) *m/e* (rel intensity) 166 (100). $C_{11}H_{18}O$ requires *m/e* 166.

Bicyclo[3.3.3]undecane (1). The ketone mixture **14, 15** (166 mg, 1 mmol) in ethylene glycol (23 ml, 150 mmol) was heated with hydrazine hydrate (2.5 ml, 66 mmol) and hydrazine dihydrochloride (840 mg, 8 mmol) at 130° for 2.5 hr. Potassium hydroxide pellets (1.2 g, 22 mmol) were added cautiously and the temperature was raised slowly to 210° with distillation of hydrazine–water. The mixture was heated for a further 2.5 hr and the product, bicyclo[3.3.3]undecane (**1**), collected on the cool part of the condenser where it had steam distilled or sublimed. The analytical sample was sublimed at 50° (10 mm): 71 mg; mp *ca.* 192° (sealed tube); nmr ($CDCl_3$) δ 2.3 (m, 2, CH), 1.55 (d, 18, CH_2), shown to be identical with the sample prepared in the U. K.[3]

Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.61; H, 13.27.

1-Azabicyclo[3.3.3]undecane (2). 1-Azoniatricyclo[3.3.3.0]undecane bromide[24] (**16**) (250 mg) was added to liquid ammonia (20–50 ml) in a well-stirred, cooled flask, and small pieces of freshly cut sodium metal were added. Fresh sodium was added as the blue color disappeared, and the addition was continued until the blue color persisted. The reaction vessel was allowed to warm to room temperature and the ammonia allowed to evaporate. Water and ether were carefully added and the ether layer was washed, dried, and evaporated to dryness. The residue was sublimed at 30° (20 mm) to give a white volatile solid, **2** (100 mg, 60% conversion): mp 150–152°; (nmr ($CDCl_3$) δ 2.85 (m, 6, α CH_2's), 2.57 (m, 1, CH), 1.57–1.60 (m, 12, β,γ CH_2's); $\lambda_{\max}$ (ether) 240 nm (ϵ 2935).

Anal. Calcd for $C_{10}H_{19}N$: C, 78.36; H, 12.49; N, 9.14. Found: C, 78.12; H, 12.39; N, 8.92.

1-Azabicyclo[3.3.3]undecane Hydrochloride (17). The amine **2** was dissolved in dry ether, and anhydrous hydrogen chloride gas was passed in until no further precipitation was observed. The solid was filtered and recrystallized from a large volume of acetone: mp 305–307°; ir (Nujol) 2800–2000 cm^{-1} (NH); nmr (D_2O) δ 3.23 (m, 6, α CH_2's), 2.60 (septet, 1, CH, $J = 5$ Hz), 1.93 (m, 6, β CH_2's), 1.75 (m, 6, γ CH_2's).

Anal. Calcd for $C_{10}H_{20}ClN$: C, 63.30; H, 10.63; N, 7.38; Cl, 18.69. Found: C, 63.59; H, 10.51; N, 7.10; Cl, 18.41.

1-Azabicyclo[3.3.3]undecane Methiodide (18). The amine **2** was dissolved in dry ether, and 2 mol equiv of methyl iodide added. The solution was allowed to stand overnight and the methiodide was filtered. Three recrystallizations from ethanol afforded the analytical sample **18**: mp 273–275°; nmr (D_2O) δ 3.38 (m, 6, α CH_2's), 3.05 (s, 3, NCH_3), 2.40 (m, 1, CH), 1.90 (m, 6, β CH_2's), 1.68 (m, 6, γ CH_2's).

Anal. Calcd for $C_{11}H_{22}IN$: C, 44.74; H, 7.51; N, 4.75; I, 42.99. Found: C, 44.59; H, 7.45; N, 4.68; I, 42.74.

1-Azabicyclo[3.3.3]undecane Methochloride (19). The methiodide **18** in water was passed through a Doxex 1-X8 (Cl^- form) ion-exchange column. Exchange was incomplete after only one passage, but almost complete exchange was achieved by passing it through a second column. Recrystallization from ethanol afforded the analytical sample: mp 295–298°; nmr (D_2O) δ 3.72 (m, 6, α CH_2's), 3.52 (s, 3, NCH_3), 2.52 (sept, 1, CH), 2.1 (m, 5, β CH_2's), 1.75 (m, 6, γ CH_2's).

Anal. Calcd for $C_{11}H_{22}ClN$: C, 64.84; H, 10.89; N, 6.88; Cl, 17.40. Found: C, 64.64; H, 10.91; N, 6.41; Cl, 17.18.

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