Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.67; H, 9.09. Found: C, 66.33; H, 9.00.

B. From Carbethyoxymethylenetriphenylphosphorane.—A mixture of 7.1 g of 3,3-dimethyl-2,4-pentanedione and 19.0 g of carbethoxymethylenetriphenylphosphorane[14] was stirred at 155–160° for 24 hr, then cooled, extracted with petroleum ether (bp 60–68°), and worked up. Distillation yielded 2.4 g of unreacted ketone and 3.7 g (34% conversion, 51% yield) of the desired ester. The ester was found by infrared and nmr spectra to be identical with that obtained by procedure A. Although the presence of the *cis* isomer could not be detected in the nmr spectrum, glpc[10] showed the presence of a very small amount of another compound with a slightly shorter retention time.

Saponification of Ethyl 3,4,4-Trimethyl-5-oxo-*trans*-2-hexenoate (II).—A solution containing 0.5 g of the ester (II), 25 ml of methanol, 1.25 g of potassium hydroxide, and 2 ml of water stood at room temperature for 18 hr, then was diluted with water, acidified with 5 ml of concentrated hydrochloric acid, and concentrated under vacuum. Crystalline 3,4,4-trimethyl-5-oxo-*trans*-2-hexenoic acid (I), 100 mg, mp 128–219°, precipitated and was filtered. A mixture melting point of synthetic I and the camphor metabolite[1] was undepressed. Ultraviolet, infrared, and nmr spectra are summarized in Table I; its mass spectrum is found in Figure 1.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.53; H, 8.24; Mol wt, 170. Found: C, 63.72; H, 8.30.

The mother liquor from filtration of I was saturated with salt and extracted with ether. The ether layer was dried over anhydrous sodium sulfate; removal of solvent gave a semisolid residue which was shown by tlc (silica gel G; 9:1 benzene–acetic acid) to contain three compounds: R_f 0.65, 0.53, and 0.18 (trace). The most mobile component was identified as 3,4,4-trimethyl-5-oxo-*trans*-2-hexenoic acid (I), R_f 0.65. Chromatography over a column of silica gel using benzene containing 3% acetic acid as eluant gave 75 mg of I (total yield, 41% from saponification) and 140 mg (33%) of 4,4-dimethyl-3-methylene-5-oxohexanoic acid (II), R_f 0.53. Both compounds crystallized from benzene–pentane; compound II had mp 53°. Ultraviolet, infrared, and nmr spectra of III are summarized in Table I; its mass spectrum is found in Figure 1.

Anal. Found: C, 63.52; H, 8.26; mol wt, 170 (mass spectrometry).

Eluting the column with benzene–acetic acid (4:1) gave 10 mg of the third isomer, **3,4,4-trimethyl-5-oxo-*cis*-2-hexenoic acid,** existing predominantly as the δ-lactol (IIIb). Crystallization from benzene–pentane gave aggregates, mp 110–131°.[15] Although the small amount of compound available precluded further purification, it was found to be pure by tlc on silica gel. Ultraviolet, infrared, and nmr spectra are summarized in Table I; the mass spectrum is found in Figure 1.

Anal. Found: mol wt, 170 (mass spectrometry).

Registry No.—I, 14919-54-1; II, 6994-98-5; IIIa, 14919-56-3; IIIb, 14919-57-4; IV, 6994-96-3; V, 14919-59-6.

Acknowledgment.—This investigation was supported by a grant (No. AI 04769) from the U. S. Public Health Service, National Institute of Allergy and Infectious Diseases.

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[14] D. B. Denney and S. T. Ross., *J. Org. Chem.* **27**, 998 (1962).

[15] The compound is apparently polymorphic, since further recrystallization from ether–pentane sometimes gave mp 152–154°, sometimes mp 110–131°.

The Synthesis of Some 3,7-Dialkyl-3,7-diazabicyclo[3.3.1]nonanes and a Study of Their Conformations

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A series of 3-methyl-7-alkyl-3,7-diazabicyclo[3.3.1]nonanes (N-methyl-N′-alkylbispidines) have been prepared by Mannich cyclocondensations on 1-methyl-4-piperidone followed by Wolff-Kischner reduction of the intermediate ketones. Dipole moment and nmr studies indicate that their preferred conformation is a flattened chair-chair. All of these diamines titrate as monoamines; the formation of very stable hydrogen-bonded adamantanelike cations is proposed to account for this behavior. The reaction of N,N′-dimethylbispidine with diiodomethane is also discussed.

Of the numerous methods which have been reported for the synthesis of the 3,7-diazabicyclo[3.3.1]nonane system,[1] those which are related to the classical Robinson–Schöpf reaction[2] are among the most versatile. Without exception, however, these heterocycles are substituted on both bridgehead carbon atoms.[3] The parent diamine itself has been prepared only by multistep, relatively low yield syntheses.[4]

In the course of other investigations, we found a need for several 3-methyl-7-alkyl-3,7-diazabicyclo-[3.3.1]nonanes (hereafter referred to as N-methyl-N′-alkylbispidines (1)), and it is our studies concerning the synthesis and properties of these compounds which we now wish to report.

Results and Discussion

It occurred to us that a two-step approach to the synthesis of 1 starting with a double Mannich condensation of commercially available 1-methyl-4-piperidone with formaldehyde and alkylamine to give the diazabicyclic ketone 2 would be worthy of investigation. The success of House and coworkers[5] in

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[1] For a review, see H. Stetter, *Angew. Chem., Intern. Ed. Engl.*, **1**, 286 (1962).

[2] For a discussion of the stereochemistry of this reaction, see L. A. Paquette and J. W. Heimaster, *J. Am. Chem. Soc.*, **88**, 763 (1966).

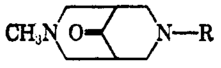
[3] (a) S. Chiavarelli, F. Toeffer, R. L. Vittori, and P. Mazzeo, *Gazz. Chim. Ital.*, **94**, 1021 (1964); (b) K. Hohenlohe-Oehringen, *Monatsh.*, **94**, 1208 (1963); (c) S. Chiavarelli and L. V. Fennoy, *J. Org. Chem.*, **26**, 4895 (1961); (d) S. Chiavarelli, G. Settimj, and H. M. Alves, *Gazz. Chim. Ital.*, **87**, 109 (1957); (e) Z.-Y. Kyi and W. Wilson, *J. Chem. Soc.*, 1706 (1951); (f) E. F. L. J. Anet, G. K. Hughes, D. Marmion, and E. Ritchie, *Australian J. Sci. Res.*, **3A**, 330 (1950); (g) C. Mannich and F. Veit, *Ber.*, **68B**, 506 (1935); (h) C. Mannich and P. Mohs, *ibid.*, **63B**, 608 (1930).

[4] (a) F. Bohlmann, N. Ottawa, and R. Keller, *Ann.*, **587**, 162 (1954); (b) H. Stetter and H. Hennig, *Ber.*, **88**, 789 (1955); (c) F. Galinowsky, F. Sparatore, and H. Langer, *Monatsh.*, **87**, 100 (1956).

[5] H. O. House, P. P. Wickham, and H. C. Müller, *J. Am. Chem. Soc.*, **84**, 3139 (1962).

TABLE I

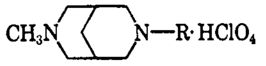
DIAMINO KETONES 2



R	Bp, °C (mm)	Formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
CH_3	88–92(0.5)	$C_9H_{16}N_2O$	64.23	64.01	9.59	9.67	16.7	17.0
C_2H_5	101–102(0.7)	$C_{10}H_{18}N_2O$	65.86	65.76	9.96	9.90	15.38	15.42
$(CH_3)_2CH$	101–103(0.5)	$C_{11}H_{20}N_2O$	67.28	67.09	10.28	10.18	14.28	14.25
$(CH_3)_3C$	97–99(0.5)	$C_{12}H_{22}N_2O$	68.51	68.71	10.56	10.66	13.33	13.30

TABLE II

PERCHLORATE SALTS OF BISPIDINES

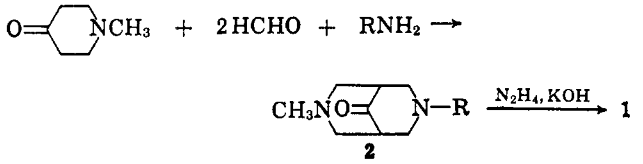


R	Mp, °C	Formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
CH_3	229–230[a]	$C_9H_{19}ClN_2O_4$	42.42	41.97	7.52	7.47	10.98	10.91
C_2H_5	241–243	$C_{10}H_{21}ClN_2O_4$	44.66	44.37	7.88	7.91	10.43	10.48
$(CH_3)_2CH$	220–222	$C_{11}H_{23}ClN_2O_4$	46.69	46.87	8.20	8.31	9.91	9.78
$(CH_3)_3C$	205–206	$C_{12}H_{25}ClN_2O_4$	48.53	48.65	8.49	8.55	9.44	9.40

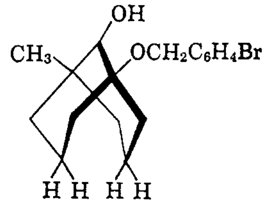
[a] All of the salts melt with decomposition.

preparing analogous azabicyclic ketones from cycloalkanones by a similar method made the approach appear particularly promising.

After investigating numerous variations on the basic reaction (such variables as solvent, temperature, concentrations of reactants, mole ratios of reactants, the chemical form of the formaldehyde, and pH all affect yield), it was found that the slow addition of a methanolic solution of the acetate salt of 1-methyl-4-piperidone (1 mole) to a refluxing methanolic solution of methylammonium acetate (1 mole) and paraformaldehyde (2 moles) gave reasonably good yields (45–55%) of **2**. Reduction of the diamino ketone to the diamine **1** by means of the usual Wolff–Kischer procedure was accomplished without any significant complications.[6] See Tables I and II for results.



The preferred conformation of the bicyclo[3.3.1]nonane system has been the subject of considerable investigation. In some cases the conformations (in the crystalline state) have been firmly established by X-ray crystallography. For example, compounds **3**[7] and **4**[8] were found to have the chair–chair conformation, although with some flattening of the rings due probably to the nonbonded interactions between the *endo* hydrogens. The reported C_3–C_7 and N_3–C_7 interatomic distances of 3.05 and 3.02 A for **3** and **4**, respectively, as opposed to expected distances of about 2.5 A for the undistorted chair–chair conformations, are a good measure of the flattening in these molecules.



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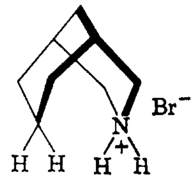

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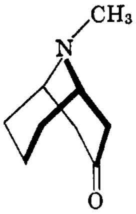
Based less securely on dipole moment and infrared and proton nmr spectral data, the chair–chair conformation has been proposed for such molecules as ψ-pelletierine (**5**),[9] 3-β-granatanol (**6**),[9] and the bicyclic amine **7**.[10] The chair–boat conformation seems to be preferred in the bicyclo[3.3.1]nonane system only when there is an *endo*-3 substituent as in structures **8**[9] and **9**.[11] To the best of our knowledge the boat–boat conformation has not been proposed for any molecule having the bicyclo[3.3.1]nonane skeleton.



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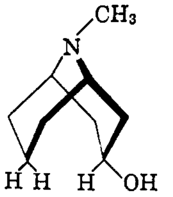

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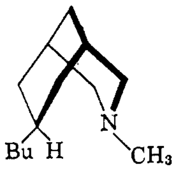

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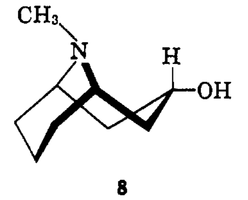

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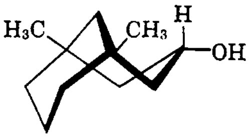

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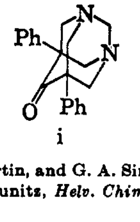
[6] However, Stetter and coworkers (*Ber.*, **91**, 598 (1958)) found that the closely related compound i was reduced normally only when sodium acetate was used as the base; the use of potassium hydroxide led to the formation of the alcohol presumably by a Meerwein–Ponndorf reduction.



i

[7] W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965).

[8] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta.*, **47**, 695 (1964).

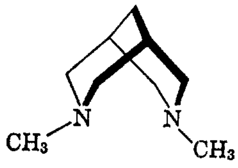
[9] (a) C.-Y. Chen and R. J. W. LeFèvre, *J. Chem. Soc., Sect. B*, 539 (1966); (b) H. S. Aaron, C. P. Ferguson, and C. P. Rader, *J. Am. Chem. Soc.*, **89**, 1431 (1967).

[10] N. W. J. Pumphrey and M. J. T. Robinson, *Chem. Ind.* (London), 1903 (1963).

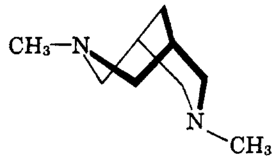
[11] W. D. K. Macrossen, J. Martin, and W. Parker, *J. Chem. Soc.*, 2589 (1695).

Within this context, then, the nature of preferred conformation of N-methyl-N′-alkylbispidines will be discussed. In order to shed some light on this problem, the physical properties of N,N-dimethylbispidine (**1**, R = CH_3) were investigated in some detail. Any conclusions which can be drawn in this case can confidently be extended to include the other bispidines.

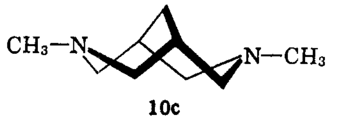
The calculated dipole moments of the chair–chair, boat–chair, and boat–boat conformations of N,N′-dimethylbispidine[12–15] are shown below structures **10a**, **b**, and **c**, respectively.



10a
1.10 D.



10b
1.10 D.



10c
1.84 D.

However, it is important to note that as the chair–chair conformation **10a** is flattened, the dipole moment increases from a calculated value of 1.10 D. to a maximum value of 1.90 D. (2 × 0.95 D.) when the axes of the lone pairs on the nitrogen atoms are parallel. The experimentally determined dipole moment of N,N′-dimethylbispidine is 2.02 ± 0.2 D., a value which clearly rules out both **10a** and **b** as the preferred conformation at room temperature. The choice, then, is between the boat–boat (probably twisted) and a flattened chair–chair conformation such as **10d**.

10d

Based upon the previously cited literature precedents, the latter appears to be the more likely. The following evidence lends support to this supposition.

Allinger and coworkers[12] have recently provided evidence for the slightly higher steric requirement of the hydrogen atom over the lone pair on nitrogen. Since hydrogen atoms occupy the same relative positions in **3** and **4** as do the lone pairs on the nitrogen atoms in **10**, and since flattened chair–chair conformations have been firmly established for **3** and **4**, it seems reasonable to infer that such a conformation should be the preferred one for N,N′-dimethylbispidine.

The nmr spectrum of **10** (Figure 1) offers additional support for this conclusion. First of all, the chemical shift (δ 1.42) of the γ-methylene protons is precisely the same as that of the γ-methylene protons in N-methylpiperidine.[16] This strongly indicates that the γ-methylene protons in **10** are in an environment quite similar to that of the corresponding protons in N-methylpiperidine, which has been shown by Allinger and coworkers[13] to have a marked preference for the chair conformation with the methyl group equatorial.[17,18] If it were otherwise, *i.e.*, if one or both of the rings in **10** were in the boat conformation, a considerable downfield shift for the γ-methylene proton *syn* to the nitrogen lone pair would be expected.[19]

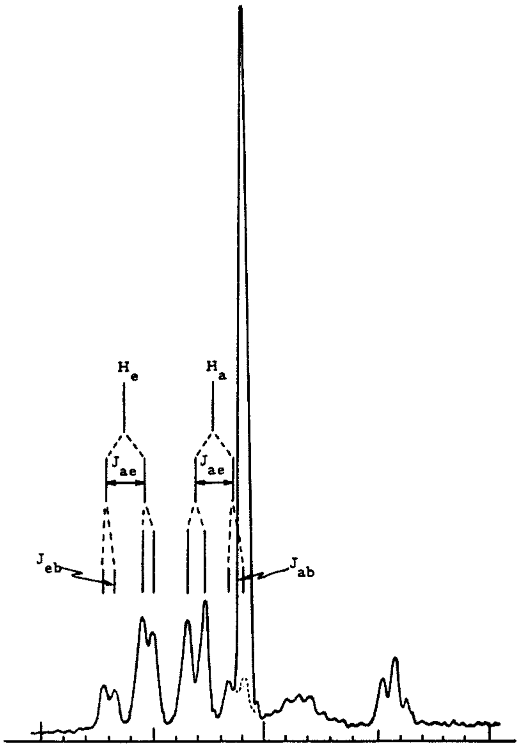
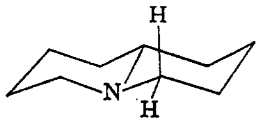


Figure 1.—The nmr spectrum of N,N′-dimethylbispidine (10) in benzene. Chemical shifts with respect to TMS.

The multiplet observed for the N-methylene protons in **10** constitutes the AB part of an ABX pattern.[20] A second-order analysis yielded chemical shifts of δ 2.22 and 2.62, which we assign to H_a and H_e, respectively. Support for these assignments comes from several recent studies[21,22] of quinolizidine (**11**) and its derivatives which show that the 4-axial proton comes at higher field (δ 2.0) than does the 4-equatorial



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[12] These values were calculated assuming that the molecule can be treated as two fused N-methylpiperidine rings. The value 0.95 D. (at 25°)[13] was used for the dipole moment of N-methylpiperidine, the direction of which was taken to lie along the axis of the lone pair of electrons on nitrogen.[13] Values of 0.80 D.[14] and 0.92 D.[15] have also been reported for this molecule.

[13] N. L. Allinger, J. D. G. Carpenter, and F. M. Karkowski, *J. Am. Chem. Soc.*, **87**, 1232 (1965).

[14] M. J. Leonard, D. F. Morrow, and M. T. Rogers, *ibid.*, **79**, 5476 (1957).

[15] M. Aroney and R. J. W. LeFèvre, *J. Chem. Soc.*, 3002 (1958).

[16] Determined on an authentic sample in our laboratory.

[17] The intense infrared absorption in the 2800–2700-cm^{-1} region shown by **10** suggests equatorial orientations for the methyl groups.[18]

[18] H. O. House, H. C. Muller, C. G. Pitt, and P. P. Wickham, *J. Org. Chem.*, **28**, 2407 (1963).

[19] For dramatic examples of this effect (as much as 1.75 ppm) in rigid molecules having hydrogen atoms constrained to positions close (2.5–2.9 A) to a nitrogen lone pair, see (a) W. Fulmor, *et al.*, *J. Am. Chem. Soc.*, **89**, 3322 (1967); (b) F. Bohlmann, D. Schumann, and C. Arndt, *Tetrahedron Letters*, 2705 (1965).

[20] In conformation **10a** (or d) there are, of course, four ABX sets, each consisting of the axial and equatorial protons of an N-methylene group and a bridgehead proton, designated H_a, H_e, and H_b, respectively.

[21] H. P. Hamlow, S. Okuda, and N. Nakagawa, *ibid.*, 2553 (1964).

[22] F. Bohlmann, D. Schumann, and H. Schulz, *ibid.*, 173 (1965).

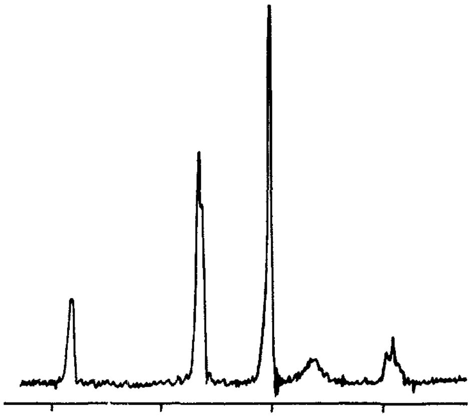
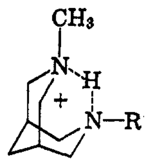


Figure 2.—The nmr spectrum of 1,3-dimethyl-1,3-diazonia-adamantane diiodide (**14**) in D_2O. Chemical shifts with respect to external TMS.

proton (2.8).[23] The geminal coupling constant, J_{ae}, is 10.2 Hz (which may be compared with a value of 11 Hz reported[22] for **11**) and is close to the value one would expect for a methylene group having tetrahedral geometry.[24]

The two vicinal coupling constants, J_{ab} (4.2 Hz) and J_{eb} (2.6 Hz), unfortunately cannot be correlated reliably with dihedral angles—and hence with conformation—without some knowledge of how the nitrogen atom interacts with the system. Both theoretical[25] and experimental[26] findings demonstrate that the Karplus equation[27] cannot be applied to systems involving a heteroatom, although there appears to be some agreement that the more electronegative the atom, the smaller will be the coupling constants, at least in six-membered rings.[26] Furthermore, as Abraham and Thomas[26a] point out, in addition to an electronegativity effect, the lone pair on nitrogen can be expected to have some effect upon the vicinal (and for that matter, the geminal) coupling constants. A detailed knowledge of these effects would be of great value in the elucidation of the structural details of complex heterocycles.

The basic properties of the bispidines proved to be quite interesting. All of them titrate as monoamines and none of them forms stable disalts, behavior which is quite contrary to that of common aliphatic diamines. These results clearly suggest that some stabilizing factor is available to the bispidines which is of much less importance in simpler diamines. Keeping in mind that the bispidines offer an ideal opportunity for intramolecular hydrogen bonding, the adamantanelike structure **12** is proposed as a reasonable possibility for these salts.



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Support for this structure was derived from a study of the properties of the perchlorate salt of N,N'-dimethylbispidine (**12a**, R = CH_3). Its pK_a of 11.88, for example, reveals that the diamine is more than an order of magnitude more basic than N-methylpiperidine (pK_a 10.08).[28] The nmr data are given in Table III. The protons of the two N-methyl groups appear as a sharp singlet at δ 2.42 in D_2O, consistent with structure **12**, although this behavior could also arise from two nonhydrogen-bonded conformations, which on the nmr time scale are in rapid equilibrium.

Table III

Chemical Shifts (δ) and Coupling Constants of Salts of N,N'-Dimethylbispidine

	γ-CH_2[a]	H_b	N–CH_3[b]	H_a[c]	H_e[d]	J_{ae}	J_{ab}	J_{eb}
12a ClO_4 (D_2O)	1.92	2.32	2.42	2.92	3.50	13.0	3.5	2
10 (CF_3CO_2H)	2.17	2.68	3.07	3.42	3.97	12.5	3.0	2

[a] Poorly resolved triplet. [b] Sharp singlet. [c] Broad doublet, clearly separated from the N-methyl singlet. [d] Doublet of doublets.

It is also interesting to note the position of the N-methyl resonance. The observed shift is some 0.6 ppm farther upfield than is commonly found when the nitrogen atom carries a full positive charge.[29] This strongly suggests that both nitrogen atoms carry something less than a full positive charge, although again this may simply reflect the average situation on the nmr time scale.[30] In any event, when the nmr spectrum of **10** is determined under conditions which should ensure protonation of both nitrogens (*e.g.*, in trifluoroacetic acid), the N-methyl resonance does fall quite close to δ 3 (see Table III).

N,N'-Dimethylbispidine reacts with diiodomethane to give either one of two products, depending upon experimental conditions. If equimolar amounts of the diamine and diiodomethane in benzene are allowed to stand at room temperature for 1 day, the only isolable product is the 1:2 adduct **13**.[31] However, when a dilute solution of diiodomethane is added slowly to a refluxing solution of **10** in ethanol, the adamantane analog **14** is formed in high yield. The elemental analyses and nmr spectrum (Figure 2) provide an unambiguous proof of structure for **14**. Because of the high degree of symmetry of the molecule, the nmr spectrum is relatively uncomplicated. The chemical shifts for the various types of protons are shown adjacent to each position. Several interesting features of the spectrum are worth noting: (1) all of the protons have experienced quite large downfield shifts with respect to their positions in **10**, including the γ-methylene protons (δ 2.84) three carbons removed from the quaternary nitrogen atoms, and (2) the broad, poorly resolved doublet (δ 4.65) due to

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[23] It has been postulated[21] that the shielding of the axial proton with respect to the equatorial arises from overlap of the p orbital on nitrogen and the σ^* orbital of the adjacent antiparallel carbon–hydrogen bond, thereby giving some double-bond character to the nitrogen–carbon bond and hence increasing the electron density at the axial hydrogen.

[24] H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

[25] M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

[26] (a) R. J. Abraham and W. A. Thomas, *Chem. Comm.*, 431 (1965); (b) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1964); (c) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963); (d) J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962); (e) K. L. Williamson and W. S. Stone, *ibid.*, **83**, 4623 (1961).

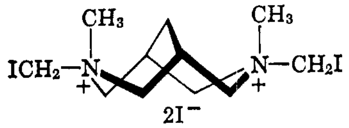
[27] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[28] S. Searles, M. Tamres, F. Blick, and L. A. Quarterman, *ibid.*, **78**, 4917 (1956).

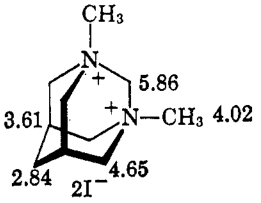
[29] For example, the N-methyl resonance in N,N,N',N'-tetramethylethylenediamine dihydriodide in D_2O appears at δ 3.02, as measured in our laboratory.

[30] This alternative was helpfully pointed out by a referee.

[31] A chair–chair conformation for this molecule is out of the question; whether or not the iodomethyl groups are *endo* as depicted is speculative.



13



14

the four N-methylene groups. The latter peak is remarkably similar to those found by Fort and Schleyer[32] for the corresponding methylene protons in symmetrically 1,3-disubstituted adamantanes. The ABX system found in **10** has collapsed to what is very close to an A_2X system in **12**, due to the near equivalence of the axial and equatorial protons of the methylene groups. That these protons are not entirely equivalent is indicated by broadness of the doublet (4.5 Hz at half-height).

Preliminary studies reveal that the bispidines react with a variety of metal ions, such as copper(II), to form very stable complexes.[33] A detailed investigation of these complexes is currently in progress.

Experimental Section

Melting points were taken on a calibrated Mel-Temp apparatus. Microanalyses were performed by Galbraith Laboratories. Infrared spectra were determined on a Perkin-Elmer 237 spectrophotometer, and nmr spectra were determined on a Varian A-60A spectrometer.

The dipole moment of N,N′-dimethylbispidine was determined at 25° in benzene using essentially the procedure of Halverstadt and Kumler.[34] Capacitance data needed for the calculations were determined using a Balsbaugh Model FL3T30 cell and a General Radio Company capacitance bridge.

N-Methyl-N′-alkylbispidones (2).—A solution of 90 g (1.50 moles) of acetic acid in 250 ml of methanol was added slowly with cooling to a solution of 170 g (1.50 moles) of freshly distilled 1-methyl-4-piperidone (obtained from Aldrich Chemical Company) in 750 ml of methanol. The resulting solution was transferred to a dropping funnel attached to a 5-l. flask which was also equipped with a mechanical stirrer and a reflux condenser. One and one-half moles of alkylamine, 1500 ml of methanol, 94 g (1.57 moles) of acetic acid, and 95 g (3.0 moles) of 95% paraformaldehyde were added to the flask. After bringing the mixture to reflux, the solution in the funnel was added with stirring over a period of about 4 hr; the mixture was heated for an additional 2 hr after the addition was complete. The mixture was kept under an atmosphere of nitrogen throughout the course of the reaction. The solution was allowed to cool to room temperature and stand overnight.

The viscous residue which was left after stripping off most of the solvent on the rotary evaporator was made strongly alkaline by the slow addition of a solution of 190 g of potassium hydroxide in 200 ml of water. An ice bath was used to keep the temperature of the solution below 20°. After filtering the mixture to remove precipitated salts, the organic layer was separated, followed by extraction of the aqueous layer with three 100-ml portions of chloroform. The combined organic material was dried over anhydrous sodium sulfate. After removing the solvent on the rotary evaporator, the residue was distilled under reduced pressure as rapidly as possible using a short-path still; following a small forerun of 1-methyl-4-piperidone, the diamino ketone was collected. The material was redistilled under reduced pressure using a 25-cm spiral-wire column. Yields were 40–55%. See Table I for data.

N-Methyl-N′-alkylbispidines (1).—Potassium hydroxide (52 g) was dissolved in 700 ml of triethyleneglycol, after which 0.40 mole of **2** and 38 ml of anhydrous hydrazine were added to the solution. The resulting solution was heated under reflux under an atmosphere of nitrogen for 4 hr during which time the temperature gradually rose to 160°. After replacing the reflux condenser with a Dean–Stark water trap, heating was continued until the pot temperature rise to 210°. The distillate which was collected during this period separated into two layers. The reaction mixture was allowed to cool to about 100°, and, after equipping the flask with a 6-in. Vigreaux column, was distilled under reduced pressure; material was collected until the head temperature reached 130° (25 mm).

This material was combined with the top layer of the initial distillate and dried over potassium hydroxide overnight. Fractional distillation under reduced pressure through a 25-cm spiral-wire column yielded the bispidines in yields of 60–70%.

The bispidine (10 mmoles) was dissolved in 10 ml of ether, and after chilling the resulting solution in an ice bath, 10 mmoles of 60% perchloric acid diluted with an equal volume of ethanol was added dropwise with continued cooling. The white precipitate which formed was filtered off, washed with a small amount of cold ethanol, and sucked dry. The solids were recrystallized from absolute ethanol to afford fine white needles. See Table II for data.

The same salts were isolated when twice the amount of perchloric acid was used.

Reaction of 10 with Diiodomethane. A.—To a stirred, refluxing solution of 1.70 g (11.0 mmoles) of **10** in 50 ml of absolute ethanol was added dropwise a solution of 2.68 g (10.0 mmoles) of diiodomethane in 25 ml of ethanol. After the addition was completed (*ca.* 1.5 hr), the mixture was heated under reflux for another 0.5 hr. Upon cooling, the precipitate which formed was filtered off, washed with a small amount of benzene, and dried. The material was recrystallized from 80% aqueous ethanol to give 3.22 g of the adamantane analog **14** as white platelets, mp 265–266° dec.

Anal. Calcd for $C_{10}H_{20}I_2N_2$: I, 60.15; N, 6.64. Found: I, 60.51; N, 6.71.

B.—A solution of 1.54 g (10 mmoles) of **10** and 5.36 g (20 mmoles) of diiodomethane in 40 ml of dry benzene was allowed to stand at room temperature for 24 hr. The white solid which formed was filtered off and recrystallized from 80% aqueous ethanol to yield 5.48 g of the diazonia salt **13**. The material melted with extensive decomposition at about 225°, although it commenced to discolor at about 130°.

Anal. Calcd for $C_{11}H_{22}I_4N_2$: I, 73.56; N, 4.06. Found: I, 73.34; N, 4.17.

Copper Complex of 10.—Compound **10** (3.08 g, 20.0 mmoles) was dissolved in 20 ml of absolute ethanol and to this was added a solution of copper perchlorate hexahydrate (3.71 g, 10.0 mmoles) in 30 ml of absolute ethanol. The lavender crystals which formed were filtered off, washed with a small amount of ethanol, and then dried. Recrystallization from acetonitrile yielded fine, deep lavender needles which sintered upon heating above 250°.

Anal. Calcd for $C_{18}H_{36}Cl_2CuN_4O_8$: Cu, 11.13; N, 9.81. Found: Cu, 11.42; N, 9.68.

Registry No.—**1a** perchlorate, 14789-40-3; **1b** perchlorate, 14789-41-4; **1c** perchlorate, 14789-42-5; **1d** perchlorate, 14901-46-3; **2a**, 14789-54-9; **2b**, 14932-19-5; **2c**, 14932-20-8; **2d**, 14789-55-0; **10**, 14789-33-4; copper complex of **10**, 12167-67-8; **13**, 14932-17-3; **14**, 14789-34-5.

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[34] See H. B. Thompson, *J. Chem. Ed.*, **43**, 66 (1966), for a recent discussion of methods for dipole moment measurements including that of Halverstadt and Kumler.