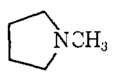
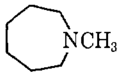
experimentally differentiating between nitrogen inversion and rotation about N–X bonds in many of these systems,[5] it has become increasingly important to have specific and independent information about both processes. We wish to report the first dnmr examples of nitrogen inversion in which angle and steric constraints have been removed and nitrogen is bonded only to saturated carbon atoms.

In order to dissociate the inversion process from single-bond rotations, open-chain systems were excluded from this study.[6] To avoid ambiguities with ring reversal,[7] six-membered rings were not used. We therefore selected N-methylpyrrolidine (I) and N-methylhomopiperidine (II) for our investigations.


I


II

Pseudorotation of the ring is the only conceivably competitive process. Particularly for five-membered rings, but also for seven-membered rings,[8] this process is of such low energy that it should not be and has not been observed on the nmr time scale.[9]

When nitrogen inversion is rapid, the α protons of I or II in Freon 22 (CHClF$_2$) are magnetically equivalent on the average and give rise to a second-order triplet, which becomes a sharp singlet when the resonance frequency of the β protons is irradiated.[10] As the temperature is lowered, the α-proton resonances reversibly broaden and ultimately produce two well-separated groupings, corresponding to the protons *cis* and *trans* to methyl. The coalescence temperature for N-methylpyrrolidine (I) is about −100° (ν_{AB} = 1.08 ppm), and for N-methylhomopiperidine (II) it is about −125° (ν_{AB} = 0.49 ppm). From these data, the free energies of activation were found to be about 8 kcal/mol for I and 7 kcal/mol for II.[11] These values correspond to the barrier to nitrogen inversion unconstrained by small valence angles or lone-pair bearing substituents.

A number of compounds were examined as controls. The spectra of pyrrolidine (III) and of homopiperidine (IV) in CHClF$_2$ were unchanged down to −150°. Atomic inversion is not expected to perturb the spectra of these compounds in this temperature range, both because the proton on nitrogen is exchanging fast[12] and because secondary amines invert more rapidly than tertiary amines.[13] If the spectral changes of I and II had been due to pseudorotation, III and IV should have exhibited similar changes. The absence of such changes is therefore consistent with a rapid pseudorotation process. The spectrum of tetrahydrofuran, in agreement with this conclusion, is also unchanged above −150°.

Ring reversal has previously been studied in N-methylpiperidine-3,3,5,5-d_4 (V).[14] The coalescence temperature for this process was found to be about −30°. Since the internal C–N–C angle for V should be bracketed by those of I and II,[15] the activation energy for the pure nitrogen inversion should also be bracketed by those for I and II. We observed no further changes in the methyl or the α-proton resonances for V down to −150°. The absence of spectral changes could result either from conformational biasing (although the ratio is only 10:1) or from chemical shift differences that are too small for observation. Alternatively, the atomic inversion process may have been appreciably altered by the operation in the same molecule of the ring reversal.[16]

We are continuing our studies in the five- and the seven-membered series in order more fully to delineate the nature of pure nitrogen inversion as a function of substituent.

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[5] (a) D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965); (b) M. Raban and G. W. J. Kenney, Jr., *Tetrahedron Lett.*, 1295 (1969).

[6] M. Raban, F. B. Jones, Jr., and G. W. J. Kenney, Jr., *ibid.*, 5055 (1968).

[7] J. B. Lambert and W. L. Oliver, Jr., *ibid.*, 6187 (1968). We prefer the term "ring reversal" to "ring inversion" in order to avoid confusion with the phrase "nitrogen inversion." In the latter context, "inversion" is adequately descriptive, but in the former it is somewhat of a misnomer, since ideally the term should refer only to configuration and not to conformation.

[8] J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

[9] This statement would not be correct for geminally disubstituted or certain unsaturated seven-membered rings.[4] The exclusion of the pseudorotation alternative, although almost certain for I, thus cannot be considered rigorous for II (however, *vide infra*).

[10] All nmr spectra were taken on the Bruker HFX-10 90-MHz spectrometer, which was purchased by an equipment grant from the National Science Foundation.

[11] A complete line-shape analysis is in progress.

[12] G. A. Yousif and J. D. Roberts, *J. Am. Chem. Soc.*, **90**, 6428 (1968).

[13] G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *ibid.*, **89**, 3396 (1967).

[14] J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *ibid.*, **89**, 3761 (1967).

[15] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 198.

[16] Evidence for concurrent and cooperative processes has been presented by J. J. Delpuech, Y. Martinet, and B. Petit, *J. Am. Chem. Soc.*, **91**, 2158 (1969).

[17] Alfred P. Sloan Foundation Fellow, 1968–1970.

[18] National Science Foundation Trainee, 1966–1967; National Institutes of Health Fellow, 1968–1970 (F1 GM-39,218).

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Bredt's Rule. IV.[1] Bicyclo[3.2.2]non-1-ene and Bicyclo[3.2.2]non-1(7)-ene, Examples of Bridged *trans*-Cycloheptenes

In previous papers we have outlined criteria for the qualitative estimation of the strain of bridgehead olefins.[1,2] Briefly, we have postulated that bicyclic olefins with bridgehead double bonds endocyclic in rings of at least eight members should be stable enough to permit their isolation and purification at normal temperatures, and that reaction intermediates with bridgehead double bonds should be possible if the double bond is endocyclic in a ring of at least seven members.[3] We have put this postulate to the test by synthesizing, isolating, and characterizing three bicyclic olefins, **1**,[2,4] **2**, and **3**,[5] which have bridgehead double bonds endocyclic in eight-membered rings. Two additional ex-

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[1] Part III: J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, in press.

[2] J. R. Wiseman, *ibid.*, **89**, 5966 (1967).

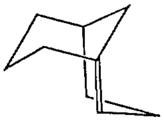
[3] In at least three cases the existence of intermediates with bridgehead double bonds endocyclic in six-membered rings has been claimed: (a) S. Beckman and O. S. Ling, *Ber.*, **94**, 1899 (1961); (b) P. C. Guha, *ibid.*, **72B**, 1359 (1939); (c) S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 21, 2997 (1965).

[4] J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **89**, 5965 (1967).

[5] J. R. Wiseman, H.-F. Chan, and C. Ahola, *ibid.*, **91**, 2812 (1969).

amples have also appeared.[6,7] These alkenes are isomeric and are formally derived from *trans*-cyclooctene by bridging of the eight-membered ring with a methylene group. They all have an *S* number[8] of 7 and, as such, transgress by two atoms on the limits set by Fawcett for isolable compounds.

We now report the preparation of the highly strained olefins, bicyclo[3.2.2]non-1-ene (**4**) and bicyclo[3.2.2]-non-1(7)-ene (**5**). Although alkenes **4** and **5** are isomeric with **1**, **2**, and **3**, and also have $S = 7$, the double bonds of **4** and **5** are endocyclic in seven-membered rings. Thus, **4** and **5** may be regarded as 1,5-ethano-*trans*-cycloheptene and 1,4-ethano-*trans*-cycloheptene and should be considerably more strained than their previously prepared isomers.[9]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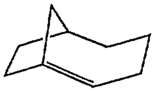
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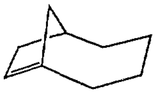
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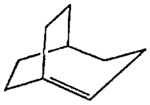
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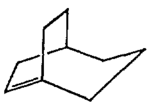
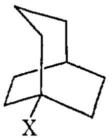
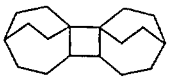

5

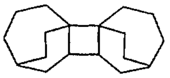
Treatment of bicyclo[3.2.2]nonan-1-ol (**6a**)[11] with sulfuric acid and sodium cyanide in acetic acid produced N-bicyclo[3.2.2]nonan-1-ylformamide (**6b**),[12] bp 105–110° (0.1 mm), in 81% yield, and reduction of the amide **6b** with lithium aluminum hydride produced the secondary amine **6c** (66%), bp 55–57° (0.5 mm). Methylation of **6c** with formic acid and formaldehyde to give the tertiary amine **6d** and reaction of the tertiary amine **6d** with iodomethane yielded the quaternary ammonium iodide **6e** (97% based on **6c**), mp 289–291°. Treatment of **6e** with an aqueous suspension of silver oxide gave the corresponding hydroxide **6f**. Pyrolysis of the quaternary ammonium hydroxide **6f** produced the olefins **4** and **5** based on the following evidence, which represents the results of several pyrolyses.

The quaternary ammonium hydroxide was pyrolyzed (155°, 1–2 min) under vacuum, and the volatile products were collected in a cold trap at −70°. A powerful odor, similar to that characteristic of olefins **1**, **2**, and **3**, was apparent if the apparatus was opened immediately after the pyrolysis. This odor disappeared within a few minutes at room temperature, and we have been unsuccessful in all attempts to isolate the alkenes **4** and **5** by a conventional work-up. When the contents of the cold trap were allowed to warm to room temperature, a white solid deposited on the walls of the trap. This white solid consists of at least four compounds which we believe to be dimers[13] of **4** and **5**; retention times[14] (relative amounts): A, mp 131–137°, 29 min (7.2); B, 33.5 min (1.04); C, 38 min (1.0); D, 47 min (2.96). The mass spectra of the two major components, A and D, show parent ions at *m/e* 244, the nmr spectra exhibit resonances due only to hydrogens bound to saturated carbon, and the infrared spectra of the dimers show no evidence of carbon–carbon double bonds and are consistent with their hydrocarbon nature. Thus the dimers may be formulated as (2 + 2) cycloadducts of **4** and **5** (*i.e.*, **7**). Addition of acetic acid to the distillate from the pyrolysis produced 3–4% of bicyclo[3.2.2]nonan-1-yl acetate (**6g**) and 1% of the corresponding alcohol **6a** (from water produced in the Hofmann elimination), along with a 61% yield of the mixture of dimers. When the pyrolysis was carried out in the presence of 1,3-diphenylisobenzofuran a Diels–Alder adduct, mp 190–194°, was isolated in 18% yield.[15]



6a, X = OH
b, X = NHCHO
c, X = $NHCH_3$
d, X = $N(CH_3)_2$
e, X = $N(CH_3)_3I$
f, X = $N(CH_3)_3OH$
g, X = $OCOCH_3$


7a


7b

The nmr spectrum ($CFCl_3$, −80°) of the distillate from the pyrolysis shows two resonances for the vinyl protons of **4** and **5**. The lower field resonance is a broadened triplet, $J = ca.$ 5 Hz, centered at δ 5.77, and the higher field resonance is a quartet, $J_{ax} = 10.5$ Hz and $J_{bx} = 4.8$ Hz, centered at δ 5.44; ratio 1.0:1.3. The sample was warmed to 0° for 40 min and then cooled to −80°. The high-field resonance had disappeared completely and the low-field resonance had diminished to about 30% of its original intensity. Since the high-field resonance originally was of greater intensity it is apparent that the least stable isomer was formed in greater amount in the Hofmann elimination.

The mass spectrum of the quaternary ammonium hydroxide **6f** showed a strong peak at *m/e* 122 in addition to peaks for the dimers and the 1-dimethylaminobicyclo-[3.2.2]nonane (**6d**).

The chemical reactivity of **4** and **5** clearly sets them apart from the isomeric bicyclic bridgehead olefins **1**, **2**, and **3** with which they are isomeric, and substantiates the postulate that the strain energy of bridgehead olefins is largely determined by the size of the larger ring containing the double bond.[1,2] Further, these results serve to negate the notion of Fawcett[8] that the strain energy of a bicyclic bridgehead alkene is directly related to the total size of the bicyclic ring system.

Acknowledgment. This work was generously supported by a grant from the Petroleum Research Fund administered by the American Chemical Society.

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[6] N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968).

[7] W. Carruthers and M. I. Qureshi, *Chem. Commun.*, 832 (1969).

[8] F. S. Fawcett, *Chem. Rev.*, 47, 219 (1950).

[9] It may also be anticipated that bridged *trans*-cycloheptenes should be more accessible than *trans*-cycloheptene[10] itself. *trans*-Cycloheptene can isomerize to *cis*-cycloheptene and thus relieve its strain, but this reaction pathway is not available to the bridgehead alkenes.

[10] E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, **87**, 934 (1965).

[11] C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

[12] All new compounds reported, except for olefins **4** and **5** and the quaternary hydroxide **6f**, gave satisfactory elemental analyses.

[13] A total of 12 dimers and cross dimers are theoretically possible.

[14] The vpc analysis was carried out on a 6 ft × 1/4 in. column packed with 6% Carbowax 20M on Chromosorb G, 180°, 60 cc of He/min.

[15] There are four possible isomeric Diels–Alder adducts derived from **4** and **5**, and we have not yet determined which of these structures our isolated adduct possesses.

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Radical Cations in the Chlorine Fluoride–Antimony Pentafluoride Systems

Sir:

Recently, Olah and Comisarow have reported[1] epr evidence for the existence of the two radical cations, Cl_2^+ and ClF^+, in both the ClF_3–SbF_5 and the ClF_5–SbF_5 systems. These data are unexpected and disagree with the following, previously observed reactions.[2–5]

$$ClF_3 + SbF_5 \rightleftarrows ClF_2^+SbF_6^-$$

$$ClF_5 + SbF_5 \rightleftarrows ClF_4^+SbF_6^-$$

According to Olah and Comisarow[1] the ClF^+ cation forms directly by combination of SbF_5 with ClF_5 or ClF_3. For ClF_5, this reaction would involve a reduction of pentavalent chlorine to the divalent state, thus requiring the simultaneous oxidation of a second species. This could be achieved by either disproportionation of pentavalent chlorine or oxidation of fluoride to fluorine.

$$5ClF_5 + 5SbF_5 \longrightarrow 2ClF^+SbF_6^- + 3ClF_6^+SbF_6^-$$

$$2ClF_5 + 2SbF_5 \longrightarrow 2ClF^+SbF_6^- + 3F_2$$

However, no evidence for either the formation of $ClF_6^+SbF_6^-$ or F_2 evolution has been observed in the ClF_5–SbF_5 system.[5] Furthermore, the Raman band at 819 cm^{-1}, observed by Olah and Comisarow in the ClF_3–SbF_5 system and ascribed to ClF^+, strongly suggests the presence of ClF_2^+, which in its AsF_6^- and SbF_6^- salts[6,7] has its strongest absorptions between 805 and 830 cm^{-1}.

The interpretation of the epr signals reported by Olah and Comisarow has also been questioned. Thus, Eachus, Sleight, and Symons recently suggested[8] the structures Cl_2O^+ and $ClOF^+$ for the epr signals attributed by Olah and Comisarow to Cl_2^+ and ClF^+, respectively. The formation of the oxygen containing species Cl_2O^+ and $ClOF^+$ in the supposedly oxygen-free ClF_x–SbF_5 system presents a mystery. Whereas Eachus and coworkers have questioned the spectroscopic interpretation of Olah's epr data, we wish to clarify some of the discrepancies in Olah's work from a chemical synthesis point of view. Furthermore, we wish to report experimental details which are completely missing in both Olah's and Symon's papers and which (as can be seen from the data given below) are extremely important for duplication of the previous work.

Contrary to the results of Olah and Comisarow, we did not obtain any epr signal for $ClF_3 \cdot SbF_5$ and $ClF_5 \cdot SbF_5$, either in the solid state or in SbF_5 solution, *provided* the samples were freshly prepared in a well-passivated stainless steel–Teflon vacuum line, and the starting materials were fractionated on the line prior to use. The epr samples were prepared directly in Teflon FEP nmr tubes. It was found necessary to avoid contact of liquid phases with metal parts owing to their ability to dissolve paramagnetic metal salts, which give rise to epr signals. However, these metal ions cannot account for the fine structure in the spectra[1] observed by Olah and Comisarow, and there is no doubt that these epr signals are caused by chlorine containing species. Our attempts to reproduce the epr signal, ascribed by Olah and Comisarow to ClF^+, in $ClF_3 \cdot SbF_5$ were successful when SbF_5, distilled in a glass apparatus and stored in a Teflon container, was used in the sample preparation without further purification. In the latter case the SbF_5 was manually transferred to the epr tubes in the dry nitrogen atmosphere of a glove box. Unfortunately, Olah and Comisarow did not give any experimental details in their paper. According to a private communication,[9] however, they handled their samples in glass vacuum systems and used quartz epr tubes. These facts might explain the difference in results and suggest that the observed paramagnetic species are due to handling procedures (such as SbF_5 purification) or to secondary reactions of the highly reactive fluorides with the container material or impurities contained in SbF_5. Since chlorine oxyfluorides and oxides might be formed in the latter reactions,[10] the observed epr signals might well be due to chlorine oxyfluorides or oxides, as suggested by Symons and coworkers.[8] It should also be pointed out that fluorosulfonic acid interacts with chlorine fluorides,[11] and thus should not be used as an inert solvent for this type of investigation. Whereas ClF_3 and ClF_5, when combined with SbF_5 under suitable conditions, do not produce paramagnetic species, ClF may behave differently. We did not study the ClF–SbF_5 system by epr but have previously observed[12] that the $ClF \cdot SbF_5$ adduct produces upon melting a highly colored (from initial orange to dark brown-green) liquid. This strong color formation may be indicative of paramagnetic species.

In summary, the combination of carefully purified SbF_5 and ClF_5 or ClF_3 does not produce any paramagnetic species but results in the formation of diamagnetic $ClF_4^+SbF_6^-$ and $ClF_2^+SbF_6^-$, respectively. Using less stringent purification and handling conditions for SbF_5, samples were produced exhibiting an epr spectrum which closely resembled that previously assigned[1] to ClF^+. However, the intensity of the epr signal indicated the paramagnetic species to be a minor constituent. Obviously the previously reported[1] epr evidence alone is insufficient to prove the exact nature of these radicals. Further experimental work to establish the role of impurities in the starting materials and of side reactions with container materials is definitely required in order to positively identify the paramagnetic species.

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(1) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **91**, 2172 (1969).
(2) J. W. Dale and D. A. MacLeod, private communication.
(3) F. Seel and O. Detmer, *Z. Anorg. Allg. Chem.*, **301**, 113 (1959).
(4) K. O. Christe and A. E. Pavlath, *ibid.*, **335**, 210 (1965).
(5) K. O. Christe and D. Pilipovich, *Inorg. Chem.*, **8**, 391 (1969).
(6) K. O. Christe and W. Sawodny, *ibid.*, **6**, 313 (1967).
(7) R. J. Gillespie and M. J. Morton, *ibid.*, in press.
(8) R. S. Eachus, T. P. Sleight, and M. C. R. Symons, *Nature*, **222**, 769 (1969).
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(11) C. J. Schack and R. D. Wilson, submitted for publication.
(12) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **8**, 212 (1969).