

with diazomethane afforded a yellow oil which was purified by vpc at 160° (SF-96 column) to give 6 mg of dimethyl homophthalate (27).⁴⁰ An unidentified minor component (3 mg) was also isolated.

Pyrolysis of 2,3-Benzobicyclo[4.2.2]deca-2,4,7,9-tetraene (25). Thermal rearrangement of 17.7 mg of 25 in the gas phase at 395° (2 mm) (N₂ atmosphere) yielded 15.3 mg of pale yellow oil. Vpc analysis showed this material to consist of 8 and 25 in the ratio of 1.0:1.17, respectively. Separation of the isomers was achieved

(40) For an infrared comparison, refer to Sadtler Infrared Prism Spectrum No. 7616.

on the SF-96 column at 150° and the two components were characterized by their nmr spectra.

Photolysis of 25. A solution of 29 mg of 25 in 8 ml of acetone containing cyclododecane as an internal standard was photolyzed with a 450-W Hanovia lamp through Pyrex glass. After 1 hr, the starting material was seen to be converted cleanly to a single product of shorter retention time (SE-30 column). This photoproduct was purified by preparative vpc at 155° (XF-1150 column) and shown by nmr analysis to be 21.

Acknowledgment. The authors wish to thank Dr. Stanley A. Lang, Jr., for his generous assistance with the 100-MHz spectra.

Stable Carbocations.¹ CXXXIII. Bicyclononyl and Methylbicyclooctyl Cations

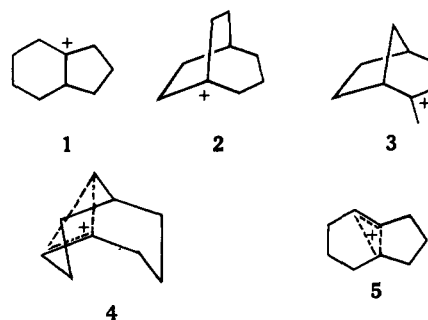
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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and The University of Michigan, Ann Arbor, Michigan 48104. Received December 4, 1971

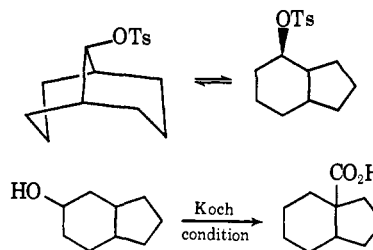
Abstract: The 2-methyl-2-bicyclo[3.2.1]octyl cation (3) is formed from several bicyclononyl precursors under long-lived ion conditions. Ion 3 is found to undergo irreversible thermal transformation to the 1-bicyclo[4.3.0]nonyl (8-hydrindyl) cation (1), which is also generated directly from bicyclo[4.3.0]nonyl precursors. The tertiary bridgehead 1-bicyclo[3.2.2]nonyl cation (2) is stable in SbF₅-SO₂ClF solution at temperatures below -50°. The proton and carbon-13 nmr spectra of ions 1, 2, and 3 are reported. The mechanism of the transformation of ion 3 to ion 1 is also discussed.

The solvolyses of bicyclononyl systems including bicyclo[3.2.2]nonyl,²⁻⁵ bicyclo[2.2.2]octanecarbonyl,⁶ bicyclo[3.3.1]nonyl,⁷ bicyclo[4.2.1]nonyl,⁸ hydrindyl,^{7,9-11} methyl-substituted cyclohexenylethyl,⁹⁻¹⁴ and 2-methylbicyclo[3.2.1]octyl derivatives^{15,16} have been reported to give products *via* the classical (carbenium) ions 1-3 and nonclassical (carbonium) ions 4-5.

In their relevant studies Foote and Woodward⁷ have reported on internal return of bicyclo[4.3.0]nonyl and 9-bicyclo[3.3.1]nonyl tosylates in acetic acid solvent, as well as the observation of *cis*- and *trans*-hydrindyl



products. Aluminum chloride catalyzed isomerization^{14,17} and the Koch reaction¹⁸ of bicyclononyl systems also reveal the stability of bridgehead cations in these systems.



Bartlett's^{19a} and Doering's studies^{19b} indicated that bridgehead cations were extremely unstable. How-

(1) Part CXXXII G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *J. Amer. Chem. Soc.*, **94**, 3554 (1972).

(2) J. A. Chong and J. R. Wiseman, presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 23, 1970.

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

(4) K. Alder, H. Drieger, and H. Weiss, *Chem. Ber.*, **88**, 144 (1955).

(5) J. P. Schaefer, L. S. Endres, and M. D. Moran, *J. Org. Chem.*, **32**, 3963 (1967).

(6) G. A. Grob, R. M. Hoegerle, and M. Ohta, *Helv. Chim. Acta*, **41**, 1823 (1962).

(7) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

(8) A. C. Cope, D. L. Nealy, P. Schneider, and G. Wood, *J. Amer. Chem. Soc.*, **87**, 3130 (1965); W. G. Dauben and J. L. Chitwood, *ibid.*, **92**, 1624 (1970).

(9) P. D. Bartlett, E. M. Micholson, and R. Owyang, *Tetrahedron*, **399** (1966).

(10) R. C. Fort, R. E. Hornish, and G. Liang, *J. Amer. Chem. Soc.*, **92**, 2558 (1970).

(11) R. E. Hornish, Ph.D. Dissertation, Kent State University, 1970.

(12) H. Felkin and C. Lion, *Tetrahedron*, **27**, 1375, 1387 (1971).

(13) H. Christol and G. Solladie, *Bull. Soc. Chim. Fr.*, 3193 (1966).

(14) J. J. Eisch and G. R. Husk, *J. Org. Chem.*, **31**, 3419 (1966).

(15) W. Kraus and P. Schmutta, *Justus Liebig Ann. Chem.*, 2259 (1966).

(16) S. H. Graham and D. A. Jonas, *J. Chem. Soc. C*, 188 (1969).

(17) N. S. Vorobeva, and A. A. Petrov, *Neftekhimiya*, **801**, 5 (1965).

(18) H. Koch and W. Haaf, *Chem. Ber.*, **94**, 1256 (1961).

(19) (a) P. D. Bartlett and L. H. Knox, *J. Amer. Chem. Soc.*, **61**, 3184 (1939); (b) W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher, and W. P. Shelan, Jr., *ibid.*, **75**, 1008 (1953).

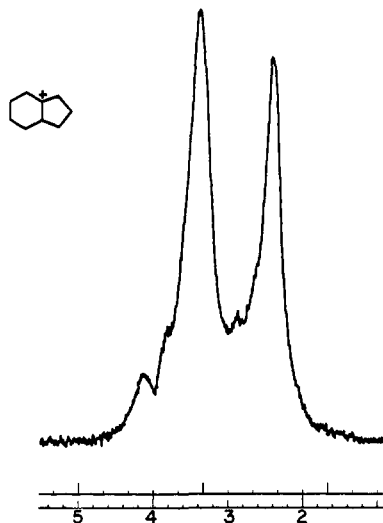
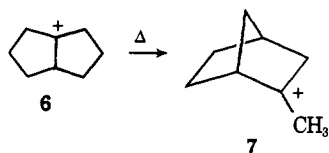


Figure 1. Pmr (60 MHz) spectrum of 8-bicyclo[4.3.0]nonyl cation (1).

ever, in molecules having nearly tetrahedral bridgehead geometries,²⁰ normal reactivity was found. For example, 1-adamantyl,²¹ 1-decyl,²² and 1-bicyclo[3.3.0]octyl^{23,24} cations were stable under long-lived ion conditions. Solvolyses of several bridgehead bicyclic alkyl derivatives also reveal the stabilities of carbocations having such geometry.

We have recently reported that the bridgehead bicyclo[3.3.0]octyl cation (6), even though the most stable of all the bicyclooctyl cations, underwent thermal transformation to 2-methylnorbornyl cation (7).²³ In continuation of our preceding studies of stable bicyclo-



decyl and bicyclooctyl cations, as well as investigation of the solvolytic behavior of bicyclononyl systems, we undertook a study to directly observe and investigate bicyclononyl and methylbicyclooctyl cations. It was considered that recently developed methods, which allowed the observation, generally in superacid solutions, of a substantial number of carbocations, would make this study feasible. We carried out these studies and present data showing that several bicyclononyl derivatives firstly rearrange to the stable 2-methylbicyclo[3.2.1]octyl cation (3) in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ or $\text{SbF}_5\text{-SO}_2\text{ClF (SO}_2\text{)}$ solutions at low temperature. The latter ion is also found to undergo thermal transformation to the 8-hydrindyl cation (1). The bridgehead 1-bicyclo[3.2.2]nonyl cation (2) can be generated directly from the chloride precursor at -78° .

(20) R. C. Fort and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

(21) (a) P. v. R. Schleyer, R. C. Fort, W. E. Watts, G. A. Olah, M. B. Comisarow, and C. A. Cupas, *J. Amer. Chem. Soc.*, **86**, 4195 (1964); (b) G. A. Olah, G. Mateescu, G. Sipos, P. v. R. Schleyer, V. Buss, and T. Gund, paper in preparation.

(22) G. A. Olah, D. P. Kelly, and R. G. Johanson, *J. Amer. Chem. Soc.*, **92**, 4137 (1970).

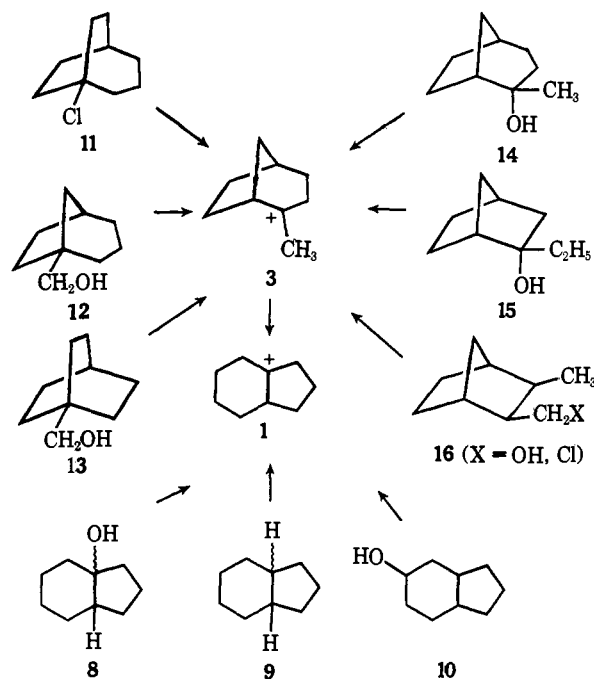
(23) G. A. Olah, and G. Liang, *ibid.*, **93**, 6873 (1971).

(24) G. A. Olah, J. M. Bollinger, and E. P. Kelly, *ibid.*, **92**, 1432 (1970).

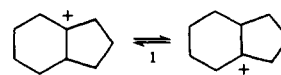
Results and Discussion

The 1-bicyclo[4.3.0]nonyl cation (1) was generated from *cis*- and *trans*-bicyclo[4.3.0]nonane (9), *cis*- and *trans*-8-hydrindanols (8), and 5-hydrindanol (10) in either SbF_5 or $\text{FSO}_3\text{H-SbF}_5$ solution diluted with $\text{SO}_2\text{ClF(SO}_2\text{)}$ at -78° (Scheme I). The solutions of

Scheme I



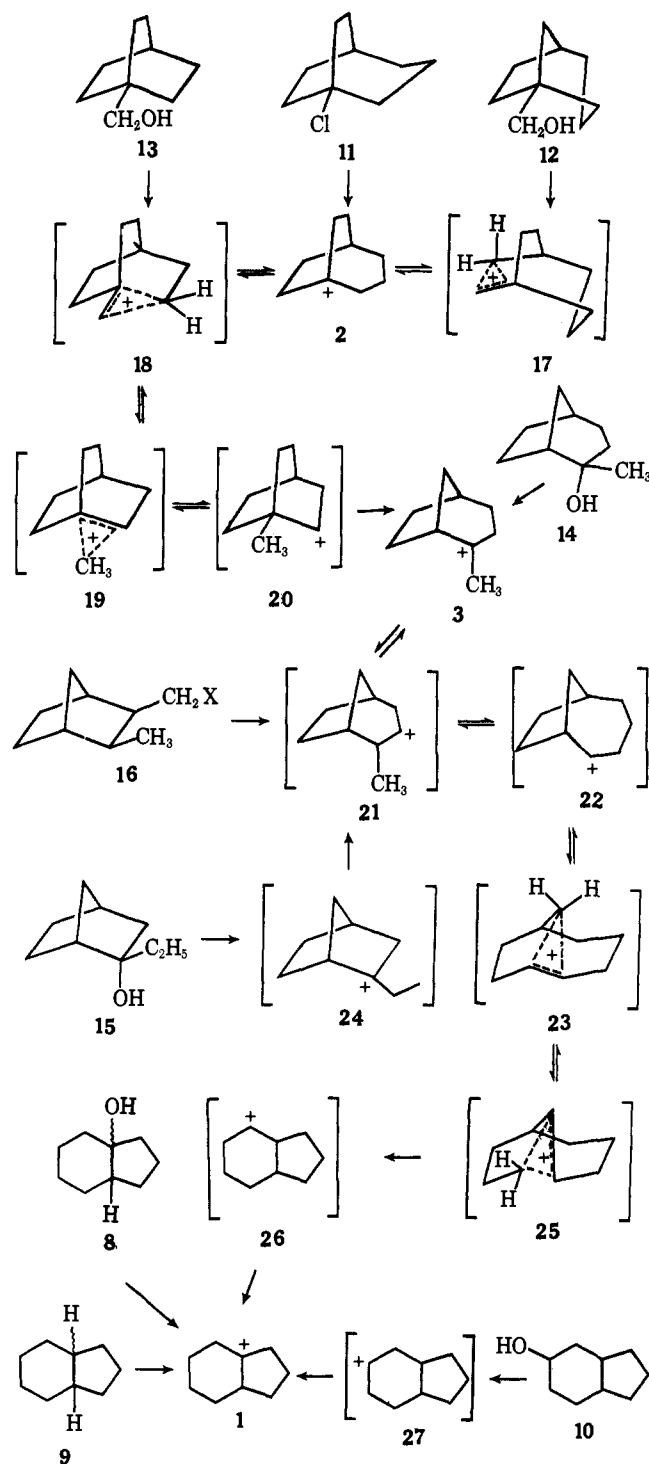
the 8-hydrindyl cation (1) in $\text{SbF}_5\text{-SO}_2\text{ClF}$ at -78° gave the pmr spectrum shown in Figure 1 with proton absorptions at δ 2.40 (broad, 6 H), 3.40 (broad, 8 H), and 4.12 (broad, 1 H). Comparison of the pmr spectrum of 1 with that of the decyl cation 7²² and bicyclo[3.3.0]octyl cation (6)^{23,24} indicates that 1 also contains a rapidly equilibrating bridgehead proton; the intensity ratio for the methylene protons α to the positive charge relative to those β to positive charge is 8:6.



The formation of 1 from *cis*- and *trans*-8 in $\text{SbF}_5\text{-SO}_2\text{ClF}$ involves only simple ionization of the hydroxy group (Scheme II). In $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ solution both alcohols must be first protonated and then quickly ionized to give ion 1. For 5-hydrindanol (10), ionization must first take place, followed by two steps of 1,2-hydride shift in order to move the positive charge to the bridgehead position.¹⁸ In $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ solution at -95° , the protonated alcohol shows the protonated hydroxy group signal at δ 9.35 (broad, 2 H), the methine proton at δ 5.61 (broad, 1 H), four methylene protons α to the protonated hydroxy group at δ 5.35 (broad, 4 H), and the remaining proton signal extending from δ 2.2 to 2.8 (10 H). The 8-hydrindyl cation can also be generated directly *via* hydride abstraction²⁵ from *cis*- and *trans*-bicyclo[4.3.0]nonanes in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -50° . The hydride abstraction could take place either at a secondary or tertiary bridgehead position (with the latter possibility

(25) G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968).

Scheme II



much more probable) to give a secondary cation (if a secondary hydride is removed), or the bridgehead cation **1** directly. The secondary cation would give **1** by intramolecular hydride shift.

The 1-bicyclo[3.2.2]nonyl cation (**2**) was generated from 1-chlorobicyclo[3.2.2]nonane²⁶ in $\text{SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$ solution at -120° . It was stable at temperatures below -75° . The pmr spectrum (Figure 2) shows two groups of proton absorptions centered at δ 2.50 (8 H) and 4.20 (6 H), and a one proton broad singlet at δ 4.43. The six methylene protons α to the

(26) The preparation of this compound, as well of **11**, **12**, and **13**, are described in connection with the solvolytic studies of J. R. Wiseman, *et al.*²

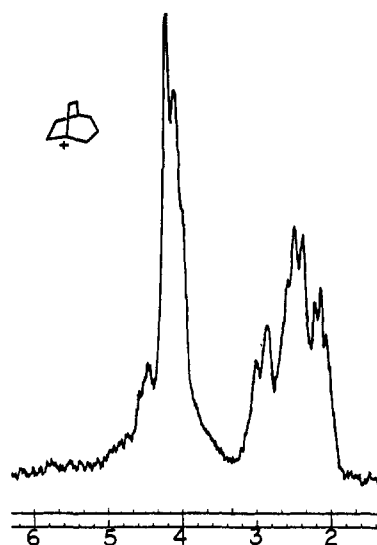
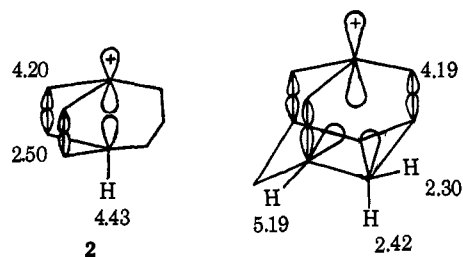


Figure 2. Pmr (60 MHz) of 1-bicyclo[3.2.2]nonyl cation (**2**).

positive charge at the bridgehead carbon show normal deshielded proton absorption. The bridgehead proton is found to be the most deshielded, with a chemical shift of δ 4.43. A similar deshielding phenomena was also observed in the 1-adamantyl cation.^{21a} Formerly it was believed that the deshielding was caused by a through space "cage effect." However, reinvestigation of the adamantyl cation^{21b} reveals that a secondary factor (through σ bond delocalization) is also involved. In the case of ion **2**, both cage effect and through σ bond delocalization are believed to be the major factors which cause deshielding of the bridgehead proton. For comparison, the chemical shifts of **2** and the 1-adamantyl cation are shown. When the solution of



2 was quenched with sodium methoxide in methanol at -90° , 1-methoxybicyclo[3.2.2]nonane was formed in 45% yield and identified by nmr.²⁷

When the superacid solution of **2** was allowed to stand at -65° for 0.5 hr, slow transformation to 2-methylbicyclo[3.2.1]octyl cation (**3**) was observed (*vide infra*). The 2-methyl-2-bicyclo[3.2.1]octyl cation (**3**) was generated either directly or indirectly from 1-chlorobicyclo[3.2.2]octane (**11**), 1-bicyclo[3.2.1]octanemethanol (**12**), 1-bicyclo[2.2.2]octanemethanol (**13**), 2-methyl-2-endo-bicyclo[3.2.1]octanol (**14**), 2-exo-ethyl-2-endo-norborneol (**15**), 3-methyl-2-hydroxymethylnorbornane (**16**) (X = OH), and 3-methyl-2-chloromethylnorbornane (**16**) (X = Cl) in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ or $\text{SbF}_5\text{-SO}_2\text{ClF}$ solutions generally -78° (Schemes I and II).

(27) The 1-methoxy derivative shows nmr (CDCl_3) δ 3.20 (s, 3 H, OCH_3) and 1.60 (m, broad, 15 H); $\nu_{\text{C-O}}$ 1076 cm^{-1} .

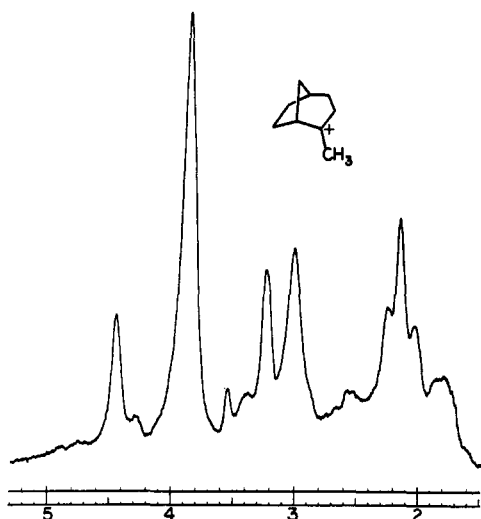
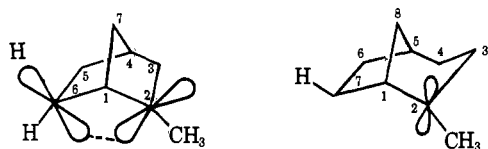
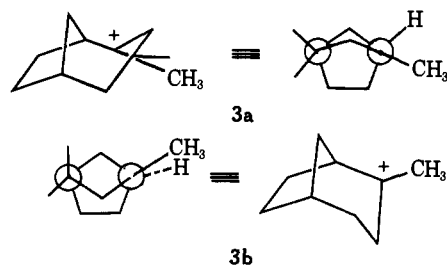


Figure 3. Pmr (100 MHz) spectrum of 2-methyl-2-bicyclo[3.2.1]-octyl cation (3).

The 100-MHz pmr spectrum of ion 3 at -78° is shown in Figure 3 with proton absorptions at δ 1.82 (broad, 2 H), 2.65 (triplet, 4 H), 2.98 (broad singlet, 2 H), 3.21 (singlet, 1 H), 3.82 (singlet, 3 H), 3.98 (broad, 2 H), and 4.45 (singlet, 1 H). The lowest deshielded peak is assigned to the bridgehead proton α to the positively charged carbon. The methyl proton absorption is in the range of that of *tert*-butyl,²⁸ methylcyclopentyl,²⁹ and methylcyclohexyl³⁰ cations (Table I). However, we did not observe any coupling between the deshielded bridgehead proton and the 7-exo proton. There is, however, substantial coupling ($J = 6.5$ Hz) between the deshielded bridgehead proton and the 6-exo proton in the 2-methylnorbornyl cation.^{31,32}



From an examination of Dreiding models of ion 3, it appears that there are two possible geometries which are represented as³³ 3a and 3b.



(28) G. A. Olah, M. B. Camisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **87**, 2997 (1965).

(29) G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *ibid.*, **89**, 2692 (1967).

(30) G. A. Olah and J. Lukas, *ibid.*, **89**, 2227 (1967); the freshly prepared methylcyclohexyl cation in $\text{SbF}_5\text{-SO}_2\text{ClF}$ at -90° shows pmr absorptions at 2.15 (m, 2 H), 2.30 (m, 4 H), 3.80 (m, 3 H), and 5.20 (m, 4 H).

(31) G. A. Olah, J. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

(32) G. A. Olah, A. M. White, J. R. DeMember, and C. Y. Liu, *ibid.*, **91**, 3958 (1969).

(33) J. A. Berson and P. R. Warnhoff, *ibid.*, **84**, 682 (1962).

Table I. Pmr Parameters (δ) of 2-Methyl-2-bicyclo[3.2.1]octyl Cation, Protonated 2-Bicyclo[3.2.1]octanone, and Model Compounds^a

	CH ₃	α -CH ₂	Bridgehead H
	3.00 ^b	2.70	4.64
	3.82	3.98	4.45
	3.98	4.20	
	3.80	4.20	4.64
		2.87	3.61
		3.40	3.75
		3.10 ^c	3.15

^a In parts per million from external TMS standard. ^b References 31 and 32. ^c Reference 36.

In 3a, the methyl group on C₂ is in the normal staggered relationship to the bridgehead hydrogen, while in 3b an eclipsed position is enforced. Therefore it seems that 3a is more favorable than 3b in spite of the former having a boat cyclohexyl conformation.

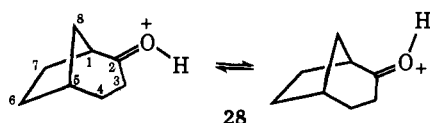
The carbon-13 nmr chemical shifts of ion 3 obtained through the indor method show that the positively charged carbon atom has a value of -128.2 ppm (from external CS₂). The value is slightly higher than that of the *tert*-butyl ($\delta_{13\text{C}} - 135.4$)³⁴ and the methylcyclopentyl ($\delta_{13\text{C}} - 142.2$)³⁵ cations. However, a value of $\delta_{13\text{C}} - 128.2$ shows that ion 3 is a classical carbocation and has substantially localized positive charge. The value is also considerably lower than that of the 2-methylnorbornyl cation 7 ($\delta_{13\text{C}} - 76.1$ ppm).³² Ion 7 has been considered as being an ion in which there is partial overlap of the vacant p orbital at C₂ and the C₆-exo-H bonding orbital at C₆ with limited decrease in the C₂-C₆ bond distance. It is very likely that this kind of σ delocalization is absent in ion 3. The introduction of the extra methylene group into the ring might very well distort the suitable geometry for the attainment of such delocalization. The absence of substantial coupling between the bridgehead proton with the 7-exo proton is further indication for the absence of such participation of σ bond. In viewing models the geometry is unfavorable for the C-2 and C-7 interaction in both 3a and 3b,

(34) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

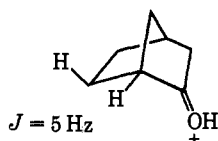
(35) Reference 34 and see also G. A. Olah and A. M. White, *ibid.*, **91**, 3954 (1969).

with better geometry in the former. However, the pmr evidence favors **3a**, but the lack of a C-2 to C-7 delocalization is consistent with either form **3a** or **3b**.

Further evidence is obtained from the pmr spectral study of the protonated 2-bicyclo[3.2.1]octanone (**28**). The chemical shifts of ion **28** are summarized in Table I. The lowest field, broad singlet (δ 3.75, 1 H) is assigned to the bridgehead proton α to the ketone functional group, whereas the two proton broad signal at 3.40 is assigned to C₃ methylene protons. The proton on the ketone oxygen appears as a doublet at δ 13.62 and 13.78; the intensities of the two lines vary according to temperature and thus correspond to two isomers.



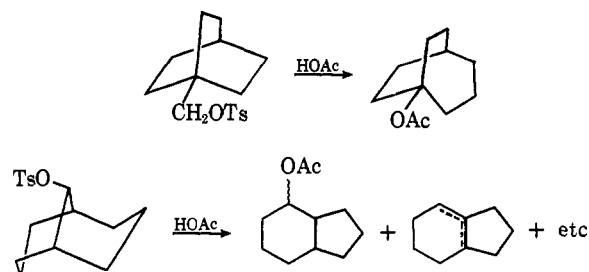
The remainder of the spectrum was complex and not analyzed in detail. It is, however, apparent that the bridgehead proton is not coupled with the 7-exo-H. It is known whether this type of coupling exists in protonated 2-bicyclo[2.2.1]heptanone (**31**).³⁶



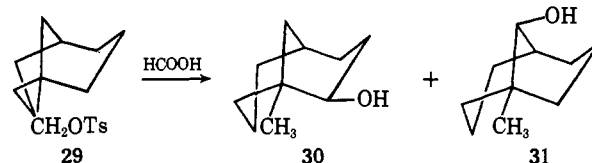
The formation of the 2-methylbicyclo[3.2.1]octyl cation (**3**) can also be accomplished through the ionization of several primary and secondary bicyclononyl or methyl-substituted bicyclooctyl precursors *via* intramolecular rearrangement. First, it can be generated in FSO₃H-SO₂ClF (SO₂) solution at -78° from 2-*exo*-methyl-2-bicyclo[3.2.1]octanol (**14**). However, **3** is not stable in this solution and decomposes into some polymer. In FSO₃H-SbF₅-SO₂ClF (SO₂) or SbF₅-SO₂ClF (SO₂) solutions, **3** is stable at temperatures below -35°. When the solutions of **3** are allowed to warm to -30°, the 8-hydrindyl cation **1** is slowly formed (*vide infra*). Ion **3** is also obtained from **2** in SbF₅-SO₂ClF solution when the latter is allowed to stand at -50° for 10 min. Surprisingly, when 1-chlorobicyclo[3.2.2]nonane is ionized in FSO₃H-SbF₅-SO₂ClF solution at -90°, ion **3** is directly formed instead of the bridgehead cation **2**. We are not able to give a full answer at the present time for the different effect that the acid systems have upon the stabilities of the cations.

In the light of the reported solvolytic data,² the conversion of ion **2** to ion **3** can be rationalized in the way shown in Scheme II. Bicyclo[2.2.2]octanecarbonyl derivatives have been found undergoing facile ring expansion to bridgehead-substituted bicyclo[3.2.2]nonyl derivatives.^{2,3,6} Also, 9-bicyclo[3.3.1]nonyl tosylate was solvolyzed⁷ into bicyclo[4.3.0]nonyl derivatives. Thus the tertiary bridgehead cation **2** directly formed from **11**, **12**, and **13** first undergoes protonated cyclopropane-type insertion to either **17** or **18**. The latter then undergoes cyclohexyl-methylcyclopentyl-type ring contraction to **20** (*via* **19**), which is followed by a Wag-

(36) D. G. Farnum and G. Mehta, *ibid.*, **91**, 3256 (1969).

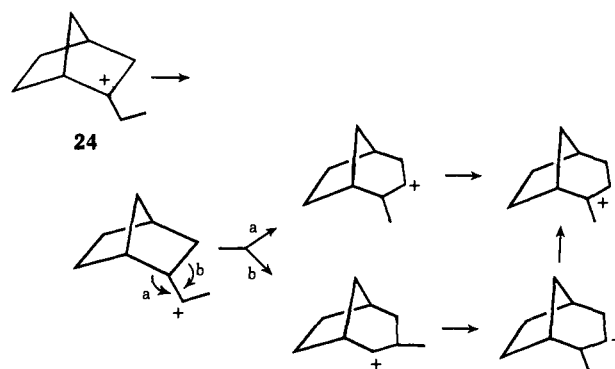


ner-Meerwein type rearrangement to **3**. The transformation of **13-OH** to **20** is preceded by the conversion of **29** into **30** and **31** in the formolysis of **29**.¹⁵



Ion **3** can also be generated from **12**. In FSO₃H-SbF₅-SO₂ClF solution at -90°, the protonated alcohol is immediately formed without ionization. Subsequently ion **3** was formed when the solution was slowly warmed to -50°. Protonated 1-bicyclo[2.2.2]octanemethanol, formed in FSO₃H-SbF₅-SO₂ClF at -95°, also gives ion **3** upon heating to -45° for 0.5 hr.

The 2-ethylnorbornyl cation (**24**)^{31,32} has been recently reported. When the freshly prepared solution of ion **24** in SbF₅-SO₂ClF is allowed to stand at -45° for 0.5 hr,³⁷ it is completely transformed into 2-methyl-2-bicyclo[3.2.1]octyl cation (**3**). Hydride shift followed by ring expansion would give **21**, which then subsequently could give **3** *via* 1,2-hydride shift (path a). An alternative way of rearrangement is that of path b.



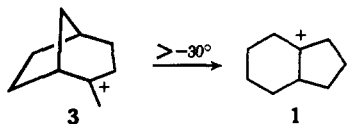
Finally, ion **3** can also be formed from either 3-methyl-2-hydroxymethylnorbornane (**16-OH**) or from 3-methyl-2-chloromethylnorbornane (**16-Cl**) in SbF₅-SO₂ClF solution at -78°. The most probable pathways for the transformation of the 3-methyl-2-bicyclo[3.2.1]heptylcarbonyl cation³⁸ to the 2-methylbicyclo[3.2.1]octyl cation (**3**) are given in Scheme II. The alcohol (**16-OH**) is first protonated in FSO₃H-SbF₅-SO₂ClF (SO₂) solutions at -78° and consequently gives ion **3** when warmed to -50°.

2-Methylbicyclo[3.2.1]oct-2-yl cation generated from the previously discussed precursors was found stable (by

(37) We have found that 2-ethylnorbornyl cation³¹ was only stable in FSO₃H-SbF₅-SO₂ClF solutions at temperatures below -45°. The observation of the rearrangement of ion **21** to **3** was not reported previously.

(38) M. G. J-Dufresne and M. Blanchard, *Bull. Soc. Chim. Fr.*, 385 (1968).

nmr) at temperatures below -30° . When the solutions of ion **3** are allowed to warm above this temperature, it gradually transforms into the 8-hydrindyl cation (**1**).³⁹



The thermal conversion of ion **3** to **1** can be rationalized in the following manner. When **3** was heated, it first reverses to **21** via 1,2-hydride shift; **21** would give **22** through a methylcyclopentyl-cyclohexyl type ring expansion. A subsequent Wagner-Meerwein rearrangement would produce **23**, which through a 1,2-hydride shift would give **25**; the latter consequently would give the secondary 1-hydrindyl cation **26**. A final hydride shift would then give ion **1**.

This rearrangement is surprising, since we have recently reported that the bicyclo[3.3.0]oct-1-yl cation is thermally unstable and rearranges to 2-methylnorbornyl cation.²³ Here, we find that the reverse reaction takes place in the bicyclononyl system. The stability of a bridgehead carbocation is known to be mainly controlled by the degree of planarity.⁴⁰ In other words, the degree of nonplanarity has a major influence on the stabilities of bridgehead cations. In the case of the bicyclo[3.3.0]octyl cation the bridgehead cation can not reach the same planarity as in the bicyclo[4.3.0]nonyl cation. In condensed ring systems,^{10,20} the stabilities of bridgehead carbocations decrease as the ring size diminishes. Thus the bicyclo[4.4.0]decyl cation should be more stable than the bicyclo[4.3.0]nonyl cation, which in turn should be more stable than the bridgehead bicyclo[3.3.0]octyl cation. In the latter case, the obvious relief of ring strain provides some driving force for the rearrangement to the 2-methylnorbornyl cation.

Conclusions

The cage effect deshielding of the bridgehead proton chemical shifts has been demonstrated first in the 1-adamantyl cation. The same effect has now been found to exist in the 1-bicyclo[3.2.2]nonyl cation. The bicyclo[4.3.0]non-1-yl (8-hydrindyl) cation is found to contain a rapidly equilibrating bridgehead proton. Under stable ion conditions the 1-methylbicyclo[3.2.1]oct-1-yl cation transforms thermally into the bicyclo[4.3.0]non-1-yl cation. The bicyclo[4.3.0]non-1-yl, bicyclo[3.2.2]non-1-yl, and 2-methylbicyclo[3.2.1]oct-2-yl cations are classical in nature as observed stable carbenium ion complexes. This does not, of course, mean that varying degrees of bridging (nonclassical nature) can not be present in relatively unstable intermediate ions or the transition states leading to them, particularly under solvolytic reaction conditions. It should be emphasized that directly observed stable ions are thermodynamically favored intermediates in low nucleophilic media (we generally try to differentiate them in

(39) Ionization of cyclononanol has been reported previously.²² As the cyclodecyl cation underwent a transannular reaction in $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$ solution and gave the bicyclo[4.4.0]decyl cation,²⁵ we were interested in whether the cyclononyl cation would give the 1-bicyclo[4.3.0]nonyl cation under identical conditions. No spectral evidence of bicyclo[4.3.0]nonyl derivatives was found in the $\text{KOH}-\text{SO}_2\text{ClF}$ quench products.

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

formulas, by bracketing not observable intermediates or transition states).

Experimental Section

Proton nuclear magnetic resonance spectra were recorded at either 60 or 100 MHz using Varian Associates Model A56/60 A and HA100 spectrometers equipped with variable temperature probes. An external TMS capillary was used as a reference signal.

Carbon-13 nuclear magnetic resonance spectra were obtained by irradiation of the 100-MHz spectrum with a swept 25.1-MHz frequency source (indor method) according to the previously described procedure.⁴¹ The ^{13}C chemical shifts were calculated with respect to TMS as a reference and converted to the $^{13}\text{C}_2$ standard by adding 194.6 ppm.

Preparation of Solutions of the Bicyclononyl Cations. A fresh solution of $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1) or a saturated solution of SbF_5 in SO_2ClF (SO_2) were prepared and cooled to -78° in a Dry Ice-acetone bath. For lower temperatures, either a liquid nitrogen-ether or a liquid nitrogen-ethanol bath was used. To the solution was then slowly added with vigorous stirring a cold solution of the bicyclononyl precursor in SO_2ClF (SO_2) to give an approximate 10–15% solution of the ion which was then transferred to an nmr tube.

Rearrangement of the 2-Methylbicyclo[3.2.1]oct-2-yl Cation to 8-Hydrindyl Cation. The solution of ion **3** prepared as described above was slowly heated in the nmr probe to the desired temperatures (-45 or -30° depending upon the precursor ions). The 8-hydrindyl cation (**1**) was slowly formed, the final solution was then cooled to -70° , and the nmr spectrum was recorded. The identical pmr spectrum was obtained directly from hydrindyl precursors (Scheme I).

Quenching of solutions of bicyclononyl cations was carried out in either $\text{MeOH}-\text{NaOMe}$ or $\text{KOH}-\text{SO}_2\text{ClF}$ by the previously described procedure.²³

Materials. *cis*- and *trans*-bicyclo[4.3.0]nonanes (**9**), 5-hydrindanol (**10**), and 3-methyl-2-hydroxymethylnorbornane (**16**) ($X = \text{OH}$) were commercially available (Aldrich Chemical Co., Milwaukee, Wis.).

cis- and *trans*-8-hydrindanols (**8**) were kindly provided by Professor Fort.^{10,11} We are indebted to Professor Fort for these samples.

cis- and *trans*-2-Methylbicyclo[3.2.1]octan-2-ols (**14**).⁴² A mixture of isomeric alcohols was prepared from 2-bicyclo[3.2.1]octanone (Aldrich) by reaction with methylmagnesium bromide in dry ether at room temperature in the usual fashion. The mixed alcohols were used directly in the preparation of ions without further separation. The *cis*:*trans* ratio was 65:35 as indicated by gas chromatography; mp $60-68^{\circ}$.

2-*exo*-Ethyl-2-*endo*-norborneol (**15**)⁴³ was prepared by reaction of norcamphor (Aldrich) with ethylmagnesium bromide (Alfa Inorganics Inc.) in absolute ether at room temperature. The alcohol was purified by vacuum distillation at 78° (8.5 mm) and had mp $39-42^{\circ}$.

3-Methyl-2-chloromethylnorbornane (**16**) was prepared by Stille and Sonnenberg's method.⁴⁴ 2-Methyl-3-hydroxymethylnorbornane (14 g, 0.10 M) (Aldrich) in dry pyridine (8.05 ml) was slowly added to thionyl chloride (10.9 ml, 0.15 M) at 0° . The resulting mixture was stirred for 1 hr at room temperature and then heated at gentle reflux on a steam bath for 30 min and kept overnight; the mixture was chilled in ice and poured into 100 ml of ice-water and extracted with ether (three 100 ml). The combined ether extracts were washed to neutral and dried (MgSO_4). The chloride (13.5 g, 85%) collected by distillation *in vacuo* had bp $51-53^{\circ}$ (2.4 mm).

Anal. Calcd for $\text{C}_9\text{H}_{15}\text{Cl}$: C, 68.41; H, 9.48. Found: C, 68.05; H, 9.21. Nmr spectrum of the chloride showed a doublet ($J = 7.8$ Hz) centered at δ 3.14, assigned to the chlorine adjacent to the methylene protons, and a doublet ($J = 6.5$ Hz) centered at δ 8.95, assigned to the methyl protons. The remaining proton signals were not assigned.

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