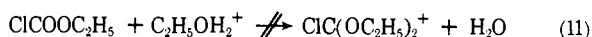
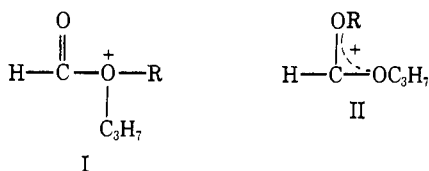


nature of the alcohol and the relative proton affinities. A further example of these requirements is illustrated by the failure to observe reaction 11, although ethanol has a higher proton affinity than ethyl chloroformate.



In short, this mechanism can be visualized under the rules established for nucleophilic displacement if attack by an oxygen of the ester is assumed to take place on the hydroxylic carbon of the alcohol.

No definite conclusions can be reached on the structure of the ions $(\text{HCO}_2\text{RC}_3\text{H}_7)^+$, as either an oxonium type structure I or an acetal (II) has been postulated as possible.²⁰ Qualitative considerations in terms of



delocalization would perhaps favor structure II, a species which is usually identified in the mass spectra of orthoformates.²⁹ Thermochemical values obtained from appearance potentials for the simplest ion of this type, namely $\text{HC}(\text{OCH}_3)_2^+$,³⁰ can be used to establish that the exothermicity of reaction 4 is below 10 kcal/mol. The species I or II can be regarded as the intermediate for gas phase transesterification as demonstrated by Munson and Field²⁰ under conditions where

(29) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 268.

(30) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 1353 (1966).

vibrational equilibration has been established for the alkyl groups. It is interesting to note that transesterification for reaction 4 would be unlikely, as decomposition of even the completely equilibrated system would result in the expulsion of CD_2 as the neutral fragment.

A meaningful comparison between reactions 4, 6, and 7 and solution studies cannot be established because of the uncertainties in our proposed mechanism. However, it is well known that esterification and hydrolysis involving tertiary alkyl groups in solution proceed *via* carbonium ion intermediates.²

Other systems can be studied which are directly related to this particular chapter of organic chemistry, and which can be explained by a variety of mechanisms. Thus, protonated methanol reacts with CH_3COCl to yield protonated methyl acetate in the gas phase, and protonated methylamine reacts with acetic acid to yield a protonated amide.³¹

The relationship between gas phase ion chemistry and solution processes is once again heavily stressed in our present results because of the importance in establishing a correct correlation between structure and intrinsic reactivity for even the most common reactions in chemistry.

Acknowledgment. This research was supported by the Conselho Nacional de Pesquisas of Brazil, and the Fundação de Amparo à Pesquisa do Estado de São Paulo (P. W. T.). We would like to thank Paulo C. Isolani for the preparation of some of the esters used in the present work, Nardy L. Lopes for initial investigations regarding these systems, and Geraldo Ayrosa for technical assistance.

(31) P. W. Tiedemann, N. L. Lopes, and J. M. Riveros, unpublished results.

Stable Carbocations. CXLV.¹ The 2,3-Dimethyl-2-norbornyl Cation and Its Rearrangement to the 1,2-Dimethyl-2-norbornyl Cation

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received December 27, 1972

Abstract: Under stable ion conditions the 2-methyl-*exo*-3-methyl-2-norbornyl cation (1) was obtained from several dimethyl-substituted norbornyl precursors at low temperature. Ion 1 is characterized as a rapidly equilibrating carbenium ion by ^1H and ^{13}C nmr spectroscopy. When 1 was allowed to warm to -60° , it slowly rearranged into the more stable 1,2-dimethyl-2-norbornyl cation 2. The structure of ion 1 and its rearrangement reaction are discussed.

Addition of hydrogen halides,² acetic acid,³ trifluoroacetic acid,⁴ and mercuric acetate⁵ to *gem*-dimethylnorbornenyl derivatives under electrophilic con-

ditions has been reported to give exclusively the *exo* products *via* nonclassical ions.²⁻⁷ Substantial an-

(1) (a) Part CXLIV: G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3706 (1973). (b) Taken in part from the Ph.D. Thesis of G. Liang, Case Western Reserve University, 1973.

(2) (a) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970); (b) M. Barthelemy, J. P. Montheard, and M. Y. B. Chretien, *Bull. Soc. Chim. Fr.*, 4881 (1968); (c) H. C. Brown and K. T. Lui, *J. Amer. Chem. Soc.*, **89**, 3898, 3900 (1967); (d) Y. C. Bessiere and J. P. Montheard, *C. R. Acad. Sci.*, **258**, 937 (1964).

(3) (a) D. E. McGree, *Can. J. Chem.*, **40**, 1554 (1962); (b) S. Beckmann and R. Bamberger, *Justus Liebigs Ann. Chem.*, **580**, 198 (1953); (c) G. Komppa and G. A. Nyman, *Ber.*, **69**, 1813 (1936).

(4) H. C. Brown, J. H. Kawakami, and K. T. Lui, *J. Amer. Chem. Soc.*, **92**, 3816 (1970).

(5) H. C. Brown, M. R. Lei, and K. T. Lui, *ibid.*, **92**, 1760 (1970).

(6) (a) H. C. Brown and K. T. Lui, *ibid.*, **92**, 3502 (1970); (b) H. C. Brown, J. H. Kawakami, and S. Misumi, *J. Org. Chem.*, **35**, 1360 (1970).

(7) (a) J. A. Berson in "Molecular Rearrangements," Vol. I, P. DeMayo, Ed., Wiley-Interscience, New York, N. Y., 1967, Chapter 3;

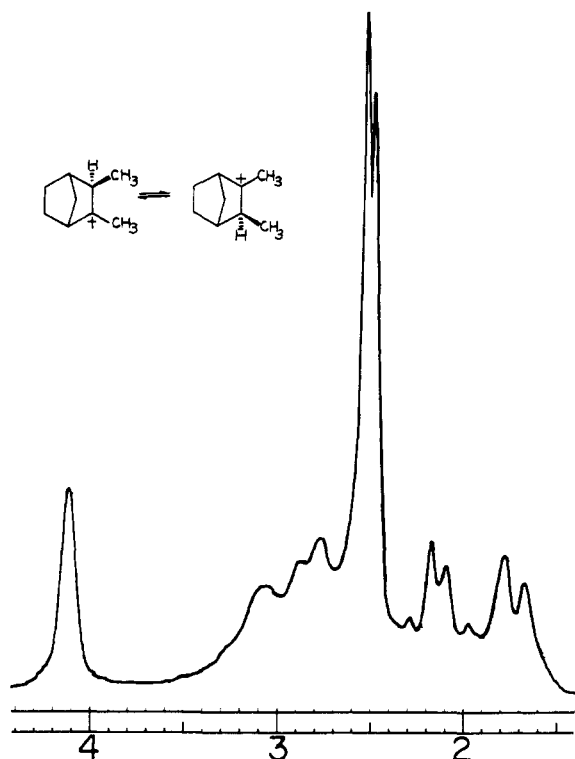


Figure 1. PMR spectrum (100 MHz) of the 2-methyl-*exo*-3-methyl-2-norbornyl cation in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ solution at -90° .

chimeric acceleration is found in the solvolysis of apoisobornyl, *exo*-camphenyl, and related derivatives suggesting bridged nonclassical dimethylnorbornyl ion intermediates, similar to the well-studied 2-norbornyl cation.⁸ Previously, study of the 1,2-dimethyl-2-norbornyl cation^{9a} generated from 1,2-dimethyl-2-norborneol, *exo*- and *endo*-2-chloro-1,2-dimethylnorbornanes, or through the rearrangement of 6,6-dimethyl-*exo*-2-norborneol under stable ion conditions showed it to be a rapidly equilibrating pair of classical ions with partial σ delocalization.^{9a} There was no intermediate ion(s) observed in the course of the rearrangement. It is, however, evident that intermediate ion(s) must have been involved.^{9,10} In continuation of our studies on stable norbornyl cations, we therefore undertook a

(b) H. C. Brown and K. T. Lui, *J. Amer. Chem. Soc.*, **92**, 200 (1970); (c) W. Huckel and A. Majumdar, *Suom. Kemistilehti B*, **42**, 115 (1969); (d) P. G. Gassman, J. L. Marshall, J. F. MacMillan, and J. M. Hornback, *J. Amer. Chem. Soc.*, **91**, 4282 (1969); (e) J. A. Berson, A. W. McRow, and R. G. Bergman, *ibid.*, **88**, 1067 (1966); (f) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965); (g) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965); (h) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965); (i) S. Winstein, *Exp. Suppl. II*, 145 (1955); (j) H. C. Brown and H. M. Bell, *J. Amer. Chem. Soc.*, **86**, 5006 (1964), and references quoted therein.

(8) (a) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970), and references quoted therein. (b) For a recent review on the 2-norbornyl cation, see G. D. Sargent in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1972, Chapter 24.

(9) (a) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *ibid.*, **93**, 1442 (1971); for further discussion see part CXLVI; (b) H. L. Goering and J. V. Clevenger, *ibid.*, **94**, 1010 (1972); (c) H. L. Goering and K. Humski, *ibid.*, **91**, 4594 (1969); (d) *ibid.*, **90**, 6213 (1968); (e) H. L. Goering, C. Brown, S. Chang, J. V. Clevenger, and K. Humski, *J. Org. Chem.*, **34**, 624 (1969); (f) H. L. Goering, C. Brown, and C. B. Schewene, *J. Amer. Chem. Soc.*, **90**, 6215 (1968).

(10) (a) M. G. J. Dufresne and M. Blanchard, *Bull. Soc. Chim. Fr.*, 385 (1968); (b) N. A. Belikova, L. I. Kovalenko, A. F. Plate, and K. E. Sterin, *Zh. Org. Khim.*, 1372 (1968); (c) L. D. Hartfield and W. D. Huntsman, *J. Org. Chem.*, **32**, 844 (1967); (d) P. Beltrame, C. A. Buntton, A. Dunlop, and D. Whitterker, *J. Chem. Soc.*, 658 (1964).

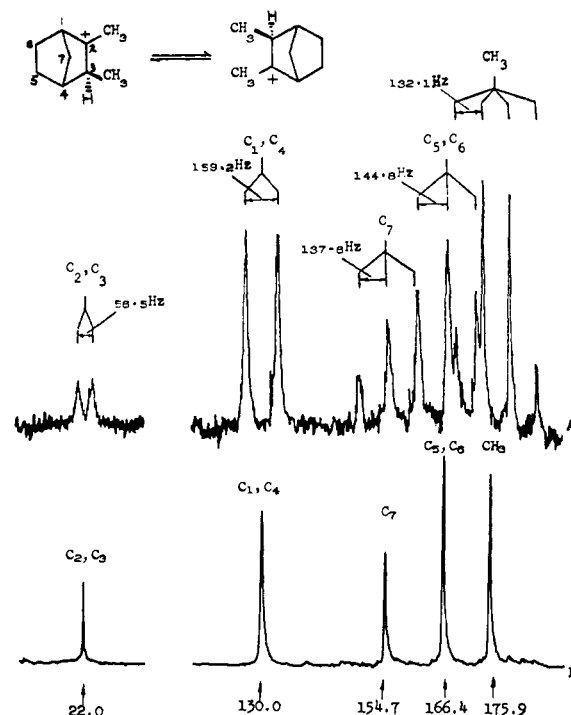


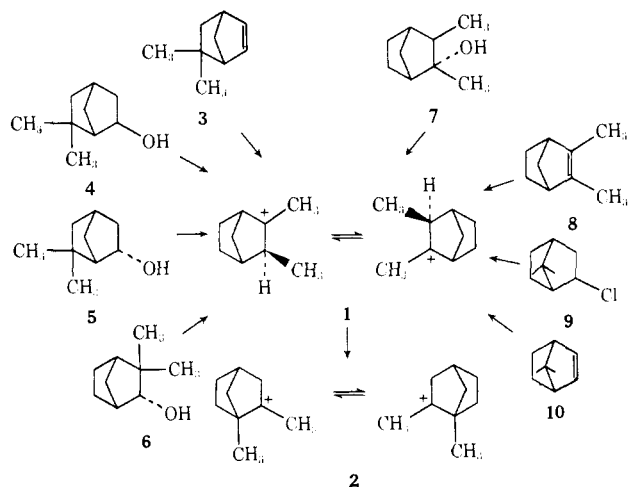
Figure 2. CMR spectra of the 2-methyl-*exo*-3-methyl-2-norbornyl cation: (A) proton coupled; (B) proton decoupled.

detailed study of the direct observation of the elusive intermediate 2,3-dimethyl-2-norbornyl cation **1** and its rearrangement to the 1,2-dimethyl-2-norbornyl cation **2**.

Results

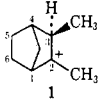




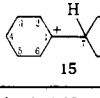
The 2-methyl-*exo*-3-methyl-2-norbornyl cation (**1**) was obtained from 6,6-dimethyl-2-norbornene (**3**), 6,6-dimethyl-*exo*- and *endo*-2-norborneols (**4** and **5**), 3,3-dimethyl-2-*endo*-norborneol (**6**), 2,3-dimethyl-2-*endo*-norborneol (**7**), 2,3-dimethyl-2-norbornene (**8**), 7,7-dimethyl-2-*exo*-norbornyl chloride (apoisobornyl chloride (**9**)), and 7,7-dimethyl-2-norbornene (**10**) in either FSO_3H , $\text{FSO}_3\text{H-SbF}_5$, or SbF_5 solutions diluted with SO_2ClF at -120° (Scheme I). The conversion of **3**,

Scheme I



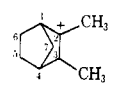
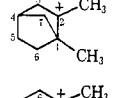
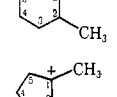
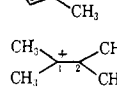
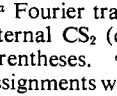
8, **9**, and **10** into **1** took place immediately at -120° . Alcohols **4**, **5**, **6**, and **7** were first protonated in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ solution and then ionized slowly into **1**

Table I. Pmr Parameters of 2,3-Dimethyl-2-norbornyl Cations and Model Cations^a

Cation	CH ₃	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇
	2.52 ^b (d, 4.2 Hz)	4.12 (b)	3.10	3.10	4.12	2.15	2.15	1.58
	2.73 (d, 3.6 Hz)		4.21 (b)	3.45	2.49	2.49	3.45	
	2.81 (d, 3.5 Hz)		3.35 (b)	3.60	2.60	3.60		
	3.32 (d, 4.2 Hz)		4.40					
			3.38	2.39	2.39	3.38	4.08	
			3.10	2.10		2.10	3.10	4.10

^a Chemical shifts (δ) are in ppm relative to external TMS. ^b Multiplicities and coupling constants (in Hz) are shown in parentheses; d = doublet, b = broad.

Table II. Cmr Parameters of 2,3-Dimethyl-2-norbornyl Cation and Model Cations^a

Cation	CH ₃	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇
	175.9 ^b (q, 132.1)	130.0 (d, 159.2)	22.0 (d, 58.5)	22.0 (d, 58.5)	130.0 (d, 159.2)	166.4 (t, 144.8)	166.4 (t, 144.8)	154.7 (t, 137.6)
	176.0 ^c (q, 130.5)	26.0 (s)	26.0 (s)	146.0 (t, 134.5)	152.5 (d, 152.6)	145.5 (t, 148.5)	167.8 (t, 127.6)	146.0 (t, 134.5)
	165.4 (q, 130.0)	-4.0 (d, 62.5)	-4.0 (d, 62.5)	138.3 (t, 144.0)	159.2 (t, 138.0)	159.2 (t, 138.0)	138.3 (t, 144.0)	
	169.8 (q, 138.0)	-9.7 (d, 51.0)	-9.7 (d, 51.0)	146.0 (t, 126.0)	158.5 (t, 124.5)	146.0 (t, 126.0)		
	151.8 (q, 132.0)	-3.4 (d, 65.0)	-3.4 (d, 65.0)					

^a Fourier transform cmr spectra were obtained using Varian XL-100 nmr spectrometer. ^b Carbon shifts (δ_{13C}) were given in ppm from external CS₂ (capillary); multiplicity (q = quartet, s = singlet, t = triplet, d = doublet) and coupling constants (in Hz) were given in parentheses. ^c Incorrect assignments were made for ion 2 previously (see ref 8). We now have obtained complete cmr spectrum for ion 2.^{9a} Assignments were made according to multiplicity and coupling constants.

at higher temperature (*ca.* -75°). When the solutions of ion 1 were warmed to -60° , a new ion was slowly formed. The pmr spectrum of the solutions cooled back to -80° was found to be identical with that of the reported 1,2-dimethyl-2-norbornyl cation 2.^{9a} The transformation of 1 into 2 was irreversible. Quenching of the solutions with ice-NaHCO₃-SO₂ClF solution at -60° gave the known 1,2-dimethyl-*exo*-2-norborneol along with a small amount of 1,2-dimethyl-2-norbornene.

The pmr (100 MHz) spectrum of ion 1 obtained at -90° is shown in Figure 1. Chemical shifts of 1 are summarized in Table I along with those of the model ions (11-15). The carbon-13 nmr spectrum of ion 1 (Figure 2) was obtained by the fast Fourier transform method using an XL-100 nmr spectrometer at -90° .

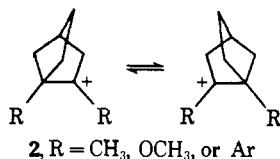
¹³C nmr parameters of ion 1 are summarized in Table II together with those of the model ions. Assignments of chemical shifts were made by comparison with those of the model ions and with the aid of the off-resonance FT spectra. Coupling constants (J_{CH} , in Hz) were directly obtained from the proton-coupled ¹³C nmr FT spectra.

Discussion

Acyclic equilibrating tertiary carbenium ions¹¹ were

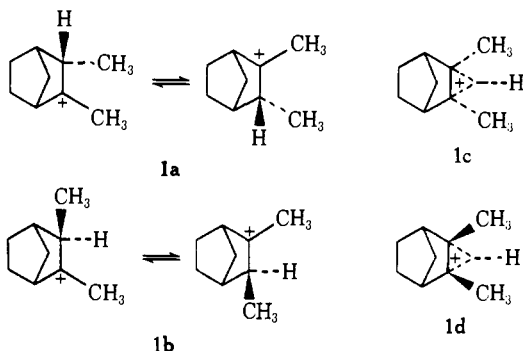
(11) (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969); (b) G. A. Olah, J. M. Bollinger, J. Lukas, and C. Cupas, *ibid.*, **89**, 2692 (1967); (c) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967); **90**, 930 (1968); (d) G. A. Olah and J. A. Olah in "Carbocation Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Interscience-Wiley, New York, N. Y., 1970, Chapter 17.

first reported from this laboratory in the case of the isopropylidimethylcarbenium ion (13). Degenerate, rapidly equilibrating ions undergoing facile Wagner-Meerwein rearrangement such as 1,2-dimethyl- (2, R = CH₃),^{9a} 1,2-dimethoxy- (2, R = OCH₃),^{12a} and 1,2-diaryl- (2, R = Ar)^{12b-c} 2-norbornyl cations have



also been extensively studied. However, rapid equilibration taking place between C₂ and C₃ in bicyclo[2.2.1]heptyl(norbornyl) cations has not been directly observed. The presently studied 2-methyl-*exo*-3-methyl-2-norbornyl cation (1)¹³ can thus be considered the first observed example for such a case.

For the 2,3-dimethyl-2-norbornyl cation, possible structures include the classical, rapidly equilibrating *exo* and *endo* ions (1a and 1b) and the *exo*- and *endo*-bridged ions (1c and 1d). Several previously reported



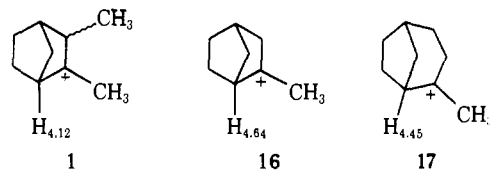
systems containing rapidly equilibrating protons all show the averaged equilibrating methine pmr absorption at about δ 4.0 (Table I). The two monocyclic systems (11 and 12) also show comparable proton absorptions for the equilibrating protons at δ 3.35 and 4.21, respectively. The equilibrating methine proton in 1 displays its absorption at δ 3.10 as a broad singlet. It is somewhat more shielded than those in the model ions, which we believe is due to the more rigid geometry in the bicycloheptyl framework. The two equivalent bridgehead protons absorb at δ 4.12, which is slightly more shielded than those in the 2-methyl-2-norbornyl (16)¹⁴ and 2-methyl-2-bicyclo[3.2.1]octyl (17)¹⁵ cations. Evidence obtained from pmr studies therefore indicates the equilibrating nature of the 2,3-dimethyl-2-norbornyl cation (either 1a or 1b). The observation of regular coupling constants between the methyl protons and the equilibrating methine proton in the 2,3-dimethyl-2-

(12) (a) A. Nickon and Y. I. Lin, *J. Amer. Chem. Soc.*, **91**, 6861 (1969); (b) P. v. R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *ibid.*, **85**, 479 (1963); (c) P. v. R. Schleyer and D. C. Kleinfelter, *J. Org. Chem.*, **26**, 3740 (1961).

(13) (a) Although 2,3-dimethyl-2-norbornyl cations have never been directly observed, all the reactions involving the formation of derivatives derived from the ion 1 indicate the unequivocal existence of such species. (b) S. Beckmann and B. Geiger, *Chem. Ber.*, **95**, 2101 (1962). (c) S. Beckmann and A. Durkop, *Justus Liebigs Ann. Chem.*, **594**, 205 (1955). (d) G. Komppa and G. A. Nyman, *Ber.*, **69**, 334 (1936). (e) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **486**, 202 (1931). (f) G. Komppa and S. V. Hintikka, *Bull. Soc. Chim. Fr.*, **22**, 15 (1917).

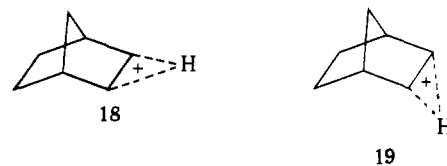
(14) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3958 (1969).

(15) G. A. Olah, G. Liang, J. R. Wiseman, and J. A. Chong, *ibid.*, **94**, 4927 (1972).



norbornyl cation further excludes the bridged structures. The pmr signal for the two equivalent methyl groups in ion 1 is split into a doublet through coupling with the equilibrating proton ($J = 4.2$ Hz). The magnitude of the coupling constant is very close to those in the model ions. Thus both pmr shifts and coupling constants indicate the structure for 1 as a pair of rapidly equilibrating ions. Among the model ions (11–15), only ions 13–15 were previously known and have been shown to contain rapidly equilibrating methine protons. The two monocyclic ions (11 and 12) have not been previously reported. Although the acid-catalyzed additions of acetic acid and hydrogen halides to both 1,2-dimethylcyclohexene and -cyclopentene have been thoroughly studied, there was no evidence reported for rapidly equilibrating cationic intermediates.¹⁶ The energy of activation for an intramolecular tertiary-tertiary 1,2-hydrogen shift is usually dependent on the degree of positive charge at the carbon atom to which the hydrogen is being transferred.^{11,17} Under stable ion conditions ions would have a much longer lifetime to become equilibrated. In the case of ions shown in Table I, energies of activation for 1,2-hydrogen shift are apparently quite low as these shifts are not "frozen out" even at -135° . Under solvolytic conditions, ions are usually captured by the strong nucleophiles or solvent molecules before they can have a chance to become equilibrated.¹⁸

In order to establish the stereochemistry for the methyl groups in ion 1, knowledge concerning the 3,2-hydrogen shift in the parent 2-norbornyl systems is imperative. Several rationalizations concerning the much greater facility of *exo,exo*-3,2-hydrogen shifts over *endo,endo*-3,2-hydrogen shifts have been given.^{8,12,17} Schleyer has calculated based on torsional effects^{17a} that the transition state required for the *exo,exo* process (18) could be up to 6 kcal/mol less energetic than that required for the *endo,endo* process (19).^{17c} In the case of the 2,3-dimethyl-2-



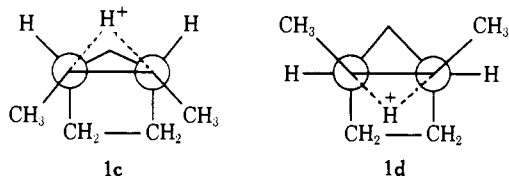
cation (1), the presence of methyl substituents may change the preference (in the parent norbornyl cation)

(16) (a) G. S. Hammond and C. H. Collins, *ibid.*, **82**, 4323 (1960); (b) R. C. Fahey and C. S. McPherson, *ibid.*, **93**, 2445 (1971).

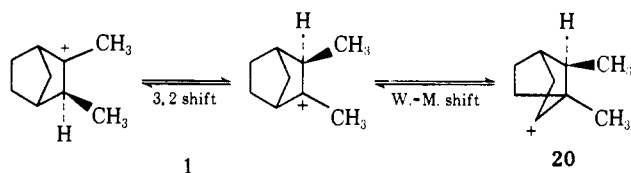
(17) (a) P. v. R. Schleyer, *ibid.*, **89**, 699, 701 (1967); (b) B. Capon, M. J. Perkins, and C. W. Rees, in "Organic Reaction Mechanism," Interscience, New York, N. Y., 1970, Chapter 1; (c) W. R. Vangham, C. T. Goetschel, M. H. Goodrow, and C. L. Watten, *J. Amer. Chem. Soc.*, **84**, 2283 (1962); (d) L. Huang, K. Ranganayakulu, and T. S. Sorensen, *ibid.*, **95**, 1936 (1973). Sorensen, *et al.*, pointed out that an *endo* 3,2 hydrogen shift cannot have a rate constant greater than 10 sec⁻¹ at -10° and a minimum of 6.9 kcal/mol difference in transition-state free energy for an *exo* hydrogen shift. This exceeded a predicted difference of 6 kcal/mol made by Schleyer.

(18) (a) A. W. Bushell and P. Wilder, Jr., *J. Amer. Chem. Soc.*, **89**, 5721 (1967); (b) P. Wilder, Jr., and W.-C. Hsieh, *J. Org. Chem.*, **36**, 2552 (1971).

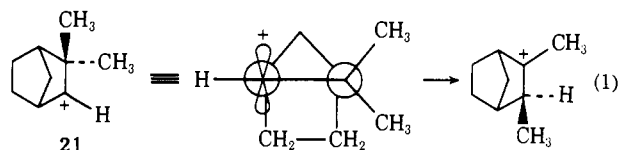
toward the relative stability of the transition states (**1c** and **1d**) required for the observed 2,3-hydrogen shift in **1**. Models show that the two methyl groups in **1c** may suffer severe steric interaction with the two endo protons ($H_{5,endo}$, and $H_{8,endo}$). On the other hand, the two methyl groups in **1d** might also suffer a slight degree of



steric repulsion with the two bridgehead protons. Therefore, the two transition states might be of comparable stability. There is considerable experimental evidence suggesting steric hindrance to endo approach in norbornyl systems.⁸ The interaction between the methyl groups and the endo protons in **1c** probably is more severe so that **1c** becomes more crowded than **1d**. This could imply that the endo,endo-3,2-hydrogen shift might be favored over the exo,exo pathway. An exception to the general assumption that in norbornyl systems the 3,2-hydrogen shift takes place exclusively in an exo,exo fashion has also been reported by Bushell and Wilder.¹⁸ The endo,endo-3,2-hydrogen shift, although being considered to be extremely slow,¹⁷ might become more feasible in the case of forming a degenerate system between tertiary-tertiary cations (*i.e.*, **1**), taking preference over undergoing Wagner–Meerwein shift between the secondary-tertiary cations (**1** \rightleftharpoons **20**).



The formation of the 2,3-dimethyl-2-norbornyl cation from all the geminally dimethyl-substituted norbornyl precursors most probably occurs *via* the unstable 3,3-dimethyl-2-norbornyl cation **21**, from which a final *exo*-methyl shift will produce the equilibrating pair of ions **1b**. The ion formed from **21** must con-

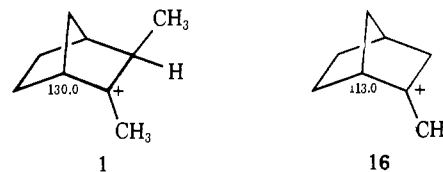


sequently adopt stereochemistry as shown in **1b**. Although an endo-3,2-methyl shift seems also possible, no analogy can be found presently in the literature for such a process.^{7a,17,19} We therefore conclude that the 2,3-dimethyl-2-norbornyl cation observed under stable ion conditions is best represented by the rapidly equilibrating structure **1b**.²⁰

(19) (a) A. M. T. Finch, Jr., and W. R. Vaughan, *J. Amer. Chem. Soc.*, **87**, 5520 (1965); (b) J. D. Roberts and J. A. Yancey, *ibid.*, **75**, 3165 (1953); (c) W. R. Vaughan and R. Perry, *ibid.*, **75**, 3168 (1953); (d) C. J. Collins and M. H. Lietzke, *ibid.*, **95**, 6842 (1973).

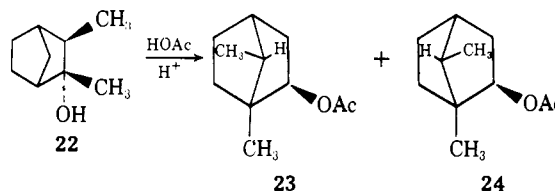
(20) (a) Sorensen, *et al.*, have reported the *exo,exo*-2,3-dimethyl-*endo*-2,3-dimethyl-2-norbornyl cation prepared in FSO_3H-SO_2ClF solution and found it also rearranged at *ca.* -20° to ion **2**. Based on both proton and carbon-13 nmr data it seems that a rapid 3,2-hydrogen

The carbon-13 nmr spectrum also provides confirmation that the 2,3-dimethyl-2-norbornyl cation **1** is a rapidly equilibrating ion, with a methine hydrogen rapidly exchanging between C_2 and C_3 . The average carbon resonance for C_2 and C_3 is found at $\delta_{13C} +22$ (Figure 2), which is shielded compared to the average carbon shifts for the corresponding carbons in model ions. This is believed to be the result of partial delocalization in ion **1b** (through the C_1-C_6 bond) as a similar effect is also found in the previously reported 2-methyl-2-norbornyl cation **16**.¹⁴ It is also reflected by the fact that the bridgehead carbons (C_1 and C_4) in ion **1** are slightly deshielded. The influence of charge



delocalization on the bridgehead positions is, however, not as substantial in **1** as in **16**, due to the presence of the rapid equilibration process in the former. The two equivalent methyl groups are found at δ_{13C} 175.9 and this shift is in good agreement with those in model ions (Table II). The average coupling constant between the methine proton and the two equivalent carbons (C_2 and C_3) in **1** ($J_{CH} = 58.5$ Hz) is also of reasonable magnitude for a rapidly equilibrating system. Both 1H and ^{13}C nmr data thus point to the same conclusion that ion **1** indeed undergoes a rapid equilibration process involving C_2 and C_3 .²⁰

The rearrangement of the 2,3-dimethyl-2-norbornyl cation **1** into the more stable 1,2-dimethyl-2-norbornyl cation **2** at temperatures higher than -60° is also expected. The fact that all dimethyl-substituted norbornyl precursors investigated in the present work first undergo rearrangement to ion **1** before they rearrange further to **2** shows that the former ion indeed is a stable intermediate with a significant energy minimum on the path of the rearrangements. In the light of solvolytic studies and electrophilic additions to dimethyl-substituted norbornyl derivatives,¹³ the mechanism for the rearrangement of **1** to **2** can be rationalized as shown in eq 2. The sulfuric acid catalyzed acetolysis of *cis*-2,3-dimethyl-*endo*-2 norborneol (**22**)¹⁰ gives a mixture of **23** and **24**, when carried out with a mixture of acetic acid

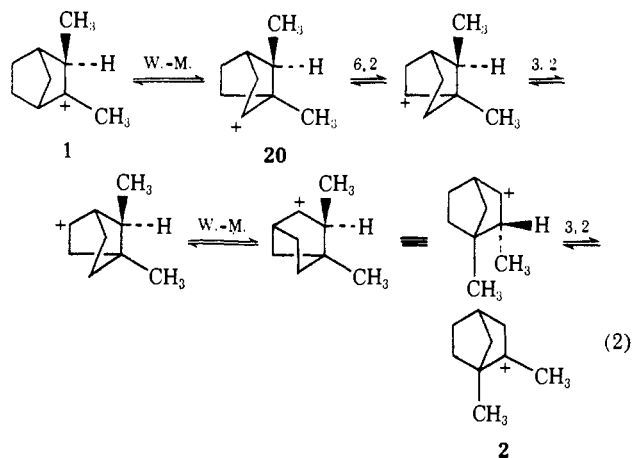


and sulfuric acid at $55-60^\circ$. When **1** is warmed in superacidic media, it probably first gives **20** *via* a Wagner–Meerwein shift. Ion **20** then can give **2** through a series of 3,2-hydrogen shifts, 6,2-hydrogen shift, and Wagner–Meerwein shifts.

Conclusion

Electrophilic additions to dimethyl-substituted nor-

bornyl cations is more likely than the process proposed by Sorensen. In addition, the irreversible formation of **2** from **1** took place even at -60° , in our hands. (b) E. H. Wang, K. Ranganayakulu, and T. S. Sorensen, *J. Amer. Chem. Soc.*, **94**, 1779, 1780 (1972). (c) T. S. Sorensen and K. Ranganayakulu, *Tetrahedron Lett.*, 2447 (1972).



bornenes^{2,7,13} have been examined in an attempt to probe more deeply the controversial classical *vs.* non-classical 2-norbornyl cation problem. Various non-classical dimethyl-substituted 2-norbornyl cations have been suggested to be involved in these reactions. Under stable ion conditions, however, only the 2-methyl-*exo*-3-methyl-2-norbornyl cation (1) is directly observed from geminally dimethyl-substituted norbornyl precursors as a long-lived ion (at temperatures below -60°). There is no evidence for any observable non-classical ion intermediates that are stable and also have long enough lifetimes to permit nmr spectroscopic detection. This does not, however, exclude the possible existence of the suggested nonclassical ions as higher energy species on the path of solvolytic reactions. Recent investigations of the 2-norbornyl cation⁸ (a σ -delocalized carbonium ion) and of 2-substituted 2-norbornyl cations⁸ (partially σ -delocalized carbenium ions) have shown the wide scope of possible σ delocalization in bicyclo[2.2.1]heptyl cations. The extent of C₁-C₆ bond delocalization to form bridged carbonium ion intermediates decreases going from secondary to tertiary norbornyl systems. A further decrease of such ability is now noticed going from static tertiary to rapidly equilibrating, degenerate tertiary norbornyl cations.

Experimental Section

Materials. 6,6-Dimethyl-2-norbornene (3),^{2b,21} 6,6-dimethyl-2-*exo*-norborneol (4),^{3a} 6,6-dimethyl-2-*endo*-norborneol (5),^{3a} 3,3-dimethyl-2-*endo*-norborneol (6),^{13d} 2,3-dimethyl-2-*endo*-norborneol (7),^{3,13d} 2,3-dimethyl-2-norbornene (8),^{3,13b} 7,7-dimethyl-2-*exo*-norbornyl chloride (9),^{6b} and 7,7-dimethyl-2-norbornene (10)^{6b} were prepared according to procedures reported.

Proton Nuclear Magnetic Resonance Spectroscopy. Pmr spectra were obtained using Varian Associates Model A56/60A and HA 100 nmr spectrometers equipped with variable-temperature probes. External tetramethylsilane (capillary) was used as reference.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Cmr spectra were obtained on a Varian Associate Model XL 100 spectrometer equipped with a Fourier transform accessory, a spin decoupler, and a variable-temperature probe. A continuous wavelength mode and no pulse delay were used. The pulse width used was 15–20 μ sec and the need to provide multichannel excitation over the region of interest (10,000 Hz) limited the data acquisition time to 0.4 sec. Approximately 2000–5000 accumulations were made to obtain satisfactory spectra depending upon the ion concentration. A Varian 620L computer was used to accumulate data. The lock used was the external fluorobenzene. Fourier transformation of the accumulated free induction signals gave the frequency spectrum, from which the chemical shift of each signal relative to the external CS₂ (obtained from the external CS₂) 5–10% enriched capillary (δ_{13C} 0) was obtained.

Preparation of the 2,3-Dimethyl-2-norbornyl Cation 1. The corresponding precursors in SO₂ClF solution were slowly added to a freshly prepared FSO₃H-SbF₅ or SbF₅ solution diluted with SO₂ClF at Dry Ice-acetone bath temperature (*ca.* -78°) with vigorous stirring, to give an approximately 20% solution of the ion.

Preparation of 1,2-Dimethyl-1-cyclohexyl and -cyclopentyl Cations. Due to the instability of both cations, they were prepared at Dry Ice-ethanol slush temperature (*ca.* -135°). Sufficient FSO₃H-SbF₅ (in SO₂ClF-SO₂F₂) was placed in an nmr tube and was cooled to -135° . 1,2-Dimethyl-1-cyclohexanol or -cyclopentanol in SO₂ClF solution was then carefully introduced along the wall of the nmr tube, where the alcohol solutions froze at this temperature. They were slowly mixed till a light yellow solution resulted. The nmr tube was then immediately transferred into the precooled nmr probe kept at -105° , at which temperature the ions were stable and their pmr and cmr spectra could be obtained without rearrangement.

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(21) J. A. Berson and S. Suzuki, *J. Amer. Chem. Soc.*, **81**, 4088 (1959).