Stable Carbonium Ions. CX.[1] The 1,2-Dimethylnorbornyl Cation

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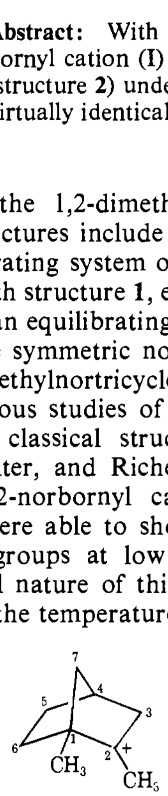
Abstract: With combined techniques of ^{13}C and ^{1}H nmr and Raman spectroscopy, the stable 1,2-dimethylnorbornyl cation (I) is shown to be the first well-characterized example of a partially σ-delocalized carbonium ion (structure **2**) undergoing a rapid 1,2 Wagner–Meerwein shift. The degree of σ delocalization in I is found to be virtually identical with that present in the 2-methylnorbornyl cation.

For the 1,2-dimethylnorbornyl cation (I) possible structures include the static classical cation **1**; an equilibrating system of equivalent classical tertiary cations with structure **1**, eq 1; a static partially delocalized ion **2**; an equilibrating partially delocalized ion **2**, eq 2; and the symmetric nonclassical ion **3** (*i.e.*, protonated 1,2-dimethylnortricyclene).

Previous studies of 1,2-diarylnorbornyl cations support a classical structure for these ions. Schleyer, Kleinfelter, and Richey[2] have investigated the 1,2-(*p*-anisyl)-2-norbornyl cation in sulfuric acid solution. They were able to show the nonequivalence of the *p*-anisyl groups at low temperature demonstrating the classical nature of this ion. Nickon[3] has recently reported the temperature-dependent pmr spectrum of the 1,2-dimethoxynorbornyl cations as evidence supporting its classical character. It is evident, however, that analogy between I and the 1,2-di(*p*-anisyl)- as well as the 1,2-dimethoxynorbornyl cations is far from complete since positive charge in the latter cases lies primarily on the oxygen atom. This property manifests itself in the very high barrier reported for the degenerate 1,2 Wagner–Meerwein shifts of the 1,2-dimethoxynorbornyl cation and is also reflected in its nmr spectra.[4]



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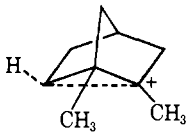

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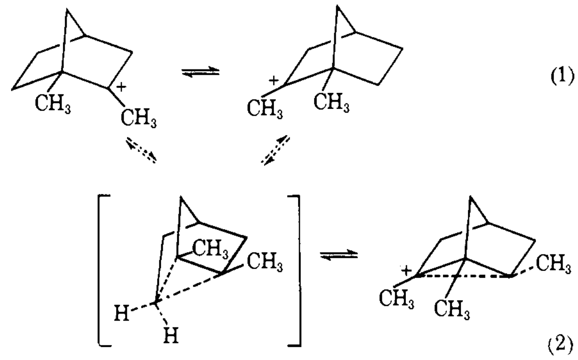
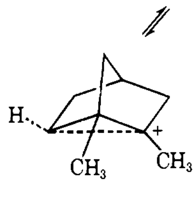


(1)

(2)



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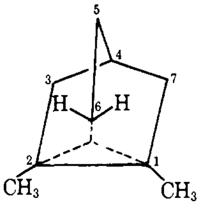

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Combined techniques of ^{13}C and ^{1}H nmr and Raman spectroscopy have demonstrated that the parent unsubstituted norbonyl cation exists as the symmetrically σ-bridged norbornonium ion in super acid and related media.[5] Similarly, the 2-methylnorbornyl cation was shown to be a static bicyclic system with a small but significant degree of $C{-}H_{6exo}{-}C_2$ σ delocalization.[5,6] Interest in the structure of the 1,2-dimethylnorbornyl cation centers primarily on the possible analogy between structures **2** and **3** for ion I and the tertiary 2-methylnorbornyl cation and the symmetrically bridged norbornyl cations, respectively. We now wish to report ^{13}C and ^{1}H nmr and Raman spectroscopic investigations of the cation I.

Results and Discussion

Ion I was generated from 1,2-dimethylnorbornyl-*endo*-2-ol or *endo*- and *exo*-2-chloride in $SbF_5{-}SO_2$ or $FSO_3H{-}SbF_5{-}SO_2$ solution. Ion I was obtained also from 6,6-dimethyl-*exo*-norbornan-2-ol in $SbF_5{-}SO_2$ or $FSO_3H{-}SbF_5{-}SO_2$ media. The conversion of the 6,6-dimethylnorbornyl cation to ion I takes place slowly at −60°. The pmr spectrum obtained for ion I at −78° is shown in Figure 1 and Table I with assignments. Assignments are based primarily on analogy

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[1] Stable Carbonium Ions. CIX: G. A. Olah and A. T. Ku, *J. Org. Chem.*, **35**, 3922 (1970).

[2] P. v. R. Schleyer, D. C. Kleinfelter, and H. B. Richey, Jr., *J. Amer. Chem. Soc.*, **85**, 479 (1963).

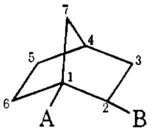
[3] A. Nickon and Y. Liu, *ibid.*, **91**, 6861 (1969).

(4) The pmr spectrum reported by Nickon[3] for the 1,2-dimethoxynorbornyl cation shows an approximate equivalence of the H_{6exo} and H_{6endo} protons (see Table I). With accumulation of positive charge on C_2, the chemical shifts of these protons should be decidedly different.[5,6] To clarify this problem further we have obtained ^{13}C nmr spectra of the C_2 carbon atom of norcamphor and protonated norcamphor. Comparison of $\Delta\delta^{13}C$ obtained for the carbonyl carbon in acetone and that in protonated acetone (43.7 ppm) with that observed for the carbonyl carbon in norcamphor and protonated norcamphor (43.7 ppm) demonstrates the absence of $C_2{-}C_6$ interaction in the α-hydroxynorbornyl cation. A substantial build-up of positive charge on C_2 would lead to a degree of σ $C{-}H_{6exo}$ delocalization which should be reflected by a measurable change in the ^{13}C nmr spectra of these cations. It is evident, therefore, that positive charge in α-hydroxy- and α-methoxynorbornyl cations lies primarily on the oxygen atom.

[5] G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).

[6] G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *ibid.*, **91**, 3958 (1969).

Table I. Pmr Spectral Parameters of Mono- and Disubstituted 2-Norbornyl Cations[a]



Ion A	Ion B	δ A	δ B	δ 3	δ 4	δ 5	δ 6	δ 7
H	CH_3	4.64 d (6.5)	3.00 t (3)	2.70	2.70	1.47	3.28 x, b, m 1.09 n	1.71
CH_3	CH_3[b]	2.43 s	2.34 s	2.42 s	2.86	1.52 t (6) d (2)	2.86	2.42 s
H	$=O^{+}H$	3.9 d (2.6)	14.1	3.1	3.1	1.9	2.7	2.25
H	$=O^{+}CH_3$[f]	3.45 s, d 3.50 a, d	4.71 s 4.65 a		*c*	*c*	*c*	*c*
CH_3	$=O^{+}CH_3$[f]	1.35 s	4.66 s	2.84 b	2.84 b	*d*	*d*	*d*
OCH_3	$=O^{+}CH_3$[f,g]	3.77	4.90 s	3.06 s, b	3.06 s, b	*e*	*e*	*e*
OCH_3	$=O^{+}CH_3$[b,f–h]	4.35 s	4.35 s	2.76 d	3.10 m	2.02 m	2.37 m	2.76 d

[a] Pmr chemical shifts in parts per million relative to TMS: b = broad; t = triplet; d = doublet; m = multiplet; s = singlet (J = Hz), s = syn; a = anti; x = exo; n = endo. [b] Time-averaged chemical shifts due to equilibration. [c] 1.2–3.2 broad multiplet. [d] Broad, 1.1–2.4. [e] Broad, 1.2–2.8. [f] Reference 3. [g] $FSO_3H-CH_2Cl_2$. [h] 38.5°.

with other related spectra shown in Table I. It should be noted that the pmr spectrum of the 1,2-dimethylnorbornyl cation has also been obtained by McFarland.[7]

For ion I, pmr equivalence of the two methyl groups, the H_{6exo} and H_{6endo} hydrogens and the H_7 and H_3 hydrogens is evident. The signal of the H_5 protons is observed as a 2 H triplet (J_{H_5,H_6} = ~6 Hz) of doublets (J_{H_4,H_5} = ~2 Hz) at δ 1.52 (external capillary of TMS). J_{H_5,H_6} and J_{H_5,H_4} are consistent with those observed in several other substituted norbornyl systems and also are in line with magnitudes predicted for the dihedral angles $\theta_{H_5,H_6} \approx 0°$ and $\theta_{H_4,H_5} \approx 45°$.[7,8] Chemical shifts of the H_4 and H_5 hydrogens of ion I are nearly identical with those reported[6] for the 2-methylnorbornyl cation with $\Delta\delta_{H_5} = 0.16$ and $\Delta\delta_{H_4} = 0.05$. The pmr chemical shift of the methyl groups of ion I predicted by calculation of the average between chemical shifts of the 2-methyl group of the 2-methylnorbornyl cation[6] and the 1-methyl group of the 1-methyl,2-methoxynorbornyl cation[3] is δ 2.17. This compares favorably with the shift of δ 2.43 observed for the methyl groups of ion I. The pmr spectrum of ion I is, therefore, in agreement with structure **2** undergoing a rapid 1,2 Wagner–Meerwein shift (eq 2).

The total cmr spectrum of ion I was obtained by the indor method and is shown in Table II with the corresponding assignments. Assignments are made by comparison with model cmr spectra of several norbornyl compounds and also are based on the magnitude of the $J_{^{13}CH}$ coupling constants. Comparison of the averaged cmr chemical shifts of the C_1 and C_2 carbon atoms of ion I and those observed or calculated for structural models provides conclusive evidence for the structure **2** of ion I. Table III contains the cmr shifts (either observed or estimated) for the C_1 and C_2 carbon atoms of ion I and model ions.

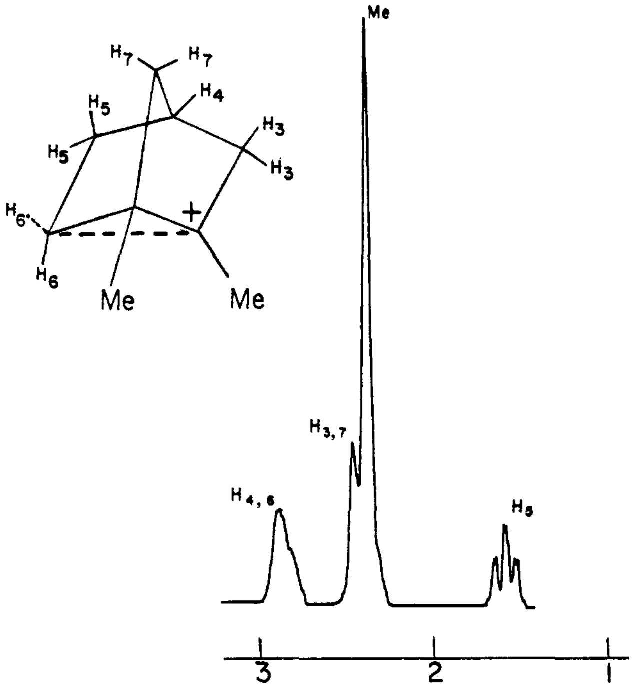


Figure 1. The 100-MHz pmr spectrum of the 1,2-dimethylnorbornyl cation in SbF_5-SO_2 at −70°.

The average of the cmr chemical shifts (which we define as an *average shift*) of the C_1 and C_2 carbon atoms in dimethyl-*tert*-butyl carbonium ion **4** (Table

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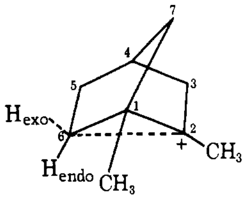
(7) J. T. McFarland, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1969.

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

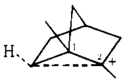
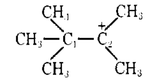
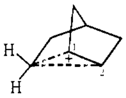
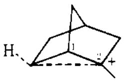
Table II. Cmr Chemical Shifts[a] of the 1,2-Dimethylnorbornyl Cation and Their Assignments[b]



Carbon atom	Chemical shifts (±1)	$J_{^{13}CH}$, Hz
C_1, C_2[c]	+26	
C_3, C_7[c]	+179	
C_4[d]	+153	152 ± 5
C_5[d]	+170	138 ± 2
C_6[c]	+147	
CH_3[d]	+176	132 ± 2

[a] Relative to $^{13}CS_2$ as external reference. [b] Structure shown is **2**. [c] Chemical shift obtained by monitoring pmr main peak enhancement. [d] Chemical shifts obtained by monitoring pmr ^{13}C statellites.

Table III. Cmr Spectra[a] of the C_1 and C_2 Carbon Atoms of Ion I and Model Ions[b]

Model ion	Model classification	^{13}C chemical shift, C_1,C_2 (obsd), ppm	Adjusted ^{13}C chemical shifts, C_1,C_2 of model ions, ppm
 2	Rapidly equilibrating partial σ delocalization	+26[c] [C_6, +147]	+26[c]
 $CH_3C_1(CH_3)_2\overset{+}{C_2}(CH_3)_2$ 4	Acyclic rapidly[e] equilibrating	−11[c,e]	−17[d]
 5	Symmetrically[f] σ delocalized	+70[c,f]	+50[d]
 6	Partial[f] σ delocalization	+21 [C_6, +141]	+20

[a] Recorded by the indor method[8] with chemical shifts reported relative to external $^{13}CS_2$. Techniques employed were main peak enhancement and monitoring the satellite whenever possible. [b] Model ions were selected on the basis of their possible analogy with the structure of ion I as described under model classification. [c] Observed as an average due to rapid rearrangement leading to equivalence on the nmr time scale. [d] Adjustments (see text) are made to correct for changes expected in going from the basic carbon skeleton of the model ion to that of ion I by analogy with changes observed for other systems (see, for example, G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969), and references therein). [e] Olah, footnote *d*, and G. A. Olah, J. R. DeMember, A. Commeyras, and J. L. Bribes, *ibid.*, **93**, 459 (1970). [f] See G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970), and references therein.

III) is a model for a classical rapidly equilibrating structure of ion I, eq 1. The average cmr chemical shifts observed for C_1, C_2 in ion **4** is −11 ppm.[8] Adjustment of this shift to an estimated average cmr shift of C_1, C_2 in ion I is based on the difference observed between cmr chemical shifts of C_1 in precursors 2,3,3-trimethylbutan-2-ol (C_1 = tertiary carbon atom) and 1,2-dimethylnorbornan-2-ol. This correction yields a corrected average C_1, C_2 shift value of −17 ppm. The average cmr chemical shift value of +26 ppm observed for C_1, C_2 in ion I is, therefore, clearly not compatible with a tertiary, classical rapidly equilibrating structure.

The only model available for structure **3** of ion I is the nonclassical norbornyl cation **5**.[5] The laser Raman spectrum of ion I in 20 mol % solution in $FSO_3H–SbF_5$ at 60°[9] does not contain lines characteristic of norbornonium ion like vibrational modes (ion **5**, 3110 cm^{-1}). Furthermore, by analogy with the observed chemical shift of +70 ppm of C_1, C_2[8] in the norbornyl cation,[5–9] we can predict (based on inductive effect of the CH_3 group) a *maximum* downfield shift to *ca.* +50 ppm for C_1, C_2 in structure **3** of ion I. The differences of 24 ppm between this estimate of the ^{13}C chemical shift of C_1, C_2 in structure **3** of ion I and that observed for ion I, the lack of norbornonium ion like CH stretch in the Raman spectrum of ion I and the chemical shift of C_6 in ion I of +149 ppm (*vide infra*) virtually eliminate **3** as a structural consideration.

C_2 in the 2-methylnorbornyl cation (**6**) has been shown to have a cmr chemical shift of −76 ppm (Table III).[6] C_1 in **6** has a cmr chemical shift of +118 ppm. Correcting this shift for the effect of methyl substitution in ion I, a downfield shift of approximately 3.5 ppm is expected (based on the norcamphor-1-methylnorcamphor model).[10] This gives a final estimate for the cmr chemical shift of C_1 in ion I of +116. The average of these two shifts, C_1 +116 ppm and C_2 −76 ppm, provides a model for the C_1 and C_2 carbon atoms of the equilibrating structure **2** of ion I. Thus, the estimated average cmr chemical shift for C_1, C_2 in a rapidly equilibrating partially delocalized ion with structure **2** is +20 ppm. This estimated shift is very similar to that (+26 ppm) observed for C_1, C_2 in ion I. In addition, the cmr spectra of ions I and **6** show that C_6 in these ions have approximately the same deshielded

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(9) For experimental conditions, see A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1969).

(10) E. Wenkert, A. O. Clouse, D. W. Cochran, and D. Doddrell, *Chem. Commun.*, 1433 (1969).

cmr shifts (C_6 in I, +147 ppm; C_6 in **6**, +141 ppm). The bridging carbon atom C_6 in the norbornyl cation **5** (Table III; the model for ion I with structure **3**) has been shown to have a relatively high cmr shift of +178 ppm.[5] The low and related cmr shifts for C_6 in ions I and **6** are compatible, therefore, only with the partially σ CH_{6exo} delocalized ion with structure **2**.

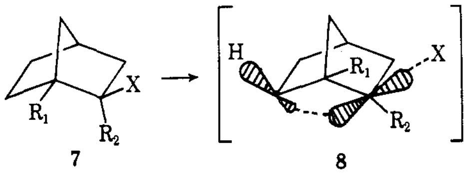
The magnitude of 6,2 σ delocalization in ion I, therefore, is nearly identical with that observed in the case of ion **6**, demonstrating that the structure of ion I may be aptly described as that of a 1-methyl-substituted 2-methylnorbornyl cation (eq 2). Although no substantial change in the amount of 6,2 σ delocalization is observed in going from HC_1 to CH_3C_1, for ion I, the barrier to C_1,C_2 Wagner–Meerwein shift is lowered sufficiently so that it cannot be frozen out on the nmr time scale even at −140°.

The combined ^{13}C and ^1H nmr and Raman spectra of ion I reveal its identity as the first well-characterized example of a partially delocalized rapidly equilibrating carbonium ion, structure **2**, eq 2.

With the structure of stable intermediate ion I verified as **2**, it is interesting to look now at the data that have been reported previously for solvolysis of 1,2-dimethylnorbornyl precursors. Goering and Humski[11] have shown that the ionization of 1,2-dimethyl-*exo*-*p*-nitrobenzoate proceeds to give retention of configuration. If limiting participation of the C_1–C_6 bond occurred in this solvolysis process, formation of a symmetric intermediate or transition state **3** should lead to racemization. Retention, therefore, was interpreted as an indication of the classical nature of ion I. With this evidence for lack of participation of the C_1–C_6 bond, Goering, *et al.*,[11,12] have assigned the $\Delta E_a^{\ddagger}$ ($\Delta E_{endo}^{\ddagger} - \Delta E_{exo}^{\ddagger}$) of 4.3 ± 0.4 kcal for 1,2-dimethylnorbornanol to steric and/or torsional effects. Brown and Rei[13] have emphasized the remarkable similarity in the Goering–Schwene diagram of the solvolysis of *exo*- and *endo*-norbornyl acetates and that of the solvolyses of 1,2-dimethyl-*exo*- and *endo*-norbornyl *p*-nitrobenzoates. They also argued that steric effects are the major contributor to the energy difference of exo and endo transition states in the solvolysis of 1,2-dimethylnorbornyl derivatives. The similarity in the Goering–Schwene diagrams led them to conclude that "...there appears to be no reason to expect that similar steric effects are involved also in the higher energy of the *endo* transition state of the secondary norbornyl system." It was, in fact, generally concluded "...that whatever factor other than (C_1–C_6) participation that is responsible for these characteristics in the tertiary derivative must also contribute to the high *exo–endo* rate and product ratios for norbornyl itself."[11–14]

Recent results in the determination of the structure of the 2-methylnorbornyl cation[14] and the presently reported structural characterization of ion I show that these ions are indeed partially σ-delocalized systems. More importantly, however, it is shown that the major contributor to charge delocalization in ions **6** and I is the CH_{6exo} bond. We have suggested also that a transition state similar to **8** may be generally involved in the ionization of exo-substituted norbornyl derivatives.[5]

We would like to suggest presently that the solvolysis data of precursors **7a–c**,[15] the retention of configuration in the products from **7c**,[12] and the similarity of the Goering–Schwene diagrams for *exo*- and *endo*-1,2-dimethylnorbornyl and those of *exo*- and *endo*-norbornyl derivatives[13] are compatible with a similar structure **8** for the transition states of all these solvolysis reactions. Although controlling steric and torsional effects cannot be ruled out definitely, a general structure of the transition state such as **8** for the solvolyses of all exo-substituted norbornyl derivatives must, therefore, be considered.



7 **8**

a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = R_2 = CH_3$

With precursors **7b**, formation of **8b** is followed by complete ionization to yield the partially σ CH_{6exo} delocalized 2-methylnorbornyl cation (**6**). The 1,2 Wagner–Meerwein shift has a relatively high barrier for this system since it is tertiary–secondary. The ion is, therefore, static and partially delocalized at −78° in super acid and related media.[5] Ionization of precursor **7c** through transition state **8c** leads to the formation of ion I with structure **2**—an equilibrating partially σ CH_{6exo} delocalized ion. The barrier to 1,2 Wagner–Meerwein shift in ion I is very low since it is a degenerate tertiary–tertiary rearrangement. The transition state of 1,2 Wagner–Meerwein shift in ion **1** is shown in eq 2 to have a structure resembling **3**—a nonclassical 1,2-dimethylnorbornonium ion. Since ion I has structure **2** and is rapidly equilibrating, it is obvious that **3** is higher in energy than the equilibrating ion **2**. Similarly, for the norbornyl cation the secondary–secondary 1,2 Wagner–Meerwein shift must involve an intermediate structure analogous to **5**. In contrast to ion I, however, the bridged intermediate structure of 1,2 Wagner–Meerwein shift must be an energy minimum since the nonclassical ion **5** is the only species observed on ionization of **7a**.

Experimental Section

^1H Nmr Spectra. All pmr spectra were recorded at both 60 and 100 MHz using Varian Associates Model A56/60A and HA-100 spectrometers equipped with a variable-temperature probe.

^{13}C Nmr Spectra. ^{13}C spectra were obtained by irradiation of the 100-MHz proton spectrum with a swept 25.1-MHz frequency source (indor method). The detailed techniques employed have been described previously.[8] ^{13}C shifts were computed with respect to TMS as a reference and converted to the carbon disulfide standard by adding 194.6 ppm.

Raman Spectra. Raman spectra were carried out on a Cary 81 Raman spectrophotometer with laser source (50 mW gas laser

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[11] H. Goering and K. Humski, *J. Amer. Chem. Soc.*, 90, 6213 (1968).

[12] H. L. Goering, C. Brown, and C. B. Schwene, *ibid.*, 90, 6214 (1968).

[13] H. C. Brown and M. H. Rei, *ibid.*, **90**, 6216 (1968), and references therein.

[14] See Table III, footnote *f*.

[15] See ref 13, 14, and K. T. Liu, Ph.D. Thesis, Purdue University, 1969, and references therein.

using the 6328 Å He–Ne line) equipped with a variable-temperature Raman cell.

Ir Spectra. Ir spectra were recorded on a Beckman IR-10 spectrophotometer.

Preparation of the Solutions of the 1,2-Dimethylnorbornyl Cations. A saturated solution of freshly distilled SbF_5 (Allied Chemical Corp.) in SO_2 was prepared and cooled to −78°. To this solution was added with continuous vigorous stirring 1,2-dimethylnorbornyl chloride to give *ca.* 10 mol % solution.

1-Methylnorcamphor.[16] Concentrated sulfuric acid (270 g) was added to a solution of 112.5 g of sodium dichromate dihydrate in 840 ml of water in a 2-l. three-necked flask fitted with a mechanical stirrer, a reflux condenser, and dropping funnel. After the resulting mixture was heated to 90°, a solution of 50 g of 2-methyl-*endo*-2-norbornanol in 12 ml of absolute ether was added slowly with vigorous stirring. Stirring was continued for 2 hr more at 90° and the product was then isolated by steam distillation (*ca.* 500 ml of distillate). The distillate was extracted with four 35-ml portions of ether and dried; the solvent was removed by a rotary evaporator at room temperature. About 34 g of the crude product was obtained. The mixture of the crude product and 4.4 g of boric anhydride (prepared by heating 5.1 g of boric acid in a drying pistol under toluene reflux) was heated with stirring at 100° for 2 hr. Fractional distillation through a 25-cm Vigreux column yielded fractions boiling at 58–62° (15 mm) and at 62–63° (15 mm): 28 g (55% yield), 99% pure by vpc. Ir showed a five-membered ring C=O at *ca.* 5.70 μ, and pmr showed a singlet for CH_3 at τ 8.9.

1,2-Dimethyl-2-*endo*-norbornanol.[17] A solution of 1-methylnorcamphor (25 g, 0.20 mol) in ether was added slowly at 0° with stirring to a solution of freshly prepared CH_3MgI (5.4 g, 0.22 mol), Mg turnings (29.5 g, 0.20 g-atom), and CH_3I. The resultant mixture was stirred overnight at room temperature, and then cooled to 0°. The subsequent procedure was the same as that for preparing 2-methyl-*endo*-norborneol. The ether solution of the product was dried over anhydrous magnesium sulfate and Drierite and was decolorized. The solvent was removed *in vacuo* and distillation of the crude product at 60° (0.5 mm) afforded 28 g of 1,2-dimethyl-*endo*-norborneol (92%), mp 32–34° (lit.[15] 34.5–36°). Pmr showed two singlets for CH_3 groups at δ 1.03 and 1.18.

1,2-Dimethyl-2-*endo*-chloronorbornane. A solution of 8 g (0.057 mol) of 1,2-dimethyl-*endo*-2-norbornanol in 14 ml of methanol was added to 68 ml of concentrated hydrochloric acid contained in a separatory funnel. A white flocculent precipitate was formed immediately. The contents in the funnel were shaken for 15 min and then allowed to stand for an additional 2 hr with occasional shaking. The aqueous solution was extracted with petroleum ether and the combined extracts were washed twice with saturated solution of $CaCl_2$ and dried over $CaCl_2$. The solvent was removed *in vacuo* to yield 8.6 g (95.4%) of white flaky solid, mp 122–123° (lit.[18] 120–122°). Infrared yielded no OH absorption. Nmr showed two singlets of CH_3 groups at δ 1.23 and 1.56.

Acknowledgment. Professor Harlan Goering is thanked for a sample of 1,2-dimethylnorbornan-2-ol. The support of the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

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[16] Prepared by modification of the method of Liu.[15]

[17] H. Toivonen, *Suom. Kemistilehti B*, **33**, 66 (1960).

[18] H. C. Brown and M. H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

The Synthesis and Rearrangement of Strained Cage Molecules[1]

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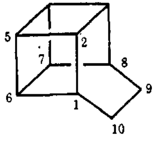
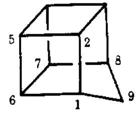
Abstract: The preparation of *cis*-9,10-dicarbomethoxypentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane (**5**, the 1,1′-bishomocubane structure) was effected by the sensitized irradiation of diene diester **4**. Photoproduct **5** was converted to bishomocubanedione **11** by a series of reactions involving saponification, bisoxidative decarboxylation, hydroboration, and two oxidations. The diketone **11**, *via* the diazo ketone **12**, was photochemically ring contracted to pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane-9-carboxylic acid (**13**, the homocubyl structure). X-Ray analyses of both homocubyl and bishomocubyl derivatives were obtained. Oxidative cleavage of dione **11** also yielded *endo,endo*-tetracyclo[4.2.0.$0^{2,5}$.$0^{3,8}$]octane (secocubane) diester **19** which, upon treatment with dimsyl anion, was converted to the isomeric diesters **17** and **21**. The Dieckmann product **23** is postulated as an intermediate in the isomerization. The 1,1′-bishomocubyl system is isomerized to the pentacyclo[4.4.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]decane structure by silver ion. The analogous reaction occurs in the homocubane and secocubane series to yield the pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl and tetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octyl systems, respectively.

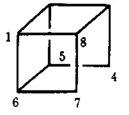
The syntheses of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane (1,1′-bishomocubane, **1**)[3,4] and pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (homocubane, **2**)[3,5] have been described earlier. We wish to report in detail the studies undertaken with cage systems **1** and **2** and to describe the synthesis and reactions of the tetracyclo[4.2.0.$0^{2,5}$.$0^{3,8}$]octane (secocubane) series (**3**).



1



2



3

The photochemical reaction of **4**, in acetone solution, proceeded with intramolecular cycloaddition to yield pentacyclic diester **5**.[3,4] However, direct irradiation of **4** in pentane did not result in formation of photoproduct **5**, indicating that acetone acts as a sensitizer.

Evidence for the correctness of structure **5** was based on spectral data consistent with that expected for the pentacyclic structure and an X-ray analysis

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[2] National Institutes of Health Predoctoral Fellow, 1967–1970.

[3] W. G. Dauben and D. L. Whalen, *Tetrahedron Lett.*, 3743 (1966).

[4] S. Masamune, H. Cuts, and M. Hogben, *ibid.*, 1017 (1966).

[5] (a) C. G. Chin, H. Cuts, and S. Masamune, *Chem. Commun.*, 880 (1966); (b) G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *Tetrahedron Lett.*, 37 (1966); (c) K. V. Scherer, R. S. Lunt, and G. A. Ungefug, *ibid.*, 1199 (1965); (d) P. v. R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, **89**, 698 (1967); (e) R. L. Cargill and T. Y. King, *Tetrahedron Lett.*, 411 (1970).