3-Hydroxycycloalk-1-enecarboxylic Acid (3a,b). The bromo ester (**2a,b**; 0.2 mol) was dissolved in Me_2SO (200 mL) and then a solution of KOH (20 g) in water (35 mL) was added at room temperature. After being stirred for 1 h, the mixture was cooled to 5 °C and filtered. The filtered K salt was suspended in water (100 mL) and dilute H_2SO_4 added (20%, 100 mL). Filtration afforded the hydroxy acids (**3a,b**). **3a:** 19.1 g; 48.2%; mp 152 °C from acetone–Et_2O; NMR (Me_2SO) 12.2 (1 H, s), 6.48 (1 H, d, J = 10 Hz), 4.8 (1 H, s), 4.6 (1 H, m), 2.5 (2 H, m), 1.4 (12 H, m); IR (Nujol) 3450, 1700, 1650 cm^{-1}; UV 215 nm (ϵ 10 500). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.46; H, 9.23.

3b: 21.5 g; 50.7%; mp 149 °C from acetone–Et_2O; NMR (Me_2SO) 6.43 (1 H, d, J = 10 Hz), 4.48 (2 H, m, CHOH and CHOH), 2.5 (4 H, m), 1.4 (12 H, m); IR (Nujol) 3400, 1710, 1680, 1650 cm^{-1}; UV 216 nm (ϵ 9100). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.44; H, 9.61.

3-Oxocycloalk-1-enecarboxylic Acid (4a,b). The hydroxy acid (**3a,b**; 0.1 mol) was dissolved in acetone (200 mL) and oxidized with an excess of Jones reagent at 10 °C. Usual workup afforded the corresponding keto acid (**4a,b**). **4a:** 17.4 g; 89%; mp 144 °C from Et_2O–pentane; NMR ($CDCl_3$) 11.2 (1 H, s), 7.32 (1 H, s), 2.6 (4 H, m), 1.9–1.2 (10 H, m); IR (Nujol) 1700, 1635 cm^{-1}; UV 232 nm (ϵ 5800). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.44; H, 8.18.

4b: 19.9 g; 95%; mp 94 °C from Et_2O–pentane; NMR ($CDCl_3$) 10.7 (1 H, s), 7.33 (1 H, s), 2.8 (2 H, m), 2.55 (2 H, m), 1.9–1.2 (12 H, m); IR (Nujol) 1695, 1630 cm^{-1}; UV 239 nm (ϵ 7300). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.36; H, 8.54.

3-Oxocycloalk-1-enecarbonyl Azide (5a,b). To a solution of the keto acid (**4a,b**; 0.1 mol) in acetone (150 mL) and water (50 mL) at 0 °C was added triethylamine (0.12 mol) followed by the slow addition of ethyl chloroformate (0.11 mol) in acetone (25 mL). The mixture was stirred for 30 min at 0 °C and then a solution of sodium azide (0.15 mol) in water (30 mL) was added dropwise. After 30 min of stirring, the mixture was poured into water (300 mL) and extracted with Et_2O (2 × 150 mL). The ether extract was washed with water and dried. Solvent was removed in vacuo at room temperature to leave the 3-oxocycloalk-1-enecarbonyl azide (**5a,b**). **5a:** 17.9 g; 81%; mp 73–75 °C from pentane; NMR ($CDCl_3$) 7.34 (1 H, s), 2.6 (4 H, m), 1.9 (2 H, m), 1.6–1.2 (8 H, m); IR (Nujol) 2160, 1700, 1640 cm^{-1}; UV 237 nm (ϵ 11 600). Anal. Calcd for $C_{11}H_{15}O_2N_3$: C, 59.71; H, 6.83; N, 18.99. Found: C, 59.59; H, 6.90; N, 18.81.

5b: 21.6 g; 92%; mp 55.5–56.5 °C from pentane; NMR ($CDCl_3$) 7.27 (1 H, s), 2.77 (2 H, m), 2.5 (2 H, m), 1.9–1.2 (12 H, m); IR (Nujol) 2150, 1700, 1630 cm^{-1}; UV 247 nm (ϵ 9400). Anal. Calcd for $C_{12}H_{17}O_2N_3$: C, 61.25; H, 7.28; N, 17.86. Found: C, 61.16; H, 7.32; N, 17.78.

Cycloalkane-1,3-dione (6a,b). The 3-oxocycloalk-1-enecarbonyl azide (**5a,b**; 0.1 mol) was dissolved in dry benzene (300 mL) and the solution was then heated until no more nitrogen evolved (1 h). Removal of benzene in vacuo afforded a liquid which was dissolved in dioxane (90 mL); 15% aqueous hydrochloric acid (300 mL) was then added and the mixture heated under reflux for 1.5 h. After cooling, the mixture was extracted with Et_2O (3 × 100 mL). The Et_2O extract was washed with water and dried. Vacuum distillation of the residue from the solvent evaporation afforded pure cycloalkane-1,3-dione (**6a,b**). **6a:** 11.1 g; 66%. **6b:** 12.2 g; 67%.

Methyl Ester of 4a. This compound was obtained in quantitative yield by esterification of **4a** with CH_2N_2: mp 69.5–70.5 °C from hexane; NMR ($CDCl_3$) 7.29 (1 H, s), 3.78 (3 H, s), 2.55 (4 H, m), 2–1.1 (10 H, m); IR (Nujol) 1705, 1685, 1610 cm^{-1}; UV 230 nm (ϵ 7600). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.51; H, 8.67.

Irradiation of the Methyl Ester of 4a. The methyl ester of **4a** (1 g) was dissolved in benzene (300 mL), N_2 was bubbled through the solution for 5 min, and irradiation (high-pressure Hg lamp, 125 W, Pyrex filter) was carried out for 8 h. After solvent evaporation, silica gel (30 g) column chromatography of the residue (eluant hexane–Et_2O, 9:1 v/v) afforded (*Z*)- (353 mg) and (*E*)-3-(methoxycarbonyl)cyclodec-3-enone (560 mg).

The NMR ($CDCl_3$) spectrum of the photolysate mixture at short-time irradiation (1.5 h) shows the presence of four unsaturated products: the starting Δ^2 isomer (17%, s, δ 7.29), the (*E*)-Δ^3 isomer (54%, t, δ 6.98), the (*Z*)-Δ^3 isomer (12%, t, δ 6.17), and the stereoisomer of the starting material (17%, s, δ 6.46).

Communications

Relative Stabilities of Secondary Methylnorbornyl Cations

Summary: Force-field calculations are used to examine alternative comparisons for the energetics of rearranging secondary carbocations in the alicyclic and norbornyl series to their tertiary isomers.

Sir: The heat of isomerization of the secondary 4-methyl-2-norbornyl cation (**1**) to the tertiary 2-methyl-2-norbornyl cation (**2**) (eq 1) has been recently reported.[1] Comparison with the isomerization of the secondary butyl to the tertiary butyl cation (eq 2) led to the conclusion that **2** enjoys special thermodynamic stability amounting to ca. 7.6 kcal/mol, but the source of this difference could not be established by this single experiment.[1,2] Since no other stable secondary ions could be found whose heat of isomerization in solution might reasonably be determined ex-

$$; \Delta H_1 = -6.6 \text{ Kcal/mol} \qquad (1)$$

$$; \Delta H_2 = -14.2 \text{ Kcal/mol} \qquad (2)$$
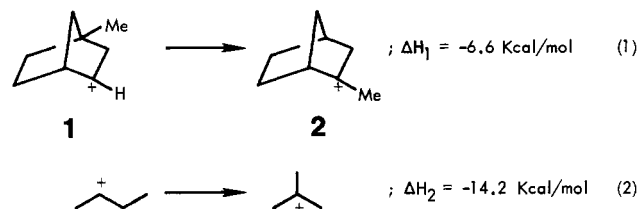
perimentally,[2] it appeared that our base of comparison could be expanded through molecular mechanics (force field) calculations. This method has been applied fruitfully for the calculation of carbocation stabilities and those of related transition states.[3] Until other experimental ex-

(1) Arnett, E. M.; Pienta, N.; Petro, C. *J. Am. Chem. Soc.* **1980**, *102*, 398.

(2) Arnett, E. M.; Pienta, N., personal communication; the present work has benefited substantially from extensive discussions and correspondence with Professor E. M. Arnett.

(3) (a) The application of force-field calculations on carbocations was pioneered by Professor P. v. R. Schleyer; cf.: Gleicher, G. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 582. (b) The method of calculation and references to other uses of it is given in: Fărcaşiu, D. *J. Org. Chem.* **1978**, *43*, 3878. (c) The BIGSTRAIN program was used: Andose, J. D.;

Table I. Calculated Heats of Formation of Secondary Methyl-2-norbornyl Cations

ion	1-Me	3-exo-Me	3-endo-Me	4-Me	5-exo-Me	5-endo-Me	6-exo-Me	6-endo-Me	7-syn-Me	7-anti-Me
ΔH_f°, kcal/mol	-14.12	-11.69	-11.05	-14.24	-11.65	-10.95	-12.02	-11.84	-10.33	-10.18
$\Delta\Delta H_f^\circ$, kcal/mol	0.12	2.55	3.19	0	2.59	3.29	2.22	2.40	3.91	4.06

amples of secondary to tertiary rearrangements can be found, these calculations should serve to partially illuminate the problems of comparing substituted bicyclic cations with acyclic models.

I report here on empirical force-field calculations[3] on 1 and its isomers with the methyl substituent in different positions of the norbornane skeleton, undertaken in order to assess the contribution of the stability of the hydrocarbon skeleton in 1 and 2 to the energetics of eq 1. The results (heats of formation of carbocations) are given in Table I. It must be noted that such comparisons are valid only for closely related species; we do not attempt to include in the same correlation the tertiary ion 2 or the parent 2-norbornyl cation. For limited reaction series, such as the isomers in Table I, the results of force-field calculations are probably reliable within 1 kcal/mol or less.[3]

The calculations indicate that the isomers with the substituent at the bridgehead are more stable. This is a rather general effect in hydrocarbons[4] and it was also observed by Sorensen[5] for tertiary analogues of 1 and 3. The 2,4-dimethylnorbornyl cation (analogue of 1) was found "much more stable" than other isomers, like the 2,3-dimethylnorbornyl cation (analogue of 3), none of which was found in equilibrium with the former and the 1,2-dimethyl isomer.[5] The calculations agree with his findings.

In order to eliminate such second-order effects, the secondary ion 1 should be replaced in eq 1 by an isomer (e.g., exo- or endo-3)[6] with the same skeleton as 2 (eq 3).

$$\Delta H_3 = -9.1 \ldots -9.8 \text{ Kcal/mol} \quad (3)$$
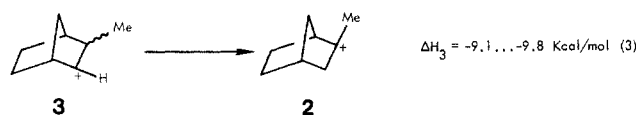
The model used in eq 2 suffers from the same drawback, since the measured ΔH_2 reflects not only the secondary/tertiary difference but also the rearrangement of the chain from linear to branched. Equations 4 and 5 offer

$$\Delta H = -2; -3 \text{ Kcal/mol} \quad (4)$$

$$\Delta H = -6 \text{ Kcal/mol} \quad (5)$$
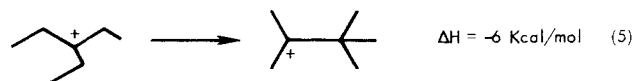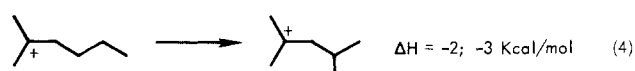
examples of the latter effect in tertiary carbocations.[7] Actually, from studies of the composition of mixtures of isomeric alkyl carbocations in super acids it has been concluded that their relative stability is determined more by nonbonded interactions than by electronic effects.[8] Therefore, an appropriate model to test the secondary/tertiary difference should be a pair with the same carbon skeleton, like 4 and 5 in eq 6. The enthalpy change for

(a) R = R' = H; (b) R = Me, R' = H; (c) R = R' = Me
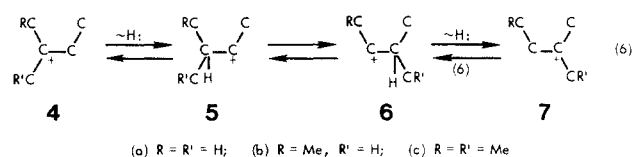
the conversion of 4 to 5 can be calculated as the difference between the activation enthalpy for the isomerization of 4 to 7 and the activation enthalpy for the alkyl group shift 5 → 6, as discussed already by Saunders.[9a]

From the study of several such carbocation rearrangements, Brouwer and Hogeveen have concluded that the alkyl shift is the rate-determining step; it has a higher barrier than the hydride migrations 4 → 5 and 6 → 7.[8]

For R = R[1] = H, eq 6a represents the methyl group scrambling in the tertiary pentyl cation. Its activation enthalpy has been measured in two laboratories:[9] $\Delta H^\ddagger$ = 14.3 ± 0.5 kcal/mol ($\Delta S^\ddagger$ = -1.2 ± 1.1 eu[10]). A similar $\Delta H^\ddagger$ value (13.4 kcal/mol) was determined for the isomerization of the 3-methyl-3-pentyl (4b) to the 2-methyl-2-pentyl cation (7b, eq 6b).[8] No $\Delta H^\ddagger$ value was reported for the conversion of 4c to 7c (ethylpentyl cations, eq 6c) but the $\Delta G^\ddagger$ value is very close to that for the lower homologue (eq 6b).[8]

The activation enthalpy of the methyl migration could not be measured for any of the pairs 5 and 6. A reasonable model exists in the methyl shift in the 2,3,3-trimethyl cation, which has $\Delta G^\ddagger$ = 3.5 kcal/mol at -136 °C.[12] At such low a temperature $\Delta G^\ddagger$ is very close to $\Delta H^\ddagger$. The

Engler, E. M.; Collins, J. B.; Hummel, J. P.; Mislow, K.; Schleyer, P. v. R. QCPE, 1979, 11, 348. (d) For other pertinent work, see: Harris, J. M.; Shafer, S. G.; Smith, M. R.; McManus, S. Tetrahedron Lett. 1979, 2089.

(4) (a) These stabilization effects have been found reasonably constant for wide series of compounds: Allinger, N. L., personal communication. (b) See also: Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. J. Am. Chem. Soc. 1973, 95, 8005. (c) I acknowledge the suggestion of Professor H. C. Brown that this factor could contribute to the difference reported in ref 1.

(5) Haseltine, R.; Ranganayakulu, K.; Wong, N.; Sorensen, T. S. Can. J. Chem. 1975, 53, 1901.

(6) It has been stated (ref 13) that in order to estimate the energy difference between the "hypothetical classical secondary 2-norbornyl cations" 1 and 3, a correction for the electronic stabilizing effect of the β-methyl group in 3 (mostly the difference between C^+-C-CH$_3$ and C^+-C-H hyperconjugation) should be introduced. The importance of such effects has been questioned even for acyclic carbocations in super acids (cf. text and ref 8). In rigid systems, which cannot orient themselves to provide optimum geometry for such interactions, the effect should be even smaller. This is shown even in one of the papers cited in ref 13 (footnote 4b) in which elimination of the correction would explain better the newer experimental data (Schleyer, P. v. R.; Grubmüller, P.; Maier, W. F.; Vostrowsky, O.; Skatebøl, L.; Holm, K. H. Tetrahedron Lett. 1980, 21, 921). In other similar studies, introduction of this correction would result in a poorer correlation of data, and no correction was used: Bingham, R. C.; Schleyer, P. v. R. J. Am. Chem. Soc. 1971, 93, 3189. On the other hand, even for nonrigid systems, where the geometry could allow stronger hyperconjugative interactions in nonbridged ions, the electronic effect of methyl substituents in bridged ions is unimportant (Wilcox, C. F., Jr.; Loew, L. M.; Jesaitis, R. G.; Belin, S.; Hsu, J. N. C. J. Am. Chem. Soc. 1974, 96, 4061). Therefore, no correction of the kind proposed in ref 13 can be used in order to evaluate the possible stabilization by bridging in 3.

(7) These values are for ions in the gas phase: Meot-Ner, M.; Solomon, J. J.; Field, F. H. J. Am. Chem. Soc. 1976, 98, 1025. In each pair, the number of β-C-C and β-C-H bonds is the same for the two isomers, so that hyperconjugative stabilization should be roughly the same.

(8) Brouwer, D. M.; Hogeveen, H. Prog. Phys. Org. Chem. 1972, 9, 179.

(9) (a) Saunders, M.; Hagen, E. L. J. Am. Chem. Soc. 1968, 90, 2436 ($\Delta H^\ddagger$ = 14.8 kcal/mol, $\Delta S^\ddagger$ = -0.05 eu). (b) Brouwer, D. M. Recl. Trav. Chim. Pays-Bas 1968, 87, 210 ($\Delta H^\ddagger$ = 13.75 kcal/mol, $\Delta S^\ddagger$ = -2.29 eu).

(10) The reported $\Delta S^\ddagger$ values[9a,b] are both within the usual range for rearrangements by hydride and alkyl shifts in carbocations, which is from 0 to -6 eu.[11]

(11) Examples of activation parameters for carbocation rearrangements can be obtained from: (a) Telkovski, L. A.; Saunders, M. In "Organic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 15; (b) ref 8; (c) Brouwer, D. M. Recl. Trav. Chim. Pays-Bas 1968, 87, 611; (d) Olah, G. A.; White, A. M.; DeMember, J. R.; Commeyras, A.; Lui, C. Y. J. Am. Chem. Soc. 1970, 92, 4627; (e) Saunders, M.; Vogel, P. Ibid. 1971, 93, 2561; (f) Haseltine, R.; Huang, E.; Rangayanakulu, K.; Sorensen, T. S. Can. J. Chem. 1975, 53, 1056; (g) Hewett, A. P. W. Ph.D. Thesis, Yale University, 1975; (h) Borodkin, G. I.; Shakirov, M. M.; Shubin, V. G.; Koptyug, V. A. Zh. Org. Khim. 1976, 12, 1297.

secondary–secondary ion conversion **5** → **6** might have a lower barrier than the tertiary–tertiary ion conversion involved in the model.[13] Taking 3 kcal/mol as a rough estimate of the activation enthalpy of the methyl shift in **5**,[14] we can calculate the energy differences between cations **4a** and **5a** (eq 6a), and between cations **4b** and **5b** (eq 6b) as shown in eq 7a and 7b, respectively. Comparison of

$$\Delta H_7^{(a)} = 14.3 - 3 = 11.3 \text{ kcal/mol} \qquad (7a)$$

$$\Delta H_7^{(b)} = 13.4 - 3 = 10.4 \text{ kcal/mol} \qquad (7b)$$

eq 3 and 7 provides a measure of the excess stability of the 3-methyl-2-norbornyl cations **3** over the acyclic models 3-methyl-2-butyl and 3-methyl-2-pentyl cations: 1.5–2.2 and 0.6–1.3 kcal/mol, respectively. It has to be remembered that the range in each case is determined by the difference in strain between the two stereoisomers of **3**; the lower limits would have to account for any electronic stabilization in the 3-*endo*-methyl-2-norbornyl cation.[15]

The excess stability of the 2-norbornyl cation over "normal" secondary cations has been discussed in terms of structure (bridged or not bridged) for the former.[16] As Arnett pointed out, stabilization over a model cannot by itself prove the existence of bridging, since the latter is a structural characteristic. An abnormal stability of a secondary ion indicates, however, that there should be a structural reason for it.[1,17] Naturally, parameters like the tertiary/secondary ion energy difference are influenced by several structural features, so that a range should be expected, rather than a constant value in all cases.[18] Thus, the value for 2-nonbornyl cations (eq 3) is better considered in the perspective of not only simpler models, like eq 6, but also more complex models, like the recently reported 2-adamantyl/1-adamantyl ion pair (eq 8).[19]

$$\Delta H_8 = -4 \text{ kcal/mol} \qquad (8)$$

Addendum: In the accompanying paper, Schleyer and Chandrasekhar[13] offer a criticism of the present analysis. I will not comment further upon their selection and treatment of data.[6,14,15] I am somewhat puzzled by the trust which they place in MINDO/3 calculations,[20] as well

as by an apparent lack of consistency: if MINDO/3 can be used to determine indirectly the stabilization of the "nonclassical" 2-norbornyl cation,[13] why should we not trust the direct MINDO/3 calculation which predicts the nonbridged 2-norbornyl cation to be the more stable by 2 kcal/mol?[21,22]

I want to emphasize, however, that the actual structure of the 2-norbornyl cation(s) is at best of peripheral interest for this work. Two types of methods have been consistently used to ascertain carbocation structures. The first is the direct structure analysis, basically by spectroscopic means; the second is the energy comparison method by which the actual energy content of an ion is compared with the value predicted for a certain structure of the ion (normally the nonbridged structure). If there is a discrepancy, a different structure is assigned (usually a bridged one). Each such comparison involves four species (e.g., eq 3 and 6a, eq 3 and 6b, eq 3 and 8). For each species the energy content is determined by a number of factors, electronic and steric; the contribution of bridging in one species, if any, is normally less important than the combined variability of all other factors for the four species involved in comparison. In particular, the energy difference for eq 3, which includes a secondary 2-norbornyl cation is very close to the figures for the model eq 6a, and especially 6b, and is larger than the figure for the model eq 8. Therefore, it appears that at the present level the energy comparison method cannot be used reliably to assign carbocation structures; instead, direct structure determinations should be attempted.[23]

(12) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 7082.

(13) Schleyer, P. v. R.; Chandrasekhar, J. *J. Org. Chem.*, following paper in this issue. Professor P. v. R. Schleyer is acknowledged for sending me a copy of that work prior to its publications.

(14) In ref 13 the barrier is taken as zero. This implies that in the process **4a** → **7a** the system is effectively at the tranisition state from **5a** to **6a**. Alternatively, **5a** would be an energy maximum. As mentioned in the text, studies on other carbocation rearrangements contradict this assumption and indicate the methyl shift as the rate-determining step (ref 8). Moreover, the relative rates of hydrogen and carbon exchange for the 2-propyl cation in super acid indicate that even the primary 1-propyl cation is not a transition state, but a real intermediate, for which both hydride shift to the secondary ion and cyclization to protonated cyclopropane (equivalent to methyl shift in **5a**) involve energy barriers, the former being actually slightly lower (Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *6*, 53). The same conclusion was reached for 1-propyl cations generated electrochemically (Laurent, E.; Thomalla, M.; Marquet, B.; Burger, U. *J. Org. Chem.* **1980**, *45*, 4193).

(15) Because only *exo*-**3** and **5a** are discussed in ref 13 the stabilization energy of **3** arrived at in that work is apparently higher.

(16) Brown, H. C. "The Nonclassical Ion Problem" (with comments by P. v. R. Schleyer); Plenum Press: New York, 1977.

(17) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522.

(18) The equivalent of this parameter in solvolysis reactions, the α-methyl group effect on rates, has been discussed: Fărcaşiu, D. *J. Am. Chem. Soc.* **1976**, *98*, 5301. See also: Brown, H. C.; Ravindranathan, M.; Gundu Rao, C.; Chloupek, F. J.; Rei, Min-Hon *J. Org. Chem.* **1978**, *43*, 3667.

(19) Wesdemiotis, C.; Schilling, M.; Schwarz, H. *Angew. Chem.* **1979**, *91*, 1017. Houriet, R.; Schwarz, H. *Ibid.* **1979**, *91*, 1018.

(20) From the papers cited in ref 13 we find that MINDO/3 (a) predicts *n*-butane to be more stable than isobutane by 6.5 kcal/mol (Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294), (b) predicts the 2-propenyl cation to be more stable than the allyl cation by 8.4 kcal/mol (Köhler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1979**, *101*, 3479), and (c) predicts the 7-norbornyl cation, "a species legendary in its inertness", to be more stable than the 2-norbornyl cation by 3.1 kcal/mol (Schleyer, P. v. R. In ref 16, p 100; the discussion on that page of the MINDO/3 method is illuminating).

(21) Reference 16, p 97.

(22) This is not a denial of the usefulness of the MINDO/3 method for any case; as any other parametric method, however, it is reliable only inside its range of parameterization; also, one should not reach conclusions based on differences well below the recognized uncertainty of the method.

(23) (a) Reference 13 cites measurements indicating a bridged structure. (b) For a different interpretation of data in super acid solution, see: Kramer, G. M. *Adv. Phys. Org. Chem.*, **1975**, *11*, 177. (c) See also: Beauchamp, J. L. "Abstracts of Papers", 177th National Meeting of the Americal Chemical Society, Honolulu, HI, Apr 1979; American Chemical Society: Washington, D.C., 1979; ORGN-3. (d) For a report on trapping the unsymmetrical 2-norbornyl cation in solvolyses, see: Saito, S.; Moriwake, T.; Takeuchi, K.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2634.

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Evaluation of the Extra Stability of the Bridged 2-Norbornyl Cation

Summary: The extra stabilization due to bridging in the nonclassical secondary 2-norbornyl cation is evaluated to be 6 ± 1 kcal/mol in stable ion media.