

crystallized: mp 129 °C; IR (CHCl₃) 2970, 1140 cm⁻¹; ¹H NMR (CDCl₃) δ 4.10 (2 H, m), 3.85 (1 H, s), 2.6-0.6 (11 H, complex); mass spectrum, *m/e* (relative intensity) 188/186 (11/36), 79 (100).

4-anti-Bromo-1-isopropyl-2-oxadamantane (10). A 350-mg sample of **1a** (1.77 mmol) was treated with thionyl bromide as described for the synthesis of **8**. The yield was 118 mg (26%) of **10** as a yellowish oil: IR (CHCl₃) 2950, 1050 cm⁻¹; ¹H NMR (CDCl₃) δ 4.55 (1 H, m), 4.04 (1 H, m), 2.6-1.1 (11 H, complex), 0.88 (6 H, d); mass spectrum, *m/e* (relative intensity) 260/258 (15/16, M⁺), 217/215 (7/7), 179 (17), 174 (51), 172 (54), 123 (70), 91 (90), 43 (100).

2-anti-Iodo-4,4-dimethyladamantane (23). A 185-mg sample of **1a** (0.93 mmol) was refluxed overnight in 57% hydriodic acid. After cooling the reaction mixture was diluted with water and extracted with methylene chloride. After the usual workup, 149 mg (52%) of **23** as a colorless liquid was obtained which turned dark after some hours at room temperature: IR (CHCl₃) 2950, 1460 cm⁻¹; ¹H NMR (CDCl₃) δ 5.37 (1 H, m), 2.5-1.2 (12 H, complex), 1.10 (6 H, s); ¹³C NMR (CDCl₃) δ 47.0 (C³), 44.6 (C²), 39.0 (C⁴), 37.4 (C¹), 36.7 (C⁵), 34.9 (C⁸), 34.7 (C⁹), 34.1 (C⁶), 28.8 (C¹⁰), 28.5 (C⁷), 27.5 (2CH₃); mass spectrum, *m/e* (relative intensity) 163 (100) (M⁺ - I).

2-anti-Bromo-4,4-dimethyladamantane. A 158-mg sample of **1a** (0.81 mmol) was refluxed overnight in 48% hydrobromic acid. After cooling, the reaction mixture was diluted with water and extracted with methylene chloride. The usual workup afforded 33 mg (16%) of 2-anti-bromo-4,4-dimethyladamantane as a colorless liquid: IR (CHCl₃) 2950, 1460 cm⁻¹; ¹H NMR (CDCl₃) δ 5.12 (1 H, m), 2.5-1.2 (12 H, complex), 1.10 (6 H, s); ¹³C NMR (CDCl₃) δ 61.7 (C²), 45.7 (C³), 38.9 (C⁴), 36.4 (C⁵), 36.1

(C¹), 34.6 (C⁹), 33.6 (C⁶), 33.2 (C⁸), 28.1 (C¹⁰), 27.4 (2CH₃), 27.1 (C⁷); mass spectrum, *m/e* (relative intensity) 163 (100) (M⁺ - Br).

Adamantane-2,4-dione (17). A 200-mg sample of **1c** (1.10 mmol) were dissolved in 20 mL water and 25 mL concentrated sulfuric acid. The mixture was refluxed overnight, and after it cooled, 50 mL water was added. The usual workup with chloroform afforded 50 mg (22%) of **17** as a white solid: mp 282-283 °C; IR (CHCl₃) 2940, 2860, 1730, 1700 cm⁻¹; ¹H NMR (CDCl₃) δ 3.40 (1 H, m), 2.76 (2 H, m), 2.5-1.5 (9 H, complex); ¹³C NMR (CDCl₃) δ 207.6 (C^{2/4}), 68.3 (C³), 45.0 (C^{1/5}), 44.0 (C¹⁰), 38.2 (C^{6/8}), 30.0 (C⁹), 26.0 (C⁷); mass spectrum, *m/e* (relative intensity) 164 (100, M⁺), 136 (14), 79 (78).

Anal. Calcd for C₁₀H₁₂O₂: C, 73.14; H, 7.37. Found: C, 73.08; H, 7.54.

The ¹³C NMR data of 4-oxa-5-homoadamantane derivatives will be published in a forthcoming paper.

Acknowledgment. We are indebted to Professor Dr. E. Wenkert for helpful discussions. We are also grateful to Dr. D. Müller (Bochum) for recording the mass spectra as well as to Mrs. E. Sauerbier for her skillful assistance in some syntheses. This work was supported by the Fonds der Chemischen Industrie.

Registry No. **1a**, 66483-57-6; **1b**, 66483-52-1; **1c**, 79499-77-7; **6**, 78726-35-9; **7**, 78726-38-2; **8**, 78726-36-0; **9a**, 79499-78-8; **9b**, 79499-79-9; **10**, 78726-37-1; **12a**, 79499-80-2; **17**, 19214-00-7; **19a**, 79548-72-4; **19b**, 79499-81-3; **19c**, 56820-19-0; **21**, 18971-91-0; **23**, 79499-82-4; **24**, 56781-86-3; **25**, 56781-85-2; *endo*-bicyclo[3.3.1]non-6-ene-3-carboxylic acid, 21932-98-9; 2-anti-bromo-4,4-dimethyladamantane, 79499-83-5.

Vinyl Cations. Comparison of Gas-Phase Thermodynamic and Solvolysis Data with ab Initio MO Calculations

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Ab initio MO calculations with the STO-3G basis set level on cyclic and acyclic methyl- and phenyl-substituted vinyl cations have been used, in combination with the experimental heat of formation of the parent vinyl cation, to evaluate ΔH_f° values for a set of vinyl cations. Comparison of these thermodynamic values with solvolysis data shows that only one-quarter of the stabilizing influence of substituents is effective in the solvolysis transition states. The slow solvolysis rates of vinyl compounds are thus not primarily due to the low stability of vinyl cations but to an unusually high kinetic barrier between vinyl derivatives and the corresponding ionic intermediates.

A knowledge of relative carbenium ion stabilities is essential for the interpretation of reactions involving carbocations and is being used to help design syntheses via cationic intermediates.¹ In principle, such relative stabilities may be obtained from solvolysis data or from thermochemical studies. However, only a few gas-phase heats of formation have been determined. Utilization of reactivity data in solution requires that solvolysis transition states resemble the corresponding carbenium ions energetically. Furthermore, published solvolysis rates have been measured under different conditions with varying leaving groups so that a consistent set of data is not available. Therefore, we have now used molecular orbital calculations to gather such thermochemical information.

Earlier computational treatments of vinyl cations concentrated on structures and the relative stabilizing abilities of α or β substituents.² We now extend this work on polysubstituted and cyclic systems in order to obtain heats of formation of vinyl cations with widely varying substitution patterns (1-13).


Calculations were carried out at the restricted Hartree-Fock level by using the ab initio SCF-MO GAUSSIAN 70 series of programs.³ Partial geometry optimizations

(1) (a) Mayr, H. *Angew. Chem., Int. Ed. Engl.* 1981, 20, 184. (b) Mayr, H.; Schütz, F. *Tetrahedron Lett.* 1981, 925. (c) Mayr, H.; Seitz, B.; Halberstadt-Kausch, I. K. *J. Org. Chem.* 1981, 46, 1041.

(2) (a) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1973, 95, 6531. (b) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Org. Chem.* 1977, 42, 3004. (c) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* 1977, 99, 5901. (d) Apeloig, Y.; Collins, J. B.; Cremer, D.; Bally, T.; Haselbach, E.; Pople, J. A.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* 1980, 45, 3496. (e) Krishnan, R.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1981, 103, 5649.

(3) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A.; QCPE Program No. 236, Indiana University Bloomington, IN.

Table I. STO-3G Optimized Structures of Cyclic Vinyl Cations 9-11 in Comparison with 4

	angle, deg; bond length, Å			
	2-butenyl (4)	1-cyclohexenyl (9)	1-cyclopentenyl (10)	1-cyclobutenyl ^{2d} (11)
C ₂ C ₁ C ₄	179.0	155.6	140.7	124.2
C ₁ C ₁ C ₃	125.8	106.8	93.3	71.5
C ₁ C ₁ C ₅		100.1	89.2	
C ₁ C ₂	1.284	1.270	1.274	1.250
C ₁ C ₄	1.481	1.457	1.483	1.479
C ₂ C ₃	1.543	1.577	1.587	1.733

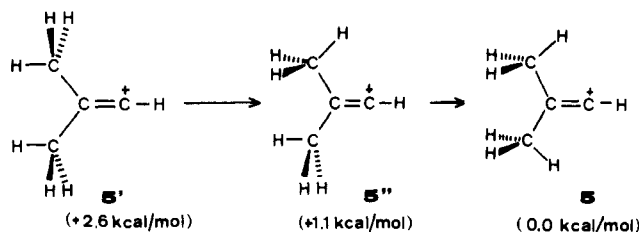
involving the heavy-atom framework and the CCH angles were performed with the STO-3G minimal basis set⁴ by using analytically calculated gradients.^{5,6} Complete optimizations were carried out for the linear systems with less than five carbon atoms.⁷

Results and Discussion

Geometry. Acyclic vinyl cations prefer linear arrangements at the positive carbon; for systems in which exact linearity is not allowed by symmetry, deviations of less than 1° are calculated. The C=C bond lengths are practically unaffected by substitution (1.281–1.286 Å). This value for 1 is 1.262 Å with the much larger 6-31G* basis.^{2e}

For 7 and 8, the previously calculated minimum energy conformation with a perpendicular phenyl ring^{2b} was enforced by symmetry constraints. Optimization of the benzene ring of 7 resulted in elongation of the C_r-C_o (1.440 Å) and the C_m-C_p bonds (1.407 Å) and in shortening of the C_o-C_m bond (1.372 Å); an energy gain of 2.9 kcal/mol relative to the partially optimized structure^{2b} resulted. The benzene ring geometry is closely similar to that calculated for the benzyl cation.⁸

In agreement with findings for the β-methylvinyl cation 3,^{2a} the β,β-dimethylvinyl cation 5 prefers the conformation



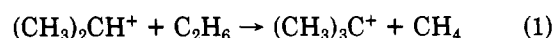
with the cis hydrogens in the plane of the empty p orbital. Consequently, similar conformations were selected for 6 and 8. Eclipsed conformations were chosen for the α-methyl groups in 4 and 6. Such conformations were calculated to be slightly more stable than the perpendicular arrangement in cation 2.^{2a}

The geometries of the cyclic vinyl cations 9–11 reflect the tendency of vinyl cations to adopt linear arrangements. Unusually large C₂C₁C₄ angles, almost complete flattening of the rings, and decrease of the adjacent C₁C₂C₃ and C₁C₄C₅ angles result (Table I).

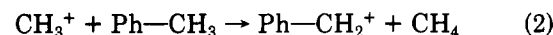
In the cyclohexenyl and cyclopentenyl cations, 9 and 10, the C₁C₂ double bond is slightly reduced in length relative to that in 4 whereas C₂C₃ is considerably elongated (+0.04 Å) in both cases. These trends continue in the 1-cyclo-

butenyl cation 11, which is indicated to have a partially opened (bridged) structure.^{2d}

Energy. Inherent deficiencies of the computational methods are most efficiently eliminated or reduced by employing isodesmic reactions. Thus, reliable energy differences of various carbenium ions may be obtained from high level ab initio MO calculations.^{2e} Naturally, this procedure is limited to small systems. However, if the isodesmic reactions considered involve only one class of carbenium ions, even from STO-3G minimal basis set data, reliable energy values can be obtained. Equations 1 and 2 demonstrate the coincidence of calculated and experimental ΔE values of methyl and phenyl transfer reactions in alkyl cations.⁹



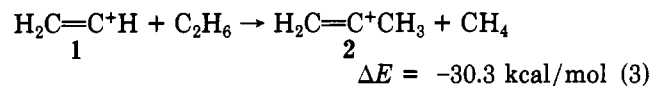
$$\Delta E(\text{STO-3G}) = -20.2 \text{ kcal/mol}^{11}; \Delta E(\text{exptl}) = -20.7,^{12} -22.0^{13} \text{ kcal/mol}$$



$$\Delta E(\text{STO-3G}) = -79.0 \text{ kcal/mol}^{14}; \Delta E(\text{exptl}) = -79.9 \text{ kcal/mol}^{15}$$

In addition, we have reported that there is an excellent agreement between calculated (STO-3G) and experimental ΔE values for methyl-transfer reactions in the series of methyl substituted allyl cations.¹⁰ Therefore, we believe the stabilization energies of eq 3–11, which are based on the total STO-3G energies of Table II, will also be reliable.

α Substitution



(9) Methyl-transfer reactions involving C₂H₅⁺ are not considered in this context because of the problems arising with the nonclassical structure of the ethyl cation (see reference 2e).

(10) Mayr, H.; Förner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 6032; **1980**, *102*, 3663.

(11) Total STO-3G energy for (a) isopropyl cation (-116.027 65 au): Radom, L.; Pople, J. A.; Buss, V.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 311. (b) For ethane (-78.306 18 au) and methane (-39.726 86 au): Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808. (c) For *tert*-butyl cation (-154.639 18 au): Hehre, W. J. In "Applications of Electronic Structure Theory"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. III.

(12) ΔH_f^o for isopropyl (192 kcal/mol) and *tert*-butyl cation (169 kcal/mol): Lossing, F. P.; Semeluk, G. P. *Can. J. Chem.* **1970**, *48*, 955.

(13) ΔH_f^o for isopropyl (187.3 kcal/mol) and *tert*-butyl cation (162.9 kcal/mol): Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.

(14) Total STO-3G energy for (a) CH₃⁺ (-38.779 48 au) and CH₄: ref 11b. (b) For toluene (-266.473 82 au): Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1496. (c) For PhCH₂⁺ (-265.652 31 au): ref 11c.

(15) ΔH_f^o for (a) methyl cation (261 kcal/mol): ref 12. (b) For benzyl cation (211 kcal/mol): Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290.

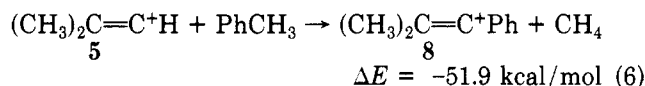
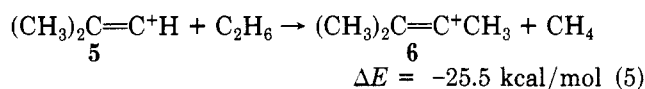
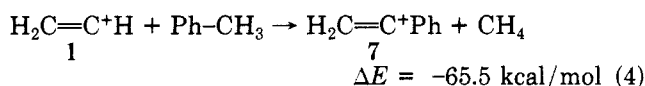
(4) Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2647.

(5) Schlegel, H. B.; Wolfe, S.; Bernardi, F. *J. Chem. Phys.* **1975**, *63*, 3632.

(6) Optimization criterion: δf/δx < 0.01 or until the total energy was constant to better than 0.05 kcal/mol.

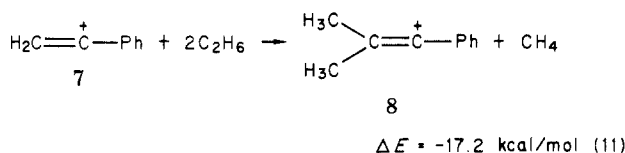
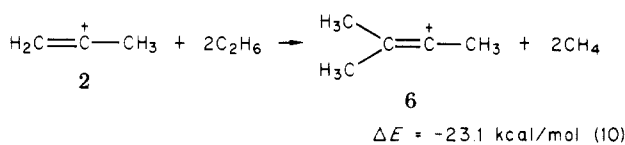
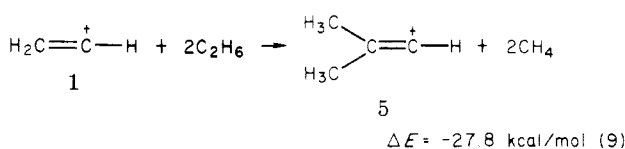
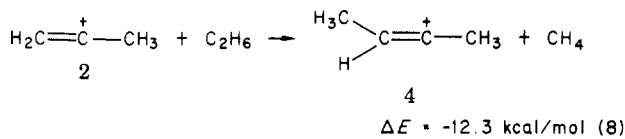
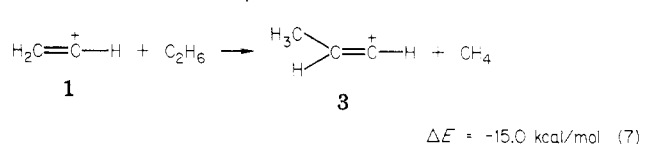
(7) For the extent of optimization see the footnotes of Table II.

(8) Wolf, J. F.; Harch, R. G.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1975**, *97*, 2902.



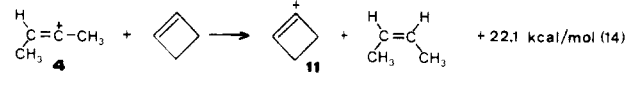
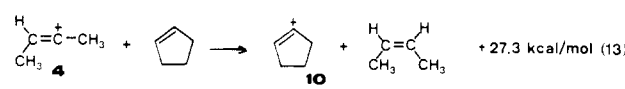
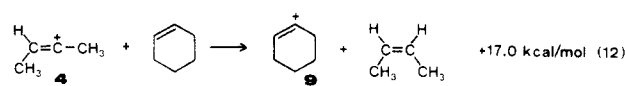
Equations 3 and 4 show that the stabilizing effect of phenyl is approximately twice that of methyl. A similar ratio is found in saturated carbenium ions.¹⁶ From eq 5 and 6 it is evident that the stabilizing effect of α sub-

β Substitution

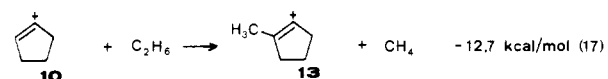
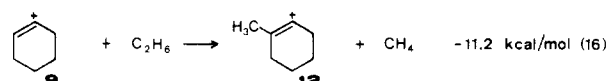
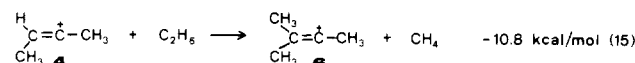


stituents is somewhat reduced if the β -carbon is methyl substituted. Methyl groups at the β -carbon stabilize vinyl cations by 15 (eq 7) and 12 kcal/mol (eq 8), though this position is formally uncharged. This effect has been attributed to hyperconjugation.^{2c} As expected, the β -methylation effect decreases the more the positive charge is stabilized by α substituents (eq 9–11).

Cyclic Vinyl Cations.¹⁸ Cyclic vinyl cations are less stable than the acyclic analogues. According to eq 12 and 13, 1-cyclohexenyl and 1-cyclopentenyl cations are destabilized by 17 and 27 kcal/mol relative to their acyclic counterpart, 4. With a $\text{C}=\overset{\oplus}{\text{C}}-\text{C}$ angle of 155° , the 1-cyclohexenyl cation is not very different from acyclic species. Therefore, eq 12 can be expected to give a reliable ΔE value for the reasons discussed above. In the isodesmic reactions, 13 and 14, carbenium ions of widely different structures are correlated, however, and we cannot be sure that the calculated numbers are accurate. This fact is



stressed by the finding that the isodesmic reaction comparing 2 and 11 displays considerable basis set dependence.^{2d} Eqs 16 and 17 show that methylation of the β -carbon has approximately the same effect in cyclic vinyl cations as in acyclic species (eq 15).



Heats of Formation. The calculated ΔE values of eq 3–17 may be used to evaluate heats of formation of vinyl cations 2–13 on the basis of the experimental ΔH_f° values of the neutral hydrocarbons¹⁹ and of the unsubstituted vinyl cation 1.²⁰ Comparison of the resulting calculated ΔH_f° values (Table II) with the few available experimental data (in kilocalories/mole; see below) show satisfactory agreement. Our assumptions are verified.

	ΔH_f° (calcd)	ΔH_f° (exptl)
$\text{H}_2\text{C}=\overset{\oplus}{\text{C}}\text{CH}_3$	233	230 ²⁰ , 237 ²¹
$\text{CH}_3\text{CH}=\overset{\oplus}{\text{C}}\text{CH}_3$	218	215 ²⁰ , 218 ²²
$(\text{CH}_3)_2\text{C}=\overset{\oplus}{\text{C}}\text{CH}_3$	205	202 ²²

Comparison with Solvolysis Data. On the basis of the Hammond–Leffler postulate,²³ one can expect a linear correlation between activation free enthalpies of solvolysis reactions (ΔG^\ddagger) and the dissociation free enthalpies (ΔG). If no specific solvation effects exist, the ΔG^\ddagger (solvolysis) values should also be related to the gas-phase stabilities of the corresponding vinyl cations (Table III).

Figure 1 shows the linear correlation between the solvolysis free enthalpies of vinyl triflates and the heat of

(16) Streitwieser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962; pp 42, 43.

(17) Since the phenyl ring of 8 is not optimized, the total energy (–303.01200 au) of partially optimized 7^b was used for this equation.

(18) Total STO-3G energies of (a) cyclohexene (–230.26065 au) and cyclopentene (–191.67362 au): complete optimization except CH bond lengths. (b) For cyclobutene (–153.04028 au) and *cis*-butene (–154.24109 au): Hehre, W. J.; Pople J. A. *J. Am. Chem. Soc.* 1975, 97, 6941.

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(30) (a) Grob, C. A.; Cseh, G. *Helv. Chim. Acta* 1964, 47, 194. (b) Derocque, J.-L.; Sundermann, F.-B.; Youssif, N.; Hanack, M. *Justus Liebig's Ann. Chem.* 1973, 419.

(31) Hanack, M.; Bentz, H.; Märkl, R.; Subramanian, L. R. *Justus Liebig's Ann. Chem.* 1978, 1894.

Table II. Total Energies (au, STO-3G) of Vinyl Cations and Calculated Heats of Formation (kcal/mol)

cation				total energy	degree of optimization ^a	ref	ΔH_f° (calcd)
	R ¹	R ²	R ³				
1	H	H	H	-76.165 40	I	11b	266 ^c
2	CH ₃	H	H	-114.792 96	I	2a	233
3	H	CH ₃	H	-114.768 54	I	2a	249
4	CH ₃	CH ₃	H	-153.391 86	I		218
5	H	CH ₃	CH ₃	-153.368 36	I		234
6	CH ₃	CH ₃	CH ₃	-191.988 34	I		205
7	Ph	H	H	-303.016 67 ^b	II		230
8	Ph	CH ₃	CH ₃	-380.197 98	III		209
9	1-cyclohexenyl			-229.384 33	IV		236
10	1-cyclopentenyl			-190.780 94	IV		(255) ^d
11	1-cyclobutenyl			-152.155 81	I	2d	(280) ^d
12	2-methyl-1-cyclohexenyl			-267.981 44	V		222
13	2-methyl-1-cyclopentenyl			-229.380 56	V		(240) ^d

^a I = complete optimization; II = heavy-atom framework fully optimized; III = (CH₃)₂C=C⁺ fragment as calculated for 6, with phenyl as reported in ref 2d; IV = complete optimization except for C-H bond lengths; V = geometries of 9 and 10, respectively, methyl groups with standard geometry. ^b Complete optimization in C_{2v} symmetry except for aromatic C-H results in an energy gain of 2.9 kcal/mol relative to the structure with phenyl in standard geometry. ^{2b} ^c Experimental reference value. ^d Uncertain; see text.

Table III. Solvolysis Rates of Vinyl Triflates in 50% Ethanol-H₂O at 75 °C

R-OTf	solvolyses			ΔH_f° (ion)	ΔH_f° (precursor) ^a	ΔH^f
	k_1, s^{-1}	$\Delta G^\ddagger, kcal/mol$	ref			
	3.3×10^{-4}	26.0	24	233	-34.3	267
	1.75×10^{-4}	26.4	24	218	-41.2	259
	2.94×10^{-4}	26.0	24	205	-49.7	255
	2.74×10^{-1}	21.3	b	230	-3.6	234
	1.68	20.0	c	209	-18.9	228
		32.6	25	236	-39.8	276
		>35.5	25, d	(255)	-30.4	(285)
		27.0	e	(280)	-1.5	(282)
		30.8	25	222	-48.2	270
		>31.3	26, d	(240)	-38.8	(279)

^a Calculated from group increments;²⁷ since the absolute value is not of interest, OTf has been replaced by OCH₃ for simplicity. ^b From k_1 (80% ethanol)²⁸ by using the "mY equation" (ref 38), $m = 0.568$ from ref 29. ^c From rate ratio (CH₃)₂C=C(Br)Ph/H₂C=C(Br)Ph at 120 °C.³⁰ ^d Since solvolysis has been shown to proceed via S-O cleavage³¹ this value represents a lower limit. ^e From relative rates of 1-cyclobutenyl and 1-cyclohexenyl nonaflates (see ref 22, p 242). ^f $\Delta H = \Delta H_f^\circ(\text{ion}) - \Delta H_f^\circ(\text{precursor})$ (ref 38).

formation differences between the cations and the precursors. However, two points deviate, those for 2-propenyl and for 1-cyclobutenyl triflates. Since the deviation of cyclobutenyl triflate can be attributed to the inadequacy of our computational approach (see discussion above), 11 has been omitted from the graph. On the other hand, the displacement of 2-propenyl triflate must have a physical meaning; the calculated heat of formation of vinyl cation 2 is in agreement with the experimental gas-phase value. The finding that 2-propenyl triflate solvolyses faster than expected from the gas-phase stability of cation 2 supports a previous suggestion that systems with β -hydrogens trans to the leaving group experience specific solvation effects

in the solvolysis transition states.²⁴ To eliminate this effect in 4, the solvolysis data of (*E*)-2-buten-2-yl triflate and not of its *Z* isomer has been included to the plot.

From the correlation line one can expect activation free enthalpies for the formation of cyclopentenyl cations which are not very different from those observed for O-S cleavage in 1-cyclopentenyl triflates.^{31,32} Probably, O-S cleavage is only slightly favored over the formation of vinyl cations. This assumption is supported by a recent report that 1-cyclopentenyl cations are formed readily via π cyclization.^{1c}

(32) This conclusion is based on the assumption that STO-3G calculations are still appropriate for 1-cyclopentenyl cations.

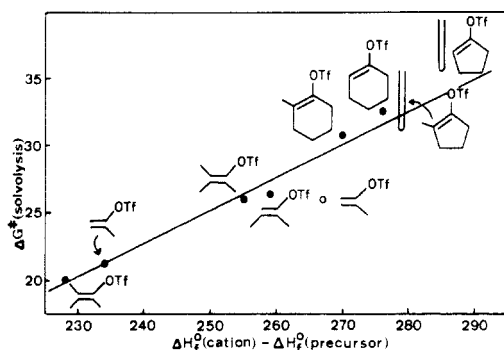
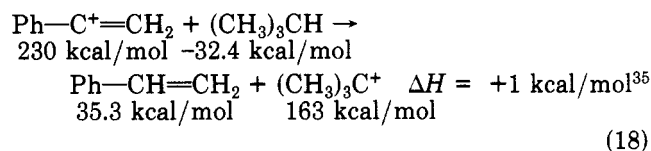


Figure 1. Correlation between activation free enthalpies of solvolysis reactions of vinyl triflates and gas-phase stabilities of vinyl cations.

If the questionable data for 2-propenyl triflate and 1-cyclobutenyl triflate are omitted, regression analysis yields a linear correlation ($r^2 = 0.980$) with a slope of 0.26. This shows that only a small fraction of carbenium ion character is developed in the solvolysis transition states. Corresponding plots for solvolyses of allylic chlorides in formic acid and of tertiary alkyl chlorides in ethanol gave slopes of 0.51¹⁰ and 0.66,³³ respectively, indicating a higher cationic character in these transition states.

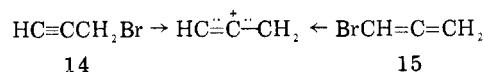
Conclusions

The slow solvolysis rates of vinylic compounds have been considered to indicate low stability of vinyl cations. This interpretation may be erroneous, however, since eq 18



(33) Schleyer, P. v. R.; Mayr, H., unpublished.

shows that *tert*-butyl and α -phenylvinyl cations have similar hydride affinities (i.e., similar thermodynamic stabilities) though *tert*-butyl bromide³⁴ solvolyses ten powers of ten faster than α -bromostyrene.^{30a} Instead, the transition states for vinyl solvolyses reflect the energies of the fully developed ions to a much smaller extent than do the transition states in alkyl solvolyses. Thus, vinyl cations are formed much more slowly than trivalent carbenium ions of equal thermodynamic stability. This point is illustrated nicely by the fact that propargyl bromide 14



solvolyses 4000 times faster than allenyl bromide 15 though both give the same carbenium ion.³⁶ Ground-state effects cannot be responsible since 14 and 15 have similar thermodynamic stabilities.³⁷ We suspect that the transition states for vinyl solvolyses are less effectively solvated even when solvent "ionizing power" rather than solvent nucleophilicity is involved. Alternatively, there may be a larger barrier in going from a sp^2 ground state to an sp ion pair transition state than that for a corresponding sp^3 - sp^2 change.

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Registry No. 1, 14604-48-9; 2, 50457-57-3; 3, 50457-58-4; 4, 79449-26-6; 5, 79449-27-7; 6, 79449-28-8; 7, 62698-27-5; 8, 56126-11-5; 9, 60690-49-5; 10, 60690-50-8; 12, 79449-29-9; 13, 79449-30-2.

- (34) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 1602.
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Active Metals from Potassium-Graphite.¹ Highly Dispersed Nickel on Graphite as a New Catalyst for the Stereospecific Semihydrogenation of Alkynes

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The reduction of NiBr₂·2DME by means of potassium-graphite affords highly dispersed nickel on the graphite surface (Ni-Gr1). Freshly prepared Ni-Gr1 is used "in situ" as a catalyst for semihydrogenation of alkynes to alkenes in the presence of ethylenediamine as catalyst modifier. Unconjugated and conjugated (*Z*)-alkenes with a stereospecificity of 96-99% and 94%, respectively, are obtained.

Alkynes are unreplaceable tools in organic chemistry for the facile construction of carbon-carbon bonds through acetylides and for the reduction to (*E*)- or (*Z*)-alkenes by a variety of stereospecific methods.

Heterogeneous catalytic hydrogenation is a topic in organic synthesis,² especially in the field of natural products, since it allows alkynes to be used as masked (*Z*)-alkenes.³ For this purpose the most widely used catalysts consist in palladium dispersed on suitable supports, the Lindlar catalyst affording the best stereospecificity, since

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