Influence of Bond Angle Distortion and $\sigma-\pi$ σ-Delocalization on the Stability and Chemistry of Allylic Cations

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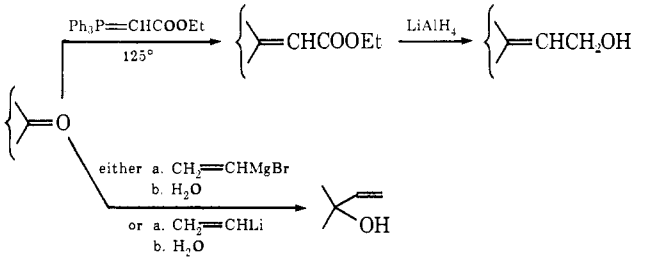
Abstract: The rate and products of solvolysis of a number of exocyclic primary allylic 3,5-dinitrobenzoates and their tertiary isomers have been investigated. The results obtained prompt the following generalizations. (1) Constriction of the endocyclic C–C–C angle at the γ position of a primary allylic ester diminishes both the rate of solvolysis of the ester and the positive charge density at the γ position of the resulting allylic cation. (2) If the appropriate orbital orientation can be achieved, and in particular if it is rigidly maintained by the geometrical constraints of a bicyclic system, $\sigma-\pi$ σ-delocalization may lead to the stabilization of an incipient allylic cation. In fact, solvolysis of suitably selected allylic esters may be one of the most sensitive probes for participation of this type. (3) Stabilization of an incipient allylic cation may also result from $\pi-\pi$ σ-delocalization from suitably oriented π-electron nucleophiles. Participation of this type is favored when the nucleophile can interact in a symmetrical sense with the p orbital at the γ position of the allylic ester.

The influence of substituents on the solvolytic reactivity of allylic derivatives has been extensively investigated.[1] Alkyl substituents at either the α or γ position have a marked and nearly identical rate-enhancing effect in the solvolysis reaction. For γ-alkyl substituents this effect appears to be virtually independent of the nature of the substituent; *e.g.*, the relative rate of formolysis for *trans*-$CH_3CH{=}CHCH_2Cl$ and *trans*-$(CH_3)_3CCH{=}CHCH_2Cl$ is 1.57 and for $(CH_3)_2C{=}CHCH_2Cl$ and $C_2H_5(CH_3)C{=}CHCH_2Cl$, 1.25.[2] When our interest in primary allylic derivatives featuring an exocyclic double bond was first aroused by their potential as model substrates for the investigation of $\pi-\pi$ σ-delocalization,[3] little was known about their solvolytic reactivity. Since no significant rehybridization at the sp^2-hybridized γ position should accompany ionization at the primary center, it seemed unlikely that alteration in torsional interactions or bond angle deformation energy on passing from ground state to transition state, effects which lead to marked differentiation in the rates of ionization at sp^3-hybridized cyclic centers,[4] should intrude in this case. This expectation, coupled with the apparent insensitivity to alteration in the nature of the γ-alkyl substituent exhibited by acyclic systems, would lead one to predict that the rates of solvolysis of primary allylic derivatives with exocyclic double bonds should be monotonously similar. For this reason the experimental observation that the rates of solvolysis of the 7-norbornylidene (**5b**) and cyclopentylidene (**2b**) derivatives differ by a factor of 128 (Table V) was totally unexpected. In order to attempt to interpret this differential reactivity, we have conducted an extensive investigation of the rates and products of solvolysis of allylic esters of this type. The results of this investigation lead us to propose the following generalizations. (1) Constriction of the endocyclic C–C–C angle at the γ position of a primary allylic ester diminishes both the rate of solvolysis of the ester and the positive charge density at the γ position of the resulting allylic cation. (2) If the appropriate orbital orientation can be achieved, and in particular if it is rigidly maintained by the geometrical constraints of a bicyclic system, $\sigma-\pi$ σ-delocalization may lead to the stabilization of an incipient allylic cation. In fact, solvolysis of suitably selected allylic esters may be one of the most sensitive probes for participation of this type. (3) Stabilization of an incipient allylic cation may also result from $\pi-\pi$ σ-delocalization from suitably oriented π-electron nucleophiles. Participation of this type is favored when the nucleophile can interact in a symmetrical sense with the p orbital at the γ position of the allylic ester.

Results

The primary allylic alcohols were prepared from the corresponding ketones *via* a Wittig reaction with carbethoxyethylidenetriphenylphosphorane followed by reduction of the resulting α,β-unsaturated ester with lithium aluminum hydride (Scheme I). This synthetic

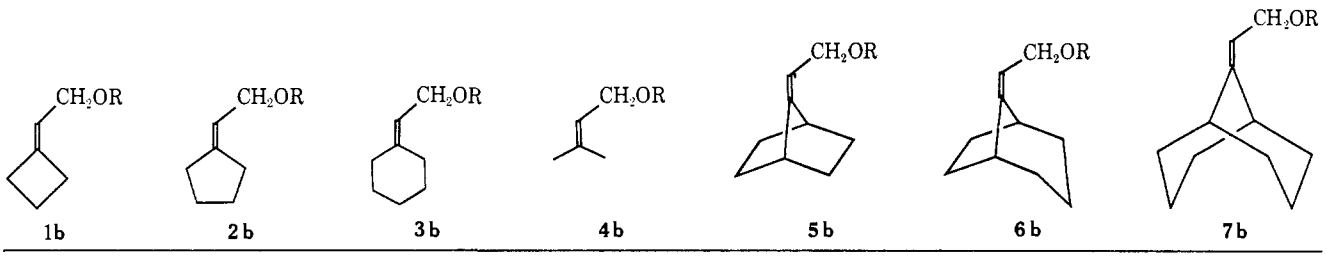
Scheme I



route resulted in the unambiguous formation of the required alcohol in each case except that of 2-(2′-hydroxyethylidene)bicyclo[2.2.1]hept-5-ene (**16a**). This alcohol was produced as a mixture of two isomers with the $-CH_2OH$ group either cis or trans to the C(1)–C(2) bond on the norbornyl skeleton. The composition of the mixture, after formation of the dinitrobenzoate ester, was determined by nmr (CCl_4, δ). The bridgehead proton resonances appeared as three broad singlets at δ 3.65, 3.15, and 3.05 with an integrated area ratio of 1:4.4 between the lowest field signal and the other

(1) Reviews: R. H. De Wolfe and W. G. Young in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, pp 681–738; *Chem. Rev.*, **56**, 753 (1956); N. C. Deno in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 783–806.
(2) C. A. Vernon, *J. Chem. Soc.*, 425, 4462 (1954).
(3) G. D. Sargent, J. A. Hall, M. J. Harrison, W. H. Demisch, and M. A. Schwartz, *J. Amer. Chem. Soc.*, **91**, 2379 (1969).
(4) See, for example, P. v. R. Schleyer, *ibid.*, **86**, 1854 (1964).

Table I. Solvolysis Rate Constants and Activation Parameters for the Series of Saturated Primary Allylic Dinitrobenzoates in 70% Aqueous Acetone

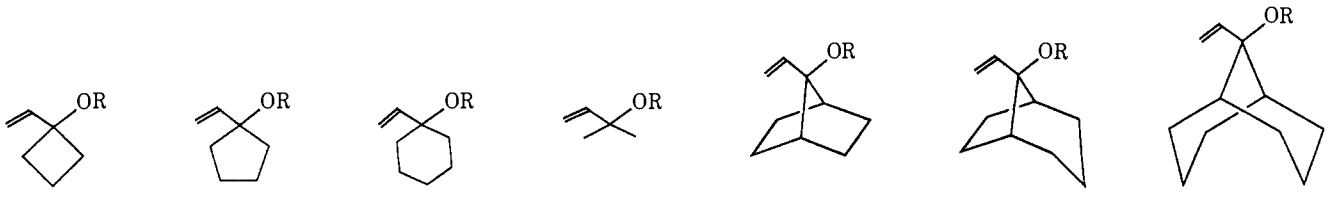


1b 2b 3b 4b 5b 6b 7b

Compd[a]	1b		2b		3b		4b		5b		6b		7b	
Temp, °C[b]	125	100	100	75	120	100	125	100	150	125	125	100	125	100
10^5k, sec^{-1}[c]	33.2	3.84	43.1	4.02	58.2	9.15	82.0	9.38	29.3	3.61	167.0	17.9	110.0	12.6
$\Delta H^{\pm}$, kcal/mol	24.7		23.8		26.2		26.4		27.3		25.6		24.8	
$\Delta S^{\pm}$, eu	−12.9		−10.7		−7.2		−12.0		−10.9		−7.4		−10.2	

[a] Series a, R = H; b, R = 3,5-dinitrobenzoyl. [b] Bath temperature ±0.05°. [c] Mean of two runs, reproducibility ±3%.

Table II. Solvolysis Rate Constants and Activation Parameters for the Series of Saturated Tertiary Allylic Dinitrobenzoates in 70% Aqueous Acetone



8b 9b 10b 11b 12b 13b 14b

Compd[a]	8b		9b		10b		11b		12b		13b		14b	
Temp, °C[b]	125	100	50	40	100	75	75	60	150	125	151	125	70	50
10^5k, sec^{-1}[c]	27.1	2.59	15.4	4.64	122.0	8.75	22.4	4.70	11.4	1.13	57.7	6.77	41.2	5.62
$\Delta H^{\pm}$, kcal/mol	27.0		23.4		26.5		23.3		30.2		26.6		21.8	
$\Delta S^{\pm}$, eu	−7.6		−3.8		−1.4		−8.7		−5.8		−11.3		−10.7	

[a–c] See Table I.

pair. We assign the signal at 3.65 to the C(1) proton of the trans isomer and attribute the slight upfield shift of the corresponding proton of the cis isomer to shielding by the ester function. This leads to a calculated isomer ratio of 60:40 in favor of the cis isomer, the same as that obtained from the analogous preparation of 2-(2′-ethylidenyl)bicyclo[2.2.1]heptane dinitrobenzoate (**19b**).[5,6] In the synthesis of **7a**, *ca.* 10% of bicyclo[3.3.1]nonan-9-ol was found to be a contaminant. The secondary alcohol was produced as a result of lithium aluminum hydride reduction of unreacted bicyclo[3.3.1]nonan-9-one carried through from the Wittig reaction. Since the solvolysis rate of the dinitrobenzoate of this alcohol was very slow (less than 5% reaction after 10 half-lives for the solvolysis of **7b**), kinetics were determined for the mixture of esters.

The tertiary allylic alcohols were prepared from the corresponding ketones by reaction with either vinylmagnesium bromide or vinyllithium in tetrahydrofuran followed by hydrolysis (Scheme I). The resulting alcohols were single isomers with the exception of the product of reaction between bicyclo[2.2.1]hept-2-en-7-one and vinyllithium. In this case a 1:3 mixture of anti:syn OH was formed. This ratio contrasts with that of 4:1 obtained in the corresponding synthesis using vinylmagnesium bromide.[7] The isomers were separated by preparative glc on Carbowax 20M, on which the syn alcohol **17a** has the shorter retention time due to the presence of intramolecular hydrogen bonding. Confirmation of this configurational assignment, which is in accord with that of Berson and Jones,[7] can be found in the solvolysis data for the dinitrobenzoate esters. The anti isomer **18b** shows considerable rate enhancement due to participation by the remote C(2)–C(3) double bond (Table III). The vinyllithium addition to bicyclo[3.2.1]octan-8-one produced an alcohol which was assumed to be one isomer on the basis of a single glc peak on a variety of columns and the sharp melting point for the dinitrobenzoate derivative. The hydroxyl group was assigned the configuration anti to the cyclopentane ring by analogy to the results of reduction of the ketone with sodium borohydride,[8] or hydrogen over platinum[9] which produces, in each case, a preponderance of alcohol anti to the cyclopentane ring.

The 3,5-dinitrobenzoate esters were prepared by standard procedures and all gave satisfactory elemental analyses. The solvolysis rates were measured using the ampoule technique in 70% (by volume) acetone in water, in the presence of urea, and are reported in Tables I–III. Good first-order plots were obtained to 60% reaction in most cases using the experimental infinity titer determined after 10 half-lives. The solvolysis of **5b** is characterized by a downward-drifting first-order rate constant. After 2 solvolytic half-lives the

(5) H. G. Richey, Jr., R. Fletcher, and R. G. Overmayer, *Tetrahedron Lett.*, 3703 (1970).

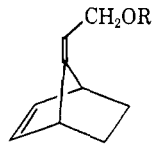
(6) For both **16b** and **19b**, the rates of solvolysis were measured on the mixture of isomers.

(7) J. A. Berson and M. Jones, Jr., *J. Amer. Chem. Soc.*, **86**, 5019 (1964).

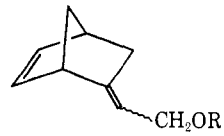
(8) C. S. Foote, Ph.D. Thesis, Harvard University, 1961.

(9) A. C. Cope, J. M. Grisar, and P. E. Peterson, *J. Amer. Chem. Soc.*, **82**, 4299 (1960).

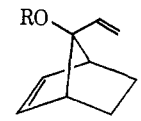
Table III. Solvolysis Rate Constants and Activation Parameters for the Series of Unsaturated Allylic Dinitrobenzoates in 70% Aqueous Acetone



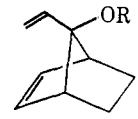
15b



16b



17b



18b

Compd[a]	**15b**		**16b**		**17b**		**18b**	
Temp, °C[b]	125	100	100	76	150	125	100	75
10^5k, sec^{-1}[c]	80.6	8.93	21.4	2.20	13.8	1.38	91.7	6.82
$\Delta H^{\ddagger}$, kcal/mol	25.2		23.7		30.0		26.1	
$\Delta S^{\ddagger}$, eu	−9.9		−12.3		−5.9		−2.9	

[a–c] See Table I.

products were extracted into ether; then, after the removal of solvent and trituration with pentane, the residual solid was examined by nmr and found to contain some of the isomeric tertiary ester **12b**. Clearly, during the solvolysis of **5b**, some return of the dinitrobenzoate ion to the tertiary position of the allylic cation takes place to form the less reactive tertiary dinitrobenzoate **12b** and it is this return which results in the anomalous kinetics observed. However, the first-order rate plot closely approaches linearity for nearly 1 half-life and it is the initial value for the rate constant which is reported (Table I). In the solvolysis of **14b** good first-order kinetics are again observed to 1 half-life, but the infinity titer is 20% below theoretical. Using the same procedure as above this substrate was found to solvolyze with return to the less reactive primary ester **7b**, but here again the initial kinetics accurately represent the solvolysis rate of **14b**.

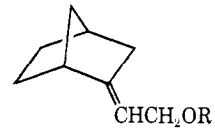
Products were determined after 4 solvolytic half-lives at 100° in the presence of an excess of urea. The products were analyzed by glc using an internal standard and the alcohol products are reported as percentages of the total theoretical yield (Table IV). Some solvolyses produced considerable olefinic material but this was not analyzed. In all cases, the stability of the alcohol products to the reaction conditions was investigated, but only for derivatives of the bicyclo[3.3.1] skeleton was any instability found. Between 1 and 4 half-lives the tertiary/primary alcohol product ratio was found to change from 1.0 to 0.50 for **7b** and 1.20 to 0.75 for **14b**. In these cases the kinetic product ratio is quoted as greater than that obtained after 1 half-life (Table IV).

All of the esters of the bicyclic alcohols yielded the expected primary and tertiary alcohol products, but the solvolysis of **16b** produced an additional alcohol. This third product, whose glc retention time on Carbowax 20M was intermediate between that of the primary and tertiary allylic alcohols, was formed in 12% yield. We propose that this alcohol is the product formed by nucleophilic attack at C(5) on the cation generated by double bond delocalization to the developing allylic cation at C(2), the ring-closed tricyclic secondary alcohol **20**: nmr (CCl_4) δ 6.10 → 5.65 (1 H, four singlets) and 5.20 → 4.88 (2 H, three doublets), the vinyl protons, 4.00 (s, 1 H, proton α to OH), 2.50 (s, 1 H, hydroxyl proton), 2.05 (m, 2 H, bridgehead protons), 1.80 → 1.30 (complex, 5 H, remaining protons). The tertiary alcohol produced in this solvolysis was

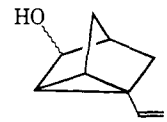
Table IV. Products from the Solvolysis of Primary and Tertiary Esters in 70% Acetone[a]

ODNB	% tertiary OH	% primary OH	T/P (prods)	T/P (equil)
1b	22	62	0.35	
				57.0
8b	19	31	0.61	
2b	52	25	2.10	
				0.3
9b	33	15	2.20	
3b	17	46	2.70	
				4.0
10b	8	24	3.00	
4b	35	14	2.50	
11b	21	7	3.00	
5b	30	70	0.43	
				12.0
12b	35	64	0.56	
6b	89	11	8.1	
				4.2
13b	85	15	5.7	
7b[b]	50	50	1.0	
				0.12
14b[b]	54	45	1.2	
15b	96 (**18a**)	2		
17b	85 (**18a**)	4		
	10 (**17a**)			
18b	100 (**18a**)	0		
16b[c]	34 (**21**)	44	0.8	

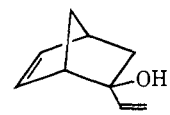
[a] Product reported as % of total theoretical yield relative to an internal standard, accuracy ±5%. [b] Products after 1 half-life. [c] Alcohol **20** produced in 12% yield.



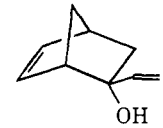
19a, R = H
b, R = DNB



20



21

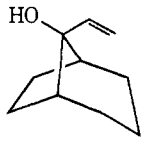


22

shown to be >95% exo-OH **21** by comparison with an authentic sample of the endo-OH isomer **22** prepared by vinylmagnesium bromide addition to 2-norbornenone. Although the isomers were not completely separable

by glc on Carbowax 20M, DEGS, or Ucon 2000, slight separation was achieved by tlc on silica gel using 20% ether–pentane. The endo-OH (5%) in a mixture of isomers could be detected by this method, but none was found in the alcohol mixture obtained from solvolysis. The nmr spectrum of the exo alcohol (CCl_4, δ) displays a complex pattern at high field 2.30 → 1.35 (4 H) which appears to be two merged AB quartets, one of which has a lower field doublet (1 H) at 2.15 (J = 8 Hz) and the other a high-field doublet (1 H) at 1.55 (J = 12 Hz). The high-field complex pattern for the endo alcohol differs from the above in that the highest field doublet from an AB quartet (1 H) at 1.1 (J = 12 Hz) is well clear of the highest field signal in the spectrum of **21**. No trace of this signal was detected in the nmr spectrum of the product alcohol, which confirms 5% as the upper limit on the amount of endo alcohol which may be present in the solvolysis product **21**.

The tertiary alcohol produced in the solvolysis of **6b** and **13b** proved to have a very similar glc retention time on a variety of columns to that for **13a**. The nmr spectrum of the glc separated tertiary alcohol product, though similar to that of **13a** in the complex pattern between δ 2.25 and 1.00 (13 H), differs markedly in the signals of the vinyl protons. The pattern observed for the vinyl protons of **13a** reveals a separation of 25 Hz between the highest signal of the single vinyl proton multiplet and the lowest field signal of the terminal $=CH_2$ proton multiplet. In the product alcohol this separation is expanded to 40 Hz. The nmr splitting pattern for the vinyl protons of the bicyclo[2.2.1] and [3.3.1] tertiary alcohols, **12a** and **14a**, shows corresponding separations of 30 and 40 Hz, respectively. We propose that this nmr evidence is in accord with our assignment of the configuration of **13a**, where the vinyl group is *syn* to a cyclopentane ring as in **12a**, and further that the product alcohol is of inverted configuration **23**

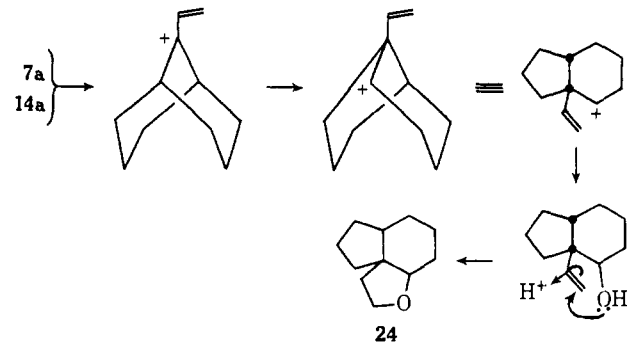


23

with the vinyl group syn to a cyclohexane ring as in **14a**.[9a] Amplification of the nmr spectrum of **23** revealed no signals for the vinyl protons of **13a** in the region δ 2.25 → 5.60. With the limits of nmr detection under the conditions of the experiment at about ±5% this allows the isomeric purity of **23** to be estimated as better than 95% (±5%).

The acid-catalyzed equilibration ratios for a number of the allylic alcohols at 100° in 70% acetone were determined and are reported (Table IV). Equilibration was accompanied by some elimination for the monocyclic alcohols. The bicyclic alcohols equilibrated normally except in the case of the bicyclo[3.3.1] isomer where a third compound was produced in 30% yield under the standard conditions employed. This product, whose retention time is less than that of the tertiary alcohol **14a**, was isolated by preparative glc on Carbowax 20M. We propose that this compound is decahydroindeno[7,7-*ab*]furan (**24**) produced by the carbonium ion rearrangement shown (Scheme II). The bond

Scheme II



24

migration leading to the indenyl skeleton is analogous to that observed in the acetolysis of bicyclo[3.3.1]nonan-9-yl tosylate (**26**)[8,10] although **24** was not produced in the solvolysis of either **7b** or **14b**. The infrared spectrum of **24** (CCl_4) showed no O—H, C=C, or C=O stretching frequencies, but absorptions at 1030, 1050, 1084, and 1126 cm^{-1} indicate the presence of C—O bonds. The nmr spectrum of **24** (CCl_4, δ) was also consistent with the assigned structure: 3.90 → 3.45 complex (3 H, protons α to oxygen) and 2.20 → 1.15 complex (15 H, remaining protons). Using the nmr shift reagent Eu(fod)$_3$ (60 mg) with **24** (23 mg) in 0.5 ml of CCl_4 the lower field complex pattern was resolved into three single proton patterns: δ 10.35, a six-peak multiplet with splitting, J = *ca.* 4 Hz; δ 9.85, triplet, J = *ca.* 4 Hz; δ 9.32, an AB-type quartet with J = 7.5 Hz. The triplet pattern can be assigned to the tertiary proton α to the oxygen and the other pair to the methylene protons α to the oxygen. The remaining 15 protons form a broad complex pattern δ 4.50 → 1.25 except for a single proton resonance shifted downfield as a multiplet 6.15 → 5.60, which may be assigned to the next-nearest proton to the coordinated europium atom, a methylene proton, β to the oxygen, on the cyclohexane ring.

Discussion

Primary Allylic Esters. The compounds **1b** → **7b** comprise a series of symmetrically γ,γ-dialkyl substituted primary allylic esters. To a first approximation, one might expect that the double bond in each of these substrates would provide a similar degree of transition state stabilization of the incipient allylic cation during ionization. The observed first-order rate constants for the solvolysis of the dinitrobenzoate esters in 70% acetone, however, illustrate that this is not the case (Table I). If the acyclic ester **4b**, where the bond angle at the sp^2 hydridized γ position is "normal," is used as a model substrate, then the ester **5b** shows a markedly reduced first-order rate of solvolysis. If one postulates that the in-plane bending force constants are greater for cationic carbon than for neutral sp^2-hybridized carbon, then the ionization of **5b**, which has a badly pinched endocyclic C–C–C angle, would be associated with an increase in angle strain not attendant upon the ionization of **4b** as positive charge is developed at the γ position. Whereas little is known about

(9a) NOTE ADDED IN PROOF. These assignments have been confirmed by analysis of the lanthanide shifted nmr spectra of **13a** and **23** utilizing the method of Willcott and Davis (M. R. Willcott, III, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1742 (1972); R. E. Davis and M. R. Willcott, III, *ibid.*, **94**, 1744 (1972). We are grateful to Professor Willcott for conducting this analysis, the details of which will be published elsewhere.

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

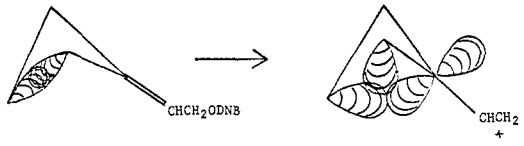


Figure 1. $\sigma-\pi$ σ-delocalization of electron density during the ionizationof **1b**.

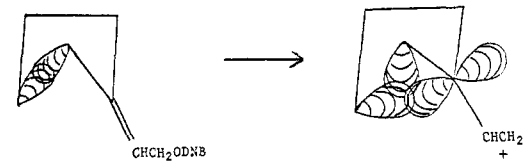


Figure 2. $\sigma-\pi$ σ-delocalization of electron density during the ionization of **2b**.

bending force constants for positively charged carbon, the observation that radicals appear to be generated more readily than cations at identically strained bridgehead positions[11] suggests that at least the out-of-plane bending force constants for cationic carbon may exceed those for neutral carbon. Corroborative evidence for this view is found in the distribution of products derived from the solvolysis of **5b** and **1b**, for which unusually low tertiary/primary product ratios of 0.43 and 0.35 are observed (Table IV). These results are unique among symmetrically disubstituted allylic esters in that they demonstrate that a preponderance of product is derived from attack at the primary carbon. Normally, kinetically controlled products derived from allylic cations generated under limiting SN1 conditions primarily arise from attack at the tertiary position,[1] for example, from **4b** the tertiary/primary ratio is 2.5. This observation is generally rationalized in terms of the greater degree of positive charge which resides at the more highly substituted terminus of the allylic cation. If, indeed, the in-plane bending force constants for sp^2 hybridized cationic carbon exceed those for sp^2 hybridized neutral carbon, one might expect a shift of π-electron density from the primary to the tertiary carbon in the intermediates generated from **1b** and **5b** relative to the distribution which obtains in the unstrained allylic cation.

Although this hypothesis provides an attractive rationale for the gross trends in solvolytic activity for the series of substrates **1b** → **7b**, it is clearly not the only controlling factor. An estimate of the angle strain at the γ position for these substrates may be obtained from the infrared carbonyl stretch frequencies of the corresponding ketones[8] (Table V). From these values

Table V. Relative Rates of Solvolysis at 100° and Ketone Ir Frequencies

Primary ODNB	k_{rel}	$\nu_{C=O}$, cm^{-1}	Tertiary ODNB	k_{rel}
1b	11.5	1791	**8b**	31.5
2b	128.0	1750	**9b**	28,700[a]
3b	27.0	1717	**10b**	1490
4b	27.0	1719	**11b**	2600[a]
5b	1.0[a]	1768	**12b**	1.0[a]
6b	53.0	1751	**13b**	8.0[a]
7b	37.0	1726	**14b**	7100[a]
15b	26.0		**17b**	1.4
16b	63.0		**18b**	115
32	54.0[b]	1704[b]		
19b	270.0[b]	1751[b]		

[a] Extrapolated rates. [b] Reference 5 calculated by using the relative rate of solvolysis compared with **2b** in 80% acetone at 100°.

it is evident that the endocyclic angle in the cyclobutyl derivative **1b** ($\nu_{C=O}$ 1791 cm^{-1}) is considerably more constrained than that of the 7-norbornyl derivative **5b** ($\nu_{C=O}$ 1768 cm^{-1}). Using an angle strain argument, one would therefore predict that the solvolysis rate of **1b** would be slower than that of **5b**, whereas kinetic measurements show a rate factor of 11.5 in favor of the former. This result can be rationalized if one postulates partial $\sigma-\pi$ σ-delocalization of electron density from the 2,3-σ bond to the developing allylic cation during the ionization of **1b** (Figure 1). Such a postulate finds precedent in the observed[12] and calculated[13] delocalization of electron density from the 2,3-σ bond to the developing cationic center in the solvolysis of cyclobutyl derivatives. A comparable $\pi-\pi$ σ-delocalization is observed in the solvolysis of **15b** leading to a rate enhancement of 26 compared with the rate of **5b** (Table V).

The rate of solvolysis of **2b** is faster than that of **4b** by a factor of 4.7 despite an unfavorable constriction of the endocyclic angle in the former ($\nu_{C=O}$ 1750 cm^{-1}). Since the cyclopentylidene ring in **2b** has available a conformation which allows the geometrical relationship of the 2,3-σ bond to the tertiary carbon to mimic that calculated to lead to σ-delocalization in the cyclobutyl cation (Figure 2), an observable, though markedly diminished, contribution of such delocalization to the stabilization of the transition state for the solvolysis of **2b** does not appear unreasonable. Indeed, since sharp discontinuities are rarely encountered by the physical organic chemist, it would be surprising that, with σ-delocalization during the generation of the cyclobutyl cation well grounded in both theory and experiment, some such delocalization did not accompany generation of the cyclopentyl cation. The failure to observe direct evidence for such delocalization most likely results from the fact that the intrusion of two competing effects, generation of increased bond angle strain and relief of ground state torsional strain, renders impossible a *precise* prediction of the relative rates of solvolysis expected from cyclobutyl, cyclopentyl, and cyclohexyl derivatives in the absence of σ-delocalization.

The contribution to transition state stabilization by σ-delocalization in the monocyclic series would be expected to diminish sharply with the increase in ring size **1b** > **2b** > **3b**, so that a peaking of the solvolysis rate for **2b** might result from the competing effects of endocyclic angle deformation and σ-bond delocalization. The distribution of alcohol products from the solvolysis of **2b** is "normal" despite the presence of a constrained endocyclic angle at the tertiary allylic carbon. Similarly, the product mixture from **1b** does not contain significantly less tertiary product than that from **5b**.

(11) R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 284 (1966).

(12) K. B. Wiberg and J. G. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 553 (1970), and references cited therein.

(13) K. B. Wiberg and J. G. Pfeiffer, *ibid.*, **92**, 571 (1970); J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968); K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); *cf.*, however, R. E. Davis and A. Ohno, *ibid.*, **24**, 2063 (1968).

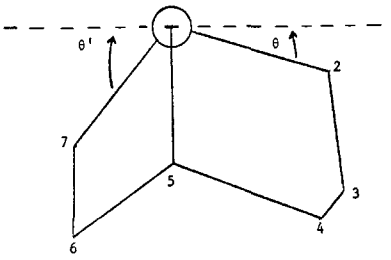


Figure 3. Newman projection along C(8)–C(1) bond of **6b**.

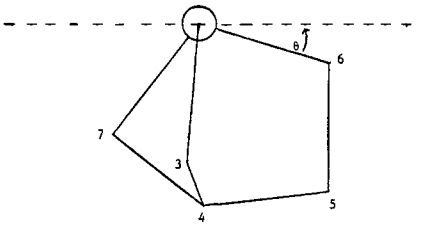


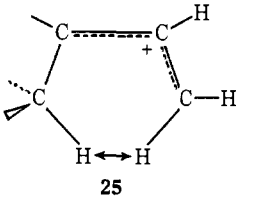
Figure 4. Newman projection along C(2)–C(1) bond of **19b**.

Both of these observations would appear to implicate σ-delocalization as a possible source of additional stabilization to the tertiary carbonium ion centers during ionization.

In order to test further the hypothesis that bond angle deformation at cationic carbon is energetically more costly than comparable deformation at neutral carbon, the bicyclic esters **6b** and **7b** were synthesized. These substrates bear a marked resemblance to the ester **5b** and, for this reason, factors extraneous to bond-angle deformation effects, such as steric inhibition to solvation or hyperconjugation, would be expected to remain reasonably constant within the series. In addition, although **6b** is a cyclopentylidene derivative, the relationship of the 2,3-σ bonds to the tertiary center, like that in **5b**, is such as to minimize incursion of $\sigma-\pi$ σ-delocalization. Since the carbonyl stretching frequencies of the bicyclic ketone analogs of **5b**, **6b**, and **7b** (1768, 1751, and 1726 cm^{-1}, respectively) indicate a marked decrease in endocyclic bond angle constriction within the series, a pronounced increase in rate of solvolysis in the order of $k_{5b} < k_{6b} < k_{7b}$ is anticipated by the bond-angle deformation hypothesis. The observed rates of solvolysis for this series, however, make it clear that although the solvolysis of **5b** is predictably slow and that of **7b** is comparable with **3b**, the rate observed for **6b** is not in line with the above predictions, being nearly 50% greater than that of **7b**.

We propose that the enhancement to the rate of solvolysis of **6b** is due to some $\sigma-\pi$ delocalization from the 2,3-σ bond on the fused cyclohexane ring. A Newman projection of **6b** along the C(8)–C(1) axis is shown in Figure 3 with the axis of the p orbitals which form the exocyclic double bond at the bridge (C(8)) position shown as a dotted line. The dihedral angle θ between these orbitals and the C(1)–C(2) bond is *ca.* 16°.[14] A similar projection along the C(9)–C(1) bond of **7b** reveals a dihedral angle of *ca.* 27°. A recent series of *ab initio* calculations of the stabilities of various conformations of simple carbonium ions has shown that considerable stability attends conformations in which the C(2)–C(3) σ bond is coplanar with the empty p lobe of the carbonium ion (for the *n*-propyl cation this conformation is favored by 2.3 kcal/mol).[15] It seems reasonable therefore to conclude that optimum conditions for $\sigma-\pi$ σ-delocalization in the ionization of primary allylic esters would require a dihedral angle of 0° and that such delocalization would decrease as this angle is increased. Thus, the enhanced rate of solvolysis of **6b** could be ascribed to the more favorable smaller dihedral angle in this molecule. For both of these systems the 2,3-σ bond and the ethylidene group are part of a cyclohexane ring; the corresponding dihedral angle subtended by C(1)–C(7) bond of the cyclopentane ring of **6b** (θ') is found to be *ca.* 60° which would seem to preclude the possibility of any delocalization from this side of the molecule. The 7-norbornyl derivative **5b** exhibits a markedly slow rate of solvolysis which can be correlated with an unfavorably large dihedral angle of 37° and thus ascribed primarily to the constricted endocyclic angle with little, if any, assistance to ionization from delocalization of the C(1)–C(2) bond. The rate of solvolysis of the 2-norbornyl derivative **19b** is an order of magnitude greater than that of **3b** in 80% acetone at 100°[5] and consequently a factor of about 5 faster than **6b**. Since the endocyclic angle for this substrate is constricted ($\nu_{C=O}$ 1751 cm^{-1}), clearly some rate enhancement attends the solvolysis of **19b**. A Newman projection along the C(2)–C(1) bond for this molecule (Figure 4) reveals a dihedral angle of *ca.* 17° between the p orbitals of the double bond and the C(1)–C(6) bond. The small dihedral angle is favorable for delocalization, and the greater rate enhancement observed for this compound compared with **6b** is probably a result of the greater bond angle strain in the cyclohexane ring of the former. The bond-angle deformations cause more p character to be incorporated into the orbitals which combine to form the C(1)–C(6) σ bond and, hence, convey upon the electrons of this bond a greater propensity for delocalization.[16]

Richey, *et al.*,[5] have suggested that the generation of the allylic cation in the solvolysis of **5b** may produce a nonbonded interaction, indicated by the arrow in **25**,



25

that might be partly responsible for its retarded rate of solvolysis. Such an interaction might inhibit planarity of the allylic system and result in the slow solvolysis rate. The observed rates of solvolysis of **5b**, **6b**, and **7b** would appear to discount this factor since all three incipient allylic cations would have almost identical nonbonded interactions with the bridgehead protons.

Examples of 2,3-σ-bond delocalization from a cyclohexane ring to the developing carbonium ion center can be found in the acetolyses of the secondary derivatives **26** → **31**. Foote and Woodward[10] have concluded that

(14) Bond angles were measured using Cenco Petersen Molecular Models.

(15) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970); **93**, 1813 (1971).

(16) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

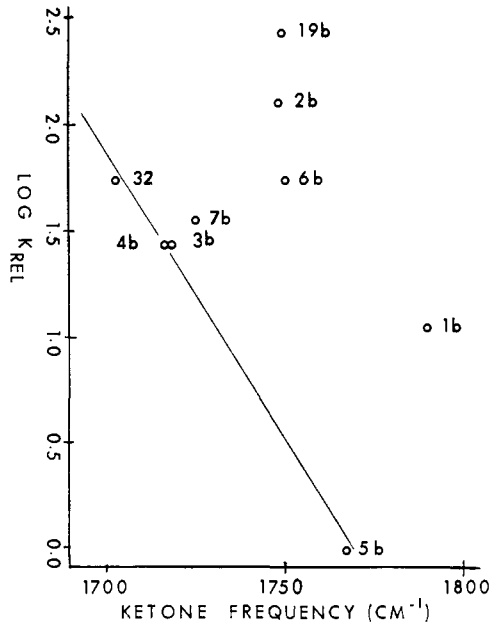
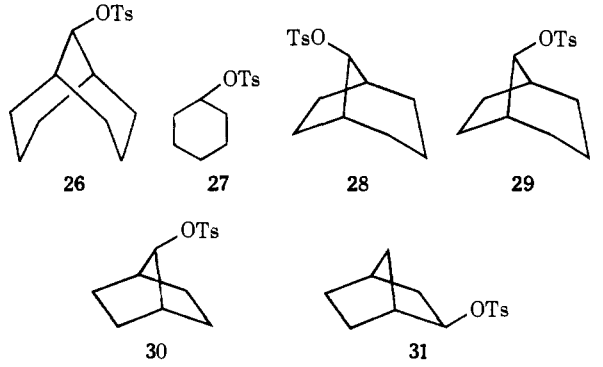


Figure 5. Correlation of solvolysis rates of primary dinitrobenzoates $R_1R_2C{=}CHCH_2ODNB$ with the carbonyl stretching frequencies of the corresponding ketones $R_1R_2C{=}O$.



whereas the rates of solvolysis of **27**, **29**, and **30** are explicable in terms of endocyclic bond angle deformation, the solvolysis of **28** and, to a lesser extent, that of **26** are anchimerically assisted by delocalization of the 2,3-σ bonds from the anti-fused cyclohexane rings. The considerable enhancement to the solvolysis rate of **31** has also been ascribed to σ-bond delocalization.

Following a study of the preferred retention observed in the products of solvolysis of *cis*- and *trans*-5-methyladamant-2-yl derivatives, Whiting, *et al.*,[17] have suggested that in branched systems where C–H bond participation is stereoelectronically frustrated, C–C bond participation occurs instead quite generally, but that this may involve little change in internuclear distances and little transfer of electronic charge. Traylor, *et al.*,[18] have proposed a similar effect, "vertical stabilization," through which polarizable σ bonds may stabilize neighboring cationic centers without altering the bond lengths or angles around such bonds as the transition state is approached. We propose that, through such a process, the σ-bond delocalization observed in the acetolysis of the secondary tosylates ($k_{31} > k_{28} > k_{26}$) is also expressed, though to a diminished extent, in the solvolysis of the allylic dinitrobenzoate derivatives

(17) J. A. Bone and M. C. Whiting, *J. Chem. Soc. D*, 115 (1970).
(18) T. G. Traylor, W. Hanstein, H. G. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971).

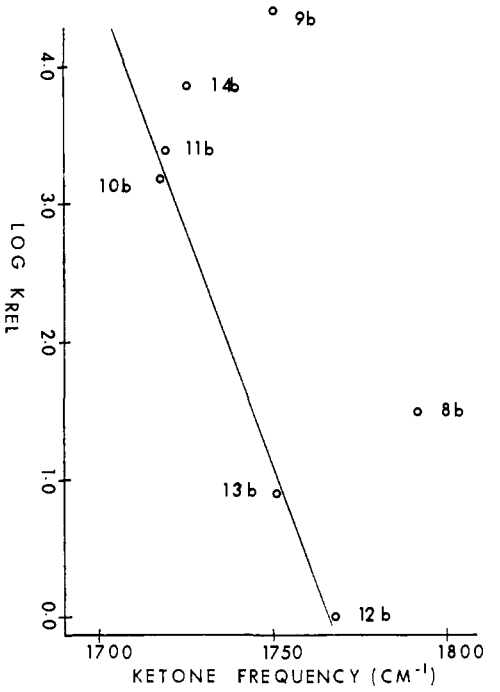


Figure 6. Correlation of solvolysis rates of tertiary dinitrobenzoates $R_1R_2C(CH{=}CH_2)ODNB$ with the carbonyl stretching frequencies of the corresponding ketones $R_1R_2C{=}O$.

($k_{19b} > k_{6b} > k_{7b}$). The preponderance of **23** (95 ± 5%) observed as the tertiary alcohol product in the solvolysis of **6b** and **13b** parallels the predominant inversion observed in the acetolysis products of **29**[10] and is in accord with the above proposal.

These results are graphically illustrated using a Foote correlation[19] of solvolysis rate with corresponding ketone ir frequency (Figure 5). Compounds **3b**, **4b**, **5b**, **7b**, and 2′-ethylidenylcycloheptane dinitrobenzoate[5] (**32**) are all seen to be on a reasonably good line indicating a direct relationship between endocyclic angle and first-order solvolysis rate. Clearly, however, the substrates **1b**, **2b**, **6b**, and **19b** all exhibit enhanced rates of solvolysis which we ascribe to varying degrees of 2,3-σ–π σ-bond delocalization.

Tertiary Allylic Esters. The solvolyses of the series of tertiary esters **8b** → **4b** were studied in order to determine the extent to which the initial cation formed in the ionization of these substrates would lead to the same product distribution as that from the corresponding primary derivatives. As may be seen from Table IV, the tertiary/primary alcohol product ratios from each pair of esters are quite similar. In most cases, a slightly smaller ratio was obtained from the solvolysis of the primary derivative. It is reasonable to attribute these small discrepancies to the intrusion of some direct solvent displacement during the ionization of the primary ester. An interesting feature of the rates of solvolysis of these tertiary esters (Table II) is the remarkably slow rate of the 8-bicyclo[3.2.1] tertiary ester **13b** which is only a factor of 8 times faster than that of **12b** (Table V). A Foote type correlation[19] of ketone ir frequency with tertiary ester solvolysis rate for this series (Figure 6) reveals that **13b** does not exhibit an abnormally slow rate in terms of endocyclic angle strain. Such a plot reveals instead that both cyclopentyl **9b** and cyclobutyl **8b**

(19) C. S. Foote, *ibid.*, **86**, 1853 (1964).

tertiary esters have anomalously fast solvolysis rates. It is probable that the fast rate of the former is due primarily to the relief of torsional strain in going to the transition state for solvolysis.[20] It is possible that the solvolysis of **8b** is also accompanied by some 2,3-σ-bond delocalization.

The acetolysis rate of *anti*-7-norbornenyl tosylate is a factor of 10^{11} faster than that of the saturated derivative.[21] Gassman[22] has reported that the presence of a 7-phenyl substituent reduces this factor to 34 for the solvolyses of the tertiary dinitrobenzoates in 70% dioxane. This marked attenuation of the rate factor has been ascribed to a stabilization of the developing carbonium ion center by the phenyl group which limits the tendency for π-electron delocalization from the remote double bond. Further, using substituted phenyl groups, it was shown that such delocalization was directly related to the electron demand of the incipient carbonium ion. The nmr study of a variety of 7-arylnorbornenyl cations has supported this conclusion.[23] 7-*p*-Anisylnorbornyl cation was found to be effectively classical whereas other aryl-substituted carbonium ions involved varying degrees of double bond delocalization. The rate ratio for the solvolysis of 7-*syn*-vinylnorbornenyl *anti*-dinitrobenzoate (**18b**) compared with the saturated analog **12b** is 1100 at 100° in 70% acetone. This result clearly indicates that a vinyl substituent is less effective than a phenyl group in reducing remote double bond participation in ionization.

In a study of the solvolysis of a series of tertiary benzylic *p*-nitrobenzoates in 60% acetone, Padwa and Alexander[24] have observed that, whereas 7-phenyl-7-norbornyl, phenylisopropyl, and phenylcyclobutyl derivatives exhibit normal reactivity on the basis of angle strain at the displacement center, the solvolysis of phenylbicyclo[1.1.1]pentyl nitrobenzoate is anomalously fast. This result was interpreted as meaning that in this system the stabilization of the incipient carbonium ion by a phenyl group is not efficient enough to preclude neighboring group participation by the 2,3-σ bond. It does not therefore seem unreasonable to conclude that, in the case of a vinyl substituent, which is less effective than phenyl in stabilizing the incipient tertiary cation, such participation should manifest itself in the form of an anomalously fast rate for solvolysis of the cyclobutyl derivative **8b**.

Since all three of the bicyclic tertiary vinyl esters studied show "normal" solvolysis rates as predicted by endocyclic angle strain considerations, we may assume that σ-bond delocalization is not a significant rate controlling factor in these solvolyses. However, the inversion noted in the tertiary alcohol solvolysis product from **13b** would seem to implicate σ-bond delocalization as a product controlling factor.

Remotely Unsaturated Allylic Esters. The solvolytic reactivity of the unsaturated allylic esters **15b** and **16b** was investigated in order to ascertain whether π–π σ-delocalization from a C–C double bond can stabilize an incipient allylic cation. Interactions of this type, for which no precedent had been established prior to the preliminary communication[3] of this work, are required if, as has been suggested,[25] the polycyclization step in the squalene oxide–lanosterol conversion is a wholly concerted process.

At 100°, the rate of solvolysis of **15b** is enhanced relative to that of **5b** by a factor of 26. This effect is substantial and clearly in the direction predicted were the endocyclic double bond in **15b** to initiate nucleophilic attack at C-7 during heterolysis of the allylic ester. The influence of the endocyclic double bond on the kinetically controlled product distribution is even more dramatic. Both **5b** and **12b**, which lack the double bond, yield virtually identical product mixtures, in which the primary alcohol **5a** predominates over the tertiary alcohol **12a** by a factor of 2:1. Since the equilibrium distribution (acid catalysis) of **5a** and **12a** favors the tertiary alcohol by a factor of at least 12:1, the observed product distribution is clearly kinetically controlled and must derive from nucleophilic attack by water on a common cation. The predominance of primary product would seem to indicate that, unlike most unsymmetrically substituted allylic cations,[1] this cation is possessed of greater positive charge density at the primary than at the tertiary position.

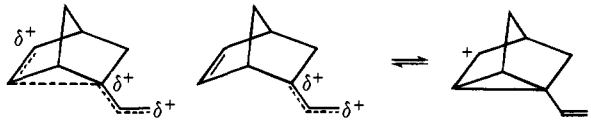
In sharp contrast, the product mixture derived from solvolysis of **15b** consists largely of the tertiary alcohol, 7-vinyl-*anti*-7-norbornenol (**18a**), which predominates over the primary alcohol **15a** by a factor of at least 43:1. No 7-vinyl-*syn*-7-norbornenol (**17a**) could be detected in the product mixture. Clearly the intermediate involved in solvolysis of ester **15b** must distribute a much greater percentage of the positive charge density to C-7 than does the intermediate derived from **5b** and **12b**. In addition, the absence of **17a** from the **15b** solvolysis product mixture is strongly reminiscent of results obtained with the 7-norbornenyl cation,[21] for which there is strong evidence for interaction between the endocyclic double bond and the vacant p orbital at C-7, but contrasts markedly with the lack of stereospecificity observed in the product distribution from the 7-*p*-anisyl-7-norbornenyl cation,[26] in which interaction between the double bond and the electron-deficient center appears to be absent. Both observations point to the interaction of the π electrons of the endocyclic double bond with the electron-deficient allylic π system in the cation resulting from ionization of ester **15b**. The fact that the rate of solvolysis of **15b** is accelerated by a factor of 26.0 strongly suggests that this interaction is already well developed in the transition state for bond heterolysis. For these reasons, we conclude that the endocyclic double bond does, indeed, participate during solvolysis of ester **15b** in a manner directly analogous to the behavior of the nucleophile in an S$_N$2′ displacement reaction.

With the ability of a suitably oriented, nonconjugated double bond to stabilize a developing allylic cation by π–π σ-delocalization thus firmly established, the solvolysis of allylic ester **16b** was investigated in an attempt to determine whether an unsymmetrically situated

(20) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).
(21) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955).
(22) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **91**, 1545 (1969); **92**, 2549 (1970).
(23) H. G. Richey, Jr., J. D. Nichols, P. G. Gassman, A. F. Fentiman, Jr., S. Winstein, M. Brookhart, and R. K. Lustgarten, *ibid.*, **92**, 3783 (1970).
(24) A. Padwa and E. Alexander, *ibid.*, **92**, 5674 (1970).
(25) A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955); G. Stork and A. W. Burgstahler, *J. Amer. Chem. Soc.*, 77, 5068 (1955).
(26) P. G. Gassman, J. Zeller, and J. Trevor Lumb, *Chem. Commun.*, 69 (1968).

double bond can also participate in this manner. The results are ambiguous. Ester **16b** solvolyzes 4.3 times more slowly than its analog **19b** which lacks the potentially nucleophilic endocyclic double bond. However, since the solvolysis of **19b** is itself accelerated (*vide supra*), a direct comparison of the reactivity of **16b** and **19b** is not a valid criterion by which to assay possible nucleophilic participation by the endocyclic double bond during solvolysis of **16b**. Clearly, the rate of solvolysis of **16b** is enhanced over that of the simple cyclohexylidene derivative **3b**. In the absence of anchimeric assistance, one would expect that both bond-angle deformation at the γ position and the presence of the inductively electron withdrawing sp^2-hybridized carbon atoms of the endocyclic double bond to cause the rate of solvolysis of **16b** to be *less* than that of **3b**. Since the opposite is true, we conclude that either the endocyclic double bond does participate during solvolysis of **16b** or that the $\sigma-\pi$ σ-delocalization which assists in ionization of **19b** is also manifest in the transition state for ionization of **16b**. Our results to date do not permit us to differentiate between these two possibilities.

The isolation in 12% yield of alcohol **20** from the solvolysis of ester **16b** does make clear that a cation electronically deficient at the more remote terminus of the endocyclic double bond must be generated at some stage in this reaction. This intermediate might be either the fully delocalized cation **33** or a cyclopropyl-



33 34 35

carbinyl isomer **35** of the allylic cation **34**.

Experimental Section

Proton magnetic resonance spectra were taken with a Varian A-60 nmr spectrometer. Chemical shifts (δ in ppm) are reported relative to the internal standard tetramethylsilane in carbon tetrachloride. A Varian Aerograph Series 1520 gas chromatograph was employed throughout for both analytical and preparative glc using 5 ft × 0.25 in. metal columns, helium as the carrier gas, and a thermal conductivity detector. Microanalyses were determined at the University of Massachusetts microanalytical laboratory. All melting points and boiling points are uncorrected.

Kinetic Measurements. The first-order rate constants were determined using the ampoule technique. Dinitrobenzoate ester (0.01 *M*) with urea (0.02 *M*) dissolved in 70% by volume acetone (Baker Analyzed Reagent) in distilled water. Each 5-ml aliquot was titrated with aqueous sodium hydroxide (0.01 *M*) using phenolphtnalein as indicator.

Product Studies. The substrate (0.01 *M*) in the presence of urea (0.04 *M*) and a suitable internal glc standard in 25 ml of solvent was allowed to solvolyze at 100° for 4 half-lives. The solution was then diluted with diethyl ether (200 ml) and washed with saturated sodium chloride (3 × 25 ml), saturated sodium bicarbonate (25 ml), and water (5 × 25 ml) before drying over magnesium sulfate. After the removal of most of the solvent at atmospheric pressure through a Vigreux column, the products were analyzed by glc using columns packed with either 10% Carbowax 20M or 15% SE-30 on Chromosorb W. For most product analyses, *n*-decyl alcohol was used as the internal standard except for the solvolyses of the esters of the dimethylallyl alcohols (**4b** and **11b**) and the bicyclo[3.3.1] alcohols **7b** and **14b** where isoamyl alcohol and benzyl alcohol were used, respectively. The molar response factors for the alcohol products relative to the internal standard were determined and used to calculate the absolute yield of each isomer formed.

Alcohol equilibrations were carried out at 100° in 70% acetone. Typically the alcohol (50 mg), in each of several ampoules each containing 70% acetone (5 ml) with two drops of perchloric acid (70% Baker Analyzed Reagent), was equilibrated until aliquots from either isomer of a pair, worked up as described above, gave the same alcohol distribution by glc.

Materials. The isomeric primary and tertiary alcohols were prepared from the corresponding ketones obtained either commercially or *via* a known synthetic route. Since the procedures were similar for each pair of isomers, a typical synthesis of the cyclopentyl allylic alcohols is reported and thereafter only deviations from these techniques are reported. The dinitrobenzoate (ODNB) derivatives were prepared in the usual manner.

Carbethoxymethylenecyclopentane. Carbethoxymethylenetriphenylphosphorane[27] (38 g, 0.11 mol) and 8.4 g (0.10 mol) of cyclopentanone (Eastman) were heated together in a sealed tube at 125° for 20 hr. The tube was then cooled and the contents were removed and extracted into 300 ml of refluxing pentane over 4 hr. The extract was filtered and reduced to small bulk on a rotary evaporator at room temperature and 20 mm. The product was distilled as a colorless oil: bp 95–96° (14 mm); yield 8.9 g (68%); nmr δ 5.68 (m, 1 H, vinyl), 4.15 3.93 (d, 2 H, CH_2 of ethyl, J = 7.5 Hz), 2.95 → 1.50 (complex, 8 H, ring methylenes), 1.20 (t, 3 H, CH_3 of methyl, J = 7.5 Hz).

2′-Hydroxyethylidenecyclopentane (2a). Carbethoxymethylenecyclopentane (8.9 g, 0.058 mol) in 25 ml of anhydrous diethyl ether was added dropwise to an ice-cooled, stirred suspension of 2.4 g (0.063 mol) of lithium aluminum hydride. After complete addition, the mixture was stirred at room temperature for a further 20 hr. The product was worked up in the normal alkaline manner and distilled as a colorless oil: bp 93–95° (12 mm); yield 4.9 g (45%); nmr δ 5.38 (m, 1 H, vinyl), 3.92 (d, 2 H, $-CH_2O$, J = 7.5 Hz), 3.85 (g, 1 H, -OH), 2.40 → 2.00 (m, 4 H, 2-ring methylenes α to sp^2 center), 1.90 → 1.40) (m, 4 H, other 2 ring methylenes).

2′-Ethylidenylcyclopentane 3,5-Dinitrobenzoate (2b): mp 94–95°; nmr δ 9.10 (s, 3 H, aromatic), 5.55 (m, 1 H, vinyl), 4.90 (d, 2 H, $-CH_2O$, J = 7.5 Hz), 2.65 → 2.15 (m, 4 H, 2 ring methylenes α to sp^2 center), 2.05 → 1.50 (m, 4 H, other 2-ring methylenes). *Anal.* Calcd for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.89; H, 4.59; N, 9.04.

1-Vinylcyclopentyl Alcohol (9a). Vinylmagnesium bromide[28] was prepared on a 0.1 *M* scale using 3 g of magnesium turnings and 14 g of vinyl bromide in a total of 60 ml of tetrahydrofuran under argon. This solution was cooled and stirred at 0° and 8.4 g (0.1 mol) of cyclopentanone (Eastman) was added dropwise, keeping the reaction temperature below 10° (1 hr). After complete addition the stirring was continued at room temperature for a further 1.5 hr; then, after cooling, the reaction was worked up by the dropwise addition of 20 ml of saturated ammonium chloride solution. After filtering off the solid material, the filtrate was dried over magnesium sulfate and then concentrated at atmospheric pressure using a Vigreux column. The product was distilled from the residue as a colorless oil: bp 71–74° (15 mm); yield 4.5 g (40%); nmr δ 6.18, 6.00, 5.86, and 5.70 (s, 1 H, single vinyl), 5.30 (d), 5.00 (t), 4.81 (d, 2 H, terminal vinyl CH_2), 3.10 (s, 1 H, hydroxyl), 2.15 → 1.40 (complex, 8 H, 4 ring methylenes).

1-Vinylcyclopentyl 3,5-Dinitrobenzoate (9b): mp 89–90°; nmr δ 9.10 (s, 3 H, aromatic), 6.52, 6.35, 6.23, and 6.05 (s, 1 H, single vinyl), 5.38, 5.25, and 5.08 (d, 2 H, terminal vinyl CH_2), 2.65 → 1.65 (complex, 8 H, 4-ring methylenes). *Anal.* Calcd for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.88; H, 4.58; N, 8.95.

Carbethoxymethylenecyclobutane: bp 80–82° (14 mm); yield 56%; nmr δ 5.45 (m, 1 H, vinyl), 4.15 and 3.93 (d, 2 H, CH_2 of ethyl, J = 7.5 Hz), 3.30 → 1.85 (complex, 6 H, ring methylenes), 1.20 (t, 3 H, CH_3 of ethyl, J = 7.5 Hz).

2′-Hydroxyethylidenecyclobutane (1a): bp 71–73° (12 mm); yield 35%; nmr δ 5.20 (m, 1 H, vinyl), 3.85 (d, 2 H, $-CH_2O$, J = 7.5 Hz), 2.95 → 1.40 (complex, 7 H, hydroxyl + ring methylenes).

2′-Ethylidenylcyclobutane 3,5-Dinitrobenzoate (1b): mp 65–67°; nmr δ 9.10 (s, 3 H, aromatic), 5.35 (m, 1 H, vinyl), 4.80 (d, 2 H, $-CH_2O$, J = 7.5 Hz), 3.10 → 1.60 (m, 6 H, ring methylenes). *Anal.* Calcd for $C_{13}H_{12}N_2O_6$: C, 53.43; H, 4.14; N, 9.59. Found: C, 53.45; H, 4.12; N, 9.33.

1-Vinylcyclobutyl Alcohol (8a): bp 64–65° (25 mm); yield 52%; nmr δ 6.30, 6.13, 6.02, and 5.83 (s, 1 H, single vinyl), 5.32,

(27) M. Gerecke, G. Ryser, and P. Zeller, U. S. Patent 2,912,467 (1959); *Chem. Abstr.*, **54**, 2254 (1960).

(28) D. Seyforth, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 258.

5.05, and 5.88 (d, 2 H, terminal vinyl CH_2), 3.60 (s, 1 H, hydroxyl), 2.45 → 1.40 (m, 6 H, ring methylenes).

1-Vinylcyclobutyl 3,5-Dinitrobenzoate (8b): mp 119–121°; nmr δ 9.10 (s, 3 H, aromatic), 6.48, 6.30, 6.19, and 6.02 (s, 1 H, single vinyl), 5.50 (d), 5.35 (d), 5.20 (m, 2 H, terminal vinyl CH_2), 2.75 → 1.65 (complex, 6 H, ring methylenes). *Anal.* Calcd for $C_{13}H_{12}N_2O_6$: C, 53.43; H, 4.14; N, 9.59. Found: C, 53.43; H, 4.11; N, 9.37.

Carbethoxymethylenecyclohexane: bp 51–52° (0.4 mm); yield 65%; nmr δ 5.50 (m, 1 H, vinyl), 4.15 and 3.93 (d, 2 H, CH_2 of ethyl, J = 7.5 Hz), 2.80 and 2.15 (m, 4 H, ring methylenes α to C=C), 1.60 (m, 6 H, remaining 3-ring methylenes), 1.20 (t, 3 H, CH_3 of ethyl, J = 7.5 Hz).

2′-Hydroxyethylidenecyclohexane (3a): bp 55–56° (0.3 mm); yield 65%; nmr δ 5.25 (t, 1 H, vinyl, J = 7 Hz), 3.95 (d, 2 H, $-CH_2O$, J = 7 Hz), 3.50 (s, 1 H, hydroxyl), 2.10 (m, 4 H, 2 ring methylenes α to C=C), 1.55 (m, 6 H, remaining 3-ring methylenes).

2′-Ethylidenylcyclohexane 3,5-Dinitrobenzoate (3b): mp 88–89°; nmr δ 9.10 (s, 3 H, aromatic), 5.45 (t, 1 H, vinyl, J = 7 Hz), 4.95 (d, 2 H, $-CH_2O$, J = 7 Hz), 2.25 (m, 4 H, 2-ring methylenes α to C=C), 1.60 (m, 6 H, remaining 3-ring methylenes). *Anal.* Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.05; N, 8.75. Found: C, 56.25; H, 5.18; N, 8.50.

1-Vinylcyclohexyl Alcohol (10a): bp 68–71° (7 mm); yield 40%; nmr δ 6.15, 5.98, 5.85, and 5.70 (s, 1 H, single vinyl), 5.30, 5.00, and 4.83 (d, 2 H, terminal vinyl CH_2), 2.05 (s, 1 H, hydroxyl), 1.55 (m, 10 H, ring methylenes).

1-Vinylcyclohexyl 3,5-Dinitrobenzoate (10b): mp 118–120°; nmr δ 9.10 (s, 3 H, aromatic), 6.40, 6.20, 6.08, and 5.90 (s, 1 H, single vinyl), 5.35 (d), 5.25 (s), 5.07 (d, 2 H, terminal vinyl CH_2), 2.50 → 1.30 (complex, 10 H, ring methylenes). *Anal.* Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.05; N, 8.75. Found: C, 56.19; H, 5.12; N, 8.74.

3,3-Dimethylallyl Alcohol (4a). 3,3-Dimethylacrylic acid (10 g, 0.1 mol) (Aldrich) in 25 ml of diethyl ether was added dropwise to an ice-cooled, stirred suspension of 4 g (0.105 mol) of lithium aluminum hydride in 75 ml of ether. After complete addition the solution was refluxed for 2 hr and worked up in the usual manner. After drying (magnesium sulfate) and removal of the solvent, the product was distilled: bp 140–142°; yield 8.0 g (90%); nmr δ 5.25 (m, 1 H, vinyl), 3.95 (d, 2 H, $-CH_2OH$, J = 7 Hz), 3.60 (s, 1 H, hydroxyl), 1.65 (d, 6 H, 2 methyl, J = 4 Hz).

3,3-Dimethylallyl 3,5-Dinitrobenzoate (4b): mp 69–70°; nmr δ 9.10 (s, 3 H, aromatic), 5.50 (m, 1 H, vinyl), 4.94 (d, 2 H, $-CH_2O$, J = 7.5 Hz), 1.84 (s, 6 H, 2 methyl). *Anal.* Calcd for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.32; N, 10.00. Found: C, 5.45; H, 4.30; N, 9.89.

1,1-Dimethylallyl 3,5-Dinitrobenzoate (11b). The ester was prepared from 1,1-dimethylallyl alcohol (Aldrich): mp 102–104°; nmr δ 9.10 (s, 3 H, aromatic), 6.50, 6.31, 6.20, and 6.03 (s, 1 H, single vinyl), 5.45 (d), 5.31, (d), 5.15 (m, 2 H, terminal vinyl CH_2), 1.75 (s, 6 H, 2 methyl). *Anal.* Calcd for $C_{12}H_{12}N_2O_6$: C, 51.43; H, 4.32; N, 10.00. Found: C, 51.34; H, 4.28; N, 10.11.

7-Carbethoxymethylenebicyclo[2.2.1]heptane. Bicyclo[2.2.1]heptan-7-one, prepared by the method of Gassman and Pape,[29] was used in the synthesis: bp 75–77° (1.5 mm); yield 51%; nmr δ 5.42 (s, 1 H, vinyl), 4.15 and 3.93 (d, 2 H, CH_2 of ethyl, J = 7.5 Hz), 3.50 and 2.40 (bs, each 1 H, bridgehead), 1.90 → 1.20 (complex, 8 H, 4-ring methylenes), 1.15 (t, 3 H, CH_3 of ethyl, J = 7.5 Hz).

7-(2′-Hydroxyethylidene)bicyclo[2.2.1]heptane (5a): bp 78–80° (1.3 mm); yield 67%; nmr δ 5.22 (t, 1 H, vinyl, J = 7 Hz), 4.05 (d, 2 H, $-CH_2O$, J = 7 Hz), 3.30 (s, 1 H, hydroxyl), 2.68 and 2.32 (bs each 1 H, bridgehead), 2.05 → 1.00 (complex, 8 H, 4 ring methylenes).

7-(2′-Ethylidenyl)bicyclo[2.2.1]heptane 3,5-Dinitrobenzoate (5b): mp 76–77°; nmr δ 9.10 (s, 3 H, aromatic), 5.35 (t, 1 H, vinyl, J = 7 Hz), 4.90 (d, 2 H, $-CH_2O$, J = 7 Hz), 2.85 and 2.40 (bs, each 1 H, bridgehead), 1.90 → 1.20 (complex, 8 H, 4 ring methylenes). *Anal.* Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 58.02; H, 5.10; N, 8.37.

7-Hydroxy-7-vinylbicyclo[2.2.1]heptane (12a). To a stirred solution of 10 g (0.09 mol) of bicyclo[2.2.1]heptan-7-one in 250 ml of dry tetrahydrofuran at 0° under argon, 62 ml of a 1.91 *M* solution of vinyllithium in tetrahydrofuran (Alfa Inorganics) was added dropwise over 1.5 hr. After stirring for a further hour at 0°, 110 ml of water was added cautiously over 2 hr. The resulting two-phase solution was separated and the lower aqueous phase extracted with 2 × 25 ml of diethyl ether. The extracts were combined with the organic phase, washed with saturated sodium chloride, dried over magnesium sulfate, and then concentrated at atmospheric pressure using a Vigreux column. The product was distilled: bp 100–110° (35 mm); yield 7.2 g (72%); nmr δ 6.50, 6.30, 6.20, and 6.02 (s, 1 H, single vinyl), 5.54 (d), 5.25 (m), 5.05 (d, 2 H, terminal vinyl CH_2), 2.75 (s, 1 H, hydroxyl), 2.50 → 1.10 (complex, 10 H, ring protons).

7-Vinylbicyclo[2.2.1]heptan-7-yl 3,5-Dinitrobenzoate (12b): mp 144–145°; nmr δ 9.10 (s, 3 H, aromatic), 6.68, 6.50, and 6.38 (s), 6.22 (s, 1 H, single vinyl), 5.68 and 5.50 (d), 5.35 (m, 2 H, terminal vinyl CH_2), 2.75 (m, 2 H, 2 bridgehead), 2.10 → 1.25 (complex, 8 H, 4 ring methylenes). *Anal.* Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.82; H, 4.78; N, 8.37.

8-Carbethoxymethylenebicyclo[3.2.1]octane. Bicyclo[3.2.1]octan-8-one, prepared by the method of Foote and Woodward,[10] was used in the synthesis: bp 94–96° (1.5 mm); yield 60%; nmr δ 5.57 (s, 1 H, vinyl), 4.25 and 4.03 (d, 2 H, CH_2 of ethyl, J = 7 Hz), 2.55 (bs, 1 H, bridgehead proton), 1.70 (m, 11 H, remaining ring protons), 1.15 (t, 3 H, CH_3 of ethyl, J = 7 Hz).

8-(2′-Hydroxyethylidene)bicyclo[3.2.1]octane (6a): bp 108–109° (4.5 mm); yield 65%; nmr δ 5.30 (t, 1 H, vinyl, J = 7 Hz), 4.05 (d, 2 H, $-CH_2O$, J = 7 Hz), 3.90 (s, 1 H, hydroxyl), 2.45 and 2.80 (bs, each 1 H, bridgehead), 1.60 (m, 10 H, 5-ring methylenes).

8-(2′-Ethylidenyl)bicyclo[3.2.1]octane 3,5-Dinitrobenzoate (6b): mp 70.5–71.5°; nmr δ 9.10 (s, 3 H, aromatic), 5.50 (t, 1 H, vinyl), J = 7.5 Hz), 5.07 (d, 2 H, $-CH_2O$, J = 7.5 Hz), 3.05 and 2.60 (bs, each 1 H, bridgehead), 1.70 (m, 10 H, 5 ring methylenes). *Anal.* Calcd for $C_{17}H_{18}N_2O_6$: C, 58.98; H, 5.20; N, 8.09. Found: C, 58.80; H, 4.97; N, 8.05.

8-Hydroxy-8-vinylbicyclo[3.2.1]octane (13a) was prepared using the vinyllithium method: bp 75–76° (4 mm); yield 60%; nmr δ 6.35, 6.17, 6.05, and 5.88 (s, 1 H, single vinyl), 5.45. 5.15, and 4.95 (d, 2 H, terminal vinyl CH_2), 2.25 → 1.00 (complex, 13 H, ring protons + hydroxyl).

8-Vinylbicyclo[3.2.1]oct-8-yl 3,5-Dinitrobenzoate (13b): mp 180–181°; nmr δ 9.10 (s, 3 H, aromatic), 6.50, 6.35, 6.25. and 6.05 (s, 1 H, single vinyl), 5.62 and 5.65 (d), 5.30 (m, 2 H, terminal vinyl CH_2), 2.75 (m, 2 H, 2 bridgehead), 2.00 → 1.30 (complex, 10 H, 5 ring methylenes). *Anal.* Calcd for $C_{17}H_{18}N_2O_6$: C, 58.98; H, 5.20; N, 8.09. Found: C, 58.86; H, 5.10; N, 8.06.

9-Carbethoxymethylenebicyclo[3.3.1]nonane. Bicyclo[3.3.1]nonan-9-one, prepared by the method of Foote and Woodward,[10] was used in the synthesis: bp 86.87° (0.6 mm); yield 30%; nmr δ 5.57 (s, 1 H, vinyl), 4.20 and 4.00 (d, 2 H, CH_2 of ethyl, J = 7 Hz), 2.34 (bs, 1 H, bridgehead), 2.10 → 1.50 (complex, 13 H, remaining ring protons), 1.22 (t, 3 H, CH_3 of ethyl, J = 7 Hz).

9-(2′-Hydroxyethylidene)bicyclo[3.2.1]nonane (7a): bp 85–90° (0.5 mm); yield 80%; nmr δ 5.37 (t, 1 H, vinyl, J = 7 Hz), 6.40 (d, 2 H, $-CH_2O$, J = 7 Hz), 2.82 and 2.30 (bs, each 1 H, bridgehead), 2.20 → 1.25 (complex, 13 H, 5 ring methylenes + hydroxyl).

9-(2′-Ethylidenyl)bicyclo[3.3.1]nonane 3,6-Dinitrobenzoate (7b): mp 97–98.5°; nmr δ 910 (s, 3 H, aromatic), 5.58 (t, 1 H, vinyl, J = 7.5 Hz), 5.10 (d, 2 H, $-CH_2O$, J = 7.5 Hz), 3.00 and 2.40 (bs, each 1 H, bridgehead), 2.30 → 1.30 (complex, 12 H, 6 ring methylenes). *Anal.* Calcd for $C_{15}H_{20}N_2O_6$: C, 60.02; H, 5.55; N, 7.77. Found: C, 60.35; H, 5.90; N, 7.37.

9-Hydroxy-9-vinylbicyclo[3.3.1]nonane (14a) was prepared using the vinyllithium method: bp 67–68° (0.7 mm); yield 70%; nmr δ 6.60, 6.45, 6.32, and 6.14 (s, 1 H, single vinyl), 5.48 (d), 5.20 and 5.03 (m, 2 H, terminal vinyl CH_2), 2.50 → 1.20 (complex, 15 H, ring protons + hydroxyl).

9-Vinylbicyclo[3.3.1]non-9-yl 3,5-Dinitrobenzoate (14b): mp 152–153°; nmr δ 9.10 (s, 3 H, aromatic), 6.80, 6.60, 6.48, and 6.30 (s, 1 H, single vinyl), 5.70 and 5.55 (s), 5.40 (d, 2 H, terminal vinyl CH_2), 2.70 (m, 2 H, 2 bridgehead), 2.20 → 1.30 (complex, 12 H, 6 ring methylenes). *Anal.* Calcd for $C_{15}H_{20}N_2O_6$: C, 60.02; H, 5.55; N, 7.77. Found: C, 60.15; H, 5.79; N, 7.60.

7-Carbethoxymethylenebicyclo[2.2.1]hept-2-ene. Bicyclo[2.2.1]-hept-2-en-7-one, prepared by the method of Gassman and Pape,[29] was used in the synthesis: bp 112° (14.5 mm); yield 59%; nmr δ 6.20 (m, 2 H, 2-ring vinyl protons), 5.05 (s, 1 H, single vinyl proton), 4.15 (m, 1 H, bridgehead), 4.15 and 3.95 (d, 2 H, CH_2 of ethyl, J = 7 Hz), 3.00 (m, 1 H, bridgehead), 1.80 (m, 2 H, 2-ring methylene protons), 1.40 → 1.05 (complex, 5 H, other 2-ring methylene protons + CH_3 of ethyl).

7-(2′-Hydroxyethylidene)bicyclo[2.2.1]hept-2-ene (15a): bp 108–109 (14.5 mm); yield 69%; nmr δ 6.10 (s, 2 H, 2 ring vinyl protons), 4.75 (t, 1 H, single vinyl proton, J = 7 Hz), 4.47 (s, 1 H, hydroxyl), 3.82 (d, 2 H, $-CH_2O$, J = 7 Hz), 3.25 and 2.90 (bs, each 1 H, bridge-

(29) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

head), 1.90 → 1.40 and 1.20 → 0.70 (m, each 2 H, ring methylene protons).

7-(2′-Ethylidenyl)bicyclo[2.2.1]hept-2-enyl 3,5-Dinitrobenzoate (15b): mp 81–82°; nmr δ 9.10 (s, 3 H, aromatic), 6.28 (m, 2 H, ring vinyl), 4.95 (m, 3 H, $-CH_2O$ + single vinyl proton), 3.55 and 3.15 (bs, each 1 H, bridgehead), 2.00 → 1.60 and 1.30 → 1.00 (m, each 2 H, ring methylene protons). *Anal.* Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.13; H, 4.32; N, 8.55.

7-*anti*-Vinyl-7-*syn*-hydroxybicyclo[2.2.1]hept-2-ene (17a) and 7-*syn*-vinyl-7-*anti*-hydroxybicyclo[2.2.1]hept-2-ene (18a) were preparedas a mixture of isomers by the vinyllithium reduction of bicyclo[2.2.1]hept-2-en-7-one: bp 70–120° (20 mm); yield 58%. The mixture contained 75% **17a** and 25% **18a** which were separated by preparative glc on a 30 ft × 3/8 in. metal column packed with 30% Carbowax 20M on 30–60 Chromosorb W at 145° with helium carrier gas flow of 120 ml/min. The anti-OH isomer **18a** had shorter retention time and was collected as a colorless liquid and **17a** was a white solid: mp 55–57°; nmr **17a**: δ 6.25, ~6.05, 5.98, and 5.82 (s, 1 H, single vinyl), 6.05 (t, 2 H, 2 ring vinyl protons, J = 2 Hz), 5.53 (d), 5.22 (t), 5.02 (d, 2 H, terminal vinyl CH_2), 2.90 (s, 1 H, hydroxyl), 2.52 (m, 2 H, 2 bridgehead protons), 1.95 → 1.60 and 1.10 → 0.75 (m, each 2 H, ring methylene protons). Nmr **18a**: δ 6.62, 6.45, 6.34, and 6.15 (s, 1 H, single vinyl), 6.02 (t, 2 H, 2 ring vinyl protons, J = 2 Hz), 5.42, 5.20, and 5.00 (d, 2 H, terminal vinyl CH_2), 2.50 (m, 2 H, 2 bridgehead protons), 2.30 (s, 1 H, hydroxyl), 2.30 → 1.90 and 1.20 → 0.85 (m, each 2 H, 4 ring methylene protons).

7-*anti*-Vinylbicyclo[2.2.1]hept-2-enyl 7-*syn*-3,5-Dinitrobenzoate (17b): mp 129–130°; nmr δ 9.10 (s, 3 H, aromatic), 6.55, 6.37, 6.25, and ~6.10 (s, 1 H, single vinyl), 6.10 (t, 2 H, 2 ring vinyl protons, J = 2 Hz); 5.63 and 5.48 (d), 5.32 (m, 2 H, terminal vinyl CH), 3.45 (m, 2 H, 2 bridgehead protons), 2.05 → 1.67 and 1.27 → 0.95 (m, each 2 H, 4 ring methylene protons). *Anal.* Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.25; H, 4.38; N, 8.39.

7-*syn*-Vinylbicyclo[2.2.1]hept-2-enyl 7-*anti*-3,5-Dinitrobenzoate (18b): mp 150–151°; nmr δ 9.10 (s, 3 H, aromatic), 6.49, 6.31, 6.20, and ~6.08 (s, 1 H, single vinyl), 6.05 (t, 2 H, 2 ring vinyl protons, J = 2 Hz), 5.45 → 5.25 and 5.10 (m, 2 H, terminal vinyl CH_2), 3.23 (m, 2 H, 2 bridgehead protons), 2.15 → 1.75 and 1.45 → 1.02 (m, each 2 H, 4 ring methylene protons). *Anal.* Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.26; H, 4.38; N, 8.39.

2-Carbethoxymethylenebicyclo[2.2.1]hept-5-ene. Bicyclo[2.2.1]-hept-5-en-2-one, prepared by the method of Bartlett and Tate,[30] was used in the synthesis: bp 116–117 (12 mm); yield 55%; nmr δ 6.30 → 5.48 (complex, 3 H, 3 vinyl protons), 4.15 and 3.93 (d, 2 H, CH_2 of ethyl, J = 7 Hz further split J = 2 Hz), 3.25 and 3.05 (bs, each 1 H, bridgehead protons), 2.60 → 1.20 (complex, 4 H, bridge and C(3) methylene), 1.25 (t, 3 H, CH_3 of ethyl, J = 7 Hz further split, J = 2 Hz).

2-(2′-Hydroxyethylidene)bicyclo[2.2.1]hept-5-ene (16a): bp 79–81° (1.2 mm); yield 70%; nmr δ 5.95 (s, 2 H, 2 ring vinyl protons), 5.35 (m, 1 H, single vinyl proton), 3.90 (t, 2 H, $-CH_2O$, J = 7 Hz), 3.40, 3.05, and 2.90 (bs, total 2 H, bridgehead protons from the two isomers present), 3.00 (s, 1 H, hydroxyl), 2.15 and 1.65 (d, 2 H, protons at C(3), J = 15 Hz), 1.55 and 1.35 (d, 2 H, bridge protons, J = 8 Hz).

2-(2′-Ethylidenyl)bicyclo[2.2.1]hept-5-enyl 3,5-Dinitrobenzoate (16b): mp 80–81°; nmr δ 9.10 (s, 3 H, aromatic), 6.10 (m, 2 H, 2 ring vinyl protons), 5.60 (m, 1 H, single vinyl proton), 4.90 (t, (2 H, $-CH_2O$, J = 8 Hz), 3.65, 3.15, and 3.05 (bs, total 2 H, bridgehead protons from the two isomers present), 2.38 and 1.92 (d, 2 H, protons at C(3), J = 14 Hz), 1.67 and 1.47 (d, 2 H, bridge protons, J = 8 Hz). *Anal.* Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.40; H, 4.35; N, 8.40.

2-*exo*-Vinyl-2-*endo*-hydroxybicyclo[2.2.1]hept-5-ene (22) was prepared by the vinylmagnesium bromide method: bp 77–59° (15 mm); yield 65%; nmr δ 6.40 → 5.80 (complex, 3 H, 2 ring vinyl protons + single vinyl), 5.30 (d), 5.10 (t), 4.82 (d, 2 H, terminal vinyl CH_2), 2.90 → 2.52 (m, 2 H, bridgehead protons), 1.70 (s, 1 H, hydroxyl), 2.05 → 0.90 (complex, 4 H, protons at bridge and C(3)).

2-*endo*-Vinyl-2-*exo*-hydroxybicyclo[2.2.1]hept-5-ene (21) was obtained by glc separation of the products from the solvolysis of **16b**: nmr 6.40 → 5.65 (3 H, complex consisting of a multiplet at 6.10 for the endocyclic vinyl proton (2 H), and four singlets for the single vinyl proton), 5.38, 5.13, and 4.93 (d, 2 H, terminal vinyl CH_2), 3.00 and 2.66 (bs, each 1 H, the bridgehead protons), 2.30 → 1.35 (complex, 4 H, bridge protons and CH_2 β to the vinyl group).

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(30) P. D. Bartlett and B. E. Tate, *J. Amer. Chem. Soc.*, 78, 2473 (1956).

Perfluoroaromatics. Tris(polyfluoroaryl) Carbocations

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Abstract: A series of polyfluorinated triarylmethanols has been synthesized, and the effects of fluorine substitution on the stability of carbenium ions, generated in concentrated sulfuric acid, have been evaluated. An interesting additive effect of the *o*-, *m*-, and *p*-fluoro substituents is observed. A satisfactory correlation is found between carbenium ion stability, as measured by pK_{R^+} values, and Hammett σ^+ constants for a number of para-substituted cations. The experimentally determined pK_{R^+} and pK_a values of three polyfluorinated triarylmethanols and the corresponding hydrocarbons provide a linear correlation and suggest a method for estimating one from the other.

Since the observation of the first stable, long-lived triphenylmethyl cations,[1] extensive studies have been carried out[2] on mono-, di-, and triaryl carbenium ions by ultraviolet, infrared, X-ray, and nmr techniques. Olah and coworkers[3] studied the influence of substitution of heteroatoms such as fluorine on the stability of carbenium ions. They observed that, in contrast to

(1) F. Kehrmann and F. Wentzel, *Chem. Ber.*, 34, 3815 (1901); 35, 622 (1902).

(2) For an extensive review, see G. A. Olah, *Science*, 168, 1298 (1970).

(3) G. A. Olah, M. B. Comisarow, and C. A. Cupas, *J. Amer. Chem. Soc.*, 88, 362 (1966).