

structures. It provides specific structural information about the number of differently substituted pyrrole rings, the particular pairs of substituents (alkyl, side-chain ester, nuclear ester, vinyl, formyl, acyl, and cyano) at the β -pyrrole positions as well as substituents on the internal nitrogens, and the sequence of adjacent pyrrole rings about the porphyrin macrocycle. A particularly illustrative example was given in the full spectrum of 4-acetyldeuteroporphyrin IX DME (**4**) presented in the preliminary communication.¹⁸ It does not, however, distinguish isomeric porphyrins which arise from interchange of the substituents on an individual pyrrole ring. Although not examined here, NH_3 D/CIMS may also be of value for elucidation of other kinds of porphyrin structures such as chlorins and corroles.

The NH_3 D/CIMS of porphyrins themselves is much more informative than EIMS of the separately formed and isolated porphyrinogens.⁷ The use of ammonia rather than hydrogen as the reagent gas is to be preferred since the extensive β -cleavage fragments formed by using the latter gas clutter the MS and may obscure the identification of particular intact pyrrolic and dipyrrolic fragment ions.

Finally, NH_3 D/CIMS does not, of course, supplant porphyrin structural analysis via other physical methods—notably, by X-ray crystallography, NMR, or absorption and IR spectroscopy. Its advantage is that much smaller samples are required in order to obtain a nearly complete description of the porphyrin structure.

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On the Mechanism of Alkyne-Forming Elimination Reactions: A Theoretical Study

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Abstract: A theoretical study employing ab initio molecular orbital calculations on the elimination of HX from halosubstituted alkenes to form alkynes is described. Upon substitution of fluorine in the β -position of ethylene anion, the inversion barrier drops ~ 20 kcal/mol while an α -fluoro or α -chloro substituent raises the inversion barrier of a vinyl anion by ~ 50 kcal/mol. The activation barrier for the elimination of fluoride ion from syn 2-fluorovinyl anion was calculated to be 4.1 kcal/mol higher in energy than that of the corresponding anti anion. We conclude that essentially all of the activation barrier in these alkyne-forming elimination reactions may be ascribed to electronic effects associated with inversion at the carbanionic center.

The stereochemistry of alkene- and alkyne-forming E2 eliminations has been intensively studied, and many factors that contribute to the overall syn or anti stereochemical course of these reactions have been identified.¹ Mechanistic rationale for this important class of reactions developed simultaneously with stereochemical studies on the $\text{S}_{\text{N}}2$ nucleophilic substitution reaction. Hughes² recognized that 1,2-elimination reactions may be thought of as an internal nucleophilic substitution at the carbon bearing the leaving group by the developing electron pair at the β carbon. One of the features essential for the description of a concerted 1,2-elimination process is the dihedral angle about the $\text{C}_{\alpha}\text{-C}_{\beta}$ bond in the activated complex. It was first suggested by DePuy,³ and

supported by experiments on various systems, that arrangements in which the $\text{C}_{\alpha}\text{-X}$ and the $\text{C}_{\beta}\text{-H}$ bonds are antiperiplanar (dihedral angle 180°) or synperiplanar (dihedral angle 0°) will be preferred in the transition state of an HX elimination reaction. Ingold⁴ and Sicher⁵ have suggested that if $\text{C}_{\beta}\text{-H}$ bond cleavage in a concerted syn elimination were considerably advanced in the transition state (such as in the E1cb-like process), sufficient ionicity could develop on the β carbon for the charge to spread on both sides of this carbon and thus proceed with inversion of configuration at the β carbon prior to elimination. In today's mechanistic parlance such alkene-forming reactions could be said to proceed by an antarafacial mode of elimination but still exhibit syn-stereospecificity with respect to the leaving group and the β -hydrogen undergoing elimination.⁶

In a recent theoretical study, we corroborated the above suggestion.⁶ Employing ab initio calculations on a series of model carbanions, we found that halogenated aliphatic compounds do

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Table I. Optimized Geometries and Total Energies for Syn **1**, Anti **2**, and Planar 2-Fluorovinyl Anions and Syn **3**, Anti **4**, and Planar 1,2-Difluorovinyl anions

	STO-3G			4-31G					
	1	2	planar anion ^a	1	2	planar anion ^b	3	4	planar anion ^c
	Bond Lengths (Å)								
C _α -C _β	1.320 ₂	1.319 ₃	1.238 ₁	1.341 ₁	1.309 ₇	1.230 ₄	1.330 ₉	1.330 ₅	1.213 ₈
C _β -H(F)	1.117 ₄	1.119 ₈	1.047 ₂	1.109 ₀	1.101 ₉	1.049 ₁	1.498 ₇	1.472 ₀	1.352 ₀
C _α -H	1.100 ₇	1.095 ₈	1.124 ₁	1.079 ₉	1.072 ₇	1.067 ₁	1.069 ₃	1.068 ₆	1.061 ₉
C _α -F	1.399 ₄	1.403 ₆	1.437 ₀	1.461 ₀	1.493 ₂	1.700 ₉	1.423 ₅	1.428 ₀	1.733 ₅
	Bond Angles (deg)								
C _β -C _α -F	122.341 ₇	127.830 ₈	127.275 ₁	121.322 ₈	126.065 ₃	125.725 ₂	118.897 ₁	127.252 ₃	125.151 ₀
C _β -C _α -H	130.768 ₀	124.761 ₁	131.809 ₅	134.965 ₂	130.332 ₈	144.086 ₁	130.990 ₅	123.350 ₈	145.970 ₄
C _α -C _β -H(F)	104.961 ₂	105.627 ₃	180.000	108.328 ₅	112.563 ₆	180.000	103.655 ₅	109.436 ₄	180.000
total energy, au	-173.2086 ₁	-173.7108 ₄	-173.6489 ₈	-175.9739 ₃	-175.9787 ₈	-175.9529 ₃	-274.7328 ₂	-274.7314 ₉	-274.6555 ₆

^aAll geometric parameters were optimized except the C_α-C_β-H angle, which was held constant at 180.0°, and the C_α-F bond length. ^bAll geometric parameters were optimized except the C_α-C_β-H angle which was held constant, and the C_α-F bond length. The C_α-F bond length was held constant at the optimized value for the C_α-F bond length (1.7009 Å) for the last thermodynamically stable anion along the reaction pathway. ^cAll geometric parameters were optimized except the C_α-C_β-F bond angle which was held constant, and the C_α-F bond length. The C_α-F bond length was held constant at the optimized value for the C_α-F bond length (1.7335 Å) for the last thermodynamically stable anion along the reaction pathway.

Table II. Optimized Geometries and Total Energies of the Transition Structures of Syn (**1a**) and Anti (**2a**) 2-Fluorovinyl Anions and Syn (**3a**) and Anti (**4a**) 1,2-Difluorovinyl Anions and Their Corresponding Planar Anions

	4-31G							
	1a	planar anion ^a	2a	planar anion ^a	3a	planar anion ^a	4a	planar anion ^{a,b}
	Bond Lengths (Å)							
C _α -C _β	1.230 ₄	1.222 ₃	1.226 ₄	1.208 ₂	1.214 ₉	1.195 ₇	1.213 ₈	1.195 ₇
C _β -H(F)	1.054 ₂	1.048 ₉	1.056 ₆	1.048 ₉	1.358 ₆	1.340 ₂	1.346 ₁	1.340 ₂
C _α -H	1.061 ₇	1.060 ₀	1.049 ₉	1.047 ₉	1.048 ₄	1.046 ₄	1.044 ₇	1.046 ₄
C _α -F	1.785 ₅	1.786 ₀	1.967 ₄	1.967 ₀	1.955 ₄	1.955 ₀	2.105 ₁	1.955 ₀
	Bond Angles (deg)							
C _β -C _α -F	122.656 ₀	125.665 ₂	126.678 ₁	126.509 ₄	118.796 ₆	125.459 ₃	132.078 ₁	125.459 ₃
C _β -C _α -H	150.676 ₃	147.999 ₉	152.357 ₇	158.367 ₁	163.695 ₂	158.592 ₈	156.488 ₁	158.592 ₈
C _α -C _β -H(F)	153.047 ₉	180.000	146.244 ₂	180.000	148.553 ₈	180.000	150.284 ₇	180.000
total energy, au	-175.9517 ₃	-175.9549 ₁	-175.9631 ₇	-175.9596 ₇	-274.6598 ₂	-274.6646 ₆	-274.6731 ₃	-274.6646 ₆

^aAll geometric parameters of the planar anions were fully optimized except the C_α-C_β-H(F) angle, which was held constant at 180.0°, and the C_α-F bond length. ^aThe C_α-F bond lengths were held constant at the C_α-F bond length of the corresponding sp² anion. ^bThe planar anion corresponding to **4a** could not be fully optimized while maintaining the C_α-F length at 2.105 Å; the C_α-F bond length was maintained at 1.9550 Å.

in fact undergo syn elimination by an antarafacial mode. In the case where the syn anion of 1-fluoroethane was formed by the action of base, it was found by following the reaction pathway that the syn carbanion undergoes inversion at the developing β carbanionic center prior to elimination. These observations prompted us to postulate that the rate of both syn and anti elimination will be increased by maximizing overlap of the developing carbanion at C_β with the backside of the C_α leaving group. We now report the results of a theoretical study on elimination of HF from substituted alkenes to form alkynes. We are particularly interested in examining the effect of the relative energies of the inversion barriers of halogen-substituted vinyl anions on the barrier to E2 elimination of vinyl substrates.

There have been a number of syntheses of fluoroacetylenes reported, as well as of aryl- and alkyl-substituted acetylenes.⁷ Fluoroacetylenes have been synthesized by the elimination of HF under E2 conditions.⁸ Recently halogenated alkynes have been extensively utilized as latent functionality in the synthesis of fairly complex molecules.⁹

Theoretical studies on such elimination reactions have been somewhat limited. Houk has examined the influence of electron-withdrawing substituents on the geometries and barriers to inversion of vinyl anions by ab initio calculations.¹⁰ Electron-

withdrawing substituents on the carbanionic center were found to lower the inversion barrier. Using a 4-31G basis set, he found an inversion barrier of 36.6 kcal/mol for the ethylene anion, whereas the inversion barrier for an α-cyano-substituted vinyl anion was calculated to be 10.3 kcal/mol. Dykstra obtained an inversion barrier for ethylene anion of 37.9 kcal/mol using a double-ζ basis set augmented with diffuse s functions.¹¹

Beauchamp has examined the effects that various bases have on fluoroethylenes in the gas phase.¹² He observed that as the number of fluorine substituents attached to ethylene increases from one to three, the product ratios for the reaction with methoxide ion changes. For the reaction of fluoroethylene with methoxide ion in the gas phase the major product was that of elimination of HF. When *gem*-difluoroethylene was reacted with methoxide ion, the major product was nucleophilic addition. Finally, when *trans*-difluoroethylene was subjected to methoxide ion the only product obtained was that of proton transfer to the base. This is a reflection of the gas-phase stability of the dihalo-substituted vinyl anion and its reluctance to undergo elimination (*supra* *vida*).

Methods of Calculation

The calculations were performed with the Gaussian 82 series of programs with standard MO theory.¹³ Both minimal STO-3G and extended 4-31G basis sets were used. A diffuse function augmented 4-31+G basis set¹⁴ was also utilized on structures 1-4.

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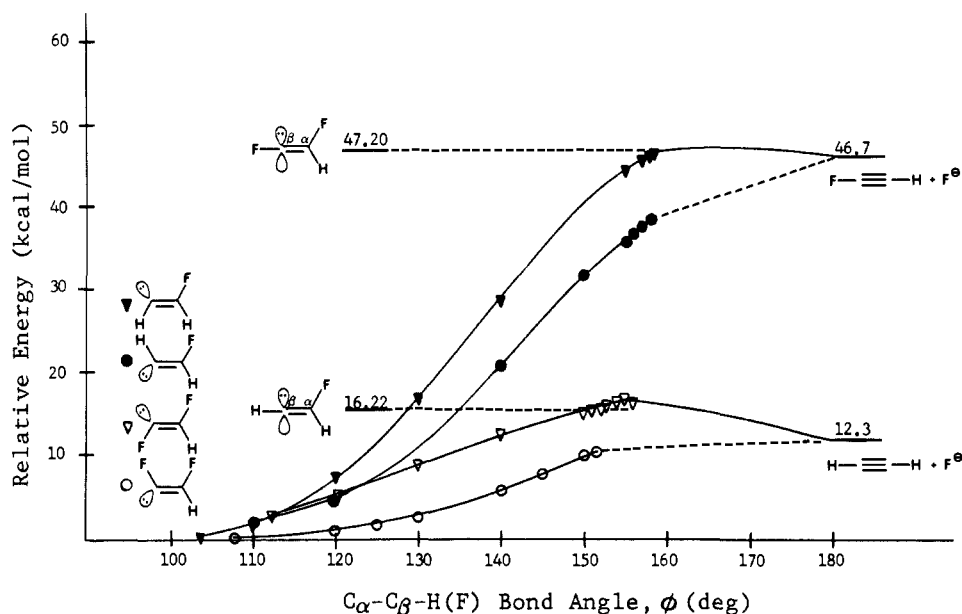


Figure 1. Reaction pathway for elimination of fluoride ion from vinyl anions 1-4 (4-31G).

Structures 1 through 4 were fully optimized without any geometric constraints (Table I). The corresponding planar anions are obviously thermodynamically unstable since the $C_\alpha-C_\beta-H(F)$ bond angle of 180° exceeds that of the transition-state structures for F^- elimination (Table II). An approximate transition-state geometry for fluoride ion expulsion from anions 1 through 4. The $C_\alpha-C_\beta-H(F)$ bond angle ϕ (Figure 1) was systematically varied from its ground-state geometry in the sp^2 anion with all other geometric parameters being fully optimized. The last thermodynamically stable point prior to expulsion of fluoride ion was taken as the initial guess for the transition-state structure. Transition structures 1a through 4a were then fully optimized at 4-31G with use of energy gradients^{13b} (Table II). The activation barriers are calculated relative to the fully optimized sp^2 vinyl anions 1 through 4 (Figure 2).

The inversion barriers for a series of α and β halo-substituted vinyl anions have been calculated (Table III). Anions 5, 6, and 7 were fully optimized without any geometric constraints. In anions 8 through 11 the C-Cl bond distance was constrained at 1.7779 Å, the optimized bond distance (4-31G) in vinyl chloride. Consequently, the inversion barriers have been calculated in three different ways (Table III). In the first method, to prevent expulsion of halide ion from the linear sp -hybridized anion, the carbon-halogen bond distance of the planar anion was constrained to that of the corresponding vinyl halide. This method is adequate to provide a series of relative inversion barriers. Since a static inversion barrier of this kind would be artificially high, a better estimate of the actual barrier was calculated while the carbon-fluorine bond distance of the planar anion was maintained at that of the corresponding fully optimized sp^2 -hybridized anion (column 2). The third and most meaningful inversion barrier (4-31G and 4-31+G) utilized the carbon-fluorine bond distance calculated in the last thermodynamically stable point prior to expulsion of fluoride ion from the corresponding sp^2 anions (column 3 and 4). The corresponding decrease in the barrier attending carbon-fluorine bond elongation is a consequence of a greater interaction of the carbanion with the σ^* carbon-fluorine orbital as that antibonding orbital is declining in energy.

Results and Discussion

Elimination of HX from vinyl halides resulting in alkyne formation involves an electronic reorganization that closely parallels simple inversion of an $\sim sp^2$ vinyl carbanion. The temperatures that are required for an E2 elimination of HX in vinyl halides to form alkynes are often higher than those for the elimination of HX from saturated substrates to form alkenes. One of the principal objectives of the present study was to qualitatively evaluate what portion of the overall activation barrier could be attributed to the inversion process associated with the involvement of an sp^2 carbanionic center. Intuitively, one would think that the transition state for a syn elimination would closely resemble

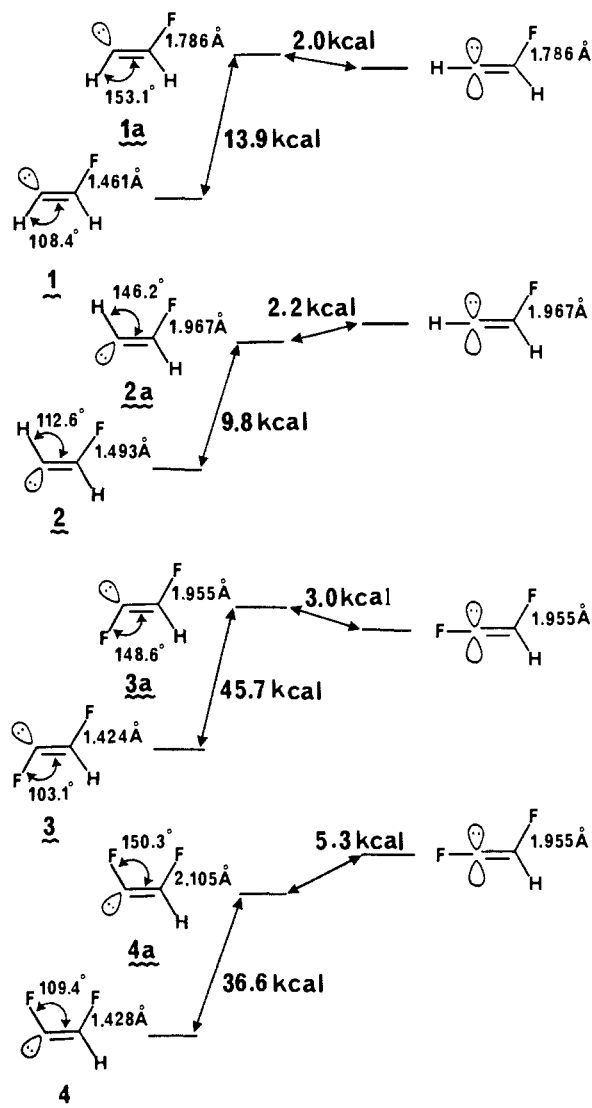


Figure 2. Calculated activation barriers for elimination of fluoride ion from 1, 2, 3, and 4 and the relative energies of the corresponding planar anions (4-31G, kcal/mol).

an anion (E1cb-like)⁶ and that the syn anions described herein could serve as satisfactory models for such a study. Since inversion

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Table III. Inversion Barriers for a Series of Vinyl Anions (4-31G)

	static inversion barrier (kcal mol ⁻¹)	inversion barrier ^b (kcal mol ⁻¹)	inversion barrier ⁱ (kcal mol ⁻¹)	inversion barrier (4-31+G, kcal mol ⁻¹)
	8.1			
1	36.6 ^a			
2	22.5 ^b	21.0	16.22	20.90
3	19.4 ^b	19.4	13.22	17.42
4	63.2 ^c	58.0	47.20	46.03
5	63.3 ^c	56.8	46.30	45.83
6	85.1			
7	86.5			
8	54.2 ^d			
9	60.2 ^e			
10	61.4 ^f			
11	21.4 ^g			
11	24.8 ^g			

^aHouk, K. N.; Caramella, P. *Tetrahedron Lett.* **1981**, 22, 819. ^bThe inversion barriers for the syn and anti anions ($\sim sp^2$) were calculated relative to the planar anion ($\phi = 180^\circ$) where the C_α -F bond distance was maintained at that of vinyl fluoride (1.461 Å). ^cThe ground-state syn and anti anions of 1,2-difluorovinyl anions were fully optimized and the inversion barriers were calculated relative to a planar anion ($\phi = 180^\circ$) where the C_α -F bond distance was maintained at that of 1,2-difluoroethylene (1.367 Å). ^dThe inversion barrier of the syn anion ($\sim sp^2$) was calculated relative to the planar anion ($\phi = 180^\circ$) where the C_α -F bond distance was maintained at that of vinyl fluoride (1.461 Å). ^eThe ground state syn anion 1-fluoro-2-chlorovinyl was fully optimized and the inversion barrier was calculated relative to a planar anion ($\phi = 180^\circ$) where the C_α -Cl bond distance was maintained at that of vinyl chloride (1.7779 Å). ^fThe ground-state anion ($\sim sp^2$) for anti 1-fluoro-2-chlorovinyl anion was optimized while maintaining the C_α -Cl bond distance at 1.7779 Å, and the inversion barrier was calculated relative to a planar anion ($\phi = 180^\circ$). ^gThe ground-state 2-chlorovinyl anion ($\sim sp^2$) was optimized while holding the C_α -Cl bond distance constant (1.7779 Å) and the inversion barrier was calculated relative to a planar anion ($\phi = 180^\circ$) where the C_α -Cl bond distance was maintained at that of vinyl chloride (1.7779 Å). ^hThe inversion barriers were calculated relative to a planar anion, where the C_α -F bond distance was held constant at the appropriate C_α -F bond distance of the ground-state anions. ⁱThe inversion barriers were calculated relative to the planar anions, where the C_α -F bond distances of the planar anions were held constant at the C_α -F bond distance of the last thermodynamically stable ($\sim sp^2$) anion along the reaction coordinate (Figure 1). The C_α -F bond distances that the planar anions were maintained at are listed in Table I.

barriers at vinyl carbon are characteristically much higher than those of aliphatic carbanions, we anticipate that the activation energy for an E2 elimination should exhibit a parallel trend. For example, the inversion barrier of a simple carbanion is typically lower than that of its corresponding amine. A secondary goal was to examine what effects α - and β -halo substituents have on the inversion barriers of vinyl anions and on the corresponding activation barrier for alkyne formation.

Examination of the data in Table III provides an estimate of the effect of α - and β -halo substituents on the inversion barrier at vinylic carbon. The inversion barrier for vinyl anion is 36.6 kcal/mol (4-31G).¹⁰ When a fluorine is substituted in the β position, as in **1** or **2**, the inversion barrier drops by ~ 20 kcal/mol, while an α -fluoro or α -chloro substituent (**5** and **6**) raises the barrier by ~ 50 kcal/mol. The inversion barrier for a 1,2-dihalo

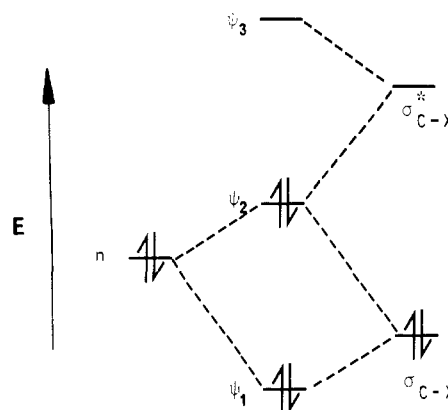


Figure 3. Three MO four-electron model for the stabilization of a carbanion by an adjacent σ bond.

vinyl anion is about 20 kcal/mol higher than that of the parent anion. These data are in good accord with an indirect experimental estimate of 25–35 kcal/mol for the activation energy for the isomerization of vinyl carbanions derived from 1,2-dihaloethenes.¹⁵ The α -halo substituent can increase the barrier by lowering the relative ground-state energy of the parent $\sim sp^2$ anion inductively and by contributing to the barrier by lone-pair repulsion in the planar anion. A similar electronic effect has been noted for the inversion barrier of *N*-fluoroformimine and formaldoxime.¹⁶ The β -halo substituent can stabilize a carbanion by a net two-electron interaction with the carbon-halogen σ^* orbital, as discussed in detail below. Houk¹⁰ noted that placing the carbanion in conjugation with a multiple bond (e.g., CN, CHO) results in an even lower barrier to inversion. The vinyl anion is still partially pyramidal even though the possibility for forming a planar resonance stabilized anion exists.

One way to follow the reaction coordinate for the dehydrohalogenation of vinyl halides is to measure the relative energy changes in going from the fully optimized ground-state anionic structures ($\sim sp^2$ hybridized) to the transition structure, as a function of the C_α - C_β -H(F) bond angle (ϕ , Figure 1). The C_α - C_β -H or C_α - C_β -F bond angle (ϕ) was systematically varied with the optimization of all the other geometric parameters for anions **1**, **2**, **3**, and **4** until that geometry was obtained where elimination of fluoride ion was exothermic. The last intermediate point on the reaction coordinate for each of the four anions was remarkably close to the actual calculated transition-state structure (Table II).

As anticipated, the barrier (9.8 kcal/mol) for elimination of fluoride ion from the anti anion **2** was lower by 4.1 kcal/mol than that of the syn anion **1**, reflecting the differences in ground-state energies and the greater efficiency of overlap of the anti anion with the leaving group. The attending angle of inversion (146°) was also smaller, which is consistent with an anticipated earlier transition state for an anti vs. a syn elimination pathway.⁶ The same trend was noted for the difluorovinyl anions **3** and **4**; however, in the latter case the barriers are much higher. The faster rate of methoxide ion induced hydrogen/deuterium exchange for (*Z*)-1,2-dibromoethene than for the (*E*) isomer is also consistent with a greater stability of the anti vinyl anion.¹⁵ Significantly, the rate of exchange was ~ 25 times greater than the rate of elimination, providing a clear-cut example of an E1cb mechanism. The same observation was made by Modena¹⁷ for the elimination of HX from β -halogenated styrenes with different alkoxide bases.

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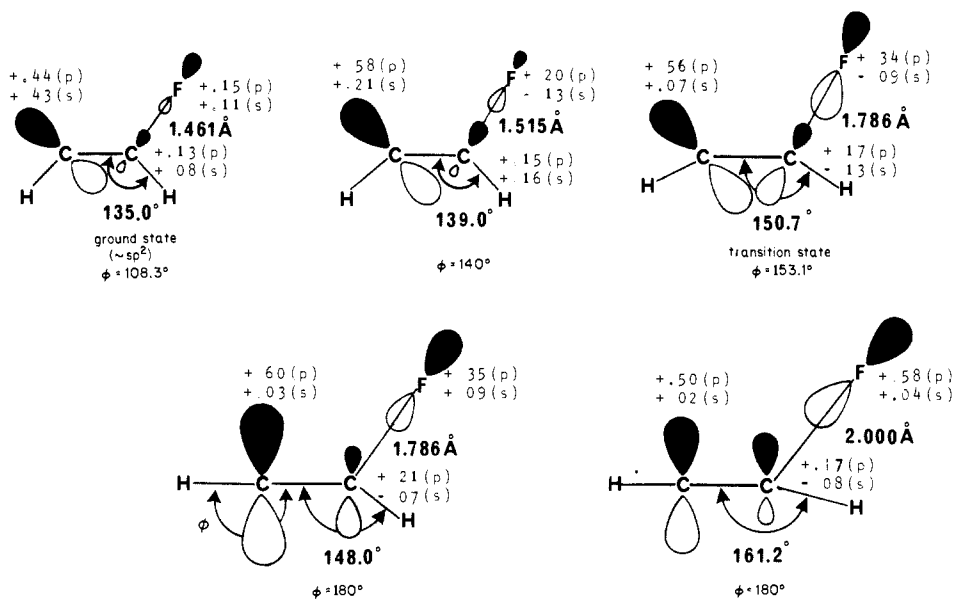
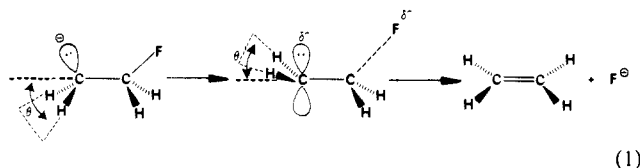


Figure 4. Development of HOMO (ψ_2) as the $\text{H}-\text{C}_\beta-\text{C}_\alpha$ bond angle ϕ is altered along the reaction coordinate for the elimination of fluoride ion from syn 2-fluorovinyl anion **1** (4-31G).

He concluded that the mechanism for dehydrohalogenation lies somewhere between the E1cb and E2 extremes.

Inversion at the anionic center makes a substantial contribution to the overall activation barrier for halide elimination. In the corresponding aliphatic series, the syn carbanion (eq 1) undergoes inversion at C_β without an energy of activation, but exothermic elimination of F^- does not proceed until positive values of θ are observed at $\sim 50\%$ C-F bond elongation (4-31G).⁶ Neither the syn nor the anti β anion of ethyl fluoride were stable anions in

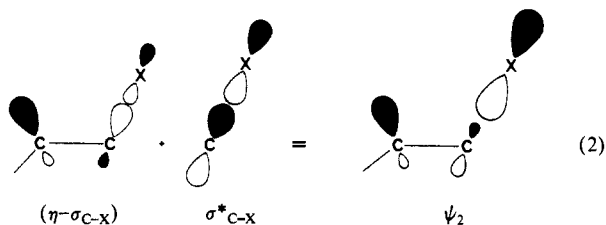


the gas phase and elimination of F^- was exothermic (without activation) with enthalpies of -19.6 and -14.3 kcal/mol, respectively. It is interesting to note that a trigonal anion that is gauche to the β -fluoro substituent is thermodynamically stable and 6.8 kcal/mol higher in energy than the corresponding trigonal α -fluoro anion.⁶ In contrast, vinyl anions **1-4** exhibit significant barriers to F^- elimination (Table III).¹⁸ The calculated activation barriers for loss of F^- from syn and anti 1,2-difluorovinyl anions **3** and **4** are 45.7 and 36.6 kcal/mol (Figure 2), respectively. Our best estimate for the inversion barriers for those anions with a fixed C-F bond distance (planar anions) is 47.3 and 46.3 kcal/mol, respectively (Table III). In both cases, expulsion of F^- appears to precede full inversion at the anionic center. A close examination of the data in Figure 1 is also revealing. The position of the transition state along the reaction coordinate was estimated by altering the $\text{H}-\text{C}_\beta-\text{C}_\alpha$ bond angle ϕ in anions **1** and **2**. At $\phi = 155^\circ$ the syn anion was 17.0 kcal/mol above the ground state and at a fixed $\text{C}_\beta-\text{F}$ bond distance (1.6567 Å) we calculated an inversion barrier of 16.22 kcal/mol. Thus, we conclude that essentially all of the activation barrier in these elimination reactions may be ascribed to electronic effects associated with inversion at the carbanionic center. It should also be emphasized that in solution in the presence of a counterion, anions **1** and **2** have barriers low enough to allow syn-anti isomerization.

(18) The loss of F^- from anions **1**, **2**, **3**, and **4** is calculated (4-31G) to be endothermic by 12.3, 9.2, 45.9, and 46.7 kcal/mol, respectively. The difference in gas-phase stability of 2-fluoroethyl anion and the vinyl anions **1** and **2** can largely be accounted for by the difference in the enthalpy of carbon-carbon double and triple bond formation upon expulsion of fluoride ion. For an extensive discussion of the stability of these anions see: Schleyer, P. v. R.; Alexander, J. K. *Tetrahedron* **1983**, *39*, 1141.

Examination of Figure 2 also provides data consistent with this contention. The energy of the planar anions relative to that of the transition-state structure is particularly revealing. The $\text{C}_\alpha-\text{F}$ bond distances of the planar anions were not altered and the $(\text{F})\text{H}-\text{C}_\beta-\text{C}_\alpha$ bond angles were constrained to 180° . The planar anions derived from syn transition structures **1a** and **3a** were lower in energy than the transition structures while the opposite was true for the planar anions corresponding to the anti transition structures **2a** and **4a**. These observations are consistent with an earlier transition state for an anti elimination and suggest that a negligible inversion barrier exists for transition structures **1a** and **2a**. Although, syn elimination in a vinyl substrate may not necessarily require complete inversion at the anionic center, the potential energy surface for $\text{H}-\text{C}_\beta-\text{C}_\alpha$ angular motion in that region of the reaction coordinate is very shallow.

We also wish to comment on the electronic consequences of inversion of the syn anion on the overall elimination mechanism. We employ an extension of frontier MO theory to gain a better understanding of the elimination step.¹⁹ Within the concepts of the three molecular orbital, four-electron model (Figure 3), the β -carbanion in **1** will interact with both the σ and σ^* orbitals of the C-F bond. The anion may be stabilized by mixing the higher lying filled orbital, comprised of the lone pair of electrons on carbon (n) antibonding to the filled $\sigma_{\text{C-X}}$ bond, into the $\sigma_{\text{C-X}}^*$ orbital in a bonding manner (eq 2). Upon examination of the phasing in the HOMO of **1** (ψ_2) it is evident that σ^* makes a major contribution to ψ_2 . The net result of the balance between the four-electron ($n-\sigma_{\text{C-X}}$) and two-electron interactions with the $\sigma_{\text{C-X}}^*$ is such that the electronic contribution to the overall activation barrier is net stabilizing. The resultant HOMO is an anion bonding to the $\sigma_{\text{C-X}}^*$ and the diminution of the coefficient on the α -carbon is a result of phase cancellation¹⁹ between the $\sigma_{\text{C-X}}$ and $\sigma_{\text{C-X}}^*$ orbitals as depicted in eq 2. The relatively small contribution



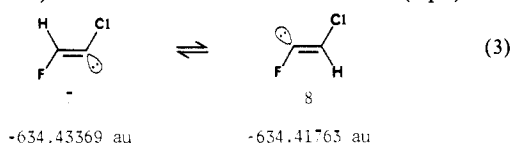
from the carbon 2p atomic orbital, however, provides clear evidence

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that the interaction between the filled σ_{C-X} orbital and the carbanion (n) is essential to the formation of the HOMO orbital ψ_2 (Figure 3). A comparison between the HOMO (ψ_2) arising from this hypothetical argument and that determined (4-31G) for the transition state (Figure 4) is gratifying. The ground-state sp^2 anionic center has a significant contribution from the carbon 2s orbital. As one proceeds along the reaction coordinate for elimination, the carbon 2s coefficient decreases from 0.43 to 0.07 at the transition state. The electron density is essentially equally distributed on both sides of the carbon in consonance with the idea of inversion of configuration attending the elimination step (Figure 4).

The HOMO level of the syn ground state anion **1** is 1.2 kcal/mol higher in energy than that of the corresponding anti anion **2**, reflecting their relative stabilities. At the transition state the HOMO of the syn anion **1a** is 7.2 kcal/mol higher in energy than the anti anion **2a**. In going from the ground state anion **1** to the transition state **1a**, a carbon-carbon bond contraction (0.1 Å) is evident, as well as an elongation of the $C_\alpha-X$ bond length as a result of the $H-C_\beta-C_\alpha$ bond angle expanding.

Finally, we wish to address the question of competitive elimination of HX from a 1,2-dihaloalkene. Examination of the relative energies of the isomeric anions derived from 1-chloro-2-fluoroethylene shows that the α -chloro anion **7** is about 10 kcal/mol (4-31G) more stable than α -fluoro anion **8** (eq 3). If



the transition state for a syn elimination from either anion is E1cb-like, and the relative rates reflect the stability of the incipient anion, then one would predict a preferential elimination of HF provided that the inversion barrier of the two anions were comparable. Thus, the leaving group abilities of F^- and Cl^- would be compromised and the course of the reaction would be controlled

by carbanion stability. In a recent study of the elimination of HX from erythro-1-chloro-2-fluoro-1,2-diphenylethane, Baciocchi²⁰ made the striking observation of a k_{Cl}/k_F value for syn elimination that was substantially less than unity. In that process it was concluded that fluorine is eliminated in preference to chlorine. A favorable coordination between the base counteranion and the leaving group along with conformational arguments concerning the carbanion was invoked in explanation of these interesting results. We suggest that the relative stabilities of the two potential incipient anions are an equally plausible explanation.

In conclusion, vinyl anions bearing a β -halo substituent will exhibit a lower inversion barrier while α -halo substituents have the opposite effect and will add to the inversion barrier. The activation energies for β -elimination from vinyl substrates are markedly higher than those of halo-substituted aliphatic substrates. The activation barriers for elimination of vinyl substrates may be largely, if not entirely, attributable to the electronic effects associated with inversion of the carbanionic center. Finally, these data suggest that 1,2-dihaloalkenes should exhibit E1cb-like behavior. As a consequence of the inversion barriers, the potential for observing hydrogen-deuterium exchange under elimination reaction conditions¹⁵ should be quite high if nucleophilic substitution at vinyl carbon can be excluded. Many of the mechanistic suggestions that we have presented on the basis of this theoretical study were made many years ago by Miller in his insightful series of papers on vinyl anions.¹⁵

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We are also grateful to the Wayne State University Computing Center for their generous amounts of computational time, Professor H. B. Schlegel for his assistance with the computations, and Professor H. F. Koch for his helpful discussions.

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Determination of the Singlet-Triplet Splitting and Electron Affinity of *o*-Benzyne by Negative Ion Photoelectron Spectroscopy

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Abstract: The photoelectron spectrum of the *o*-benzyne negative ion displays transitions to both the \bar{X}^1A_1 and \bar{a}^3B_2 states of the neutral molecule. Results yield adiabatic electron affinities of 0.560 (10) and 0.551 (10) eV for C_6H_4 and C_6D_4 , respectively. These values are consistent with extrapolations from studies of larger strained cycloalkynes and imply that the lowest unoccupied MO of *o*-benzyne is primarily an antibonding acetylenic orbital. The *o*-benzyne singlet-triplet splitting is determined to be 37.7 (6) kcal/mol. Several new vibrational frequencies for the neutral and anionic species are also reported.

I. Introduction

The determination of the electronic and molecular structure of *o*-benzyne (1,2-dehydrobenzene, C_6H_4) has attracted considerable interest since the first demonstration of its existence by Roberts et al.¹ over 30 years ago. This species is among the simplest of highly strained conjugated hydrocarbons. Thus, it

provides a benchmark system for theoretical models² of the structural and energetic consequences of ring strain. Much attention has focussed on the effects of its unique geometry on the well-studied solution chemistry³ of this reactive intermediate.

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