required the unreasonable assumption that solvation reverses the order of electron affinities of benzyl cations, even though such reversal does not occur with trityl cations.[17] Rate-determining formation of the benzyl cations undoubtedly explains the reactivity orders in the reactions investigated by Chalvet.[13]

A theoretical study,[18] which will be reported at a later date, will consider in more detail the origins of selectivity in "early" transition states.

Acknowledgment. Financial support of this research by the National Science Foundation in gratefully acknowledged. We thank Professor F. P. DeHaan for very helpful comments.

References and Notes

(1) C. D. Johnson, *Chem. Rev.*, **75,** 755 (1975); A. Pross, *Adv. Phys. Org. Chem.*, **14**, (1977); B. Giese, *Angew. Chem., Int. Ed. Engl.*, **16,** 125 (1977).

(2) (a) H. C. Brown and L. K. Nelson, *J. Am. Chem. Soc.*, **75,** 6292 (953); (b) L. M. Stock and H. C. Brown, *ibid.*, **81,** 3323 (1959); (c) L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1,** 35 (1963), and references therein.

(3) (a) G. A. Olah, *Acc. Chem. Res.*, **4,** 240 (1971); (b) G. A. Olah, F. Pelizza, S. Kobayashi, and J. A. Olah, *J. Am. Chem. Soc.*, **98,** 296 (1976), and previous references in the series on "Aromatic Substitutions"; (c) G. A. Olah, S. Kobayshi, and M. Tashiro, *ibid.*, **94,** 7448 (1972); (d) G. A. Olah and S. Kobayshi, *ibid.*, **93,** 6964 (1971); (e) G. A. Olah, H. C. Lin, J. A. Olah, and S. C. Narang, *Proc. Natl. Acad. Sci. U.S.A.*, **75,** 1045 (1978).

(4) G. Klopman, *J. Am. Chem. Soc.*, **90,** 223 (1968); R. F. Hudson and G. Klopman, *Tetrahedron Lett.*, 1103 (1967); G. Klopman, "Chemical Reactivity and Reaction Paths", Wiley-Interscience, New York, 1974, pp 81, 82.

(5) K. Fukui, T. Yonezawa, and H. Singu, *J. Chem. Phys.*, **20,** 722 (1952).

(6) N. D. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, **100,** 29 (1978).

(7) C. Decoret, J. Royer, and O. Chalvet, *Tetrahedron*, **31,** 973 (1975).

(8) P. F. Christy, J. H. Ridd, and N. D. Stears, *J. Chem. Soc. B*, 797 (1970); R. G. Coombes, R. B. Moodie, and K. Schofield, *ibid.*, 800 (1968); J. H. Ridd, *Acc. Chem. Res.*, **4,** 248 (1971).

(9) C. L. Perrin, *J. Am. Chem. Soc.*, **99,** 5516 (1977).

(10) P. Rys, P. Skrabal, and H. Zollinger, *Angew. Chem., Int. Ed. Engl.*, **11,** 874 (1972).

(11) A. Modro, G. H. Schmid, and K. Yates, *J. Org. Chem.*, **42,** 3673 (1977).

(12) F. Cacace and A. Caronna, *J. Chem. Soc., Perkin Trans. 2*, 1604 (1972); F. Cacace and P. Giacomello, *J. Am. Chem. Soc.*, **99,** 5477 (1977).

(13) It has been shown recently that some anomalies in benzylations of toluene and benzene arise from experimental difficulties in measurements of k_T/k_B: F. P. DeHaan, W. D. Covey, M. S. Anisman, R. L. Ezelle, J. E. Margetan, K. D. Miller, S. A. Pace, S. L. Pilmer, M. J. Sollenberger, and D. S. Wolf, *J. Am. Chem. Soc.*, **100,** 5944 (1978).

(14) The experimental proton affinity of toluene is 6.3 kcal/mol higher than that of benzene: Y. K. Lau and P. Kebarle, *J. Am. Chem. Soc.*, **98,** 7452 (1976).

(15) J. M. McKelvey, S. Alexandratos, A. Streitwieser, Jr., J. L. M. Abboud, and W. J. Hehre, *J. Am. Chem. Soc.*, **98,** 244 (1976).

(16) This model was used to better mimic a solvated electrophile. The stabilization energy of a "bare" proton and benzene, with $r_{C\text{-}H^+} = 2.0$ Å is still 113.9 kcal/mol.

(17) D. H. Plesch and I. Šestáková, *J. Chem. Soc. B*, 1337 (1971).

(18) C. Santiago, N. G. Rondan, and K. N. Houk, unpublished results.

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Influence of Molecular Distortions upon Reactivity and Stereochemistry in Nucleophilic Additions to Acetylenes

Sir:

We report here ab initio molecular orbital studies which show that the changes in frontier molecular orbital energies and shapes upon bending distortions of acetylene and ethylene explain several preplexing, but general, phenomena: (1) alkynes are much more reactive than alkenes toward nucleophiles;[1-4] (2) nucleophilic additions to alkynes generally proceed with anti stereochemistry,[1] although some highly activated alkynes give syn adducts with amines;[1,5] (3) nucleophiles, N, are predicted to attack acetylenes, RCCR, with an RCN angle of 120°,[6] even though this would seem to require an unreasonable NCC angle of 60°.

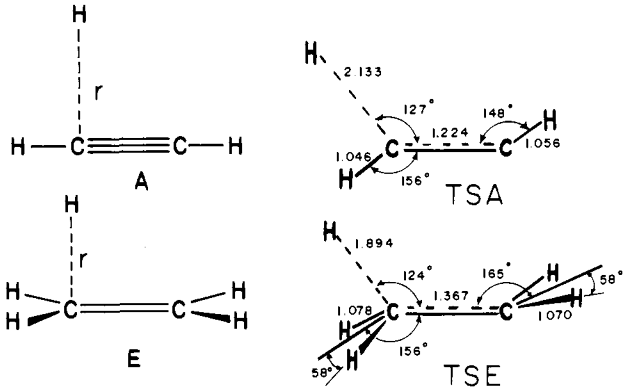

Figure 1. Geometries of complexes between hydride and acetylene (A) or ethylene (E) used in calculations reported in Table I. TSA and TSE are the 4-31G transition states for addition of hydride to acetylene and ethylene, respectively.

Frontier molecular orbital theory adequately accounts for the greater reactivity of electrophiles toward alkenes than toward similarly substituted alkynes:[1,7] the HOMO of ethylene (IP = 10.5eV) is higher in energy than that of acetylene (IP = 11.4 eV) and provides more charge-transfer stabilization upon interaction with the LUMO of an electrophile. However, the LUMO of acetylene (EA = −2.6 eV)[8] is higher in energy than that of ethylene (EA = −1.8 eV),[9] suggesting that acetylene is less capable of charge-transfer (CT) stabilization upon interaction with the HOMO of a nucleophile. This implication gains numerical support from an energy decomposition analysis[10] of the ab initio SCF 4-31G calculations[11] (Table I) for the interaction of hydride (at 2 Å) with the equilibrium geometries of acetylene and ethylene (Figure 1, structures A and E, r = 2 Å). The stabilizing CT interaction is smaller upon interaction of hydride with undistorted acetylene than with undistorted ethylene. The exchange repulsions (EX) are largely reponsible for the overall enormously repulsive interaction energies, but differences in CT control the relative interaction energies. This simple picture changes dramatically as molecular distortions occur along the reaction pathway.

The transition states (TS) for hydride addition to acetylene and ethylene calculated here with the 4-31G basis set are shown in Figure 1 (TSA and TSE, respectively).[12] Using 4-31G optimized geometries of reactants and transition states, and 4-31G plus 3 × 3 configuration interaction (CI) calculations, activation energies of 16.7 and 16.6 kcal/mol are predicted for the additions of hydride to acetylene and ethylene, respectively. Overall reaction energies compare favorably with those calculated by others.[12-15] Even for these relatively early transition states, the attack of hydride on acetylene is essentially as easy as attack on ethylene, and preferential attack on acetylene should become pronounced for a less reactive nucleophile.

Bending of the hydrogens out of linearity or planarity is the most significant distortion occurring in these transition states, along with a change of attack angle away from 90°; CC stretching is of minor importance. The "driving force" for bending of acetylene or ethylene upon attack by nucleophiles can be deduced from Figure 2, which shows that the LUMOs of both species are lowered in energy[17] and change shape appreciably upon bending to the transition-state geometries. Calculations on cis bending or one-end bending of these molecules reveal the same trends shown in Figure 2: for compa-

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Table I. 4-31G Energy Decomposition Analysis[a] for Interaction of Hydride with Acetylene and Ethylene

	energy components,[b] kcal/mol							
molecular species	E_{rel} (+CI)[c]	E_{rel} (no CI)	DIS	ΔE	ES	PL	EX	CT
			$HC\equiv CH + H^-$					
A (r = 2 Å)[d]	46.1	30.1	0	30	−11	−6	55	−7
"TSA" (r = 2 Å)[e]	16.1	3.2	11	−8	−15	−12	41	−22
TSA[f] (r = 2.133 Å)	16.7	3.2	11	−8	−9	−10	28	−17
vinyl anion	−34.8	−49.5						
			$H_2C{=}CH_2 + H^-$					
E (r = 2 Å)[d]	41.6	24.7	0	25	−12	−8	56	−12
"TSE" (r = 2 Å)[e]	17.1	2.0	7	−5	−11	−13	41	−23
TSE[f] (r = 1.894 Å)	16.6	1.9	7	−5	−18	−14	55	−29
ethyl anion	−2.0	−20.7						

[a] STO-3G energy decompositions parallel these except that CT is much larger realtive to the other terms, as has been observed in other systems. For example, for TSA, the terms E_{rel} through CT are −14.2, 16, −30, −1, −7, 20, and −42 kcal/mol, respectively. [b] These were calculated by the method of Morokuma.[10] Positive energies are destabilizing; negative are stabilizing. E_{rel} is the difference in energy between the isolated equilibrium species and the complex in the given geometry at the computational level noted. DIS is the energy required to distort acetylene or ethylene to the geometry of the complex. ΔE is the energy of interaction between hydride and the distorted unsaturated species. ES, PL, EX, and CT are electrostatic, polarization, exchange repulsion, and charge-transfer terms, respectively. CT also contains small terms resulting from higher order mixing of the other terms.[10] [c] These numbers arise from separately carrying out 3 × 3 CI on each isolated reactant and on the "complexes". CI stabilizations for isolated hydride, acetylene, and ethylene are 5.6, 10.4, and 14.1 kcal/mol, respectively. [d] Undistorted unsaturated species plus hydride (see Figure 1). [e] This species corresponds to TSA or TSE in Figure 1, except that the hydride carbon distance is changed to 2 Å. [f] This is TSA or TSE shown in Figure 1.

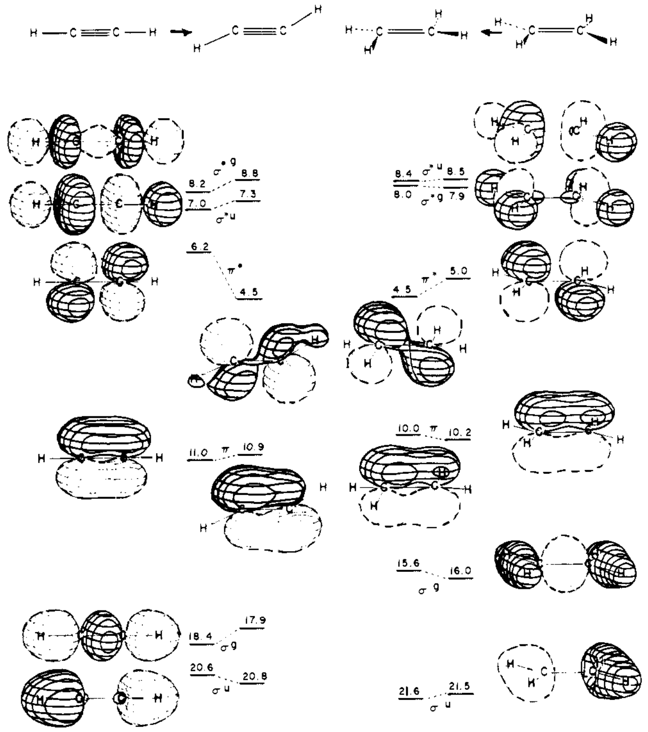


Figure 2. Orbital energies (4-31G) and shapes for acetylene and ethylene in the equilibrium and transition-state geometries. The STO-3G orbital drawings were drawn by the program written and kindly provided to us by Professor William L. Jorgensen of Purdue University.

rable bending distortions, the LUMO of acetylene drops two to three times faster than the LUMO of ethylene. We attribute this to the fact that the σ^*_{CH} orbitals of acetylene are closer to the π^* orbital, and are more concentrated on H, than the σ^*_{CH} orbitals of ethylene (Figure 2). Both of these factors cause greater σ^*_{CH}–π^* mixing and a more precipitous drop of the LUMO upon bending of acetylene. In the isolated molecules distorted to transition-state geometries, the LUMOs have the same energy (4.5 eV), and according to a simple frontier orbital analysis should provide equal CT stabilization upon interaction with the hydride HOMO.

Computational support for this model is obtained by the energy decomposition analysis, which reveals an additional consequence of bending distortions. When the hydride–carbon distance is kept at 2 Å, but the molecules are distorted to transition-state geometries (Table I, "TSA" and "TSE"), the large increase in CT and decrease in EX practically eliminates the repulsion for hydride, in spite of the increase in distortion (DIS) energy. At this stage, hydride interactions with acetylene and ethylene are nearly equally favorable, owing primarily to larger increases of CT and ES stabilization for acetylene upon bending. The greater CT stabilization increase for acetylene arises from the faster LUMO drop upon bending of acetylene. The increase in ES stabilization arises from a drift of electron density from C to H upon bending (C charges are −0.32 for acetylene, −0.24 for TSA-distorted acetylene, and −0.33 for ethylene and TSE-distorted ethylene). This greater "charge drift" upon bending of acetylene arises both from the greater distortion of acetylene in the transition state and from the greater mixing of the σ^*_{CH} orbitals into π orbitals upon distortion of acetylene.

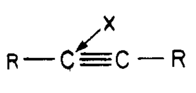
Bending of acetylene is easier than bending of ethylene,[18] but acetylene also prefers to bend more than ethylene in the TSs for reaction with hydride, because of the larger increase of ES and CT in TSA, which more than compensates for the larger DIS than is present in TSE. The increase in CT stabilization occurs more rapidly for a given bend of acetylene than of ethylene, so that CT (and ES) stabilization overcomes repulsive interactions earlier along the r_{CH} reaction coordinate for acetylene than ethylene. In effect, it is the relatively easy bending of acetylene, the accompanying rapid drop of the LUMO, and the resulting increase of CT and ES which makes acetylenes more reactive than ethylenes toward nucleophiles. By contrast, CC stretching is more difficult and has a less dramatic influence on LUMO energies,[19] so that this distortion is minor in TSA and TSE. Bending has very little effect on HOMO energies, so that no "driving force" for bending is present upon interactions with electrophiles. Indeed, protonation of acetylene and ethylene leaves these molecules essentially linear and planar, respectively.[20]

The preferential trans bending of acetylene in the transition state for hydride attack provides an explanation of the experimentally observed anti addition of nucleophiles to simple alkynes.[1-4] This trans bending will cause the vinyl anion to be "born" in a conformation with the lone pair anti to the nucleophile. Since the inversion barrier in simple (alkyl or aryl substituted) vinyl anions is high (37 kcal/mol by 4-31G, and cf. ref 14), protonation of the anion intermediate will result in overall anti addition. However, alkynes substituted by one or more strongly electron-withdrawing groups may give the anti anion, but then invert and undergo intramolecular proton transfer to give predominantly syn addition in the absence of good external proton donors.[5,21] This mechanism requires carbanion inversion to be competitive with intermolecular proton transfer, compatible with the inversion barriers of 10, 4, and −1 kcal/mol predicted by our 4-31G calculations for 1-cyanovinyl, 1-methoxycarbonylvinyl, and 1-formylvinyl anions, respectively.

Why is trans bending preferred in the nucleophilic addition transition states? According to model calculations to be reported in the full account of this work, the trans bending in TSA results from the fact that trans bending of ground-state acetylene is considerably easier than cis bending. The cis-bent geometry corresponding to TSA is 8 kcal/mol higher in energy than TSA, owing mainly to the 7-kcal/mol greater distortion energy of the cis-bent acetylene. The corresponding one-end-bent transition-state geometry has less distortion energy (6 kcal/mol), but is less stable owing to diminished CT since the LUMO energy is lowered less. The same trends are observed for ethylene, but the differences in distortion energies are much smaller.

The preference for trans bending can be rationalized readily in terms of the relative magnitudes of filled-vacant and filled-filled orbital interactions occurring upon different distortions. The highest lying σ_{CH} orbital of acetylene ($\sigma^{g}{}_{CH}$) shown in Figure 2 can mix with the π^* LUMO upon trans bending, but only a lower energy σ orbital ($\sigma^{u}{}_{CH}$) can mix with the LUMO upon cis bending. Similarly, the lowest σ^* orbital ($\sigma^{*u}{}_{CH}$) mixes with the π HOMO upon trans bending, but only a higher energy ($\sigma^{*g}{}_{CH}$) orbital mixes with π upon cis bending.[22] Furthermore, $\sigma^{g}{}_{CH}$ mixes with π upon cis bending, leading to more exchange repulsion than that which occurs for $\sigma^{u}{}_{CH}$-π mixing upon trans bending.

The consequences of the facile trans bending of acetylene upon interaction wtih nucleophiles and of the large LUMO drop upon bending are considerable. (1) Based on empirical evidence, Baldwin recently suggested that electrophiles (E) and nucleophiles (N) attack alkynes with a trajectory (**1**) having an RCX angle of 120°.[6] Theory now predicts a somewhat altered attack geometry (**2**), but with a large HCN angle. The transition state for attack of electrophiles (**3**) also has a large HCE angle, but the two transition states are in other ways very different. (2) Easy bending of acetylene and the consequential increase in interaction of the acetylene LUMO with the HOMO of a second species provide an explanation for the surprising observation that alkynes undergo various sigmatropic shifts as readily as the corresponding alkenes.[23] An extension of the conclusions reported here suggests that a bent transition state (**4**) for the Cope rearrangement of 1,5-hexadiyne will be as readily achieved as that commonly accepted for 1,5-hexadiene (**5**). (3) Incorporation of an alkyne into a ring (e.g., benzyne), should increase reactivity of such a species toward nucleophiles more than toward electrophiles. Superimposed on this selective activation toward nucleophiles is the overall increase in reactivity owing to strain.



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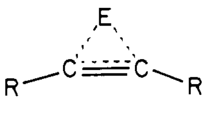

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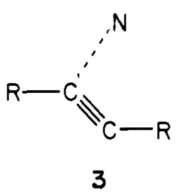

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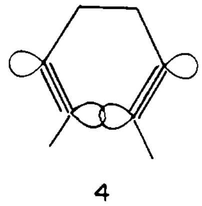

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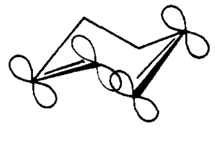

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Bending distortions have profound consequences upon orbital energies and shapes. The general consideration of such effects, combined with frontier orbital concepts, promises to be a fruitful approach to the understanding of organic reactivity on a quantitative level.[24-26]

Acknowledgments. We thank Drs. Tada Fukunaga and S. Nagase and Professor W. T. Borden for helpful discussions, the National Science Foundation for financial support of this research, and the CNR (Rome) for a NATO Senior Fellowship to P.C.

References and Notes

(1) J. Dale in "Acetylenes", H. G. Viehe, Ed., Marcel Dekker, New York, 1969, Chapter 1; J. L. Dickstein and S. I. Miller, "The Chemistry of the Carbon-Carbon Triple Bond, Part 2", S. Patai, Ed., Wiley, New York, 1978.

(2) F. Bohlmann, *Angew. Chem.*, **69**, 82 (1957).

(3) S. I. Miller and R. Tanaka in "Selective Organic Transformations", Vol. I, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, 1970, p 1414.

(4) S. I. Miller, *J. Org. Chem.*, **21**, 247 (1956).

(5) B. Giese and R. Huisgen, *Tetrahedron Lett.*, 1889 (1967), and references therein.

(6) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 734 (1976).

(7) K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H.-W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, **95**, 160 (1973), and references therein.

(8) K. D. Jordan and P. D. Burrow, *Acc. Chem. Res.*, **11**, 341 (1978).

(9) P. D. Burrow and K. D. Jordan, *Chem. Phys. Lett.*, **36**, 594 (1975).

(10) W. A. Lathan, G. R. Pack, and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 6624 (1975). We thank Professor Morokuma for the energy-partitioning subroutine.

(11) Gaussian 70, QCPE 236, by W. J. Hehre, W. A. Pople, R. Ditchfield, M. D. Newton, and J. A. Pople, was used for these calculations.

(12) After completion of our surface calculations, we were informed of calculations carried out by C. E. Dykstra, A. J. Arduengo, and T. Fukunaga (*J. Am. Chem. Soc.*, **100**, 6007 (1978)) for hydride attack on acetylene, using an extended basis set with diffuse s functions on each atom and SCEP correlation corrections. An activation energy of 16 kcal/mol was found, with a transition-state geometry (r_{CH^-} = 2.097, r_{CC} = 1.277 Å; $\angle H^-CC$ = 128.0, $\angle H_1C_1C_2$ = 147, $\angle H_2C_2C_1$ = 128°, where C_1 is the carbon being attacked) very similar to that reported here. The energy of reaction is calculated to be −26 kcal/mol at this computational level. The trajectory of attack of hydride on acetylene has also been studied recently by O. Eisenstein, G. Proctor, and J. D. Dunitz, *Helv. Chim. Acta*, **61**, 2538 (1978).

(13) Using radical heats of formation, estimated electron affinities of 1.1 and 0.2 eV for the vinyl and ethyl radicals, respectively, and an estimation of 7 kcal/mol for the increase in zero-point energies for these reactions,[14] "experimental" reaction energies of −56 ± 6 and −33 ± 5 kcal/mol can be estimated for the acetylene and ethylene reactions.

(14) J. E. Williams, Jr., and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **97**, 2634 (1975).

(15) Cf. −3.3 kcal/mol calculated for the reaction of hydride with acetylene: H. Kollmar, *J. Am. Chem. Soc.*, **100**, 2665 (1978).

(16) H. Schmidt, A. Schweig, and A. Krebs, *Tetrahedron Lett.*, 1471 (1974); C. Santiago, K. N. Houk, G. J. DeCicco, and L. T. Scott, *J. Am. Chem. Soc.*, **100**, 692 (1978).

(17) The acetylene LUMO drop upon bending was noted long ago (A. D. Walsh, *J. Chem. Soc.*, 2288 (1953); see also R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, **74**, 127 (1974)), but acetylene and ethylene have not been compared directly. Other computations on acetylene distortions have also been reported that show the LUMO lowering (R. Hoffmann, *Tetrahedron*, **22**, 521 (1966); W. E. Kammer, *Chem. Phys. Lett.*, **6**, 529 (1970); K. Tatsumi, T. Fueno, A. Nakamura, and S. Otsuka, *Bull. Chem. Soc. Jpn.*, **49**, 2170 (1976); A. Gavezotti and M. Simonetta, *Chem. Phys. Lett.*, **48**, 434 (1977)), but these have been applied only to explain geometries of acetylene excited states (C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702, 2725 (1953); K. K. Innes, *J. Chem. Phys.*, **22**, 863 (1954); J. L. Hardwick and D. A. Ramsey, *Chem. Phys. Lett.*, **48**, 399 (1977)) or addition of electrophiles (J. Duchesne, *J. Chem. Phys.*, **18**, 1120 (1950); L. Burnelle, *Tetrahedron*, **20**, 2403 (1964); **21**, 49 (1965)). The calculations of Chu and Goodman on the acetylene radical anion indicate a strong preference for trans bending owing to the π^* orbital stabilization upon bending: S. Y. Chu and L. Goodman, *J. Am. Chem. Soc.*, **97**, 7 (1975).

(18) The force constants for bending of acetylene and ethylene hydrogens out of plane are 0.0105 and 0.0240 kcal/(mol deg), respectively.[1]

(19) According to 4-31G calculations, stretching of acetylene by 0.055 Å requires 4.1 kcal/mol, raises the HOMO by only 0.35 eV, and lowers the LUMO by 0.47 eV. Stretching ethylene by 0.074 Å requires 4 kcal/mol, raises the HOMO by 0.46 eV, and lowers the LUMO by 0.49 eV.

(20) J. Weber and A. D. McLean, *J. Am. Chem. Soc.*, **98**, 875 (1976); A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, 3835 (1971); W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).

(21) K. Herbig, R. Huisgen, and H. Huber, *Chem. Ber.*, **99**, 2546 (1966).

(22) Similar arguments have been applied independently to rationalize the

preferred trans bending of ethylene.[25] The same explanation has been given, in part, by K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970).

(23) For a summary, see R. A. Firestone, *Tetrahedron*, **33**, 3009 (1977).

(24) During the course of this work, we became aware of independent investigations of ethylene bending distortions[25] and an energy decomposition analysis of the addition of the hydrogen atom to acetylene.[26]

(25) W. V. Volland, E. R. Davidson, and W. T. Borden, *J. Am. Chem. Soc.*, in press.

(26) S. Nagase and C. W. Kern, submitted for publication.

(27) On leave from the University of Pavia, Pavia, Italy.

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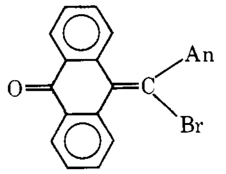
Vinylic Cations from Solvolysis. 27.[1] Solvolysis of an Optically Active Vinyl Bromide

Sir:

Two conflicting reactivity-selectivity relationships exist for the reaction of carbonium ions with nucleophiles. For solvolytically generated ions, their selectivities, measured by the relative reaction rates with two nucleophiles, e.g., $k_{N_3^-}/k_{H_2O}$, increase with the increased solvolytic reactivity of the precursor RX.[2] By Hammond's postulate, this reflects a reactivity-selectivity relationship (i.e., lower reactivity or higher stability is associated with higher selectivity), a well-documented phenomenon.[3] In contrast, Ritchie reported many cases of a "constant selectivity" relationship for the directly measured reaction of stable carbonium ions with nucelophiles, where the rate ratio for two nucleophiles was independent of the cation.[4] Ritchie[4,5] ascribes part of this discrepancy to the derivation of the selectivity term in solvolysis from the product ratio in a competitive reaction of two nucleophiles. Since the products are probably derived from both free ions and ion pairs, their ratio does not measure the selectivity of a single species.



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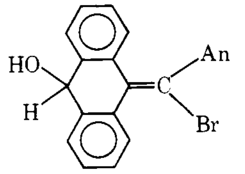

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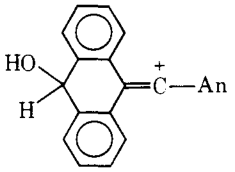

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An = p-MeOC$_6$H$_4$

This hypothesis can be tested if the selectivity constants could be measured when the products are formed only from a solvolytically generated free cation. For such relatively stable cations, the recombination of R^+ and X^- can compete with capture of R^+ by the solvent SOH. The accompanying common ion rate depression[2c,6] is associated with capture of only the *free* cation by X^- and SOH[6b,c] and the derived "mass law constant", $\alpha = k_{X^-}/k_{SOH}$, is a selectivity constant. The α values for the benzhydryl system obey a reactivity-selectivity relationship.[2c,6]

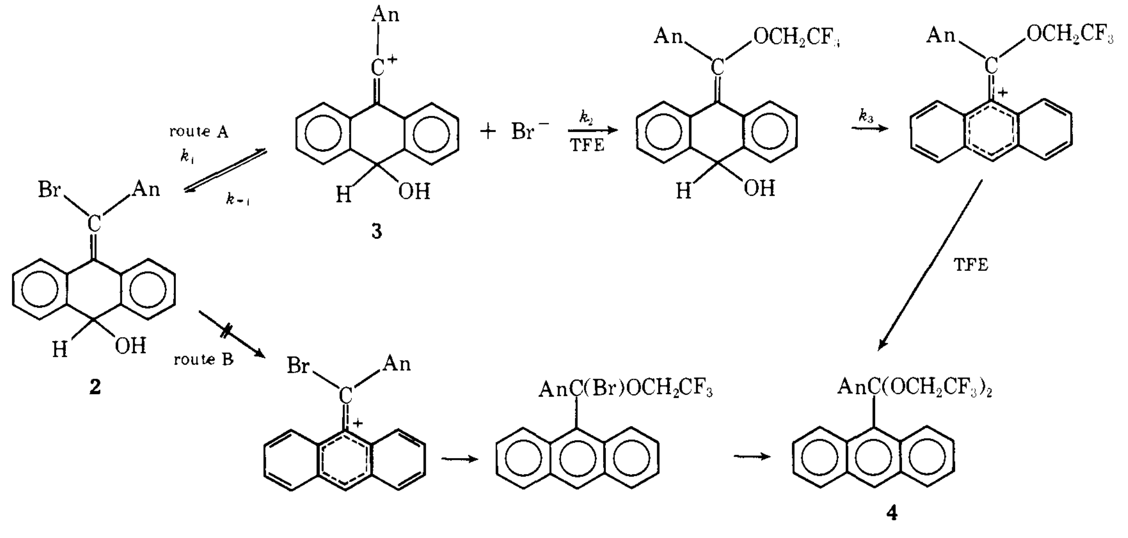
Moreover, the solvolysis rate constants which are an indirect measure of the reactivity of R^+ may differ from the ionization rate constants owing to ion-pair return,[6b,c,7] and its extent should be known for evaluation of any reactivity-selectivity relationship.

Solvolysis of triarylvinyl halides is accompanied by an extensive common ion rate depression.[8] E.g., the anthronylidene derivative **1** gives very high α values and both **1** and its p-tolyl analogue form products almost exclusively from the free ion.[8a,9] The extent of ion-pair return for several α-arylvinyl systems was evaluated by comparing the solvolysis and the cis-trans isomerization rates.[10] The more convenient comparison of titrimetric (k_t) and polarimetric (k_α) constants for optically active RX[6c,7] is usually inapplicable for the planar vinyl systems, although it was recently applied for an optically active allene.[11]

We report now the first application of this tool for a vinylic bromide which is structurally related to **1**. Reduction of **1** with LiAlH$_4$ in ether or THF in the presence of (−)-quinine, followed by chromatographic separation, gave optically active 9-(α-bromoanisylidene)-10-hydroxy-9,10-dihydroanthracene (**2**).[12] The highest rotations observed so far are $[\alpha]_{436}$ +97.5° in 2,2,2-trifluoroethanol (TFE) and $[\alpha]_{436}$ −65° in CDCl$_3$.

The solvolysis of 0.002 M **2** in TFE buffered by 0.004 M 2,6-lutidine at 49.6 °C is described in Figure 1. Extensive common ion rate depression by the formed Br$^-$ reduces the integrated first-order rate constant k_t at 75% reaction to 25% of the extrapolated initial value k_t^0 of 3.68×10^{-5} s^{-1} (line B). A selectivity constant $\alpha = 3205 \pm 99$ M^{-1} for competition between Br$^-$ and TFE[13] was calculated by assuming that the product is formed only from the free vinyl cation **3**. The rate coefficient in the presence of 0.0092 M Bu$_4$NBr remains constant (line A) but its value (1.52×10^{-6} s^{-1}) is ~4% of k_t^0, indicating that ≥96% of the product is formed from **3**.[14] The main product is anisyl 9-anthrylbis(trifluoroethyl) acetal (**4**).

Scheme I



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