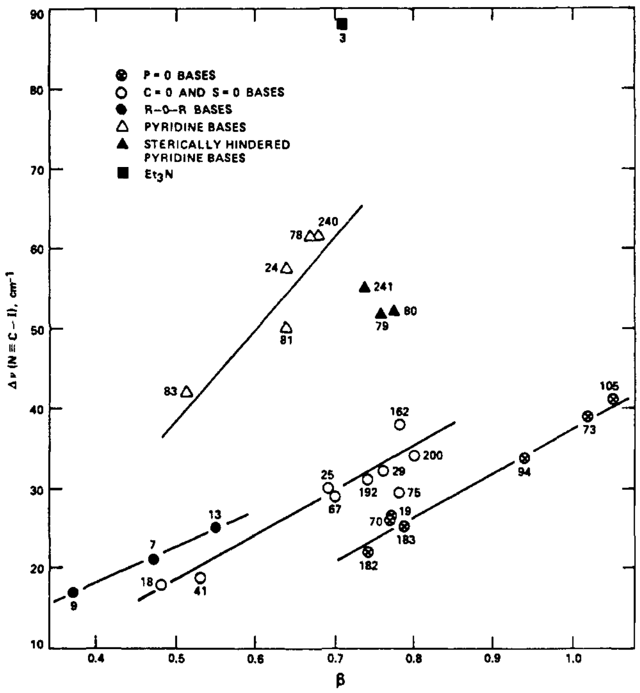

Figure 3. Values of $\Delta\nu$(C–I) of cyanogen iodide complexes with HBA bases plotted against β values of the bases. Base numbering is as in Tables I–III and ref 1.

The same workers also showed that the data also separate into families in a plot of ΔH_f vs. $\Delta\nu$(O–H) of 4-fluorophenol.

On the basis of data reported by Laurence and co-workers,[22a] $\Delta\nu$(C–I) of cyanogen iodide–HBA complexes also shows FD-type behavior with β. A plot is shown in Figure 3, where it is seen that, as might be expected of complexation by an iodine atom, steric effects seem to be quite severe. Laurence and co-workers have also shown FD-type behavior in a plot of $\Delta\nu$(C–I) against $\Delta\nu$(O–H) of phenol.

In a future paper we will show that, when used in combination with the β parameter, a new coordinate covalency parameter, ξ, allows quantitative intercomparisons between FD and FI behavior patterns through equations of the form of eq 17. Values of ξ are 0.0 for double bonded

$$XYZ = XYZ_0 + b\beta + e\xi \tag{17}$$

oxygen bases, 0.2 for single bonded oxygen bases, 0.6 for pyridine bases, and 1.0 for sp^3-hybridized amine bases. Representative e/b values in eq 17 (which are measures of separations between families in plots like Figures 2 and 3) are 0.00 ± 0.05 for most FI properties, 0.24 for ΔH_f(4-FP:HBA) 0.61 for $\Delta\nu$(O–H) of phenol, and 0.79 for $\Delta\nu$(C–I) of cyanogen iodide.

In the initial formulation of the β scale,[8a] as in the present study, we obtained β values by averaging β_i's for the HBA bases acting as both solvents and solutes in nonhydrogen bonding solvents. We wish now, in conclusion, to reemphasize that, except in the base of self-associating amphiprotic compounds (whose apparent β values are very concentration dependent), no statistical distinction between the two types of measurements was evident when appropriate corrections were made for dipolarity/polarizability effects of the neat solvents and dipole/dipole interaction effects of the solutes.

Acknowledgment. The work by T.G. was done while on sabbatical at UCI. The work by R.W.T. was supported in part by a grant from the Public Health Service. The work by M.J.K. was done under Naval Surface Weapons Center Foundational Research Task IR-210.

Butadiynyl-Substituted Vinyl Cations

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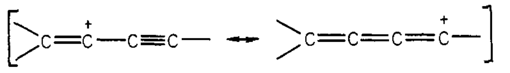
The solvolytic reactivity of various 1-(butadiynyl)vinyl triflates, $R_2C{=}C(OTf)(C{\equiv}C)_2R'$, was investigated in aqueous ethanol and 2,2,2-trifluoroethanol (TFE). Activation parameters, solvent m values, and deuterium isotope effects were determined for these compounds and compared with corresponding parameters for 1-ethynylvinyl triflates, $R_2C{=}C(OTf)C{\equiv}CR'$. For R = CH_3 and R′ = H, the diynyl ester sovolyses in 50% EtOH at 25 °C are 23.5 times faster than those for the alkynyl ester, and both compounds show almost the same isotope effects of 1.05 and 0.94 in 60% EtOH and 97% TFE, respectively. These data are consistent with a unimolecular solvolysis mechanism involving an extended vinyl cation intermediate. The transmission of substituent effects through the diynyl group is discussed.

Considerable interest has been evoked recently in the stability, structure, and nature of the reactivity of alkynylvinyl cations such as 1. Recent theoretical studies[1] indicate that α-alkynyl substitution destabilizes a vinyl cation in a manner comparable to that observed and predicted for saturated cations. Such calculations are borne out by rate measurements on the solvolysis of a number of alkynylvinyl triflates, **2–5**, reported earlier by us[2] and others.[3-5]



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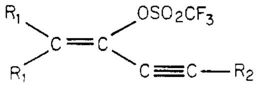


2, $R_1 = CH_3$; $R_2 = H$
3, $R_1 = CH_3$; $R_2 = D$
4, $R_1 = CH_3$; $R_2 = Si(CH_3)_3$
5, $R_1 = CH_3$; $R_2 = C(CH_3)_3$

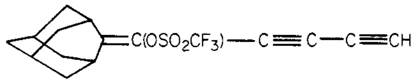
Further, these theoretical studies suggest that while α-alkyl- and α-silylvinyl cations exhibit similar stabilities, e.g., $Si(CH_3)_3$ and *t*-Bu afford comparable stabilization when attached directly to the cationic center, the effect of these groups is transmitted differently through an alkynyl moiety.

This interest, coupled with a continuing interest in vinyl cations,[6] prompted us to extend our earlier examination of the solvolysis of alkynylvinyl triflates along three lines.

First, recently developed syntheses[7,8] of butadiynylvinyl triflates, **6–9**, presented the opportunity to study the effect

$(R_1)_2C{=}C(OSO_2CF_3){-}C{\equiv}C{-}C{\equiv}C{-}R_2$

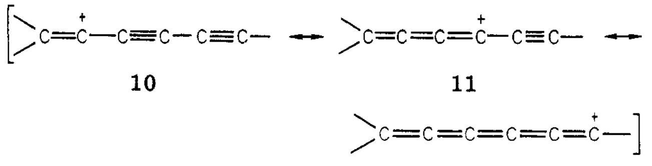
6, $R_1 = CH_3$; $R_2 = H$
7, $R_1 = CH_3$; $R_2 = D$
8, $R_1 = CH_3$; $R_2 = Si(CH_3)_3$



9

of extending π delocalization available to the cationic center in an attempt to ascertain whether such added conjugation would overcome the inductively electron-withdrawing effect of the second triple bond.

Second, suitable substitution of the triple bond should enhance the stability of **12** and thereby stabilize the cation.



10 **11** **12**

Therefore, we also investigated the nature of the effect of silyl substitution at the diynyl terminus in order to compare these results with our earlier work. These results bear also on the ability of a diynyl group to transmit substituent effects, information about which was hitherto unavailable.

Third, the ability of the triple bond to transmit substituent effects encouraged us to examine the effect of deuterium substitution at the alkynyl terminus, **3** and **7**, in an attempt to provide further mechanistic insight to these solvolyses.

Results and Discussion

Rates of solvolyses of vinyl triflates **2**, **3**, and **6–9** were measured in duplicate conductometrically in unbuffered aqueous ethanol and trifluoroethanol. First-order rates of high precision were obtained in all instances to greater than 90% reaction. Isotope effects were measured with duplicate or triplicate paired (H,D) runs by using a precise conductometric technique (see Experimental Section). Solvent *m* values, activation parameters, and first-order rate constants summarized in Table I are consistent with the direct unimolecular generation of the respective intermediate vinyl cation. The secondary deuterium isotope effects observed are summarized in Table II.

The effect of extending the alkynyl system can be seen to be a balance between the expected stabilization of the cation, **10** ↔ **11** ↔ **12**, caused by more extensive charge delocalization and the expected rate-retarding inductive effect of an additional triple bond. Thus the order of reactivity $(CH_3)_2C{=}C(OTf)CH_3 > 6 > 2$ (k_{rel} = 115:23.5:1.0; 25 °C, solvent 50E) implies an important stabilizing influence upon addition of a second alkyne function. This stabilization clearly outweighs a diminished inductive effect. The attenuation of the inductive effect in compounds containing more than one triple bond is noted in a comparison of the pK_a values for compounds **13–16**.[10] In these cases the effect of the second and third

	$C_3H_7CO_2H$	$C_2H_5C{\equiv}CCO_2H$	$C_2H_5(C{\equiv}C)_2COOH$	$C_2H_5(C{\equiv}C)_3COOH$
	13	**14**	**15**	**16**
pK_a	4.8	2.6	1.9	1.67

C–C triple bond is diminished in comparison to the presence of the first. Our solvolysis rates are yet another example of this effect.

Little is known about the effect of the diynyl moiety on transmission of substituent effects in reactions. A comparison of the rates of solvolysis of **2**, **4**, **6**, and **8** provides insight into this question. In the extended system, the effect of $Si(CH_3)_3$ is found to be rate-enhancing relative to H by a factor of 15.1 (k_8/k_6; 50E, 25 °C) whereas $Si(CH_3)_3$ enhances the rate of solvolysis compared to H by a factor of 61 (k_4/k_2; 50E, 25 °C) in the monoalkynyl series. Thus the extended conjugation is seen to attenuate the effect of the trimethylsilyl group by about fourfold. Another view suggests that greater delocalization of charge in **10** ↔ **11** ↔ **12** as compared to **1** results in greatly diminished electronic demand on the substituent. Nonetheless the transmission of an effect of this magnitude through five bonds is not unexpected. Proton coupling has been observed through diynyl functionalities in **17** and **18**

$CH_3C{\equiv}CC{\equiv}CCH_3$ **17** $CH_3C{\equiv}CC{\equiv}CCH_2OH$ **18**

$HOCH_2C{\equiv}CC{\equiv}CH$ **19** $HC{\equiv}CC{\equiv}CH$ **20**

where ${}^7J_{H,H}$ = 1.3 and 1.1 Hz, respectively.[11,12] Similarly in **19** ${}^5J_{C,H}$ = 1.5 Hz,[13] and in **20** ${}^5J_{H,H}$ = 2.2 Hz.[11] To our knowledge these results represent the first quantitative measurement of the ability of a diynyl group to transmit a substituent effect in a reaction.

The secondary isotope effects observed (Table II) also are consistent with the proposed intermediacy of a vinyl cation. The effect of remote deuterium substitution on solvolytic reaction rates is normally small and inverse or unity.[14-16] To our knowledge only one example of a remote

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Table I. Rates of Solvolysis, Solvent m Values, and Activation Parameters for Ethynyl- and Butadiynylvinyl Triflates

compd	temp, °C	solvent[a]	10^5k, s^{-1}	m_{OTs}[b]	m_{Cl}[c]	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu (65 °C)
$(CH_3)_2C{=}C(OTf)C{\equiv}CH$ (**2**)	25.0	50E	4.63×10^{-4}[f]				
	85.6 ± 0.1	60E	1.066 ± 0.008	0.77	0.54	28.7	−0.5
	95.8 ± 0.2	97T	1.32 ± 0.03				
$(CH_3)_2C{=}C(OTf)C{\equiv}CD$ (**3**)	85.6 ± 0.1	60E	1.015 ± 0.009[d]				
	95.8 ± 0.2	97T	1.39 ± 0.04[d]				
$(CH_3)_2C{=}C(OTf)(C{\equiv}C)_2H$ (**6**)	25.0	50E	0.0109[f]				
	75.05 ± 0.05	50E	11.86 ± 0.04	0.66	0.46	28.4	5.4
		60E	6.74 ± 0.09				
		97T	11.65 ± 0.30				
	85.6 ± 0.1	50E	38.6 ± 1.5				
$(CH_3)_2C{=}C(OTf)(C{\equiv}C)_2D$ (**7**)	75.05 ± 0.05	50E	11.25 ± 0.03[e]				
		60E	6.44 ± 0.15[e]				
		97T	12.4 ± 0.12[e]				
$(CH_3)_2C{=}C(OTf)(C{\equiv}C)_2Si(CH_3)_3$ (**8**)	25.0	50E	0.165[f]				
	65.09 ± 0.03	60E	15.44 ± 0.14	0.71	0.58	25.8	−3.0
		70E	6.74 ± 0.13				
		80E	3.41 ± 0.033				
	85.6 ± 0.1	80E	32.24 ± 0.13				
$Ad{=}C(OTf)(C{\equiv}C)_2H$ (**9**)	25.0	50E	0.637[f]				
	65.09 ± 0.03	70E	40.3 ± 1.5	0.65	0.51	26.3	0.5
		80E	31.6 ± 0.5				
		90E	8.62 ± 0.25				
	75.05 ± 0.05	90E	27.2 ± 1.2				

[a] 50E = 50:50 (v/v) ethanol/water; 60E, 70E, 80E, 90E similarly; 97T = 97:3 (w/w) 2,2,2-trifluoroethanol/water. [b] Solvent dependence based on $Y_{2\text{-AdOTs}}$ from ref 9. [c] Solvent dependence based on Y from ref 9. [d] Uncorrected, material is 92.1% d_1 by mass spectral analysis. [e] Uncorrected, material is 90.6% d_1 by mass spectral analysis. [f] Extrapolated from this work or ref 2.

Table II. Secondary Isotope Effects in the Solvolyses of **2**/**3** and **6**/**7** at 75 °C

compd	solvent	k_H/k_D[a]	$\Delta\Delta G^{\ddagger}$, cal mol^{-1}
2/**3**	50E	1.059 ± 0.006	40.1
	60E	1.046 ± 0.014	34.3
	97T	0.94 ± 0.02	−47.2
6/**7**	60E	1.054 ± 0.014	37.7
	97T	0.95 ± 0.02	−39.6

[a] Corrected to 100% deuteration.

secondary isotope effect involving an alkynyl group has been reported.[17] The isotope effect upon deuterium substitution in the 1-position of 3-chloro-3-methyl-1-butyne is reported to be $k_H/k_D = 1.00 \pm 0.04$. Clearly then, the effects reported here represent the first precise measurement of a remote deuterium isotope effect transmitted through an alkynyl moiety. The origin of such effects is attributed typically to an inductive effect on the isotopic atom.[16] In the present case, however, the observation of a "normal" isotope effect in aqueous ethanol implies an origin other than an inductive effect. Further speculation seems premature, yet the marked reduction of the isotope effect when the solvolysis rates are measured in the less nucleophilic aqueous trifluoroethanol implies the nucleophilic involvement of solvent at the transition state in TFE. In a less nucleophilic solvent, conversion of a tight ion pair to a solvent-separated ion pair is slowed relative to the rate of this process in aqueous ethanol, and external attack by solvent at the terminal alkynyl or diynyl group may become rate-limiting. A similar scheme has been proposed by Shiner et al. for the solvolysis of cyclopentyl brosylate.[18] Total rehybridization (sp → sp^2) at the terminal position should result in a maximum isotope effect of $k_H/k_D = 0.78$,[19] placing the observed value of 0.95 well within the expected region for incomplete rehybridization. Unfortunately product studies which might assist in determining whether attack at the terminal carbon does occur are not feasible in these extremely labile systems.

Finally, the increased reactivity of the adamantyl compound **9** ($k_{Ad}/k_{Me_2} = 59$; 50E, 25 °C) is ascribed to ground-state destablization arising from interaction of bridgehead hydrogens with the leaving triflate and the α-substituent.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer. Solvents and reagents were purified and dried by standard procedures immediately prior to use.

Vinyl triflates **2**,[20] **6**,[7] **8**,[7] and **9**[8] were prepared and characterized as previously reported.

Vinyl triflate 7 was prepared from the corresponding trimethylsilylvinyl triflate **8** in a manner similar to nondeuterated analogue **6**.[7] Into a 50-mL three-necked flask maintained under argon and equipped with a stirrer was added a solution of anhydrous KF (0.60 g, 10.3 mmol; 230% excess) in CH_3OD (20 mL) and D_2O (0.4 mL), followed by triflate **8** (1.00 g, 3.08 mmol). The mixture was stirred at room temperature for 30 min and worked up as previously described,[7] yielding 700 mg (89.7%) of **7** as a colorless oil with a deuterium content of 90.6% (as determined by mass spectrometry):[21] IR (neat) 2580 (C—D), 2210 cm^{-1} (C≡C).

Vinyl triflate 3 was prepared from triflate **4** (1.00 g, 3.33 mmol) by following the same procedure as described for the preparation of triflate **7**. It was obtained (660 mg, 86.5%) as a colorless oil with a deuterium content of 92.1%, as determined by mass spectrometry:[21] IR (neat) 2593 (C—D), 2160 cm^{-1} (C≡C).

Kinetic Studies. Ethanol was purified according to Wiberg.[22] Trifluoroethanol was purified according to Shiner et al.[23] or

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(21) The deuterium content can be increased by subsequent exchange with D_2O (50-fold excess) in DME with Et_3N (50% excess) as a base at room temperature for 2 h (for triflate **7**) or 4 h (for triflate **3**).

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Rappoport.[24] Solvents were prepared by weight from conductivity water (Millipore Systems) and appropriate organic solvents. Conductivity measurements were performed in sealed, paired cells by using a Hewlett-Packard Model 4274A LCR bridge, providing 5.5-digit precision, interfaced with a Hewlett-Packard Model 3497A multiplexer and a Hewlett-Packard Model 9826 BASIC microcomputer. From 1 to 10 μL (depending on concentration) of a pentane solution of the triflate was utilized (in-cell concentration of triflate was ca. 2×10^{-4} M) for each run. Approximately 200 points at equal changes in percent reaction were collected over the range 5–95% reaction. Rate constants were calculated by using a BASIC version nonlinear least-squares program written for the HP 9826 in our laboratories. Temperature control and measurement were accomplished by using a PRT-regulated proportional temperature controller and Hewlett-Packard quartz thermometer.

Acknowledgment is made to the donors of the Petroleum Research fund, administered by the American Chemical Society, for the partial support of this research. M.D.S. thanks the National Science Foundation 2- and 4-year college Research Equipment Program for funds used in the purchase of the rate data acquisition instrumentation. Financial support by the NSF (Grant No. CHE81-07629) is further gratefully acknowledged. We are indebted also to the University of Utah Mass Spectrometry Laboratory funded by the NSF (Grant No. CHE-8100424) and the University of Utah Institutional Funds Committee.

Registry No. 2, 71451-07-5; **3**, 83027-30-9; **6**, 74711-40-3; **7**, 83027-31-0; **8**, 77350-69-7; **9**, 79140-87-7; D_2, 7782-39-0.

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[1,5] Hydrogen Sigmatropy within Isodicyclopentadiene. Cycloadditive Capture of a Fleeting Isomer with Dienophiles of Low Reactivity

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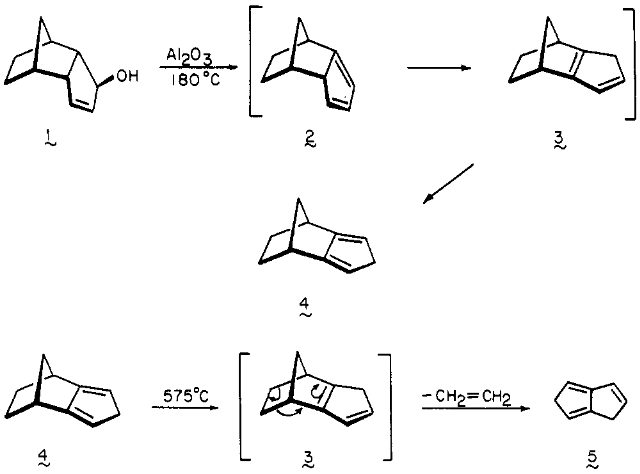
The ability of isodicyclopentadiene (**4**) to experience [1,5] sigmatropic hydrogen migration within its unsaturated five-membered ring has been established by Diels–Alder cycloaddition chemistry. By making recourse to elevated temperatures and dienophiles which react sluggishly with **4**, it becomes possible for one to trap the more reactive isomer **3**, with addition occurring invariably on the exo face. Alternatively, **4** may be preequilibrated with **3** (e.g., at 169 °C) prior to dienophile addition if higher levels of angular adducts are desired with more reactive dienophiles. The dienophiles examined are *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethene (**6**), *trans*-1,2-dichloroethene (**11**), phenyl vinyl sulfide (**13**), phenyl vinyl sulfoxide (**19**), and phenyl vinyl sulfone (**22**). Appropriate chemical transformations of the adducts have given rise to the fused norbornadiene **8** and norbornene **9**. The presence of an *endo*-methyl substituent as in **25** fosters [1,5] hydrogen sigmatropy to give **26**, which, although not spectroscopically detectable, is easily trapped.

Dehydration of tricyclic alcohol **1** over alumina at 180 °C yields the hydrocarbon **4** known as isodicyclopentadiene[2,3] (Scheme I). Since loss of water from **1** cannot lead directly to **4**, this reaction is probably mediated by dienes **2** and **3**, although these isomers have been neither observed nor isolated. The involvement of **3** in the pyrolytic conversion of **4** to dihydropentalene (**5**) and ethylene, the key reaction leading to formation of the pentalenyl dianion, has additionally been claimed by Katz and co-workers.[3] Although no doubt persists that **4** is more thermodynamically favored than **2** or **3**, it remained to detect these less stable isomers or, at a minimum, to gain some reasonable appreciation of the facility for [1,5] hydrogen migration within these systems.[4]

Scheme I



The Diels–Alder reactivity of isodicyclopentadiene has been the subject of intense investigation recently because of the exceptionally high π-facial stereoselectivity exhibited during the course of its cycloaddition reactions. Thus, in the presence of reactive dienophiles, **4** enters into [4 + 2] bonding predominantly, if not exclusively, from its endo surface to produce *syn*-sesquinorbornene derivatives.[5-7] It

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(1) Author to whom inquiries regarding the X-ray crystal structure analysis should be addressed at Hoffmann-La Roche.

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