Solvolysis of 2,2-Dialkylvinyl Iodonium Salt: Alkyl Participation and Possibility of a Primary Vinylic Cation Intermediate

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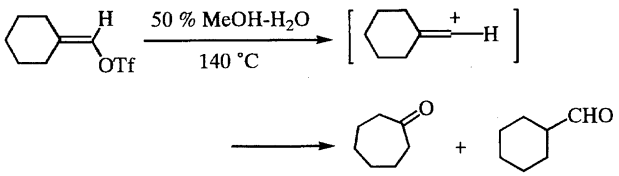
Solvolysis of (*E*)- and (*Z*)-2-methyl-5-phenyl-1-pentenyl(phenyl)iodonium tetrafluoroborate (**1**·BF_4) was carried out in various alcohols, acetic acid, and aqueous solutions at 60 °C. Products (after acid hydrolysis) include iodobenzene and 2-methyl-5-phenylpentanal as well as rearranged ones: 6-phenyl-2-hexanone, 6-phenyl-3-hexanone, 6-phenyl-2-hexyne, 6-phenyl-1,2-hexadiene, and 6-phenyl-2,3-hexadiene. The products of α-elimination, including 1-methyl-3-phenyl-1-cyclopentene, were also obtained in methanol and ethanol. Solvolysis of the *E* isomer (***E***)-**1** is faster than that of (***Z***)-**1** in every solvent examined. The percentage of rearrangement is higher with (***E***)-**1** than with (***Z***)-**1**, and the main rearranged products are those of migration of the alkyl group *trans* to the iodonio group, but migration of the *cis* alkyl group is also involved. Theoretical calculations suggest that interconversion between the secondary vinylic cations by 1,2-hydride shift is rapid. These results show that a major heterolysis reaction occurs with β-alkyl participation to directly give a secondary vinylic cation, but stereochemistry of the unrearranged substitution products suggests that formation of the primary vinylic cation is also involved in less nucleophilic solvents like acetic acid and 2,2,2-trifluoroethanol.

Vinyl iodonium salts are good precursors for vinyl cations due to a high nucleofugality of the iodonio group. A 1-cyclohexenyliodonium salt readily undergoes solvolysis in hydroxylic solvents through a cyclohexenyl cation intermediate.[1] Solvolysis of styryliodonium salt occurs via β-phenyl participation with 1,1-vinylenebenzenium ion as an intermediate.[2] Primary 1-alkenyliodonium salts undergo vinylic S_N2 substitution with inversion of configuration,[3—5] but no sign of formation of primary vinylic cation was detected. Primary vinylic cations are considered generally to be unstable[6—9] and can be generated only under some forced conditions; i.e., by a nuclear decay from tritiated ethene,[10] by photolysis,[11] or in a superacid.[12] Acid-catalyzed hydration of acetylene was also suggested to occur via a vinyl cation intermediate but in strong sulfuric acid.[13]

These results must be closely related to the stability of a putative primary vinylic cation which carries a hydrogen atom at the α position. Theoretical calculations as well as thermochemical data show that the β-alkyl substitution does stabilize vinyl cation.[7—9] There is a possibility for generation of such a β-substituted stabilized primary vinylic cation during solvolysis. Hinkle and Thomas[14] have recently found that thermolysis of 2-methyl-1-propenyl(aryl)iodonium triflate in chloroform gives rearranged products and suggested formation of a primary vinylic cation as an intermediate, but the observed rearrangement is obviously not enough evidence for the primary cation. A cycloalkylidenemethyl triflate was suggested to undergo solvolysis via the corresponding primary cation (a 2,2-dialkylvinyl cation) in aqueous solution at high temperature (Eq. 1).[15]



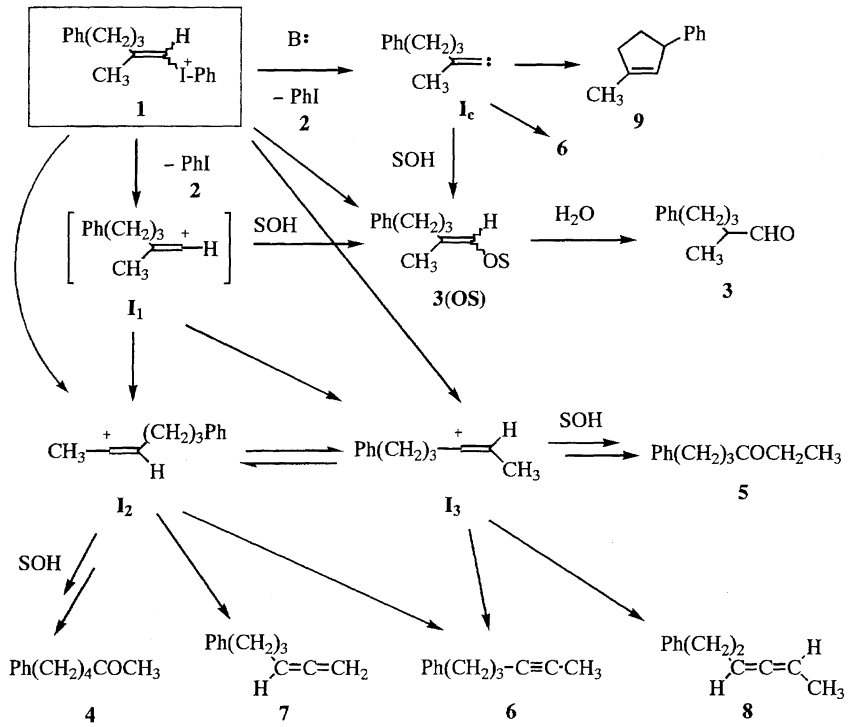
(1)

We have examined similar possibilities with an unsymmetrically substituted 2,2-dialkylvinyl substrate bearing a still better nucleofuge of phenyliodonio group to more closely look into the reactive intermediate from the stereochemical point of view. Solvolysis of a 2,2-dialkylvinyliodonium salt resulted in extensive rearrangement mainly via β-alkyl participation, and the primary vinylic cation seemed to be involved only in a minor reaction pathway in some solvents. These results will be presented in this paper.[16]

Results

Solvolysis of (*E*)- and (*Z*)-2-methyl-5-phenyl-1-pentenyl(phenyl)iodonium tetrafluoroborate (**1**·BF_4) was carried out in some alcohols, acetic acid, and aqueous solvents at 60 °C. The reaction resulted in extensive rearrangements to lead to both substitution and elimination. The products were

gas-chromatographically analyzed both before and after the treatments with aqueous hydrochloric acid by extraction with pentane containing tetradecane as an internal standard for determination. The products include iodobenzene (**2**), carbonyl compounds **3**—**5** and elimination products **6**—**8** (Scheme 1). The carbonyl products must be derived from hydrolysis of the initial substitution products, enol ethers or esters. Some of the enol products could be identified in the product mixture extracted immediately after the solvolysis reaction. Yields of the products determined by gas chromatography are given in Table 1, and possible reaction pathways leading to these products are illustrated in Scheme 1.



Scheme 1.

Table 1. Product Distribution for the Solvolyis of **1** at 60 °C[a)]

Struct.		Reaction	Product yield/%									(**4** + **7**)	%
of **1**	Solv.	time/h	**2**	**3**[b)]	**3(OS)** (*Z*/*E*)[c)]	**4**	**5**	**6**	**7**	**8**	**9**	(**5** + **8**)	rearr.[b)]
E	MeOH	16	80	26 (2.2)	22 (27/73)	12	Trace	25	7.0	0.3	2.8	Large	63 (95)
Z	MeOH	46	68	61 (15)	41 (25/75)	Trace	3.7	12	Trace	2.7	5.4	Small	23 (54)
E	EtOH	14	98	27 (5.5)	18 (32/68)	16	0.8	38	12	0.9	4.6	94/6	73 (92)
Z	EtOH	40	89	62 (10.5)	51 (25/75)	0.8	5.6	15	Trace	3.9	11	8/92	37 (69)
E	MEA[d)]	15	80	7.4	2.7 (44/56)	18	0.7	38	12	0.8	0	95/5	90
Z	MEA[d)]	15	68	15	0.7 (43/57)	1.8	12	34	0.6	7.8	0	11/89	79
E	TFE[e)]	30	85	0.9	Nd	15	8.9	30	0.5	0.2	0	63/37	98
Z	TFE[e)]	80	62	2.9	Nd	11	17	34	0.3	0.4	0	39/61	96
E	AcOH	40	63	2.0	0.4 (trace/0.4)	21	3.4	50	2.7	(1)[f)]	0	84/16	98
Z	AcOH	80	70	9.0	4.9 (20/80)	7.7	22	47	0.5	(3)[f)]	0	25/75	91
E	H_2O[g)]	25	38	1.1		18	0.8	10.5	2.9	Trace	0	96/4	97
Z	H_2O[g)]	75	37	0.6		1.7	11	6.3	Trace	1.0	0	13/87	97
E	50M(H^+)[h)]	20	78	2.3		15	1.0	39	9.9	0.9	0	93/7	97
Z	50M(H^+)[h)]	70	52	6.2		1.8	13	25	Trace	5.0	0	9/91	88
E	50ET[i)]	40	78	9.5		11.4	1.3	36	4.9	0.7	3.8	89/11	86
Z	50ET[i)]	80	81	10.3		2.2	6.4	29	0.7	4.0	1.5	22/78	81
E	20MT[j)]	25	74	2.0		14	2.4	42	3.7	1.9	1.0	80/20	97

a) Carbonyl products were determined after treatments with aqueous hydrochloric acid. b) Values in parentheses are those ascribable to the reactions other than α-elimination. c) Percent yields of **3(OS)** along with *Z*/*E* isomeric ratios in parentheses before the acid treatments. d) 2-Methoxyethanol. e) 2,2,2-Trifluoroethanol. f) The gas-chromatographic peak was partially overlapped with another one. g) H_2O containing 1% of MeOH. h) 50% (v/v) aqueous methanol containing 0.001 mol dm^{-3} trifluoroacetic acid. i) 50% (v/v) ethanol–TFE. j) TFE containing 20% (v/v) methanol.

The unrearranged product **3(OS)**, where **OS** stands for the fragment of the hydroxylic solvent SOH, may be formed directly from the iodonium substrate **1** (S_N2) or via an intermediate primary vinylic cation $\mathbf{I_1}$ (S_N1), and can take one of two geometrical forms: *E* or *Z*. In aqueous solutions, the enol **3(OH)** directly results in the aldehyde **3**, while the enol products **3(OS)** formed in alcohol and acetic acid undergo acid hydrolysis to give **3**.

The rearranged products must be formed via secondary vinylic cations, $\mathbf{I_2}$ and $\mathbf{I_3}$, which can be generated by migration of the β-alkyl groups, 3-phenylpropyl and methyl, respectively. This migration can occur not only from the primary vinylic cation $\mathbf{I_1}$, if formed, but also directly from **1** by β-alkyl participation. Possible substitution products derived from $\mathbf{I_2}$ and $\mathbf{I_3}$ would have included two pairs of geometrical isomers of enol ethers or esters. Although there were some small gas-chromatographic peaks (less than a few %) in the product mixture extracted immediately after reaction that seemed to correspond to these products, those minor products could not be identified. Instead, they were determined as hydrolysis products, **4** and **5**. Three possible elimination products, **6**, **7**, and **8**, derived from the rearranged cations could be identified and determined.

A cyclic product **9** was also detected in methanol and ethanolic solutions and is considered to be derived from α-elimination via the alkylidenecarbene $\mathbf{I_c}$. This reaction occurs very readily in the presence of an added base. The reaction was very rapid in solutions containing sodium acetate or triethylamine as a base, and the products were exclusively those of α-elimination in alcoholic and aqueous solutions. However, some usual solvolysis products with rearrangement were also observed in acetic acid. These results are summarized in Table 2.

Rate constants for solvolysis were determined spectrophotometrically at 60 °C in various solvents. Results are not precise enough, due to the effects of unknown impurities of the solvents, but careful manipulations gave consistent data, as listed in Table 3. The *E* isomer (***E***)-**1** is always more reactive than (***Z***)-**1**. This relative reactivity is in marked contrast to that observed in the reaction of **1** with halide ions, where (***Z***)-**1** is more reactive than (***E***)-**1**.[17] The reaction of **1** in the presence of sodium acetate in methanol is instantaneous at 60 °C, and the rates were measured at 25 °C. The observed rate constants are similar for the two isomers, as shown in Table 3.

Table 3. Observed Rate Constants for Solvolysis of **1** at 60 °C

Solvent	$10^5 k_{obsd}/s^{-1}$	
	(*E*)-**1**	(*Z*)-**1**
MeOH	5.96	1.60
EtOH	6.0	2.00
H_2O	6.0	1.54
TFE	3.0	0.47
80E[a]	7.7	2.34
60E[a]	7.5	2.36
40E[a]	6.9	1.98
20E[a]	6.8	1.66
80ET[b]	5.7	1.70
60ET[b]	5.5	1.33
40ET[b]	5.2	0.85
20ET[b]	4.3	0.62
90Tw[c]	4.2	0.61
70Tw[c]	5.0	1.02
50Tw[c]	4.8	1.10
MeOH (0.05 AcONa)[d]	980	940
MeOH (0.01 AcONa)[e]	930	910

a) 80E = 80 : 20 (v/v) EtOH–H_2O, 60E = 60 : 40 (v/v) EtOH–H_2O, and so on. b) 80ET = 80 : 20 (v/v) EtOH–TFE, and so on. c) 90Tw = 90 : 10 (w/w) TFE–H_2O, and so on. d) Reaction at 25 °C in MeOH containing 0.05 mol dm^{-3} sodium acetate. e) Reaction at 25 °C in MeOH containing 0.01 mol dm^{-3} sodium acetate. The ionic strength was adjusted at 0.05 with tetrabutylammonium perchlorate.

Discussion

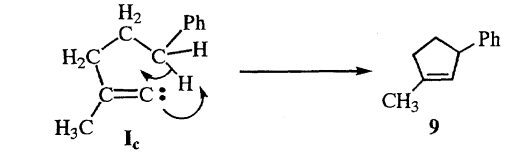
The data summarized in Table 1 are complicated because of competing parallel reaction pathways, as illustrated in Scheme 1. The reactions may be divided into two categories: solvolysis and α-elimination. The solvolysis is a nucleophilic reaction that occurs at the vinylic carbon and may involve pathways via vinylic cation intermediates and/or a bimolecular nucleophilic substitution (S_N2). By contrast, the α-elimination occurs at the α-hydrogen by a base and proceeds via an alkylidenecarbene intermediate. Our primary concern is the former pathways, and we call them sim-

Table 2. Product Distribution in the Solvolyis of **1** in the Presence of a Base at 60 °C

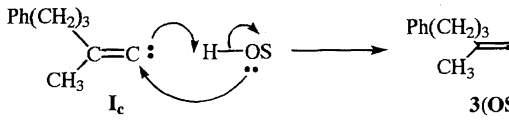
Struct. of **1**	Solv.	Base (concn/ mol dm^{-3})	Time h	Product yield/%							
				2	**3(OS)** (*Z*/*E*)		**4**	**5**	**6**	**7**	**8**	**9**
E	MeOH	AcONa (0.1)	1.0	79	80	(27/73)	0	0	1.7	0	0	9.3
E	MeOH	Et_3N (0.1)	1.0	90	80	(27/73)	0	0	1.7	0	0	10.0
Z	MeOH	AcONa (0.1)	1.0	70	64	(26/74)	0	0	1.3	0	0	8.1
E	EtOH	AcONa (0.06)	0.5	81	78	(28/72)	0	0	2.0	0	0	17
Z	EtOH	AcONa (0.06)	0.5	84	71	(27/73)	0	0	1.6	0	0	15
E	MEA	AcONa (0.05)	2.5	71	41	(33/67)	0	0	2.6	0	0	17
E	TFE	AcONa (0.1)	3.0	84	14.4	(28/72)	0	0	24	0	0	42
E	TFE	Et_3N (0.1)	3.0	86	12.5	(27/73)	0	0	22	0	0	46
Z	TFE	AcONa (0.1)	3.0	91	14.0	(28/72)	0	0	24	0	0	42
E	AcOH	AcONa (0.1)	3.0	79	56	(43/57)	9.3	1.0	27	3.7	0.8	3.3

ply solvolysis. We will focus our attention on how vinylic cation intermediates are formed; that is, whether the primary vinylic cation is generated or not, and how much β-alkyl participation occurs during the heterolysis.

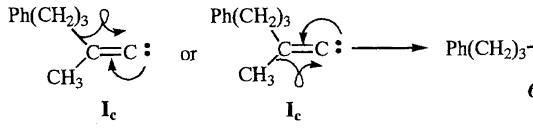
α-Elimination. Before looking into the vinylic cation pathways (solvolysis), let us first examine the α-elimination, results of which are summarized in Table 2. In the presence of a base like acetate ion or triethylamine, the reaction becomes very rapid and occurs essentially via α-elimination, except for the reaction in acetic acid. The three kinds of products must result from the alkylidenecarbene intermediate $\mathbf{I_c}$. First of all, both geometrical isomers of the substrate, (***E***)-**1** and (***Z***)-**1**, gave essentially the same product distribution at nearly the same rate (last two runs in Table 3), reflecting the loss of the original geometry in the intermediate state. This implies that the intermediate involved is a free carbene.[18] The three ensuing reactions are: an intramolecular insertion to give the cyclic product **9** (Eq. 2), a solvent insertion reaction to lead to **3(OS)** of the same isomeric ratio from (***E***)-**1** and (***Z***)-**1** (Eq. 3), and a migration of a β-alkyl group (1,2-shift) to afford alkyne **6** (Eq. 4),[19] where we cannot differentiate which alkyl group migrates. However, there are good reasons for asserting that the phenylpropyl group preferentially migrates over the methyl group,[21] as is also the case in β-alkyl participation (see below).



(2)



(3)



(4)

The fraction of the solvent insertion product **3(OS)** decreases in the order: MeOH > EtOH > 2-methoxyethanol (MEA) > 2,2,2-trifluoroethanol (TFE). This order of solvent reactivity seems to reflect solvent nucleophilicity and probably steric effects. The stable form of an alkylidenecarbene is singlet and electron-deficient in nature,[18,22] and nucleophilic attack of the alcohol on a vacant p orbital of the carbene may be an important factor to govern this reactivity. The ratio of the two intramolecular reactions, cyclization and 1,2-shift, (**9/6**) could be independent of the solvent used. However, it is not the case. The ratio of **9/6** ranges from 5 to 9 in MeOH, EtOH, and MEA, while it is 1.8 in TFE. That is, the intramolecular C–H insertion is relatively retarded in TFE compared with the 1,2-shift. The intramolecular reactivity of the electron-deficient center of the singlet carbene must be lowered by nucleophilic solvation by an electron-pair-donor solvent. The 1,2-alkanide shift no doubt occurs toward the electron-deficient center of the carbene. It is theoretically suggested that there is a slight preference for the π approach (reaction of the electron-deficient center) in the insertion of vinylidene ($H_2C = C$) into the C–H bond,[23] but the σ approach (reaction toward the sp orbital) is also possible in the insertion reaction. So, the electron-pair-donor solvation on the electron-deficient center must affect the 1,2-alkanide shift more influentially to reduce the reactivity than it does the C–H insertion. On the contrary, a hydrogen-bond-donor solvent may retard the insertion more greatly than the 1,2-shift. These two modes of solvent effects must be responsible for the low value of **9/6** ratio in TFE. A similar observation of solvent effects on the relative ease of the cyclization and 1,2-shift of alkylidenecarbene was previously noted for the solvents H_2O and THF.[18]

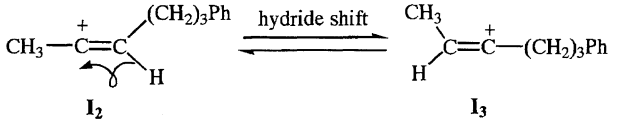
The α-elimination route obviously takes part in the reaction in neutral methanol and ethanolic solvents, as is implied by formation of the cyclic product **9** (Table 1). If we assume that **9** solely arises from the α-elimination and that the 1,2-shift and the solvent insertion occur at the same ratio as in the basic solution, then we can calculate the amounts of **3** and **6** derived from this reaction among the overall products in neutral methanol and ethanol. The unrearranged product **3** is evaluated to be formed mainly from α-elimination in these solvents. The calculated yields of **3** due to the other reactions (solvolysis) are given in parentheses following the overall yields in Table 1, but reliable evaluation of the calculated yields of **3(OS)** was impossible.

Solvolysis Products. Solvolysis products include both unrearranged (**3**) and rearranged products (**4**—**8**). Fractions of the percent rearranged products are summarized in the last column in Table 1, where the corrected values for the solvolysis pathways in methanol and ethanol are given in parentheses. In the reactions in less basic solvents, MEA, TFE, AcOH, and aqueous solvents, where the cyclic product **9** was not detected, the carbene route may be negligible, and product distributions observed are due to the usual solvolysis pathways. Including the corrected values for solvolysis, the rearranging tendency of (***E***)-**1** (> 90%) is always greater than that of (***Z***)-**1**, which increases with increasing polarity (or decreasing nucleophilicity) of the solvent. Values of the % rearrangement in solvolysis of (***Z***)-**1** are 54, 69, 79, 91, 96, and 97% in MeOH, EtOH, MEA, AcOH, TFE, and H_2O, respectively.

The 1,2-shift of the 3-phenylpropyl group leads to **4**, **6**, and **7** through the cation $\mathbf{I_2}$, while that of the methyl group affords **5**, **6**, and **8** through $\mathbf{I_3}$. So, the relative extent of migration of the phenylpropyl and methyl groups can be evaluated by the ratio of the yields of **4**+**7** and **5**+**8** (the second last column of Table 1), assuming that $\mathbf{I_2}$ and $\mathbf{I_3}$ react similarly (i.e., **6** is formed similarly from both $\mathbf{I_2}$ and $\mathbf{I_3}$). It is apparent that the group *trans* to the leaving iodonio group migrates more readily than the *cis* group. This difference is large in MeOH, EtOH, MEA, and aqueous solvents, being 9/1 or greater, but it becomes smaller in mixed methanol–TFE (20 MT)

and acetic acid (about 8/2) and in TFE (6/4). Migration of the *cis* alkyl group seems to compete with nucleophilic and basic trapping by the solvent. A less reactive solvent allows more migration of the *cis* group. Furthermore, the phenylpropyl group seems to show a slightly higher tendency to migrate than the methyl group in the same stereochemical arrangement, judging from the magnitudes of (**4**+**7**)/(**5**+**8**) value for the *E* and *Z* isomers as well as from their total rearranging tendencies.

Results of the rearrangement that the *trans* alkyl group migrates more readily (but not exclusively) than the *cis* group can be explained in two ways: First, simple heterolysis of **1** would give an ion-molecule pair of the primary vinylic cation $\mathbf{I_1}$ and iodobenzene **2**, and the 1,2-alkyl shift from the opposite side of **2** within this pair (*trans*-alkyl migration) could be easier than a similar shift from the same side (A) (Chart 1). Alternatively, participation of the *trans* β-alkyl group may occur in concert with the departure of the leaving group (B). The latter process should be stereospecific due to the stereoelectronic requirement, but apparent migration of the *cis* alkyl group can occur if the interconversion of the rearranged secondary vinylic cations, $\mathbf{I_2}$ and $\mathbf{I_3}$, can be induced by the 1,2-hydride shift (Eq. 5). If this interconversion takes place readily and can compete with trapping by the solvent, then the initially formed secondary cation, $\mathbf{I_2}$ or $\mathbf{I_3}$, can rearrange to the other and eventually affords the product of migration of the *cis* alkyl group.



(5)

In the first possibility, however, the stereoselectivity of rearrangement would not be so good since the pairing nucleofuge **2** is neutral and the solvent could also participate in this process. Differentiation of the two faces should be weak. Furthermore, is the primary cation $\mathbf{I_1}$ stable enough to exist as a discrete intermediate? Any discrete intermediate should have a lifetime longer than 10^{-13} s.[24] Primary alkyl cations are not considered to have a long enough lifetime in aqueous solution. On the other hand, a 2,2-dialkylvinyl cation is evaluated to be nearly as stable as a saturated primary alkyl cation, although the simple vinyl cation is less stable.[6] So, it is predicted that a 2,2-dialkylvinyl cation can seldom exist as an intermediate in aqueous solution. However, it may exist as a transient intermediate in less reactive solvents.

In the second possibility, how easy is the 1,2-hydride shift of the secondary vinylic cations? The parent vinyl cation $\mathbf{V_1}$ was found both theoretically and spectroscopically to be less stable than the hydrogen-bridged isomer $\mathbf{V_{\Delta 1}}$.[25] Thus a similar hydrogen-bridged isomer of an alkyl-substituted vinyl cation can also be stable, and the 1,2-hydride shift of a secondary vinylic cation like $\mathbf{I_2}$ and $\mathbf{I_3}$ may occur readily through a hydrogen-bridged species. However, available calculations at the HF level[25] show that secondary 1-methylvinyl cation is more stable than the hydrogen-bridged one. Such calculations are largely dependent on the level of theory; although the MP2 or higher levels of calculations reproduced the gas-phase observation that $\mathbf{V_{\Delta 1}}$ is more stable than $\mathbf{V_1}$, the HF calculations led to the opposite result.[25] In order to know how easy the 1,2-hydride shift of 1,2-dialkylvinyl cation is, the degenerate 1,2-shifts of hydride in 1-methyl-1-propenyl cation $\mathbf{V_2}$ (Eq. 6) as well as in parent vinyl cation $\mathbf{V_1}$ were examined by the ab initio MO calculations at the MP2/6-31G(d) level. Optimized structures and energetics of these processes are summarized in Fig. 1 and Table 4, respectively. The results show that the bridged structures are on the local minima and are slightly more stable than the open cations for both systems (ca. 1 kcal mol^{-1} for $\mathbf{V_{\Delta 2}}$) (1 cal = 4.184 J). It may be worth pointing out that the respective angles H–C–C and C–C–C of the bridged cations $\mathbf{V_{\Delta 1}}$ and $\mathbf{V_{\Delta 2}}$ are nearly 180°. The transition state ($\mathbf{V_{TS2}}$) for the degenerate hydride shift of $\mathbf{V_2}$ was found nearly in the middle between the initial ($\mathbf{V_2}$) and the bridged states ($\mathbf{V_{\Delta 2}}$) and lies only 0.32 kcal mol^{-1} above $\mathbf{V_2}$. So, the 1,2-hydride shift within a similar 1,2-dialkylvinyl cation must occur very readily, and the product of *cis*-alkyl migration in the present solvolysis

Chart 1.

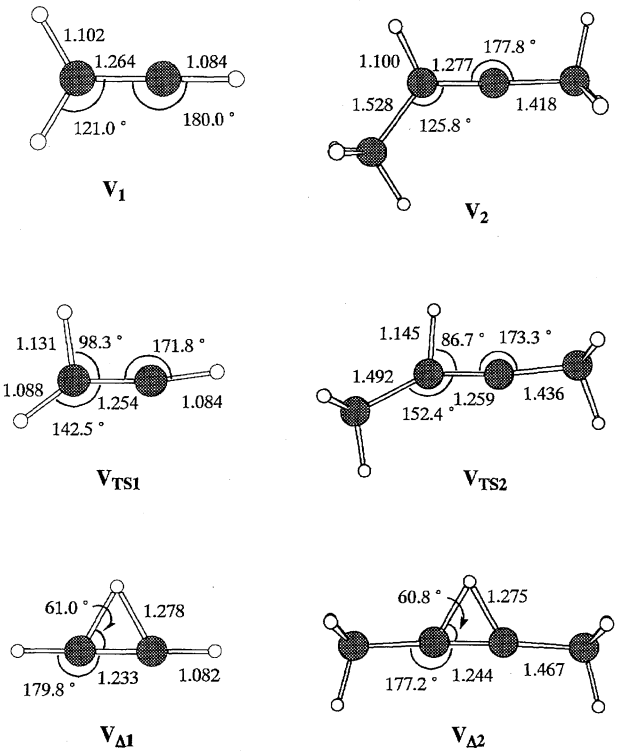
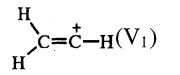
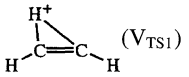
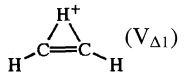
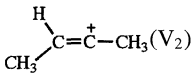
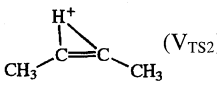
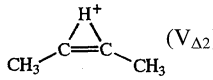


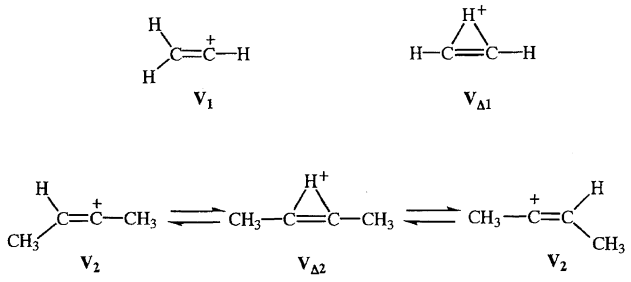
Fig. 1. Optimized geometries of vinyl cations, hydrogen-bridged cations, and transition states for their conversions. Values given are bond lengths (in Å) and bond angles.

Table 4. Calculated Energies for Vinylic Cations[a)]

Cation	$-E$/a.u.	Relative energy/kcal mol^{-1}
 (V_1)	−77.307083	0 (0)
 (V_{TS1})	−77.306347	0.46 (0.09)
 ($V_{\Delta 1}$)	−77.314246	−4.50 (−4.41)
 (V_2)	−155.701512	0 (0)
 (V_{TS2})	−155.700292	0.77 (0.32)
 ($V_{\Delta 2}$)	−155.703064	−0.97 (−1.56)

a). Calculated with the 6-31G(d) basis set at the MP2 level. Numbers in parentheses are free energies at 298 K.

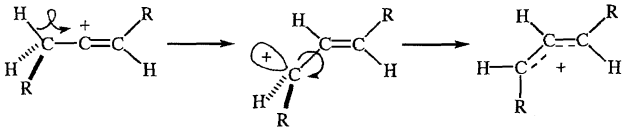
can be explained by the β-alkyl participation followed by partial 1,2-hydride shift. We need not consider formation of the primary cation $\mathbf{I_1}$.



(6)

Although the theoretical calculations suggest a very low barrier against the 1,2-hydride shift, the observed difference in distributions of the rearranged products for the isomeric substrates indicates that there is some barrier in solution and that the solvent trapping of the incipient cation can compete with the rearrangement. A more nucleophilic and basic solvent can more rapidly react with the cation and should result in a larger fraction of the products of *trans* migration. The results given in Table 1 seem to be accounted for largely by a mechanism involving the β-alkyl participation. Hinkle and Thomas[14] have suggested formation of a primary vinylic cation, from the observed rearrangement during the reaction of 2-methyl-1-propenyliodonium salt. However, this is obviously not enough evidence for this cation and the rearrangement very likely occurred via β-methyl participation.

Allylic cations $\mathbf{I_4}$ and $\mathbf{I_5}$ are isomers of the intermediate vinylic cations that could be generated by the hydride shift across the single bond from $\mathbf{I_2}$ and $\mathbf{I_3}$, respectively, and are possible intermediates of this reaction. However, no sign of products derived from these cations was detected. Although the allylic cations are obviously more stable than the isomeric vinylic cations, the barrier to 1,2-hydride shift across the single bond should be high. Allylic conjugation can contribute little to the stabilization of the transition state of the hydride shift since the vacant orbital is perpendicular to the π system (Eq. 7).



(7)

This could be reproduced by the present ab initio calculations (MP2/6-31G(d)). (*E*)-2-Butenyl cation $CH_3CH{=}CHCH_2^+$ is 19.4 kcal mol^{-1} more stable than the isomeric 1-methyl-1-propenyl cation $\mathbf{V_2}$ but the transition state for the hydride shift is 20.3 kcal mol^{-1} higher than the vinylic cation $\mathbf{V_2}$.

We must now consider how unrearranged products, **3(OS)** and **3**, are formed. The unrearranged products **3(OS)** are largely provided by the α-elimination, followed by solvent insertion in methanol and ethanol, but there is still a considerable remaining fraction of **3** due to solvolysis via the S_N2 and/or S_N1 mechanism. The stereochemistry of the product will be informative on this problem. The *Z*/*E* ratios of the **3(OS)** obtained in MEA and AcOH which are due to the solvolysis show that both isomeric substrates, (*E*)-**1** and (*Z*)-**1**, resulted in nearly the same compositions of isomeric **3(OS)** with a larger fraction of (*E*)-**3(OS)**. These results may be taken as indicating formation of the primary vinylic cation $\mathbf{I_1}$ in these less nucleophilic solvents. Although **3(OS)** could not be determined in TFE, the fact that the unrearranged product **3** was identified in this solvent suggests formation of the primary cation $\mathbf{I_1}$. The S_N2 pathway in this poorly nucleophilic solvent is unlikely as was found for the reaction of styryliodonium salt.[2]

Kinetics. Solvolysis rates summarized in Table 3 show that (*E*)-**1** is more reactive than (*Z*)-**1**, contrary to the reactivity values toward bimolecular nucleophilic reaction.[17] This is in accord with a mechanism involving β-alkyl participation. The observed rate constants for (*E*)-**1** and (*Z*)-**1** are plotted logarithmically against the solvent ionizing power Y_{OTs}[26a] and the solvent nucleophilicity N_T[26b] in Figs. 2 and 3. Solvent dependency of the rate is rather small, and complete scatterings are obvious in the plots against Y_{OTs} (a). Nonetheless, increasing tendencies of the rate with increasing solvent nucleophilicity N_T are seen in (b) of both Figs. 2 and 3. Since the heterolysis rates of a charged substrate are generally little influenced by solvent polarity,[1] the present observation of the

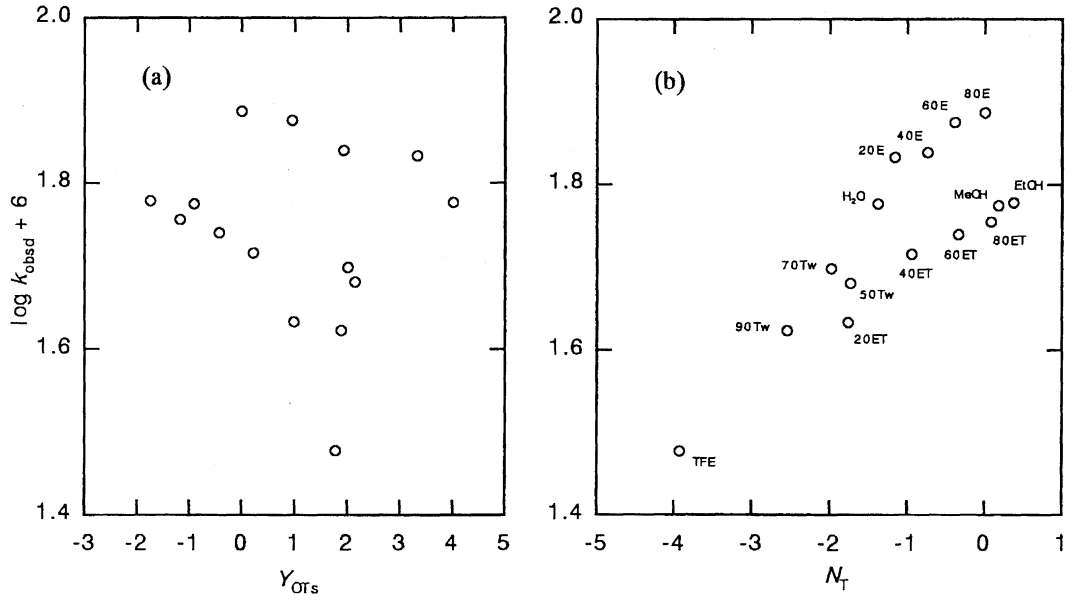


Fig. 2. Observed rate constants k_{obsd} for solvolysis of (*E*)-**1** plotted against Y_{OTs} (a) and N_T (b).

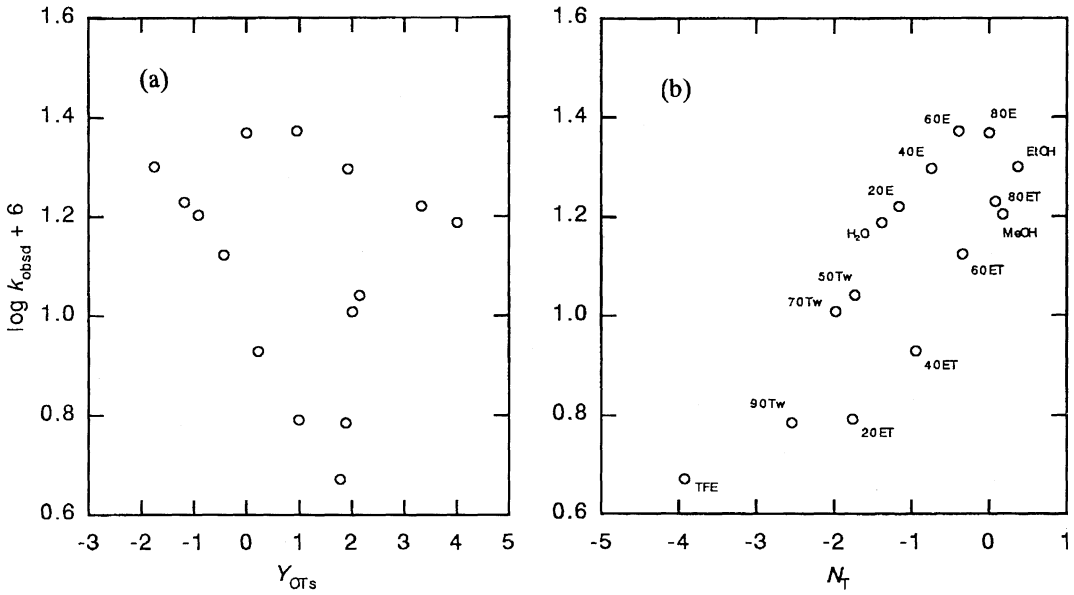


Fig. 3. Observed rate constants k_{obsd} for solvolysis of (*Z*)-**1** plotted against Y_{OTs} (a) and N_T (b).

independence of the solvent ionizing power is not surprising. The dependence of the rate on the nucleophilicity N_T may be ascribed to the α-elimination pathway that should depend on the solvent basicity which is parallel to the nucleophilicity.[27]

In conclusion, solvolysis of the 2,2-dialkylvinyliodonium salt occurs mainly via β-alkyl participation, leading to a rearranged secondary vinylic cation, and the 1,2-hydride shift within the secondary vinylic cation is rapid. This leads to an extensive rearrangement involving apparent *cis*-alkyl migration. Formation of the primary vinylic cation intermediate also seems to be involved in less nucleophilic solvents. Another facile reaction of this salt is α-elimination under mildly basic conditions.

Experimental

Most of the experimental procedures are essentially the same as before.[4] Instruments used for analyses were a gas chromatograph Shimadzu GC-14B with a capillary column DB-1 (0.25 mm×30 m) and an integrator C-R6A, a spectrophotometer Shimadzu UV-2200, an IR spectrometer JASCO IRA-1, an NMR spectrometer Varian INOVA 500, and mass spectrometers JMS-DX303HF and JMS-SX102A.

Materials. Solvents and salts used were obtained as before[4] or of the best analytical grade available.

(*E*)- and (*Z*)-2-methyl-5-phenyl-1-pentenyl(phenyl)iodonium tetrafluoroborate (1·BF_4): (*E*)- and (*Z*)-2-methyl-5-phenyl-1-trimethylsilyl-1-pentene obtained by the method of Fleming[28] were treated as described previously.[29]

(*E*)-1·BF_4: Needles, mp 75.5—76.5 °C (CH_2Cl_2–Et_2O);

^{1}H NMR ($CDCl_3$) δ = 1.83 (quint, J = 7.6 Hz, 2H), 2.17 (d, J = 0.5 Hz, 3H), 2.48 (br t, J = 7.6 Hz, 2H), 2.59 (t, J = 7.6 Hz, 2H), 6.70 (br s, 1H), 7.07—7.32 (m, 5H), 7.45 (br t, J = 7.5 Hz, 2H), 7.60 (br t, J = 7.5 Hz, 1H), 7.94 (br d, J = 7.5 Hz, 2H); No signal for the contaminated isomer was detected. HRFAB MS: Found: *m/z* 363.0623. Calcd for $C_{18}H_{20}I$: [$M^+ - BF_4$], 363.0610. Found: C, 47.51; H, 4.45%. Calcd for $C_{18}H_{20}BF_4I \cdot (1/4)H_2O$: C, 47.56; H, 4.43%.

(*Z*)-1·BF_4: Needles, mp 72.5—73.0 °C (CH_2Cl_2–Et_2O); ^{1}H NMR ($CDCl_3$) δ = 1.77 (quint, J = 7.5 Hz, 2H), 2.18 (s, 3H) 2.48 (br t, J = 7.5 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H), 6.71 (s, 1H), 7.08—7.38 (m, 5H), 7.43 (dd, J = 8.1, 7.4 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.82 (d, J = 8.1 Hz, 2H); No signal for the contaminated isomer was detected. HRFAB MS: Found: *m/z* 363.0641. Calcd for $C_{18}H_{20}I$: [$M^+ - BF_4$], 363.0610. Found: C, 47.58; H, 4.48%. Calcd for $C_{18}H_{20}BF_4I \cdot (1/4)H_2O$: C, 47.56; H, 4.43%.

6-Phenyl-2-hexyne (6): The authentic sample of **6** was prepared by methylation of 5-phenyl-1-pentyne, and also isolated as an oil from the products. ^{1}H NMR ($CDCl_3$) δ = 1.79 (quint, J = 7.5 Hz, 2H), 1.80 (t, J = 2.5 Hz, 3H), 2.08—2.22 (m, 2H), 2.71 (t, J = 7.5 Hz, 2H), 7.13—7.34 (m, 5H). MS: *m/z* (%) 158 (M^+; 52), 143 (72), 129 (66), 115 (18), 104 (100), 91 (66), 77 (20), 65 (21).

6-Phenyl-1,2-hexadiene (7): The authentic sample of **7** was prepared by the reaction of 3-phenylpropylmagnesium bromide with propargyl bromide, and was also isolated as an oil from the products. ^{1}H NMR ($CDCl_3$) δ = 1.66—1.84 (m, 2H), 1.99—2.17 (m, 2H), 2.65 (t, J = 7.7 Hz, 2H), 4.68 (dt, J = 7.0, 3.2 Hz, 2H), 5.13 (quint, J = 7.0 Hz, 1H), 7.12—7.34 (m, 5H). MS: *m/z* (%) 158 (M^+; 10), 143 (41), 129 (21), 115 (10), 104 (100), 91 (49), 77 (10), 65 (13). HRMS: Found: *m/z* 158.1096. Calcd for $C_{12}H_{14}$: M, 158.1096.

6-Phenyl-2,3-hexadiene (8): The authentic sample of **8** was prepared from 6-phenyl-3-hexyn-2-ol according to a procedure developed by Myers:[30] ^{1}H NMR ($CDCl_3$) δ = 1.60 (dd, J = 6.3, 3.8 Hz, 3H), 2.21—2.38 (m, 2H), 2.72 (t, J = 8.1 Hz, 2H), 4.96—5.19 (m, 2H), 7.11—7.34 (m, 5H). MS: *m/z* (%) 158 (M^+; 13), 143 (44), 129 (100), 115 (17), 104 (9), 91 (84), 77 (12), 65 (29). HRMS: Found: *m/z* 158.1090. Calcd for $C_{12}H_{14}$: M, 158.1096.

1-Methyl-3-phenyl-1-cyclopentene (9): ^{1}H NMR ($CDCl_3$) δ = 1.66—1.92 (m, 1H), 1.83 (s, 3H), 2.20—2.61 (m, 3H), 3.79—4.00 (m, 1H), 5.38 (br s, 1H), 7.11—7.45 (m, 5H). MS: *m/z* (%) 158 (M^+; 45), 143 (100), 128 (36), 115 (18), 91 (9), 77 (8). HRMS: Found: *m/z* 158.1080. Calcd for $C_{12}H_{14}$: M, 158.1096.

Product Analysis. Gas-chromatographic determination of solvolysis products was typically carried out as follows. A sample of **1** (5 mg) was dissolved in 5 mL of the solvent and kept at 60 °C for the reaction time. The reaction mixture was diluted with water and the products were extracted 3 times with pentane after addition of tetradecane as an internal standard. The combined organic layer was washed with water, dried over $MgSO_4$, and analyzed by gas chromatography before and after concentration. Relative molar sensitivities of the gas-chromatographic peaks were determined with the available authentic samples and the same sensitivities were used for the isomeric carbonyl and elimination products. The concentrated residues were treated with 1 mol dm^{-3} HCl overnight and the products were again extracted with pentane for analysis. The same sample was also applied to GC MS. The NMR measurements were performed on the products obtained from 10—20 mg of **1**.

The following solvolysis products were assigned by ^{1}H NMR and MS spectra. The alleged isomers of **3(OS)** showed essentially the same MS spectra and their acid hydrolysis resulted in formation of the aldehyde **3**. The geometrical structure of **3(OMe)** was assigned from the NMR spectra, and the peak of shorter GC retention time of the two was the *Z* isomer as was usually the case for other enol ethers. The isomers of the shorter retention time of the other enol products **3(OS)** were also assumed to be in a *Z* form. Gas-chromatographic retention times under the standard analytical conditions are given to show the relative values for different products below.

2-Methyl-5-phenylpentanal (3): GC retention time, 15.8 min. MS: *m/z* (%) 176 (M^+; 33), 143 (8), 129 (8), 117 (25), 104 (52), 91 (100), 77 (10), 65 (16).

6-Phenyl-2-hexanone (4): Isolated as an oil from the products. GC retention time, 16.5 min. ^{1}H NMR ($CDCl_3$) δ = 1.52—1.68 (m, 4H), 2.12 (s, 3H), 2.44 (2H), 2.62 (2H), 7.03—7.39 (m, 5H). IR ($CHCl_3$) 1716 cm^{-1}. MS: *m/z* (%) 176 (M^+; 52), 158 (12), 143 (6), 129 (22), 118 (86), 105 (12), 91 (100), 85 (21), 77 (11), 71 (35), 65 (16), 43 (78). HRMS: Found: *m/z* 176.1197. Calcd for $C_{12}H_{16}O$: M, 176.1201.

6-Phenyl-3-hexanone (5): GC retention time, 16.2 min. MS: *m/z* (%) 176 (M^+; 33), 147 (9), 129 (3.5), 104 (100), 91 (41), 72 (5), 65 (8), 57 (10).

(*E*)- and (*Z*)- 1- Methoxy- 2- methyl- 5- phenyl- 1- pentene (3(OMe)): The product mixture was obtained from the reaction of (*E*)-**1** in methanol containing 0.1 mol dm^{-3} sodium acetate. Gas chromatography shows two peaks corresponding to the isomers in a ratio of 27/73, both peaks giving a similar mass spectrum. GC retention times, 16.53 (*Z*) and 16.95 (*E*) min. MS: *m/z* (%) 190 (M^+; 100), 158 (12), 143 (14), 129 (27), 117 (8), 104 (43), 99 (11), 98 (10), 91 (34), 85 (94), 77 (5), 65 (6), 55 (35). ^{1}H NMR ($CDCl_3$) δ = 1.53 (d, J = 1.5 Hz, 2-Me of *Z*), 1.59 (d, J = 1.5 Hz, 2-Me of *E*), 3.52 (s, OMe of *Z*), 3.54 (s, OMe of *E*), 5.77 (olefinic H). The configuration of the isomer was assigned from the observed NOESY between the 2-methyl and methoxy (the major *E* isomer) or olefinic proton (the minor *Z* isomer).

(*E*)- and (*Z*)-1-Ethoxy-2-methyl-5-phenyl-1-pentene (3(OEt)): The product mixture was obtained in the same way as **3(OMe)**. GC retention times, 17.7 (*Z*) and 18.2 (*E*) min. MS: *m/z* (%) 204 (M^+; 70), 158 (15), 143 (15), 129 (35), 117 (12), 104 (58), 99 (95), 91 (49), 77 (10), 71 (100), 65 (11). ^{1}H NMR ($CDCl_3$) δ = 1.125 (t, J = 7.0 Hz, ethoxy Me of *Z*), 1.142 (t, J = 7.0 Hz, ethoxy Me of *E*), 1.49 (d, J = 1.5 Hz, 2-Me of *Z*), 1.51 (d, J = 1.5 Hz, 2-Me of *E*), 3.65 (q, J = 7.0 Hz, OCH_2 of *Z*), 3.67 (q, J = 7.0 Hz, OCH_2 of *E*), 5.83 (olefinic H).

(*E*)- and (*Z*)-2-Methyl-5-phenyl-1-(2,2,2-trifluoroethoxy)-1-pentene (3(OCH_2CF_3)): GC retention times, 16.26 (*Z*) and 16.70 (*E*) min. MS: *m/z* (%) 258 (M^+; 54), 167 (9), 153 (73), 143 (7), 129 (10), 117 (24), 104 (100), 91 (43), 77 (8), 67 (9), 65 (9), 55 (18).

(*E*)- and (*Z*)-1-(2-Methoxyethoxy)-2-methyl-5-phenyl-1-pentene (3(OME)): GC retention times, 19.35 (*Z*) and 16.70 (*E*) min. MS: *m/z* (%) 234 (M^+; 16), 158 (43), 143 (15), 129 (39), 117 (10), 104 (32), 91 (33), 77 (11), 65 (10), 59 (100).

(*E*)- and (*Z*)- 1- Acetoxy- 2- methyl- 5- phenyl- 1- pentene (3(OAc)): GC retention times, 19.35 (*Z*) and 19.88 (*E*) min. MS: *m/z* (%) 218 (M^+; 18), 176 (63), 158 (13), 143 (9), 129 (8), 118 (12), 117 (11), 104 (100), 91 (39), 78 (8), 77 (8), 71 (35), 65 (9), 43 (47).

Kinetic Measurements. Reactions were followed spectrophotometrically at 240 nm on a Shimadzu UV 2200 spectrophotometer, and rate constants were determined as described previously.[1] Freshly distilled solvents stored in quartz flasks were used.

Theoretical Calclulations. Ab initio molecular orbital calculations were carried out for vinyl cations ($\mathbf{V_1}$ and $\mathbf{V_2}$) and dimethylvinyl cations ($\mathbf{V_3}$ and $\mathbf{V_4}$) at the second-order Møller–Plesset perturbation (MP2) level[31] with the standard 6-31G(d) basis set by using

the Gaussian 94 program.[32] All structures were fully optimized and were identified by means of a full analysis of the vibrational modes.

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