Solvolysis of Vinyl Iodonium Salts. New Insights into Vinyl Cation Intermediates

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ABSTRACT

Solvolysis of some vinyl iodonium salts carrying an excellent leaving group is examined, focusing on whether or not a classical primary vinyl cation can be generated. Formation of the primary cation is avoided, when possible, by participation of the β substituent in the heterolysis to form a vinylenebenzenium ion or a secondary vinyl cation. Definitive evidence against a primary vinyl cation is provided by a chirality probe approach in the solvolysis of 4-methylcyclohexylidenemethyl iodonium salt.

Carbocation chemistry has been explored largely through studies of solvolysis reactions of appropriate precursors. This is also the case for vinyl cation chemistry, and the development was greatly accelerated by the introduction of a "super" leaving group, triflate, in this field in the 1970s.[1,2] These developments, made in the first stage of vinyl cation chemistry, were reviewed in a monograph, *Vinyl Cations*, published in 1979.[3] In the next two decades, modern techniques of chemistry widened the scope of vinyl cation chemistry, which was summarized in a book, *Dicoordinated Carbocations*, published in 1997.[4]

Vinyl iodonium salts have only recently become easily available.[5,6] The enormously enhanced nucleofugality[7] of the iodonio group allowed studies of simpler, more labile vinyl cations. This Account summarizes our recent results on the chemistry of vinylic cations,[8] explored by way of the reactions of vinyl iodonium salts. Our attention was focused on the generation of a primary vinyl cation in solution. Secondary vinyl cations carrying an α substituent were readily generated from the vinyliodonium precursors, but the primary cation seemed too elusive to exist in solution under the usual conditions. Formation of a primary vinyl cation is usually avoided by rearrangement if possible: the β-phenyl group participates in the heterolysis of styryliodonium salt to give 1,1-vinylenebenzenium ion as the intermediate. The β-alkyl group can also participate in heterolysis to give a rearranged secondary vinyl cation from β,β-disubstituted vinyliodonium salt. However, β-monoalkylvinyl derivatives give no ionic intermediate but undergo S_N2 substitution and elimination. Finally, a chirality probe approach using a cyclo-

hexylidenemethyl derivative conclusively disproved formation of a classical primary vinyl cation under solvolytic conditions.

Stability of Vinyl Cations. Parent and primary vinyl cations, $H_2C=C^+H$ and $RHC=C^+H$, are very unstable both thermodynamically and kinetically and could be generated thermally only under forced conditions in solution. Lucchini and Modena[9] suggested from kinetic analysis the formation of a vinyl cation as an intermediate in the acid-catalyzed hydration of ethyne in strong sulfuric acid (>15 mol dm^{-3}). In a superacid, $FHSO_3-SbF_5$, 2-butyne was partly trapped by carbon monoxide as a rearranged primary vinylic derivative.[10] Fornarini and Speranza[11] used the nuclear decay of tritiated ethene to generate the parent vinyl cation in solution. The radioactive tritium undergoes β^- decay to give ^3He, which works as an extreme leaving group. Another class of compounds having a very good leaving group N_2, vinyldiazonium salts, has also been tested. Decomposition of β,β-disubstituted vinyl diazonium salts gives rearranged products via either direct participation of the β group or rearrangement of the incipient primary cation, but no evidence has been presented to differentiate between these possibilities.[12]

Gas-phase spectroscopic studies[13] show that the smallest vinylic cation, $C_2H_3^+$, has the structure of protonated acetylene I_2 but not that of the classical vinyl cation I_1.[14] Recent ab intio MO studies are consistent with the
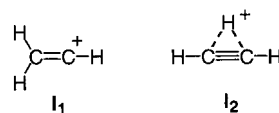
experimental results.[14] Thus, primary vinyl cations generated in solution may also be in a bridged form. α-Phenyl and α-alkyl substitutions markedly stabilize the cation,[15] and such stabilized secondary vinyl cations are common intermediates in vinylic solvolysis and electrophilic addition to alkynes.[4] Substituents at the β position also affect significantly the stability of vinyl cation: gas-phase thermochemical data and theoretical calculations show that a β-alkyl group stabilizes the classical vinyl cation, while a β-phenyl group destabilizes it.[15,16] The 1,2-participation of the β substituent within such a cation stabilizes it and easily leads to rearrangement to a more stable vinyl cation.
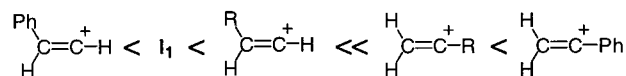

The kinetic stability of a vinyl(phenyl)iodonium salt is largely due to the instability of the corresponding vinyl cation formed on departure of the iodobenzene nucleofuge. Thus, α-phenyl- or α-alkyl-substituted vinyl iodonium ions could not yet be prepared as isolable salts.[6]

1-Cyclohexenyliodonium salt is moderately stable due to the stability of the secondary vinyl cation and the ring strain of the cyclic structure. We first studied solvolysis

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Scheme 1

Scheme 2
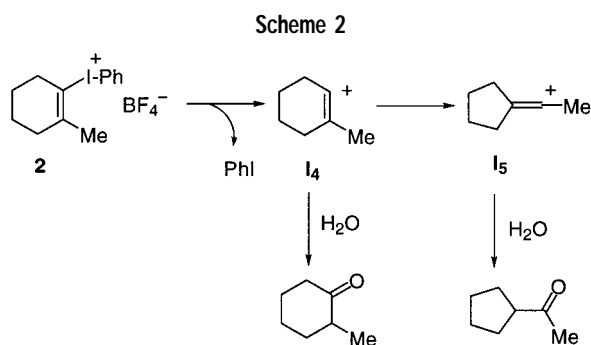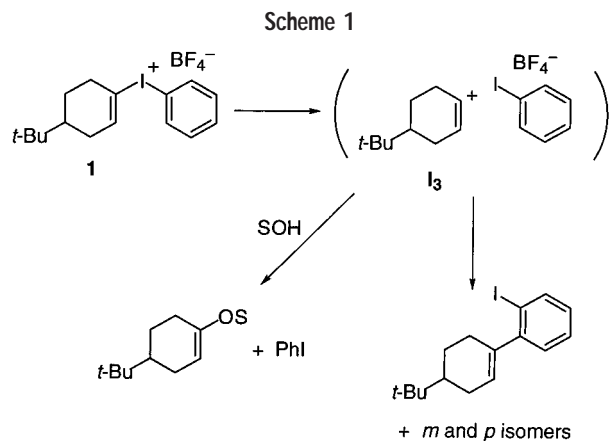
of 4-*tert*-butyl-1-cyclohexenyl(phenyl)iodonium tetrafluoroborate (**1**) in various alcoholic and aqueous solutions.[17] The main products are those expected for a cyclohexenyl cation intermediate **I₃**, the enol ether, and/or cyclohexanone as well as iodobenzene (Scheme 1). In addition to these expected solvolysis products, (4-*tert*-butyl-1-cyclohexenyl)iodobenzenes were obtained in yields of about 13−15% in methanol and aqueous solutions and of 30−40% in 2,2,2-trifluoroethanol (TFE). The *ortho* derivative is the predominant isomer of these products and must be derived from the internal return of the contact ion−molecule pair of cyclohexenyl cation **I₃** and iodobenzene. The solvolysis rates are affected only slightly (the Winstein−Grunwald[18] $m = 0.12$) by the solvents employed, as expected for a reaction of an ionic substrate to give an ionic product in the rate-determining step. From comparison of the rate constant with that for 1-cyclohexenyl triflate,[19] the phenyliodonio group was evaluated to be about 10^6 times as effective a nucleofuge as the triflate leaving group or 10^{12} times more reactive than the iodo group itself; this value shows that the iodonio group is the most efficient leaving group ever determined quantitatively.

The intermediacy of the cyclohexenyl cation was further supported by the observation of a carbocation rearrangement during the solvolysis of 2-methyl-1-cyclohexenyl(phenyl)iodonium tetrafluoroborate (**2**). The strained bent vinyl cation formed, 2-methyl-1-cyclohexenyl cation (**I₄**), rearranges to a more stable linear secondary vinyl cation, **I₅** (Scheme 2). Solvolysis of **2** in 60% aqueous ethanol at −20 °C gave both rearranged and un-rearranged ketones in a ratio of 14:86. This 1,2-rearrangement is characteristic of electron-deficient carbon species. The 2-methyl iodonium salt **2** decomposes very readily, and

the solvolysis rate in 60% aqueous ethanol shows that the 2-methyl group enhances the reactivity of **1** by about 250-fold (if the influence of the 4-alkyl group is small). This is in accord with a prediction that a β-methyl group stabilizes vinyl cation intermediates.[14]

Although no free-radical products were detected under the usual solvolysis conditions, careful examinations of the products in the presence of a good hydrogen donor, 1,4-cyclohexadiene, or in 2-propanol showed formation of about 1% of 4-*tert*-butyl-1-cyclohexene. Apparent heterolysis could take place via the initial homolysis followed by a single electron transfer (SET). However, this possibility is inconsistent with the observed effects of substituents at the leaving iodobenzene.[17] Electron-withdrawing groups, which would destabilize the iodobenzene cation radical, accelerate the solvolysis with $\rho = +1.7$. The major reaction must occur via rate-determining heterolysis. The free radical products may be formed via reverse SET (eq 1), since the ionization potentials of the cyclohexenyl radical and iodobenzene are close to each other.[17]
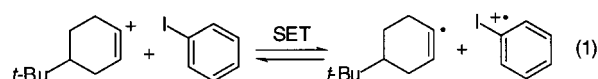

β-Alkylvinyliodonium Salts. As a typical primary vinylic substrate, we have examined the reactivity of (*E*)-1-decenyl(phenyl)iodonium tetrafluoroborate (**3**) under solvolytic conditions.[20] Although solvolysis of **3** was expected to be sluggish due to the high energy of the possible primary vinyl cation intermediate, it proceeds smoothly and as rapidly as that of **1** in alcoholic and aqueous solvents. However, the solvolysis rates are dependent on the nucleophilicity of the solvents but not on their ionizing power.[20] The products include those of both substitution (enol ether or aldehyde) and elimination (1-decyne) at varying ratios, depending on the basicity of the medium (eq 2). The enol products are essentially found with
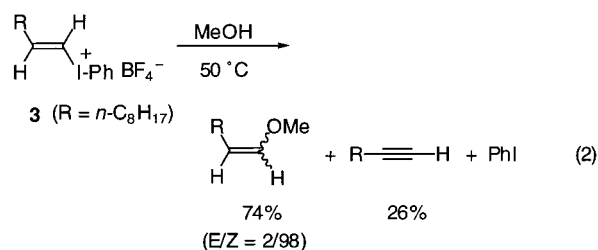

inversion of configuration and are concluded to be derived from S_N2 reactions but not from an intermediate primary vinyl cation. Both the in-plane σ^* route and the out-of-plane π^* route are theoretically feasible for vinylic S_N2 pathways, leading to inversion and retention of configuration, respectively (Scheme 3).[21] The major reaction of **3** follows the former route and the accompanying minor reaction the latter route.[22]

No sign of formation of the primary 1-alkenyl cation was detected. If it were formed, the rearrangement via a facile 1,2-hydride shift[23] should have been observed to give the more stable secondary cation (Scheme 4). Furthermore, the possibility of an alkyl-bridged cation and an

Scheme 3. Vinylic S_N2 Mechanisms
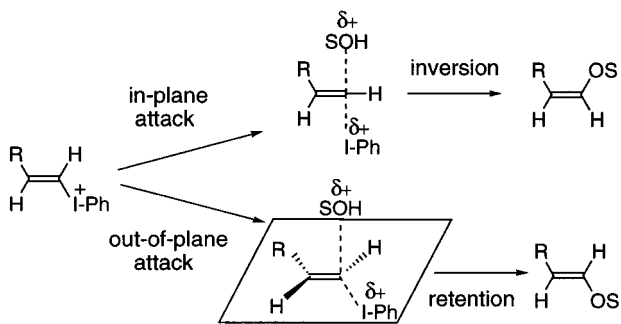
Scheme 4
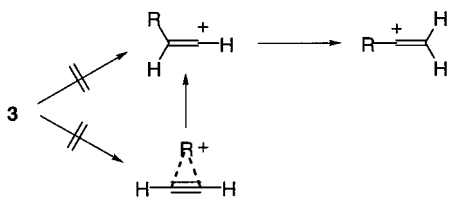
alkyl participation mechanism were ruled out on the basis of the lack of isotope scrambling in the product from the deuterium-labeled substrate (Scheme 4).[24a] The elimination product can be formed via α and β elimination pathways, depending on the reaction conditions. In neutral methanol, the ratio of α to β elimination was evaluated to be about 3:1.[20]

β-**Phenylvinyliodonium salts** would not afford the primary vinyl cation, which is predicted to be unstable.[15,16] Solvolysis of (E)-styryl(phenyl)iodonium tetrafluoroborate (**4**) took place at a reasonable rate at 60 °C.[24] The only product of trifluoroethanolysis was the (E)-styryl ether. The α-deuterated substrate **4-αD** gave a 1:1 mixture of α- and β-deuterated products (eq 3). These results of stereochemistry and H/D scrambling are best explained by a symmetric 1,1-vinylenebenzenium ion intermediate (**I$_6$**).[25] In acetic acid and methanol, (Z)-styryl enol derivatives were also obtained (eq 4). In these products of inversion
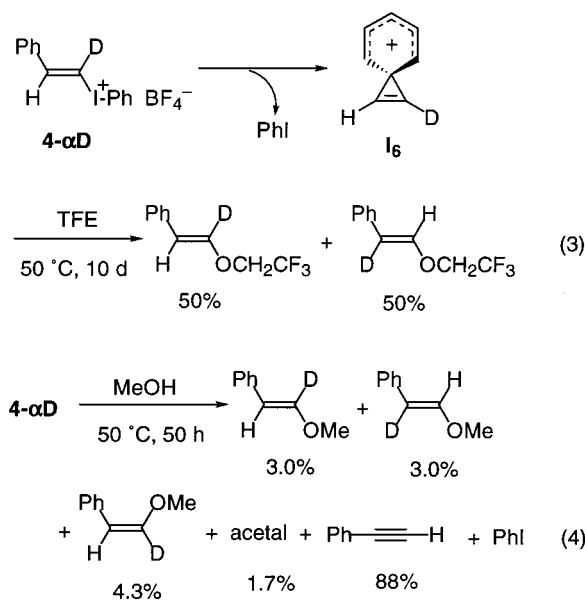
of configuration obtained from **4-αD**, the deuterium remained completely at the original α position, and it was concluded that they are formed via the in-plane S_N2 pathway. The benzenium ion intermediate **I$_6$** was formed by participation of the β-phenyl group, but the primary vinyl cation was not involved in this reaction. The participation should occur from the trans position with respect to the nucleofuge for stereoelectronic reasons, and this can be confirmed by comparison of the E/Z isomers of the substrate.

Solvolysis of (E)- and (Z)-2-phenyl-1-propenyl(phenyl)-iodonium tetrafluoroborate (**5**) was examined,[26] since the Z isomer of **4** is too unstable to be isolated as a salt due to the facile β elimination.[27] As is anticipated, solvolysis of the E isomer **E-5** was much faster than that of **Z-5**, e.g., by 4000 times in TFE at 60 °C. The product distributions from the isomeric substrates are quite different from each other (Table 1). The E substrate **E-5** gives mainly the phenyl-migrated product **7** and two elimination products, **9** and **10**, which are derived from the phenyl-migrated cation **I$_8$** (and/or **I$_7$**). In less nucleophilic solvents, the methyl-migrated product **8** is also yielded. In contrast, **Z-5** gives the un-rearranged **6** and the methyl-migrated products, **8** and **9** (Scheme 5). The phenyl-migrated products have never been obtained from **Z-5**. These results are consistent with participation of the trans β substitutent in departure of the iodobenzene nucleofuge. In a less nucleophilic solvent, also a 1,2-hydride shift across the double bond of the vinyl cation **I$_8$**, formed from **E-5**, also occurs to give the more stable cation **I$_9$**, but the reverse rearrangement does not take place. The phenyl group has a higher migratory aptitude than the methyl group: **Z-5** can afford the un-rearranged product **6**, but **E-5** gives only rearranged products. These results indicate that the primary vinyl cation **I$_{10}$** is never formed during the thermal solvolysis of **E-5** or **Z-5**.

Photosolvolysis of **5** was found to give similar distributions of the products from both **E-5** and **Z-5**, which are quite different from those of the thermal solvolysis.[26] Although products of homolysis and phenyl–iodine bond cleavage were also observed (about 30% in methanol) in photolysis, heterolysis products derived from vinyl–iodine bond cleavage in methanol include **6** (38%), **7** (5%), **8** (15%), and **9** (12%) in similar ratios from both isomeric substrates. These results strongly suggest the photochemical formation of the primary vinyl cation **I$_{10}$**, which gives the same distribution of rearranged products from **E-5** and **Z-5**. The contrasting results of the thermal and photochemical solvolyses of **5** strongly argue for the lack of thermal generation of the primary cation.

β,β-**Dialkylvinyliodonium salts** may have more chances to afford a primary vinyl cation due to the stabilizing effect of the β alkyl substituents. Solvolyis of (E)- and (Z)-2-methyl-5-phenyl-1-pentenyl(phenyl)iodonium tetrafluoroborate (**11**) gave various products of extensive rearrangements (Scheme 6).[28] Although this unsymmetrically substituted substrate gave the products derived from migration of the trans alkyl group more favorably than those of the cis alkyl migration, the latter products were

Table 1. Product Distributions[a] (in Percent Yields) in the Solvolysis of 5 at 60 °C

substrate	solvent	reaction time/h	6 (E/Z)[a]	7 (E/Z)[b]	8 (E/Z)[c]	9	10	PhI
E-5	MeOH	1	0	29 (15/0)	0	28	30	97
Z-5	MeOH	95	5.8 (5.8/0)	0	4.9	81	0	87
E-5	AcOH	1	0	42 (35/7.1)	8.1 (3.1/5.0)	35	7.3	97
Z-5	AcOH	122	12.8 (5.2/7.6)	0	56 (20/36)	30	0	92
E-5	TFE	0.5	0	20	11	17	6.4	85
Z-5	TFE	170	0	0	14	6.7	0	22

[a] For structures of the products, see Scheme 5. [b] Total yields of **6** and **6c** with the isomer yields of **E-6**/**Z-6** in parentheses. [c] Total yields of **7** and **7c** with the isomer yields of **E-7**/**Z-7** in parentheses. [d] Total yields of **8** and **8c** with the isomer yields of **E-8**/**Z-8** in parentheses.

Scheme 5

Scheme 6
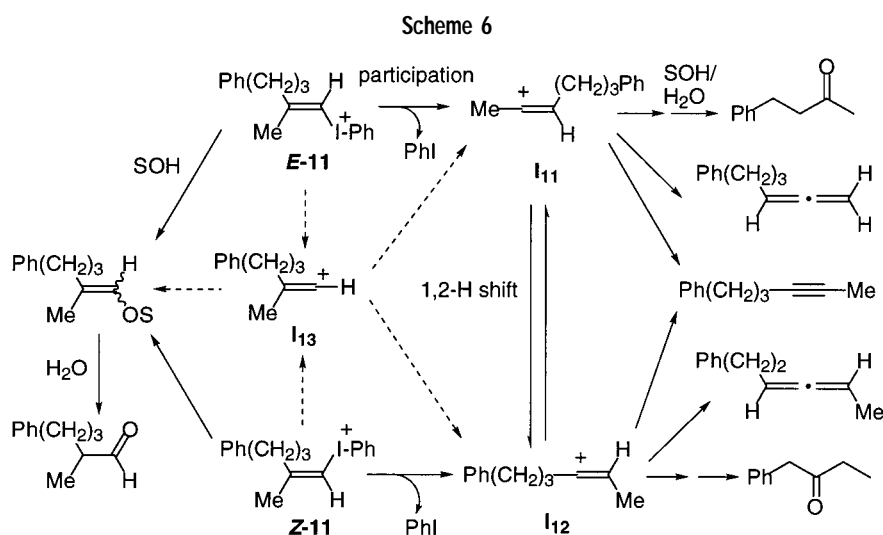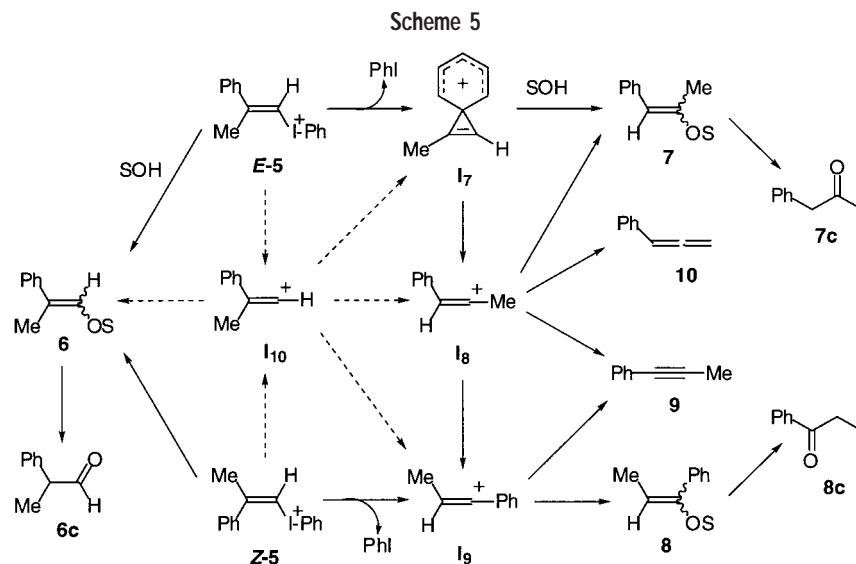
also observed. The amount of the latter was very small in methanol but substantial in less nucleophilic solvents. If the migration of the alkyl group was solely due to the participation in the heterolysis, only the trans group could have migrated, and the migration of the cis β-alkyl group could have been taken as evidence for the formation of the classical primary vinyl cation. However, the cis alkyl-migrated products can also be formed via a very facile interconversion of the intermediate secondary vinyl cations, I_{11} and I_{12}, by a 1,2-hydride shift.

Model calculations for the α,β-dimethylvinyl cation system at the MP2/6-31G* level show that the hydrogen-bridged cation is more stable than the secondary cation and also that the barrier for the degenerate hydride transfer is very low (<1 kcal mol^{-1}, Figure 1).[28b,29] The isomeric allylic cation, which could be generated by a 1,2-hydride shift across the single bond of the secondary vinyl cation, is much more stable than the isomeric vinylic cations. However, the barrier for this 1,2-hydride shift is very high, since allylic conjugation cannot contribute to the stabilization of the transition state.

Un-rearranged enol ether products were also obtained, but without stereoselectivity, which seemed to suggest the formation of the primary cation I_{13}. However, these
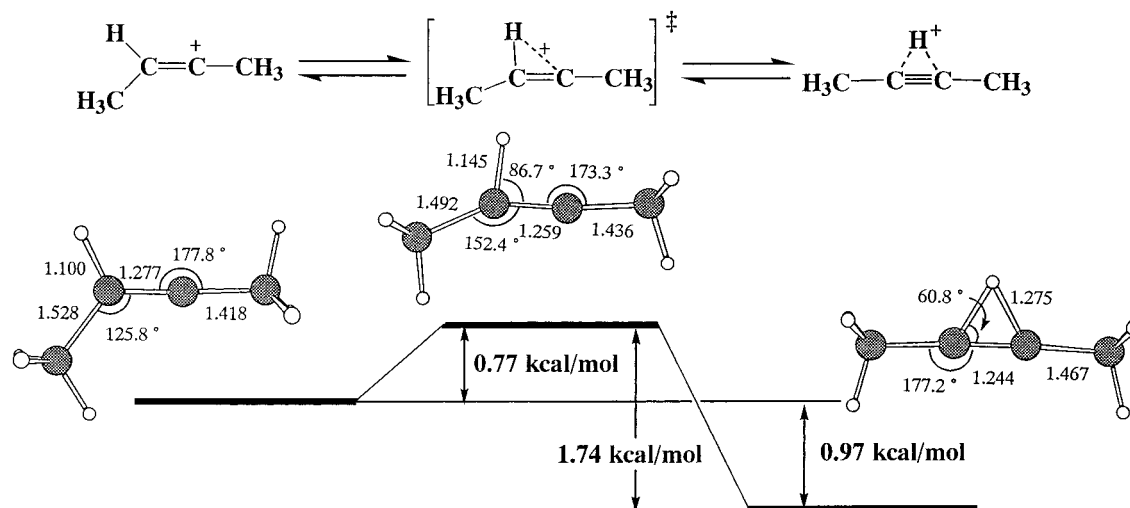
FIGURE 1. Calculated energy barrier for the 1,2-hydride shift in the 1,2-dimethylvinyl cation system at the MP2/6-31G* level. Numbers in the ball-and-stick structures show selected bond lengths (Å) and bond angles (°).

products in methanol and ethanol were concluded to be derived mostly from alkylidenecarbene formed by α elimination (eq 5), while those obtained in more polar solvents are less than a few percent. We now think that the latter obervation is not definitive to support formation of I_{13}, since alternative direct routes to give these products cannot be strictly excluded.
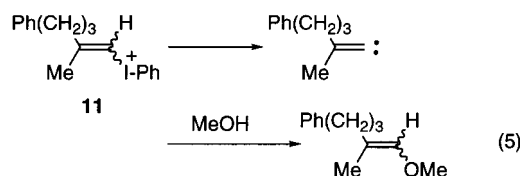
Hinkle and co-workers[30] have recently found that thermal decomposition of (*E*)- and (*Z*)-2-ethyl-1-hexenyl-(aryl)iodonium triflates in chloroform gave both isomers of the un-rearranged triflates as well as two pairs of the rearranged triflates. Formation of both the *E* and *Z* isomers of the un-rearranged products together with kinetic observations was originally considered as evidence for the primary vinyl cation intermediate in this reaction,[30] but details of these results are needed before their conclusion can be judged.[30b]

Chiral 4-Methylcyclohexylidenemethyliodonium Salt. The product analyses of solvolysis of unsymmetrically substituted β,β-dialkylvinyl substates could not provide definitive information about primary vinyl cation intermediates, mainly due to the facile 1,2-hydride shift of the intermediate vinyl cations. It can be predicted that the cyclic vinyl cation should have a high barrier for this rearrangement, since the hydrogen-bridged vinylic cation has a structure similar to that of a protonated acetylene; a small-ring acetylene has a large strain. In fact, ab initio MO calculations (MP2/6-31G*) of the cycloheptenyl cationic system show a barrier as high as 23 kcal mol^{-1} for the 1,2-hydride shift (Figure 2).[31] So, solvolysis of optically active (*R*)-4-methylcyclohexylidenemethyl(phenyl)iodonium tetrafluoroborate (**12**) should give optically active (*R*)-4-methylcycloheptanone if the rearrangement occurs with

β C−C bond participation with complete retention of enantiomeric purity of the substrate (Scheme 7). In contrast, if the primary vinyl cation I_{15} was generated during the reaction, extensive racemization should occur due to the loss of chirality in the intermediate stage: the linear vinyl cation is achiral. A further advantage of this chiral system is that the two β substituent groups are identical, and the complications arising from different migratory aptitudes of the β-alkyl groups of an unsymmetrical substrate such as **11** are avoided.

The product cycloheptanone obtained from solvolysis of (*R*)-**12** of 69% ee (enantiomeric excess) in methanol, aqueous methanol, TFE, and HFIP (1,1,1,3,3,3-hexafluoro-2-propanol) was the *R* isomer of 68−69% ee, the ee being unchanged within experimental errors.[32] So, the primary vinyl cation is not formed under the reaction conditions, even in a highly ionizing non-nucleophilic solvent.

Hanack and co-workers[33] have suggested the formation of a primary vinyl cation during the solvolysis of cyclo-hexylidenemethyl triflate in 50% aqueous methanol at 140 °C, on the basis of their observation that the solvolysis gave the rearranged cycloheptanone as well as cyclohex-anecarboxaldehyde despite its lack of reactivity in less polar pure methanol. Therefore, a similar chirality probe approach was applied to this system:[34] solvolysis of the optically active (*R*)-4-methylcyclohexylidenemethyl triflate (**13**, 73% ee) was carried out under the same conditions as those employed by Hanack and co-workers.[33] The main product was (*R*)-4-methylcycloheptanone with 71% ee (eq 6). That is, the rearranged product retained the optical
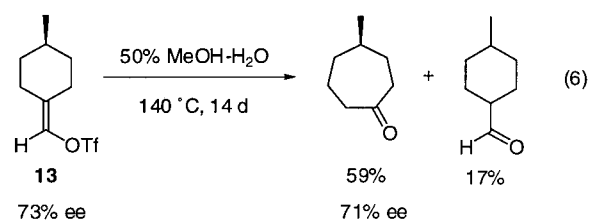
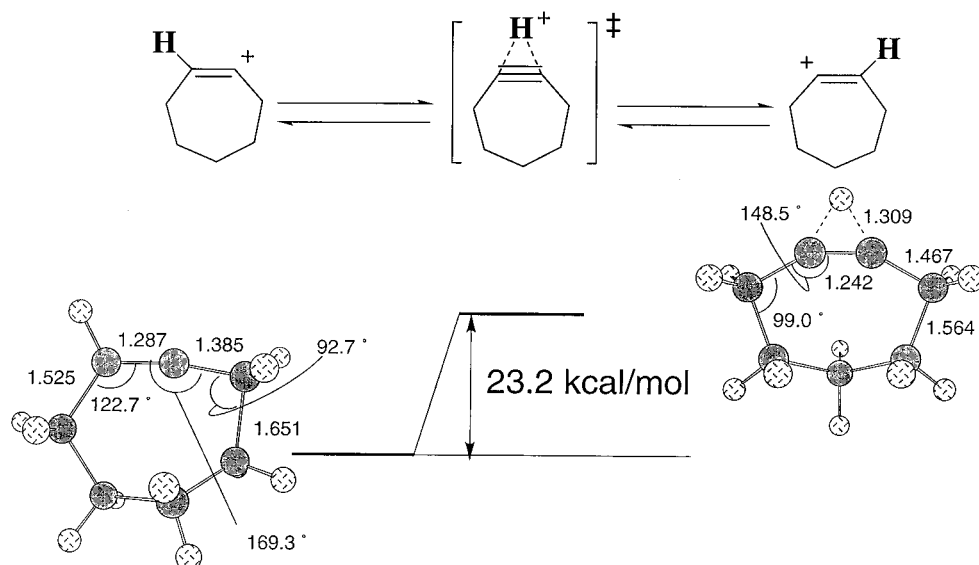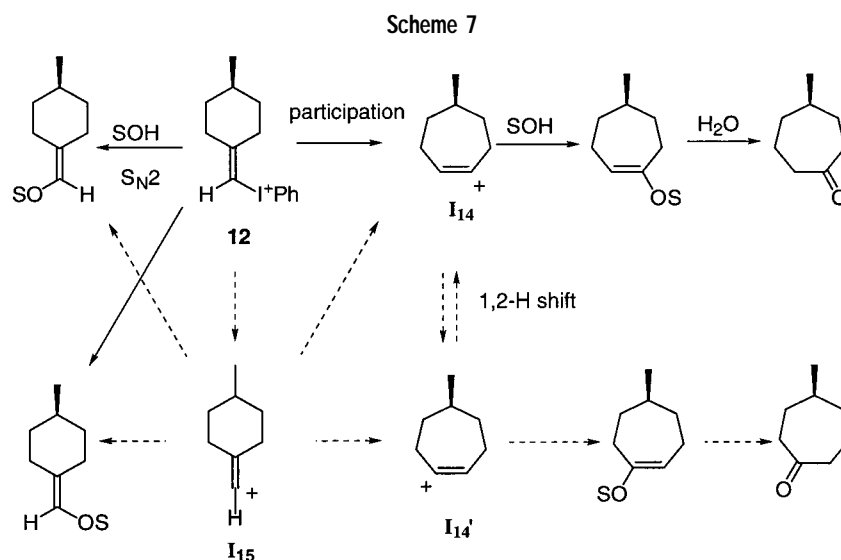purity of the substrate, and this is taken as definitive

FIGURE 2. Calculated energy barrier for the 1,2-hydride shift of 1-cycloheptenyl cation at the MP2/6-31G* level. Numbers in the ball-and-stick structures show selected bond lengths (Å) and bond angles (°).

Scheme 7

evidence against the formation of the primary vinyl cation I_{15}. The rearrangement must occur via β-C$-$C bond participation, as was concluded for the solvolysis of the iodonium salt **12**. The aldehyde product might be formed via a nucleophilic reaction at the sulfonate sulfur to give an enol intermediate.

In conclusion, generation of classical primary vinyl cation has never been demonstrated from vinyliodonium salts, good precursors of cationic intermediates. A chirality probe approach using optically active cyclohexylidenemethyl derivatives definitively ruled out the possibility of formation of the achiral primary vinyl cation. Many of the previous reports suggested formation of a vinyl cation intermediate based on the observation of 1,2-rearrangement, but this does not necessarily mean that the primary vinyl cation was involved. The extensive rearrangements observed can occur in most cases via σ-bond participation in the heterolysis, leading to more stable bridged or secondary vinyl cations.

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