

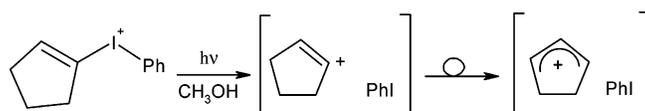
Photochemical Generation of Six- and Five-Membered Cyclic Vinyl Cations

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The photochemical solvolyses of 4-*tert*-butylcyclohex-1-enyl(phenyl)iodonium tetrafluoroborate (**1**) and cyclopent-1-enyl(phenyl)iodonium tetrafluoroborate (**2**) in methanol yield vinylic ethers and vinylic cycloalkenylidobenzenes and cycloalkenylbenzene, which are the trapping products of the geometrically destabilized C₆-ring and C₅-ring vinyl cation with the solvent and with the leaving group iodobenzene. Iodonium salt **2** also yields an allylic ether and allylic cyclopentenylidobenzenes and cyclopentenylbenzene, which are the trapping products of the C₅-ring allylic cation produced from the C₅-ring vinyl cation by a hydride shift in a typical carbocationic rearrangement.

Introduction

The reactivity of vinyl cations, one of the most unstable types of intermediates known to organic chemists,¹ has been the subject of extensive scrutiny in the past decades.^{1,2} This research has culminated in the determination of the crystal structure of a tamed, i.e., highly stabilized, vinyl cation.³ At the other end of the reactivity spectrum, destabilized vinyl cations are found. Destabilization may be caused by electronic effects of electron-withdrawing groups at the α - or β -position,⁴ or by geometric effects if the vinyl cation is part of a cyclic system.

Vinyl cations are sp²-hybridized, and possess a linear orientation at the positive carbon atom. A theoretical comparison of

the prop-1-enyl cation with the cyclohex-1-enyl cation and the cyclopent-1-enyl cation shows that decreases in the angle from 179° via 156° to 141° are accompanied by decreases in the relative stabilities of 17.0 and 27.3 kcal/mol, respectively.⁵ The cyclopent-1-enyl cation may well be the ultimate in geometrical destabilization of simple cyclic vinyl cations: calculations indicate that while this cation exists as a classical vinyl cation, the cyclobut-1-enyl cation is a bridged nonclassical ion.⁶ The solvolysis products of cyclobut-1-enyl nonaflate can indeed be interpreted as stemming from such a nonclassical intermediate.⁷

Several research groups have sought to generate and trap cyclic vinyl cations in thermal solvolysis reactions. But, whereas 1-methylprop-1-enyl triflate readily solvolyzes via an S_N1 mechanism in trifluoroethanol, cyclohex-1-enyl triflate does so very slowly, and cyclopent-1-enyl triflate does not exhibit

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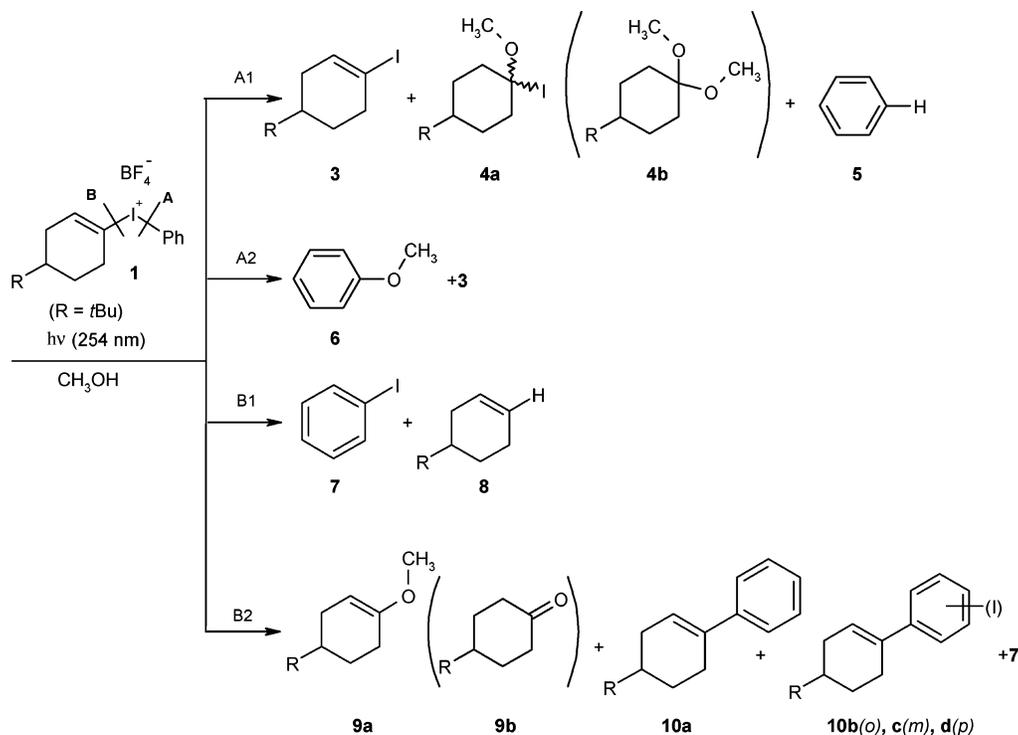
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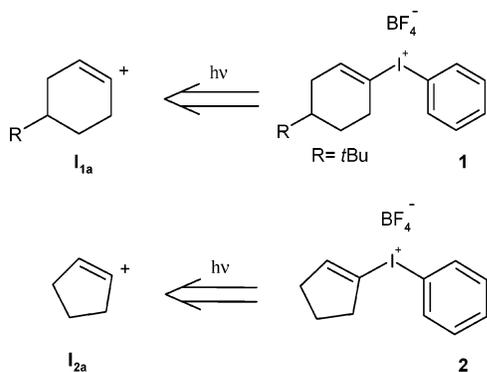
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SCHEME 1. Product Formation upon Photolysis of **1** in Methanol

unimolecular dissociation.⁸ Due to the extremely good leaving group ability of neutral iodobenzene, 4-*tert*-butylcyclohex-1-enyl(phenyl)iodonium tetrafluoroborate solvolyzes much faster than cyclohex-1-enyl triflate, but cyclopent-1-enyl(phenyl)iodonium tetrafluoroborate still displays no reactivity.^{9,10}

Employing photolysis, it has been possible to generate a score of vinyl cations from their vinyl halide precursors.¹¹ Recent photochemical studies have shown that pseudohalides, such as vinyl(phenyl)iodonium salts, are an even better source of vinyl cations.¹² We surmised that the latter method is powerful enough to generate geometrically destabilized vinyl cations.

Here we report the results of the photolysis of 4-*tert*-butylcyclohex-1-enyl(phenyl)iodonium tetrafluoroborate (**1**) and cyclopent-1-enyl(phenyl)iodonium tetrafluoroborate (**2**) in methanol. Our findings unambiguously demonstrate that not only the 4-*tert*-butylcyclohex-1-enyl cation (**I_{1a}**) but also the cyclopent-1-enyl cation (**I_{2a}**) is accessible through photochemistry.



Results and Discussion

Formation of Photoproducts. Irradiation of **1** in methanol, at $\lambda_{\text{exc}} = 254$ nm, yields the product mixture depicted in Scheme 1, in the composition recorded in Table 1. Next to the two

TABLE 1. Product Composition^a after 90 min of Irradiation of **1** at $\lambda_{\text{exc}} = 254$ nm (ca. 10% conversion^b)

3	4a	4b	5	6	7	8	9a	9b	10a	10b-d
20	3.9	11.7 ^c	16.8	5.2	80	1.3	2.9	1.5 ^d	3.0	1.5/0.8/1.2

^a As percentages of converted starting material. ^b 1.7% **3** and 8.2% **7** (GC yields relative to internal standard). ^c Secondary photoproduct (see text). ^d Secondary thermal product (see text).

leaving groups **3** and **7**, two reductive dehalogenation products, **5** and **8**, are produced by replacement of the phenyliodonium group by a hydrogen atom. Along with the nucleophilic vinylic substitution product, vinyl ether **9a**, four different products of Friedel–Crafts aromatic arylation are formed, **10a** and **10b-d**. Anisole (**6**) results from a nucleophilic aromatic substitution reaction. Product **4a** is the formal Markovnikov addition product of methanol to the vinylic double bond of 4-*tert*-butyl-1-iodocyclohexene (**3**). The products are grouped along the proposed mechanisms for their formation (Scheme 2). In

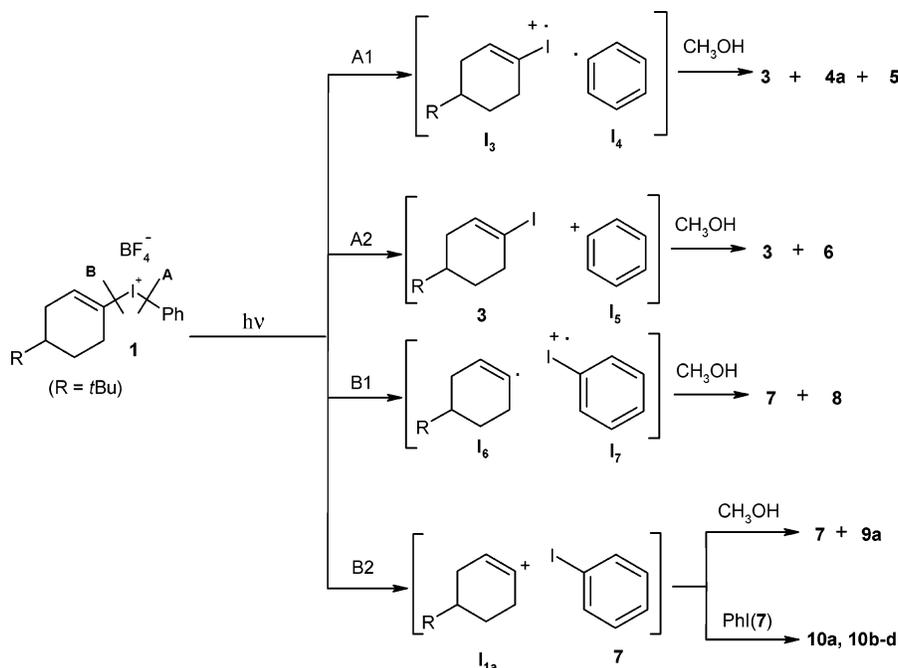
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SCHEME 2. Mechanism of Formation of Photoproducts from **1** in Methanol

molecule **1** two bonds are prone to photolysis, the phenyl–iodonium (A) bond and the vinyl–iodonium (B) bond. Both bonds are subject to homolytic (A1, B1) and heterolytic (A2, B2) cleavage.

Homolytic cleavage of the A bond (Route A1) yields the 4-*tert*-butyl-1-iodocyclohexene radical cation **I**₃ and the phenyl radical **I**₄. The radical cation **I**₃ can acquire an electron from its environment to form 4-*tert*-butyl-1-iodocyclohexene (**3**) or undergo addition of methanol with Markovnikov orientation, followed by abstraction of a hydrogen atom (vide infra, Scheme 5), to form 4-*tert*-butyl-1-iodo-1-methoxycyclohexane (**4a**). Benzene (**5**) is formed after hydrogen atom abstraction from the solvent by **I**₄. Upon heterolytic cleavage of bond A (Route A2), **3** is formed, alongside phenyl cation **I**₅. In methanol this elusive reactive intermediate will be trapped immediately, forming anisole (**6**).

Photohomolysis of bond B (Route B1) will yield the 4-*tert*-butylcyclohex-1-enyl radical **I**₆ and the iodobenzene radical cation **I**₇. Radical **I**₆ will abstract a hydrogen atom from the solvent and form 4-*tert*-butylcyclohex-1-ene (**8**). Radical cation **I**₇ forms iodobenzene (**7**) by acquiring an electron. Upon heterolysis of the B bond (Route B2), leaving group **7** and vinyl cation **I**_{1a} are formed. The vinyl ether 4-*tert*-butyl-1-methoxycyclohexene (**9a**) is the trapping product of **I**_{1a} with methanol. Vinyl ether **9a** is found to hydrolyze under the experimental conditions or upon workup, in part, to 4-*tert*-butylcyclohexanone (**9b**). The 4-*tert*-butylcyclohex-1-enyliodobenzenes **10b** (ortho), **10c** (meta), and **10d** (para) are products of the Friedel–Crafts reaction of cation **I**_{1a} with **7**. Electrophilic aromatic substitution on the ipso position of **7** results in the formation of 4-*tert*-butylcyclohex-1-enylbenzene (**10a**). In principle, product **10a** may also have been formed by attack of the phenyl cation **I**₅ on the leaving group **3** (Route A2) or by recombination of the radical pairs **I**₃ and **I**₄ (Route A1) or **I**₆ and **I**₇ (Route B1). Alternative routes toward the formation of the radical pairs may be photoheterolysis to **3** and **I**₅ (route A2) and to **I**_{1a} and **7** (Route B2) followed by electron transfer within the ion–molecule pairs.¹³ These alternatives would make routes A1 and

B1 superfluous, which is unlikely in view of the observation of radical cation **I**₇ as transient in the picosecond flash photolysis of diphenyliodonium salts.¹⁴

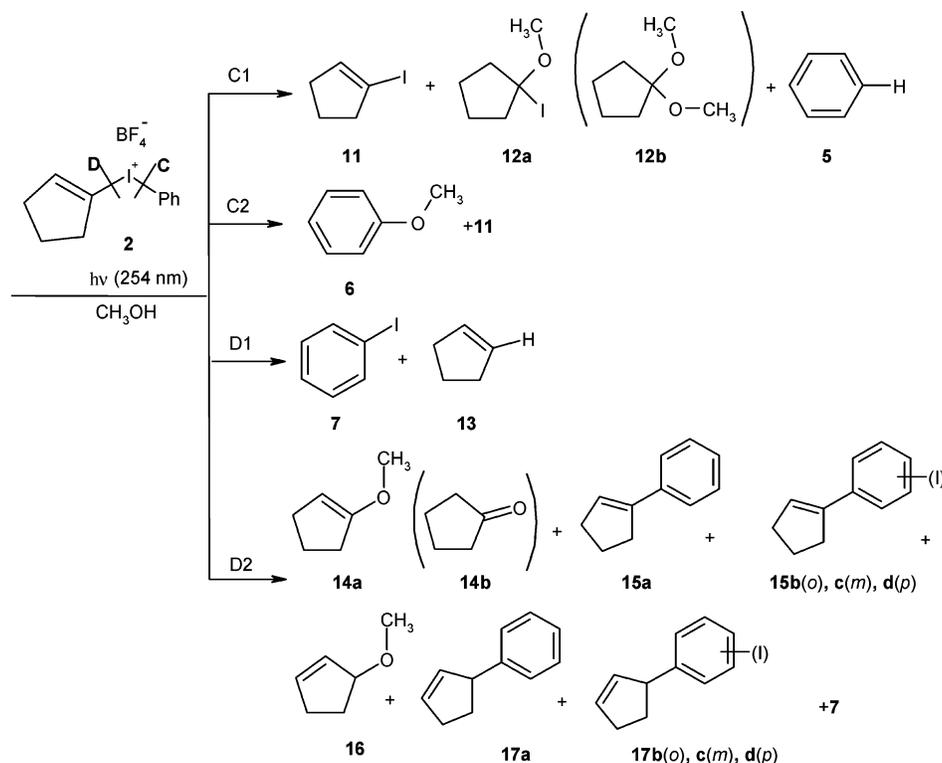
The results obtained in the photolysis of **1** encouraged us to photolyze the cyclopent-1-enyl compound **2** in methanol at $\lambda_{\text{exc}} = 254 \text{ nm}$ (Scheme 3, Table 2). Most rewarding is the formation of two nucleophilic substitution products, the vinylic ether 1-methoxycyclopent-1-ene (**14a**) (and its hydrolysis product cyclopentanone (**14b**)), and the allylic ether 3-methoxycyclopent-1-ene (**16**). Also four Friedel–Crafts vinylation products, cyclopent-1-enylbenzene **15a** and cyclopent-1-enyliodobenzenes **15b–d**, and four allylation products, cyclopent-2-enylbenzene **17a** and cyclopent-2-enyliodobenzenes **17b–d**, are produced.

Again, both carbon–iodine bonds (C and D) are photolabile and proposed to be subject to homolytic and heterolytic cleavage. Homolysis of the C bond (Route C1) will form the radical cation of 1-iodocyclopentene and the phenyl radical **I**₄. The products of these intermediates are 1-iodocyclopentene (**11**), 1-iodo-1-methoxycyclopentane (**12a**) (vide infra), and **5**. The heterolytic cleavage of the C bond (Route C2) yields the leaving group **11** and the phenyl cation **I**₅, which is trapped by methanol to yield anisole (**6**). Homolytic cleavage of the D bond (Route D1) yields the radical cation of iodobenzene **I**₇ and the cyclopent-1-enyl radical. These intermediates will produce **7**, after electron transfer, and cyclopentene (**13**), after hydrogen atom abstraction, respectively.

Crucial in this report is the photoheterolysis of bond D (Route D2) as depicted in Scheme 4. This cleavage generates **7** and vinyl cation **I**_{2a}. In the product mixture the trapping product of **I**_{2a} and methanol, the vinyl ether **14a** (+**14b**), is accompanied by the allylic ether **16**, which is the trapping product of the

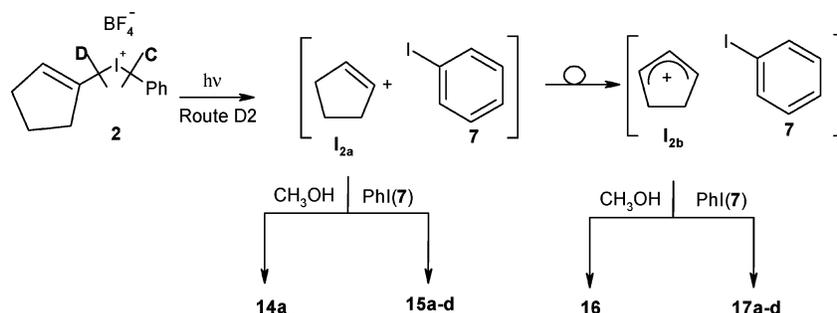
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SCHEME 3. Product Formation upon Photolysis of **2** in MethanolTABLE 2. Product Composition^a after 90 min of Irradiation of **2** at $\lambda_{\text{exc}} = 254 \text{ nm}$ (ca. 15% conversion^b)

11	12a	12b	5	6	7	13	14a	14b	15a	15b–d	16	17a	17b–d
38	6.7	11 ^c	61 ^d	19	62	8.9	<i>e</i>	0.8 ^f	3.8	8.8/4.7 ^g /2.3	2.5	5.6	<i>e</i>

^a As percentages of converted starting material. ^b 5.8% **11** and 9.3% **7** (GC yields relative to internal standard). ^c Secondary photoproduct (see text). ^d In part secondary photoproduct of **7**. ^e These products could only be identified on GC-MS. ^f Secondary thermal product (see text). ^g The GC peak of **15c** somewhat overlaps with that of the internal standard)

SCHEME 4. Mechanism of Formation of Photoproducts **14–17** from **2** in Methanol

allylic cation **I_{2b}**. Further, next to the products of the electrophilic aromatic substitution reaction of **7** and **I_{2a}** (**15a** (ipso), **15b** (ortho), **15c** (meta), **15d** (para)), also products reasoned to stem from the trapping of **I_{2b}** by **7**, the cyclopent-2-enylidobenzenes **17a, b–d**, are observed.

All reactions were checked to be photochemical of origin. A “dark” thermal reaction of **1** in methanol, at 25 °C for 3 h, yielded no appreciable amount of product. Thermal solvolysis of **2** in methanol shielded from light at 25 °C yielded no products at all after 3 h. Study of the composition of the photoproduct mixtures of **1** and **2** as a function of the time of irradiation shows that 4-*tert*-butyl-1,1-dimethoxycyclohexane (**4b**) and 1,1-dimethoxycyclopentane (**12b**) (presented in parentheses in Schemes 1 and 3) are secondary products, apparently produced

from their 1-iodo-1-methoxycycloalkane precursors **4a** (see Scheme 5) and **12a**, respectively.

Quantum Chemical Studies. To assess the nature and plausibility of the possible cationic intermediates in the photolysis of **1** and **2**, CBS-Q calculations¹⁵ were carried out on the structures and stabilities of the parent six- and five-membered cyclic vinyl and allyl cations **I_{1a}** and **I_{1b}** (R = H) and **I_{2a}** and **I_{2b}** (see Table 3, Figure 1). Such calculations have been shown to reproduce the relative stabilities of cations within experimental errors for a wide range of cationic species.¹⁶ Also, some related species (cf. Scheme 6) were studied. The cyclohex-1-enyl cation **I_{1a}** is found to be less stable than the cyclohex-

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SCHEME 5. Mechanism of Formation of Photoproducts 4a and 4b

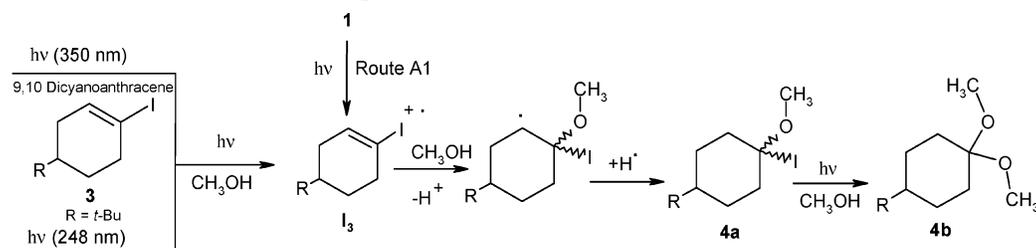


TABLE 3. Relative Stabilities of the Cyclic Vinyl Cations and Isomers

I_{1a}^+ (R=H)		I_{1b}^+ (R=H)	
27.8 kcal/mol		0 kcal/mol	
I_{2a}^+		I_{2b}^+	
47.8 kcal/mol		0 kcal/mol	
I_{2c}^+			I_{2e}^+
		23.3 kcal/mol	
I_{2e}^+			I_{2r}^+
0 kcal/mol			14.0 kcal/mol

2-enyl cation I_{1b} by 27.8 kcal/mol. In the cyclopentenyl cations the vinyl cation is 47.8 kcal/mol less stable than the allyl cation.

Vinyl cation I_{2a} is a planar species (C_2 symmetry) that corresponds to a real minimum at the potential energy surface at both the B3LYP/6-311G(2d,2p) and MP2/6-311G(2d,2p) levels of theory. While the positive charge, obtained with NBO analysis, is highest at the formally positively charged vinylic C^+ atom (+0.431), the remainder is delocalized significantly over the rest of the molecule. Of specific interest is that the charges of the CH and CH_2 moieties next to this vinylic C^+ atom are less positive (+0.093 in both cases) than at the remaining CH_2 moieties (+0.209 for the CH_2 next to the first CH_2 and +0.175 for the CH_2 next to the CH moiety). The strain in this molecule is significant. This is shown in two ways: first, the $CH-C^+-CH_2$ angle is 149.9° , which is significantly different from the 180° observed for an unstrained vinyl cation; second, the lengths of specifically the CH_2-CH_2 bonds are larger than in unstrained species: 1.611 Å for the $C-C$ bond farthest away from the C^+ atom, and 1.642 Å for the other CH_2-CH_2 bond with a concomitantly low bond order of 0.822.

For the six-membered 1-cyclohexenyl cation (I_{1a} , R = H), similar observations are made. In this species the $CH-C^+-CH_2$ angle is 156.3° , which indicates a more relaxed structure. The vinylic C^+ atom bears a charge of +0.450 while the remainder of the charge is delocalized over the rest of the ring.

The C_6 -Ring Vinyl Cation. The parent cyclohex-1-enyl cation (I_{1a} , R = H) has already been postulated as an intermediate in thermal solvolyses several times. The major indication for its generation is the formation of a vinyl ether accompanied by or completely converted to its hydrolysis product. Whereas cyclohex-1-enyl tosylate and brosylate are

unreactive in 50% methanol at $130^\circ C$ for 17 days,¹⁷ the unimolecular solvolysis of cyclohex-1-enyl triflate in deuterated acetic acid ($130^\circ C$, for 4 weeks) does yield a mixture of cyclohex-1-enyl acetate and its hydrolysis product cyclohexanone.⁸ In ethanol/water, cyclohexanone is the sole product. This is also the case for the corresponding cyclohex-1-enyl nonaflate, which solvolyzes a factor of 2 faster than the triflate (ethanol/water $150^\circ C$, 2 days).¹⁸ In the thermal solvolysis of **1** in methanol ($25^\circ C$, for 9 days), which occurs about 10^6 times faster than that of the triflate/nonaflate, the formation of **10b-d**, next to **9a** and **9b**, provides additional evidence for the generation of the cyclic vinyl cation, these compounds being the trapping products of I_{1a} by iodobenzene **7**.⁹ The photosolvolysis of **1** in methanol takes only hours at $20^\circ C$, using a standard light source. The difference in reaction conditions needed to prepare the C_6 -ring vinyl cation attests to the tremendous effect of photoexcitation upon leaving group abilities.^{11,12}

The cyclohex-1-enyl cation (I_{1a} , R = H) has also been proposed as the product-forming intermediate in the photolysis of 1-iodocyclohexene (**3**, R = H) in methanol.¹⁹ In this photoreaction, at almost complete conversion, the only product, next to cyclohexene (**8**, R = H), is 1,1-dimethoxycyclohexane (**4b**, R = H), which according to the authors was apparently a secondary product arising from acid-catalyzed addition of methanol to the nucleophilic trapping product 1-methoxycyclohexene (**9a**, R = H).¹⁹ In the photolysis of **1**, reported here, 4-*tert*-butyl-1,1-dimethoxycyclohexane (**4b**) is proposed to be a secondary photoproduct, formed at the expense of 1-iodo-1-methoxycyclohexane **4a**. The contradictory results prompted us to study the origin of **4a** and **4b** in more detail.

Irradiation of a solution of vinyl iodide **3** (R = *tert*-butyl) in methanol in the presence of 9,10-dicyanoanthracene at $\lambda_{exc} = 350$ nm (well outside the UV absorption band of **3**) produced **4a** (Scheme 5). Under these electron-transfer photosensitization conditions alkenes are known to give radical cations. Here the radical cation I_3 is generated, which adds to methanol and yields **4a** after a hydrogen atom transfer.²⁰ Compound **3** even yields **4a**, next to **8**, in the absence of the sensitizer and upon irradiation in methanol at $\lambda_{exc} = 248$ nm (Scheme 5). This means that radical cation I_3 is also produced by a direct photoinduced ejection of an electron from the substrate into the solvent.²¹ No vinyl ether **9a** (or its hydrolysis product **9b**) is formed. Only after prolonged

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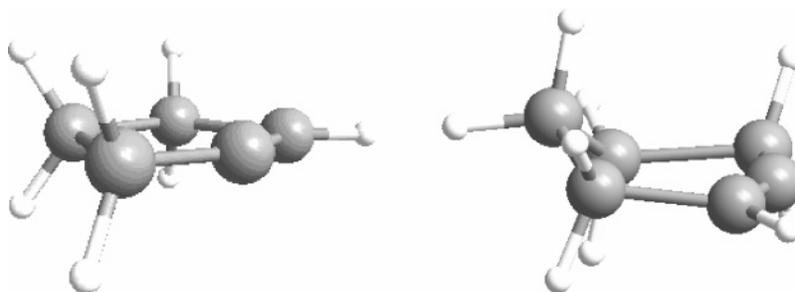


FIGURE 1. The B3LYP/6-311G(2d,2p)-calculated structures of the vinyl cations I_{2a} and I_{1a} ($R = H$).

irradiation of **3** are the reaction products cyclohexene **8** and 1,1-dimethoxycyclohexane **4b**, indicating that **4b** is a secondary photoproduct of **4a**. 1-Iodo-1-methoxycycloalkanes are known to be photolabile and give the corresponding 1,1-dimethoxyalkanes as photoproduct.²²

In the photolysis of **1**, the formation of enol ether **9a** as primary photoproduct signals the generation of I_{1a} and its subsequent trapping by methanol. Vinyl cation I_{1a} also reacts with iodobenzene (**7**) yielding **10b–d**. These products are found in an o:m:p ratio of 43:22:34. This ratio is different from the ratio found in the thermal solvolysis of **1** (o:m:p = 87:6:9).⁹ Another difference between the thermal and photochemical reaction of **1** is that only the light-induced reaction yields ipso alkylation product **10a**, in a 1:1.2 ratio relative to the Friedel–Crafts products **10b–d**. Such ipso substitution is frequently observed in iodonium salt photolysis.^{12b,23} Also, the relative importance of the two product-forming pathways from I_{1a} , reaction with the solvent and with the leaving group, is significantly different in the thermal and photochemical methanolysis of **1**. Upon thermolysis the ratio of products **9** and **10b–d** is 6:1,⁹ and upon photolysis the ratio of products **9** and **10** is 1:1.5. Clearly, the photogenerated C₆-ring vinyl cation differs from the thermally generated species in its regioselectivity toward iodobenzene and in its chemoselectivity toward the nucleophiles methanol and iodobenzene. The differences may be due to the formation of an aliphatic vinyl cation of high energy (a “hot” vinyl cation) in the photochemical reaction.^{19,24} We speculate that the species generated in the photolysis is the triplet state of I_{1a} , produced upon heterolytic cleavage of the C–I⁺ bond of the triplet excited state of **1**. This triplet cation reacts (in part) faster with nucleophiles than it deactivates, by spin-inversion, to its singlet ground state.²⁵ As in the case of triplet aryl cations,²⁶ triplet vinyl cations are expected to prefer reaction with π -nucleophiles, such as iodobenzene, over reaction with n -nucleophiles, such as methanol.

In theory, as observed in the photochemistry of **2**, the C₆-ring vinylic cation I_{1a} can convert, by a hydride shift, to the allylic cation I_{1b} . However, neither in the thermal solvolysis of cyclohex-1-enyl triflate, cyclohex-1-enyl nonaflate, and iodonium salts nor upon irradiation of **1** are allylic products observed. The CBS-Q calculated stabilities (see Table 3) of I_{1a} and I_{1b} show that the production of allyl cation I_{1b} from I_{1a} is exothermic by 27.8 kcal/mol, but considerably less so than for the five-membered ring where 47.8 kcal/mol is gained in converting the vinyl cation I_{2a} into the allyl cation I_{2b} . A 1,2-hydride shift does occur in a benzannellated form of I_{1a} , the 1,2-dihydronaphthyl vinyl cation,²⁷ where the driving force is 57 kcal/mol.²⁸ Apparently, for I_{1a} the driving force for a hydride shift is not large enough for that shift to compete with reaction of the vinyl cation with the solvent or the leaving group.

The C₅-Ring Vinyl Cation. In the irradiation of **2** in methanol the heterolytic cleavage of bond D yields cation I_{2a} . This conclusion is based on the formation of vinyl ether **14a**, next to its hydrolysis product **14b**, as well as on the formation of **15a**, and of three isomers of cyclopent-1-enyliodobenzene (**15b–d**), the trapping products of I_{2a} with iodobenzene. The conclusion is strongly supported by the formation of allylic ether **16** and the allylic, aromatic trapping products of I_{2b} (**17a,b–d**). These products imply that upon generation of I_{2a} , it is converted through a hydride shift to the allylic cation I_{2b} , which is trapped by methanol or iodobenzene. Hydride shifts are typical of carbocation behavior and therefore products from I_{2b} provide direct evidence that a cation, i.e., I_{2a} , is generated photochemically in methanol. The driving force for the 5-ring vinyl cation I_{2a} to undergo a hydride shift is much larger (see Table 3) than that for the 6-ring vinyl cation I_{1a} , allowing the conversion of I_{2a} to allyl cation I_{2b} to compete with the trapping by the solvent or the leaving group. The ratio between vinyl and allyl cation-derived products is about 2.5:1.

The trapping of the C₅-ring vinyl cation I_{2a} by the leaving group **7** yields **15b–d** in an o:m:p ratio of about 56:30:14. The C₅-ring vinyl cation reacts less abundantly at the ipso position than at the combined o:m:p positions compared to the C₆ ring ion: a ratio of 1:4 between these two pathways is found. For the C₅-ring vinyl cation, the ratio between solvent trapped products versus leaving group trapped products is 1:25, com-

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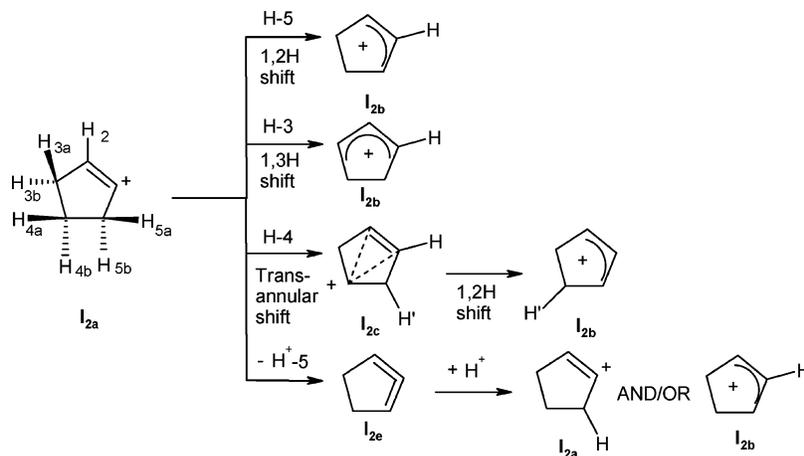
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SCHEME 6. Possible Mechanisms of Conversion of I_{2a} into I_{2b} 

pared to the 1:1.5 ratio for the C_6 -ring vinyl cation. This difference in preference for the reaction with iodobenzene (**7**) over methanol probably reflects the higher reactivity of the C_5 -ring species. As discussed for the C_6 -ring vinyl cation, this species may be (in part) the triplet state of I_{2a} .²⁵

The formation of C_5 -ring vinyl cation I_{2a} -derived products also occurs in the irradiation of a derivative of **2** with a 4-tolyl instead of a phenyl ligand, cyclopent-1-enyl(4-methylphenyl)-iodonium tetrafluoroborate, in methanol ($\lambda_{exc} = 254$ nm). The photolysis of the tolyl salt proceeds 1.6 times more efficiently than the photoreaction of the phenyl salt. The product formation resembles that of the photolysis of **2**. The formation of vinyl ether **14a** through the presence of **14b** is confirmed in this experiment and also allyl ether **16** was found. The ratio between vinyl- and allyl cation-derived products is about 1.6:1. Vinyl cation I_{2a} reacts with the leaving group 4-iodotoluene to yield the ipso product 4-cyclopent-1-enyltoluene, and the Friedel–Crafts products 3-(cyclopent-1-enyl)-4-iodotoluene and 2-(cyclopent-1-enyl)-4-iodotoluene. The latter two are produced in a 3:1 ratio, which resembles the ratio obtained in the thermal solvolysis of the 4-tolyl derivative of **1** (76:24).⁹ The Friedel–Crafts products are formed in a 3.3-fold excess over the ipso products. The C_5 -ring vinyl cation again shows a large preference for reaction with 4-iodotoluene over methanol. An exact ratio could not be determined because the GC peak of **14b** is obscured by that of toluene.

For the mechanism of conversion of the C_5 -ring vinylic cation I_{2a} into the allylic cation I_{2b} , four possibilities come to mind (Scheme 6). First, a 1,2-H shift across the single bond toward the carbon–carbon double bond. As already discussed, the resulting allylic cation is far more stable than the vinylic cation (data in Table 3), which thermodynamically allows this reaction. However, the activation energy for such a 1,2-H shift has both experimentally and computationally been shown to be considerable (18–20 kcal/mol) in linear systems.^{29,30,31} Allylic stabilization as in the product cannot be achieved in the bent transition state because of the lack of overlap between the newly created empty orbital and the double bond. In the rigid cyclopentenyl

ring, the difficulty in creating the initial overlap may significantly add to an already high activation energy.

Second, a 1,3-H shift across the double bond, also yielding allylic cation I_{2b} . The activation energy for such a 1,3-H shift is calculated to be 11.4 kcal/mol in the linear prop-1-enyl cation, considerably less than the activation energy for the corresponding 1,2-H shift.³¹ This kinetic preference for a 1,3- over a 1,2-H shift for linear vinyl cations is probably even more pronounced for the ring vinyl cation, because of the higher conformational freedom of C-3 compared to C-5.³²

Third, a trans-annular hydride shift³³ from C-4 to C-1 producing the homoallylic cation I_{2c} , which in turn may undergo a 1,2 H shift to yield allylic cation I_{2b} . Several reports on the generation and reactivity of the cyclopent-3-enyl cation I_{2c} have appeared.³⁴ When generated in a nonnucleophilic environment, the homoallylic cation I_{2c} yields allylic products, in a more nucleophilic reaction medium a mixture of homoallylic and allylic products is formed. Thus I_{2c} is easily converted, through a 1,2 H shift, in an allyl cation in competition with trapping by the solvent. In our experimental setup, however, employing the nucleophilic solvent methanol, the trapping product of cation I_{2c} should have been present, if this mechanism is operative. This is not the case, no 4-methoxycyclopentene is produced. Therefore this sequence of reaction steps is unlikely.

Fourth, proton loss from C-5 of I_{2a} forming the highly strained cyclic allene I_{2e} ,^{35,36} which upon reprotonation may yield the allyl cation I_{2b} , or the vinyl cation I_{2a} , depending on the site of protonation. Proton loss from C-2 of I_{2a} , yielding cyclopentyne, is less likely because CBS-Q calculations show (data Table 3) that cyclopentyne (I_{2f}) is 14 kcal/mol less stable than cyclopenta-1,2-diene (I_{2e}). It is doubtful whether the deprotonation of I_{2a} to I_{2e} is thermodynamically feasible, the more so because only

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methanol or iodobenzene is available as base in the solvent cage.^{12b} However, if a vinyl cation of higher energy is involved or if it is the triplet state of **I_{2a}** that is involved, the propensity for proton loss may be enhanced.^{19,37} Anyhow, the preferred reaction for structurally unbiased linear allenes is reprotonation at the terminal allene carbons atoms,³⁸ here yielding **I_{2a}** and not **I_{2b}**. This reaction sequence is not productive toward allylic ether formation and is therefore disregarded.

Summarizing, we propose that **I_{2b}** is produced from **I_{2a}** by a 1,3-H shift. As far as we know, this mode of rearrangement is unprecedented in vinyl cation chemistry.³⁹

The data presented here constitute the first unambiguous case for the direct formation of C₅-ring vinyl cation **I_{2a}**.⁴⁰ Attempts to thermally generate vinyl cation **I_{2a}** from cyclopent-1-enyl triflate or nonaflate did yield cyclopentanone, but in both cases the reaction occurred through S–O bond fission rather than vinyl–O bond fission.^{8b,41} **I_{2a}** has been proposed as an intermediate in the photolysis of 1-iodocyclopentene in methanol at –25 °C, which yielded 1,1-dimethoxycyclopentane (**12b**) next to cyclopentene (**13**).¹⁹ It may, however, well be that **12b**, in analogy with **4b**, is a radical cation-derived rather than a vinyl cation-derived product. The nonformation of vinyl ether **14a** (and hence no cyclopentanone **14b**), or allyl ether **16**, is in line with this idea.

Relative Photoefficiencies. Comparison of the rates of formation of the leaving groups from **1** and **2** (at low conversion) showed that photolysis of **2** is 1.4 times more efficient than that of **1**. Thus **2** is more photolabile than **1**, while **2** is far less thermolabile than **1**. Presumably, the cyclopentenyl ligand contributes less electron density to the carbon–iodine bond in the reactive excited state than the cyclohexenyl moiety, which lowers the photostability.

In the irradiation of **1**, almost 5 times more iodobenzene (**7**) is cleaved off (B-bond fission) than vinyl iodide **3** (A-bond fission); in the photoreaction of **2** only 1.8 times more **7** than vinyl iodide **11** is produced. These efficiencies reflect the instability of the intermediates that are generated in these light-induced reactions, the phenyl cation, the cyclohex-1-enyl cation, and the cyclopent-1-enyl cation. This is in agreement with a report about thienyl(aryl)iodonium salts that the cationic iodine center allows π electron communication between the two ligands via its d-orbitals.⁴² There is a substantial effect of one ligand at the iodonium center on the bond to the other ligand.

In summary, we have demonstrated that not only the C₆-ring vinyl cation, but also the C₅-ring vinyl cation can be generated photochemically, under mild reaction conditions. Compelling evidence for the formation of the C₅-ring vinyl cation **I_{2a}** is the production, next to the direct trapping products **14a** (and **14b**), of the allylic ether **16**, which is the trapping product of the hydride shifted intermediate **I_{2b}**. The formation of **17a** next to

15a, and their iodine substituted counterparts, further substantiates this conclusion.

Experimental Section

Materials. The iodonium salts 4-*tert*-butylcyclohex-1-enyl-(phenyl)iodonium tetrafluoroborate (**1**), cyclopent-1-enyl(phenyl)iodonium tetrafluoroborate (**2**), and cyclopent-1-enyl(4-methylphenyl)iodonium tetrafluoroborate were synthesized as described in refs 9 and 43. Methanol (HPLC grade) was checked to be UV transparent and purged with Argon prior to use. *n*-Hexane and *n*-hexadecane were used as received as were all available reference compounds (**5**, **6**, **7**, **9b**, **13**, **14b**, and **16**). Nonavailable reference compounds were synthesized following literature procedures with use of commercially available starting materials.

Photochemistry. All reaction mixtures were purged with Argon prior to irradiation. The solutions are irradiated in a quartz reaction tube that was sealed with a rubber septum (to allow sampling) and placed in a merry-go-round apparatus. A Hanau TNN-15/32 low-pressure mercury lamp placed in a water-cooled quartz tube is used to supply light with a main emission at $\lambda = 254$ nm.

In a typical experiment 10 mL of a 5 mM solution of the iodonium salt, containing 10 μ L *n*-hexadecane as internal standard, was irradiated. At appropriate time intervals 50 μ L samples were taken, using a syringe piercing through the septum. In kinetic runs, samples are taken every 5 min. The samples were injected in a test tube containing \sim 1 mL demineralized water and 100 μ L of *n*-hexane or diethyl ether. Extraction was ensured by shaking the stoppered test tube. After settling of the layers, the organic layer was removed with a rinsed syringe and analyzed on GC and GC-MS. At the end of the irradiation, the remainder of the reaction mixture was reduced in volume by purging with nitrogen and, if necessary, redissolved in 1 mL of diethyl ether. This sample is also analyzed on GC and GC-MS. Experiments were carried out in triplicate.

The $\lambda_{\text{exc}} = 248$ nm irradiations of **3** (R = *tert*-butyl) are carried out in a different setup. A high-pressure Hg/Xe arc, from which the IR output was removed by a water filter, was used as the irradiation source. The light beam was guided through a 77250 model Oriel monochromator to select the desired wavelength, and aimed at a 3 mL quartz cell, equipped with a glass stopper with Teflon septum. Per experiment 3 mL of 5 mM solutions of **3** and 1 mM *n*-hexadecane were used. The $\lambda_{\text{exc}} = 350$ nm 9,10-dicyanoanthracene-sensitized irradiation of **3** is carried out in a Rayonet Photochemical Reactor, RPR 200, equipped with 350 nm lamps, which was placed in a cool room (4 °C). Reaction mixtures of 6 mM sensitizer and 50 mM starting material (in methanol, 10 mL) in Pyrex were used.

Products. All reaction products were characterized by comparison of their retention times on analytical GC and of their mass spectra (by GC-MS) with those of authentic samples, using equipment described in ref 12b. In many cases the product mixture was co-injected with the alleged product. Benzene (**5**), anisole (**6**), iodobenzene (**7**), 4-*tert*-butylcyclohexanone (**9b**), cyclopentene (**13**), cyclopentanone (**14b**), and 3-methoxycyclopentene (**16**) are commercially available. Most other products were synthesized according to literature procedures: 4-*tert*-butyl-1-iodocyclohexene (**3**),^{19b} 4-*tert*-butyl-1,1-dimethoxycyclohexane (**4b**),⁴⁴ 4-*tert*-butylcyclohexene (**8**),⁴⁵ 4-*tert*-butylcyclohex-1-enylbenzene (**10a**),^{46,47} 1-iodocyclopentene (**11**),^{19b,48} 1,1-dimethoxycyclopentane (**12b**),⁴⁴ 1-meth-

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oxycyclopentene (**14a**),⁴⁹ cyclopent-1-enylbenzene (**15a**),⁵⁰ and 3-phenylcyclopentene (**17a**).⁵⁰ Four products, 4-*tert*-butyl-1-methoxycyclohexene (**9a**) and the isomeric 4-*tert*-butylcyclohex-1-enylidobenzene **10b–d**, are assigned by comparison of the thermal solvolysis⁹ products of **1** with the products of the photolysis. The isomeric cyclopent-1-enylidobenzene (**15b–d**) are tentatively assigned just as the cyclopent-2-enylidobenzene isomers (**17b–d**) are. The MS patterns of the allylic products **17b–d** differ from those of the vinylic compounds **15b–d**, which do resemble the patterns obtained for the vinylic products **10b–d**. In the irradiation of **1** two products with a molecular mass of the diastereoisomers **4a** are formed. The occurrence of these products has been certified by comparing their retention times and mass spectra with the products of the (9,10-dicyanoanthracene sensitized) photoreaction of 4-*tert*-butyl-1-iodocyclohexene in methanol yielding **4a**. The formation of just one product **12a**, identified by its mass spectrum, in the photolysis of **2** is in line with these findings. Finally, two reference compounds were synthesized that turned out to be no products in the photolysis experiments. The homoallylic products 4-methoxycyclopentene⁵¹ and 4-phenylcyclopentene,⁵⁰ synthesized

alongside **15a** and **17a**, are not present in the photoproduct mixture of **2**.

Quantum Chemical Calculations. The computations were performed with the Gaussian 03 program, version B3.⁵² All optimizations on singlet and triplet states of **I_a** and **I_{2a}** were performed with B3LYP/6-311G(2d,2p) computations to properly account for ring strain effects. Relative thermodynamics on the compounds under study (Table 3) were obtained by using the CBS-Q model chemistry method.¹⁵

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