Selective alkylation by photogenerated aryl and vinyl cation

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Chapter 5 | **Photochemical generation of six- and five-membered cyclic vinyl cations**

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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 stabilised, vinyl cation[3]. At the other end of the reactivity spectrum, destabilised vinyl cations are found. Destabilisation 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.

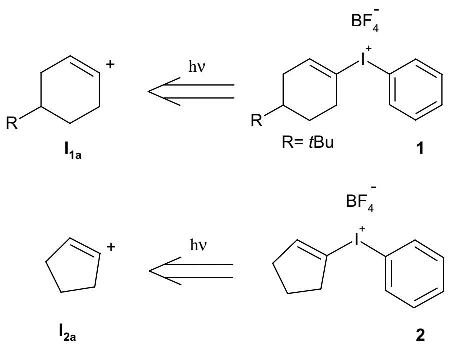
Vinyl cations are sp-hybridised, and possess a linear orientation at the positive carbon atom. A theoretical comparison of the prop-1-enyl cation with the cyclohex-1-enyl cation and the cylopent-1-enyl cation shows that decreases in the angle from 179° via 156° to 141° are accompanied by decreases in 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 destabilisation 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 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 pseudo halides, 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 destabilised 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 ($\mathbf{I}_{1a}$) but also the cyclopent-1-enyl cation ($\mathbf{I}_{2a}$) is accessible through photochemistry (Chart 1).

Chart 1: Cyclic vinyl cations produced from their corresponding iodonium salts.



Results and Discussion

Formation of photoproducts

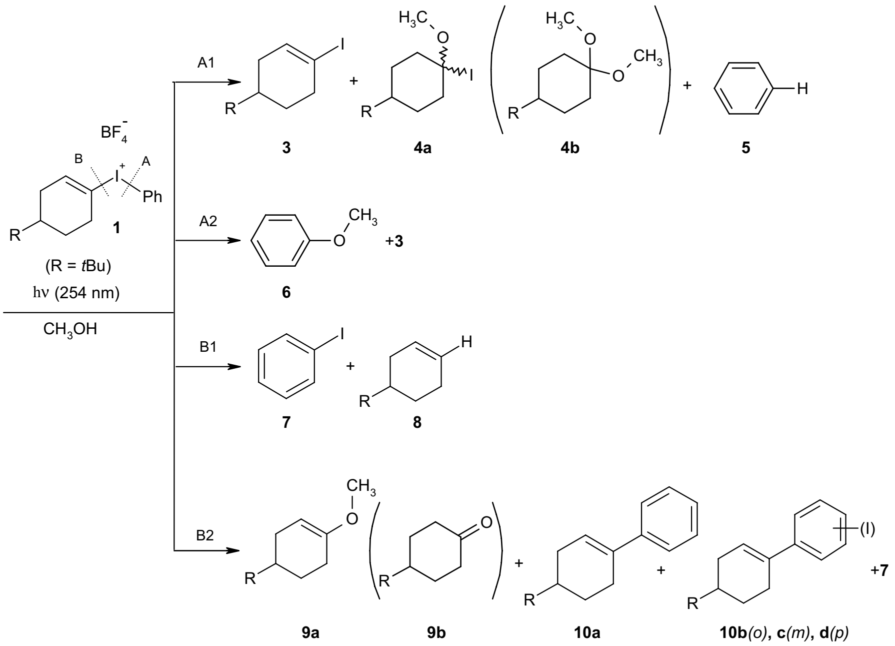
Irradiation of **1** in methanol, at λ_{exc} = 254 nm, yields the product mixture depicted in Scheme 1, in the composition recorded in Table 1. Next to the two leaving groups **3** and **7**, two reductive dehalogenation products, **5** and **8**, are produced by replacement of the phenyliodonium group by a hydrogen atom. Along with the nucleophilic vinylic substitution product, vinyl ether **9a**, four different products of Friedel-Crafts aromatic vinylation are formed, **10a** and **10b**-**d**. Anisole (**6**) results from a nucleophilic aromatic substitution reactionProduct **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 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.

Table 1: Product composition[a] after 90 minutes of irradiation of **1** at λ_{exc} = 254 nm (ca. 10% conversion[b]).

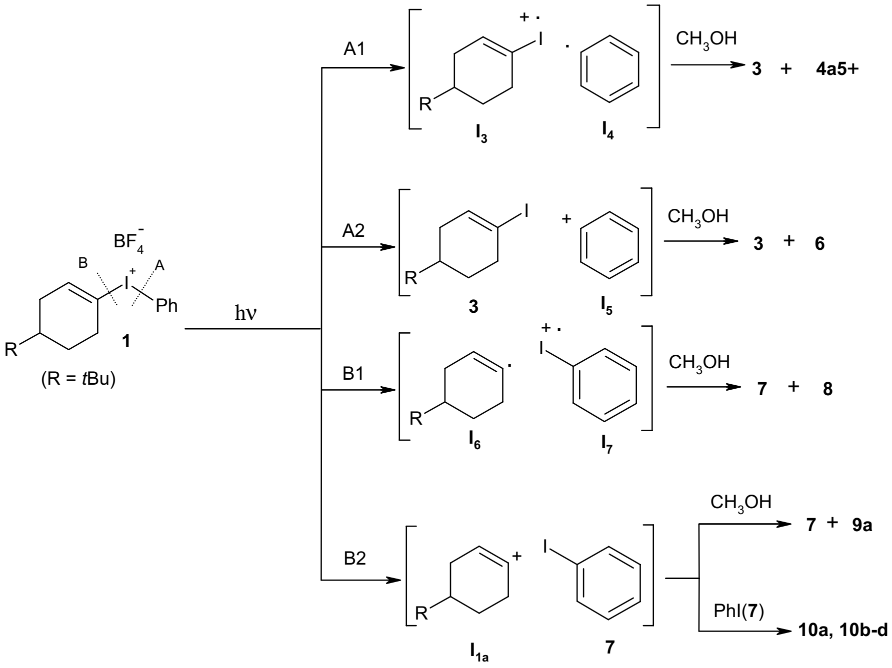
3	**4a**	**4b**	**5**	**6**	**7**	**8**	**9a**	**9b**	**10a**	**10b-d**
20	3.9	11.7[c]	16.8	5.2	80	1.3	2.9	1.5[d]	3.0	1.5/0.8/1.2

[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).

Scheme 1: Product formation upon photolysis of **1** in methanol.



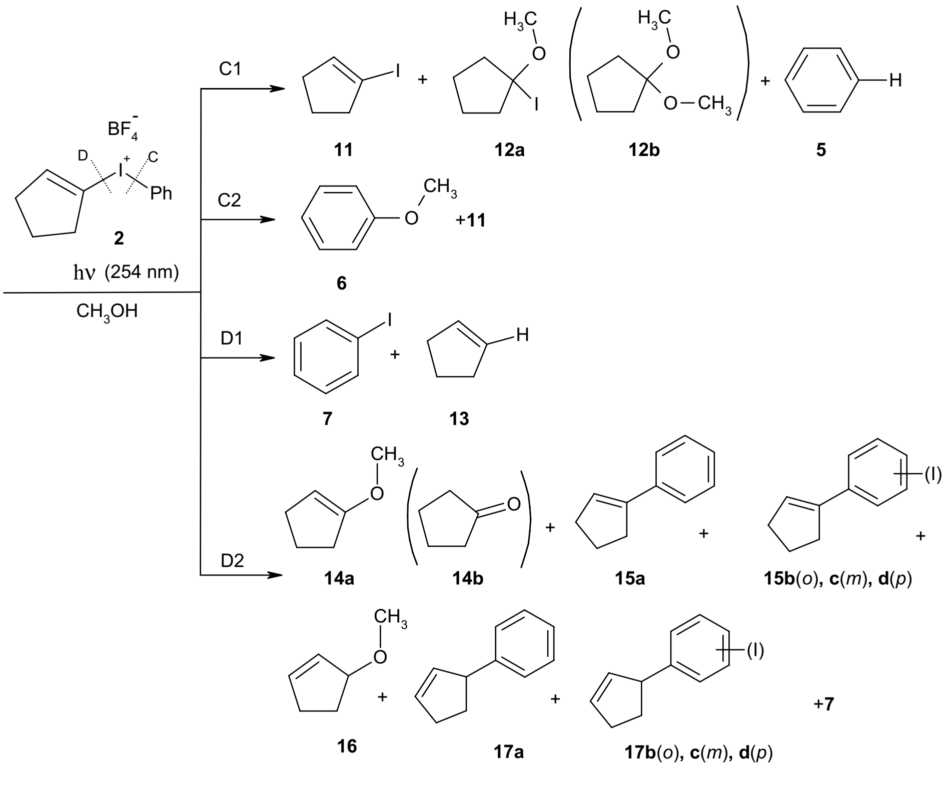
Scheme 2: Mechanism of formation of photoproducts from **1** in methanol.



Homolytic cleavage of the A bond (Route A1) yields the 4-*tert*-butyl-1-iodocyclohexene radical cation $\mathbf{I}_3$ and the phenyl radical $\mathbf{I}_4$. The radical cation $\mathbf{I}_3$ 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 $\mathbf{I}_4$. Upon heterolytic cleavage of bond A (Route A2), **3** is formed, alongside phenyl cation $\mathbf{I}_5$. 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 $\mathbf{I}_6$ and the iodobenzene radical cation $\mathbf{I}_7$. Radical $\mathbf{I}_6$ will abstract a hydrogen atom from the solvent and form 4-*tert*-butyl-cyclohex-1-ene (**8**). Radical cation $\mathbf{I}_7$ forms iodobenzene (**7**) by acquiring an electron. Upon heterolysis of the B bond (Route B2), leaving group **7** and vinyl cation $\mathbf{I}_{1a}$ are formed. The vinyl ether 4-*tert*-butyl-1-methoxycyclohexene (**9a**) is the trapping product of $\mathbf{I}_{1a}$ with methanol. Vinyl ether **9a** is found to hydrolyze under the experimental conditions or upon work-up, in part, to 4-*tert*-butyl-cyclohexanone (**9b**). The 4-*tert*-butylcyclohex-1-enyliodobenzenes **10b** (*ortho*), **10c** (*meta*), and **10d** (*para*) are products of the Friedel-

Scheme 3: Product formation upon photolysis of **2** in methanol.



Crafts reaction of cation $\mathbf{I}_{1a}$ 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 $\mathbf{I}_5$ on the leaving group **3** (Route A2) or by recombination of the radical pairs $\mathbf{I}_3$ and $\mathbf{I}_4$ (Route A1) or $\mathbf{I}_6$ and $\mathbf{I}_7$ (Route B1). Alternative routes toward the formation of the radical pairs may be photoheterolysis to **3** and $\mathbf{I}_5$ (route A2) and to $\mathbf{I}_{1a}$ 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 $\mathbf{I}_7$ as transient in the picosecond flash photolysis of diphenyliodonium salts[14].

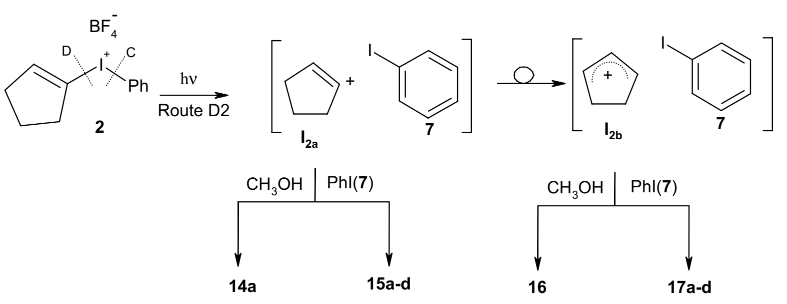
The results obtained in the photolysis of **1**, encouraged us to photolyse the cyclopent-1-enyl compound **2** in methanol at λ_{exc} = 254 nm (Scheme 3, Table 2). Most rewarding is the formation of two nucleophilic substitution products, the vinylic ether 1-methoxycyclopent-1-ene (**14a**) (and its 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.

Table 2: Product composition[a] after 90 min. of irradiation of **2** at λ_{exc} = 254 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	[e]	0.8[f]	3.8	8.8/4.7[g]/2.3	2.5	5.6	[e]

[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.



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 $\mathbf{I}_4$. 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 $\mathbf{I}_5$, which is trapped by methanol to yield anisole (**6**). Homolytic cleavage of the D bond (Route D1) yields the radical cation of iodobenzene $\mathbf{I}_7$ 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 $\mathbf{I}_{2a}$. In the product mixture the trapping product of $\mathbf{I}_{2a}$ and methanol, the vinyl ether **14a** (+**14b**), is accompanied by the allylic ether **16**, which is the trapping product of the allylic cation $\mathbf{I}_{2b}$. Further, next to the products of the electrophilic aromatic substitution reaction of **7** and $\mathbf{I}_{2a}$ (**15a** *(ipso)*, **b***(ortho)*, **c***(meta)*, **d***(para)*), also products reasoned to stem from the trapping of $\mathbf{I}_{2b}$ by **7**, the cyclopent-2-enyliodobenzenes **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 hours, 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 calculations[15] were carried out on the structures and stabilities of the parent six- and five-membered cyclic vinyl and allyl cations $\mathbf{I}_{1a}$ and $\mathbf{I}_{1b}$ (R=H) and $\mathbf{I}_{2a}$ and $\mathbf{I}_{2b}$ (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 $\mathbf{I}_{1a}$ is found to be less stable than the cyclohex-2-enyl cation $\mathbf{I}_{1b}$ by 27.8 kcal/mol. In the cyclopentenyl cations the vinyl cation is 47.8 kcal/mol less stable than the allyl cation.

Table 3: Relative stabilities of the cyclic vinylic cations and isomers.

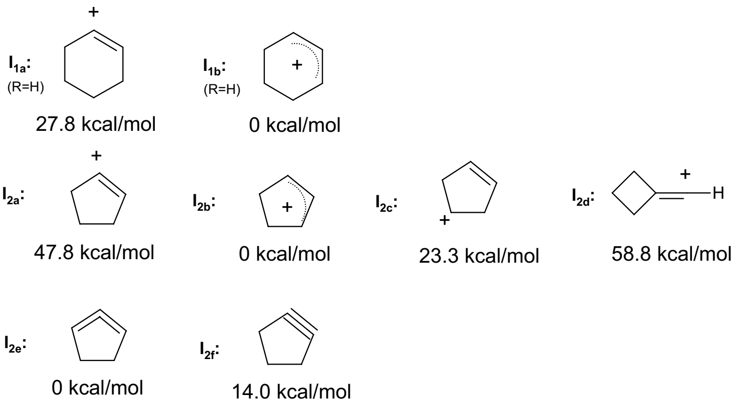
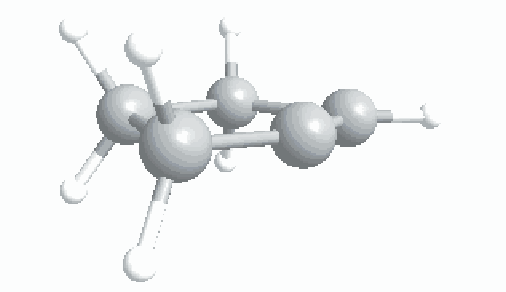
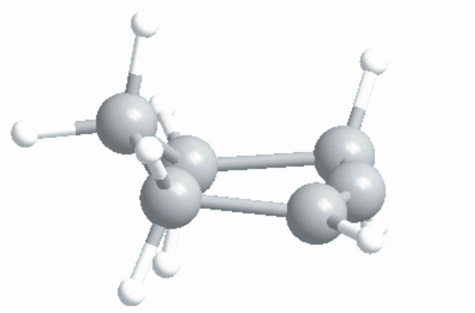


Figure 1: The B3LYP/6-311G(2d,2p)-calculated structures of the vinyl cations **I_{2a}** and **I_{1a}** (R=H).



Vinyl cation **I_{2a}**



Vinyl cation **I_{1a}**

Vinyl cation **I_{2a}** is a planar species (Cs 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 delocalised 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.

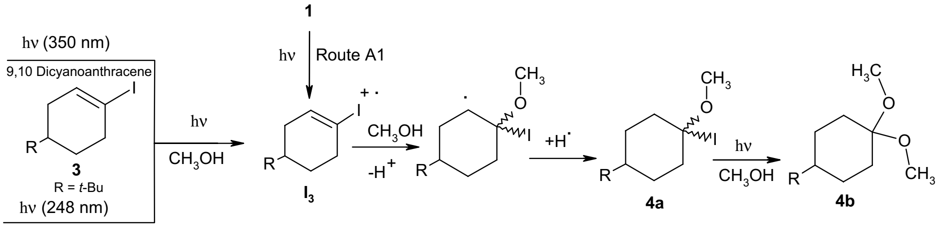
For the six-membered 1-cyclohexenyl cation (**I_{1a}**, R=H), similar observations are made. In this species the CH-C^+-CH_2 angle is 156.3°, which indicates a more relaxed structure. The vinylic C^+ atom bears a charge of +0.450 while the remainder of the charge is delocalised over the rest of the ring.

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 solvolyzes 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 °C for 17 days[17], the unimolecular solvolysis of cyclohex-1-enyl triflate in deuterated acetic acid (130 °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 °C, 2 days)[18]. In the thermal solvolysis of **1** in methanol (25 °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 °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 cylohex-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.

Scheme 5: Mechanism of formation of photoproducts **4a** and **4b**.



Irradiation of a solution of vinyl iodide **3** (R = *tert*-butyl) in methanol in the presence of 9,10-dicyanoanthracene at λ_{exc}= 350 nm (well outside the UV absorption band of **3**) produced **4a** (Scheme 5). Under these electron-transfer photosensitisation conditions alkenes are known to give radical cations. Here the radical cation $\mathbf{I_3}$ 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 sensitiser and upon irradiation in methanol at λ_{exc}= 248 nm (Scheme 5). This means that radical cation $\mathbf{I_3}$ 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 irradiation of **3** are the reaction products cyclohexene **8** and 1,1-dimethoxy-cyclohexane **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 $\mathbf{I_{1a}}$ and its subsequent trapping by methanol. Vinyl cation $\mathbf{I_{1a}}$ 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 $\mathbf{I_{1a}}$, 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, and upon photolysis the ratio of products **9** and **10** is 1:1.5. Clearly, the photogenerated C_6-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 $\mathbf{I_{1a}}$, 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 phenyl 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 C_6-ring vinylic cation $\mathbf{I_{1a}}$ can convert, by a hydride shift, to the allylic cation $\mathbf{I_{1b}}$. However, neither in the thermal solvolysis of cyclohex-1-enyl triflate, -nonaflate, and iodonium salts nor upon irradiation of **1**, are allylic products observed. The CBS-Q calculated stabilities (see Table 3) of $\mathbf{I_{1a}}$ and $\mathbf{I_{1b}}$ show that the production of allyl cation $\mathbf{I_{1b}}$ from $\mathbf{I_{1a}}$ 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 $\mathbf{I_{2a}}$ into the allyl cation $\mathbf{I_{2b}}$. A 1,2-hydride shift does occur in a benzannellated form of $\mathbf{I_{1a}}$, the 1,2-dihydronaphthyl vinyl cation[27], where the driving force is 57 kcal/mol[28]. Apparently, for $\mathbf{I_{1a}}$ 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 C_5-ring vinyl cation

In the irradiation of **2** in methanol the heterolytic cleavage of bond **D** yields cation $\mathbf{I_{2a}}$. 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 $\mathbf{I_{2a}}$ with iodobenzene. The conclusion is strongly supported by the formation of allylic ether **16** and the allylic, aromatic trapping products of $\mathbf{I_{2b}}$ (**17a**, **17b**-**d**). These products imply that upon generation of $\mathbf{I_{2a}}$, it is converted through a hydride shift to the allylic cation $\mathbf{I_{2b}}$, which is trapped by methanol or iodobenzene. Hydride shifts are typical of carbocation behavior and therefore products from $\mathbf{I_{2b}}$ provide direct evidence that a cation, i.e., $\mathbf{I_{2a}}$ is generated photochemically in methanol. The driving force for the 5-ring vinyl cation $\mathbf{I_{2a}}$ to undergo a hydride shift is much larger (See Table 3) than that for the 6-ring vinyl cation $\mathbf{I_{1a}}$, allowing the conversion of $\mathbf{I_{2a}}$ to allyl cation $\mathbf{I_{2b}}$ 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 C_5-ring vinyl cation $\mathbf{I_{2a}}$ by the leaving group **7** yields **15b**-**d** in an *o: m: p* ratio of about 56:30:14. The C_5-ring vinyl cation reacts less abundantly at the *ipso* position than at the combined *o*: *m*: *p* positions compared to the C_6-ring ion: a ratio of 1:4 between these two pathways is found. For the C_5-ring vinyl cation, the ratio between solvent trapped products versus leaving group trapped products is 1:25, compared 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 $\mathbf{I_{2a}}$[25].

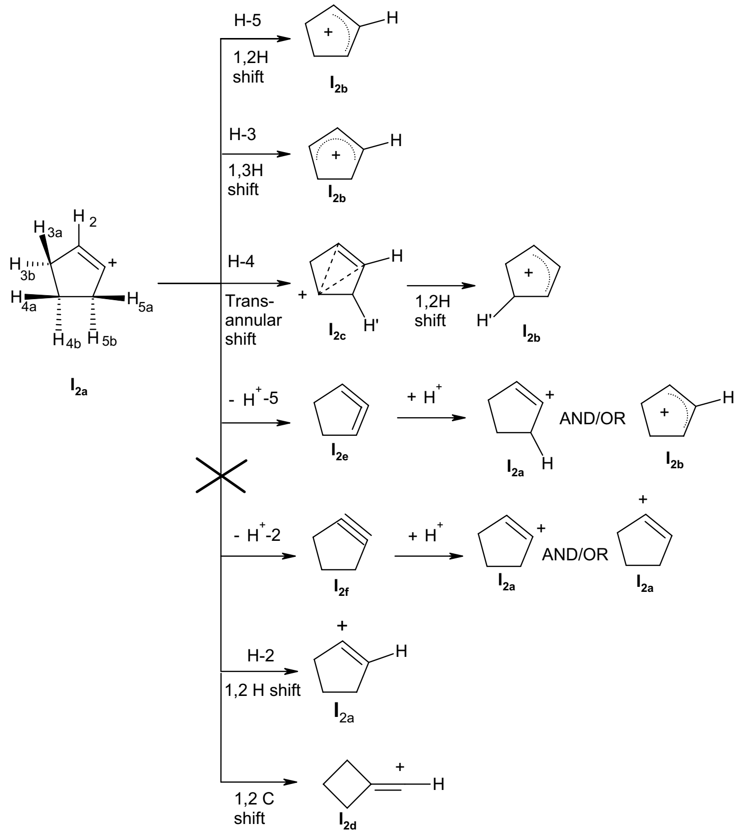
The formation of C_5-ring vinyl cation $\mathbf{I}_{2a}$-derived products also occurs in the irradiation of a derivative of **2** with a 4-tolyl instead of a phenyl ligand, cyclopent-1-enyl(4-methylphenyl)-iodonium tetrafluoroborate, in methanol (λ_{exc}= 254 nm). The photolysis of the tolyl salt proceeds 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 $\mathbf{I}_{2a}$ 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 $\mathbf{I}_{2a}$ into the allylic cation $\mathbf{I}_{2b}$, 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 stabilisation 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 $\mathbf{I}_{2b}$. 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 shift[33] from C-4 to C-1 producing the homo allylic cation $\mathbf{I}_{2c}$, which in turn may undergo a 1,2 H shift to yield allylic cation $\mathbf{I}_{2b}$. Several reports on the generation and reactivity of the cyclopent-3-enyl cation $\mathbf{I}_{2c}$ have appeared[34]. When generated in a non nucleophilic environment, the homoallylic cation $\mathbf{I}_{2c}$ yields allylic products, in a more nucleophilic reaction medium a mixture of homoallylic and allylic products is formed. Thus $\mathbf{I}_{2c}$ 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 $\mathbf{I}_{2c}$ should have been present, if this mechanism is operative. This is

Scheme 6: Possible mechanisms of conversion of $\mathbf{I}_{2a}$ into $\mathbf{I}_{2b}$.



not the case, no 4-methoxycyclopentene is produced. Therefore this sequence of reaction steps is unlikely.

Fourth, proton loss from C-5 of $\mathbf{I}_{2a}$ forming the highly strained cyclic allene $\mathbf{I}_{2e}$[35,36], which upon reprotonation may yield the allyl cation $\mathbf{I}_{2b}$ or the vinyl cation $\mathbf{I}_{2a}$, depending on the site of protonation. Alternatively, a proton may be lost from C-2 of $\mathbf{I}_{2a}$, yielding cyclopentyne ($\mathbf{I}_{2f}$). The latter proton-loss pathway is less likely because CBS-Q calculations show (data Table 3) that cyclopentyne $\mathbf{I}_{2f}$ is 14 kcal/mol less stable than cyclopenta-1,2-diene $\mathbf{I}_{2e}$. It is doubtful whether the deprotonation of $\mathbf{I}_{2a}$ to $\mathbf{I}_{2e}$ is thermodynamically feasible, the more so because only methanol or iodobenzene is available as base in the solvent cage [12b]. However, if a vinyl cation of higher energy is involved or if is the triplet state of $\mathbf{I}_{2a}$ that is involved, the propensity for proton loss may be enhanced[24,37]. Anyhow, the preferred reaction for structurally unbiased linear allenes is reprotonation at the terminal allene carbons atoms[38], here yielding $\mathbf{I}_{2a}$ and not $\mathbf{I}_{2b}$. This reaction sequence is not productive toward allylic ether formation and is therefore disregarded.

Other possible shifts, a 1,2-H shift across the double bond, or a 1,2-alkyl shift, do not contribute to $\mathbf{I}_{2b}$ formation. This particular 1,2-H shift would yield an intermediate indistinguishable from $\mathbf{I}_{2a}$. Formation of the primary vinyl cation $\mathbf{I}_{2d}$ from $\mathbf{I}_{2a}$ via a 1,2-alkyl shift is endothermic by 11 kcal/mol (see Table 3) and therefore thermodynamically not feasible. Also no products stemming from $\mathbf{I}_{2d}$ are observed.

Summarizing, we propose that $\mathbf{I}_{2b}$ is produced from $\mathbf{I}_{2a}$ 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 C_5-ring vinyl cation $\mathbf{I}_{2a}$[40]. Attempts to thermally generate $\mathbf{I}_{2a}$ 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]. $\mathbf{I}_{2a}$ 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 non formation 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(phenyl)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 C_6-ring vinyl cation, but also the C_5-ring vinyl cation can be generated photochemically, under mild reaction conditions. Compelling evidence for the formation of the C_5-ring vinyl cation $\mathbf{I}_{2a}$ 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 $\mathbf{I}_{2b}$. 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 synthesised as described in references [9,43]. 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**). Non available reference compounds were synthesised 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 μL *n*-hexadecane as internal standard, was irradiated. At appropriate time intervals 50 μL 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 ~1 mL demineralised water and 100 μL 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 $\lambda_{exc} = 248$ nm irradiations of **3** (R = *tert*-butyl) are carried out in a different set up. 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 $\lambda_{exc} = 350$ nm 9, 10-dicyanoanthracene-sensitised 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 sensitiser and 50 mM starting material and 1 mM *n*-hexadecane (in methanol, 10 mL) in Pyrex were used.

Products

All reaction products were characterised 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 synthesised 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*-butyl-cyclohex-1-enylbenzene (**10a**)[46,47], 1-iodocyclopentene (**11**)[19b,48], 1,1-dimethoxycyclopentane (**12b**)[44], 1-methoxycyclopentene (**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*-butyl-cyclohex-1-enyliodobenzenes **10b-d**, are assigned by comparison of the thermal solvolysis[9] products of **1** with the products of the photolysis. The isomeric cyclopent-1-enyliodobenzenes (**15b-d**), are tentatively assigned just as the cyclopent-2-enyliodobenzene 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 sensitised) 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 synthesised that turned out to be no products in the photolysis experiments. The homoallylic products 4-methoxycyclopentene[51], and 4-phenylcyclopentene[50], synthesised alongside **15a** and **17a,** are not present in the photoproduct mixture of **2**. Also 1-methoxymethylenecyclobutane[52] and cyclobutane carbaldehyde[53], the vinyl ether and its hydrolysis product that could have been formed if $\mathbf{I_{2d}}$ would have been an intermediate in the photolysis of **2**, are not present.

Quantum Chemical Calculations

The computations were performed with the Gaussian 03 program, version B3[54]. All optimisations on singlet and triplet states of $\mathbf{I_a}$ and $\mathbf{I_{2a}}$ 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].

Equipment

UV spectra were recorded at room temperature on a double beam Varian DMS 200 Spectrophotometer, if applicable with pure solvent in the reference cell. ^{1}H-NMR spectra were recorded on a DMX 300, using DMSO D_6 as solvent. As analytical GC a Hewlett-Packard 6890 model was used, equipped with a automatic injector, fitted with a CP-Sil5-CB column (25 m, ø = 0.25 mm, 1.2 µm) using hydrogen as carrier gas. The Flame-Ionisation Detector (FID) was calibrated using commercially available reference chemicals. HP Chemstation was used for the analysis of the analytical data. Mass spectra were measured on a GC-MS set-up consisting of a Hewlett-Packard 5890 series 2 model GC, equipped with a automatic injector, fitted with a AT-5MS column (30 m, ø = 0.25 mm, 0.25 µm) using helium as carrier gas. The GC was coupled to a Finnigan Mat SSQ 710 mass spectrometer, employing electron-impact as the ionisation method. The GC-MS data was analyzed with Xcaliber.

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