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Observation of Cationic Intermediates in the Photolysis of 1-Phenylcyclohexene

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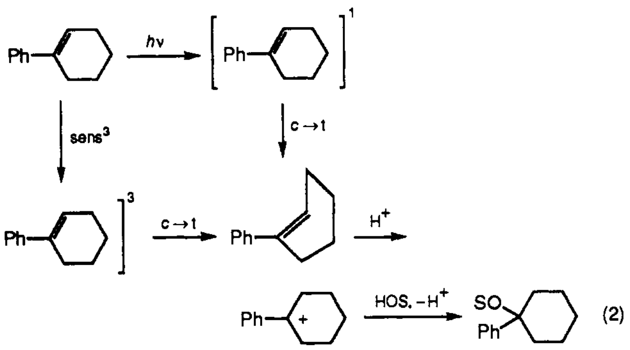
Abstract: The photochemistry of *cis*-1-phenylcyclohexene and its *m*-methoxy derivative has been examined in 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP). The only photoproduct is the Markovnikov adduct of the solvent, arising from an intermediate 1-arylcyclohexyl cation. This cation is observed as a transient species with laser flash photolysis, for both direct irradiation at 248 nm and benzophenone sensitized irradiation at 308 nm. As suggested in previous studies with phenylcyclohexene in other solvents, the mechanism involves protonation of a strained *trans*-1-arylcyclohexene formed from both the singlet and triplet excited states. The *trans*-cyclohexene is not observed in HFIP because of its very rapid protonation by this solvent. Direct protonation of the singlet excited state to give the cyclohexyl cation cannot be ruled out, but it is likely a minor pathway. There is, however, unambiguous evidence for protonation of the singlet, with the protonation occurring on the aromatic ring to give a 2-benzenonium ion. This cation is observed as a second transient in the flash photolysis experiments involving direct 248-nm irradiation while it is not detected with sensitized irradiation. The 2-benzenonium ion intermediate returns to parent *cis*-1-phenylcyclohexene, and thus results in no overall photoreaction. Its presence, however, is clearly demonstrated in experiments carried out in deuterated HFIP, where exchange of aromatic ring protons in unreacted cyclohexene is observed. In addition to reacting with the solvent, the 2-benzenonium ion is efficiently quenched by unphotolyzed phenylcyclohexene, with a rate constant of 1.4×10^9 $M^{-1}\,s^{-1}$ at 20 °C. This reaction involves the cyclohexene acting as the base, and it results in the formation of additional 1-phenylcyclohexyl cation. The occurrence of a sequence involving aryl ring protonation followed by proton transfer to unreacted phenylcyclohexene is demonstrated through the observation that a portion of the ether product formed in $(CF_3)_2CHOD$ arises from the formal addition of $(CF_3)_2CHOH$.

Acyclic styrenes undergo a Markovnikov addition of the solvent upon irradiation in water and methanol.[1] The reaction is acid catalyzed, but it employs considerably lower acid concentrations or weaker acids than required for thermal addition. The proposed mechanism is however analogous to the thermal one, with protonation of the first excited singlet state giving a carbocation intermediate. Protonation of the excited state (by H^+) is estimated to be 10^{11}- to 10^{14}-fold more rapid than thermal protonation.

$$\mathrm{ArCR{=}CH_2} \xrightarrow{h\nu} \{\mathrm{ArCR{=}CH_2}\}^1 \xrightarrow{\mathrm{HA},\,-\mathrm{A}^-} \mathrm{Ar}\overset{+}{\mathrm{C}}\mathrm{R{-}CH_3} \xrightarrow{\mathrm{HOS},\,-\mathrm{H}^+} \mathrm{ArC(OS)R{-}CH_3} \quad (1)$$

cis-1-Phenylcyclohexene also undergoes photoaddition, but the mechanism is quite different, with isomerization to *trans*-1-phenylcyclohexene as the initial photochemical reaction.[2] This occurs from the singlet state upon direct irradiation and from the triplet state upon sensitized irradiation. The highly strained trans isomer is subsequently protonated in the ground state to give the 1-phenylcyclohexyl cation followed by solvent trapping.



(2)

Several experimental observations are consistent with this mechanism. The presence of an intermediate common to the direct and sensitized irradiations has been established.[2c] Singlet-to-triplet intersystem crossing is however inefficient,[3] ruling out the triplet as this intermediate. Direct protonation of the triplet has been ruled out since its lifetime is no different in inert and proton-donating solvents.[4] Laser flash photolysis studies carried out in methanol have revealed a transient with λ_{max} at 380 nm that has been assigned to the *trans*-1-phenylcyclohexene, this transient being observed upon both direct[5] and sensitized irradiation.[6] In the latter case the triplet *cis*-1-phenylcyclohexene with λ_{max} at 325 nm could be observed as a precursor to the 380-nm transient. The decay of the *trans*-cyclohexene was

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(1) (a) Woolridge, T.; Roberts, T. D. *Tetrahedron Lett.* **1973,** 4007–4008. (b) Wan, P.; Culshaw, S.; Yates, K. *J. Am. Chem. Soc.* **1982,** *104,* 2509–2515. (c) Wan, P.; Yates, K. *J. Am. Chem. Soc.* **1983,** *48,* 869–876. (d) McEwen, J.; Yates, K. *J. Am. Chem. Soc.* **1987,** *109,* 5800–5808. (e) Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984,** *5,* 157–181. (f) Except nitrostyrenes, where the addition is anit-Markovnikov: Wan, P.; Davis, M. J.; Teo, M.-A. *J. Org. Chem.* **1989,** *54,* 1354–1359.

(2) (a) Kropp, P. J. *J. Am. Chem. Soc.* **1969,** *91,* 5783–5791. (b) Rosenberg, H. M.; Serve, M. P. *J. Org. Chem.* **1972,** *37,* 141–142. (c) Dauben, H. G.; van Riel, H. C. H. A.; Hauw, C.; Leroy, F.; Joussot-Dubien, J.; Bonneau, R. *J. Am. Chem. Soc.* **1979,** *101,* 1901–1903. (d) Dauben, H. G.; van Riel, H. C. H. A.; Robbins, J. D.; Wagner, G. J. *J. Am. Chem. Soc.* **1979,** *101,* 6383–6389.

(3) Zimmerman, H. E.; Kamm, K. S.; Werthermann, D. P. *J. Am. Chem. Soc.* **1974,** *97,* 3718–3725.

(4) Ni, T.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989,** *111,* 457–470.

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(6) Bonneau, R, *J. Photochem.* **1979,** *101,* 439–449.

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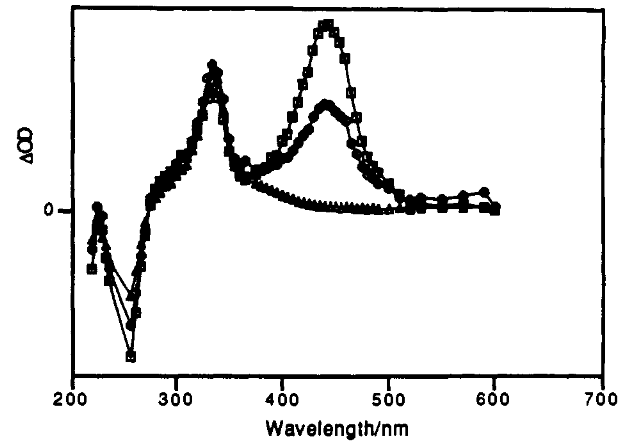


Figure 1. Transient spectra obtained upon 248-nm laser photolysis of *cis*-1-phenylcyclohexene in HFIP. Spectra were recorded at times of 150 ns (□), 750 ns (○) and 6.5 ms (△).

accelerated by acids,[5] consistent with thermal protonation to the 1-phenylcyclohexyl cation.

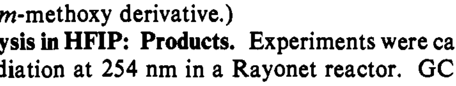
The cation intermediate, however, was not observed in these experiments. This is not surprising, since methanol is a highly nucleophilic solvent, expected to react with benzylic-type cations such as 1-phenylcyclohexyl extremely quickly.[7] We have recently employed the considerably less nucleophilic 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) as a solvent to observe reactive cations with flash photolysis.[8] This solvent has the additional property of being sufficiently acidic to protonate excited styrenes without the addition of stronger acids. Thus, styrene and α-methylstyrene undergo Markovnikov addition of HFIP upon irradiation in the solvent alone, and the 1-phenylethyl and cumyl cations are readily detected as intermediates in laser photolysis experiments.[8d]

In this paper we examine the photochemical behavior of *cis*-1-phenylcyclohexene and its *m*-methoxy derivative in HFIP. The 1-arylcyclohexyl cations derived from these were indeed observed as transients. To our surprise there was a second transient, also with characteristics consistent with a cation structure. This has been identified as a cyclohexadienyl cation obtained by protonation of the aryl ring. This explains a previous observation with *cis*-1-phenylcyclohexene, namely the quenching of fluorescence in methanol by added acids.[2d] Since this same study ruled out protonation of the cyclohexene C=C, a different acid deactivation mechanism is required. We now suggest that this involves protonation on the aryl ring.

Results

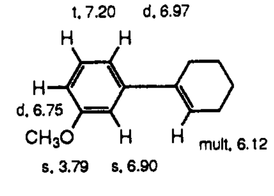
Flash Photolysis in HFIP: Direct Irradiation. The transient absorption spectra obtained upon 248-nm irradiation of *cis*-1-phenylcyclohexene in HFIP show two bands with maxima at 335 and 445 nm, along with bleaching below 300 nm due to consumption of the precursor (Figure 1). Both the 335- and 445-nm bands decay in a first-order fashion. However, the observed rate constants differ by over two orders of magnitude (Table I), indicating that two different transients are being produced. Partial return of the bleaching below 255 nm is observed, with a rate constant that is identical with that for the decay at 455 nm. Also occurring with this same rate constant is a small amount of delayed appearance of absorbance at 335 nm, the increase here accounting for $\sim$5–10% of the ultimate total optical density. No absorbance remains in the region above 300 nm at long times after the laser pulse, indicating that no long-lived species absorbing in this region is present after the two transients decay. There is, however, permanent bleaching below 300 nm. Very similar behavior is observed with *cis*-(*m*-methoxyphenyl)cyclohexene (Figure 2), with the transients having λ_{max} at 340 and 480 nm. The *m*-methoxy substituent has only a small effect on the rate constant for the decay of the transient at the lower wavelength, but it results in a considerable increase in the lifetime of the transient at higher wavelength (Table I). With both systems the initial absorbances due to the transients increase in a linear fashion with increasing intensity of the laser pulse, and both the absorption spectra and the observed rate constants are unchanged on proceeding form argon-saturated to oxygen-saturated HFIP. The rate constants are, however, increased significantly by the addition of tetrabutylammonium bromide and simple alkanols ranging from methanol to *tert*-butyl alcohol. In these cases plots of k_{decay} vs the concentration of the added reagent are excellently linear. Second-order rate constants obtained as the slopes of these plots are given in Table I. In experiments with *cis*-1-phenylcyclohexene, the rate constant for the decay at 445 nm was also found to increase in a linear fashion with increasing initial concentrations of the substrate, with a second-order rate constant of 1.4×10^9 M^{-1} s^{-1}. The decay at 335 nm was however unaffected. (A similar study was not carried out with the *m*-methoxy derivative.)

Photolysis in HFIP: Products. Experiments were carried out with irradiation at 254 nm in a Rayonet reactor. GC analysis showed that only one product was formed as the cyclohexenes disappeared, even up to 50–80% conversions. These products were isolated and identified by NMR and MS as the Markovnikov solvent adducts.



(3)

Experiments carried out in the deuterated solvent $(CF_3)_2CHOD$ revealed that there was partial exchange into unreacted cyclohexene. In the case of the parent compound, this was demonstrated by GC/MS, in terms of an increase with increasing irradiation time in the ratio at 159:158 corresponding to (P + 1):P. At low conversions exchange increased in a manner linear in the formation of the product of solvent addition, with the latter occurring approximately twice as fast. In the case of the *m*-methoxy compound the actual position of exchange was determined by isolating the unreacted material and recording a ^{1}H NMR spectrum. At 400 MHz the four aromatic protons and the alkene proton are separated and readily identified from their splitting patterns.[10]



Only the signal at δ 6.90 corresponding to the proton ortho to both the methoxy and cyclohexenyl groups is decreased in intensity on irradiation in $(CF_3)_2CHOD$. Within experimental error there is no change in the relative intensity of any of the other signals.

The ether product obtained from irradiation of *cis*-1-phenylcyclohexene in $(CF_3)_2CHOD$ was also examined for deuterium incorporation, with a sample obtained in an experiment with 1 mM *cis*-1-phenylcyclohexene showing the presence of ions at *m/e* 326 and 327 in a ratio of 1:3. The material with *m/e* 327 is expected

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(7) (a) Richard, J.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361–1372. (b) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913–6914.

(8) (a) McClelland, R. A.; Mathivanan, N.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 4857–4861. (b) Steenken, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 9648–9649. (c) Mathivanan, N.; Cozens, F.; McClelland, R. A.; Steenken, S. *J. Am. Chem. Soc.* **1992**, *114*, 2198–2203. (d) McClelland, R. A.; Chan, C.; Cozens, F.; Modro, A.; Steenken, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1337–1339.

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(10) Some long-range coupling is also observed in the aromatic signals.

Table I. Rate Constants at 20 °C for the Reaction of Transient Cations Produced on 248-nm Irradition of *cis*-1-Phenylcyclohexene, *cis*-1-(*m*-Methoxyphenyl)cyclohexene, α-Methylstyrene, and Anisole in 1,1,1,3,3,3-Hexafluoroisopropyl Alcohol

	1-PhC$_6$H$_9$[a]		1-(m-MeOC$_6$H$_4$)C$_6$H$_9$[b]		α-MeSty[c]	anisole[d]
reactant	k_{335}[e]	k_{445}[f]	k_{340}[g]	k_{480}[h]	k_{325}[i]	k_{370}[j]
HFIP,[k] s^{-1}	5×10^3	1.2×10^6	7×10^3	5×10^3	9×10^3	6×10^5
Br$^-$, M^{-1} s^{-1}	5.4×10^9	7.9×10^9	4.2×10^9	1.0×10^8	6.7×10^9	4.9×10^9
MeOH, M^{-1} s^{-1}	2.2×10^6	4.5×10^7	3.5×10^6	1.5×10^6	4.1×10^6	2.2×10^7
EtOH, M^{-1} s^{-1}	9.9×10^5	3.8×10^7	2.0×10^6	1.9×10^6	3.7×10^6	1.9×10^7
iPrOH, M^{-1} s^{-1}	2.9×10^5	3.3×10^7	5.9×10^5	1.8×10^6	7.0×10^5	2.0×10^7
tBuOH, M^{-1} s^{-1}	1.5×10^5	3.6×10^7	4.8×10^5	1.7×10^6	3.2×10^5	1.9×10^7

[a] *cis*-1-Phenylcyclohexene. [b] *cis*-1-(*m*-methoxyphenyl)cyclohexene. [c] α-Methylstyrene, data from refs 8d, 9. [d] Data from ref 9. [e] 1-Phenylcyclohexyl cation. [f] 2-Cyclohexenylbenzenonium ion. [g] 1-(*m*-Methoxyphenyl)cyclohexyl cation. [h] 2-Cyclohexenyl-6-methoxybenzenonium ion. [i] Cumyl cation. [j] 2-Methoxybenzenonium ion. [k] First-order rate constant for the decay in the solvent alone. Number can vary by ±30% depending on the amount of water in the solvent. Errors in the other rate constants are ±5%.

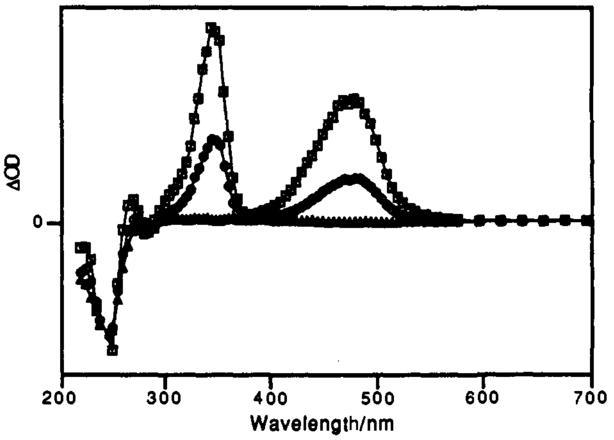


Figure 2. Transient spectra obtained upon 248-nm laser photolysis of *cis*-1-(*m*-methoxyphenyl)cyclohexene in HFIP. Spectra were recorded at times of 520 ns (□), 20 ms (○) and 320 ms (△).

since this corresponds to the parent ion of the ether containing one deuterium atom. However, the ion at m/e 326 is unexpected, since a sample obtained in nondeuterated solvent shows very little P - 1 peak, the (P - 1):P ratio (325:326) being less than 0.05 in this case. The implication is that a portion of the hexafluoroisopropyl ether obtained in (CF$_3$)$_2$CHOD is in fact not deuterated.

Flash Photolysis in HFIP: Sensitized Irradiation. These experiments were carried out in argon-saturated solutions with excitation of benzophenone at 308 nm, a wavelength where there is little optical density due to the arylcyclohexenes. In acetonitrile and methanol, the benzophenone triplet is quenched by the addition of the two cyclohexenes, with a transient at 380 nm growing in with the same rate constant. Such observations have been made previously by Bonneau in studies involving triplet sensitizers and the parent system,[5] and the 380-nm transient is therefore identified as the *trans*-1-arylcyclohexene.[4,5] In HFIP (Figure 3), the two cyclohexenes also increase the rate of decay of the benzophenone triplet, but the new transients that appear have λ_{max} at 335–340 nm, being identical in both their absorption spectra and kinetics of decay to the transients observed at the same λ_{max} upon direct irradiation at 248 nm. In particular the transients that are produced with the sensitizer are quenched by added alkanols with rate constants identical to those obtained under direct irradiation. Sensitized irradiation, however, does not produce any of the transient absorbance at the higher wavelength that is seen on direct irradiation.

When a similar triplet sensitization experiment was carried out with benzophenone in the presence of α-methylstyrene in HFIP, triplet decay was observed to be accelerated, but there was no new absorbance above 300 nm. The cumyl cation has λ_{max} at 325 nm, and it is sufficiently long-lived in HFIP to be observed after decay of the benzophenone triplet. The conclusion is that triplet sensitized excitation of α-methylstyrene does not lead to C=C protonation in HFIP.

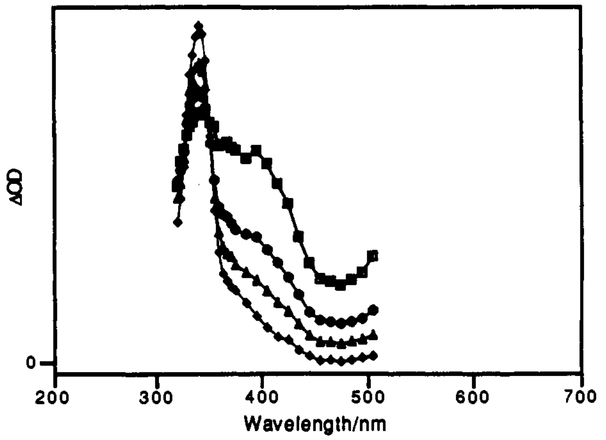


Figure 3. Transient spectra generated in argon-saturated HFIP upon 308-nm excitation of 0.2 mM benzophenone in the presence of 3 mM *cis*-1-phenylcyclohexene. Spectra were recorded at times of 40 ns (□), 100 ns (○) , 200 ns (△) and 375 ns (◇).

Flash Photolysis in HFIP–MeOH and HFIP–CH$_2$Cl$_2$ Mixtures. These experiments were carried out to investigate whether there is a solvent mixture where both the *trans*-cyclohexene transient at 380 nm and the transient at 335–340 nm could be detected. In 100% methanol, the *trans*-cyclohexenes at 380 nm are readily observable,[4] but there is no appearance of the transient at the lower wavelength. The addition of HFIP accelerates the decay of the *trans*-alkene, and by ~50% HFIP its lifetime is approaching the limit of the nanosecond flash technique. Starting in 100% HFIP, the 335-nm transient is observed. This decay is accelerated by the addition of methanol, and by ~10% MeOH the limit is reached. Thus, as illustrated for the parent system in Figure 4, HFIP quenches the *trans*-alkene while methanol quenches the 335-nm transient, and no combination of these two solvents exists where both are observed in the same experiment on the time scale of our apparatus. In fact, from 50 to 90% HFIP both transients are too short lived to be detected.

The *trans*-cyclohexene is also observed in 100% dichloromethane. In this solvent, quenching by HFIP is very efficient, and by ~5% by volume, the decay of the *trans*-alkene is reaching the limit. No other transient is observed however. The 335 nm transient first appears around 10% HFIP, being formed completely within the laser pulse. By this concentration of HFIP the *trans*-alkene is no longer observed, being quenched within the laser pulse. The 440 nm transient is not seen in 10% HFIP, this species requiring a solvent containing at least 50% HFIP to become observable.

Discussion

1-Arylcyclohexyl Cations. The cumyl cation has been characterized by Olah and co-workers under strongly acidic conditions and a UV spectrum provided, showing bands with λ_{max} 326 nm

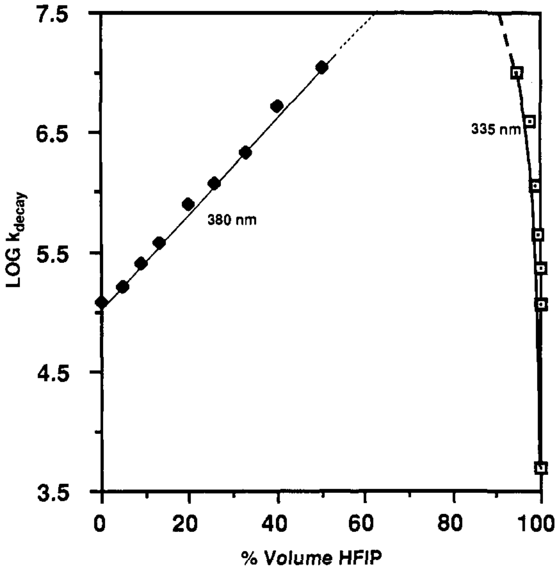
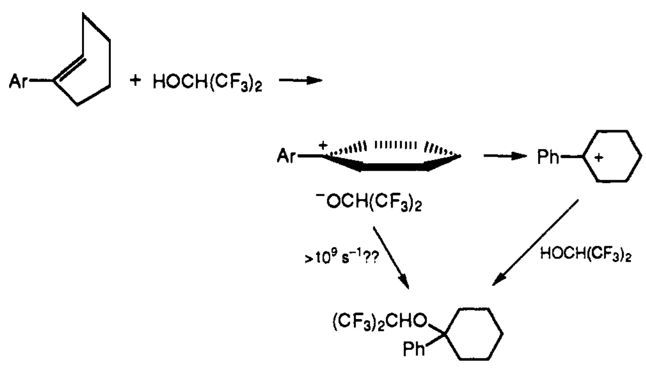


Figure 4. Rate constants (20 °C, s^{-1}) for the decay of transients produced upon 248-nm laser irradiation of *cis*-1-phenylcyclohexene in mixtures of methanol and 1,1,1,3,3,3-hexafluoroisopropyl alcohol: (◆) *trans*-1-phenylcyclohexene, λ_{max} = 380 nm; (☐) 1-phenylcyclohexyl cation, λ_{max} = 335 nm.

($\epsilon = 1.1 \times 10^4$) and 390 nm ($\epsilon = 1.4 \times 10^3$).[11] The transient cumyl cation formed on photoprotonation of α-methylstyrene in HFIP is in excellent agreement, with a band with λ_{max} at 325 nm and a weaker, more poorly defined one at λ_{max} ~390 nm, with the ratio of intensities at the two maxima of about 10:1.[8d] The cumyl cation decays in HFIP with a rate constant of 9×10^3 s^{-1}.

With this background, the transients with lower λ_{max} observed in this study can clearly be assigned as 1-arylcyclohexyl cations. The rate constants, the shapes of the absorption bands, and the λ_{max} are all similar to those of the cumyl cation. The 1-phenylcyclohexyl cation even shows the second, less intense, band at higher wavelengths.[12] As shown in Table I, further evidence comes in the close similarities in the rate constants for the reactions with nucleophiles. The order MeOH > EtOH > iPrOH > tBuOH, with about a 10-fold decrease across the series, is common for the reaction of alcohols with short-lived cationic species.[13] Arylcyclohexyl cations as intermediates are obviously also consistent with the observation of the Markovnikov ether as the product of irradiation in HFIP. And, as a final piece of evidence, similar rate constants are expected for the parent and *m*-methoxyphenyl systems, since the *m*-methoxy group is only weakly electron withdrawing relative to hydrogen.

In the experiment involving triplet sensitization (Figure 3), the 1-arylcyclohexyl cation must be arising after the initial formation of *trans*-1-cyclohexene, and not from direct protonation of triplet *cis*-cyclohexene. The best evidence for this is the failure to observe the cumyl cation on triplet-sensitized excitation of α-methylstyrene in HFIP. Previous workers have also demonstrated that triplet styrenes do not undergo acid-catalyzed photoaddition in water.[1b] The *trans*-cyclohexene is not observed as a transient in HFIP, since it is rapidly quenched by the solvent. That this is the case is demonstrated by the experiments in the mixed solvents CH_2Cl_2–HFIP and MeOH–HFIP (Figure 4). The *trans*-alkene can be observed in mixtures with low HFIP content, but HFIP accelerates the decay, and at some point the limit of the nanosecond flash photolysis method is reached. Interestingly, HFIP proves to be a significantly better quencher in CH_2Cl_2 than in methanol. This is likely caused by a hydrogen bonding interaction $\{(CF_3)_2CHO\text{–}H\cdots O(H)\text{–}CH_3\}$ in methanol that decreases the inherent acidity of the HFIP hydroxyl group. With both of the solvent combinations investigated, no mixture could be found where the *trans*-cyclohexene and the arylcyclohexyl cation were observed in the same experiment.[14] In the mixtures with methanol, solutions where the amount of HFIP present is sufficiently low that *trans*-alkene is detected have a high concentration of the excellent nucleophile methanol, and this rapidly traps the cation. At the other extreme where the methanol concentration is reduced so that cation is observed, there are large amounts of HFIP that rapidly quench the *trans*-alkene. In the CH_2Cl_2 mixtures, *trans*-alkene is only observed at relatively low concentrations of HFIP. Cation is not observed is these solutions, presumably because the solvent is not sufficiently polar to separate the ion pair that is initially formed in the protonation. This ion pair is expected to collapse on the picosecond time scale.[15]



In more polar mixtures where free cation can form through separation of the ion pair, the HFIP content is sufficiently high that *trans*-alkene cannot be observed.

For the direct irradiation in HFIP, there is ambiguity as to whether the cyclohexyl cation that is observed arises from protonation of the *trans*-cyclohexene or from a direct protonation of the singlet excited state. The rapid protonation of the former prevents the demonstration that it is the precursor, at least for experiments conducted on the nanosecond time scale.[16] For experiments with *cis*-1-phenylcyclohexene in methanol, the singlet state has been excluded as the intermediate that is protonated in

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[11] Olah, G. A.; Pittman, C. U.; Waack, R.; Doran, M. *J. Am. Chem. Soc.* **1966**, *88*, 1488–1495.

[12] This band appears as a shoulder and is only evident at the completion of the decay of the second transient (see Figure 1). The similar rates of decay of the two transients from (*m*-methoxyphenyl)cyclohexene make it impossible to tell if there is any absorbance at higher wavelength for the (*m*-methoxyphenyl)cyclohexyl cation.

[13] For other examples see: (a) Kobayashi, S.; Kitamura, T.; Taniguchi, H.; Schnabel, W. *Chem. Lett.* **1983**, 1117–1120. (b) Kobayashi, S.; Zhu, Q. Q.; Schnabel, W. *Z. Naturforsch. B* **1988**, *43*, 825; **1992**, *43*, 825. (c) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462–2464. (d) Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 7710–7716.

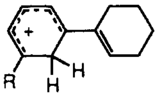
[14] A referee has suggested the use of acetonitrile/HFIP mixtures for this experiment. This, however, does not work, for the same reasons as in the case of the methanol/HFIP mixtures. In particular, acetonitrile is considerably more nucleophilic in its reactions with carbocations than HFIP, so that in mixtures with significant acetonitrile content the 1-phenylcyclohexyl cation is too short-lived to be observed.

[15] (a) The importance of solvent polarity in separating ions is illustrated by experiments with diphenylmethyl chloride in mixtures of acetonitrile–CH_2Cl_2. With nanosecond flash photolysis, the diphenylmethyl cation is readily observed in acetonitrile-rich mixtures, but not in CH_2Cl_2-rich ones.[15b] When a picosecond apparatus is employed, however, the cation is observed throughout. In acetonitrile-rich solutions, its decay is two component, a decay on the picosecond time associated with partial collapse of the ion pair in competition with separation, followed by decay on the nanosecond scale representing the reaction of the free ion. In CH_2Cl_2-rich solutions, however, decay is complete on the picosecond time scale as the only reaction undergone by the ion pair is bond formation.[15c] Similar observations have been made with cation radical–anion ion pairs.[15d] (b) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918–6928. (c) Hilinski, E. Personal communication. (d) Masnovi, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7880–7893.

[16] Depending on the relative rates of the two steps in the sequence singlet → *trans*-cyclohexene → cyclohexyl cation, it is possible that the *trans*-alkene could be observed on the picosecond time scale. This, however, will require monitoring in the 300–400-nm region.

the pathway leading to the ether adduct.[2d] On this basis, we suspect that a similar protonation in HFIP is at best a minor pathway.

2-Cyclohexenylbenzenonium Ions. The transient observed at higher wavelength in HFIP is assigned the structure of a 2-cyclohexenylbenzenonium ion, a cyclohexadienyl cation obtained by protonation in the ring moiety of the *cis*-1-arylcyclohexene.



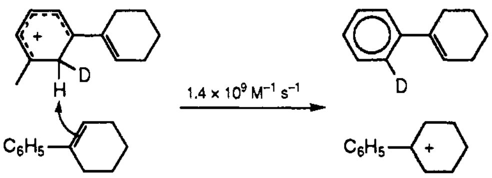
R = H, OMe

The quenching by bromide and alkanols coupled with the lack of an effect of oxygen clearly points to a cationic structure for this transient. Noteworthy also is the absence of a photoproduct that could be associated with this species, the implication being that this transient decays to starting material. There is in fact evidence that this does occur, in terms of a return of the bleaching of the latter with the same rate constant as observed for decay of the transient. A cyclohexadienyl cation is obviously consistent with this, since it should deprotonate to return to parent compound.

The ability of the solvent HFIP to protonate excited aromatic compounds has been described previously for systems such as mesitylene[8b] and 1,3-dimethoxybenzene.[8c] In the case of the latter compound, evidence additional to that from flash photolysis was obtained through a study of Ar–H exchange on irradiation in $(CF_3)_2CHOD$. These experiments in particular established that protonation in the excited state occurs at the 2-position of 1,3-dimethoxybenzene, as opposed to thermal protonation that favors the 4-position. In the present study, experiments in deuterated HFIP do indeed show that there is exchange in unreacted 1-arylcyclohexene during the formation of the ether product. In the case of the *m*-methoxy derivative this was established to be occurring solely at the 2-position of the aromatic ring between the methoxy and cyclohexenyl substituents. Thus the cation in this case can be identified as above, that is, as the 2-cyclohexenyl-6-methoxybenzenonium ion. Our assumption is that protonation in the parent compound also occurs ortho to the cyclohexenyl group. There is some support for this. An *o*-methoxy substituent in a cyclohexadienyl cation results in a 40 ± 5 nm bathochromic shift in λ_{max} relative to hydrogen.[8c] The difference in the λ_{max} of the two cations in the present case, 35 nm, thus lies well within this range. Ortho and para substituents have very different effects on the λ_{max} of a cyclohexadienyl cation, a *p*-methoxy, for example, resulting in a large hypsochromic shift relative to hydrogen.[8c] Thus it is highly unlikely that there would be only a 35-nm difference if the cation obtained with the parent system were the 4-cyclohexenylbenzenonium ion. Interestingly, the present results signify that an *o*-cyclohexenyl substituent in a cyclohexadienyl cation causes a 100–110 nm bathochromic shift in λ_{max} relative to hydrogen.

Further consistency in the assignment as a cyclohexadienyl cation is seen in the actual kinetic measurements. The methoxy substituent, for example, increases the lifetime of the transient at higher wavelength by a factor of 240. This is consistent with a cation where this substituent can directly conjugate with the positive charge. In fact, the effect is very similar to the difference—a factor of 140—between the 2-methoxybenzenonium ion obtained from the photoprotonation of anisole in HFIP and the 2,6-dimethoxybenzenonium ion from 1,3-dimethoxybenzene.[8c] The lack of a significant difference across the series MeOH, EtOH, iPrOH, tBuOH (Table I) also points to a cyclohexadienyl cation. This pattern, which reflects the alcohols reacting as bases, contrasts with the order observed in their reactions as nucleophiles.

The effective quenching of the cyclohexadienyl cation by starting phenylcyclohexene can be rationalized by a reaction in which the latter acts as a carbon base.



Consistent with this mechanism are the observations of a small amount of delayed formation of the 1-phenylcyclohexyl cation and the formal addition of $(CF_3)_2CHOH$ in a portion of the ether product obtained upon irradiation in $(CF_3)_2CHOD$. As shown above, the proton transfer exchanges a benzenonium ion for a phenylcyclohexyl cation. Thus, as the former decays the latter should form at the same rate, as is observed. Moreover, forming a monodeuterated cyclohexadienyl cation by aromatic protonation in $(CF_3)_2CHOD$ followed by transfer of H to parent cyclohexene provides a nondeuterated phenylcyclohexyl cation, and derived from this, a nondeuterated ether.

It is interesting that 1-phenylcyclohexene is a much better kinetic base than a simple alcohol such as methanol in the above reaction. We have previously found that styrenes are highly effective carbon nucleophiles in HFIP, reacting, for example, with the 9-fluorenyl cation with a rate constant of $3 \times 10^9\ M^{-1}\ s^{-1}$.[17] This number is independent of substituent in the styrene, and likely it represents an encounter-controlled reaction. Thus the above reaction is also occurring at a rate that is close to the diffusion limit. The lower kinetic basicity of methanol and the other alcohols is likely associated with a hydrogen bonding interaction with the solvent tieing up the alcohol lone pairs and reducing their reactivity. A similar effect has been described previously in considerations of the nucleophilicities of oxyanions[18] and amines[19] in water.

The benzenonium ions undoubtedly arise through direct protonation of the singlet excited state of the 1-arylcyclohexene. A pathway involving the triplet can be ruled out on the basis that this transient is not observed on triplet-sensitized irradiation, whereas the cyclohexyl cation is detected under the same conditions. This observation also rules out protonation on the aryl ring of the *trans*-cyclohexene. Reasonably large amounts of HFIP (~50% by volume) are required in CH_2Cl_2–HFIP mixtures before the benzenonium ions are observed, in contrast to the situation with the arylcyclohexyl cations. The latter transient arises from a competition for the *trans*-cylcohexene, a relatively long-lived species, and thus low concentrations of the proton donor can be effective. The former, however, involves a short-lived intermediate, the singlet excited state, and larger amounts of the proton donor are required for effective trapping to occur in competition with other deactivation pathways.

Although protonation of the aromatic ring has not been considered as a deactivation route of *cis*-1-phenylcyclohexene, previous results do suggest that this occurs. Thus, Dauben and co-workers found that the fluorescence of this compound in methanol is quenched upon the addition of moderately low concentrations of sulfuric acid.[2d] This quenching was fairly effective, but it did not correlate quantitatively with the formation of the solvent adduct. This implied that the latter did not arise from direct protonation of the singlet excited state[4d] but that there was some other acid deactivation pathway. The present results suggest that this involves protonation on the aromatic ring.

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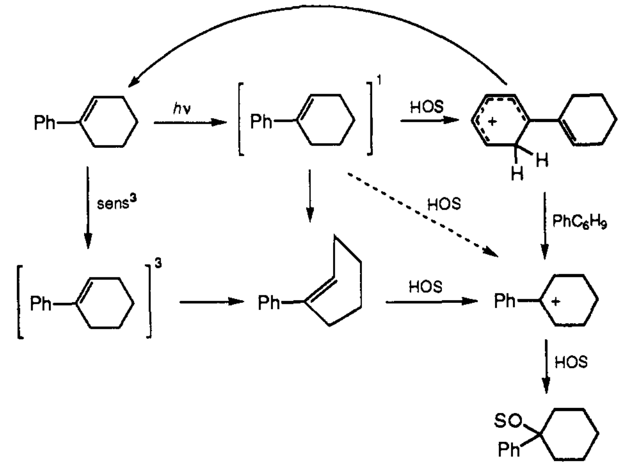
Scheme I



Summary. The photochemical reactions that occur on excitation of *cis*-1-phenylcyclohexene in HFIP (HOS) are summarized in Scheme I. The Markovnikov ether is the only photoproduct, being obtained from a 1-phenylcyclohexyl cation that is observed by flash photolysis on both direct and sensitized irradiation. This cation arises through protonation of the *trans*-1-phenylcyclohexene formed by cis–trans isomerization in both the singlet and triplet excited states. The *trans*-cyclohexene is not observed by nanosecond flash photolysis because of its rapid quenching by HFIP. Direct protonation of the singlet excited state to give the cyclohexyl cation cannot be ruled out, but it is likely a minor pathway. The singlet is however quenched by a protonation mechanism, producing a 2-benzenonium ion that is also observed with flash photolysis. This cation decays to parent *cis*-1-phenylcyclohexene by deprotonation; its presence can also be demonstrated by the observation of aromatic proton exchange in the cyclohexene upon irradiation in deuterated HFIP. 1-Phenylcyclohexyl cation can also arise from the benzenonium ion by an intermolecular proton transfer to starting *cis*-1-phenylcyclohexene.

Experimental Section

1,1,1,3,3,3-Hexafluoroisopropyl alcohol was dried over 4A molecular sieves and distilled under nitrogen through a 40-cm Vigreux column before use. $(CF_3)_2CHOD$ was prepared and purified as recently described.[8c] *cis*-1-Phenylcyclohexene was commercially available and was distilled before use. *cis*-1-(*m*-Methoxyphenyl)cyclohexene was prepared by the reaction of (*m*-methoxyphenyl)magnesium bromide with cyclohexanone, followed by dehydration of the alcohol so obtained over potassium hydrogen sulfate. The product was purified by column chromatography on basic alumina. ^{1}H NMR δ 1.5–1.8 (m, 4H), 2.15 (m, 2H), 2.4 (m, 2H), 3.79 (s, 3H), 6.12 (m, 1H), 6.75 (dd, 1H, J = 1, 8 Hz), 6.90 (t, 1H, J = 1 Hz), 6.97 (dd, 1H, J = 1, 8 Hz), 7.20 (t, 1H, J = 8 Hz). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.61; H, 8.69. Products of the irradiation of the *cis*-1-arylcyclohexenes were obtained by irradiation of ~0.07 M solutions in HFIP with 254-nm light from a low-pressure mercury lamp until GC analysis showed that the product to starting material ratio had reached about 1:1. These were separated by chromatography on basic alumna. 1,1,1,3,3,3-Hexafluoro-2-propyl 1-phenylcyclohexyl ether had NMR δ 1.5–2.0 (m, 10H), 3.92 (sept, 1H, J = 6 Hz), 7.3–7.5 (m, 5H). HRMS, calcd for $C_{15}H_{16}F_6O$ 326.1105, found 326.1113. 1,1,1,3,3,3-Hexafluoro-2-propyl 1-(*m*-methoxyphenyl)cyclohexyl ether had NMR δ 1.5–2.0 (m, 10H), 3.80 (s, 3H), 3.92 (sept, 1H, J = 6 Hz), 6.90 (dd, 1H, J = 1, 8 Hz), 7.06 (t, 1H, J = 1 Hz), 7.09 (dd, 1H, J = 1, 8 Hz), 7.33 (t, 1H, J = 8 Hz). HRMS, calcd for $C_{16}H_{18}F_6O_2$ 356.1211, found 356.1201.

Solutions employed in the laser flash photolysis experiments were prepared by adding a small amount of a stock solution of the *cis*-1-arylcyclohexene (0.1–1 M) in dichloromethane to the appropriate solvent to give a solution with a final concentration of ~0.1 mM. These were flowed through a 2 by 4 mm Suprasil quartz cell (flow rates of 0.2–0.5 mL/min) and photolyzed with 20-ns pulses of 248-nm light (20–40 mJ/pulse) from a Lamda-Physik excimer laser. Experiments with triplet sensitization were carried out with benzophenone also present at 0.1 mM and irradiation at 308 nm. The light-induced optical transmission changes were digitized by Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI11/73+ computer which also controlled the apparatus and preanalyzed the data. Final data analyses were performed on a Microvax I connected to the LSI computer.

Product analysis and isotope exchange exeriments were carried out with solutions of ~1–10 mM concentration being photolyzed with 254-nm light using a Rayonet RPR-100 reactor. The irradiated solutions were injected directly into a Varian Aerograph series 2700 Gas chromatograph with a DB5 fused silica column. Irradation for times required for 50–70% disappearance of starting material resulted in only one new product, whose GC retention time and GC/MS were identical with those of the ether sample isolated following irradiation on a larger scale.

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