

# Making Photochemically Generated Phenyl Cations Visible by Addition to Aromatics: Production of Phenylcyclohexadienyl Cations and Their Reactions with Bases/Nucleophiles

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**Abstract:** The benzenediazonium cation and its 4-fluoro, 4-chloro, 4-bromo, 4-methyl, and 4-methoxy derivatives were photolyzed in 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) with 20-ns pulses of 308-nm light from a XeCl excimer laser. This leads to a pronounced and permanent depletion of the parent compounds (quantum yields 0.89–0.96), but no signal from a transient is seen. However, on addition of aromatics such as, e.g., mesitylene, strong signals due to species with  $\lambda_{\text{max}}$  at 250–260 and 350–390 nm are detected. In the absence of bases/nucleophiles other than the aromatics, these species, which do not react with oxygen, have a lifetime in the microsecond to millisecond range. On the basis of their absorption spectra and their reactivity with typical bases/nucleophiles such as halides, alcohols, and ethers, the transients are identified as cyclohexadienyl cations formed from the photoproducted “invisible” phenyl cations by addition to the ring of the added aromatics. On the basis of competition data for reaction with HFIP and aromatic, the substituents Me, MeO, and Cl lead to a weak increase in selectivity of the phenyl cation, whereas F and Br do not influence the selectivity.

## Introduction

The reactions of arenediazonium ions have attracted considerable interest, both from a synthetic and from a mechanistic point of view.<sup>4</sup> The diazonium ions are able to undergo *homolytic* decomposition, as in the Gomberg–Bachmann reaction,<sup>5</sup> or *heterolysis*, as in, e.g., solvolysis reactions. A particularly fascinating aspect is the gradual changeover from heterolytic to homolytic dediazoniations, which leads to the question of a common intermediate for these two types of reactions.<sup>6</sup>

A point of interest for the heterolytic reactions has been whether aryl cations are real intermediates. These cations are expected to be highly reactive due to the large degree of localization of charge at C<sub>α</sub> in an orbital of significant s character.<sup>7,8</sup> This question has been positively answered on the basis of carefully performed product analysis and kinetic studies on the thermal decomposition of PhN<sub>2</sub><sup>+</sup> in H<sub>2</sub>O and in 2,2,2-trifluoroethanol.<sup>9</sup> It was, however, concluded that the phenyl cation is extremely short-lived. This result has been qualitatively supported by 337-nm laser flash photolysis studies of monosubstituted arenediazonium cations in aqueous solutions,<sup>10</sup> where it was concluded that the lifetime of the aryl cations is

probably  $\leq 0.5$  ns. In the case of *p*-amino-substituted phenyl cations, which exist in the triplet state, their lifetime in liquid solution has recently been measured to be  $< 15$  ps.<sup>11</sup> Phenyl cations stabilized by *several* methoxy groups appear to have long lifetimes in LiCl matrices at 77 K.<sup>12</sup>

We have recently found that the solvent 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)<sup>13</sup> is sufficiently weakly nucleophilic to allow the direct, time-resolved detection of highly reactive carbocations such as the (antiaromatic) 9-fluorenyl cation<sup>14</sup> or benzyl cations.<sup>15</sup> The solvent HFIP is also moderately polar ( $\epsilon = 16.6$ ),<sup>16</sup> so it should support ionic processes. Diazonium salts are obviously good precursors for carbocations because N<sub>2</sub> is such an excellent leaving group. Finally, photochemical excitation should speed up bond breakage as found in many analogous cases.<sup>17,18</sup> Therefore, the combination of benzenediazonium cations as precursors, HFIP as a solvent, and photolysis to accelerate bond rupture should provide conditions suited for the

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(2) Department of Energy, University of Madras, India.

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study of even extremely reactive carbocations such as the  $\sigma$ -type phenyl cations.

## Experimental Section

Except 4-ClC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>PF<sub>6</sub> and 4-BrC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> (from Aldrich), the (substituted) benzenediazonium compounds ArN<sub>2</sub><sup>+</sup> were synthesized (as BF<sub>4</sub><sup>-</sup> salts) using literature procedures.<sup>19</sup> The aromatic derivatives (from Aldrich, purity  $\geq$  97%) used as phenyl cation scavengers were passed over basic Al<sub>2</sub>O<sub>3</sub> in order to remove any polar impurities. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP; from Hoechst) was purified by fractional distillation over Na<sub>2</sub>SO<sub>4</sub> (to remove water), then over NaHCO<sub>3</sub> (to remove trace acid impurities), and finally by zone refining at -15 °C (to remove UV-absorbing impurities) to a purity of >99.9% (GC). The diazonium salts were dissolved in HFIP to give concentrations of 0.1–0.2 mM. Shortly after preparing the solutions (which contained in addition 0–0.2 M benzene derivative and were deoxygenated by bubbling with argon), they were pumped through the 2 × 4 mm Suprasil quartz cell (flow rates ca. 0.2–0.5 mL/min) and photolyzed with 20-ns pulses of 308-nm light (ca. 5–40 mJ/pulse) from a Lambda-Physik excimer laser. Prolonged standing of the solutions leads to trapping of moisture with a concomitant reduction of signal amplitude and lifetime. There is also a slow thermal decomposition (half-lives several hours). The light-induced optical transmission changes were digitized by Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI11/73<sup>+</sup> computer which also process-controlled the apparatus and on-line preanalyzed the data. Final data analysis was performed on a Microvax I connected to the LSI.

The error in the quantum yields and extinction coefficients is estimated as  $\pm$ 10%.

For identification of photochemical products, a  $\approx$ 1 mM solution of the diazonium salt in HFIP was photolyzed in the presence of 0.05–0.5 M benzene, toluene, or anisole with excitation at 300 nm in a Rayonet reactor. The irradiated solutions were analyzed by GC and GC–MS. Authentic samples of biphenyl, 2-methylbiphenyl, 3-methylbiphenyl, 4-methylbiphenyl, 4-methoxybiphenyl, fluorobenzene, 4-fluoroanisole (all from Aldrich), and phenyl 1,1,1,3,3,3-hexafluoroisopropyl ether and 3,5-dimethoxyphenyl 1,1,1,3,3,3-hexafluoroisopropyl ether (isolated from scaled up reactions) served as standards to verify and quantify the products. 4-Methoxyphenyl 1,1,1,3,3,3-hexafluoroisopropyl ether was identified only by GC–MS. For quantitative studies, the GC response of the particular product was determined by injecting known quantities of the standard material. Reaction of the benzenediazonium ion with the isomer ratio determined at several concentrations of toluene in the range 0.1–0.5 M was independent of concentration. The measurement of  $k_{Ar}/k_{HFIP}$  from the reaction of the benzenediazonium ion was carried out with six concentrations of benzene in the range 0.05–0.5 M in HFIP. The ratio [biphenyl]:[PhOCH(CF<sub>3</sub>)<sub>2</sub>] was obtained by GC and was linear in benzene concentration; the rate constant ratio  $k_{Ar}/k_{HFIP}$  is obtained as the slope of this plot. In all cases the reactions were carried out to approximately complete conversion, and the total yield of products (HFIP ether, fluorobenzene, and biaryls) was essentially quantitative.

## Results and Discussion

### 1. Formation of R-C<sub>6</sub>H<sub>4</sub><sup>+</sup> Adducts to 1,3,5-Trialkyl- and Hexamethylbenzenes and Their Optical Absorption Spectra.

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Deoxygenated  $\approx$ 0.1–0.2 mM solutions of the diazonium ions 4-R-C<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> (R = H, Br, Cl, Me, MeO) were irradiated in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at 20  $\pm$  1 °C with 20-ns pulses of 308-nm light. Permanent negative changes of optical density (OD) were seen at the wavelengths of the two main absorption bands of the parents (between 260 and 320 nm and between  $\leq$ 200 and 235 nm for R = H to MeO). The amount of depletion of the diazonium ions was strictly proportional to laser dose, showing that the process is monophotonic. Negative signals arise when the precursor is more absorbing at a particular wavelength than the product (or intermediate) that is formed on photolysis. With our system, the light-induced “negative” spectra were within experimental error ( $\pm$ 10%) exact mirror images of the absorption spectra of the starting materials. This shows that the products of the photolysis have much weaker absorptions than the diazonium cations. The (negative) signals were the same with respect to shape and amplitude when the solutions were saturated with oxygen, indicating that the photolysis probably does not lead to radicals since these would be scavenged by oxygen leading to peroxy radicals which absorb in the 230–250-nm region. Absence of observable transients was also reported for aqueous solutions of benzenediazonium salts on photolysis with 337-nm light.<sup>10</sup>

The quantum yields for depletion of the arenediazonium cations were determined by measuring the pulse-induced (negative)  $\Delta$ OD changes (in a range of laser dose varying by a factor of 5) at or close to the  $\lambda_{max}$  of the diazonium absorption bands and comparing them with the (positive)  $\Delta$ OD obtained at 320 nm on photolysis of a solution in acetonitrile of acetophenone of the same absorbance at 308 nm as that of the diazonium salt. With acetophenone, the transient absorbing at 320 nm is the triplet whose extinction coefficient is 12 600 M<sup>-1</sup> cm<sup>-1</sup> and which is formed with a quantum yield of unity.<sup>20</sup> On this basis, the quantum yields for destruction of the diazonium cations R-C<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> were found to be 0.91 (R = H), 0.92 (R = Me), 0.96 (R = MeO), 0.89 (R = F), 0.93 (R = Cl), and 0.91 (R = Br), which are essentially twice the values measured for (some of) the cations in water–methanol mixtures.<sup>21</sup>

To the solutions containing the diazonium ions were then added alkylated benzenes, in particular, symmetric 1,3,5-trisubstituted ones. As an example, in Figure 1 is shown the result obtained on 308-nm photolysis of 4-MeO-C<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> in the presence of 1,3,5-triisopropylbenzene (TPB). In addition to the pronounced depletion of the parent diazonium ion (at  $\approx$ 310 nm), one now observes *positive*  $\Delta$ OD at three wavelengths: approximately equally strong bands at 365 and 260 nm and a band (by a factor  $\approx$  10 stronger) at  $\approx$ 200 nm (shown in reduced size in Figure 1). These band positions and relative intensities are very similar to those of the cyclohexadienyl-type cations formed by *protonation* of these trialkylbenzenes (see Table 1). The latter cations can be formed by proton addition to the *ground-state* aromatic in superacids, where NMR studies establish that they are 2,4,6-trialkylbenzenonium ions, i.e., arising from protonation at a nonalkylated position.<sup>22,23</sup> These

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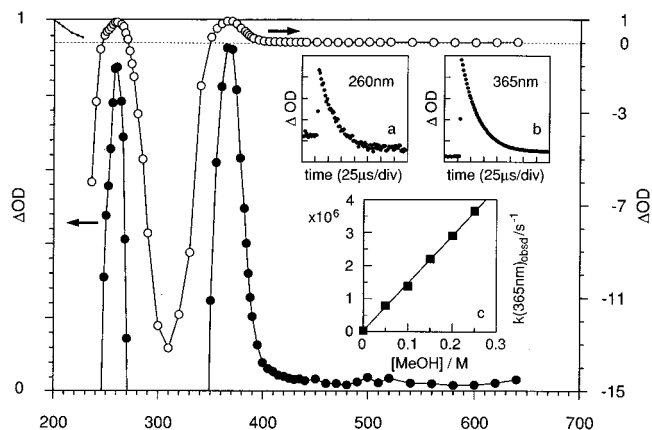
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**Table 1.** Absorption Maxima  $\lambda_1$  and  $\lambda_2^a$  (nm) of the Cyclohexadienyl (CHD) Cations Formed by Addition of  $p$ -R-C<sub>6</sub>H<sub>4</sub><sup>+</sup> to Alkyl-Substituted Benzenes (Ar) in HFIP and Partitioning of R-C<sub>6</sub>H<sub>4</sub><sup>+</sup> between Ar and HFIP

Ar <sup>b</sup>	$p$ -R-C <sub>6</sub> H <sub>4</sub> <sup>+</sup>													
	R = H		R = Me		R = OMe		R = F		R = Cl		R = Br		H <sup>+</sup> adduct	
	$\lambda_1$	$\lambda_2$	$\lambda_1$	$\lambda_2$	$\lambda_1$	$\lambda_2$	$\lambda_1$	$\lambda_2$	$\lambda_1$	$\lambda_2$	$\lambda_1$	$\lambda_2$	$\lambda_1$	$\lambda_2$
1,3,5-TMB	350	260	354	260	356	264	353	258	353	258	352	257	350 <sup>c</sup>	260 <sup>c</sup>
1,3,5-TEB	362	264	363	264	362	260	357	258	362	262	357	262	360 <sup>d</sup>	260
1,3,5-TPB	363	264	363	264	366	260	362	260	364	260	362	262	365 <sup>d</sup>	260
1,3,5-TBB	371	268	374	266	374	276	367	263	373	267	370	268	370 <sup>d</sup>	270
HMB	386	273	394	270	390	272	394	266	388	270	388	272	390 <sup>c</sup>	275 <sup>c</sup>
$k_{Ar}/k_{HFIP}^e$														
	R = H		R = Me		R = OMe		R = F		R = Cl		R = Br			
1,3,5-TEB	140		150		190		150		220		110			
1,3,5-TPB	72		100		100		120		120		80			
1,3,5-TBB					73		80		84		60			
HMB	34		42		60		30		90		40			
benzene	7 <sup>f</sup>													
Apparent Quantum Yield for Formation of CHD Cation <sup>g</sup>														
	R = H		R = Me		R = OMe		R = F		R = Cl		R = Br		H <sup>+</sup> adduct	
1,3,5-TMB	0.27		0.31		0.32		0.28		0.51		0.35		0.08 <sup>c</sup>	
HMB	0.18		0.23		0.26		0.20		0.47		0.26		0.04 <sup>c</sup>	

<sup>a</sup> The  $\lambda_{max}$  values are accurate to  $\pm 3$  nm. In all cases there is a third absorption band at  $\lambda \approx 200$  nm (see text and Figure 1). <sup>b</sup> 1,3,5-TMB = 1,3,5-trimethylbenzene; 1,3,5-TEB = 1,3,5-triethylbenzene, 1,3,5-TPB = 1,3,5-triisopropylbenzene; 1,3,5-TBB = 1,3,5-tri-*tert*-butylbenzene; HMB = hexamethylbenzene. <sup>c</sup> From ref 24. See also: Cozens, F. Ph.D. Thesis, University of Toronto, 1991. <sup>d</sup> From Cozens, F. Ph.D. Thesis, University of Toronto, 1991. <sup>e</sup> Value obtained from the competition analysis of the dependence on [Ar] (in the range 0 to  $\approx 0.1$  M) of the yield of CHD<sup>+</sup>, see eq 6. Error limits  $\pm 15\%$ . Unitless, both  $k_{Ar}$  and  $k_{HFIP}$  are expressed as second-order rate constants. <sup>f</sup> From the dependence on [benzene] of the product ratio [biphenyl]:[C<sub>6</sub>H<sub>5</sub>OCH(CF<sub>3</sub>)<sub>2</sub>] determined by GC. <sup>g</sup> Measured using 0.2 M Ar. The quantum yields are based on the assumption that the  $\epsilon$  values at  $\lambda_1$  are the same as that of the H<sup>+</sup> adduct of 1,3,5-TMB ( $\epsilon$  at 358 nm = 9200 M<sup>-1</sup> cm<sup>-1</sup>, ref 22b) or of HMB ( $\epsilon$  at 392 nm = 10 400 M<sup>-1</sup> cm<sup>-1</sup>, ref 22b), and using the acetophenone triplet for calibration (see text).



**Figure 1.** Changes in OD (normalized to 100 mJ/laser pulse) observed at 250 ns after the pulse on 308-nm photolysis of an air-saturated 0.1 mM solution of 4-MeO-C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> in HFIP at 20  $\pm$  1  $^{\circ}$ C in the presence of 50 mM 1,3,5-triisopropylbenzene. The upper part (above the dashed line) shows *positive* bands at 365, 260, and  $\leq 200$  nm (the 200-nm band is shown compressed in size by the factor 10) and a strong negative band at  $\approx 310$  nm. The part below the dashed line (OD scale is on the left-hand side) is an expansion (by the factor 16) of the positive  $\Delta$ OD of the upper part. In the insets a and b are presented the decays of the CHD cation at 260 and 365 nm. Inset c shows the dependence on [MeOH] of the rate of decay of the cation measured at 365 nm.

same cations with identical absorption spectra are produced also upon 248-nm-light-induced protonation of the first *excited singlet state* of the trialkylbenzene in the solvent HFIP.<sup>24,25</sup> The

(23) For a review, see: Koptiyuk, V. A. Arenium Ions—Structure and Reactivity. In *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer: Berlin, 1984; Vol. 122, p 96.

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(25) In a manner similar to that observed with TMB,<sup>24</sup> the H<sup>+</sup> adducts of TEB, TPB, and TBB have been produced by 248-nm photoprotonation in HFIP (Cozens, F. Dissertation, University of Toronto, 1992).

trialkylbenzenes, however, have no absorption at 308 nm, and an experiment carried out under the same conditions as that of Figure 1, but with no diazonium salt present, produced no transient upon 308-nm excitation. This rules out the possibility that the cyclohexadienyl-type spectrum obtained with the diazonium ion arises by a photoprotonation mechanism.

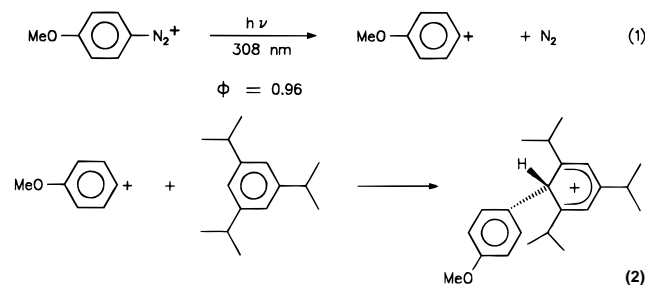
The upper part (above the dashed line) shows *positive* bands at 365, 260, and  $\leq 200$  nm (the 200-nm band is shown compressed in size by the factor 10) and a strong negative band at  $\approx 310$  nm. The part below the dashed line (OD scale is on the left-hand side) is an expansion (by the factor 16) of the positive  $\Delta$ OD of the upper part. In the insets a and b are presented the decays of the CHD cation at 260 and 365 nm. Inset c shows the dependence on [MeOH] of the rate of decay of the cation measured at 365 nm.

The absorptions were found to decay by first-order kinetics with the *same rates* in the regions 250–270 and 350–390 nm, consistent with a *single* transient. The rates were not influenced by oxygen nor was the shape of the absorption spectrum altered, evidence that there are *no detectable radicals* present in the system. However, addition of small concentrations of nucleophiles/bases such as halides, alcohols, or ethers led to a drastic reduction of the lifetime of the transient. This kinetic behavior is characteristic for carbocations,<sup>17,18</sup> including cyclohexadienyl cations generated by photoprotonation in HFIP.<sup>24</sup>

These observations, especially the absorption spectra that make it clear<sup>22–24</sup> that the cation is of the cyclohexadienyl (CHD) type, suggest a mechanism involving photoheterolysis of the diazonium ion (eq 1) followed by attachment of the aryl cation to the trialkylbenzene to form a 1-aryl-2,4,6-trialkylbenzenonium ion (e.g., eq 2).

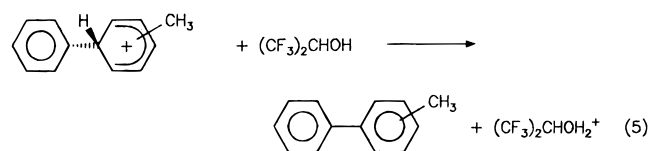
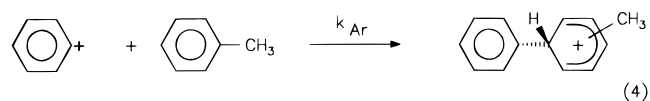
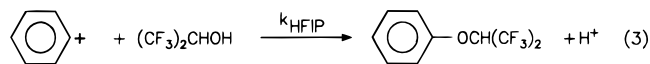
To further test whether photohomolysis is a side reaction in the dediazonium,  $\approx 0.5$  mM solutions of 4-MeO-C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> in HFIP (with 2% cyclohexane added as an H donor) were





photolyzed with a medium-pressure Hg lamp using a cutoff filter at 300 nm, and after 10–50% conversion, the solutions were analyzed by GC for anisole, the product expected from the 4-methoxyphenyl radical. No traces of anisole were found, which is strong evidence that in HFIP decomposition of the electronically excited 4-methoxybenzenediazonium cation does not proceed by homolysis. Analogously, in the case of the 3,5-dimethoxybenzenediazonium ion, photolysis in HFIP was found to lead to the 3,5-dimethoxyphenyl ether of HFIP as the product (characterized by both GC/MS and NMR) and no 3,5-dimethoxybenzene, which again shows that photodediazoni-ation occurs by *heterolysis* (analogous to eq 1).

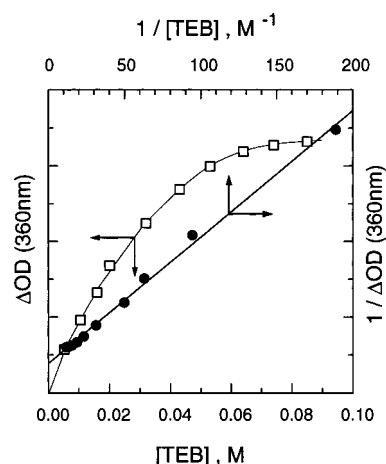
The first-order decay of the CHD cation is proposed to be due to reaction with solvent (analogous to eq 5), the latter acting as a Brønsted base. The CHD cation (the Brønsted acid) deprotonates to give the corresponding phenyl-substituted aromatic.<sup>26</sup> This is concluded from product analysis data on the reaction when  $\text{C}_6\text{H}_5^+$  is formed photochemically in HFIP containing 0.1–0.5 M toluene. In addition to the ether  $\text{PhOCH}(\text{CF}_3)_2$ , the product from reaction with the solvent (eq 3), the three methyl biphenyls are formed as products with an *o:m:p* ratio of 55:22:23 (eqs 4 and 5). This isomer ratio indicates that the phenyl cation is electrophilic but has only a low regioselectivity with toluene.<sup>27</sup> When toluene was replaced by benzene, biphenyl was a product. A similar experiment with 4-MeOC<sub>6</sub>H<sub>4</sub><sup>+</sup> in the presence of benzene yielded 4-MeOC<sub>6</sub>H<sub>4</sub>-OCH(CF<sub>3</sub>)<sub>2</sub> and 4-methoxybiphenyl (and 4-fluoroanisole, see later).



Spectra similar to that shown in Figure 1 were observed on photolysis of 4-MeO-C<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> in the presence of other benzene derivatives such as mesitylene (1,3,5-trimethylbenzene (TMB)), 1,3,5-triethylbenzene (TEB), 1,3,5-triisopropylbenzene (TPB), 1,3,5-tri-*tert*-butylbenzene (TBB), and hexamethylbenzene (HMB) or on photolysis of the diazonium cations 4-R-C<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> (R = H, Me, Br, Cl) in the presence of these aromatics.<sup>28</sup> In every

(26) In an analogous system, the rate of deprotonation from the cation was found to be larger than that for addition of the (highly nucleophilic) solvent water to the cation (see: Boyd, D. A.; McMordie, R. A. S.; Sharma, N. D.; More O'Ferrall, R. A.; Kelly, S. C. *J. Am. Chem. Soc.* **1990**, *112*, 7822).

(27) For comparison, a considerably larger regioselectivity is shown by the 9-fluorenyl cation in the reaction with toluene (*o:m:p* ratio = 5:5:90).<sup>33</sup>



**Figure 2.** Dependence on [TEB] of the yield (OD) of CHD cation (measured at 360 nm) from the reaction of 4-ClC<sub>6</sub>H<sub>4</sub><sup>+</sup> (from 308-nm photolysis of 0.1 mM of the PF<sub>6</sub><sup>-</sup> salt) with TEB in air-saturated HFIP, squares. The filled circles contain the same data, however analyzed according to competition (see text) for 4-ClC<sub>6</sub>H<sub>4</sub><sup>+</sup> between HFIP and TEB.

case the transient had a band in the region 350–390 nm, one at ≈260–270 nm, and one at ≈200 nm.<sup>29</sup> Consistent with the presence of only one species, the rate of decrease of OD (measured at 250–260 and 340–400 nm) was found to be in all cases independent of wavelength. As shown in Table 1, the spectroscopic data are characteristic for CHD cations.<sup>22–24</sup>

Examination of the effect of substituents on the position of the bands reveals that the substituent R (on the *phenyl cation*) has *no* influence, whereas substituents on the *aromatic* shift  $\lambda_{\text{max}}$  to higher wavelengths with increasing number or electron-donating power (e.g., for the first band,  $\lambda_{\text{max}}$  increases from 350 to 390 nm in going from TMB to HMB).

**2. Reactivity of 4-RC<sub>6</sub>H<sub>4</sub><sup>+</sup>.** As expected on the basis of eqs 2 and 3, the yield of CHD cations was found to increase with the concentration of the aromatic scavenger. Figure 2 (squares) shows a typical dependence of CHD<sup>+</sup> optical density on the concentration of the aromatic. The plot is not linear; at higher concentrations of the scavenger the yield tends toward a plateau. Such a dependence can be quantitatively explained in terms of competition for the aryl cation Ar'<sup>+</sup> between the aromatic Ar (eq 4) and the solvent (eq 3). This leads to eq 6,

$$1/\text{OD}(\text{CHD}^+) = \text{const} + \{[(\text{const})k_{\text{HFIP}}[\text{HFIP}]]/(k_{\text{Ar}}[\text{Ar}])\} \quad (6)$$

where  $k_{\text{HFIP}}$  and  $k_{\text{Ar}}$  are second-order rate constants for reaction of the solvent and aromatic and  $\text{const} = 1/(\epsilon(\text{CHD}^+)d[\text{Ar}'^+])$ . In the latter term,  $\epsilon(\text{CHD}^+)$  is the extinction coefficient of the cyclohexadienyl cation,  $d$  is the path length of the cell (4 mm), and  $[\text{Ar}'^+]$  is the constant concentration of Ar'<sup>+</sup> produced in the pulse at fixed  $[\text{Ar}'\text{N}_2^+]$  and laser dose. Equation 6 predicts that a plot of  $1/\text{OD}(\text{CHD}^+)$  vs  $1/[\text{Ar}]$  should be a straight line whose intercept if divided by its slope is equal to  $k_{\text{Ar}}/(k_{\text{HFIP}}[\text{HFIP}])$ .

(28) (a) Other alkylated benzenes such as toluene, the xylenes, and additional polymethylated benzenes also give absorption spectra characteristic of CHD cations. In some cases, there is evidence for the formation of more than one isomer (Ashokkumar, M.; Steenken, S. Unpublished results). (b) In the case of 4-FC<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup>, the strong absorption of the diazonium ion at ≈260–280 nm makes it impossible to measure the expected  $\lambda_2$  band of the CHD cation.

(29) Experimentally, the band at ≈200 nm is not easy to detect, due to the very low levels of analyzing light intensity typically available at this wavelength. The exact position of this band is therefore not known with sufficient precision and thus not given in Table 1.

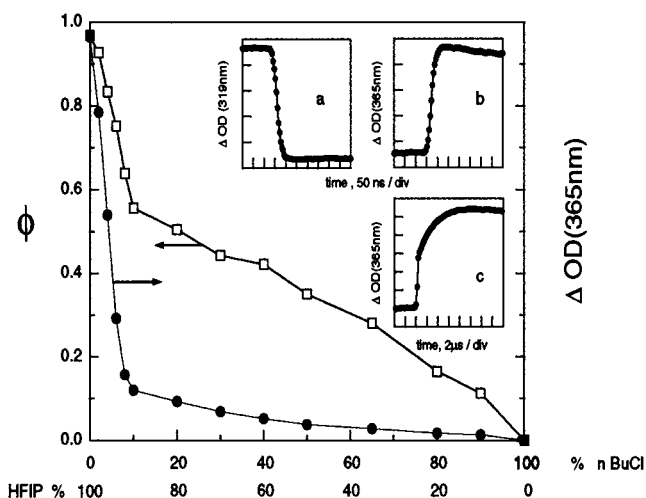
Figure 2 depicts such a competition plot for the system 4-ClC<sub>6</sub>H<sub>4</sub><sup>+</sup> plus TEB. From the slope of the straight line (full circles) and the intercept and taking [HFIP] = 9.5 M, the ratio  $k_{Ar}/k_{HFIP}$  is calculated to be 220. Values ranging between 30 and 290 thus determined for a series of phenyl cations and aromatics are presented in the second section of Table 1.

The question arises as to whether the aryl cation that is reacting here is in the ground state or in some vibrationally or electronically excited state. If the assumption is made that the aryl cation reacts with the aromatic with a rate constant  $\sim 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (see later), the lifetimes of the aryl cations in this system are on the order of a few nanoseconds. Barring some unusual behavior of excited aryl cations, such lifetimes are significantly long to ensure that the intermediate has reached its ground state before capture by nucleophiles.

These data show that the parent phenyl cation (R = H) is the least selective (most reactive) ion and that Me, MeO, and Cl increase the preference for reaction with the aromatic relative to solvent. The effect is, however, not very large (factor  $\leq 2$ ). Since the substituent is remote from the reaction site, the observed effect cannot be of steric but must be of electronic nature. It is interesting that not only MeO but also Cl appear to act as electron-donating groups with respect to the positive charge in the  $\sigma$ -orbital of the phenyl cation. This has been predicted on theoretical grounds<sup>7</sup> on the basis of through-bond interaction of the lone pairs of the substituent with the  $\sigma$ -orbital of the cationic site.<sup>30</sup> In contrast to Cl is the effect of F and of Br: These atoms do *not* increase the selectivity of the phenyl cation with respect to Ar and HFIP. It is notable that a strongly destabilizing effect predicted<sup>8</sup> for F does not show up in the reactivity of the cation.

The preference of the phenyl cations to react with the aromatic relative to HFIP decreases in going from 1,3,5-trimethyl- to the corresponding isopropyl and tert-butyl compounds. This is likely caused by the increasing steric hindrance in this series which dominates over the increasing electron-donating effect of the alkyl substituents. The fully methylated compound HMB is the most electron-rich (on the basis of the ionization potentials<sup>31</sup>) or most basic<sup>32</sup> compound of the series and is therefore expected to react most rapidly if the electron density or basicity were decisive. The aryl cation however has to add to an ipso position, i.e., an already occupied position. The steric hindrance exerted by the methyl group at the reaction site slows the addition reaction down to the extent that the resulting rate is a factor  $\approx 4$  lower than in the case of the less electron-rich or less basic but sterically more accessible TMB.

As a further check of the competition data, the quantum yields for formation of CHD cation were determined by measuring the OD changes at the CHD<sup>+</sup>  $\lambda_{\text{max}}$  values, using the acetophenone triplet for actinometry (see section 1) and assuming that the extinction coefficients of the phenyl-CHD<sup>+</sup>'s are the same as those<sup>22,24</sup> of the corresponding proton adducts. The values found are listed in the last section of Table 1. They are between 0.2 and 0.5, i.e., a factor of 2–3 lower than expected on the basis of the  $k_{Ar}/k_{HFIP}$  ratios and the scavenging capacity of Ar at 0.2 M. There is one simple explanation possible for this impfection: The extinction coefficients of the phenyl-CHD cations are lower than those<sup>22,24</sup> of the corresponding H<sup>+</sup> adducts. An additional possibility is that there is ion pairing



**Figure 3.** Dependence of the quantum yield for depletion of 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> (squares) and the yield of CHD cation (measured by the  $\Delta\text{OD}$  at 365 nm) from the reaction of 4-MeOC<sub>6</sub>H<sub>4</sub><sup>+</sup> with 0.2 M TPB in HFIP-*n*-BuCl mixtures (full circles). Inset a shows the kinetics of depletion of 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> and inset b that for formation of the CHD<sup>+</sup> on the same time scale, both in pure HFIP. Inset c shows the slow additional buildup (2  $\mu\text{s}/\text{div}$ ) of the CHD cation from 4-MeOC<sub>6</sub>H<sub>4</sub><sup>+</sup> and 0.2 M TPB in 80% *n*-BuCl/20% HFIP, see footnote 38.

between Ar<sup>+</sup>N<sub>2</sub><sup>+</sup> and BF<sub>4</sub><sup>-</sup> (or PF<sub>6</sub><sup>-</sup>) and that some of the photochemically produced phenyl cations are scavenged by the counteranion before they react with the aromatic to give the CHD cation. In support of this is the observation in yields of 20–25% of the product C<sub>6</sub>H<sub>5</sub>F from the parent or 4-MeOC<sub>6</sub>H<sub>4</sub>F from the 4-methoxybenzenediazonium salt. (The possibility also exists that these fluorinated products are derived from fluoride extraction from the solvent.)

An attempt was made to measure the rate constants  $k_{Ar}$  directly by monitoring the rate of buildup of CHD cations at low concentrations of Ar. Down to concentrations of  $\approx 10 \text{ mM}$ , the rates were found to be  $\approx 5 \times 10^7 \text{ s}^{-1}$ , essentially independent of [Ar]. The value of  $5 \times 10^7 \text{ s}^{-1}$  corresponds to the reciprocal of the laser pulse width (20 ns) and thus reflects the effective time resolution of the apparatus (see Figure 3, insets a and b, for an example). At concentrations below 10 mM the signal amplitudes (see, e.g., Figure 2) were not sufficiently strong for reliable analysis. Taking  $k_{\text{obsd}}$  for the formation of CHD<sup>+</sup> at 10 mM Ar to be  $\geq 5 \times 10^7 \text{ s}^{-1}$ ,  $k_{Ar}$  results as  $\geq 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . This number is reasonable considering the value of  $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  directly measured<sup>14c</sup> for reaction of the more stabilized and sterically more demanding 9-fluorenyl cation with TMB. The aryl cations are likely reacting at the diffusion limit (or at least very near it), and thus, a value of  $5 \times 10^9$  is not unexpected. Taking  $5 \times 10^9$  for  $k_{Ar}$ , 100–200 for  $k_{Ar}/k_{HFIP}$ , and [HFIP] in HFIP = 9.5 M, the lifetimes of the aryl cations are 2–4 ns,<sup>33</sup> shorter than the laser pulse with our instrument. It is therefore not surprising that transients<sup>11</sup> are not seen on photolysis of the diazonium salts in the absence of the aromatic scavengers.<sup>34</sup>

**3. Solvent Effects.** The substituted benzenediazonium ions were also photolyzed in other solvents, such as 2,2,2-trifluoro-

(33) (a) With lifetimes of this order of magnitude, most of the reaction of the cation with the added nucleophile is occurring through the free ion, and preassociation of the nucleophile with the precursor does not account for much of the trapping. For example, the 4-chloro-*N*-acetylnitrenium ion is estimated to have a lifetime (in water) of 0.6 ns; around 75% of its reaction with added azide ion is still occurring through the free ion.<sup>33b</sup> (b) Novak, M.; Kahley, M. J.; Lin, J.; Kennedy, S. A.; James, T. G. *J. Org. Chem.* **1995**, *60*, 8294.

(30) It is also possible that the substituent effect is due to changes in the spin multiplicity of the cation, cf. refs 11 and 12.

(31) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6* (Suppl. 1), 1.

(32) See ref 22d. For a review on basicity of aromatics, see: Perkampus, H.-H. *Adv. Phys. Org. Chem.* **1966**, *4*, 195.

**Table 2.** Rate Constants<sup>a</sup> (M<sup>-1</sup> s<sup>-1</sup>) for Reaction of 1-(*p*-R-C<sub>6</sub>H<sub>4</sub>)Benzenium Ions R-C<sub>6</sub>H<sub>4</sub>-Ar<sup>+</sup> with Bases/Nucleophiles in HFIP at 20 ± 1 °C

R	Ar	HFIP <sup>b</sup>	MeOH	EtOH	2-PrOH	<sup>t</sup> BuOH	THF	1,4-diox.	Br <sup>-</sup>
H	2,4,6-Me <sub>3</sub>	1.2 × 10 <sup>5</sup> (1 × 10 <sup>5</sup> ) <sup>c</sup>	1.2 × 10 <sup>7</sup>	1.7 × 10 <sup>7</sup>	1.5 × 10 <sup>7</sup>	1.0 × 10 <sup>7</sup>	1.7 × 10 <sup>7</sup>	5.1 × 10 <sup>6</sup>	3.5 × 10 <sup>9</sup>
H	2,4,6-Et <sub>3</sub>	4.5 × 10 <sup>4</sup> (7.4 × 10 <sup>4</sup> ) <sup>d</sup>	1.0 × 10 <sup>7</sup>				8.3 × 10 <sup>6</sup>	3.0 × 10 <sup>6</sup>	2.7 × 10 <sup>9</sup>
H	2,4,6- <sup>i</sup> Pr <sub>3</sub>	4.5 × 10 <sup>4</sup> (3.3 × 10 <sup>4</sup> ) <sup>d</sup>	1.3 × 10 <sup>7</sup>				8.5 × 10 <sup>6</sup>	1.7 × 10 <sup>6</sup>	2.9 × 10 <sup>9</sup>
H	2,4,6- <sup>t</sup> Bu <sub>3</sub>	1.6 × 10 <sup>6</sup> (1.4 × 10 <sup>4</sup> ) <sup>d</sup>	1.4 × 10 <sup>7</sup>				3.9 × 10 <sup>7</sup>	1.0 × 10 <sup>7</sup>	6.5 × 10 <sup>9</sup>
Cl	2,4,6-Me <sub>3</sub>	1.5 × 10 <sup>5</sup>	1.9 × 10 <sup>7</sup>	2.1 × 10 <sup>7</sup>	1.7 × 10 <sup>7</sup>	1.3 × 10 <sup>7</sup>	1.7 × 10 <sup>7</sup>	7.1 × 10 <sup>6</sup>	5.2 × 10 <sup>9</sup>
Cl	2,4,6-Et <sub>3</sub>	5.3 × 10 <sup>4</sup>	1.2 × 10 <sup>7</sup>				1.0 × 10 <sup>7</sup>	3.5 × 10 <sup>6</sup>	3.3 × 10 <sup>9</sup>
Cl	2,4,6- <sup>i</sup> Pr <sub>3</sub>	4.8 × 10 <sup>4</sup>	1.5 × 10 <sup>7</sup>				1.4 × 10 <sup>7</sup>	4.4 × 10 <sup>6</sup>	4.9 × 10 <sup>9</sup>
Cl	2,4,6- <sup>t</sup> Bu <sub>3</sub>	1.7 × 10 <sup>6</sup>	1.7 × 10 <sup>7</sup>				3.5 × 10 <sup>7</sup>	1.1 × 10 <sup>7</sup>	5.1 × 10 <sup>9</sup>
Br	2,4,6-Me <sub>3</sub>	2.2 × 10 <sup>5</sup>							
Br	2,4,6-Et <sub>3</sub>	6.2 × 10 <sup>4</sup>							
Br	2,4,6- <sup>i</sup> Pr <sub>3</sub>	4.5 × 10 <sup>4</sup>							
Br	2,4,6- <sup>t</sup> Bu <sub>3</sub>	2.5 × 10 <sup>6</sup>							
MeO	2,4,6-Me <sub>3</sub>	1.6 × 10 <sup>5</sup>	1.3 × 10 <sup>7</sup>	1.9 × 10 <sup>7</sup>	1.5 × 10 <sup>7</sup>	1.0 × 10 <sup>7</sup>	1.6 × 10 <sup>7</sup>	5.2 × 10 <sup>6</sup>	5.3 × 10 <sup>9</sup>
MeO	2,4,6-Et <sub>3</sub>	4.5 × 10 <sup>4</sup>	1.1 × 10 <sup>7</sup>				8.0 × 10 <sup>6</sup>	3.6 × 10 <sup>6</sup>	3.4 × 10 <sup>9</sup>
MeO	2,4,6- <sup>i</sup> Pr <sub>3</sub>	4.2 × 10 <sup>4</sup>	1.4 × 10 <sup>7</sup>	4.1 × 10 <sup>6</sup> <sup>e</sup>			1.4 × 10 <sup>7</sup>	4.6 × 10 <sup>6</sup>	4.7 × 10 <sup>9</sup>
MeO	2,4,6- <sup>t</sup> Bu <sub>3</sub>	1.8 × 10 <sup>6</sup>	1.8 × 10 <sup>7</sup>				3.8 × 10 <sup>7</sup>	1.1 × 10 <sup>7</sup>	3.7 × 10 <sup>9</sup>
H	(Me) <sub>6</sub>	4.8 × 10 <sup>3</sup>	1.0 × 10 <sup>6</sup>				1.1 × 10 <sup>6</sup>	3.8 × 10 <sup>5</sup>	8.8 × 10 <sup>8</sup>
Cl	(Me) <sub>6</sub>	3.8 × 10 <sup>3</sup>	1.3 × 10 <sup>6</sup>				1.9 × 10 <sup>6</sup>	3.3 × 10 <sup>5</sup>	6.6 × 10 <sup>8</sup>
Br	(Me) <sub>6</sub>	4.5 × 10 <sup>3</sup>							
MeO	(Me) <sub>6</sub>	4.8 × 10 <sup>3</sup>	1.1 × 10 <sup>6</sup>				2.0 × 10 <sup>6</sup>	3.9 × 10 <sup>5</sup>	6.5 × 10 <sup>8</sup>
									3.1 × 10 <sup>7</sup> <sup>f</sup>
									≥ 1.7 × 10 <sup>8</sup> <sup>g</sup>
									1.7 × 10 <sup>9</sup> <sup>h</sup>

<sup>a</sup> Determined at the  $\lambda_{\max}$  values of the cations (see Table 1). Error limits ±15%. <sup>b</sup>  $k_s$ . Units of s<sup>-1</sup>. <sup>c</sup> Rate constant for decay of H<sup>+</sup> adduct of Ar, obtained<sup>24</sup> by photoprotonation. <sup>d</sup> Rate constant for decay of H<sup>+</sup> adduct of Ar, obtained<sup>39</sup> by photoprotonation. <sup>e</sup> Value refers to reaction with H<sub>2</sub>O and was determined in the [H<sub>2</sub>O] range 0–0.1 M. <sup>f</sup> Value refers to F<sup>-</sup>. <sup>g</sup> Value refers to Cl<sup>-</sup>. <sup>h</sup> Value refers to I<sup>-</sup>.

roethanol (TFE), water, acetonitrile, dimethyl sulfoxide, tetrahydrofuran, 1,4-dioxane, cyclohexane, dichloromethane, 1,2-dichloroethane, or *n*-butyl chloride. For the case of R = MeO, the quantum yields for depletion of the diazonium cation were determined as described previously. The most acidic and least nucleophilic solvent HFIP (pK<sub>a</sub> = 9.3)<sup>35</sup> is superior to the others in promoting the photoinduced decomposition ( $\phi = 0.96$ , determined via the depletion of the arenediazonium ions, vide supra). The less acidic and more nucleophilic TFE (pK<sub>a</sub> = 12.4)<sup>35</sup> is a factor of 2 less efficient ( $\phi = 0.52$ ).<sup>36</sup> A similar value is obtained for water, for which the quantum yield (0.54) is in excellent agreement with that<sup>21</sup> obtained by product analysis techniques. Since water is even less acidic and more nucleophilic than TFE, it is probably the higher polarity which supports decomposition. In the polar solvent acetonitrile, photochemical decomposition is also quite efficient ( $\phi = 0.30$ ), as is the case for dimethyl sulfoxide (0.42) and dioxane (0.45). In contrast, in the nonpolar solvents cyclohexane and *n*-butyl chloride, the diazonium cation appears to be photostable. No decrease of OD was seen at 320 nm on photolysis ( $\phi \approx 0$ ).<sup>37</sup>

Figure 3 shows the effect on the quantum yield for depletion of 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> and on the yield of CHD cation from the reaction of 4-MeOC<sub>6</sub>H<sub>4</sub><sup>+</sup> with TPB when increasing amounts of *n*-butyl chloride are added to HFIP solutions of the reactants. The *n*-butyl chloride suppresses the decomposition of the diazonium cation very strongly and inhibits the formation of the CHD cation even more efficiently.<sup>38</sup>

An attempt was also made to produce CHD cations in TFE, which is a stronger nucleophile than HFIP. For this purpose, a 0.2 mM 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> solution containing 1 M TPB was

(34) It is likely that the extinction coefficients of phenyl cations are very low, based on analogy with phenyl radicals. This decreases further the chance of detecting the cations optically. Triplet-state phenyl cations have recently been determined<sup>11</sup> to have lifetimes of ≤15 ps.

(35) See: Schrems, O.; Oberhoffer, H. M.; Luck, W. A. P. *J. Phys. Chem.* **1984**, *88*, 4335.

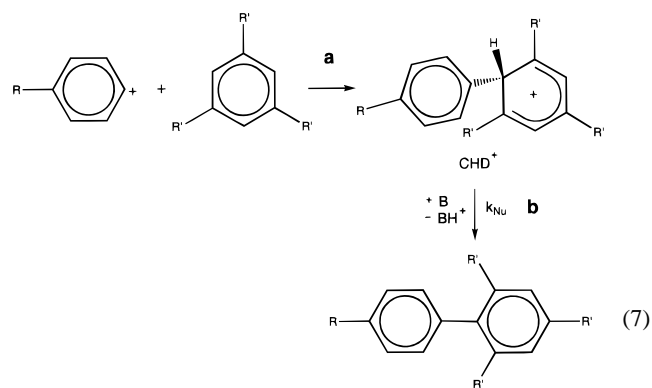
(36) A similar value ( $\phi = 0.45$ ) has been measured for decomposition of 4-morpholinobenzenediazonium tetrafluoroborate (ref 11).

(37) The high value ( $\phi = 0.52$ ) found for the weakly polar solvent tetrahydrofuran is noticeable.

photolyzed. A relatively weak transient was seen with  $\lambda_{\max} \approx 360$  nm, which reacted rapidly with O<sub>2</sub> but not with ethanol. This is a behavior opposite to that observed in HFIP. The conclusion is that this transient is a radical but not a cation. If it is assumed that (a) MeOC<sub>6</sub>H<sub>4</sub><sup>+</sup> is produced in TFE, (b) it reacts with TPB with  $k \geq 5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, and (c) the resulting CHD<sup>+</sup> has a lifetime ≥1 μs, the failure to see a CHD<sup>+</sup> means that the lifetime of MeOC<sub>6</sub>H<sub>4</sub><sup>+</sup> in TFE is ≤200 ps.

#### 4. Reactions of Phenylcyclohexadienyl Cations with Bases.

These reactions, eq 7b, were studied by adding small amounts



of alcohols, ethers, or bromide (as a tetra-*n*-butylammonium salt) to the solutions containing a benzenediazonium ion and one of the aromatic derivatives. Such addition resulted in (a)

(38) In mixtures containing, e.g., 80% *n*-butyl chloride, there is a considerably delayed, first-order further formation of CHD<sup>+</sup> on top of a rapidly formed component. The rate of this delayed process was found to be independent of the concentration of the aromatic in the range 0.09–1 M. The nature of this reaction, which was also seen with other aromatics and other diazonium ions and in other chlorinated hydrocarbon solvents, is presently unknown. In this connection, it may be interesting that benzenediazonium cations can form charge-transfer (CT) complexes with aromatics (Koller, S.; Zollinger, H. *Helv. Chim. Acta* **1970**, *53*, 78. Becker, H. G. O.; Schukat, G.; Kuzmin, M. G. *J. Prakt. Chem.* **1975**, *317*, 229), the formation constants of which increase with decreasing polarity of the solvent. However, our attempts to see CT complexes in HFIP were unsuccessful.



a decrease in the *amplitude* of the signal due to CHD cation (measured  $\approx 50$  ns after the pulse) and (b) an increase in the *rate* of decay of the CHD cation. The reduction in *amplitude* is due to scavenging of the *phenyl* cation by the added reagent presumably acting as a competing nucleophile. The increase in *rate* must represent reaction directly with the CHD cation, in most cases a simple deprotonation. The experimentally observed rate of decay increased linearly with the concentration of the base B (see inset c of Figure 1). From the slopes of the plots of  $k_{\text{obsd}}$  vs [B] the second-order rate constants for reaction of the CHD cations with B were obtained. These values and those for reaction of the CHD<sup>+</sup>s with the solvent HFIP ( $k_s$ , see, e.g., eq 5) are collected in Table 2.

From an inspection of Table 2 the following statements can be made and conclusions drawn:

1. The  $k_s$  values are essentially independent of the substituent R on the former phenyl cation. This is expected since a potential electronic effect of R is insulated by the sp<sup>3</sup>-hybridized carbon of the CHD cation.

2. With respect to the substituents on the aromatic trap, the reactivities  $k_s$  with the weak nucleophile HFIP follow the order Me > Et  $\sim$  <sup>i</sup>Pr < <sup>t</sup>Bu. The rate constant decreases by a factor of  $\approx 3$  in going from Me to Et, is essentially unchanged for <sup>i</sup>Pr, and then increases by a factor of 30–40 for <sup>t</sup>Bu. Proceeding from Me to <sup>t</sup>Bu is expected to provide a small stabilization on electronic grounds, <sup>t</sup>Bu being slightly more electron donating than Me. This however would be counterbalanced by a decrease in planarity of the dienyl system due to the steric interaction of the aryl group at C1 of the benzenium ion and the alkyl groups at the two ortho positions. The result is a decrease in stability, so that <sup>i</sup>Pr and especially <sup>t</sup>Bu have enhanced reactivity. In agreement with this,  $k_s$  values for the *proton* adducts (where there is *no* steric interaction) follow the order Me > Et > <sup>i</sup>Pr > <sup>t</sup>Bu (Table 2), as expected on the basis of only the electronic effect.

There is a *decrease* in reactivity by a factor of  $\approx 30$  in going from TMB to HMB. There are several possible explanations for this. The cation from HMB is stabilized electronically since it has more methyl substituents. There may also be a steric effect, the HMB cation allowing decreased accessibility by bases. In addition, the HMB cation cannot deprotonate directly from the benzenium ring, although it could lose a proton from one of the methyls to give a methylene-substituted cyclohexadiene. This process does not have the driving force of the aromatization that occurs when the TMB cation loses its proton.

3. The trend with the alcohols (MeOH  $\sim$  EtOH  $\sim$  <sup>i</sup>PrOH  $\sim$  <sup>t</sup>BuOH) is the one expected for these compounds reacting as *bases*; the order when these react as *nucleophiles* with carbocations is MeOH > EtOH > <sup>i</sup>PrOH > <sup>t</sup>BuOH, with over an order of magnitude decrease across the series.<sup>40</sup> The similar reactivity with tetrahydrofuran is also not surprising, since this has a similar basicity. In contrast, the less basic 1,4-dioxane has rate constants that are a factor of 3–5 lower. As in the case of reaction with the solvent, the CHD cation from HMB reacts less rapidly with MeOH, THF, and 1,4-dioxane.

4. With Br<sup>-</sup>, all systems except HMB gave rate constants of  $\approx 5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, a value which is probably close to the diffusion-controlled limit. Since the basicity of Br<sup>-</sup> is much

lower than that of alcohols and ethers, this high reactivity suggests that that Br<sup>-</sup> does not react as a base but rather as a nucleophile, i.e., by addition to the cation. This has also been observed in a previous study.<sup>24</sup> No stable product incorporating bromide has been observed, either in this work or the previous one. The adduct with bromide would be a bromo-substituted cyclohexadiene, and this likely rearomatizes at longer times by eliminating HBr.

The values for the HMB-containing systems ( $\approx 7 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>) are clearly below diffusion-controlled. It is interesting that the cation exhibits selectivity toward the halides: The reactivity (F<sup>-</sup> < Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup>) increases with increasing nucleophilicity but decreasing basicity (see the lower end of the last column of Table 2).

5. The reactivity patterns of the CHD cations produced by addition of a (substituted) *phenyl cation* to 1,3,5-trimethylbenzene and to hexamethylbenzene are *very similar* to those<sup>24</sup> of the corresponding H<sup>+</sup> *adducts*, which means that replacement of H at the methylene group of these CHD cations by phenyl has little influence on reactivity. Whether this is also true for, e.g., the corresponding tri-*tert*-butyl compounds is not known since the nucleophilic reactivity of its H<sup>+</sup> adduct has not yet been studied. It is interesting that the reactivities with the alcohols MeOH, EtOH, 2-PrOH, and <sup>t</sup>BuOH of the *phenyl*-CHD cations from TMB are on average a factor of  $\approx 6$  larger than that<sup>14c</sup> of the CHD cation produced by addition of the 9-*fluorenyl* cation to TMB.

**5. Summary and Conclusions.** It has been demonstrated that 308-nm photolysis of a series of 4-substituted benzenediazonium ions in the polar, acidic, and weakly nucleophilic solvent HFIP leads to their decomposition with quantum yields close to unity. This process is mainly if not completely a heterolysis<sup>41</sup> to phenyl cations which can be scavenged by aromatics giving cyclohexadienyl cations. From experiments involving competition for phenyl cations between HFIP and aromatics, it is deducible that the substituents Me, MeO, and Cl stabilize the phenyl cation, although this effect is not very strong (factor  $\leq 2$ ). Such a conclusion has so far not been possible since the substituent effect on phenyl cation stability cannot be discerned from solvolysis data of benzenediazonium ions.<sup>42</sup> From competition data relating to different 1,3,5-trialkylated benzenes, it is evident that addition of the phenyl cations to the aromatics is subject to steric hindrance which dominates over the counteracting electronic influences.

The CHD cations produced by covalent bond formation between the phenyl cation and the aromatic have characteristic absorption spectra with bands at  $\approx 200$ , 260–270, and 350–390 nm and show a high reactivity with bases/nucleophiles such as alcohols, ethers, and halides ( $k$  values of  $10^6$  to  $\approx 5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>). With respect to both spectral and reactivity properties, the “phenyl adducts” are very similar to the corresponding<sup>22,23,24,28</sup> “proton adducts”.

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(39) Cozens, F. Unpublished results.

(40) McClelland, R. A. *Tetrahedron* **1996**, *52*, 6283.

(41) A similar conclusion has been drawn<sup>11</sup> for similar benzenediazonium salts.

(42) For a review of the solvolysis data, see ref 9a.