

Production of carbenium ions from carbenes by protonation

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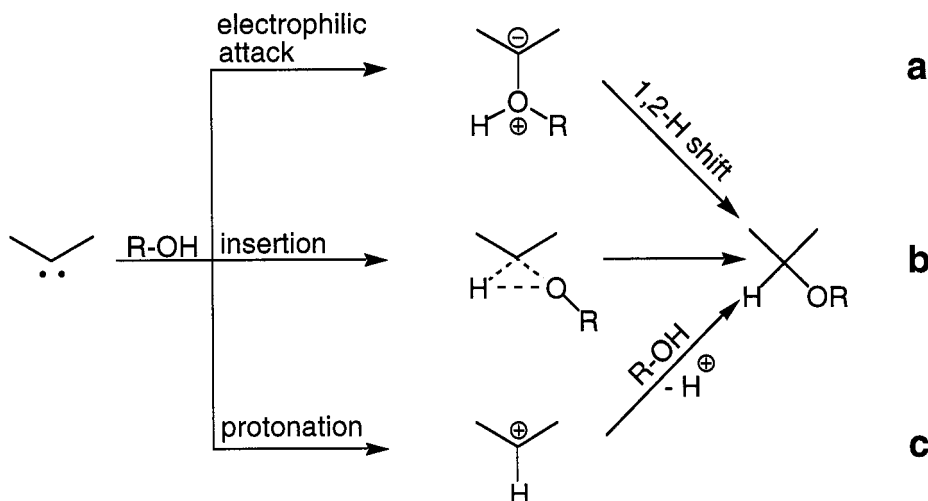
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Abstract: Diphenyl-, aryl- α -siloxy- and 2-furanyl carbenes can be protonated by even weak proton donors such as alcohols (by a bimolecular or by a pre-association mechanism involving more than one alcohol molecule) to yield the corresponding carbenium ions, whose spectra and electrophilic patterns of behavior are described.

INTRODUCTION

Proton transfer reactions to and from heteroatoms ($\equiv$ "normal" Brönsted acids and bases, with rate constants for proton transfer usually at or near the diffusion controlled limit) are different from those to and from carbon atoms.¹ In aqueous solution, the latter typically undergo proton transfer reactions more slowly than do their heteroatom counterparts and are believed to do so *directly* rather than through solvent molecules. This difference in behavior is probably due to differences in changes in hybridization, in heavy atom bond lengths and angles, in hydrogen-bonding ability, in (de)solvation in the transition state, and changes in delocalization of charge. So far, nearly all of the studies related to the acid/base chemistry at carbon atoms relate to carbanions and their conjugate acids.¹ Little is known about the acid/base chemistry of divalent carbon atoms, carbenes. However, carbenes can exhibit a considerable reactivity even towards weak proton donors such as alcohols or water, the reaction leading to carbenium ions, whose spectra and nucleophilic reactivities have been determined, using the technique of laser flash photolysis (LFP).²⁻⁴ For these cases, the mechanism of the formal insertion of (nucleophilic) carbenes into O-H bonds, which has been discussed in terms of **a**) initial formation of an oxonium ylide followed by a 1,2-hydrogen shift, **b**) a concerted mechanism, or **c**) by proton transfer (Scheme 1), has thus been decided upon in favor of reaction **c**:

Scheme 1



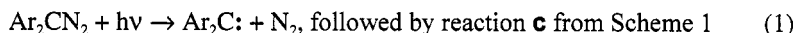
*Lecture presented at the 14th International Conference on Physical Organic Chemistry, Florianópolis, Brazil, 21–26 August 1998. Other presentations are published in this issue, pp. 1933–2040.

The proton transfer leads to the initial formation of a carbocation/alkoxy anion pair which can 1) collapse or 2) separate by solvation of the ions followed by electrophilic reaction of the carbenium ion with subsequent deprotonation (reaction **c**), to finally form formal O-H insertion products. The observation of free carbocationic intermediates after the photochemical generation of carbenes in solutions containing hydroxylic reactants, in LFP experiments, has shown that several carbenes of different structure undergo "O-H insertion" into alcohols *via* path **c**.²⁻⁴ In some other cases, proton transfers to carbenes have been implied based on product distributions.^{5,6}

The carbocations studied so far^{2,3} are all relatively strongly stabilized systems such as benzhydryl- or oxygen-substituted benzyl cations. The rate constants for protonation in acetonitrile solution of the carbenic precursors by „relatively strongly acidic“ ($pK_a \leq 14$) proton donors were found to be close to diffusion control, whereas in the case of weaker proton donors the protonation mechanism was different, i.e., *via* a pre-association path, for which the involvement of *two* alcohol molecules was suggested.³ We have recently found that this mechanism also holds for purely aliphatic carbenes, e.g., oxatetrahydrofuranylidenes.⁷ The up-to date situation is summarized in the following.

DIARYLCARBENES

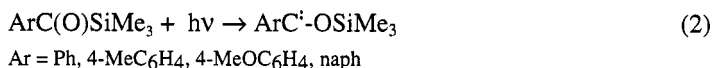
Laser-flash photolysis (LFP; 248 nm, 20-ns pulses) of 4,4'-dimethoxydiphenyldiazomethane in acetonitrile-water gave rise² to the same transient absorption ($\lambda_{\max} = 500$ nm) as that of the carbenium ion obtained by photoheterolysis of Ar_2CH-X . The decay of the transient was first-order, the rate being unaffected by oxygen and independent of the precursor concentration. Corroboration for assignment in terms of cation was by time-resolved conductance detection in weakly basic solution: The observed steep increase in conductance after the pulse is due to protonation of the carbene by H_2O to give the carbenium ion and OH^- , and the subsequent decrease of conductance to reaction of the cation with the solvent, by which the OH^- is neutralized (via the H^+ generated in the reaction of the carbocation with H_2O). LFP of 4-(mono)-methoxy- and 4,4'-dimethyldiphenyldiazomethane in acetonitrile-water also generated diarylcarbenium ion whose absorption and reactivity are in good agreement with previous measurements.^{8,9} The results can thus be summarized by:



The absorption spectra of the diarylcarbenium ions evolved within the 20-ns laser pulse. Rapid formation of the carbocations is consistent with the rates ($10^9 - 10^{10} M^{-1}s^{-1}$) at which singlet diphenylcarbene is quenched by ROH .^{10,11}

α -SILOXYARYLCARBENES

were produced³ by 248 nm laser photolysis of aroylsilanes, a reaction that proceeds via the carbonyl triplet state (Eq 2):



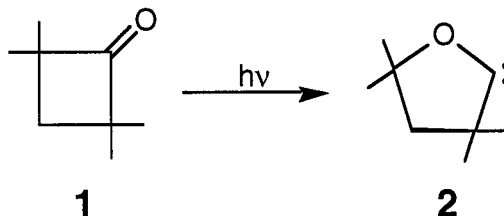
These α -siloxyphenylcarbenes have $\lambda_{\max}$ values in acetonitrile between 270 and 310 nm and lifetimes between 130 and 260 ns. In the presence of proton donors such as alcohols or water, the lifetimes of the carbenes decrease dramatically, indicating that a rapid reaction occurs between the carbene and the

proton donor. In the case of the alcohols ROH, from ethylene glycol ($pK_a = 15.1$) to 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP), $pK_a = 9.3$), the rate of decrease of carbene increases with [ROH] in a linear fashion such that the bimolecular rate constants for the carbene protonations to yield the α -siloxybenzyl-type cations (analogous to Scheme 1, **c**) can be obtained from the k_{obs} vs [ROH] plots. They are of the order $10^9 \text{ M}^{-1}\text{s}^{-1}$. With more weakly acidic alcohols, the mechanism of protonation has been suggested to involve *two* molecules of alcohol, and from the low kinetic isotope effects of ≈ 1 it was concluded that the transition state for protonation of the carbene is not linear.²

3,3,5,5-TETRAMETHYLTETRAHYDROFURANYLIDENE-2

On photochemical excitation (308 nm, 20 ns), cyclobutanones and a few larger-ring ketones undergo ring expansion.¹²⁻¹⁵ From the product analysis and matrix isolation data it was concluded that the reactive intermediates formed are oxacarbenes which, due to O-substitution at C:, should be singlet state species, e.g. eq 3¹⁶

(eq 3)



In Figure 1, circles, is shown the spectrum of the carbene **2** which has two peaks: one at $\approx 220 \text{ nm}$ and a weaker one at 360 nm , that decay predominantly in an exponential fashion with a similar rate ($(1-2) \times 10^4 \text{ s}^{-1}$), see insets **a** and **b**. The similar rate of decay at the two wavelengths indicates that the two bands belong to the same transient (lifetime $50 \mu\text{s}$).¹⁷

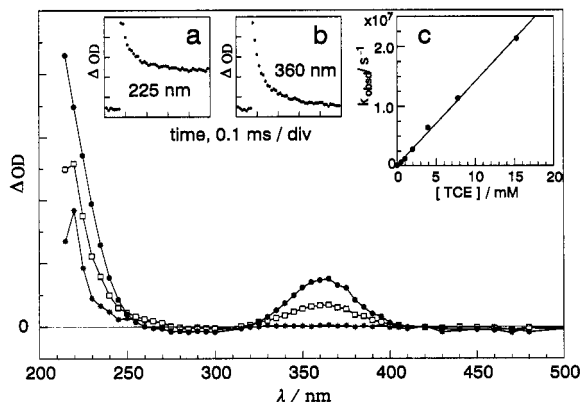


Figure 1. Time resolved absorption changes on 308 nm photolysis of a deoxygenated 0.05 mM solution of **1** in acetonitrile. Recorded at 30 ns (circles), 2 μs (squares), 400 μs (asterisks) after the 20 ns pulse.

It was found that the rate of decay is not accelerated in the presence of O_2 [8 mM], from which it is concluded that the transient is not a triplet state or a radical. A species with an absorption band at 360 nm has been observed on photolysis of **1** in matrices at 77 K and identified^{18,19} as the carbene **2** formed by ring-expansion (eq 3) and on this basis we assign the 360

nm species with the so far unreported $\approx 225 \text{ nm}$ band, produced by us at room temperature in liquid solution, also to the carbene **2**.

It was found that the lifetime of **2** is dramatically reduced if proton donors such as alcohols are added to the acetonitrile solutions. This is shown for the case of trichloroethanol (TCE) in Figure 1, inset **c**. It is seen that the rate k_{obsd} for decay of **2** increases linearly with [TCE]. From the slope of this dependence, the bimolecular rate constant for reaction of **2** with TCE is $1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, a value lower than that for diffusion ($k_{diff} = 2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$). A similar behavior of **2** was observed with respect to its interaction with other acidic alcohols, such as, e.g., trifluoroethanol (TFE), and hexafluoroisopropanol

(HFIP). From the slopes of the linear k_{obsd} (decay of **2**) vs [proton donor] dependencies, the rate constants for these reactions were determined and are collected in Table 1.

Table 1. Rate Constants for Reaction of the Oxacarbenes **2** and **4** with Proton (Deuteron) Donors ROH(D) in Acetonitrile.

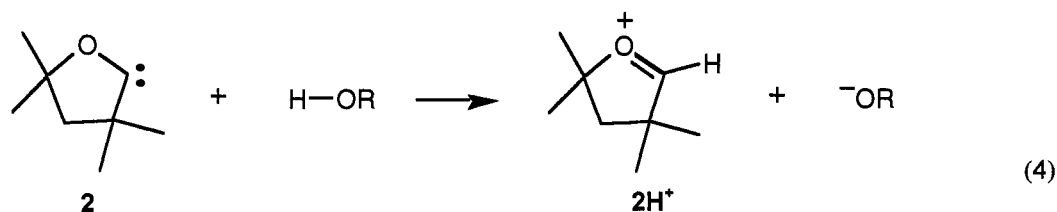
ROH(D)	$\text{p}K_{\text{a}}(\text{ROH})$	Oxacarbene 2		Oxacarbene 4	
		$k/\text{M}^{-1}\text{s}^{-1}\text{ }^a$	$k_{\text{H}}/k_{\text{D}}$	$k/\text{M}^{-1}\text{s}^{-1}\text{ }^a$	$k_{\text{H}}/k_{\text{D}}$
HClO ₄	≈ -8	7.3×10^9	0.9		
DClO ₄		8.1×10^9			
(CF ₃) ₂ CHO-H	9.3	2.6×10^9	1.0	2.7×10^9	1.0
(CF ₃) ₂ CHO-D		2.5×10^9		2.8×10^9	
CF ₃ CH ₂ O-H	12.8	6.4×10^8			
CCl ₃ CH ₂ O-H	12.24	1.5×10^9			
CHCl ₂ CH ₂ O-H	12.89	<i>b</i>			
CH ₂ ClCH ₂ O-H	14.31	<i>b</i>			
MeO-H	15.5	<i>b</i>			
EtO-H	15.9	<i>b</i>			
CH ₃ CO ₂ -H	4.75			2.2×10^9	1.1
CD ₃ CO ₂ -D				2.0×10^9	
H ₂ O	15.7	<i>b</i>			

^a Error limits $\pm 10\%$.

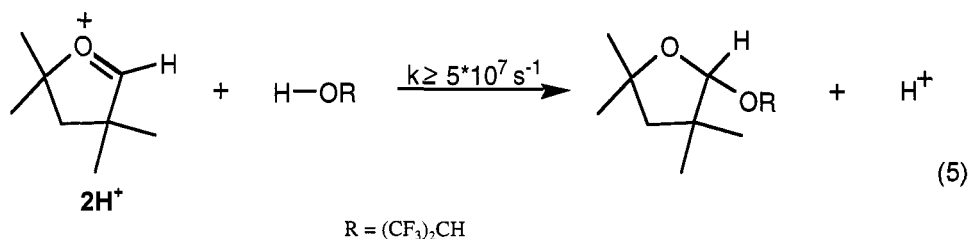
^b The k (decay of carbene) vs [ROH] plots are "curved upwards" (see text and Figure 2). A meaningful number for a bimolecular rate constant can therefore not be given.

The highest value for the alcohols is that for the most acidic one, i.e., HFIP, with $k = 2.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. This value, however, is still below that for diffusion control in the solvent acetonitrile (see above).

The product expected from the reaction of **2** with a (strong) proton donor is the corresponding carbenium ion, **2H⁺**:



An attempt was made to *directly see* this ion (**2H⁺**) using a strong proton donor such as HFIP. For this purpose, the precursor, **1**, was photolyzed in *neat* HFIP, which is a strongly acidic and also weakly nucleophilic solvent, which supports the detection of carbenium ions. However, on photolysis of **1** in *neat* HFIP, no evidence for the existence of a carbocation such as **2H⁺** was obtained. Since the carbene, **2**, as shown above, *does* react with proton donors, the non-detectability of **2H⁺** after the 20 ns pulse obviously means that its lifetime is ≤ 20 ns. This is explained by the rapid conversion of the carbocation **2H⁺** by reaction with the solvent HFIP acc to eq 5:



2 was also reacted with the acetonitrile-solvated proton or deuteron (from HClO_4 or DClO_4), the rate constant determined (Table 1) being 7.3×10^9 or $8.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, i.e., very close to diffusion control. Within experimental error ($\pm 10\%$), the two values are the same. The analogous is true for the reaction of **2** with HFIP(OH/OD), see Table 1, i.e., the kinetic isotope effect is 1. Values of $k_{\text{H}}/k_{\text{D}}$ close to one have previously been observed for protonation of dimethoxycarbene¹⁴ and of α -siloxyarylcarbenes and interpreted in terms of pre-association and a non-linear transition state for carbene protonation.^{3,20}

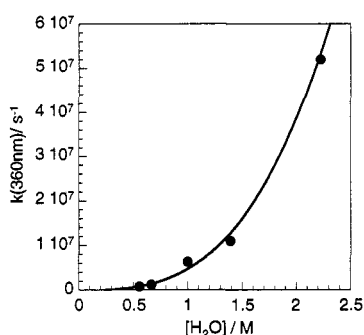
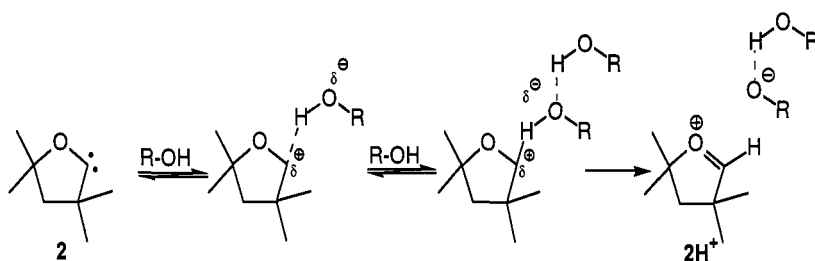


Figure 2. Dependence of the rate of decay in acetonitrile of the carbene **2** on the concentration of added water.

The carbene **2** was also reacted with *less acidic* alcohols such as mono- and di-chloroethanol, and with MeOH, EtOH, ethylene glycol, and also with water. In all these cases an increase in *reactivity* with increasing alcohol concentration was observed, i.e., the k_{obsd} (reaction of **2**) vs $[\text{R(H)OH}]$ plots are "curved-up" (for an example, see Figure 2). Also this kind of phenomenon has previously been observed, the interpretation³ involving the participation of more than one alcohol (water) molecule in the course of the protonation of the carbene:

Scheme 2

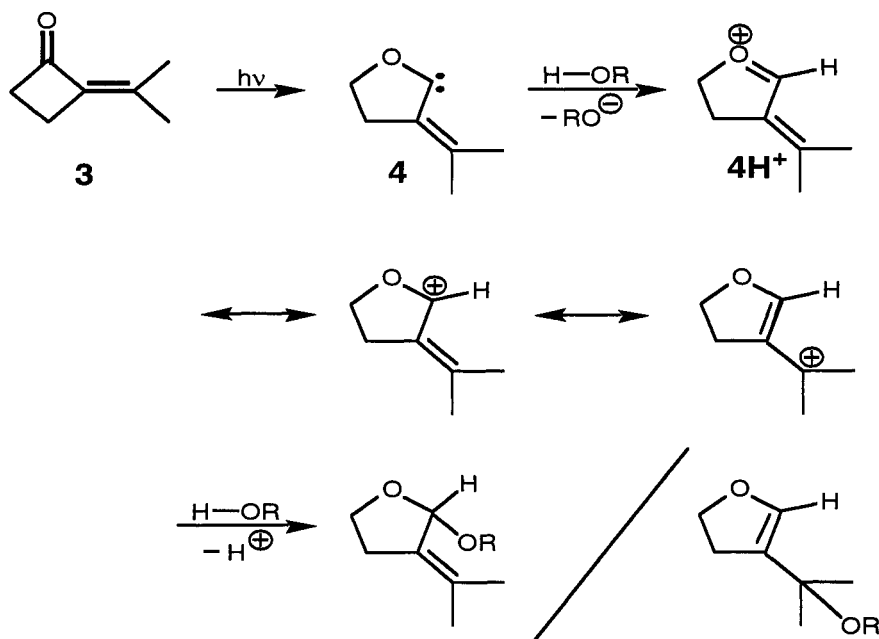


Since the attempt to detect 2H^+ was unsuccessful due to its too short lifetime, a longer-lived carbocation was aimed at. For this purpose, a different cyclobutanone, i.e. isopropylidene-cyclobutanone, **3**, (see Scheme 3), was studied in acetonitrile and in acidic alcohols.

3-ISOPROPYLIDENETETRAHYDROFURANILYDENE-2.

In the carbocation $4H^+$ expected from the olefinic cyclobutanone **3** (via the carbene, **4**, see Scheme 3) the positive charge can be delocalized and the reactivity thus decreased.

Scheme 3



$R = Ac, CF_3CH_2, (CF_3)_2CH$

In Figure 3 are shown the spectral observations made on photolyzing **3** in pure acetonitrile (squares): There is a strong *depletion* of optical density (*negative* ΔOD) at ≈ 240 nm, where the parent has an absorption band, and a *production* of optical density (*positive* ΔOD) with two maxima at ≈ 220 nm and ≈ 278 nm.²¹ The species responsible (there is only $< 10\%$ decay within $100\ \mu s$) is identified in terms of the oxacarbene **4**, formed by ring-expansion acc to Scheme 3.^{15b,c}

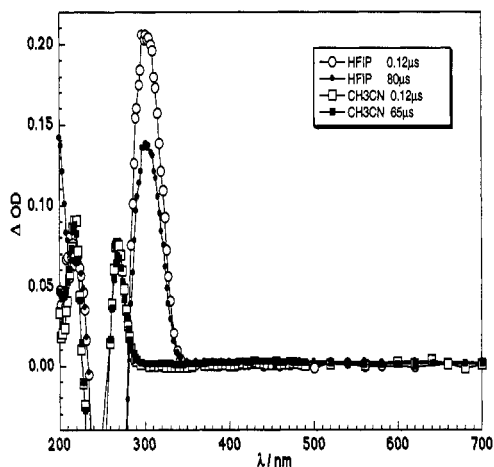


Figure 3: Absorption spectra recorded on photolyzing a deoxygenated 0.2 mM solution of 2-isopropylidenecyclobutanone **3** in a) acetonitrile (squares) and b) in HFIP (circles) at $20 \pm 2^\circ C$.

The spectrum observed was not changed in shape or intensity when O_2 was admitted to a solution in acetonitrile, demonstrating that neither the carbene nor its precursor is scavenged efficiently by O_2 . This is also evidence that the carbene is not in the triplet state.

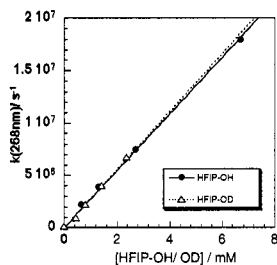
It was found that the lifetime of the carbene can be dramatically reduced by adding proton donors such as, e.g., $HClO_4$, acetic acid,

TFE or HFIP to solutions of **3** in acetonitrile, as evidenced by the decay of the peaks at ≈ 220 and ≈ 280 nm. As a result of the accelerated decay of the carbene, a new species is formed (the carbenium ion $4H^+$) which absorbs at ≈ 310 nm, whereby the rate of *decay* at ≈ 280 nm is the same as that of *formation* of the carbenium ion. If the photolysis is carried out in acetonitrile in the presence of ≈ 8 mM $HClO_4$ or in neat TFE or HFIP²² (Figure 3, circles), the carbene is not visible any more after the 20 ns pulse, and in its place the cation absorbing at 310 nm is fully developed.

The rate constants for reaction of carbene with various proton donors such as, e.g., AcOH or HFIP were determined (see Table 1) by monitoring their effect on the rate of decay of the carbene. In these cases the rates increased with increasing [proton donor], and from the slopes of the straight lines the rate constants (see Table 1) obtained are 2.2 and $2.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively, i.e. a factor ≈ 8 smaller than the diffusion limit in acetonitrile.

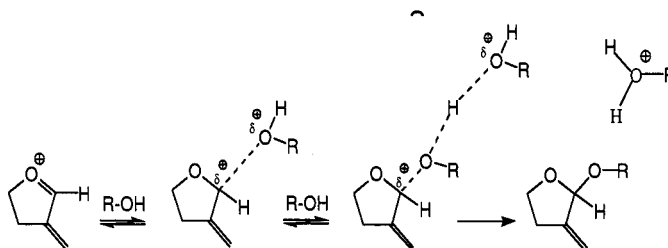
In Figure 4 is contained a comparison of the effects of O-protonated and O-deuterated HFIP on the rate of decay of the carbene.

Figure 4: Dependence of k_{decay} of **4** on [HFIP-OH/HFIP-OD].



As evident, in both cases the rate of decay increases linearly with the concentration of alcohol, and to the same extent, which means that the kinetic isotope effect for the conversion reaction is 1.0. Similarly low numbers have previously been observed^{20,23} for the reaction with proton donors of other carbenes and explained³ in terms of a *bent* alignment and/or a preassociation-mechanism analogous to Scheme 2.

In order to further show that the species produced in the solvents TFE or HFIP is a carbocation, nucleophilic compounds such as ROH, water, or halides were added. In the case of ROH or H_2O , it was found that the rate of decay of the species increased with increasing concentration of the nucleophile, as expected for a carbocation. However, the rate of decay was not linearly dependent on [ROH], but the dependence was „concave“, i.e., not only the reaction rate but also the *reactivity* increased with increasing [ROH]. This is explained in terms of pre-association (Scheme 4), i.e. reaction in the transition state of an alcohol-cation complex with a second alcohol molecule,²⁴ analogous to previously described cases³ and reciprocal to Scheme 2:



In contrast to the behavior of the alcohols, with the strong nucleophiles Cl^- and Br^- , which, in addition, are *good leaving groups*, the rate of decay of the cation *decreased* with increasing [Nu]. This is explained in terms of the reaction of the cation with Hal^- being reversible, analogous to cases previously described for reaction of Br^- with trityl cation or other delocalized cations,²⁵ the final decay of the cation being due to its irreversible reaction with solvent to give the corresponding ether(s) (see Scheme 4). In agreement with this idea is the observation that with

the weak nucleophile and *bad* leaving group F^- , the plot of k_{obsd} for decay of cation on $[F^-]$ is linear and passes through the origin, indicating that in this case the reaction is *irreversible*, and from the slope the (low) rate constant $1.6 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ (corresponds to $<0.05\%$ of the diffusion limit for a cation/anion combination reaction³ in acetonitrile) is obtained, which reflects the low nucleophilicity of F^- .

Summary and Conclusions. Examples have been given for diaryl- and α -oxygen substituted carbenes that are sufficiently nucleophilic to undergo protonation by even weak proton donors such as alcohols to yield the corresponding carbenium ions whose properties and reactivities can be measured. The mechanism of carbene protonation is often more complicated than a bimolecular proton transfer. In the cases studied, due to the mechanistic complications, unfortunately, not enough suitable data are presently available for testing for Brønsted relations.

Acknowledgment: I thank professor W. Kirmse, Universität Bochum, for the many years of fruitful collaboration.

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