The Fragmentation of Alkoxyhalocarbenes

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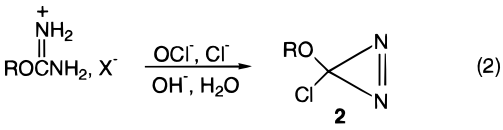
Alkoxyhalocarbenes stand at an intersection of carbene, carbocation, elimination, and substitution chemistry. Their fates are decided by several fundamental mechanisms, and we can anticipate significant contributions to mechanistic organic chemistry from an understanding of their behavior. In the 1950s, Hine[1] and Skell[2] reported that dihalocarbenes reacted with alkoxides to form alkoxyhalocarbenes, **1**, and Skell suggested that, when *sec*- or *tert*-alcohols were used, the derived carbenes fragmented to alkyl cations with the loss of CO and X^- (eq 1, X = Cl or Br). Noting the close resemblance between CO and N_2, Skell offered an analogy between reaction 1 and the decomposition of alkyldiazonium ions ($RN_2^+ \rightarrow R^+ + N_2$).

$$RO^- + :CX_2 \longrightarrow ROCX_2^- \xrightarrow{-X^-} \underset{\mathbf{1}}{ROCX} \longrightarrow R^+ + CO + X^- \qquad (1)$$

Both Hine and Skell utilized sequence 1 as a basic dehydration of alcohols to alkenes,[1,2] while Hine noted that carbene **1** could react at its divalent carbon, undergo a β-elimination reaction to form olefin and the OCCl anion (or CO + Cl^-), or afford a nucleophilic displacement with OH^- or OR^-, with loss of $OCCl^-$.[1,3]

The requirement for strong base in eq 1, however, is limiting. Neither carbenes **1** nor carbocations can survive such conditions, and direct observational studies would be severely constrained. Graham's discovery of the hypohalite oxidation of amidines to halodiazirines afforded a new avenue of attack[4] (eq 2). When isouronium salts were



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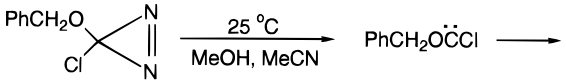
employed in this reaction, 3-alkoxy-3-halodiazirines (**2**) were obtained. In 1979, Smith and Stevens reported that diazirines **2** (R = Me or *i*-Bu) afforded the corresponding alkoxychlorocarbenes (**1**) upon thermolysis; fragmentation of **1** could be studied under neutral contions.[5]

Carbocations, Ion Pairs, and S_Ni Reactions

We found that the thermolysis of benzyloxychlorodiazirine (**2**, R = $PhCH_2$) in MeCN at 25 °C affords benzyl chloride (**3**). In MeOH/MeCN mixtures, benzyl methyl ether (**4**) also forms, its relative yield increasing with increasing MeOH (eq 3).[6] Two remarkable observations from these



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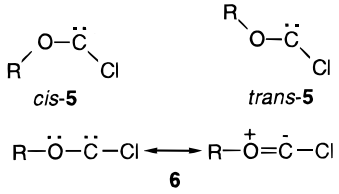
experiments are (1) even in pure methanol about 43% of chloride **3** still forms and (2) there are no products from methanolic trapping of the benzyloxychlorocarbene (e.g., benzyl dimethylorthoformate), even though the methanolysis of *i*-butoxychlorocarbene leads to very substantial carbene trapping.[5b]

We formulate eq 3 as a fragmentation of $PhCH_2OCCl$ to an ion pair, [$PhCH_2{}^+OCC1^-$], which can either collapse to **3** or react with methanol to give **4**.[6] This economical mechanism rationalizes several observations. It accounts for the persistence of chloride **3** in methanol; the chloride anion can return to its benzyl cation partner in competition with methanolic trapping of the cation. If the rate-limiting step is carbene fragmentation to the ion pair, then the absence of carbene−MeOH products implies that $PhCH_2OCCl$ fragments faster than it is trapped. For an ambiphilic carbene such as $PhCH_2OCCl$, methanolic trapping can be relatively slow, with $k \approx 10^4-10^6$ s^{-1}.[7] Moreover, the benzyl cation is more stable than the isobutyl cation, so we expect ROCCl to fragment more rapidly to [R^+OCCl^-] when R = benzyl than when R = isobutyl. Therefore, *i*-BuOCCl is trapped by MeOH,[5b] whereas $PhCH_2OCCl$ is not.[6] Additionally, there is a solvent effect: generation of $PhCH_2OCCl$ in MeOH/pentane, rather than MeOH/MeCN, affords up to 40% of MeOH−carbene trapping. In the less polar medium, fragmentation to the ion pair is slower and methanolic trapping more competitive.

Alkoxychlorocarbenes can exist as cis or trans "isomers", e.g., *cis*-**5** and *trans*-**5**. With R = Me or Ph, such isomers have been observed in cryogenic matrixes[8] and owe their existence to partial double bond character and hindered rotation at O−C due to the oxygen lone pair to vacant carbene p orbital electron donation, represented by resonance hybrid **6**.[8,9] Ab initio calculations suggest a



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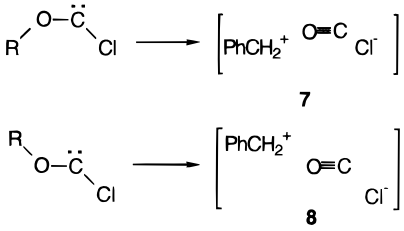
barrier of ~20 kcal/mol for cis/trans isomerization of **5** when R = $PhCH_2$,[10] with the isomeric carbenes not interconverting on the microsecond time scale of the fragmentation reaction. Fragmentation of $PhCH_2OCCl$ may, therefore, yield "isomeric" ion pairs **7** and **8**, depending on the geometry of the parent carbene. In fact,



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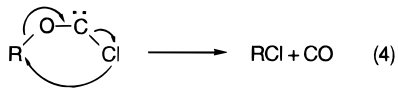
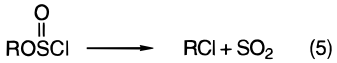
we speculate that the residual benzyl chloride formed from $PhCH_2OCCl$ in methanol may reflect efficient internal return of Cl^- in "cis" ion pair **7**, whereas the benzyl cation of CO-separated "trans" ion pair **8** may be largely diverted to ether **4** by solvolysis.[6]

In 1971, Tabushi reported that, with a large excess of CCl_2 (from 50% aqueous NaOH, chloroform, and a phase-transfer catalyst), alcohols could be converted to alkyl chlorides.[11] Substrates such as 1-adamantanol, benzyl alcohol, and *exo*-2-norbornanol were efficiently converted to the corresponding chlorides. *endo*-2-Norbornanol gave 47% of the *exo*-chloride and 44% of the *endo*-chloride, while *l*-menthol gave *l*-menthyl chloride with some racemization.[11] Tabushi formulated these reactions as a blend of carbocation and S_Ni processes: the R^+ intermediates were responsible for racemization and some rearrangement (e.g., 1-adamantylmethyl to homoadamantyl), as well as well as endo → exo conversion in the norbornyl system, whereas the S_Ni mechanism (eq 4) could account for retention in the menthyl system.[11]



$$RCl + CO \qquad (4)$$

Later, Jones et al. posited a similar mechanism to account for the formation of a 70−80% exo mixture of epimeric chlorides in the CCl_2-induced reactions of either epimer of 2-norbornyl-type alcohols.[12] Free carbocations, as well as the Woodward−Hoffmann-forbidden classical S_Ni mechanism of eq 4, were discounted in favor of the intermediacy of "a carbocation which is committed to chloride formation through intermolecular capture with retention".[12] Indeed, a careful experimental and computational reinvestigation of the "S_Ni" conversion of alkyl chlorosulfites to alkyl chlorides (eq 5) demonstrates the key role of ion pairs in this process.[13]



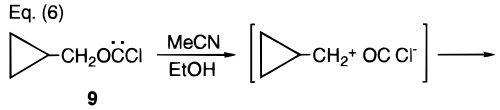
$$RCl + SO_2 \qquad (5)$$

Note that ion pairs can form from ROS(O)Cl either by S−Cl cleavage to $ROS^+ {=}O\ Cl^-$ or by R−O cleavage to R^+OSOCl^-, with the dominant pathway dependent on whether R is primary (S−Cl), secondary, or tertiary (R−O).[13] We will see below that similar questions of cleavage site (i.e., R−O or C−Cl) attend a mechanistic analysis of ROCCl fragmentation. In summary, however, ion pair mechanisms seem well-suited to rationalize most alkoxyhalocarbene fragmentations.

Cyclopropylmethoxychlorocarbene

Fragmentation of cyclopropylmethoxychlorocarbene (**9**) is a good test of the ion pair mechanism because the chemistry of the cyclopropylmethyl cation has been so extensively studied.[14] Thermolysis of diazirine **2** (R = *c*-$C_3H_5CH_2$) in MeCN at 23 °C gives carbene **9**, which fragments to chlorides **10**, **11**, and **12** (cf. eq 6).[15] The three isomeric products are those expected from the cyclopropylmethyl (or bicyclobutonium) cation,[14] but the "high" ratio of **10**/**11** (5.2) indicates a tight or intimate ion pair which collapses mainly at the initial CH_2 reaction center, rather than a "free" cyclopropylmethyl cation, from which the **10**/**11** ratio would be closer to unity.[14,16] (The high proportion of **10** does not signal the intervention of S_N2 processes because added chloride does not increase the yield of **10**.) Moreover, when carbene **9** is deuterated at C_α, we observe only ~30% of the label redistribution expected from a free cyclopropylmethyl cation.[14,16] That is, a free cyclopropylmethyl cation would rearrange rapidly, fully scrambling its α-CH_2 with its two cyclopropyl CH_2 groups.[14,16] However, the cyclopropylmethyl cation generated as part of the tight ion pair in eq 6 affords only limited CH_2 scrambling.[15]

Eq. (6)



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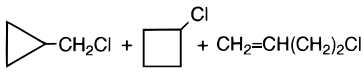
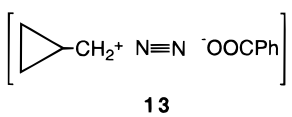


		10	**11**	**12**
Products (%): (MeCN)		78	15	7
(EtOH)	RCl:	42	5	2
	ROEt:	28	22	1

The case for ion pair intervention in eq 6 is strengthened if we recall Skell's analogy to the chemistry of alkyldiazonium ions.[2] Thus, the reactions (in ether) of cyclopropyldiazomethane with benzoic acid, or of cyclopropylmethyl diazotate with benzoyl chloride, afford cyclopropylmethyl benzoate ion pairs **13**, which yield the



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benzoate analogues of **10**−**12** in distributions very similar (79:14:7 or 78:13:9) to those of the cyclopropylmethyl cation−carbon monoxide−chloride ion pair of eq 6.[17]

When the fragmentation of **9** occurs in ethanol, we obtain 49% of chlorides **10**−**12** with a high **10**/**11** distribution (8.4), as well as 51% of the ethyl ether analogues of **10**−**12** with a much reduced cyclopropylcarbinyl/cyclo-

butyl distribution (1.3). The chloride products represent ion pair return (probably from a "cis" ion pair analogous to **8**), whereas the ether products most likely derive from solvolysis of a "trans" ion pair, or an ethanol-solvated (escaped) cyclopropylmethyl cation; the cyclopropylcarbinyl/cyclobutyl ratio is now very similar to the distribution obtained from the "free" cyclopropylmethyl cations formed in the nitrous acid deamination of cyclopropylmethylamine[14,16] or the hydrolysis of cyclopropylmethyl diazotate.[18]

Alkoxyfluorocarbenes

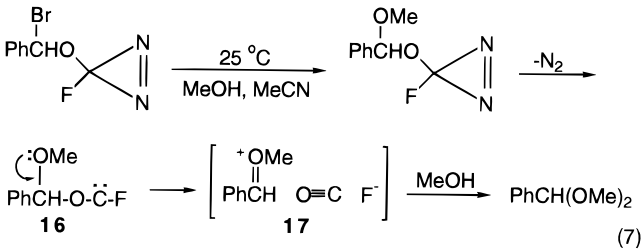
Although ROCCl (and ROCBr) readily fragment, there are closely related species that do not. Examples include phenoxychlorocarbene (**14**) and benzyloxyfluorocarbene (**15**) Phenoxychlorocarbene resists fragmentation because

scission to an ion pair (Ph^+ OC Cl^-) would produce the high-energy phenyl cation. Carbene **14**, therefore, behaves as a typical ambiphile, offering a variety of intermolecular reactions.[19]

Benzyloxyfluorocarbene (**15**), generated by thermolysis of the appropriate diazirine at 80 °C in MeCN, gave less than 10% of fragmentation to $PhCH_2F$; the major products corresponded to HF or H_2O trapping of the carbene.[20] Under comparable conditions, $PhCH_2OCBr$ completely fragmented to $PhCH_2Br$.[20] Benzyloxyfluorocarbene could also be trapped by methanol and acrylonitrile.[20]

The variations in the fragmentation behavior of $PhCH_2OCX$ presumably arise in the relative strengths of the C−X bonds; the strong C−F bond of **15** opposes facile fragmentation. This naturally strong bond will be further strengthened in **15**, where we expect significant C═F character due to the F → C lone pair to carbene 2p orbital donation.

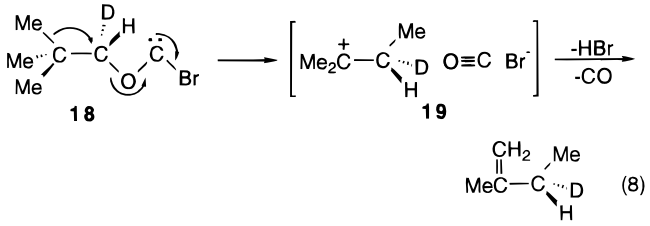
Interestingly, although **15** resists fragmentation, its α-methoxy derivative, **16**, fragments readily (eq 7).[21] With carbene **16**, the extra stability imparted to the incipient α-methoxybenzyl cation apparently compensates for the high C−F bond strength, driving the fragmentation to ion pair **17**, and thence to the product, benzaldehyde dimethylacetal.



(7)

Stereochemistry

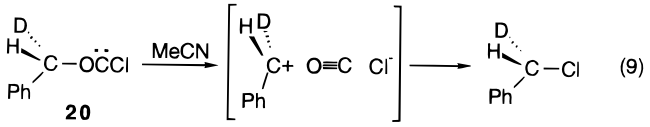
The first stereochemical study of an alkoxyhalocarbene fragmentation is due to Mosher, who reported that chiral neopentyloxybromocarbene (**18**, from neopental-l-*d* alcohol and CBr_2) fragmented with 1,2-Me migration, followed by proton loss, mainly affording 2-methyl-l-butene-3-*d* (eq 8).[22] The 1,2-Me shift occurred with ≥90% *inversion*



(8)

at the chiral center, suggesting that it was concerted with the oxabromocarbene fragmentation; a free (primary) neopentyl cation did not intervene.[22] In our formulation, carbene **18** directly gives the *t*-amyl cation (CO-separated) ion pair, **19**, from which the product arises. We shall revisit this rearrangement below.

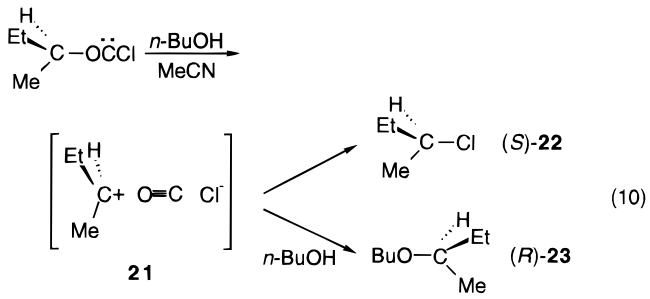
A second stereochemical example appears in eq 9. When generated thermolytically from the diazirine, (*S*)-



(9)

α-deuteriobenzyloxychlorocarbene (**20**) fragments to α-deuteriobenzyl chloride in MeCN at 25 °C with 60−80% net retention.[23] We argued above that fragmentation of $PhCH_2OCCl$ proceeds via ion pairs. Such ion pairs should collapse with stereochemical retention.[23]

A more complicated (and more informative) situation ensues when a chiral oxahalocarbene fragments in a nucleophilic solvent: for example, the scission of (*S*)-2-butoxychlorocarbene (from the diazirine) in either MeCN or 1-butanol at ambient temperature (eq 10).[24] The



(10)

"simple" fragmentation in MeCN, proceeding through ion pair **21**, affords 89% of (*S*)-2-chlorobutane, formed with 55−57% net retention. This result parallels that of eq 9 and is again consistent with dominant front-side chloride return within the ion pair.

When the fragmentation occurs in *n*-butanol, ion pair **21** partitions between chloride return (44%), solvolysis to 1-butyl 2-butyl ether (36%), and butene. Significantly, the 2-chlorobutane, (*S*)-**22**, forms with 81−83% net retention, indicative of front-side ion pair collapse, whereas the solvolysis product, (*R*)-**23**, exhibits 69−73% net *inversion*, reflecting rear-side capture of the cation.[24] The persistence

Table 1. Fragmentation Rate Constants for Alkoxychlorocarbenes[a]

carbene	$10^6\ k_{frag}$, s^{-1}	ref
$PhCH_2OCCl$	0.69−1.3	26
Me_3CCH_2OCCl (**24**)	0.3−1.3	26
1-$AdCH_2OCCl$ (**25**)	2.8−5.2	26
C_4H_9OCCl (**26**)	1.8 ± 0.35	29
Me_2CHCH_2OCCl (**27**)	1.9 ± 0.1	29

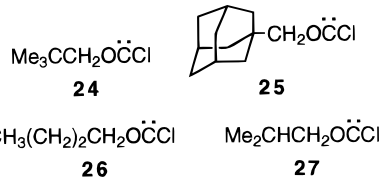
[a] The carbenes were generated by LFP of the diazirines in MeCN at 25 °C. A variable concentration of pyridine (~0.4−7.5 M) was present.

of **22** upon fragmentation in *n*-butanol is consistent with earlier observations for $PhCH_2OCCl$ in methanol (eq 3)[6] and cyclopropylmethoxychlorocarbene in ethanol (eq 6).[15] Again, "isomeric" ion pairs might be involved, with "*cis*"-**21** mainly collapsing to chloride **22** and "*trans*"-**21** solvolyzing to **23**.

Importantly, our results with CO-containing ion pairs closely resemble our earlier findings with the related nitrogen-separated ion pairs $[R^+N_2X^-]$ derived from alkane diazotates, which also exhibit return of the counterion with stereochemical retention and competitive solvolysis with inversion.[25] The intersection here of these two quite separate lines of mechanistic inquiry is very satisfying.

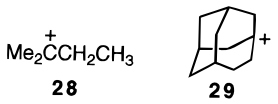
Kinetics of Fragmentation

Although alkoxyhalocarbenes **1** lack convenient UV bands, one can follow the kinetics of their fragmentation by laser flash photolysis (LFP).[26] We use the pyridine ylide methodology,[27] in which competition between the fragmentation of ROCCl and its kinetically measurable capture as an ylide by pyridine[28] permits the extraction of k_{frag}.[26] We first examined the fragmentations of benzyloxychlorocarbene, neopentyloxychlorocarbene (**24**), and (1-adamantyl)methoxychlorocarbene (**25**).[26] Rate constants appear in Table 1, along with data for *n*-butoxychlorocarbene (**26**) and isobutoxychlorocarbene (**27**),[29] which are discussed below. The k_{frag} ranges in the table reflect alternative analytical methods applied to the kinetic data. Clearly, however, the fragmentations all occur on the microsecond time scale and are all reasonably comparable.



Consider the first three entries of Table 1. It is striking that carbenes **24** and **25**, which might afford primary cations, should fragment as rapidly as $PhCH_2OCCl$, which gives the primary but relatively stabilized benzyl cation. The explanation lies in the products of the fragmentations: both **24** and **25** give rearranged products derived from tertiary carbocations, the *t*-amyl cation (**28**) from **24**, and the homoadamantyl cation (**29**) from **25**.[26,30]

For carbene **24**, fragmentation is likely concerted with the neopentyl → *t*-amyl rearrangement[22] (cf. eq 8), as

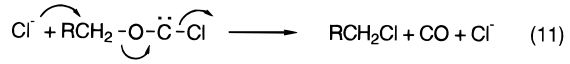


would also be expected for the **25** → **29** conversion.[11,12,26,31] Participation of the migrating alkyl group in the fragmentations of **24** and **25**, therefore, affords values of k_{frag} that are comparable to that of $PhCH_2OCCl$.

Bimolecular Carbene Fragmentation

Granted that concerted rearrangement−fragmentation accounts for the "high" k_{frag}'s of **24** and **25**, what is responsible for the comparable rate constants displayed by *n*-butyoxychlorocarbene (**26**) and *i*-butyoxychlorocarbene (**27**) (cf. Table 1)? In 5.8 M pyridine−MeCN, the major fragmentation products of **26** are 1-chlorobutane (46%) and 1-butene (24%), whereas **27** yields 7% of *i*-butyl chloride, 12% of (1,2-H shift product) 2-chlorobutane, 10% of 2-butene, and 47% of isobutene.[29] Strikingly, the yields of primary (unrearranged) chlorides from the fragmentations of **26** and **27** are very sensitive to added chloride ion (as $Bu_4N^+Cl^-$): with 0.5 M chloride in the pyridine−MeCN solvent, 1-chlorobutane from **26** increases to 63% (with 23% 1-butene), while *i*-butyl chloride from **27** increases to 38% (with 27% isobutene).[29]

These results suggest a bimolecular ("S_N2") fragmentation of carbenes **26** and **27** with chloride ion (eq 11). A



kinetic test of this idea is illustrated in Figure 1. The k_{frag} values for **26**, **27**, and $PhCH_2OCCl$ are dependent on chloride concentration, where the correlations' slopes represent the second-order rate constants (k_2) for the carbene fragmentations induced by chloride. These k_2 values ($M^{-1}\ s^{-1}$) are 8.2×10^6, 2.7×10^6, and 2.2×10^6 for **26**, **27**, and $PhCH_2OCCl$, respectively.[29] Thus, k_2 is highest for the straight-chain primary *n*-BuOCCl and lowest for the benzyloxychlorocarbene, where "unimolecular" decomposition via ion pairs (**7** or **8**) will compete with external chloride attack.[6,29]

The bimolecular fragmentation of **26** and **27** extends the analogy between the behavior of alkoxychlorocarbenes and alkyldiazonium ions. The chiral α-D-substituted *n*-butyl- and *i*-butyldiazonium ions hydrolyze in water with 96% inversion, indicative of S_N2-like solvolyses.[32] The bimolecular reactions of primary ROCCl also fulfill Hine's 1953 suggestion that ROCCl could undergo nucleophilic displacement with loss of OCCl.[1] Note that reaction of ROCCl with chloride at the carbene carbon would produce $ROCCl_2^-$, a carbanion that, in the absence of protonation, would simply revert to the carbene.

There is additional evidence for the bimolecular vs "unimolecular" (ion pair) dichotomy postulated for the fragmentations of, e.g., *n*-BuOCCl and $PhCH_2OCCl$. Thus, LFP-generated $PhCH_2OCCl$ affords benzyl cations that escape their ion pairs and can be captured by 1,3,5-trimethoxybenzene in MeCN, affording trimethoxyben-

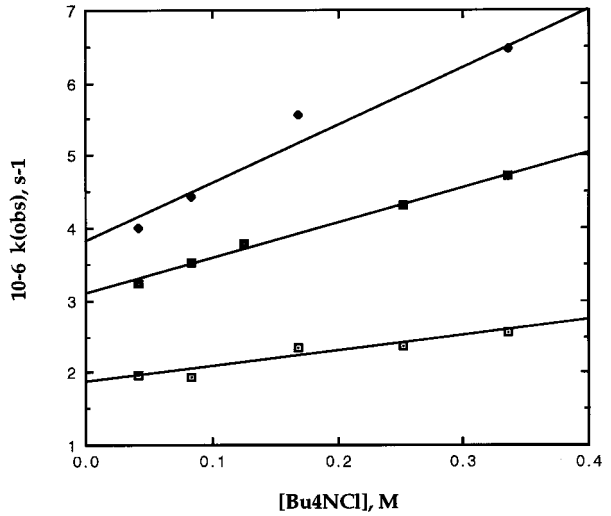


FIGURE 1. Observed rate constants (10^{-6} s^{-1}) for the formation of pyridinium ylides from carbenes **26**, **27**, and $PhCH_2OCCl$ as a function of added $Bu_4N^+Cl^-$ in 5.77 M pyridine−MeCN solution at 24 °C: (◆) **26**, (■) **27**, and (⊡) $PhCH_2OCCl$. The slopes of these correlations give the second-order rate constants for the fragmentations of the carbenes induced by chloride.[29]

zylcyclohexadienyl cations absorbing at 410−430 nm.[33,34] In contrast, a similar transient is not seen in an analogous experiment with *n*-BuOCCl, presumably because carbene fragmentation to the *n*-butyl cation does not occur.[29,33]

Conclusions

The fragmentation of alkoxyhalocarbenes unites aspects of carbene, carbocation, substitution, and elimination reactions. Structural, stereochemical, kinetic, and computational studies (the latter in progress) support this contention and suggest further analysis. If, for example, the 1-chlorobutane formed from *n*-BuOCCl and Cl^- in pyridine−MeCN is primarily a "S_N2" product, what is the origin of the accompanying l-butene? We suspect that it is largely an E2 product. Isotope effect studies to test this idea are under way.

The conclusion that ion pair formation is central to the fragmentation of those alkoxyhalocarbenes that afford relatively "stabilized" carbocations suggests kinetic, stereochemical, and trapping studies of, e.g., cycloalkyl, 2-adamantyl, and 2-norbornyl cations. The likelihood that primary ROCCl undergoes bimolecular fragmentations presents an opportunity to examine the stereochemistry of the (Cl^- + RCHD*OCCl) reaction. Many additional experiments are conceivable, including the application of photoacoustic calorimetry to these LFP-initiated reactions. The addition and insertion reactions of carbenes have engendered decades of mechanistic and synthetic chemistry. The less common fragmentation reaction may now make its contribution, too.

I am delighted to recognize the many contributions of my collaborators, whose names appear in the references. Together, we are grateful to the National Science Foundation for financial support.

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