ORGANIC
LETTERS

2002
Vol. 4, No. 14
2341−2344

The Carbene Fragmentation–Ring Expansion Route to Bridgehead Carbocations

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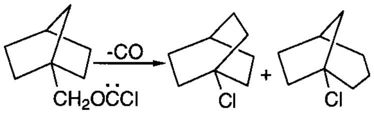
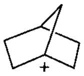
Received April 18, 2002

ABSTRACT



The products, kinetics, and activation parameters were determined for the fragmentation–ring expansions of 1-norbornylmethyloxychlorocarbene (11) and 3-noradamantylmethyloxychlorocarbene (17). Products from 11 (in dichloroethane) included 1-chlorobicyclo[2.2.2]octane (9, 56%) and 1-chlorobicyclo[3.2.1]octane (10, 37%); from 17, we obtained 1-chloroadamantane (15, 68%) and protoadamantyl chloride (16, 28%).

The energy and stability of bridgehead carbocations are directly related to the strain imposed upon them by enforced nonplanarity of the cationic carbon.[1] Accordingly, certain bridgehead carbocations are highly strained, very unstable, and difficult to form by solvolytic processes.[1] For example, acetolysis of 1-norbornyl triflate, via the 1-norbornyl cation (**1**), proceeds at 70 °C with $k = 6.5 \times 10^{-8}$ s^{-1} and $\Delta H^{\ddagger} = 28.2$ kcal/mol.[2] On the other hand, we find that the fragmentation of alkoxychlorocarbenes[3] in polar solvents provides alkyl cations (as components of ion pairs) with low activation energies (<10 kcal/mol);[4,5] cf. eq 1. Thus, cation **1** could be generated from 1-norbornyloxychlorocarbene with $k_{frag} = 3.3 \times 10^4$ s^{-1} ($E_a = 9.0$ kcal/mol) in dichloroethane (DCE) at 25 °C,[6] representing a rate enhancement of 5×10^{11} over the triflate acetolysis.[2]



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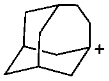

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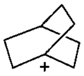

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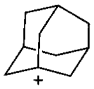

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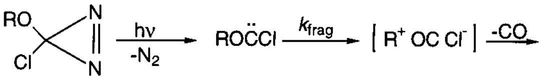

(1)

Bridgehead carbocations can also arise by ring expansions. For example, 1-adamantylmethyl tosylate undergoes concerted ring expansion−acetolysis to 1-homoadamantyl acetate via the 1-homoadamantyl cation, **2**.[7] Analogously, fragmentation of 1-adamantylmethoxychlorocarbene in MeCN or DCE affords products largely derived from ring-expanded cation **2**[5,8]

Here, we examine the 1-bicyclo[2.2.2]octyl (**3**) and 1-adamantyl (**4**) cations as generated by carbene fragmentation−ring expansion reactions or by direct fragmentations.[6] We focus on two unusual features of the ring expansion reactions: (1) due to the low activation energies associated with fragmentation−ring expansions, *competitive* ring expansions occur; (2) the ion pairs formed via ring expansion or direct

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[1] (a) Abboud, J.-L. M.; Herreros, M.; Notario, R.; Lomas, J. S.; Mareda, J.; Müller, P.; Rossier, J.-C. *J. Org. Chem.* **1999**, *64*, 6401. (b) Abboud, J.-L. M.; Castano, O.; Della, E. W.; Herreros, M.; Müller, P.; Notario, R.; Rossier, J.-C. *J. Am. Chem.* Soc. **1997**, *119*, 2262.

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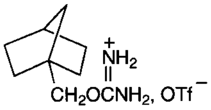
10.1021/ol020083j CCC: \$22.00 © 2002 American Chemical Society
Published on Web 06/17/2002

fragmentation reactions in methanol are not identical. Presumably they do not live long enough to equilibrate within and with their solvent cages.

1-Norbornylcarboxylic acid[9] and 3-noradamantylcarboxylic acid (Aldrich) were reduced with $LiAlH_4$ to 1-norbornylmethanol[9] and 3-noradamantylmethanol,[10] respectively. These alcohols were then converted to the isouronium salts **5** and **6** by reactions with 1 equiv each of cyanamide and trifluoromethanesulfonic acid.[11] Oxidations of **5** and **6** with 12% aqueous NaOCl[12] afforded diazirines **7a** and **7b**, which were the desired carbene precursors. The diazirines displayed UV maxima in DCE at 351 and 364 nm (**7a**), and 353 and 363 nm (**7b**).



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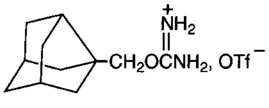

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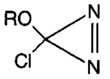

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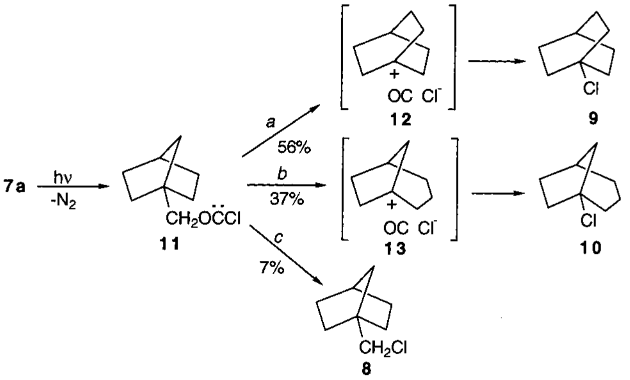
a, R = 1-norbornyl
b, R = 3-noradamantyl

Photolysis of diazirine **7a** at 25 °C in DCE ($\lambda > 320$ nm, $A_{356} = 0.5$) gave 7% of 1-norbornylmethyl chloride (**8**), 56% of 1-chlorobicyclo[2.2.2]octane (**9**), and 37% of 1-chlorobicyclo[3.2.1]octane (**10**). Product identities were confirmed by GC−MS, NMR, or GC comparisons with authentic materials.[13−16]

We formulate these reactions as shown in Scheme 1, where photolysis of diazirine **7a** generates 1-norbornylmethyloxychlorocarbene (**11**).

Scheme 1

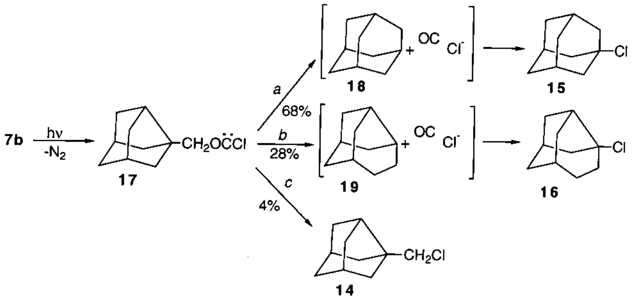


Fragmentation of the carbene,[3] mainly with ring expansion,[5,8] gives ion pairs **12** or **13**, which collapse to products **9** or **10**, respectively. In competition with ring expansion, chloride attack at the original methylene group provides 7% of chloride **8** (which might also arise by S_N2 attack of chloride directly on carbene **11**;[17] see below).

Of special note is the competition between alternative ring expansions *a* and *b* in Scheme 1. Expansion *a* (of the "short" 1-carbon bridge) exceeds expansion *b* (of the "long" 2-carbon bridge) by a statistically corrected factor of 3.0 in the carbene fragmentation reactions. In contrast, acetolysis of 1-norbornylmethyl tosylate is reported to give *only* 1-carbon bridge expansion to 1-bicyclo[2.2.2]octyl acetate.[18]

Similarly, photolysis of diazirine **7b** in DCE afforded 4% of 3-noradamantyl chloride (**14**), 68% of 1-adamantyl chloride (**15**), and 28% of protoadamantyl chloride (**16**); Scheme 2. Product **14** was identified by GC−MS and MS comparisons to literature data,[19] whereas **15** was identical to an authentic sample (Aldrich) in GC−MS and GC spiking experiments. The identity of protoadamantyl chloride, **16** (M^+ at *m*/*e* 170, 172), was assigned in analogy to the rearrangements of carbene **11** and by exclusion, because isomers **14** and **15** are already assigned.[20] Additionally, treatment of 3-noradamantylmethanol with $SOCl_2$ and pyridine (120 °C, 15 min) gave **14**, **15**, and **16** in an 11:85:4 distribution.

Scheme 2



These reactions can be formulated via 3-noradamantylmethoxychlorocarbene, **17** (Scheme 2), in parallel to the reactions of 1-norbornylmethoxychlorocarbene, **11** (Scheme 1). Ion pairs **18** and **19** are drawn in analogy, and the statistically corrected"short-bridge/long-bridge" (*a*/*b*) ring expansion ratio is ∼4.8 for the fragmentation of **17** (compared to 3.0 in the fragmentation of **11**). As in the case of 1-norbornylmethyl tosylate, acetolysis of 3-noradamantylmethyl tosylate is reported to give only short-bridge ring expansion to 1-adamantyl acetate.[21]

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[10] Tae, E. L.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 3803.

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[13] Chloride **8** was prepared from 1-norbornylmethanol,[9] $SOCl_2$, and pyridine (reflux, 30 min) and characterized by ^1H NMR comparison to the literature[14] and GC−MS. Chlorides **9** and **10** were prepared from 1-norbornylmethanol, concentrated HCl, and $ZnCl_2$,[15] which afforded an 85:15 mixture of **9** and **10**. These were characterized by GC, GC−MS, and ^{13}C NMR comparisons to the reported spectra.[15,16]

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[19] Mueller, A. M.; Chen, P. *J. Org. Chem.* **1998**, *63*, 4581.

[20] Chloride **16** has been prepared by a lengthy sequence, but no spectroscopic data were offered: Vogt, R. B. *Tetrahedron Lett.* **1968**, *9*, 1575.

[21] Schleyer, P. v. R.; Wiskott, E. *Tetrahedron Lett.* **1967**, *8*, 2845.

The kinetics of the fragmentations of carbenes **11** and **17** were determined by laser flash photolysis (LFP).[3,5,6,22] LFP at 351 nm and 25 °C of diazirine **7a** in DCE ($A_{356} = 0.5$) in the presence of pyridine[23] produced an ylide absorption at 416 nm due to pyridine trapping of carbene **11**. A correlation of the apparent rate constants for ylide formation ($k_{\mathrm{obs}} = (2.0-5.5) \times 10^6\ \mathrm{s}^{-1}$) vs [pyridine] (1.65−7.42 M) was linear (seven points, $r = 0.998$) with a slope of $5.43 \times 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, equivalent to the rate constant for ylide formation (k_y), and a *Y*-intercept of $7.72 \times 10^5\ \mathrm{s}^{-1}$, equivalent to the *overall* rate constant for fragmentation (k_{frag}) of carbene **11**. See Figure 1 in the Supporting Information. Using the product distribution shown in Scheme 1, we can partition the aggregate k_{frag} into $k_{\mathrm{frag}(a)} \sim 4.3 \times 10^5\ \mathrm{s}^{-1}$ for **11** → **9** and $k_{\mathrm{frag}(b)} \sim 2.9 \times 10^5\ \mathrm{s}^{-1}$ for **11** → **10**. Note that fragmentation *b* is twice as likely as fragmentation *a*.

Similarly, we measured the aggregate k_{frag} for carbene **17** in DCE: $k_{\mathrm{frag}} = 2.0 \times 10^6\ \mathrm{s}^{-1}$ (7 points, $r = 0.981$).[24] In this case, the appropriate partition of k_{frag} (Scheme 2) leads to $k_{\mathrm{frag}(a)} \approx 1.4 \times 10^5\ \mathrm{s}^{-1}$ for **17** → **15** and $k_{\mathrm{frag}(b)} \approx 0.6 \times 10^5\ \mathrm{s}^{-1}$ for **17** → **16**. Again, fragmentation *b* is statistically favored by a factor of 2.

An Arrhenius study of the fragmentation of carbene **11** was carried out in DCE from −40 to 30 °C; the resulting fair ($r = 0.959$) correlation of $\ln(k_{\mathrm{frag}})$ vs $1/T$ is shown in Figure 2; see Supporting Information. The derived (aggregate) values of E_a (5.1 kcal/mol) and $\Delta S^{\ddagger}$ (−17 eu, $\ln A = 21.8\ \mathrm{s}^{-1}$) are quite comparable to the analogous data for the fragmentation of 1-adamantylmethoxychlorocarbene, for which $E_a = 4.6$ kcal/mol and $\Delta S^{\ddagger} = -18$ e.u.[5]

We also determined $E_a = 5.2$ kcal/mol and $\Delta S^{\ddagger} = -14$ eu for the fragmentation of carbene **17** in DCE (seven points, −40 to +30 °C, $r = 0.944$). Although the data are no more than adequate (significant linearity at the 99% confidence level), it is clear that the aggregate activation parameters for the fragmentations of 1-adamantylmethoxychlorocarbene, carbene **11**, and carbene **17** are similar and that $E_a \approx 5$ kcal/mol in each case.

These low activation energies allow the fragmentations of **11** and **17** to explore the competitive ring expansion pathways depicted in Schemes 1 and 2. In contrast, the triflate or tosylate analogues of these carbenes undergo acetolysis with expansions *only* of their "short" bridges. The substantial activation enthalpies for these reactions (28.2 kcal/mol for 1-norbornylmethyl triflate[2] and 20.7 kcal/mol for 3-noradamantylmethyl tosylate[21]) permit sufficiently large differential activation enthalpies between short- and long-bridge ring expansions in favor of exclusive short-bridge rearrangements.

From the measured k_{frag} values of carbenes **11** and **17**, and the reported rate constants for acetolyses of their tosylate analogues,[2,21] we estimate $k_{\mathrm{frag}}/k_{\mathrm{acet}} \approx 1 \times 10^{16}$ in the 1-norbornylmethyl series and $\sim 2 \times 10^{11}$ in the 3-noradamantyl series. These huge enhancements reflect the dramatically lower activation energies associated with carbene fragmentation reactions, which empower them to explore pathways not available in tosylate solvolysis. Related effects are observed in the fragmentations of *exo*- and *endo*-2-norbornyloxychlorocarbenes.[22]

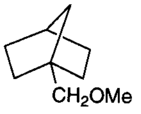
Above, we suggested that the "unrearranged" carbene fragmentation products **8** (Scheme 1) and **14** (Scheme 2) could arise (at least in part) by S_N2 reactions of chloride ions with carbenes **11** or **17**, respectively. Such reactions are known for, e.g., *n*-butoxychlorocarbene, and avoid the formation of primary carbocations.[17] Computations (see below) indicate that the unassisted fragmentation of carbene **11** to primary chloride **8** requires an activation energy of ~15.3 kcal/mol, which would not be competitive with the fragmentations of **11** to tertiary chlorides **9** or **10** ($E_a \approx 5$ kcal/mol; see above), and further suggests that the **11** → **8** conversion may be an S_N2 reaction of **11** with chloride. We expect the S_N2 reaction to have $E_a \approx 4-6$ kcal/mol[4,17] and to be competitive with fragmentation−rearrangement pathways. Note, however, that S_N2 chloride attack on carbene **11** (a "neopentyl" system) will be more difficult than comparable attack on *n*-BuOCCl, for which $E_a \approx 3$ kcal/mol.[17]

In support of these ideas, we find that decomposition of **11** in the presence of 1.2 M added $n\text{-Bu}_4\mathrm{N}^+\mathrm{Cl}^-$ in DCE affords an **8**/**9**/**10** product mixture that is enhanced in **8** (distribution 20:46:34), relative to the "normal" distribution (7:56:37, see Scheme 1, above). Moreover, LFP of diazirine **7a** in DCE with a constant concentration (5.77 M) of pyridine and varying quantities (0.042−0.504 M) of added $n\text{-Bu}_4\mathrm{N}^+\mathrm{Cl}^-$ gives a linear correlation (seven points, $r = 0.999$) of k_{obs} for ylide formation vs [Cl$^-$]. The slope of this correlation, $8.2 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, can be taken as the second-order rate constant (k_2) for quenching of carbene **11** by chloride; i.e., fragmentation of the carbene induced by chloride.[17,23,25]

Parallel results are obtained for the fragmentation of carbene **17**. In the presence of 1.26 M added $n\text{-Bu}_4\mathrm{N}^+\mathrm{Cl}^-$, the **14**/**15**/**16** distribution (Scheme 2) changes from 4:68:28 (no added chloride) to 8:61:27 (with a 4% of an unknown product), while $k_2 = 2.5 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ for the chloride-induced fragmentation.[26]

Photolysis of diazirine **7a** in MeOH gave methyl ethers **20**, **21**, and **22**, in addition to the analogous chlorides **8**, **9**, and **10**. A substantial quantity of 1-norbornylmethanol (**23**) also formed.

The structures of **20**−**22** were confirmed by GC, NMR, and MS comparisons with authentic samples made by the $\mathrm{AgClO_4}$-mediated methanolysis of 1-norbornylmethyl iodide.[27]



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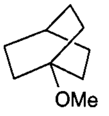

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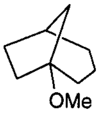

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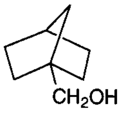

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Alcohol **23**, which forms from carbene **11** in 25% yield at even low concentrations ($\chi_{\mathrm{MeOH}} = 0.093$) of methanol in

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[23] Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.

[24] $A_{353} = 0.8$ for diazirine **7b** in DCE. The pyridinium ylide of carbene **17** had $\lambda_{\max} = 320$ nm and $k_y = 1.1 \times 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.

DCE, and in 30% yield in pure MeOH, is a carbene trapping product: MeOH captures **11** in competition with fragmentation, producing ROCH(Cl)OMe, which yields orthoformate ROCH$(OMe)_2$ and HCl by acid-catalyzed hydrolysis.[6,28] Products RCl and ROMe, however, represent competition between chloride return to R^+ vs methanol capture of R^+ in ion pairs **12** and **13**. These products (**9**, **10**, **21**, and **22**) represent ring expansion−fragmentation of **11**, whereas ether **20** may stem from solvolytic fragmentation of the carbene.

In pure methanol, the product distribution from carbene **11** is chlorides **8** (3.0), **9**, (26.0), and **10** (15.1); ethers **20** (1.3), **21** (10.5), and **22** (13.7); alcohol **23** (30.3). We note first that, even in pure methanol, alkyl chloride formation from carbene **11** persists;[3] the total chloride/ether ratio is 44:26. Thus, the lifetimes of the putative ion pairs formed upon carbene fragmentation (**12** and **13** in Scheme 1) must be comparable to the diffusive events that would remove Cl^- and fully solvate the carbocations.[29,30]

Furthermore, the bicyclo[2.2.2]octyl cation−chloride anion pair (**12**) generated by carbene fragmentation-ring expansion of carbene **11** in MeOH (Scheme 1) is *not* identical to the "same" ion pair generated by the *direct* fragmentation of 1-bicyclo[2.2.2]octyloxychlorocarbene.[6] Thus, the RCl/ROMe product ratio (**9**/**21**) is 26:10.5 ≈ 2.5 from fragmentation−rearrangement of carbene **11**, but only 19:48.6 ≈ 0.39 from fragmentation of 1-bicyclo[2.2.2]octyloxychlorocarbene.[5] Ion pair **12** **"**remembers" its carbene origin; its choice between reaction with chloride or methanol depends on its origin.[31]

Similar results obtain for ion pair **18** in Scheme 2: the RCl/ROMe ratio (**15**/1-Ad-OMe) is 37:15 ≈ 2.5 from the fragmentation−ring expansion of carbene **17** but 54.2/37 ≈ 1.5 from the direct fragmentation of 1-adamantyloxychlorocarbene.[5] That the RCl/ROMe ratios are more nearly equal when the selecting carbocation is more stable[1] (i.e., **4** vs **3**), seems reasonable, but a more extensive study of these phenomena is clearly needed.

In analogy with previous computational studies of alkoxyhalocarbene fragmentation,[4,6] we computed energies for cis-carbene **11** and the three competing fragmentation transition structures leading to **8**, **9**, and **10**. All structures were fully optimized by analytical gradient methods at the B3LYP/6-31G(d) level using the Gaussian98 suite of programs.[32] DFT calculations used Becke's three-parameter hybrid method and the LYP correlation functional of Lee, Yang, and Parr.[33] Computed gas-phase energies (unscaled) were corrected for thermal effects at 298.15 K and for zero-point energy differences. Normal coordinate analyses confirmed the nature of the computed stationary points as either ground state (no imaginary frequencies) or transition structures (one imaginary frequency). Solvation effects in dichloroethane ($\epsilon = 10.36$) were simulated via single-point energy calculations and PCM[32] methodology.

The fragmentation transition structures for the rearrangements of carbene **11** to chlorides **9** and **10** are shown in Figure 3; see Supporting Information. The computed activation energies at 298.15 K, converted from activation enthalpies, and corrected for zero-point energies, are 12.5 (**9**) and 13.8 (**10**) kcal/mol in vacuo and 4.84 (**9**) and 5.94 (**10**) kcal/mol in simulated DCE solution. The computed E_a's for these rearrangements, 4.8−5.9 kcal/mol, are in excellent agreement with the experimental (aggregate) E_a for the disappearance of carbene **11** (5.1, kcal/mol, see above).

The computed E_a for the "unimolecular" fragmentation of **11** to unrearranged **8** is 21.2 kcal/mol in vacuo and 15.3 kcal/mol in simulated DCE. The calculations therefore suggest that the **11** → **8** pathway should not be competitive with either the **11** → **9** or **11** → **10** rearrangements. The finding of 7% of **8** from the fragmentation of **11** is most likely the result of chloride ion-induced S_N2 fragmentation of the carbene, as suggested above.

The migrating carbons of the transition structures for **9** and **10** lie midway along the reaction coordinates in contrast to the "early" transition structures computed for the cyclopropylmethyl analogue[34] (E_a = 3.0 kcal/mol) and the 1-adamantylmethyl system[5,8] (E_a = 5.6 kcal/mol). Whereas strain relief provides a significant driving force for the 1-norbornylmethyl rearrangements, strain increases for the 1-adamantylmethyl rearrangement. On the other hand, incipient homoconjugation may provide significant stabilization of the cycloproplymethyl system with relatively little geometric change. What makes the present systems unique are the locations of the chloride ion in the transition structures. In most other computed transition structures for these fragmentation reactions, the Cl- - -C terminus distance ranges from 3.0 to 3.6 Å,[4,5,6,34] but in the present case it is more tightly bound at distances of 2.6−2.8 Å. The contrast reflects an unexpected variability in the geometry of "early" fragmentation transition structures.

Acknowledgment. We are grateful to the National Science Foundation for financial support and to the Center for Computational Neuroscience of Rutgers University (Newark) for computational support.

Supporting Information Available: Figures 1−3. This material is available via the Internet at http://pubs.acs.org.

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[25] The values of k_2 for carbene **11** (in DCE) and *n*-butoxychlorocarbene (in MeCN)[17] are identical.

[26] This result was obtained as described for carbene **11**. The correlation of k_{obs} with $[Cl^-]$ had $r = 0.971$ for 6 points.

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[29] From carbocation trapping experiments with trimethoxybenzene,[5,30] we could estimate the lifetimes of the cations of Scheme 1 as $\sim 7 \times 10^{-11}$ s in DCE. Thus, in methanol, the cations of the ion pairs react either with their chloride counterions or with solvent molecules in the first shell of the solvent cage.

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[31] For examples of "memory effects" in carbocation rearrangements, see: Berson, J. A. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 799.

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