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Homolytic Fragmentation of Allyloxychlorocarbene

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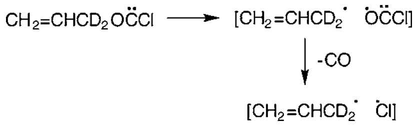
ABSTRACT



The decomposition of allyloxychlorocarbene in hydrocarbon solvents leads via homolysis to allyl and COCl radicals, which recombine to 3-butenoyl chloride or (after scission of $^•$COCl to CO and $^•$Cl) to allyl chloride. Labeling experiments show that both products are formed in part with allylic rearrangement.

The fragmentations of alkoxychlorocarbenes (ROCCl) access several mechanistic channels. When R can tolerate a positive charge (e.g., R = 3-homoadamantyl) and the solvent is polar, fragmentation occurs via an ion pair [R^+ OC Cl^-].[1] Short-lived ion pairs can sometimes be generated even in nonpolar hydrocarbon solvents (e.g., R = cyclopropylmethyl).[2] However, when R is a primary alkyl group devoid of carbocation-stabilizing features (R = *n*-butyl), S_N2 attack of chloride on the carbene itself becomes the principal fragmentation channel.[3] With secondary alkyl groups, ROCCl often fragments via effectively concerted, S_Ni-like processes, particularly in hydrocarbon solvents where escape to ion pairs is disfavored; examples include ROCCl where R = 3-nortricyclyl or cyclohexyl.[4]

There are also indications that ROCCl fragmentation can sometimes proceed *homolytically*. For example, cyclopropylmethoxychlorocarbene accesses a ring-opening, radical fragmentation pathway in the gas phase,[5] and photochemically generated benzyloxychlorocarbene fragments in Ar matrixes at 12 K to benzyl and COCl radicals, which (in part) recombine to form phenacyl chloride.[6] However, homolytic fragmentation−recombination is a minor process in the matrix, while in hydrocarbon *solution*, phenacyl chloride is *not* observed, possibly because COCl radical rapidly cleaves to CO and $Cl^•$ (which then recombines with a benzyl radical).[6] Alternatively, concerted (S_Ni) fragmentation of $PhCH_2OCCl$ to $PhCH_2Cl$ may dominate in hydrocarbon solvents, while ionic fragmentation holds sway in polar solvents such as MeCN.[6]

Finally, curved Hammett correlations of k_{frag} for $ArCH_2OCCl$ vs σ^+ in 1,2-dichloroethane (DCE) suggest that the fragmentations of X-$PhCH_2OCCl$ undergo mechanistic change from predominantly heterolytic to predominantly homolytic as X is altered from electron-donating (Me, Ph) to electron-withdrawing (CF_3, NO_2).[7] Phenacyl halides, however, are not formed in the latter cases; $ArCH_2Cl$ is the product.[7]

Here, we describe fragmentation reactions of allyloxychlorocarbene (**1**) that afford *both* allyl chloride (**2**) and 3-butenoyl chloride (**3**) in hydrocarbon solution at ambient temperature. This is the first instance of acyl chloride production from ROCCl in solution. Moreover, the formation of **3** with allylic rearrangement suggests that at least some COCl radicals recombine with allyl radical partners before

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(1) Moss, R. A.; Zheng, F.; Fedé, J.-M.; Johnson, L. A.; Sauers, R. R. *J. Am. Chem. Soc.* **2004**, *126*, 12421.

(2) Moss, R. A.; Sauers, R. R.; Zheng, F.; Fu, X.; Bally, T.; Maltsev, A. *J. Am. Chem. Soc.* **2004**, *126*, 8466.

(3) Moss, R. A..; Johnson, L. A.; Merrer, D. C.; Lee, G. E., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 5940.

(4) (a) Moss, R. A.; Ma, Y.; Sauers, R. R..; Madni, M. *J. Org. Chem.* **2004**, *69*, 3628. (b) Moss, R. A.; Fu, X.; Tian, J.; Sauers, R.; Wipf, P. *Org. Lett.* **2005**, *7*, 1371.

(5) Blake, M. E.; Jones, M., Jr.; Zheng, F.; Moss, R. A. *Tetrahedron Lett.* **2002**, *43*, 3069.

(6) Moss, R. A.; Ma, Y.; Zheng, F.; Sauers, R. R.; Bally, T.; Maltsev, A.; Toscano, J. P.; Showalter, B. M. *J. Phys. Chem. A.* **2002**, *106*, 12281.

(7) Moss, R. A.; Ma, Y.; Sauers, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 13968.

10.1021/ol050668o CCC: $30.25

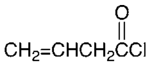
dissocation to CO and Cl. Strikingly, in polar solvents, acyl chloride **3** disappears in favor of allyl chloride **2** as the homolytic fragmentation of **1** gives way to heterolytic fragmentation via allyl cation chloride anion pairs.

$CH_2{=}CHCH_2O\ddot{C}Cl$

1

$CH_2{=}CHCH_2Cl$

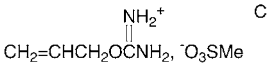
2



$CH_2{=}CHCH_2\overset{O}{\overset{\|}{C}}Cl$

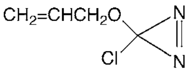
3

Allyl alcohol was converted to isouronium salt **4** with cyanamide and methanesulfonic acid.[8] The salt was fully characterized[9] and then oxidized to allyloxychlorodiazirine **5** with aqueous NaOCl.[9,10] Diazirine **5** was purified by column chromatography on silica gel with pentane elution and characterized spectroscopically by UV (λ_{max} 348 nm) and NMR.[9] The diazirine was decomposed photolytically (350 nm) or thermally at 25 °C in various solvents, with product identification by capillary GC and ^{1}H NMR comparisons to authentic materials.



$CH_2{=}CHCH_2O\overset{NH_2^+}{\overset{\|}{C}}NH_2,\ {}^-O_3SMe$

4



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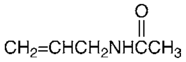


$CH_2{=}CHCH_2NH\overset{O}{\overset{\|}{C}}CH_3$

6

Photolysis or thermolysis (at 25 °C) of diazirine **5** generates allyloxychlorocarbene (**1**). In polar solvents such as DCE or MeCN, fragmentation of **1** gives allyl chloride (**2**). In MeCN, **2** is accompanied by ~36% of amide **6**, a "Ritter" product attributable to attack of an allyl cation on the solvent, followed by hydrolysis by adventitious water. Products **2** and **6** are the major products of carbene **1** observed in DCE or MeCN.[11]

However, in dodecane or cyclohexane solvents, very significant quantities of 3-butenoyl chloride (**3**)[12] accompany fragmentation product **2**. In dodecane (by GC analysis), the **2**:**3** distributions are 65:32 (photolysis of **5**) or 43:55 (thermolysis of **5**), with 2−3% of allyl formate[11] also formed. In cyclohexane-d_{12} (by ^{1}H NMR analysis), the **2**:**3** distributions are 61:39 (photolysis) or 53:47 (thermolysis).[13]

Further information was obtained from labeling experiments. Allyl alcohol-α,α-d_2[14] was converted to the isouronium salt (**4**-α,α-d_2), and the latter was oxidized to diazirine **5**-α,α-d_2, using the methods employed for their unlabeled analogues (see above). Photolysis or thermolysis of **5**-α,α-d_2 gave product mixtures that were analyzed by 300 MHz ^{1}H NMR spectroscopy.

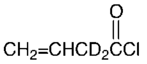
In 90:10 DCE/CDCl$_3$, only allyl chloride **2** was formed by fragmentation, and the ratio of rearranged (**2-re**) to unrearranged (**2-un**) chlorides was 34:66 ($h\nu$) or 41:59 (Δ).[15]

$CD_2{=}CHCH_2Cl$

2-re

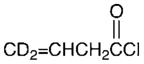
$CH_2{=}CHCD_2Cl$

2-un



$CH_2{=}CHCD_2\overset{O}{\overset{\|}{C}}Cl$

3-un

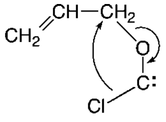


$CD_2{=}CHCH_2\overset{O}{\overset{\|}{C}}Cl$

3-re

In contrast, decomposition of **5**-α,α-d_2 in perdeuteriocyclohexane−pentane gave *both* products **2** and **3**. ^{1}H NMR analysis[16] gave the photolysis product distribution as **2-re** (19%), **2-un** (42%), **3-re** (13%), and **3-un** (26%). From thermolysis, the distribution was **2-re** (13%), **2-un** (40%), **3-re** (7%), and **3-un** (40%). Considered by product, the normalized extents of rearrangement were 31% ($h\nu$) or 24% (Δ) for allyl chloride **2**, and 33% ($h\nu$) or 15% (Δ) for 3-butenoyl chloride **3**. Allylic rearrangement is somewhat greater when carbene **1** is generated photochemically as compared to thermal generation (possibly associated with some fragmentation from the excited state of **5**), but significant rearrangement is consistently observed in the thermal formation of both **2** and **3**.

A priori, there are several mechanisms available for the genesis of these products. Allyl chloride could arise by S_Ni (**7**)[4] or S_Ni' (**8**) fragmentations of carbene **1**, with **7** giving **2-un** and **8** providing **2-re**. Alternative channels include heterolytic fragmentation of **1** to ion pair **9**, followed by ion recombination, or homolytic fragmentation to radical pair **10**, coupled with subsequent dissociation of the OCCl radical to CO and the Cl radical before recombination. Given the delocalization of both the allyl cation and radical, the allyl chloride derived from either **9** or **10** would consist of both **2-un** and **2-re**.[17]



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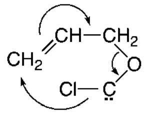


8

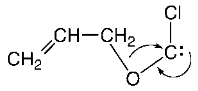
$[CH_2{=}CHCH_2^+\ OC\ Cl^-]$

9

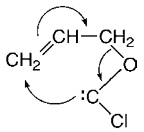
$[CH_2{=}CH\dot{C}H_2\ \dot{O}CCl]$

10

3-Butenoyl chloride **3** could form via an O → C allyl shift (**11**) or by a S_Ni' rearrangement (**12**). Here, **11** would afford **3-un**, whereas **12** would furnish **3-re**.



11



12

Finally, homolysis of **1** to radical pair **10** could yield both **3-un** and **3-re**, provided that the allyl radical can capture

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(8) Moss, R. A.; Kaczmarczyk, G. M.; Johnson, L. A. *Synth. Commun.* **2000**, *30*, 3233.

(9) See Supporting Information for details.

(10) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(11) Small quantities of allyl formate and allyl dichloromethyl ether are also observed. These result from the trapping of carbene **1** by water or HCl, respectively, and are precedented: Moss, R. A.; Ge, C.-S.; Maksimovic, L. *J. Am. Chem. Soc.* **1996**, *118*, 9792.

(12) ^{1}H NMR spectrum of **3** is described by: Tsuji, J.; Kiji, J.; Imamura, S.; Morikawa, M. *J. Am. Chem. Soc.* **1964**, *86*, 4350. An authentic sample was prepared by the method of: Marson, C. M.; Grabowska, U.; Fallah, A.; Walsgrove, T.; Eggleston, D. S.; Baures, P. W. *J. Org. Chem.* **1994**, *59*, 291.

(13) Compounds **2** and **3** were accompanied by ~10% of allyl dichloromethyl ether.

(14) Scheutz, R. D.; Millard, F. W. *J. Org. Chem.* **1959**, *24*, 297.

(15) ^{1}H NMR analysis relied on the δ 4.06 d ($J = 6.6$ Hz) signal of the α-CH$_2$ of **2-re** and the δ 5.21 dd ($J = 1.5, 9.9$ Hz) signal of the termimal vinyl proton trans to CD$_2$Cl of **2-un**.

the COCl radical (cf., **13**) competitively with the latter's scission to CO and Cl radical.[2,6,18−20]

$$\dot{O}{-}\ddot{C}{-}Cl \longleftrightarrow O{=}\dot{C}{-}Cl$$

13

Computational studies can help us decide among these alternatives. B3LYP/6-31G(d) calculations[21−23] afforded energies and structures for most of the reaction channels represented by **7**−**12**. The reactions of carbene **1** in dodecane or cyclohexane-d_{12} are best approximated by the computational results in vacuo. Here, S_Ni' transition state (TS) **8**, which affords **2-re**, has $\Delta H^{\ddagger}_{298} = 9.25$ kcal/mol. Structure **11** is a bifurcation point leading to **2-un** in one direction and **3-un** (by a 1,2-shift) in the other direction. It has $\Delta H^{\ddagger}_{298} = 7.01$ kcal/mol, so that the TS leading to **11** (which we have not located), must have $\Delta H^{\ddagger} > 7$ kcal/mol. Similarly, structure **12** is also a bifurcation point, giving either **2-un** or **3-re** (S_Ni'). It features a high activation enthalpy (12.2 kcal/mol) and can be disregarded. The computed structure for S_Ni' TS **8** appears in Figure 1A. However, we were unable to locate a TS for S_Ni fragmentation (**7**) in a vacuum, nor could we find a minimum corresponding to ion pair **9** under this condition.

Most importantly, we calculate that *homolysis* of carbene **1** to radical pair **10** requires only ∼5.5 kcal/mol in a vacuum and may well be the favored process in hydrocarbon solution.[24] Given that the further scission of $^{\bullet}$COCl into CO and Cl$^{\bullet}$ is expected to be rapid at 298 K[2,6,18] and should be competitive with allyl/COCl recombination, we suggest that the homolysis of carbene **1** may account for all four of the principal products observed in hydrocarbon solvents; cf., Scheme 1. Here, radical pairs **10**-d_2 and **14**-d_2 are presumed to form and recombine within the solvent cage.[25]

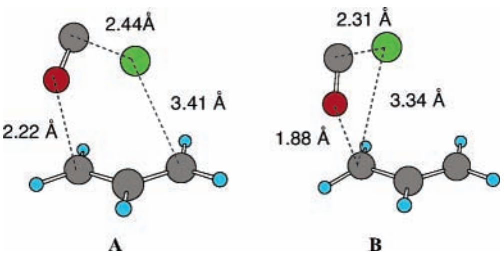
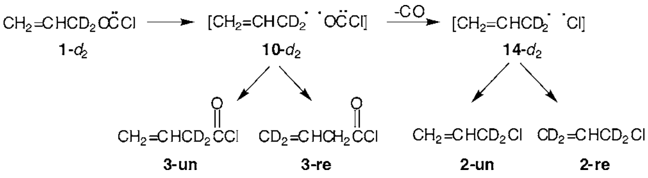


Figure 1. B3LYP/6-31G(d)-computed structures:[21] (A) TS **8** for S_Ni' rearrangement in a vacuum; (B) TS **7** for S_Ni formation of unrearranged allyl chloride in simulated MeCN.

Scheme 1



Experimentally, **2-un** and **3-un** are formed in greater quantities than their rearranged counterparts **2-re** and **3-re** in C_6D_{12} (40:13 and 40:7, respectively, for thermolysis), so that both radical pairs **10** and **14** appear to recombine predominantly at the initial scission site of carbene **1**. We also note the large excess of **3-un** over **3-re** (40:7), which could reflect the competition between recombination of allyl and COCl radicals and the dissociation of the COCl radical to CO and Cl. Alternatively, the energetically closest competitor to carbene homolysis in vacuo is the bifurcation leading to **2-un** and **3-un**. Participation of this channel could also account for the dominance of the 2 unrearranged products in C_6D_{12}.

In polar solvents, the situation is markedly altered. Decomposition of **1** in MeCN ($\epsilon = 37.5$) or DCE ($\epsilon = 10.36$) affords only the fragmentation products **2** and (in MeCN) amide **6**, while in $CDCl_3$ ($\epsilon = 4.8$ for $CHCl_3$), about 9% of **3** is formed along with 83% of **2** (and ∼8% of the carbene capture product, allyl dichloromethyl ether). Moreover, labeling experiments in 9:1 DCE/$CDCl_3$ reveal significant allylic rearrangement in the formation of **2**, with **2-re**/**2-un** = 34:66 ($h\nu$) or 41:59 (Δ).

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(16) ^{1}H NMR analysis relied on the δ 3.90 d ($J = 6.6$ Hz) signal of the α-CH_2 of **2-re**, the δ 5.30 dd ($J = 1.5$, 15.6 Hz) signal of the terminal vinyl proton cis to CD_2Cl of **2-un**, the δ 3.48 d ($J = 6.6$ Hz) signal of the α-CH_2 of **3-re**, and the δ 5.10 dd ($J = 1.5$, 10.2 Hz) signal of the terminal vinyl proton trans to CD_2COCl of **3-un**. (Note that there are small solvent-induced chemical shift changes between DCE−$CDCl_3$ and C_6D_{12}−pentane NMR solvents.)

(17) Laser flash photolysis experiments with diazirine **5** give $k_{\mathrm{frag}} = (6.5 \pm 0.1) \times 10^5\ \mathrm{s}^{-1}$ for carbene **1** in DCE and $(6.6 \pm 0.2) \times 10^5\ \mathrm{s}^{-1}$ in MeCN. These rate constants are not significantly affected by the addition of up to 1.8 M $Bu_4N^+Cl^-$, indicating that neither S_N2 nor S_N2' processes contribute to the fragmentation of **1** in these solvents. Details appear in: Ma, Y. Ph.D. Dissertation, Rutgers University, New Brunswick, NJ, 2003; pp 92f.

(18) $\Delta H^{\ddagger}_{298}$ for the dissociation of COCl radical is ∼8 kcal/mol,[19] whereas the COCl anion decays spontaneously to CO + Cl^-.[20] Therefore, a COCl radical generated by homolysis of **1** might be recaptured by allyl radical to yield **3-un** or **3-re**. However, a COCl anion from the heterolysis of **1** would dissociate to CO and Cl^- too rapidly for capture by allyl cation; only **2-un** and **2-re** would be expected from the heterolysis of **1**.

(19) Nicovitch, J. M.; Kreutter, P. H.; Wine, P. H. *J. Chem. Phys.* **1990**, *92*, 3539.

(20) Karpas, Z.; Klein, F. S. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *22*, 189.

(21) All structures were fully optimized by analytical gradient methods using the Gaussian 98 and Gaussian 03 suites[22] and density functional (DFT) calculations at the 6-31G(d) level, the exchange potentials of Becke,[23a] and the correlation functional of Lee, Yang, and Parr.[23b] Activation energies were corrected for zero-point energy differences (ZPVE) (unscaled) and thermal effects at 298.150 K. Vibrational analyses established the nature of all stationary points as either energy minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency).

(22) *Gaussian 03*, revision B.03; Gaussian, Inc: Pittsburgh, PA, 2003. See Supporting Information for the full reference.

(23) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Paar, R. G. *Phys. Rev. B.* **1988**, *37*, 785.

(24) Homolysis energy was calculated as the difference between the computed energies of carbene **1** and the allyl plus COCl radicals.

(25) Homolysis of **1** to allyl and COCl radicals is analogous to the cleavage of allylmethoxycarbenes to allyl and methoxycarbonyl radicals: Venneri, P. C.; Warkentin, J. *J. Am. Chem. Soc.* **1998**, *120*, 11182. See also the homolysis of benzyloxymethoxycarbene (Merkley, N.; El-Saidi, M.; Warkentin, J. *Can. J. Chem.* **2000**, *78*, 356) and, more distantly, the radical fragmentation of hydrazinoaminocarbenes: Cattoen, X.; Miqueu, K.; Gornitzka, H.; Bourissou, D.; Bertrand, G. *J. Am. Chem. Soc.* **2005**, *127*, 3292.

Computationally, in simulated MeCN (polarizable continuum model[22]), S_Ni fragmentation via TS **7** (see Figure 1B) becomes the favored pathway, leading to **2-un** with $\Delta H^{\ddagger}_{298} = 3.38$ kcal/mol. Intrinsic reaction coordinate analysis connects **7** to **2-un**; no S_Ni' pathway was located. The homolysis of carbene **1** in MeCN is calculated to require 8.41 kcal/mol and should not compete with S_Ni fragmentation via TS **7**.

Although we have not computationally located allyl chloride ion pairs, the heterolysis of carbene **1** to ion pair **9** very likely competes with S_Ni fragmentation in MeCN, given that 36% of Ritter amide **6** is formed; such products typically stem from initial attack of R^+ on MeCN.[26] We also suggest that heterolysis of **1** occurs in the DCE solvent, accounting for the observed label scrambling of product **2**.

In conclusion, the decomposition of allyloxychlorocarbene (**1**) in hydrocarbon solvents leads via homolysis to allyl and COCl radicals, which recombine to 3-butenoyl chloride (**3**) or (after scission of $^{\bullet}$COCl to CO and $^{\bullet}$Cl) to allyl chloride (**2**). Labeling experiments show that both products **2** and **3** are formed in part with allylic rearrangement. This is the first example of acyl chloride formation from ROCCl in solution, and it demonstrates that the COCl radical can survive within the solvent cage long enough to be captured by an allylic radical partner.

Acknowledgment. We are grateful to the National Science Foundation for financial support, to Professor Leslie Jimenez for a helpful discussion, and to the National Center for Computer Applications for allocation of time on the IBM P Series 690 (CHE 030060 to R.R.S.).

Supporting Information Available: Preparative details for compounds **4** and **5** and details of photolysis or thermolysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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[26] See Moss et al., cited in ref 11.