Pergamon

Tetrahedron Letters 43 (2002) 3069–3071

TETRAHEDRON
LETTERS

Fragmentation of alkoxychlorocarbenes in the gas phase

Michael E. Blake,[a] Maitland Jones, Jr.,[a,*] Fengmei Zheng[b] and Robert A. Moss[b,*]

[a]*Department of Chemistry, Princeton University, Princeton, NJ 08544, USA*
[b]*Department of Chemistry, Rutgers University, New Brunswick, NJ 08903, USA*

Received 30 January 2002; accepted 15 February 2002

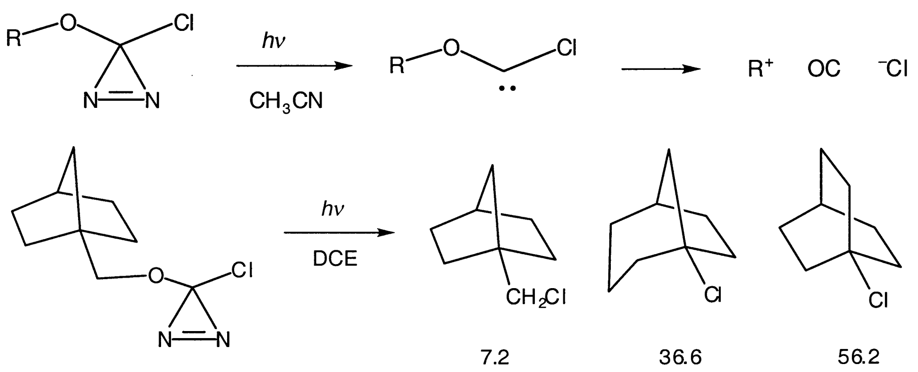
Abstract—In contrast to photolysis or thermal decomposition in solution, which is dominated by ionic reactions, flash vacuum pyrolysis of alkylchlorodiazirines in the gas phase generates radicals. The cyclopropylcarbinyl system is re-examined and the 1-norbornylcarbinyl system is studied for the first time. © 2002 Elsevier Science Ltd. All rights reserved.

Generation of alkoxyhalocarbenes in polar solvents such as acetonitrile or ethanol,[1a] and even pentane,[1b] leads to formation of ion pairs and the ultimate collapse to products of retained and rearranged structure. Two of the classic intermediates of physical organic chemistry, the cyclopropylcarbinyl cation,[2] and the 2-norbornyl cation,[3] have been recently revisited through this reaction. Here we describe another classic ion, the 1-norbornylcarbinyl cation, and show that the mechanism of carbene fragmentation strongly depends on the medium; in the gas phase radicals, not ion pairs, are the important intermediates.

In accord with this scheme, when diazirine **1** is photolyzed in dichloroethane (DCE) at room temperature, the products are the three chlorides, **2**, **3**, and **4**. The kinetic product of solvolysis of 1-norbornylcarbinyl compounds is the bicyclo[2.2.2] system;[4] thus, presence of **3** in substantial amounts argues for some measure of thermodynamic control in this reaction. Under thermodynamic conditions the bicyclo[3.2.1] system dominates the products from ring expansion of 1-bicyclo[2.2.1]carbinyl compounds.[5,6]

The small amount of **2** presumably derives from a bridged ion, or, more likely, from a minor amount of displacement by chloride at the neopentyl carbon of **1**. In any event, the amount of retained product **2** is small.

When **1** is decomposed by flash vacuum pyrolysis (FVP) at 500°C, the product mixture changes sharply. The following figure gives normalized percentages; there is about 15% of other products in the pyrolysis, mostly formates and alcohols. Although we have not been able to find a study of the 1-norbornylmethyl radical, the pyrolysis product ratios are consistent with a radical process in which the initially formed **5** is captured by a chlorine atom before substantial rearrangement. The observation of substantial retention of the bicyclo[2.2.1] skeleton is in keeping with the well-known lack of an authentic 1,2-hydrogen or alkyl shift in simple radicals.[7]

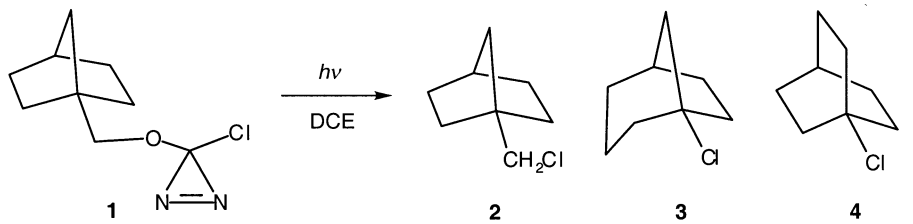


1 **2** **3** **4**

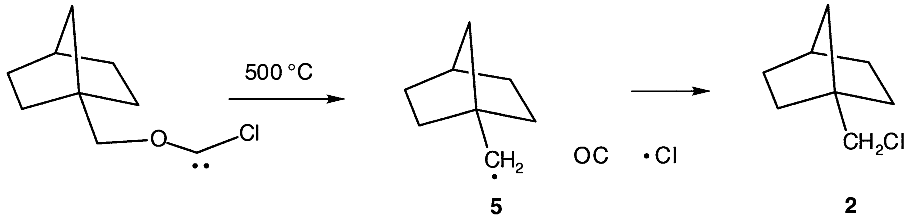
---

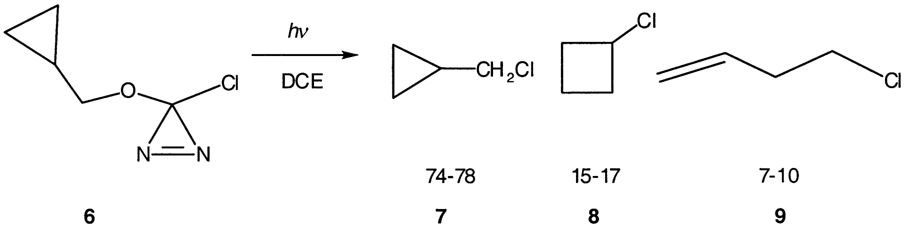
* Corresponding authors.

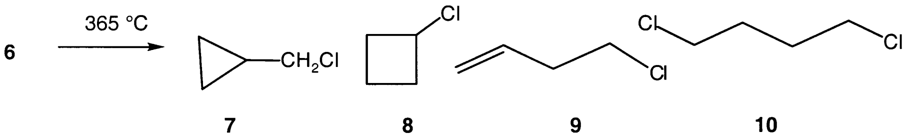
0040-4039/02/$ - see front matter
PII: S0040-4039(02)00438-0



	2	3	4
hν DCE	7.2	36.6	56.2
500 °C	45.8	22.0	32.2







	7	8	9	10
365 °C, gas phase	43.4	22.9	4.9	28.9
25 °C, solution	74-78	15-17	7-10	

Where do rearranged compounds **3** and **4** come from? We do not know for certain, but a likely possibility is a measure of concerted migration during fragmentation. Such a pathway is likely during the fragmentation of 1-adamantylmethoxychlorocarbene, which affords homoadamantyl chloride.[8] Alternatively, 500°C may be high enough to overcome the barrier to 1,2 alkyl migration.

We have put these tentative mechanistic suggestions to the test by re-examining the cyclopropylcarbinyl system **6**, and comparing the FVP results to the known decomposition in solution at room temperature.[2] Moss, et al. found the results shown above from either photolysis or pyrolysis of **6** (25°C) in dichloroethane[2] or pentane.[1b]

These results resemble closely the product spectrum under conditions in which ion pairs are important intermediates (**7**:**8**:**9**~79:14:7).[2]

We anticipated that the product spectrum from FVP of **6** would resemble that from the cyclopropylcarbinyl radical, not the cation, and be relatively rich in the ring-opened minor product, **9**.[9] In a study of the cyclopropylcarbinyl radical generated by photolysis of the diacyl peroxide, Sheldon and Kochi found about 60% of rearranged materials.[10] Our initial disappointment at the near-absence of **9** was assuaged by the observation that a fourth major product, **10** appeared in the product mixture.

Compound **10**, 1,4-dichlorobutane, is the product of the radical addition of chlorine atoms to **9**. Were cations somehow involved in the formation of **10**, the product would have been 1,3-dichlorobutane, which is not formed in any detectable amount. Thus, the formation of **10** becomes a lucky confirmation that the FVP reaction is radical in nature. Even though the cyclopropyl-carbinyl radical and its partner chlorine atom must be formed in proximity to each other, there is time for ring opening before capture. The products are stable under the reaction conditions.

It would seem that one has a choice in the decomposition of alkoxychlorodiazirines: reaction in solution leads to ionic intermediates, whereas decomposition in the gas phase generates radicals.

Acknowledgements

This work was supported at Princeton by the National Science Foundation through Grant CHE-0073373 and at Rutgers by the National Science Foundation through Grant CHE-0091368.

References

1. (a) Moss, R. A. *Acc. Chem. Res.* **1999**, *32*, 969; (b) Moss, R. A.; Zheng, F., unpublished.
2. Moss, R. A.; Zheng, F.; Johnson, L. A.; Sauers, R. R. *J. Phys. Org. Chem.* **2001**, *14*, 400.
3. Moss, R. A.; Zheng, F.; Sauers, R. R.; Toscano, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 8109.
4. Wilt, J. W.; Schneider, C. A.; Dabek, H. F., Jr.; Kraemer, J. J.; Wagner, W. J. *J. Org. Chem.* **1966**, *31*, 1543.
5. Sauers, R. R.; Ahlstrom, D. H. *J. Org. Chem.* **1967**, *32*, 2233.
6. For reviews see: (a) Walling, C. *Molecular Rearrangements*; de Mayo, P., Ed.; Wiley: New York, 1963; Chapter 7; (b) Wilt, J. W. *Free Radicals*; Kochi, J. K., Ed. Wiley: New York, 1973; Chapter 8.
7. Ref. 6b, p. 340ff.
8. (a) Moss, R. A.; Ge, C.-S.; Maksimovic, L. *J. Am. Chem. Soc.* **1996**, *118*, 9792; (b) Moss, R. A.; Johnson, L. A.; Yan, S.; Toscano, J. P.; Showalter, B. M. *J. Am. Chem. Soc.* **2000**, *122*, 11256.
9. Nonhebel, D. C. *Chem. Soc. Rev.* **1993**, 347.
10. Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395.