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Unexpected interconnection of the 7-norbornenyl and 3-nortricyclcyl/5-norbornen-2-yl cations

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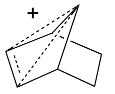
Abstract—Fragmentation of *syn*-7-norbornenyloxychlorocarbene provides products derived from both 7-norbornenyl cation-chloride anion pairs and from 3-nortricyclyl/2-norbornen-5-yl cation-chloride anion pairs. A 5,7-hydride shift within the 7-norbornenyl cation is proposed to interconnect the two cation systems.

The 7-norbornenyl cation **1** is the prime exemplar of homoallylic delocalization in organic chemistry.[1,2] Its formation via acetolysis of the *anti*-tosylate **2** is $\sim 10^{11}$ times faster than the acetolysis of (saturated) 7-norbornyl tosylate, and the *anti*-7-norbornenyl acetate (**3**) reaction product is formed stereospecifically by the capture of **1**.[1,2]



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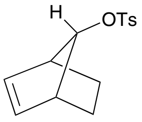

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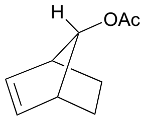

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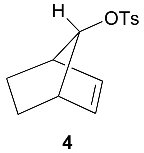

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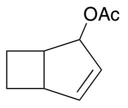

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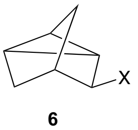
When the double bond is not in position to assist the tosylate's departure, as in the acetolysis of *syn*-tosylate, **4**, the reaction takes a very different course. Now, anchimeric assistance involves an *anti* σ bond, 1,2-carbon migration is concerted with tosylate loss, and the product is rearranged acetate **5**, formed from **4** 10^7 times more slowly than **3** is formed from **2**.[3] Not only tosylate solvolyses, but also amine deaminations follow this scenario: the aqueous HNO_2/HOAc deamination of *anti*-7-norbornenylamine gives only **3** and *anti*-7-norbornenol, whereas deamination of *syn*-7-norbornenylamine affords only **5** and the corresponding alcohol (as an epimeric mixture).[4]

Apparently unrelated are the solvolyses of 3-nortricyclyl brosylate (**6a**) and *exo*-norbornenyl brosylate (**7a**) in MeOH, HOAc, or HCOOH, which afford mixtures of **6b** and **7b**, **6c** and **7c**, and **6d** and **7d**, containing >90% of nortricyclyl products.[5,6] Similarly, diazonium ions **6e** and **7e** decompose in water to alcohols **6f** and **7f**, with **6f** strongly dominant.[7] These results can be attributed to the intermediacy of the 3-nortricyclyl and 2-norbornen-5-yl cations, **8** and **9**, which can be regarded as canonical forms of a resonance hybrid whose structure (in super acid solution) closely resembles **8**.[8]



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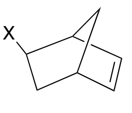

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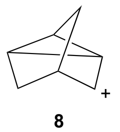

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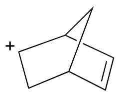

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a, X=OBs; **b**, X=OMe; **c**, X=OAc; **d**, X=OOCH; **e**, $X=N_2^+$; **f**, X=OH

We have undertaken an extensive study of carbene fragmentation, as nonsolvolytic entry to notable carbocations of organic chemistry; cf., Eq. 1.[9] Studies of the 2-norbornyl[10] and 3-bicyclo[3.1.0]hexyl[11] cations, for

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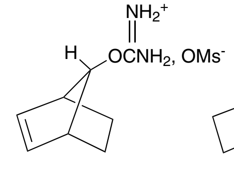
example, gave insight into the cation/anion/solvent equilibration of short-lived ion pairs.

$$\mathrm{RO\ddot{C}Cl} \rightarrow [\mathrm{R^+\ OC\ Cl^-}] \rightarrow \mathrm{RCl} + \mathrm{CO} \qquad (1)$$

Here, we report the existence of a 'wormhole' connecting the 7-norbornenyl and 3-nortricyclyl/2-norbornen-5-yl cation manifolds. This unanticipated nexus can be accessed by the fragmentation of *syn*-7-norbornenyloxychlorocarbene.

anti-7-Norbornenol was prepared in two steps from norbornadiene by literature methods,[12–14] while *syn*-7-norbornenol was obtained from norbornene in two steps by the method of Baird.[15] These alcohols were converted to *anti*- and *syn*-isouronium salts **10** and **11** by reaction with cyanamide and methanesulfonic acid.[16] The salts were obtained as oils admixed with urea. They were not purified, but directly converted to diazirines **12** and **13** by oxidation with NaOCl.[17] Both diazirines were unstable on silica, but could be purified by rapid chromatography on short, neutral alumina columns, eluted with very cold pentane. The diazirines were characterized by ^{1}H and ^{13}C NMR,[18] as well as IR and UV spectroscopy. In particular, there were characteristic[17] N=N bands in their IR (1540 cm^{-1}) and UV (349 nm, pentane) spectra.



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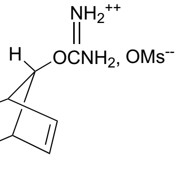

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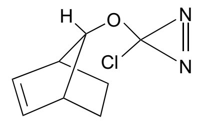

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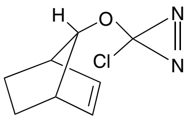

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Photolysis of *anti*-diazirine **12** in CDCl$_3$ at 350 nm and 25 °C gave *anti*-7-norbornenyl chloride (**15**), most reasonably understood as arising via the fragmentation of carbene **14** to (ion pair) **1**, followed by chloride capture; see Scheme 1. The identity of **15** followed from its NMR spectra, and GC and NMR spiking experiments with authentic **15** prepared from *anti*-7-norbornenol and SOCl$_2$ in ether.[19]

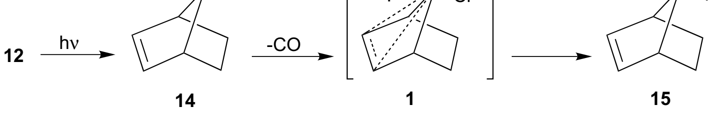
Conversion of diazirine **12** to chloride **15** via carbene **14** was quite clean; about 3% of dichloride (ROCHCl$_2$) and 4% of formate (ROOCH), trapping products[20] of **14** by HCl or H$_2$O, respectively, accompanied 93% of **15**. Photolyses of **12** in cyclohexane-d_{12} or CD$_3$CN gave 79% or 86% of **15**, respectively, with the balance as dichloride and formate.

Fragmentation of **14** in the presence of excess Bu$_4$N$^+$Cl$^-$in dichloroethane led only to *anti*-chloride **15**; there was no evidence for the formation of the *syn*-chloride isomer by a S$_N$2 reaction[21] at C-7. Thus, the fragmentation of *anti*-carbene **14** to chloride **15** is stereospecific, joining the acetolysis of tosylate **2**,[1] and the deamination of *anti*-7-norbornenylamine,[4] as reactions, which funnel through the delocalized 7-norbornenyl cation, **1**.

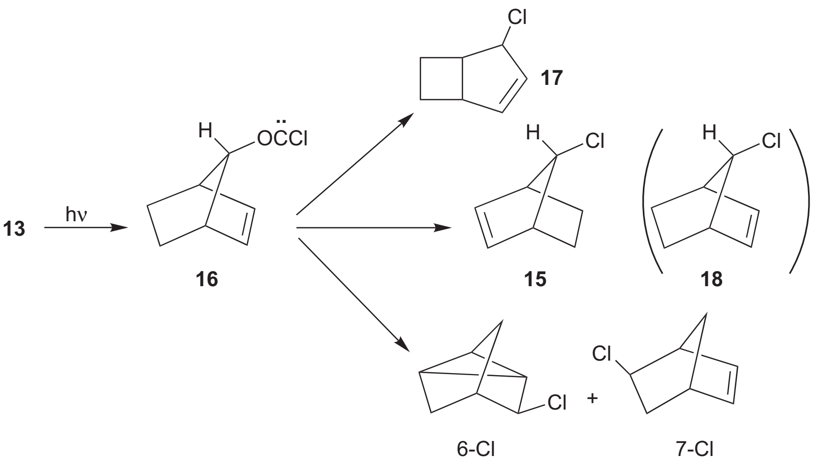
The photolysis of *syn*-diazirine **13** in CDCl$_3$, however, is considerably more complicated, affording 4-chlorobicyclo[3.2.0]hept-2-ene (**17**), *anti*-7-chloronorbornene (**15**), 3-chloronortricyclene (**6-Cl**), and *exo*-5-chloro-2-norbornene (**7-Cl**); cf., Scheme 2. Not shown in the scheme are the dichloride (ROCHCl$_2$) and formate (ROOCH) trapping products of carbene **16**, which account for $\sim$22% and $\sim$4%, respectively, of the product mixture.[22]

Product identities were established by GC–MS and ^{1}H and ^{13}C NMR comparisons (including spiking experiments) with authentic materials. Chloride **17**[23] was prepared by reaction of *anti*-bicyclo[3.2.0]hept-2-en-4-ol[3] with SOCl$_2$ and pyridine in ether. *anti*-7-Chloronorbornene (**15**) is described above.[19] Nortricyclcyl chloride (**6-Cl**) was prepared from nortricyclanol[24] and SOCl$_2$ in THF.[25] *exo*-5-Chloro-2-norbornene (**7-Cl**) was made from *exo*-5-norbornen-2-ol[26] and SOCl$_2$ in pyridine/ether.[27] Importantly, the key vinyl and C–Cl regions of the ^{1}H and ^{13}C NMR spectra of the product mixtures from carbene **16** did not show signals (<5%) that could be attributed to *syn*-7-chloronorbornene (**18**). By capillary GC, the normalized product distribution in Scheme 2 was **17** (74%), **15** (3.6%), **6-Cl** (8.6 %) and **7-Cl** (13.7%).

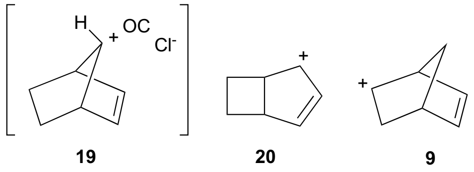
In that bicyclic chloride **17** is the major product from *syn*-oxychlorocarbene **16**, the fragmentation reaction follows the pattern established in the acetolysis of *syn*-tosylate **4**,[3] and the deamination of *syn*-7-aminonorbornene:[4] 1,2-alkyl migration *anti* to the leaving group is the dominant process in each case. In contrast to the earlier reactions, however, 1,2-alkyl migration (to **17**) *is not the exclusive process*, in the fragmentation of **16**: appreciable quantities of nortricylclyl chloride **6-Cl** and 5-norbornenyl chloride **7-Cl** are also formed.



Scheme 1.



Scheme 2.



This unprecedented outcome must, in part, reflect the low activation energy required for the fragmentation of carbene **16**. Laser flash photolysis[21] of diazirines **12** and **13** in dichloroethane, with pyridine ylide visualization of the carbene,[28] gave[20] $k_{\text{frag}}(\mathbf{14}) = 1.7(\pm 0.3) \times 10^5\ \text{s}^{-1}$ and $k_{\text{frag}}(\mathbf{16}) = 1.5 \pm 0.2 \times 10^6\ \text{s}^{-1}$. For *syn*-carbene **16**, an Arrhenius study from −30 to 30 °C gave $E_a = 7.4\ \text{kcal mol}^{-1}$.[29]

The low E_a required for the fragmentation of **16** obviates the need for extensive anchimeric assistance from a migrating ethano carbon, as occurs in the acetolysis of **4**. The carbene fragmentation is 'disconnected' from alkyl group migration, and other processes can compete. A similar disconnection occurs in the fragmentation of 3-bicyclo[3.1.0]hexyloxychlorocarbene.[11]

How does carbene **16** access the products of Scheme 2? We suggest that fragmentation of **16** initially affords short-lived ion pair **19**, from which 1,2-ethano migration affords the bicyclo[3.2.0]hept-2-ene-4-yl cation, **20**, and then chloride **17** by collapse with a chloride counterion. A small quantity of **19** evidently also undergoes intraion pair reorganization, ultimately leading to *anti*-7-norbornenyl chloride, **15**.

Further in Scheme 2, we note that the simplest connection between the 7-norbornenyl cation of **19** and the 2-norbornen-5-yl cation (**9**) involves a 5,7-hydride shift, which would directly transform **19** into **9**. Chloride collapse with **9** then affords **7-Cl**, while **8** also provides nortricyclyl chloride, **6-Cl**. The postulated hydride shift that converts **19** to **8/9** must compete with the ethano shift that transforms **19** to **20**. We suspect that the chloride anion of **19** plays an important part in the **19** → **9** conversion; otherwise we would also expect the deamination of *syn*-7-aminonorbornene to give nortricyclyl and 5-norbornenyl products (which it does not).[30]

In summary, fragmentation of *syn*-7-norbornenyloxychlorocarbene provides products derived from both 7-norbornenyl cation-chloride anion pairs and (surprisingly) from 3-nortricyclyl/2-norbornen-5-yl cation-chloride anion pairs. A 5,7-hydride shift within the 7-norbornenyl cation is postulated to interconnect the two cation systems.

Acknowledgements

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References and notes

1. (a) Winstein, S.; Shavatsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183; (b) Winstein, S.; Shavatsky, M. *J. Am. Chem. Soc.* **1956**, *78*, 592.
2. For a discussion and leading references, see: March, J. *Advanced Organic Chemistry*; 4th ed.; Wiley: New York, 1992, p 314*f*.
3. Winstein, S.; Stafford, E. T. *J. Am. Chem. Soc.* **1957**, *79*, 505.
4. Tanida, H.; Tsuji, T.; Irie, T. *J. Org. Chem.* **1966**, *31*, 3941.
5. Cristol, S. J.; Seifert, W. K.; Johnson, D. W.; Jurale, J. B. *J. Am. Chem. Soc.* **1962**, *84*, 3918.
6. Roberts, J. D.; Lee, C. C.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 3034.
7. Kirmse, W.; Knöpfel, N. *J. Am. Chem. Soc.* **1976**, *98*, 4672.

8. Jarret, R. M.; Veniero, J. C.; Byrne, T. P.; Saunders, M.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 8287, and references cited therein.
9. Moss, R. A. *Acc. Chem. Res.* **1999**, *32*, 969.
10. Moss, R. A.; Zheng, F.; Sauers, R. R.; Toscano, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 8109.
11. Moss, R. A.; Fu, X. *Org. Lett.* **2004**, *6*, 981.
12. Weiss, R. G.; Snyder, E. I. *J. Org. Chem.* **1970**, *35*, 1627.
13. Tanida, H.; Tsuji, T. *J. Org. Chem.* **1964**, *29*, 849.
14. Franzus, B.; Snyder, E. I. *J. Am. Chem. Soc.* **1965**, *87*, 3423.
15. Baird, W. C., Jr. *J. Org. Chem.* **1966**, *31*, 2411.
16. Moss, R. A.; Kaczmarczyk, G. M.; Johnson, L. A. *Synth. Commun.* **2000**, *30*, 3233.
17. Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.
18. Diazirine **12**: ^{1}H NMR (δ, CDCl$_3$): 6.01 (q, $J = 4$ Hz, 2H, vinyl H), 3.92 (s, 1H, *H*–C–O), 2.82 (m, 2H, bridgehead H), 1.57 and 1.00 (m's, 2H each, C-5 and C-6 H). ^{13}C NMR (δ, CDCl$_3$): 133.6, 86.3, 68.2, 43.8, 21.3. Diazirine **13**: ^{1}H NMR (δ, CDCl$_3$): 5.93 (m, 2H, vinyl H), 4.10 (s, 1H, *H*–C–O), 3.03 (m, 2H, bridgehead H), 1.77 and 1.04 (m's, 2H each, C-5 and C-6 H). ^{13}C NMR (δ, CDCl$_3$): 131.0, 92.0, 68.2, 44.7, 21.6. The diazirine carbon resonances at 68.2 ppm are very weak.
19. Tanida, H.; Hata, Y. *J. Org. Chem.* **1965**, *30*, 977, Key NMR resonances (δ, CDCl$_3$): ^{1}H: 6.07 (dd, $J = 2.0$, 1.2 Hz, 2H, vinyl H), 3.70 (d, $J = 1.2$ Hz, 1H, *H*–C–Cl), 2.75 (m, 2H, bridgehead H). ^{13}C: 135.3 (vinyl C), 68.1 (*C*–Cl), 47.0 (C-l, C-4), 21.3 (C-5, C-6).
20. Moss, R. A.; Ge, C.-S.; Maksimovic, L. *J. Am. Chem. Soc.* **1996**, *118*, 9792. Traces of water are responsible for carbene trapping, with the ultimate formation of formates.
21. Moss, R. A.; Johnson, L. A.; Merrer, D. C.; Lee, G. E., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 5940.
22. The dichloride is suppressed when the reaction is run in the presence of pyridine, which scavenges HCl.
23. Key resonances (δ, CDCl$_3$): ^{1}H NMR: 6.10, 5.97 (m, 2H, vinyl H), 4.74 (m, 1H, *H*–Cl–Cl). ^{13}C NMR: 139.4, 131.2 (vinyl C), 69.8 (*C*–Cl).
24. Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 1927.
25. Trecker, D. J.; Henry, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 3204, Key resonances (δ, CDCl$_3$): ^{1}H NMR: 3.89 (s, 1H, *H*–C–Cl). ^{13}C NMR: 65.8 (*C*–Cl).
26. Posner, G. H.; Ting, J.-S.; Lentz, C. M. *Tetrahedron* **1976**, *32*, 2281.
27. For ^{1}H NMR, see: Steele, W. C.; Jennings, B. H.; Botyos, G. L.; Dudek, G. O. *J. Org. Chem.* **1965**, *30*, 2886, Key ^{13}C NMR resonances (δ, CDCl$_3$): 140.8, 133.7 (vinyl C), 58.9 (*C*–Cl).
28. Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595.
29. We were unable to complete an Arrhenius study of carbene **14** due to weak carbene–pyridine ylide signals.
30. E_a for the decomposition of the *syn*-7-norbornenyldiazonium ion is likely to be quite low.