JOC Article

Nortricyclyl−Norbornenyl Cation System Accessed by Carbene Fragmentation

Robert A. Moss,* Yan Ma, Ronald R. Sauers,* and Mahvash Madni

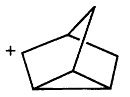
Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

moss@rutchem.rutgers.edu

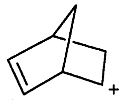
Received January 28, 2004

Fragmentation of nortricyclyloxychlorocarbene **5** in pentane occurs by an S_Ni-like process which yields nortricyclyl chloride **3g**. In more polar solvents, fragmentation leads to nortricyclyl cation chloride anion pairs (**9**) that give mainly **3g**, accompanied by ~10% of *exo*-2-norbornenyl chloride **4g**. From *exo*-2-norbornenyloxychlorocarbene **6** in hydrocarbon solvents, "S_Ni" reactions lead mainly to *exo*- (**4g**) and *endo*-2-chloro-5-norbornenes (**4g′**). Leakage to ion pairs adds ~16% of nortricyclyl chloride **3g**. In more polar solvents, the main product remains chloride **4g**, but increasing quantities of **3g** appear due to enhanced participation of ion pairs. Fragmentations of **5** and **6** in MeOH afford chlorides **3g** and **4g** as well as the corresponding methyl ethers **3b** and **4b**. Nortricyclyl cation and norbornenyl cation chloride anion pairs and methanol-solvated nortricyclyl cations are invoked to rationalize the results.

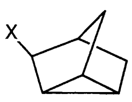
Formally, the nortricyclyl cation (**1**) and 5-norbornen-2-yl cation (**2**) are connected by a homoallylic rearrangement. However, structures **1** and **2** can also be regarded as canonical forms of a single resonance hybrid, whose structure (e.g., in superacid solution) is very close to that of **1**.[1] Not surprisingly, solvolyses of the related brosylates, **3a** and **4a**, afford mixtures of nortricyclyl and (exo) norbornenyl products in which the former are dominant; cf. Table 1.



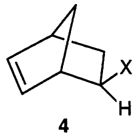
1



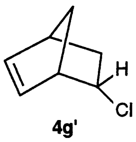
2



3



4



4g'

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

For example, solvolyses of **3a** or **4a** in methanol, acetic acid, or formic acid give mixtures of **3b** and **4b**, **3c** and **4c**, and **3d** and **4d** containing >90% of nortricyclyl product.[2,3] Similarly, decompositions of diazonium ions **3e** and **4e** yield alcohols **3f** and **4f** with **3f** strongly predominant.[4]

TABLE 1. Products from Nortricyclyl and Norbornenyl Precursors[a]

precursor	conditions	X	% 3-X	% 4-X	ref
3a	MeOH, 25 °C	OMe	93	7	2
4a	MeOH, 25 °C	OMe	92	8	2
3a	HOAc, 25 °C	OAc	95	5	2
4a	HOAc, 25 °C	OAc	92	8	2
4a	HOAc, 45 °C	OAc	89	11	3
4a	HCOOH, 45 °C	OOCH	96	4	3
3e	0.1 N aq NaOH	OH	96	4	4
4e	0.1 N aq NaOH	OH	96	4	4

[a] Product distributions are rounded to the nearest percent.

Much attention has been devoted to the nature of the carbocationic intermediates(s) that intervene in these reactions. Winstein[5] and Roberts[3] rationalized slight differences in product distributions from precursors **3a** and **4a**, together with labeling studies,[3] by postulating two cationic intermediates: a symmetrical nortricyclyl cation from **3a** and an unsymmetrical, but closely related, cation from **3b**. However, later deuterium-labeling experiments by Cristol were interpreted with ion-pair intermediates in which the cation was best represented as **1**, even from precursor **4a**.[2,6,7] Similar conclusions were reached from labeling studies carried out with diazonium ions **3e** and **4e**.[4] And, the cation generated from either 3-nortricyclanol (**3f**) or 5-norbornen-2-ol (**4f**) in superacid

---

[1] 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.

[2] Cristol, S. J.; Seifert, W. K.; Johnson, D. W.; Jurale, J. B. *J. Am. Chem. Soc.* **1962**, *84*, 3918.

[3] Roberts, J. D.; Lee, C. C.; Saunders: W. H., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 3034.

[4] Kirmse, W.; Knöpfel, N. *J. Am. Chem. Soc.* **1976**, *98*, 4672.

[5] Winstein, S.; Kosower, E. M. *J. Am. Chem. Soc.* **1959**, *81*, 4399.

[6] Cristol, S. J.; Morrill, T. C.; Sanchez, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 3087.

[7] Cristol, S. J.; Beimborn, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 3651. See also: Lee, C. C.; Hahn, B.-S. *J. Am. Chem. Soc.* **1970**, *92*, 2583.

10.1021/jo0401218 CCC: $27.50

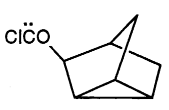
solution is best represented as **1**, with extensive charge delocalization into the cyclopropyl ring.[1,8−10]

Although the weight of evidence favors a single nortricyclyl-like cation as the key intermediate in the reactions of Table 1, when this cation is generated by solvolysis from precursors **3a** or **4a**, it arises as part of an ion pair. Olah made the important suggestion that the symmetrical or unsymmetrical nature of the cation "clearly depends on the degree of ionization, the acid strength, the nucleophilicity of the solvent system, and possible ion pair effects".[9] From this perspective, product distributions that exhibit "memory" of their precursor (i.e., **3** or **4**) can be traced to subtle differences in ion pairing, rather than to structurally distinct carbocations.

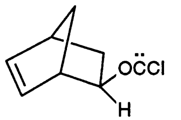
We have been exploring carbene fragmentation (eq 1) as an alternative, nonsolvolytic entry to important carbocationic intermediates of organic chemistry.[11] Studies of the 2-norbornyl system, for example, revealed differences in product distributions from exo or endo precursors that were attributed to incomplete cation/anion/solvent equilibration of short-lived ion-pair intermediates, which therefore transmitted (limited) memories of their origins to the products.[12] Related phenomena were encountered with bicyclo[2.2.2.]octyl cations generated either directly by the fragmentation of 1-bicyclo[2.2.2]-octyloxychlorocarbene or via the ring expansion-fragmentation of 1-norbornylmethoxychlorocarbene.[13]

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

Here, we describe the fragmentation of 3-nortricycloxychlorocarbene (**5**) and *exo*-5-norbornen-2-oxychlorocarbene (**6**), which afford products of series **3** and **4** and transit ion pairs that (at least in part) must differ from those arising from brosylates **3a** and **4a**.



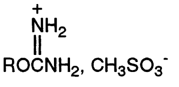
5



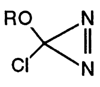
6

Results

Products. 3-Nortricyclanol[14] (**3f**) and *exo*-5-norbornen-2-ol[15] (**4f**) were converted[16] to their respective isouronium salts (**7a** or **7b**) with cyanamide and methanesulfonic acid. In neither case could we purify the oily mixture of isouronium salt and urea that we obtained. ^{1}H NMR spiking experiments with urea established that both mixtures contained about 33% of **7a** or **7b** and 67% of urea.



7



8

a, R = 3-nortricyclyl
b, R = *exo*-5-norbornen -2- yl

TABLE 2. Products from Photolyses of Diazirines 8a and 8b[a]

diazirine	carbene	solvent	nortricyclyl Cl (**3g**)	norbornenyl Cl (**4g**)	rearr[b]
8a	**5**	pentane	100		0.00
8a	**5**	DCE	89.2 (± 0.01)	10.8 (± 0.01)	0.12
8a	**5**	MeCN	89.9 (± 0.4)	10.1 (± 0.4)	0.11
8b	**6**	pentane[c]	16.4 (± 0.1)	56.1 (± 0.1)	0.20[d]
8b	**6**	C_6D_{12}[e]	16.0 (± 0.5)	53.0 (± 0.5)	0.19[d]
8b	**6**	DCE	32.4 (± 0.2)	67.6 (± 0.2)	0.48
8b	**6**	MeCN	43.0 (± 0.4)	57.0 (± 0.4)	0.75

[a] Results are averages of two experiments. Product distributions (%) are from GC analysis. [b] Rearrangement is the ratio of rearranged chloride/unrearranged chloride. [c] The products also contained 27.5(± 0.2)% of *endo*-5-chloro-2-norbornene (**4g′**). [d] The extent of rearrangement is **3g**/(**4g** + **4g′**). [e] Product distributions were obtained by NMR using the singlet C*H*Cl signal of **3g** as an internal standard. The products included 31.0(± 0.01)% of *endo*-5-chloro-2-norbornene.

Graham oxidation[17] with aqueous NaOCl of crude **7a** or **7b** to diazirines **8a** or **8b**, however, gave products that could be purified by column chromatography and characterized by IR, UV, and ^{1}H and ^{13}C NMR spectroscopy; details appear in the Experimental Section. Both **8a** and **8b** exhibited λ_{max} ~350 nm in 1,2-dichloroethane (DCE).

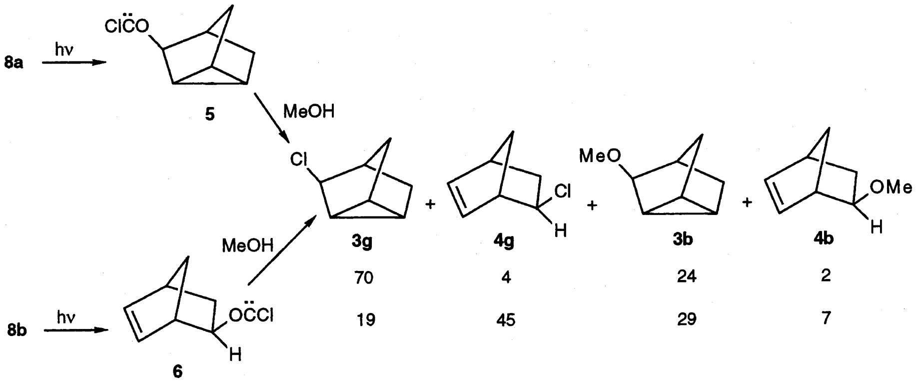
Photolyses of diazirines **8a** and **8b** ($\lambda > 320$ nm, $A_{350} = 1.0$) were carried out in pentane, DCE, or MeCN at 25 °C. Products were analyzed by capillary GC and NMR, with product identities confirmed by NMR, GC−MS, and GC spiking experiments with authentic samples.[18] The products and their distributions appear in Table 2. They include 3-nortricyclyl chloride (**3g**), *exo*-5-norbornenyl-2-chloride (**4g**), and (from diazirine **8b** in pentane or cyclohexane-d_{12}) *endo*-5-norbornenyl-2-chloride (**4g′**). These products are most readily understood as arising via fragmentations of carbenes **5** or **6**, formed upon photolysis of diazirines **8a** or **8b**, respectively.

Key observations contained in Table 2 include the following. (1) Fragmentation of carbene **5** in pentane gives *only* nortricyclyl chloride. (2) In the more polar solvents, DCE and MeCN, fragmentation of **5** gives ~90:10 distributions of nortricyclyl chloride (**3g**) and *exo*-norbornenyl chloride (**4g**), resembling the solvolytic product distributions from brosylates **3a** or **4a** in MeOH or HOAc (Table 1). (3) Fragmentation of carbene **6** in hydrocarbon solvents gives 27−31% of *endo*-norbornenyl chloride (**4g′**), as well as a mixture of chlorides **4g** and **3g**, heavily weighted toward **4g**. (4) In the more polar DCE and MeCN solvents, *endo*-chloride **4g′** is not formed, but the **4g**/**3g** product mixture still favors **4g**. (5) The fragmentation of carbene **6** responds to solvent polarity

---

(8) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1973**, *95*, 3792.
(9) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 1920.
(10) Saunders, M.; Jarret, R. M.; Pramanik, P. *J. Am. Chem. Soc.* **1987**, *109*, 3735.
(11) Moss, R. A. *Acc. Chem. Res.* **1999**, *32*, 969.
(12) Moss, R. A.; Zheng, F.; Sauers, R. R.; Toscano, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 8109.
(13) Moss, R. A.; Zheng, F.; Fedé, J.-M.; Sauers, R. R. *Org. Lett.* **2002**, *4*, 2341.
(14) Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 1927.
(15) Posner, G. H.; Ting, J.-S.; Lentz, C. M. *Tetrahedron* **1976**, *32*, 2281.
(16) Moss, R. A.; Kaczmarczyk, G.; Johnson, L. A. *Synth. Commun.* **2000**, *30*, 3233.
(17) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.
(18) Chloride **3g** was prepared from nortricyclanol (**3f**) and $SOCl_2$ in THF (Trecker, D. J.; Henry, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 3204). Chloride **4g** was prepared from *exo*-5-norbornen-2-ol (**4f**) and $SOCl_2$ in ether/pyridine (^{1}H NMR: Steele, W. C.; Jennings, B. H.; Botyos, G. L.; Dudek, G. O. *J. Org. Chem.* **1965**, *30*, 2886.) *endo*-2-Chloro-5-norbornene (**4g′**) was identified by its NMR spectrum (Moen, R. V.; Makowski, H. S. *Anal. Chem.* **1967**, *39*, 1860).

SCHEME 1



in that the extent of rearrangement (to **3g**) increases from 0.20 to 0.48 to 0.75 as the solvent is altered from pentane to DCE to MeCN. These observations will be explicated in the Discussion.

Carbenes **5** and **6** were also generated in MeOH and in MeOH−DCE mixtures. The fragmentation products and their distributions in pure MeOH are shown in Scheme 1. Note that we did not observe products from trapping of the carbenes by methanol. As previously noted,[11] fragmentations of many alkoxychlorocarbenes are faster than methanol trapping.

From nortricyclyloxychlorocarbene **5**, chloride products **3g** and **4g** form in a distribution of 70:4 (~95:5), similar to distributions observed for the fragmentations of **5** in DCE or MeCN (~90:10, Table 2), the dediazoniation of **3e** (96:4, Table 1), or various solvolyses of **3a** (Table 1). However, the chlorides formed by fragmentation of the norbornenyloxychlorocarbene **6** are heavily weighted toward *exo*-norbornenyl chloride; i.e., **3g**/**4g** = 19:45. This "memory effect" is specific to the fragmentation of **6**; solvolyses of brosylate **4a** or dediazoniation of **4e** give product mixtures that are strongly biased toward nortricyclyl derivatives (Table 1).

Significantly, the distribution of methyl ethers formed from carbene **6** (**3b** and **4b**, Scheme 1) also obeys the nortricyclyl-rich pattern (**3b**/**4b** = 29:7~80:20). The contrasting distributions of chlorides (**3g**/**4g**) and ethers (**3b**/**4b**) formed from **6** suggest important differences in their immediate precursors, where the precursor of the ethers is likely similar to the product-determining intermediate formed from carbene **5**.

The relative yields of chlorides **3g** and **4g**, and ethers **3b** and **4b**, were determined by capillary GC analysis in various blends of MeOH and DCE. The distributions are plotted against the mole fraction of MeOH in Figure 1; the original data appear in Table S1 in the Supporting Information. Not surprisingly, yields of chlorides **3g** and **4g** decrease, while those of the corresponding ethers, **3b** and **4b**, rise with increasing methanol concentration. More importantly, the nortricyclyl/norbornenyl product ratios, **3**/**4**, are 0.41−0.46 for the chlorides and 3.0−4.2 for the ethers over the range of MeOH mole fractions, suggesting that the chlorides and ethers arise from distinct intermediates or ion pairs. Similar phenomena were encountered for the fragmentations of *exo*- and *endo*-2-norbornyloxychlorocarbenes in MeOH/MeCN.[12]

Kinetics. Absolute rate constants for the fragmentations of carbenes **5** and **6** were determined by laser flash photolysis (LFP)[19] using the pyridine ylide method of carbene visualization.[20,21] Carbene **5** is illustrative: LFP at 351 nm and 25 °C of diazirine precursor **8a** in DCE (A_{350} ~1.0) in the presence of pyridine gave an absorbance at 416 nm assigned to the carbene **5**-pyridine ylide.

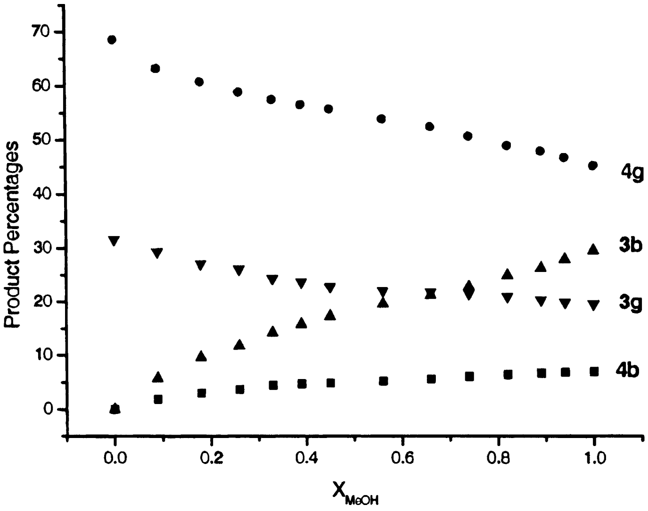


FIGURE 1. Product distributions (%) from the fragmentations of carbene **6** in MeOH−DCE vs mole fraction (X) of MeOH. See Scheme 1 for product identities.

A correlation of the apparent rate constants for ylide formation, k_{obs} ($2.01 \times 10^5 - 5.85 \times 10^5$ s^{-1}), vs pyridine concentration (1.65−7.42 M) was linear (eight points, $r = 0.999$) with a slope of 6.70×10^4 M^{-1} s^{-1}, taken as the rate constant for ylide formation, k_y. The *Y*-intercept of the correlation was 8.84×10^4 s^{-1}, which we take as k_{frag}, the rate constant for fragmentation of carbene **5**.[21] (This correlation is shown in Figure S1 of the Supporting Information.) Repetition gave a second value, $k_{frag} = 9.53 \times 10^4$ s^{-1}, leading to an average rate constant of 9.19 ($\pm$0.35) $\times 10^4$ s^{-1}. The average rate constant for ylide formation was $k_y = 6.84(\pm 0.14) \times 10^4$ M^{-1} s^{-1}.

Similarly, we measured k_{frag} for carbene **6** in DCE (see Figure S2 of the Supporting Information). Two

---

[19] For a description of our LFP apparatus, see: Moss, R. A.; Johnson, L. A.; Merrer, D. C.; Lee, G. E., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 5940. The 1000 W Xe monitoring lamp described there has been replaced by a Photophysics LS.1 150 W pulsed Xe light source.

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

[21] Moss, R. A.; Ge, C.-S.; Maksimovic, L. *J. Am. Chem. Soc.* **1996**, *118*, 9792.

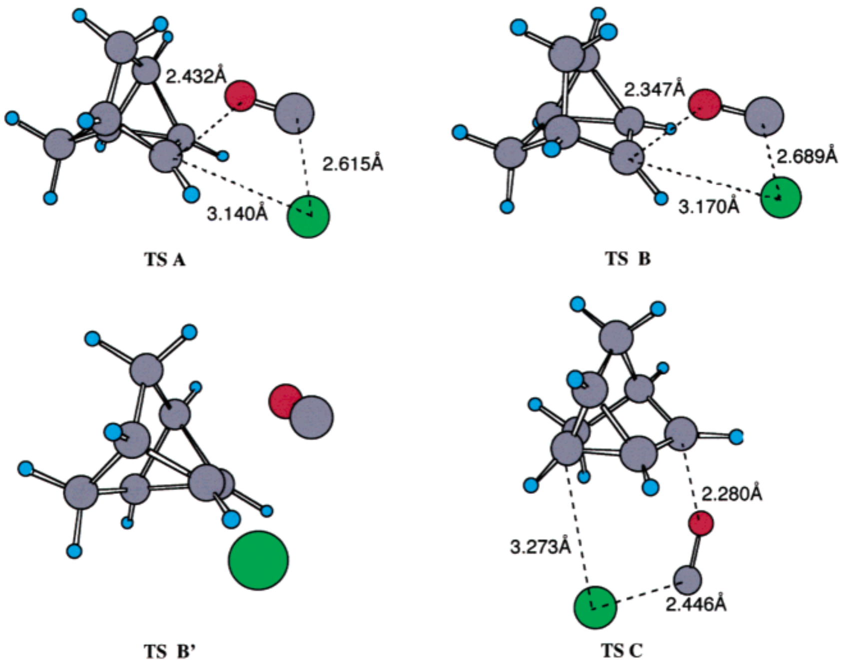


FIGURE 2. Computed transition states for the fragmentations of carbene **5** to nortricyclyl chloride (**3g**) with retention (**TS A**), to chloride **3g** with inversion (**TS B**), and for rearrangement to *endo*-2-chloro-5-norbornene **4g′** (**TS C**).

LFP runs gave $k_{\text{frag}} = 4.05(\pm0.09) \times 10^4\ \text{s}^{-1}$ and $k_y = 5.13(\pm0.01) \times 10^4\ \text{M}^{-1}\ \text{s}^{-1}$. In DCE, the fragmentation of carbene **5** is about twice as fast as that of carbene **6**, an order which is reversed in the acetolyses of brosylates **3a** and **4a**, where **4a** solvolyses about 3.5 times faster than **3a**.[22]

Fragmentations of carbenes **5** and **6** are orders of magnitude faster than solvolyses of **3a** and **4a** because the activation energies for the carbene fragmentations are low. We determined k_{frag} for carbene **5** in DCE at 5 temperatures over the range −9.6 to 29.9 °C. An Arrhenius correlation of ln k_{frag} vs $1/T$ (Figure S3 in the Supporting Information) gave $E_a \sim 6.3$ kcal/mol, $\Delta S^{\ddagger} \sim -16$ eu for the fragmentation of **5**. An attempted Arrhenius correlation for carbene **6** gave data that was too scattered for meaningful analysis, probably reflecting a very low E_a for this fragmentation.

Discussion

The principal results from fragmentations of carbenes **5** and **6** can be rationalized by ion-pair intermediates which are responsive to solvent polarity and vary in "tightness". In the limiting case of nonpolar solvents such as pentane, the ion pairs approach covalency and display characteristics associated with the S_Ni mechanism. The idea of a spectrum of ion pairs ranging from solvent-separated, through intimate, to near covalent, is associated with Winstein, who noted that "...there is no sharp distinction between formation of an intimate ion pair followed by internal return and a cyclic rearrangement [i.e., S_Ni reaction], and marginal cases may be expected."[23] More recently, Schleyer et al. provided experimental and computational evidence for an S_Ni-ion-pair continuum in the decomposition of alkyl chlorosulfites, a reaction analogous to the fragmentation of alkoxychlorocarbenes.[24] Jones et al. presented a related scenario in which certain alkoxychlorocarbenes were suggested to fragment via "a carbocation which is committed to chloride formation through intermolecular capture with retention."[25]

In the present instance, fragmentation of nortricyclyloxychlorocarbene **5** in pentane gives only nortricyclyl chloride **3g** (Table 2), a reaction that seems to approximate the S_Ni mechanism. We examined this fragmentation computationally.[26−28] A conformational search for carbene **5** located conformers which led to the three transition states (TS) pictured in Figure 2. **TS A** led to nortricyclyl chloride **3g** with retention ($\Delta G^{\ddagger} = 12.0$ kcal/mol), **TS B** gave **3g** with inversion ($\Delta G^{\ddagger} = 11.1$ kcal/mol),

---

[22] Winstein, S.; Walborsky, H. M.; Schreiber, K. *J. Am. Chem. Soc.* **1950**, *72*, 5795.

[23] Winstein, S.; Robinson, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 169.

[24] (a) Schreiner, P. R.; Schleyer, P. v. R.; Hill, R. K. *J. Org. Chem.* **1993**, *58*, 2822. (b) Schreiner, P. R.; Schleyer, P. v. R.; Hill, R. K. *J. Org. Chem.* **1994**, *59*, 1849.

[25] Likhotvorik, I. R.; Jones, M., Jr.; Yurchenko, A. G.; Krasutsky, P. *Tetrahedron Lett.* **1989**, *30*, 5089.

[26] All structures were fully optimized by analytical gradient methods using the Gaussian98 and Gaussian03 suites[27] and density functional (DFT) calculations at the 6-31G(d) level, the exchange potentials of Becke[28a] and the correlation functional of Lee, Yang, and Parr.[28b] Activation energies were corrected for zero-point energy differences (ZPVE) (unscaled) and thermal effects at 298.150 Kelvin. Vibrational analyses established the nature of all stationary points as either energy minima (no imaginary frequencies) or first order saddle points (one imaginary frequency). Solvation effects in acetonitrile ($\epsilon = 36.64$) utilized PCM[27] methodology.

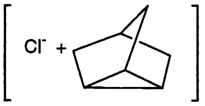
[27] Gaussian98, Revision A.9: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheesman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

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

while **TS C** afforded *endo*-norbornenyl chloride (**4g′**, $\Delta G^{\ddagger} = 14.7$ kcal/mol).[29] (Another view of **TS B**, emphasizing its inverting nature, is shown in **TS B′**.) **TS C**, due to its higher enthalpy of activation, should not be competitive in vacuo (or in pentane) with the "direct" fragmentations of **5** to **3g** via **TS A** and **TS B**.[30] Indeed, **4g′** is not formed from carbene **5** under the experimental conditions (Table 2).

TS A and **TS B** can be construed as "S_Ni" transition states: positive charge buildup on the nortricyclyl C(H) reaction center is only ~0.05 unit, and the C(terminus)–Cl separations of **TS A** and **TS B** are 3.14 and 3.17 Å, respectively. The computational results recall those obtained for alkyl chlorosulfite decompositions, where retention and inversion transition states were also encountered.[24b]

The S_Ni-like transition states of Figure 2 account for the sole production of chloride **3g** from carbene **5** in the nonpolar solvent pentane ($\epsilon = 1.84$). In the more polar solvents DCE ($\epsilon = 10.4$) and MeCN ($\epsilon = 36.6$), carbene **5** probably fragments via a tight nortricyclyl chloride ion pair which yields both chloride **3g** and *exo*-norbornenyl chloride **4g** in a ratio of ~9:1 (Table 2). This ion pair likely resembles the species formed during the solvolysis of brosylate **3a**, or the decomposition of diazonium ion **3e**, where high nortricyclyl/norbornenyl product ratios are also observed (Table 1). We have not been able to locate this nortricyclyl chloride ion pair computationally taking carbene **5** as the starting point. However, we imagine that its chloride anion must initially reside near C3 of the nortricyclyl skeleton, cf. **9**.



9

The product distributions from *exo*-norbornenyloxychlorocarbene **6** are more complex. In pentane or cyclohexane-d_{12}, three products form: *exo*-**4g** and *endo*-2-chloro-5-norbornene (**4g′**), as well as nortricyclyl chloride (**3g**); cf. Table 2. The extent of "rearrangement" is low; only ~16% of **3g** is formed. Computational studies reveal three conformations of carbene **6** which furnish three transition states (Figure 3): **TS D** leads to norbornadiene by HCl elimination ($\Delta G^{\ddagger} = 12.3$ kcal/mol), **TS E** affords *exo*-norbornenyl chloride **4g** with retention ($\Delta G^{\ddagger} = 12.1$ kcal/mol), and **TS F** gives *endo*-chloride **4g** with inversion ($\Delta G^{\ddagger} = 11.6$ kcal/mol).[29]

The prediction that HCl elimination should be the least favored pathway accords with experiment. Careful examination of the ^{1}H NMR product spectra limits the yield of norbornadiene to 5% in cyclohexane-d_{12}, 2% in $CDCl_3$, and <1% in CD_3CN. On the other hand, *exo*- and *endo*-norbornenyl chlorides are formed as major products from carbene **6** in hydrocarbon solvents, along with some nortricyclyl chloride. The norbornenyl chlorides can arise directly via "S_Ni" transition states **TS E** and **TS F**. However, somewhat more exo (**4g**) than endo (**4g′**) chloride is formed from carbene **6** despite the 0.5 kcal/mol higher computed $\Delta G^{\ddagger}$ for the former pathway.

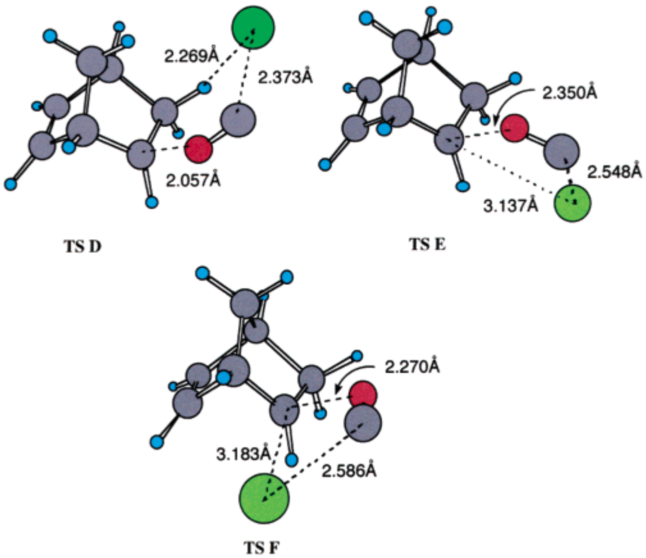


FIGURE 3. Computed transition states for the fragmentations of carbene **6** with elimination to norbornadiene (**TS D**), with retention to *exo*-2-chloro-5-norbornene (**TS E**), and with inversion to *endo*-2-chloro-5-norbornene (**TS F**).

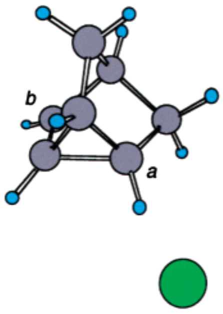


FIGURE 4. "Ion pair" intermediate derived from **TS F**; see text for discussion.

How does chloride **3g** arise from carbene **6** in pentane? We suggest leakage to a tight norbornenyl cation chloride anion pair during the fragmentation of **6**. This ion pair must differ from **9**, the nortricyclyl cation chloride anion pair formed from carbene **5** (which gives mainly chloride **3g**). Presumably, the ion pairs differ in the relative positions of C^+ and Cl^-. We have computationally approximated the ion pair from carbene **6** in the following way. **TS F** (Figure 3) was subjected to optimization in simulated MeCN solvent by the PCM method. This optimization did not succeed. However, after arbitrary removal of the CO, optimization proceeded to the ion pair pictured in Figure 4, which was indeed an energy minimum. Here, return of Cl^- to carbon *a* (separation 3.35 Å) to form **4g** should be favored over Cl^- return to carbon *b* (separation 5.59 Å) to form **3g**. This accords with the experimental preference for **4g** (and **4g′**) observed in the fragmentation of carbene **6**.

As solvent polarity increases (DCE and MeCN), the *endo*-norbornenyl chloride (**4g′**) disappears in favor of nortricyclyl chloride **3g**, while the yield of *exo*-chloride **4g** remains nearly constant (Table 2). We suggest that in the more polar solvents, **TS F** is diverted to the ion

---

(29) The TS → product connections were verified by intrinsic reaction coordinate methodology.[27]

(30) The sterochemical outcome of the **5** → **3g** transformation could be examined with optically active materials; such experiments are contemplated in the future.

pair of Figure 4, which enjoys a greater lifetime with increasing solvent polarity, consequently reorganizing more effectively to nortricyclyl chloride ion pair **9**, and thence to chloride **3g**. There are stereochemical predictions that can be extracted from such a mechanistic pathway that, at least in principle, could be tested.

Fragmentation of carbene **6** differs from the solvolysis of brosylate **4a** or the dediazoniation of **4e** in that the product mixture from the fragmentation reaction is weighted toward norbornenyl chlorides (Table 2), whereas the latter two reactions are biased toward nortricyclyl chloride (Table 1). Similarly, Spurlock and Cox, who examined the rearrangement and isomerization of nortricyclyl and norbornenyl thiocyanates in MeCN at 150 °C,[31] reported that the product mixture obtained from the norbornenyl thiocyanate contained significantly more "unrearranged" *exo*-5-norbornenyl-2-isothiocyanate than obtained from the nortricyclyl thiocyanate. The reverse was true for nortricyclyl thiocyanate, where nortricyclyl isothiocyanate was produced in larger quantities than from the norbornenyl thiocyanate. Spurlock and Cox postulated ion pairs that differed in the position of the anion relative to the faces of the cation,[31] much as we have invoked ion pairs which differ in the relative position of chloride, depending on whether the carbene precursor is **5** or **6**.[32]

Finally, we consider the fragmentations of **5** and **6** in MeOH (Scheme 1, Table S1 (Supporting Information), Figure 1). Even in pure methanol (Scheme 1), chlorides **3g** and **4g** remain the major reaction products, and their distributions reflect their origins: from carbene **5**, **3g** > **4g**, while from carbene **6**, **4g** > **3g**. These results are similar to those obtained in DCE or MeCN (Table 2) and can be understood in terms of a solvent-dependent blend of S_Ni reactions and chloride return from either ion pair **9** or the ion pair of Figure 4. In contrast, the methyl ethers formed from either carbenes **5** or **6** are nearly identical in distribution, heavily favoring nortricyclyl ether **3b** over norbornenyl ether **4b**. This suggests that, in MeOH, the initial chloride-containing ion pairs are partly diverted to methanol-solvated nortricyclyl cations which largely react at C3 to give **3b**. A minor competitive pathway involves MeOH attack at C6 leading to **4b**.

In summary, fragmentation of nortricyclyloxychlorocarbene **5** occurs by a S_Ni-like process in pentane which yields nortricyclyl chloride **3g**. In more polar solvents, fragmentation leads to nortricyclyl chloride ion pairs (**9**) that give mainly **3g**, accompanied by ~10% of norbornenyl chloride **4g**. From norbornenyloxychlorocarbene **6** in hydrocarbon solvents, "S_Ni" reactions lead mainly to *exo*- (**4g**) and *endo*- (**4g′**) 2-chloro-5-norbornenes. Leakage to ion pairs adds ~16% of nortricyclyl chloride **3g**. In more polar solvents, the main product remains chloride **4g**, but increasing quantities of **3g** appear due to enhanced participation of ion pairs. Fragmentations of **5** and **6** in MeOH afford chlorides **3g** and **4g** as well as the corresponding methyl ethers, **3b** and **4b**. Nortricyclyl chloride and norbornenyl chloride ion pairs, as well as methanol-solvated nortricyclyl cations, can be invoked to rationalize the results.

Experimental Section

Solvents. Acetonitrile and pyridine were dried by reflux over CaH_2, followed by distillation and storage over 5A molecular sieves. Dichloroethane was used as purchased. Pentane and cyclohexane were stored over 5A molecular sieves.

***O*-(Nortricyclyoxy)isouronium Methanesulfonate (7a).** In a 100 mL round-bottom flask, equipped with a stirring bar and protected with a $CaCl_2$ tube, was stirred a mixture of nortricyclyl alcohol (**3f**)[14] (5 g, 45 mmol), cyanamide (0.96 g, 22.5 mmol), and methanesulfonic acid (1.50 mL, 2.18 g, 22.5 mmol) for 24 h. The reaction mixture was poured into ether and kept in the refrigerator. After 15 days, it was still an oil. The oil was washed with a large amount of ether and dried under vacuum for 8 h. Yield: 4.06 g, 24%. (This crude material was spiked with urea, which proved that it contained 67% of urea by ^1H NMR). ^1H NMR (δ, DMSO-d_6): 8.50 (br, 4H), 4.65 (s, 1H), 2.49 (s, 3H), 1.73−1.69 (m, 2H), 1.43−1.20 (m, 5H), 1.06 (m, 1H). ^{13}C NMR (δ, DMSO-d_6); 161.9 (urea), 161.8, 86.1, 40.4, 33.9, 30.7, 30.5, 14.4, 13.9, 12.3.

***O*-(*exo*-5-Norbornen-2-oxy)isouronium Methanesulfonate (7b).** In a 100 mL round-bottom flask, equipped with a stirring bar and protected with a $CaCl_2$ tube, was stirred a mixture of *exo*-5-norbornen-2-ol (**4f**)[15] (2 g, 18 mmol), cyanamide (0.74 g, 18 mmol), and methanesulfonic acid (1.18 mL, 1.75 g, 18 mmol) for 24 h. The reaction mixture was poured into ether and kept in the refrigerator. After 15 days, it was still an oil. The oil was washed with a large amount of ether and dried under vacuum for 8 h. Yield: 2.94 g, 23%. (This crude material contained 67% of urea by ^1H NMR.) ^1H NMR (δ, DMSO-d_6): 8.52 (br, 4H), 7.28 (br, urea), 6.45 (m, 1H), 6.0 (m,1H), 4.6 (s, 1H), 2.46 (s, 3H), 1.83−1.30 (m, 5H), 1.06 (m, 1H). ^{13}C NMR (δ, DMSO-d_6): 161.9 (urea), 162.3, 142.3, 132.5, 81.8, 47.7, 46,5, 40.9, 40.3, 35.2.

Diazirines 8a and 8b. A Graham oxidation[17] was used to convert isouronium salts **7a** and **7b** to the diazirines. To a mixture of lithium chloride (4.2 g) in DMSO (90 mL) was added 1.0 g of isouronium salt and 40 mL of pentane. The mixture was kept under 20 °C while 150 mL of 12% commercial aqueous sodium hypochlorite, saturated with sodium chloride, was added dropwise with stirring over about 30 min. The mixture was then transferred to a separatory funnel and the aqueous layer was drained. The pentane layer was washed twice with ice−water. The diazirine−pentane solution was dried over anhydrous calcium chloride at 0 °C for 2 h and then purified by column chromatography over silica gel eluted with cold pentane. The pentane was removed by rotary evaporation and replaced by DCE or MeCN to a volume of ~30 mL.

3-(3-Nortricyclyloxy)-3-chlorodiazirine (8a). ^1H NMR (δ, $CDCl_3$): 4.23 (s, 1H), 2.12−2.00 (m, 2H), 1.51−1.26 (m, 6H). ^{13}C NMR (δ, $CDCl_3$); 84.6, 70.9, 33.8, 30.5, 30.2, 14.1, 13.3, 11.5 IR (film): 1540 cm^{-1}. UV: 350 nm (pentane, DCE).

3-(*exo*-5-Norbornen-2-oxy)-3-chlorodiazirine (8b). ^1H NMR (δ, $CDCl_3$): 6.27−6.24 (m, 1H), 5.98−5.95 (m, 1H), 4.25 (d, $J = 6$ Hz, 1H), 3.06−2.83 (m, 2H), 1.76−1.26 (m, 4H). ^{13}C NMR (δ, $CDCl_3$): 141.8, 132.3, 80.4, 71.0, 47.6, 46.2, 40.8, 34.6 IR (film): 1539 cm^{-1}. UV: (350 nm, pentane, DCE).

3-Chloronortricyclene (3g). This chloride was prepared by the method of Trecker and Henry.[18] 3-Nortricyclanol (**3f**)[14] (4 g, 36 mmol) and thionyl chloride (5.28 mL, 270 mmol) were stirred together for 15 min at room temperature, and then 10 mL of THF was added. The mixture was refluxed overnight, and a brown liquid was obtained. Thionyl chloride was stripped at the water pump. Then the residue was dissolved in 100 mL of ethyl ether and washed with 2 × 100 mL of brine, 100 mL of saturated aqueous sodium bicarbonate, and then again with 100 mL of brine. The ether layer was dried over sodium sulfate and vacuum stripped. The product, 3.1 g (67%), was then purified by column chromatography with 4:1 hexanes and ethyl

---

(31) Spurlock, L. A.; Cox, W. G. *J. Am. Chem. Soc.* **1971**, *93*, 146.

(32) Moss, R. A.; Johnson, L. A.; Kacprzynski, M.; Sauers, R. R. *J. Org. Chem.* **2003**, *68*, 5114.

acetate as eluent. GC/MS (*m/e*): M$^+$, 126:128 = 3:1. ^{1}H NMR (δ, CDCl$_3$, lit.[18]): 3.89 (s, 1H), 2.04−1.95 (m, 2H), 1.39−1.26 (m, 6H). ^{13}C NMR (δ, CDCl$_3$, lit.[33]): 65.8, 37.5, 32.0, 30.6, 18.2, 14.2, 11.6.

***exo*-5-Chloro-2-norbornene (4g).** This compound was prepared by a modification of the method of Trecker and Henry.[18] *exo*-5-Norbornen-2-ol (**4f**)[15] (1 g, 9 mmol) was dissolved in dry ethyl ether. To this mixture were added dropwise pyridine (0.83 mL, 9 mmol) and then thionyl chloride (0.98 mL, 13.5 mmol). The mixture was refluxed overnight, and a brown liquid was obtained. Thionyl chloride was stripped at the water pump. Then the residue was dissolved in 100 mL of ethyl ether and washed with 2 × 100 mL of brine, 100 mL of saturated aqueous sodium bicarbonate, and then again with 100 mL of brine. The ether layer was dried over sodium sulfate and vacuum stripped. The product, 0.7 g (60%), contained 56% of *exo*-5-chloro-2-norbornene **4g** and 44% of 3-chloronortricyclene **3g** by GC analysis. It was purified by column chromatography over silica gel with 4:1 pentane and ethyl acetate as eluent. GC/MS (*m/e*): M$^+$, 126:128 = 3:1. ^{1}H NMR (δ, CDCl$_3$, for literature data, see ref 18): 6.19−6.17 (m, 1H), 5.99−5.97 (m, 1H), 3.73 (m, 1H), 2.96−2.89 (m, 2H), 2.03−1.76 (m, 4H). ^{13}C NMR (δ, CDCl$_3$): 140.8, 133.7, 58.9, 51.8, 46.4, 42.1, 38.6.

***endo*-5-Chloro-2-norbornene (4g′)** was identified by its ^{1}H NMR spectrum.[18,34]

3-Methoxynortricyclene (3b) and *exo*-5-Methoxy-2-norbornene (4b). These ethers were prepared as a mixture.[35] To a solution of 5.2 g of 96% sulfuric acid in 50 g of absolute methanol (10% sulfuric acid solution in methanol) was added 10 g (0.10 mol) of norbornadiene. The mixture was heated under slow reflux for 2 h. The mixture was poured into 150 mL of water and extracted with 3 × 100 mL of pentane. The pentane solution was washed with 2 × 100 mL of water, 2 × 100 mL of saturated aqueous sodium bicarbonate solution, and 100 mL of water and dried over anhydrous magnesium sulfate. The solvents were removed by rotary evaporation to give 10.5 g (85% yield) of crude product. This crude product contained 27% of **4b** and 63% of **3b** by GC analysis. The mixture was further purified by column chromatography over silica gel using 5:1 pentane/ethyl acetate as eluent, giving **4b** with 92% purity and **3b** with 95% purity by GC analysis.

3b. ^{1}H NMR (δ, CDCl$_3$, lit.[36]): 3.29 (t, J = 1.5 Hz, 1H), 3.16 (s, 3H), 1.87 (“s”, 1H), 1.60−1.65 (m, 1H), 1.20−1.24 (m, 1H), 1.00−1.13 (m, 5H). ^{13}C NMR (δ, CDCl$_3$): 86.1, 56.6, 32.3, 30.6, 29.7, 14.0, 13.0, 11.1.

4b. ^{1}H NMR (δ, CDCl$_3$, lit.[37]): 6.10−6.06 (m, 1H), 5.95−5.92 (m, 1H), 3.39 (t, J = 1.5 Hz, 1H), 3.31 (s, 3H), 2.87, (“s”, 1H), 2.76 (“s”, 1H), 1.60−1.62 (m, 1H), 1.51−1.48 (m, 2H), 1.26−1.24 (m, 1H). ^{13}C NMR (δ, CDCl$_3$): 140.8, 133.3, 82.3, 57.1, 46.2, 46.1, 40.6, 34.5.

Acknowledgment. We are grateful to the National Science Foundation for financial support and to the Center for Neurosciences at Rutgers University (Newark Campus) for computational support.

Supporting Information Available: Table S1 (product distributions from carbene **6** in MeOH/DCE) and Figures S1−S3 (determinations of absolute rate constants for fragmentations of carbenes **5** and **6**, Arrhenius correlation for carbene **5**). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0401218

---

(33) Lajunen, M. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1551.

(34) Laszlo, P.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 2709; **1964**, *86*, 1171.

(35) Youngblood, G. T.; Trivette, C. D., Jr.; Wilder, P., Jr. *J. Org. Chem.* **1958**, *23*, 684.

(36) Coulson, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 200.

(37) McConaghy, J. S., Jr.; Bloomfield, J. J. *J. Org. Chem.* **1968**, *33*, 3425.