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2-Norbornyl Ion-Pair Leakage in Electrophilic Addition of HCl to Nortricyclene and Norbornene

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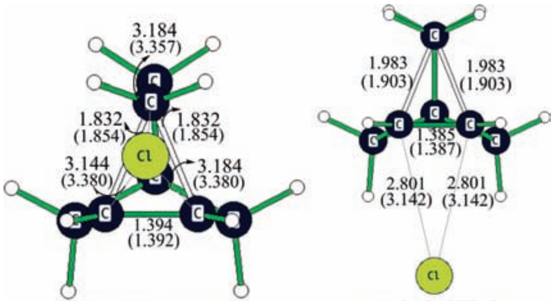
ABSTRACT



(nonclassical min, Cs) (nonclassical TS, Cs)

Ion pair "leakage" pathways, located computationally by means of multidimensional potential energy surface scans, rationalize the unsymmetrical D-label scrambling observed experimentally in the DCl addition products of nortricyclene and norbornene. "Classical" addition transition structures can interconvert ("leak") to symmetrical nonclassical 2-norbornyl ion pair species, either TS's or a minimum, before products form.

Controversies concerning the mechanistic interpretations of carbocationic 2-norbornyl reactions were among the most contentious disputes in chemistry during the last half-century.[1,2] But they were never resolved.[3] Rather than free ions,[2a,b] ion pair intermediates, first postulated by Wilson[4] in Wagner−Meerwein rearrangements and then established by Winstein and Trifan[5] in 2-norbornyl sulfonate solvolyses, provide the key insights needed to fully understand the details of the reaction mechanisms.

Electrophilic DCl additions to nortricyclene[6,7] (eq 1) and to norbornene[7,8] (eq 3) to give 2-*exo*-norbornyl chloride in nonpolar solvents like CH_2Cl_2 illustrate the interpretive problems. In both cases, the distribution of the D label

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deviated significantly from expectations based on symmetrical nonclassical (bridged) 2-norbornyl cation intermediates. Brown proposed a rapidly interconverting pair of classical 2-norbornyl cations, trapped before full equilibrium was complete, to explain the results.[1c] In contrast, nonclassical carbocation advocators suggested that "leakage" from classical addition mechanisms to pathways involving bridged ion intermediates was incomplete.[1d] Neither of these two contrasting ad hoc hypotheses has been proven.

Our initial computational explorations of these two HCl additions gave startling results. Direct HCl−nortricyclene addition gave the "wrong" product, 2-*endo*- instead of 2-*exo*-norbornyl chloride, and there was no D-scrambling (eq 2)! Likewise, the computed direct *cis-exo* HCl-norbornene addition proceeded via a 4-center ion-pair transition structure. Although the product was 2-*exo*-norbornyl chloride, D-scrambling was absent as well (eq 4)!

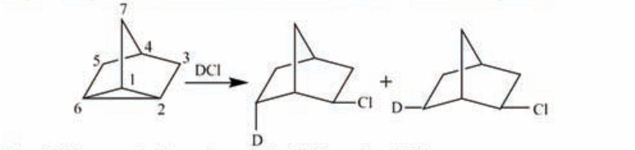
We now elucidate the mechanisms of these reactions by locating the nonclassical 2-norbornyl ion pair "leakage" pathways, which account for the discrepancies between eqs 1 and 2 as well as between eqs 3 and 4.

Computational Methods. The computations used the Gaussian 03 program[9] at the B3LYP/6-311+G** density functional level.[10] All computed harmonic frequencies of fully optimized minima were real, whereas transition structures had a single imaginary frequency. Intrinsic reaction coordinate analyses of the minimum energy pathways (MEPs) confirmed the connection of transition structures to the reactants and products, as described in the text. We used the polarized continuum model (PCM)[11] implemented in the Gaussian 03 program to evaluate the stabilizing effect of simulated CH_2Cl_2 bulk solvation, which was substantial on the ion pairs.[12,13] PCM-based single-point energy computations were carried out on the intermediate geometries of the "leakage" pathways (Figures 2 and 4). However, continuum-based SCI-PCM simulations[13,14] with full geometry optimizations were applied to all stationary points **1**−**10**. The united atom topological model (UAKS) was used to specify the molecular cavity. The small energy differences between PCM and SCI-PCM in Figure 3 justify our use of PCM for the scans in Figures 2 and 4.

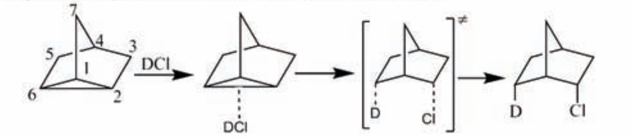
Addition of HCl to Nortricyclene (NT). Brown et al.[7] observed that DCl addition to nortricyclene gave 2-*exo*-norbornyl chloride exclusively and that the D label was scrambled about equally to the 6-*endo* and 6-*exo* positions (eq 1). In contrast, our initial computational exploration of the addition of "DCl" to nortricyclene gave quite different results (eq 2). (The actual use of an isotope label is obviated by following the reaction course.) The optimized geometries (**1**−**8**) involved are depicted in Figure 1. The direct addition pathway involves an initial weakly bound C_s-symmetrical H-bonded cyclopropane−HCl complex[15] (**1**). The computed reaction barrier via the unsymmetrical ion-pair transition structure **2** is 21.2 kcal/mol in "CH_2Cl_2" medium (35.2 kcal/mol in isolation). Although **2** has some nonclassical character (note the 1.7 Å C_1−C_6 distance), it collapses to the "wrong" product, 6-*endo*-D-2-*endo*-(not 2-*exo*)-norbornyl chloride (**3** instead of **8**), and there is no D scrambling (eq 2). The IRC of **2** confirms its connection with **1** and **3**.

How can these computational discrepancies with the experimental results (eq 1) be reconciled? Although *exo*-**8** is ∼1 kcal/mol less stable than the *endo*-**3** (in isolation and "CH_2Cl_2" medium), simple *endo* → *exo* epimerization via TS **6** is precluded by a large **3** → **6** barrier (51.0 kcal/mol in isolation; 35.4 kcal/mol in CH_2Cl_2 medium). Furthermore, the *exo* products from this "classical" pathway (**1** → **2** → **3** → **6** → **8**) would still have unscrambled D labels.

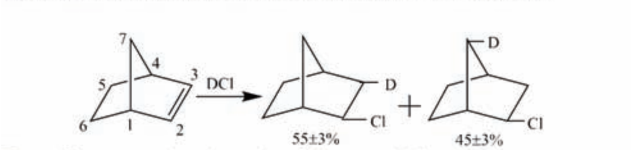
Eq. 1 Experimental result: DCl addition to nortricyclene[7]



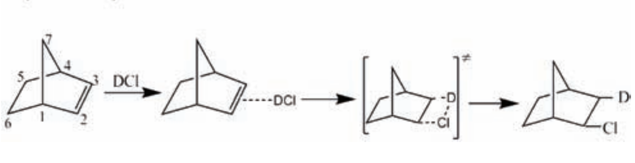
Eq. 2 Computational result of direct addition



Eq. 3 Experimental result: DCl addition to norbornene[7]



Eq. 4 Computational result of direct addition



However, we were able to locate a "leakage" pathway leading from **1** to D-scrambled product (**8**) involving non-

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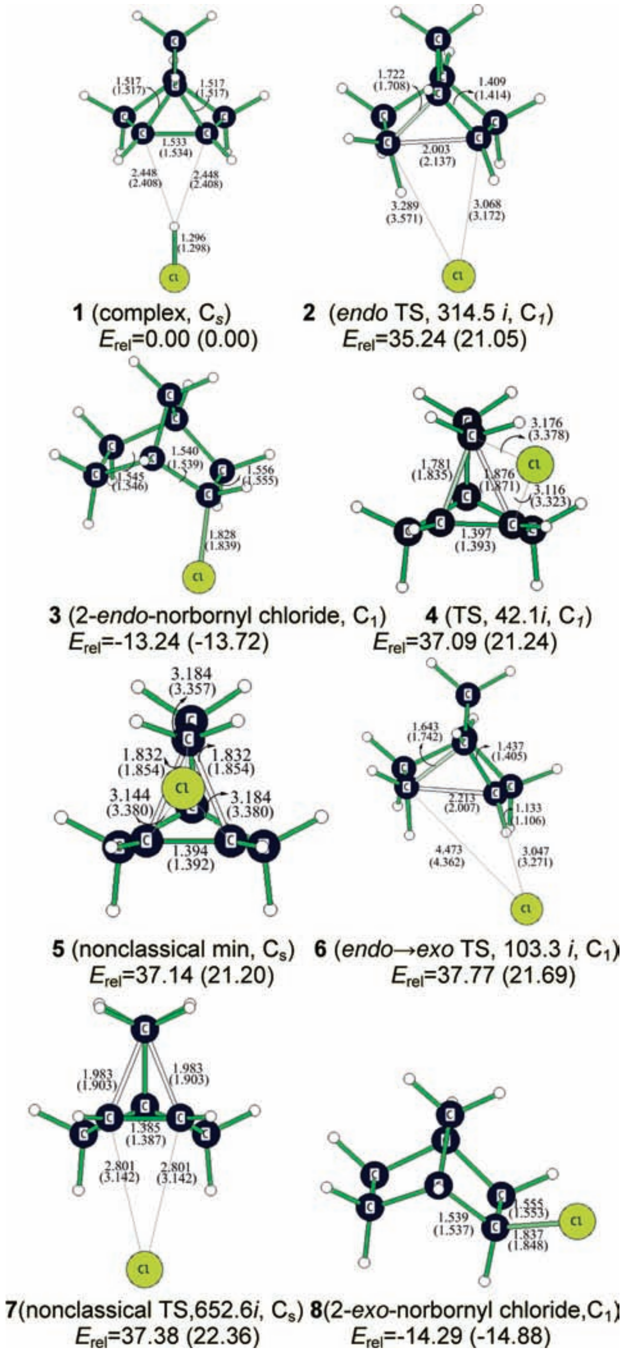

Figure 1. Geometries **1**−**8** involved in the NT-HCl addition. E_{rel} is the relative E + ZPE (unscaled) at B3LYP/6-311+G**. Bond lengths are in Å and E_{rel} are in kcal/mol, both in isolation and in SCI-PCM-simulated CH_2Cl_2 solvation (in parentheses).

classical 2-norbornyl ion pairs. This competing, but unexpectedly complex "nonclassical" mechanism, explains the formation of D-scrambled *exo*-**8**. The remarkable reaction pathway (**1** → **4** → **5** → **7** → **8**, Figure 1) involves HCl attack on NT via TS **4**, which is distinctly different from TS **2** but has nearly the same energy (see Figure 1).[10] However, TS **4** does not lead to covalent product directly. Instead, its IRC connects with **5**, a C_s-symmetrical ion pair minimum! This "nonclassical" intermediate also has nearly the same energy as both **4** and **2**, but its Cl^- counterion is located over the center of the C-1,2,6 face of the bridged 2-norbornyl cation. Notably, intermediate **5** is related to TS **4** and to its enantiomeric TS but is not involved directly in the racemization of 2-*exo*-norbornyl chloride (**8**). Instead, this enantiomerization involves TS **7**, which, like **5**, also has C_s symmetry and a bridged 2-norbornyl cation moiety; however, the Cl^- ion position in **5**, equidistant to C-1 and C-2, but far from C-6, is very differerent from that in **7**.

Consequently, an unconventional "leakage" pathway, connecting the two nonclassical 2-norbornyl ion pairs, i.e., **5**, a minimum, and **7**, a TS, must be involved; it was located straightforwardly by two-dimensional potential energy surface (PES) scan, which moves the Cl^- anion from the position in **5** to the position in **7**.[16] Figure 2 shows that the interconversion barrier is about 6 kcal/mol in isolation, but only 3 kcal/mol barrier in simulated CH_2Cl_2. After C_s **7** is reached, the bifurcating Wagner−Meerwein rearrangement leads to the enantiometic *exo* products (**8**) but with the D label scrambled to the 6-*endo* and 6-*exo* positions.

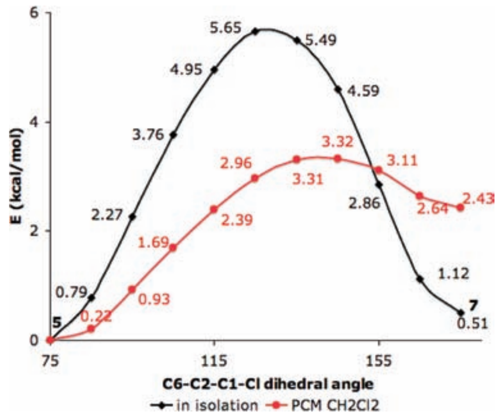

Figure 2. Interconversion scans between the nonclassical minimum (**5**) and the nonclassical TS (**7**) in isolation and in PCM-simulated CH_2Cl_2. (The relative energies were not ZPE-corrected, but the ZPE difference between **5** and **7** is only 0.3 kcal/mol.)

In summary, the NT-HCl addition PES is quite flat. The energies of TS **2**, TS **4**, intermediate **5**, TS **6**, and TS **7** are all quite close to one another, both in isolation and in simulated CH_2Cl_2 (Figure 1).[10] A nonclassical 2-norbornyl ion pair "leakage pathway" leads to 2-*exo*-norbornyl chloride products with 6-*endo*- and 6-*exo*-D-scrambling, in general accord with Brown's NT-DCl experimental observations.[7]

Addition of HCl to Norbornene (NB). Experimentally, DCl addition to norbornene[7] resulted exclusively in 2-*exo*-norbornyl chloride, but the D-label was distributed 55 ± 3% to *exo*-C_3 and 45 ± 3% to *syn*-C_7 (eq 3). Computationally, direct NB−HCl addition proceeds via a C_s weakly H-bonded

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[16] The leakage pathway was found using a two-dimensional PES scan with C_s symmetry. All coordinates were optimized except the $C_6C_2C_1Cl$ dihedral angle, which was constrained incrementally in 10° steps from the 75° in **5** to the 175° in **7**. The resulting, partially optimized intermediate geometries are given in the Supporting Information.

π-complex[15] (**9**) and passes through a C_1 four-center ion-pair transition state (**10**) to give 2-*exo*-norbornyl chloride (**8**) (Figure 3, left side). No D-label scrambling with DCl would occur by this mechanism (eq 4), contrary to experiment (eq 3).

A "leakage" mechanism from TS **10** to TS **7** (see Figures 3 and 4) rationalizes this discrepancy. The subsequent bifurcation from the nonclassical ion-pair TS **7** leads to the 3-*exo*, 7-*syn* D scrambling shown on the right side of Figure 3.

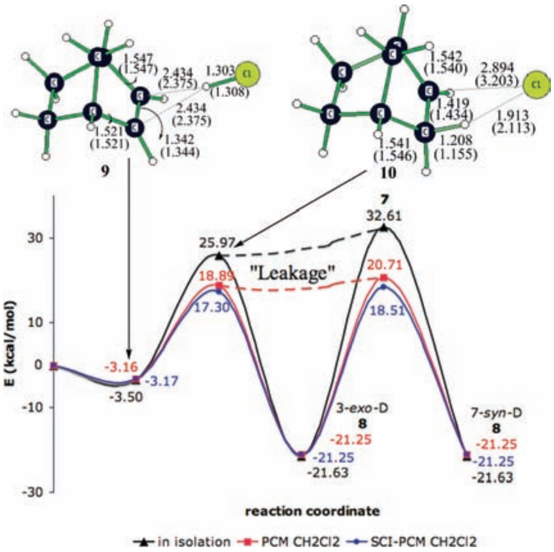

Figure 3. PES profiles for the *cis*-*exo* HCl addition to NB (left side) and for degenerate Wagner−Meerwein rearrangement (right side). The "leakage" pathways in dash lines join these processes (see Figure 4). *E* (in kcal/mol) are in isolation, PCM CH_2Cl_2, and SCI-PCM simulated CH_2Cl_2, respectively. D-label isotope calculations show negligible energy difference between 3-*exo* and 7-*syn*-*D*-2-*exo*-norbornyl chloride (**8**).

A "leakage" pathway for the conversion of **10** to **7** is shown in Figure 4; the geometries of the intermediate points (in the Supporting Information) map the course of bridging from the rather classical 2-norbornyl ion-pair geometry **10** (Figure 3) to the nonclassical (bridged) ion pair **7** (Figure 1): the C_1-C_6 distance lengthens, and the C_2-C_6 and the C_1-C_2 distances shorten. These changes are accompanied by delocalization of the C_1-C_6 electron density as well as alteration in ring strain. While the energy of **7** is almost 7 kcal/mol greater than **10** in isolation (Figure 4, black curve), this leakage pathway is facilitated by bulk CH_2Cl_2 simulation; the difference is only ~2 kcal/mol in simulted CH_2Cl_2 (Figure 4, red curve).

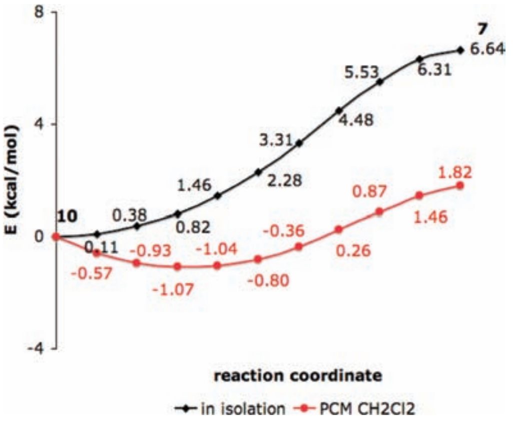

Figure 4. "Leakage" PES profiles from the *exo* HCl-NB addition TS (**10**) to the nonclassical TS (**7**) in isolation and in PCM-simulated CH_2Cl_2. (The relative energies were not ZPE corrected.)

Simulated SCI-PCM CH_2Cl_2 solvation generally increases the cation−anion separations in the ion-pair TS's and intermediates from the distances in isolation (compare the data in Figures 1 and 3). The considerable energetic bulk medium stabilization of ion pairs by simulated CH_2Cl_2 solvation facilitates the "leakage" between different mechanistic pathways by decreasing the interconversion energies (Figures 2 and 4).

Ion pair "leakage" pathways rationalize the experimental results of DCl additions to nortricyclene and to norbornene and reconcile discordant computational findings. The computed "classical" HCl addition pathways involving classical 2-norbornyl ion pair geometries can interconvert "leak" to pathways involving nonclassical (bridged) 2-norbornyl ion pair structures.

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Supporting Information Available: Full citation of ref 9. Optimized structures **1**−**10** and intermediates in leakage pathways as well as energetic data both in isolation and simulated CH_2Cl_2 medium. This material is available free of charge via the Internet at http://pubs.acs.org.

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