Fascinating Organic Transformations: Rational Mechanistic Analysis

1. The Wagner Meerwein Rearrangement and the Wandering Bonds

Subramania Ranganathan

After nearly a three-decade long innings as an inspiring teacher and researcher at IIT Kanpur, S Ranganathan is now at RRL, Trivandrum. He and his chemist wife, Darshan, plan to set up (without government assistance) "Vidyanantha Education Centre", to promote education, art and culture.

A carbocation can stabilize itself by a series of C-H and C-C shifts to reach the most stable form. Several examples are shown in which relatively strained systems upon such cationic rearrangements produce diamondoid systems.

The Ganges flows to neutralize the water potential, electricity flows to compensate an electron gradient. Naturally therefore, an electron deficiency in a carbon framework generates a "bond flow". This phenomenon, in its most simple representation *(Figure 1)*, is the Wagner Meerwein rearrangement.

A natural property of an electron deficient centre is to make the system dynamic, thus opening the possibilities for charge dissipation. This can be illustrated with what is called the Grotus mechanism *(Figure 2)*. One can see how effectively the proton excess on the left side is transmitted by the medium to the right. Similarly, charge deficiency created at a location can be evenly, and quite effectively, spread swiftly. The process that takes place
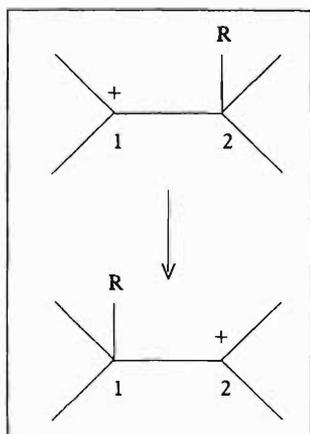

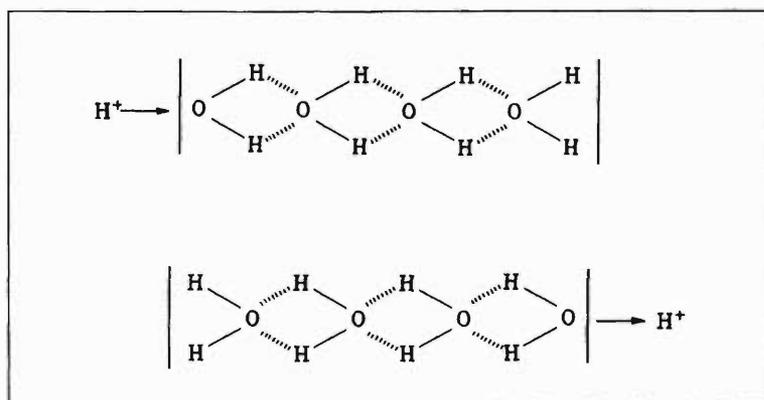*Figure 1 The Wagner Meerwein rearrangement.*

Figure 2 The Grotus mechanism.

The Series on Fascinating Organic Transformations: Rational Mechanistic Analysis

Rational analysis of organic reaction mechanisms was initiated in the early decades of this century, when the now well-known 'arrow pushing' *, to describe the flow of an electron pair, gained popularity among chemists. Subsequently, in the 1930-1960 period, the combined efforts of several great organic chemists established mechanistic organic chemistry on a firm ground. Every organic transformation is, however, unique, in the sense that there is always some twist when you carry out a new reaction (or else many of us would have been out of business!). Thus, in order to understand new transformations, one must have a very good appreciation of the basic principles of mechanistic analysis.

Many of us feel that at the undergraduate level

rational mechanistic analyses of exciting transformations are seldom taught. The examples available in many textbooks tend to be somewhat routine (and perhaps boring), and many good examples are left out. S Ranganathan, one of the most popular organic chemistry teachers at IIT, Kanpur for almost three decades, has put together for **Resonance** readers, six examples that demonstrate a step-by-step approach to rationalize fascinating organic transformations.

In this series of articles, he will cover Wagner-Meerwein rearrangement, molecular self- assembly, Woodward-Hoffmann rules, 'lone pairs', von Richter reaction and synthesis vs biosynthesis of indigo. We are certain that students and teachers alike will enjoy the simple and classroom-type discussions provided in each of these examples.

* When organic chemists started using curved arrows a well-known chemist reportedly remarked: "Curved arrows never hit the target".

Uday Maitra

in the norbornyl cation system (**1**, *Figure 3*), leads to a total charge dissipation, as shown in *Figure 4*.

Figures 3,4 permit the definition of very basic aspects associated with this type of bond migrations. By definition, whenever a sigma bond (other than a C-H bond) shifts, it is called the Wagner Meerwein shift [WM]. The hydrogen sigma bond migrations are denoted as proximate [1,2] or through-bridge [1,3] shifts.

The WM shift in substituted derivatives of **1** [1,2 $\rightleftharpoons$ 2,1] takes place with incredible speed*, of the order of $\approx 10^{12}$ sec^{-1} at room temperature [RT]. This is an estimate, since no 'eye' can see this because of the swiftness of the operation. We enjoy the video because we cannot 'see' it! The frames move at a rate faster than the

1,2-alkyl shift $\equiv$ WM and
1,2 H· shift $\equiv$ [3,2]
1,3 H· shift $\equiv$ [6,2] if one uses norbornane system.

*The structure of the unsubstituted 2-norbornyl cation is highly controversial. Do 1 and 2 rapidly interconvert or does the ion exist as an intermediate 'non-classical' form? Spectroscopic and theoretical studies are currently interpreted in favour of the latter proposal. However, tertiary derivatives have classical structures and undergo fast WM shifts.
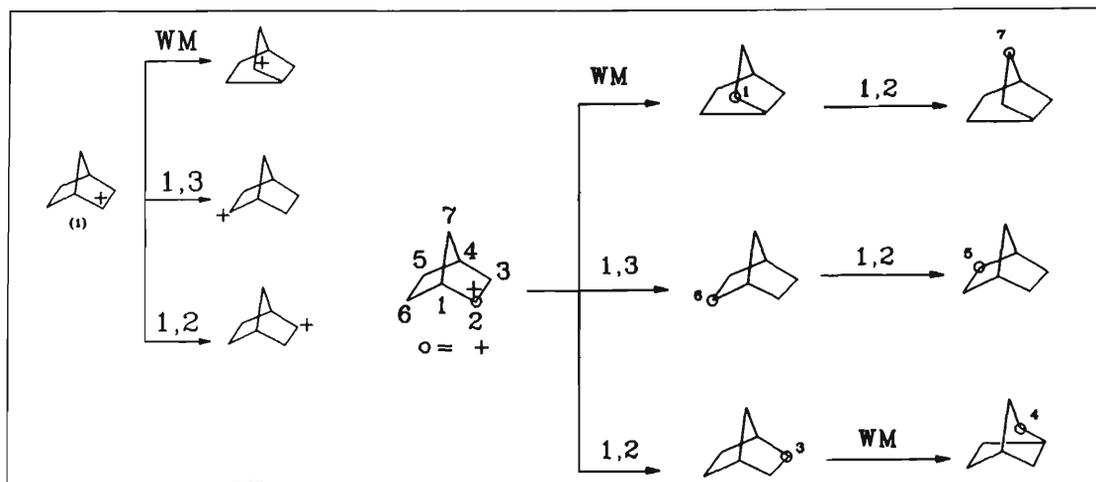
Figure 3,4 Rearrange-
ments in the norbornyl cat-
ion system.

Figure 5 A profile of the
diamond structure. Note
how beautifully the chair
cyclohexanes are stacked
leading to a thermodynami-
cally stable constellation.

eye can discern [≈ 16 frames sec^{-1}]; thus one frame merges into another creating an illusion of continuity. At one time the WM in 1 was called the windshield wiper [WW] effect. The WW of a car operates (if at all!) at the rate of one per second. So one can see how rapid the WM in 1 is. The [1,3] is slower [$\approx 10^8$ sec^{-1}], and the [1,2] even more so [$\approx 10^6$ sec^{-1}]. The last two could be focused to the eye of the NMR which can distinguish events that take place at 10^4 sec^{-1}. So, cooling down the norbornyl cation 1 can bring down the rates to lie in the vision range of NMR and this has been done. Charge dissipation naturally opens avenues for equilibration leading to stable systems from not so stable precursor cations. This is well documented in organic chemistry, and in this presentation is taken to esoteric heights leading to options for making diamond!
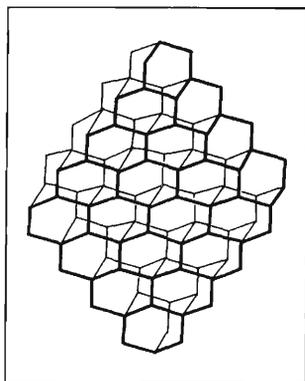
A profile of diamond structure is shown in *Figure 5*. Note how beautifully the chair cyclohexanes are stacked leading to a thermodynamically stable constellation. This would imply that such shuffling of bonds can lead to diamondoids from unrelated precursors having the same carbon framework. This was dramatically illustrated with the transformation of 2 - readily formed by hydrogenation of cyclopentadiene dimer - to adamantane (3) in excellent yields, thus making a rather expensive compound very commonplace! Like in a 'random walk jogging' we can start in
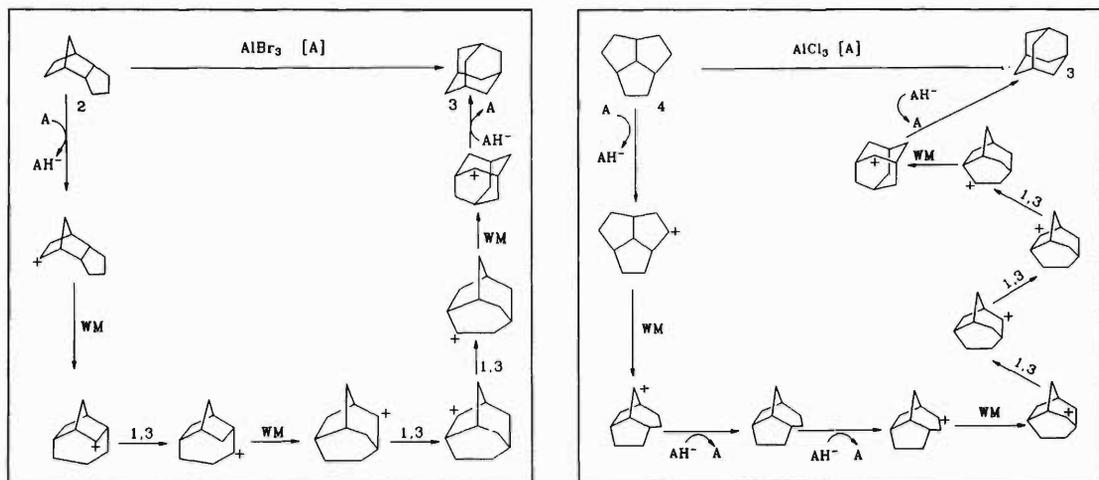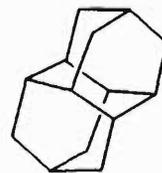
several directions from 2 and reach 3. We have shown here one such pathway (*Figure 6*). One can trace other pathways and doing so can be fun! To reinforce the notion of equilibration leading to diamondoids, another example is given in *Figure 7*, wherein the aesthetically pleasing C-10 triquinane (4) possessing a three fold axis of symmetry, is transformed to adamantane (3).

While adamantane (3) was known before the era of the understanding of carbocation rearrangements, its logical homolog 5, notionally formed by placement of additional chair cyclohexanes was unknown. The fascination for this molecule was such that it was the motif for an international congress (IUPAC Conference in 1963) and the compound itself was named, before birth, as *Congressane;* additionally, a reward was offered for anyone who could make it before the next congress, scheduled in two years. But no one could claim this reward! The facile synthesis of adamantane (3) by wandering of sigma bonds opened up possibilities, not only for congressane, but also for higher members of the family. In the event, congressane, now formally called diamantane (5) was magically made, in excellent yields from 6 and 7 which are easily derived from the dimerization of the C-7 bicycloheptadiene. Indeed, dimer 6 gave a 90% yield of 5 under equilibrating conditions! The transformation of 6 and 7 to diamantane (5) has been rationalized in *Figure 8* and *Figure 9*, respectively, by pathways

Figure 6 (top left) Rear-rangement of compound 2 to adamantane (3).

Figure 7 (top right) The aes-thetically pleasing C-10 triquinane (4) transformed to adamantane (3).

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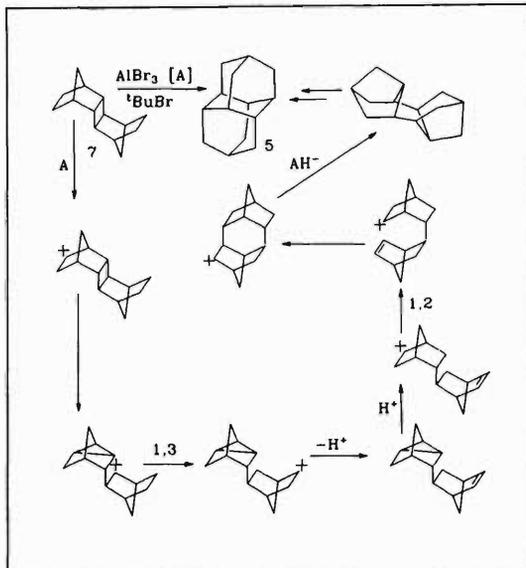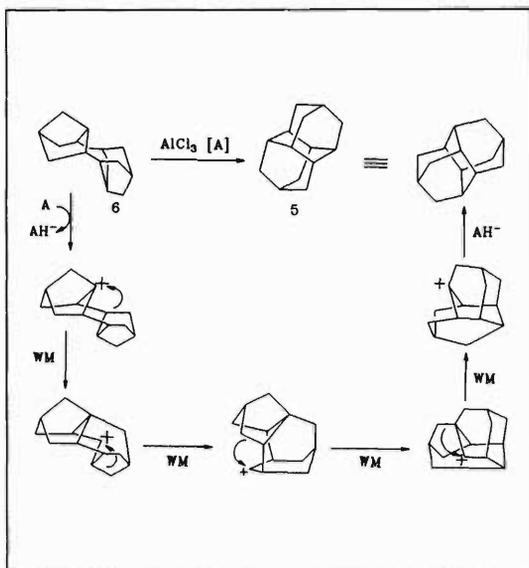
Figure 8,9 Rearrangement (top left) of compound (6) and (top right) compound 7 to diamantane (5).

precisely similar to those discussed earlier. A recent addition to this family is triamantane (8), which has a true tetrahedral carbon, attached to four other carbons as in diamond.
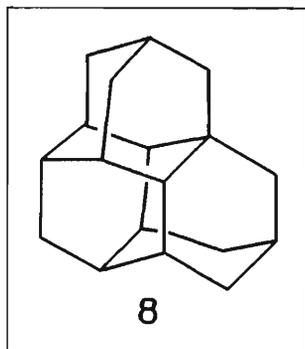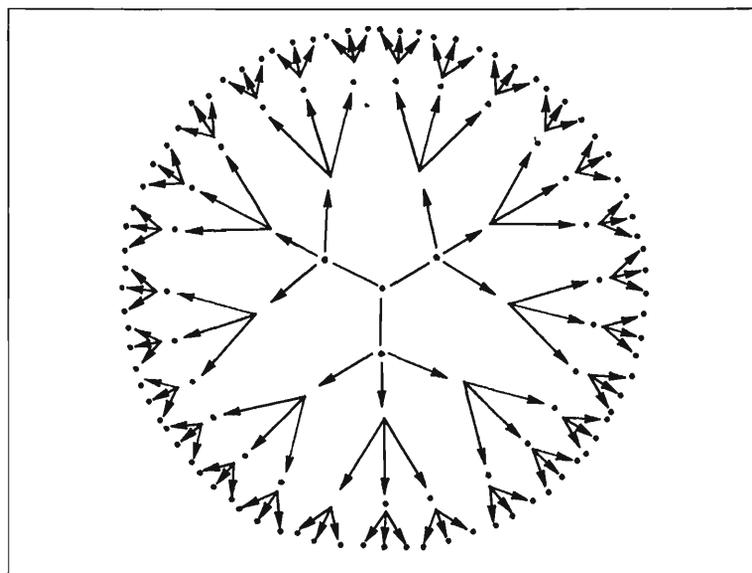
Based on the above principles and illustrations, one could develop a computer program to identify appropriate precursors for a

Figure 10 Triamantane (8).

Figure 11 (right). Iterative pattern search for diamandoid precursors on the basis of a retro-analysis program.

specific diamondoid. Even in the case of C-10 adamantane (3), the number of possible C-10 precursors would be huge. For higher members of the series the options could be astronomical. A reasonable guess is that it would take 500-1000 such rearrangements for substances that would have the properties of diamond. Thus it is obvious that if the carbocation strategy is to be adopted to make diamondoids, a listing of all possible precursors be secured using a computer and based on the three pathways involved. The task could be simplified by incorporating restrictions in the program. Although using this strategy for diamond appears far fetched, it could lead to novel diamondoids and related precursors having desirable properties. The iterative pattern is simple, and each generation produces three possibilities, as shown in *Figure 11* (the three arrows here represent, WM, [1,3] and [1,2]).

One could develop a computer program to identify appropriate precursors for a specific diamondoid.

Suggested Reading

P D Batlett. Nonclassical Ions. Benjamin, New York. 1965.
   Read this book for a historical account.
N Anand, J S Bindra, S Ranganathan. Art in Organic Synthesis. 2nd edition. 1988. p.148.
P v R Schleyer. My Thirty Years in Hydrocarbon Cages: From Adamantane to Dodecahedrane, from Cage Hydrocarbons, Ed. G A Olah, Chapter 1. Wiley. 1990.

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Newton's Inheritance ... After Newton's death on 20 March 1727, his liquid assets, which totalled some £32,000 were to be divided equally among his eight nieces and nephews, but the estate at Woolsthorpe was now legally the property of the next surviving Newton. He turned out to be one John Newton, descendant of a brother to Newton's father, who was described as "a poor representative of so great a man". This assessment proved to be accurate: John Newton gambled and drank his inheritance away, dying by accident when, after a round of drinking, he stumbled and fell with a pipe in his mouth, the broken stem lodging in his throat.