Fascinating Organic Transformations: Rational Mechanistic Analysis

1. The Wagner Meerwein Rearrangement and the Wandering Bonds

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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

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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 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 \[\rightarrow\] 2,1] takes place with incredible speed*, of the order of \(\approx 10^{12} \text{ sec}^{-1}\) 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.