

Think It Over



This section of Resonance is meant to raise thought-provoking, interesting, or just plain brain-teasing questions every month, and discuss answers a few months later. Readers are welcome to send in suggestions for such questions, solutions to questions already posed, comments on the solutions discussed in the journal, etc. to Resonance Indian Academy of Sciences, Bangalore 560 080, with "Think It Over" written on the cover or card to help us sort the correspondence. Due to limitations of space, it may not be possible to use all the material received. However, the coordinators of this section (currently R Nityananda and C S Yogananda) will try and select items which best illustrate various ideas and concepts, for inclusion in this section.

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1. How Many Functional Molecules?

A gene on a bacterial chromosome codes for a polypeptide. The same gene is also present on a plasmid in the cell. Two units of this polypeptide are needed to make a functional protein. Now consider that a mutation in the chromosomal gene makes a defective polypeptide. The plasmid, however, continues to synthesize the normal polypeptide. If the rate of transcription from the chromosome and the plasmid is the same, out of all the protein molecules produced what proportion will be functional?

A biochemist and a mathematician argued over this problem. The biochemist said that three types of proteins will be produced. One with both defective polypeptides (D-D), the other with one normal and one defective (N-D) and the third with both normal (N-N). But the third type will be a functional protein. Because there are three types of molecules, one third of the total molecules will be functional. If, say, 3000 protein molecules are produced, 1000 will be functional.



The mathematician thought that there will be four types of molecules, D-D, N-D, D-N and N-N and one fourth of the total molecules will be functional. That is, out of 3000, only 750 will be functional.

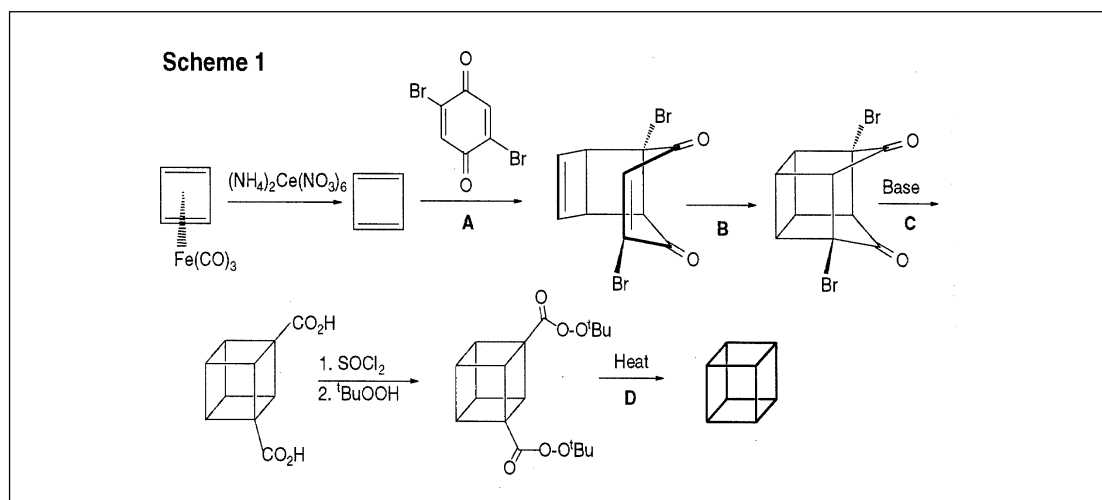
Whose statement do you think is correct? The biochemist's or the mathematician's? And why?

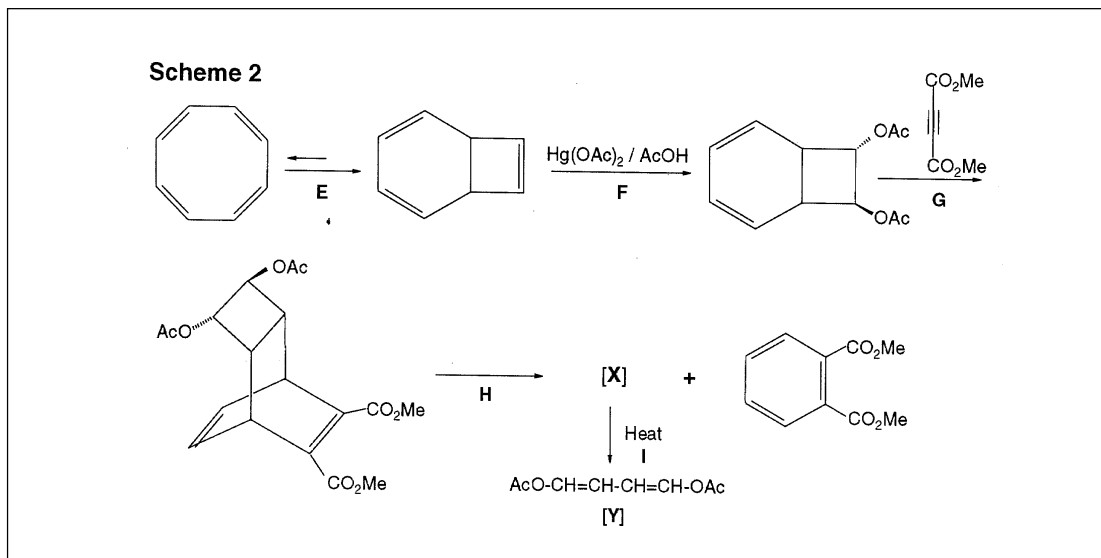
2. Organic Reaction Mechanisms

In the February 1997 issue of *Resonance*, two multi-step reaction sequences involving some pericyclic reactions and a few other important reactions were shown (*Schemes 1 and 2*). We had posed questions concerning the mechanistic details of the steps marked A-I and also on the stereochemistry of the products X and Y.

Discussion of the questions raised in the series article - A tale of two topologies - by S Ranganathan in *Resonance*. Vol.2. No.2. p.41, 1997.

Steps A and G are Diels-Alder reactions. Being $\pi 4s + \pi 2s$ type processes, they are thermally allowed. Note that the dienophiles are activated due to the presence of carbonyl groups. Step H is a related reaction, occurring in the reverse direction. It is a *retro*-Diels-Alder reaction. The symmetry rules governing this process are the same as in normal cycloadditions.





Therefore, H is also a thermal reaction and the product X is *trans*-3, 4-diacetoxy-cyclobutene. Step B is a $\pi 2s + \pi 2s$ type cycloaddition, and it is photochemically allowed but not thermally. Steps E and I are both electrocyclic reactions. However, the stereochemical modes are different for these two thermal reactions. Whereas step E is a 6-electron *dis*-rotatory process, step I is a 4-electron *con*-rotatory reaction. As a direct consequence, the stereochemistry of compound Y is *trans-trans* (the alternative *cis-cis* diene which can also be formed via the *con*-rotatory mode involves a sterically crowded transition state, and so is not observed).

The non-pericyclic reaction steps are C, D and F. Step C is the well-known *Favorsky rearrangement* which results in ring contraction. Step D corresponds to the pyrolysis of a *per*-ester, eventually leading to decarboxylation. The mechanism involves the homolytic cleavage of the (weak) O-O bond, loss of CO_2 , and then abstraction of a hydrogen atom by the resulting radical. Step F is an electrophilic addition of acetoxy groups to a double bond mediated by Hg^{2+} ions.