

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.

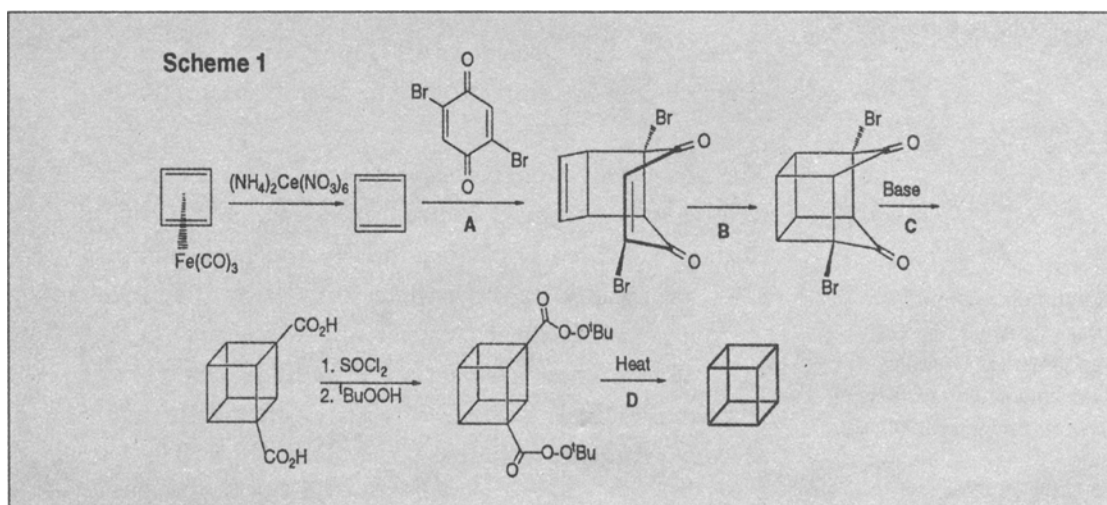
Whose statement do you think is correct? The biochemist's or the mathematician's? And why?

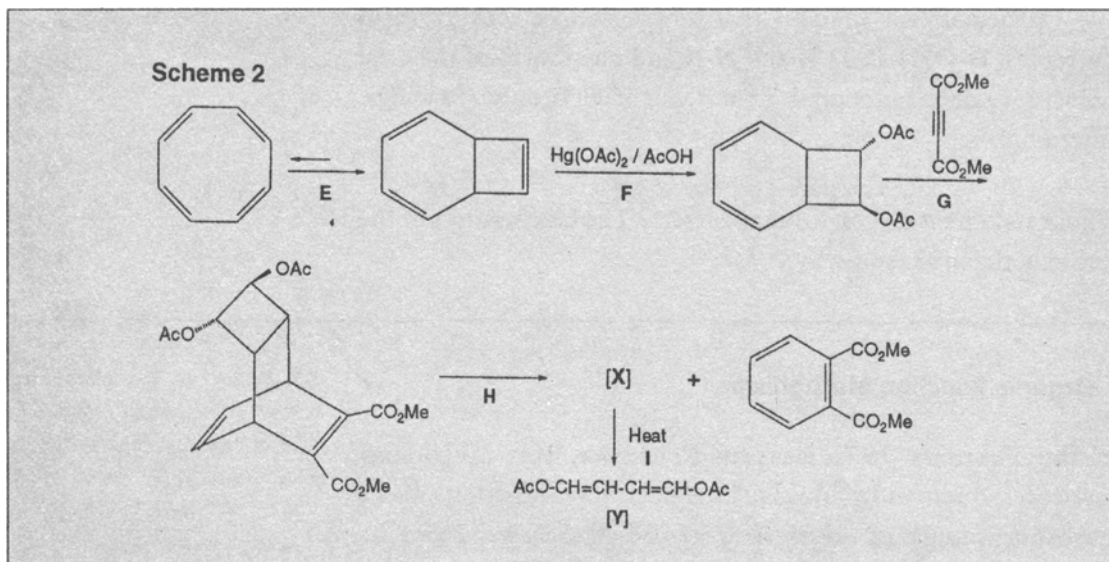
2. Organic Reaction Mechanisms

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.

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.

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.





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.

J Chandrasekhar and
 Uday Maitra
 Department of Organic
 Chemistry, Indian Institute of
 Science, Bangalore 560 012,
 India.