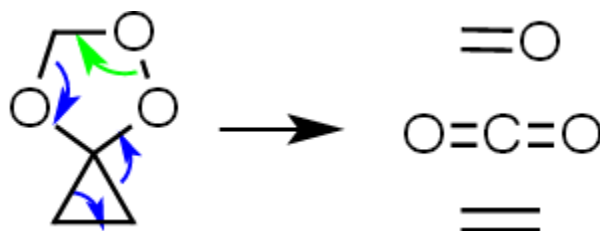
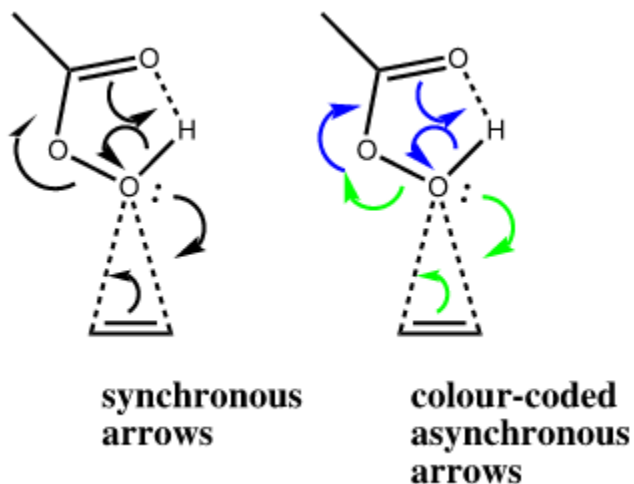


Coarctate reactions as a third fundamental organic-mechanistic type

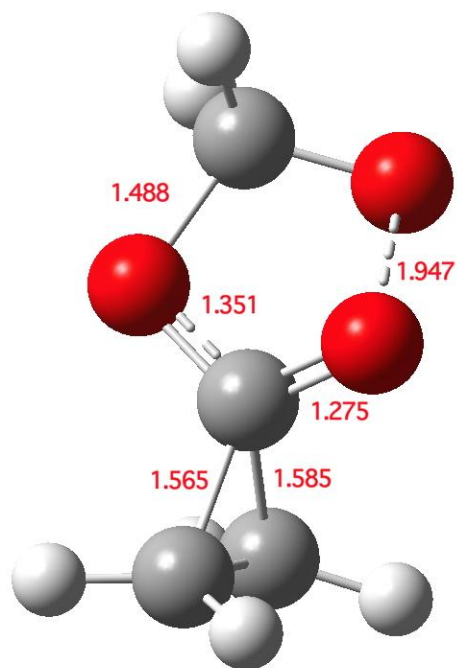
According to Herges^{[1],[2]} the mechanism of single-step (concerted) reactions can be divided into three basic types; **linear** (e.g. substitution, elimination etc), **pericyclic** (e.g. Diels Alder) and a third much rarer, and hence very often overlooked type that was named **coarctate**. This is based on the topology of bond redistribution patterns, an explicit real example^[3] illustrating:



It happens that this reaction bears a close similarity to **epoxidation using peracid**, the characteristic feature being that the central (spiro) atom has two bonds forming to it and two bonds breaking from it in both reactions.^{†,‡} I had noted for the latter reaction that in fact the bond redistribution, although concerted, was asynchronous. This asynchrony was represented by the green arrows preceding the blue ones (or *vice-versa* for the reverse reaction).

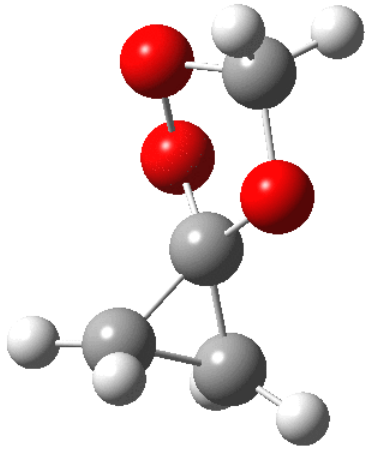


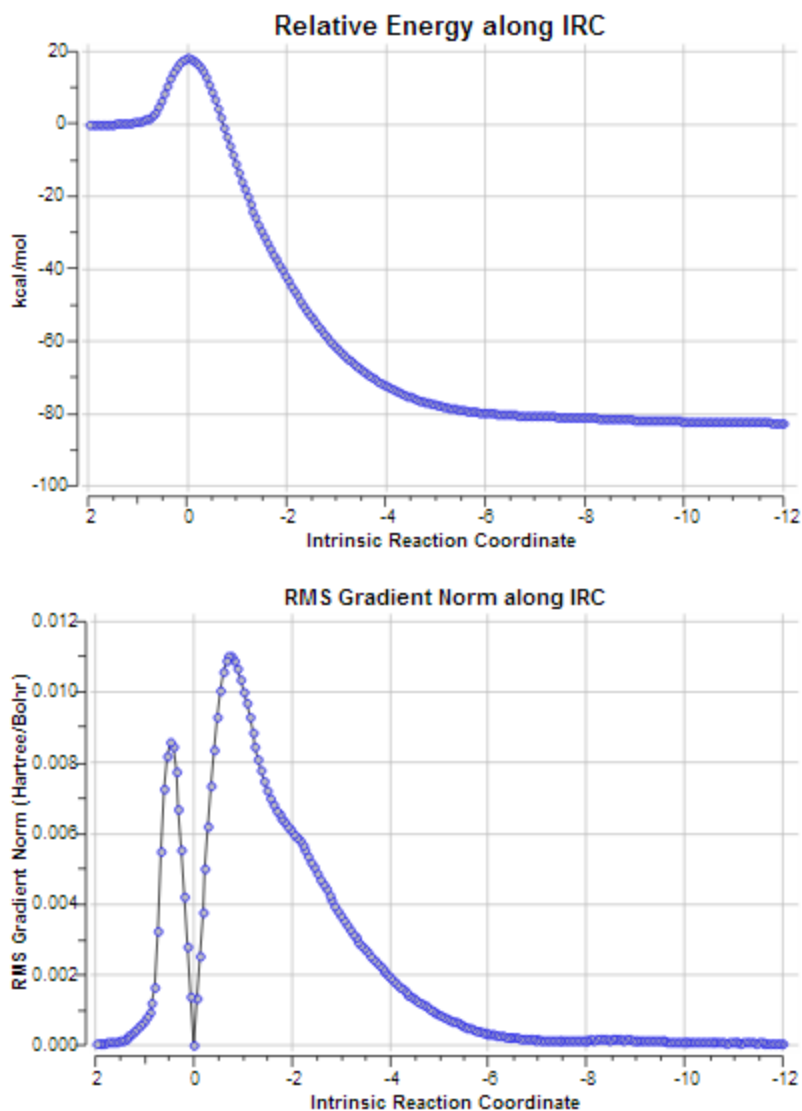
So here I decided to investigate if the same might be true of the coarctate reaction shown above (ω B97XD/6-311G(d,p)/SCRF=water.^[4]



Click for 3D

The transition state is indeed interestingly asynchronous. The O-O bond (shown green above) is clearly the first to break; neither of the C-C bonds has really started to do so at the transition state. But the process remains resolutely concerted.





The IRC above shows clearly that the reaction has a room-temperature barrier (*i.e.* it is a very facile process). But missing really from this process is any hidden intermediate either (there is the merest hint at IRC = -2). So this reaction is interesting for

1. its classification apart from the normal two types of organic mechanism, as a concerted type
2. Its asynchrony in the bond redistributions
3. but this asynchrony not resulting in any hidden intermediates.

[†] Another example was the topic of [this post](#).

[‡] One can contrive an [even higher-order reaction](#) (thus far un-named) in which (formally) three bonds break and three bonds form at a single atom.

References

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4. Henry S. Rzepa., "Gaussian Job Archive for C4H6O3", 2013.<http://dx.doi.org/10.6084/m9.figshare.787693>

Source: <http://www.ch.imperial.ac.uk/rzepa/blog/?p=11110>