Lecture XIV: Organic Photochemistry - Naphthoicyclic Reactions

1. Norrish reactions
2. Chemiluminescence
3. Singlet oxygen reactions
4. Radical clocks

Reactions of carbonyl compounds can occur from either singlet or triplet states.

\[ R^1R^2 \xrightarrow{hv} \left[ \begin{array}{c} \cdot R^1 \\ \cdot R^2 \end{array} \right] \xrightarrow{ISC} \left[ \begin{array}{c} \cdot R^1 \\ \cdot R^2 \end{array} \right] \]

Norrish type I (acyl cleavage)

\[ R^1R^2 \xrightarrow{A} R^* + \cdot R^1 \]

Recombine

\[ \xrightarrow{B} -CO \]

If \( R^* = RCH_2CH_2 \cdot \)/\( R'\cdot \)

\[ \xrightarrow{C} \]

If \( R^* = RCH_2 \cdot \) and \( R^1\cdot R^1 = R^1CH_2 \cdot \)

A variety of products is formed, slightly more selective in cyclic ketones:

\[ \xrightarrow{D} -R^1 \]

\[ \xrightarrow{E} \]

Ketene

Use of this reaction in synthesis is limited, but:

\[ \text{Org. Synth., 1967, 47, 34} \]

\[ \text{Et}_3\text{~N} \xrightarrow{\Delta} [2+2] \]

\[ \text{hv} \xrightarrow{-CO} \]

\[ \text{hv} \xrightarrow{-CO} \]
Norrish type II fragmentation

Synthetic example:

Chemiluminescence: thermal reactions that produce electronically excited product; its relaxation gives back ground state product and light.

Examples: Luminol:

Cyglume (used in glow sticks):

\[ \text{H}_2\text{O}_2 \rightarrow \text{dye} \]
Depending on the dye, color of chemiluminescence changes:

- Blue, green, \( X=4 \)
- Yellow, \( X=1 \)

Chemiluminescence occurs in nature, too:

Lucifεrin
  
in fire-flies
  Lucifer = fire-bringer

\[
\text{Lucifεrin} \xrightarrow{\text{enzyme}} \text{ATP} \xrightarrow{\text{enzyme}} \text{Molecule's } H_2O_2 \xrightarrow{\text{hv}} \text{ground state}
\]

**3 Singlet oxygen reactions**

Ground state of \( O_2 \) is a triplet. Singlet has much different chemical properties. It can be prepared through the use of sensitizers (e.g., methylene blue) or chemically:

\[
\text{H}_2\text{O}_2 + \text{NaOCl} \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{NaCl}
\]

Engages into Diels–Alder reactivity, making endoperoxides:

\[
\text{C} + \text{O}_2 \rightarrow \text{C} \xrightarrow{\text{reaction}} \text{H}_2\text{O}_2 + \text{H}_2\text{O}
\]

\[
\text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}
\]
Detection of these (and other) radicals can be done using radical clocks: radicals that rearrange intramolecularly with well-defined rates. Used for determining the kinetics of radical reactions. Examples:

\[
\text{ cyclopropane} \quad k = 1.3 \times 10^8 \text{s}^{-1} \\
\text{ at } 25^\circ \text{C}
\]

How does one use these things? Attach them onto a molecule and monitor what happens in a radical reaction. If the clock reacts as it is supposed to then it is more reactive than the other radical (i.e., other radical has a shorter or longer lifetime). An example:

All three products were detected, meaning that the lifetime of the Ar-OH radical is comparable to that of the radical clock used.