Cyclobutadienes via an Organocascade

**Significance:** The Wang group reports an organocatalytic [2+2] cycloaddition between \( \alpha,\beta \)-unsaturated aldehydes and ynals. This reaction is catalyzed by secondary amines and generates cyclobutadienes in high yields under mild conditions.

**Comment:** The authors suggest that the reaction follows a dienamine–iminium–allenamine cascade sequence furnishing cyclobutadienes as products. Typically high temperatures are required for the synthesis of cyclobutadienes. This method requires only room temperature, hence overcoming a limitation of previous methods.

**Proposed mechanism:**

- **Steps:**
  1. **Dienamine formation:** The dienal forms a dienamine with the secondary amine catalyst.
  2. **Iminium formation:** The dienamine reacts with the iminium ion to form an allenamine.
  3. **Cyclization:** The allenamine undergoes a [2+2] cycloaddition to form a cyclobutadiene.

**Selected examples:**

- **PhCHO, PhCHO, Ar:** 87% yield
- **PhCHO, 3-MeC₆H₄CHO:** 84% yield
- **PhCHO, 2-MeC₆H₄CHO:** 83% yield
- **ArCHO, 2-ClC₆H₄CHO:** 62% yield
- **ArCHO, 3-MeOC₆H₄CHO:** 83% yield
- **MeCHO, PhCHO:** 78% yield

**Proposed mechanism:**

1. **Dienamine formation:** The dienal forms a dienamine with the secondary amine catalyst.
2. **Iminium formation:** The dienamine reacts with the iminium ion to form an allenamine.
3. **Cyclization:** The allenamine undergoes a [2+2] cycloaddition to form a cyclobutadiene.

**Key words:**

- cyclobutadienes
- ynals
- \( \alpha,\beta \)-unsaturated aldehydes
- [2+2] cycloaddition