The Power of Light in Hexadehydro-Diels–Alder Chemistry

**Significance:** The authors demonstrate the efficient formation of reactive benzyne intermediates through photochemically initiated hexadehydro-Diels–Alder (HDDA) cycloisomerization reaction of multi-yne precursors. The reported photochemical transformation occurs at lower temperatures than the thermal version of the HDDA.

**Comment:** The authors also report that the resulting benzyne intermediates behave identically to those obtained through thermal HDDA reactions. The subsequent, highly efficient trapping reactions with π-donors and nucleophilic agents demonstrate the application of this method to access more elaborate structures.

**Selected examples:**

- 71% yield
- 69% yield
- 84% yield
- 68% yield
- 44% yield
- 77% yield
- 47% yield
- 83% yield

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Photochemical Hexadehydro-Diels–Alder Reaction