Aryne’t You Doubly Impressed with this Cyclopropenone Insertion?

Significance: The authors demonstrate a method to formally insert two arylene units into the carbon–oxygen double bond of a ketone, producing spirocyclic xanthene–cyclopropene scaffolds 1. Mechanistically, a direct formal [2+2] cycloaddition of an arylene with cyclopropenone is followed by the subsequent cycloaddition of the ortho-quinone methide intermediate with the second arylene equivalent.

Comment: The reaction relies on the strong nucleophilicity of the ketone oxygen: cyclopropenone proved to be one of the best candidates due to its zwitterionic structure, and attempts to generalize the reaction with other ketones failed. Interestingly, the more electron-rich arylene precursor, when exposed to trace acid, ring-opened to produce xanthylum triflate 2.

Selected examples:

1. MeCN, 30–60 °C, 24 h
   - 80% yield, 30 °C, 24 h
   - 78% yield, 30 °C, 24 h
   - 0% yield
   - 56% yield, 30 °C, 24 h

2. MeCN, 35 °C, 24 h
   - 37% yield

Xanthylum triflate formation:

- 80% yield, 30 °C, 24 h
- 78% yield, 30 °C, 24 h
- 56% yield, 30 °C, 24 h

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