J. Wallbaum, P. G. Jones, D. B. Werz* (Technische Universität Braunschweig, Germany)
Reacting Cyclopropenones with Arynes: Access to Spirocyclic Xanthene–Cyclopropene Motifs
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Aryne’t You Doubly Impressed with this Cyclopropenone Insertion?

Significance: The authors demonstrate a method to formally insert two aryne 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 aryne with cyclopropenone is followed by the subsequent cycloaddition of the ortho-quinone methide intermediate with the second aryne 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 aryne precursor, when exposed to trace acid, ring-opened to produce xanthylum triflate 2.

Selected examples:

1. 80% yield, 30 °C, 24 h
2. 78% yield, 30 °C, 24 h
3. 0% yield
4. 56% yield, 30 °C, 24 h

Xanthylum triflate formation:

1. 80% yield, 30 °C, 24 h
2. 78% yield, 30 °C, 24 h
3. 56% yield, 30 °C, 24 h

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