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 xanthylium triflate 2.

Selected examples:

- 80% yield, 30 °C, 24 h
- 78% yield, 30 °C, 24 h
- 0% yield
- 56% yield, 30 °C, 24 h

Xanthylium triflate formation:

- 37% yield

SYNFACTS Contributors: Timothy M. Swager, Sarah P. Luppino

Synfacts 2015, 11(6), 0601  Published online: 18.05.2015
DOI: 10.1055/s-0034-1380808; Reg-No.: S04715SF