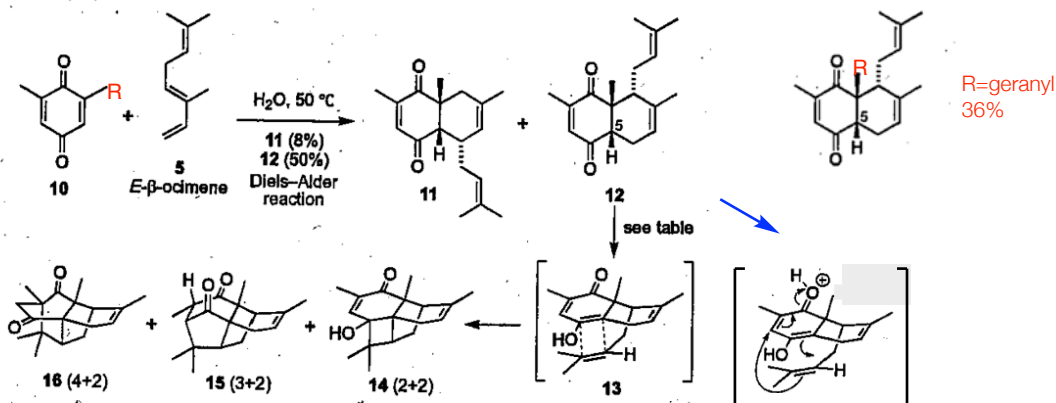


Total Synthesis of Atrachinenins A and B: Sarah A. French, Christopher J. Sumbly, David M. Huang, and Jonathan H. George* [Cite this:](#) J. Am. Chem. Soc. 2022, 144, 50, 22844–22849

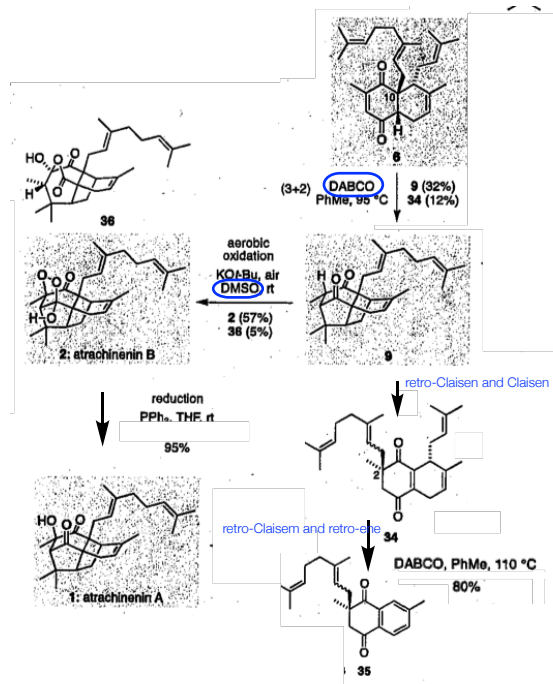
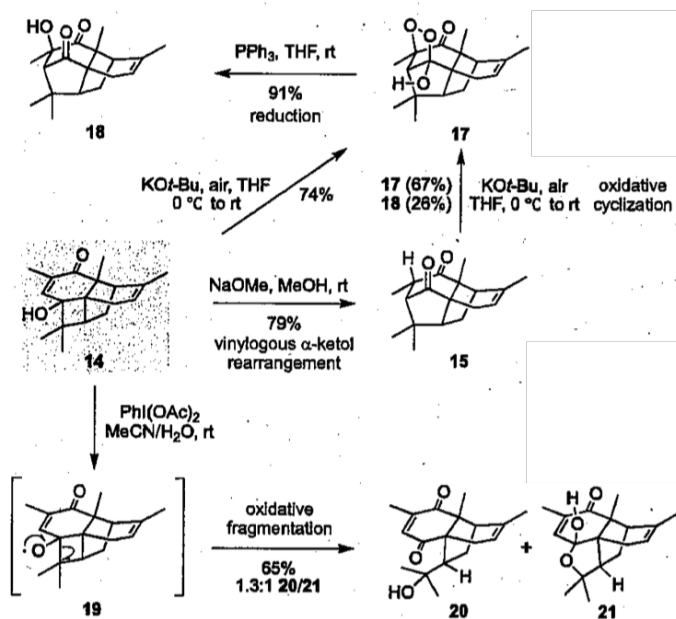
Scheme 2. Intramolecular Cycloadditions of Enedione 12



	Conditions	Products
1	NaOMe, MeOH, rt, UV light	complex mixture
2	NaOMe, MeOH, rt, purple LED	15 (60%)
3	NaOMe, MeOH, rt, no light	5- <i>epi</i> -12 (69%)
4	[Ru(bpy) ₃] ₂ Cl ₂ , Et ₃ N, HCO ₂ H, MeCN, rt, blue LED	14 (58%), 15 (14%), 16 (7%)
5	DABCO, MeCN, rt, blue LED	14 (31%), 15 (17%)
6	CSA, CHCl ₃ , 60 °C	15 (65%)
7	DABCO, PhMe, 95 °C	15 (55%)

Mechanism from DFT calculation:

1. acid catalyzed (3+2) cycloaddition concerted but asynchronous
2. acid catalyzed (2+2) cycloaddition and vinylogous α -ketol rearrangement
3. a stepwise (2+2) cycloaddition involving triplet state biradical via photoexcitation and vinylogous α -ketol rearrangement



Scheme 4. Proposed Structure Revision of Atrachinenin C

