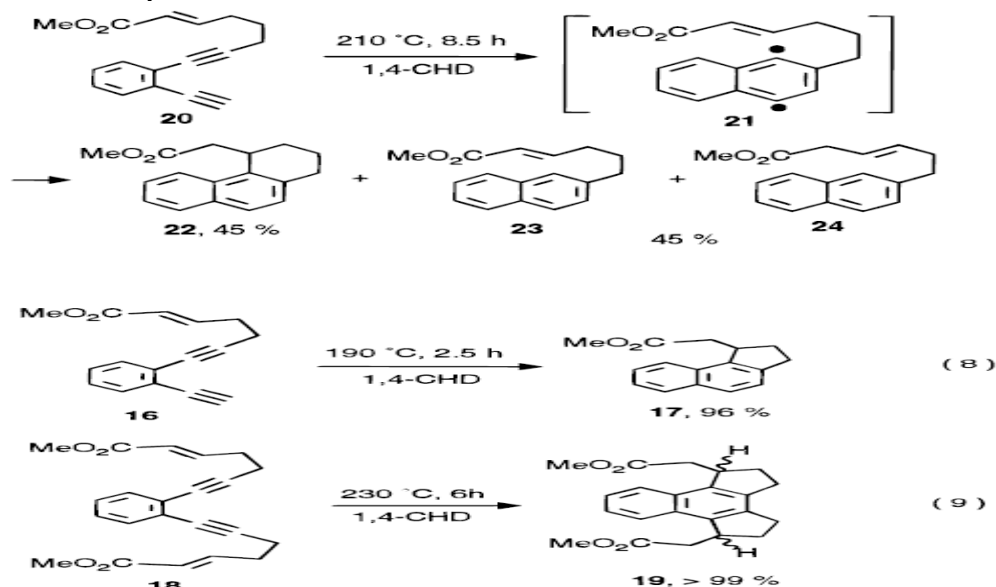


## Bergman Cyclization Cascade Reaction Polymerizations

By Robert B. Login rloginconsulting.com

The Bergman Cyclization(BC) and related reactions produce diradical transitory intermediates which can react with unsaturated moieties also attached to said BC compound. For example:



Wang, K. K. (1996). Cascade radical cyclizations via biradicals generated from enediynes, enyne-Allenenes, and enyne-ketenes. *Chemical reviews*, 96(1), 207-222.

Although this reference explains the preference for cyclopentane containing products, because Baldwin's Rules indicate that exo-trig producing 5-membered rings is very favorable but less favorable (slower) for exo-trig 6-membered ring formation.

Contributing also to this reactivity, I think because the above tether resulting in six-membered derivatives is more flexible while the one for five membered rings is more rigid with less degrees of freedom resulting in quicker 5-membered cyclization. In addition although Baldwin's rules show that the exo-trig is favored, I think with stabilizing groups such as vinyl carbonyl types, the following proposals for endo-trig are even more favorable.

Baldwin dis/favored ring closures

	3		4		5		6		7	
type	ex	en	ex	en	ex	en	ex	en	ex	end
tet	✓		✓		✓	✗	✓	✗	✓	✗
trig	✓	✗	✓	✗	✓	✗	✓	✓	✓	✓
dig	✗	✓	✗	✓	✓	✓	✓	✓	✓	✓

Alabugin, I. V., & Gilmore, K. (2013). Finding the right path: Baldwin "Rules for Ring Closure" and stereoelectronic control of cyclizations. *Chemical Communications*, 49(96), 11246-11250.

Majumdar, K. C., Basu, P. K., & Chattopadhyay, S. K. (2007). Formation of five- and six-membered heterocyclic rings under radical cyclisation conditions. *Tetrahedron*, 63(4), 793-826.

The Wang reference above also has many additional unrelated examples. The above examples employ 1,4-CHD as a proton source to trap the intermediate radicals, but if no source of protons are available then polymerization is possible. I cannot find any references to this type of chain polymerization, however.

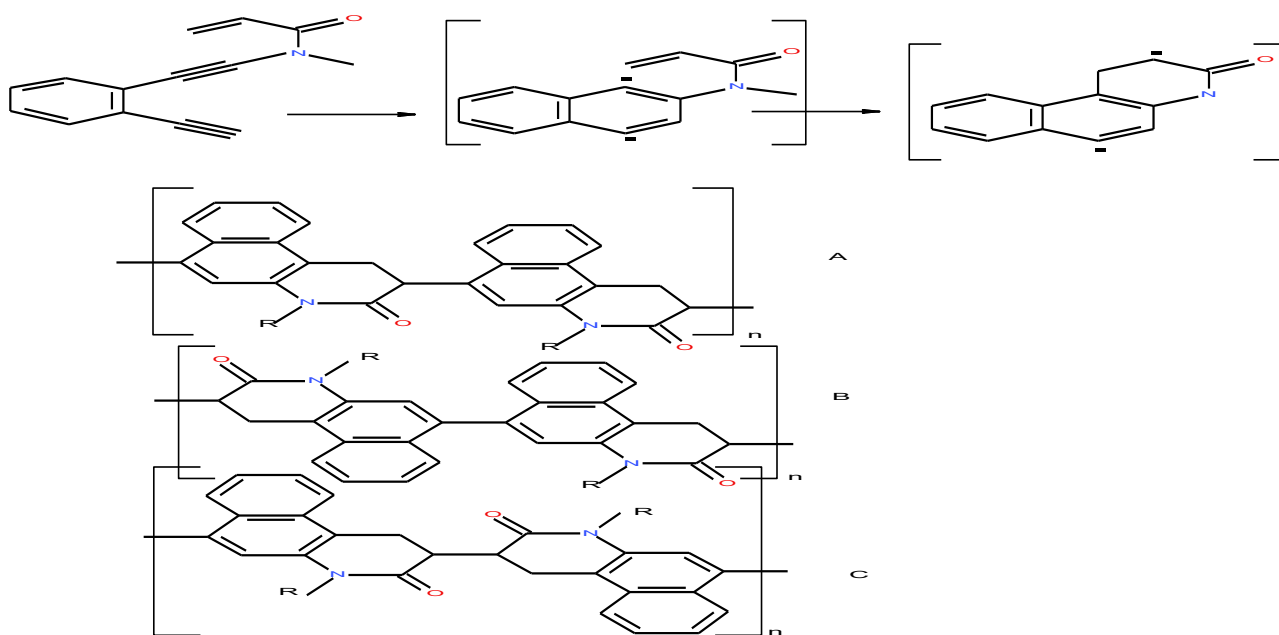
### BC polymer reviews:

Xiao, Y., & Hu, A. (2011). Bergman cyclization in polymer chemistry and material science. *Macromolecular rapid communications*, 32(21), 1688-1698.

Wang, Y., Chen, S., & Hu, A. (2017). Construction of Polyarylenes with Various Structural Features via Bergman Cyclization Polymerization. In *Polymer Synthesis Based on Triple-bond Building Blocks*(pp. 97-126). Springer

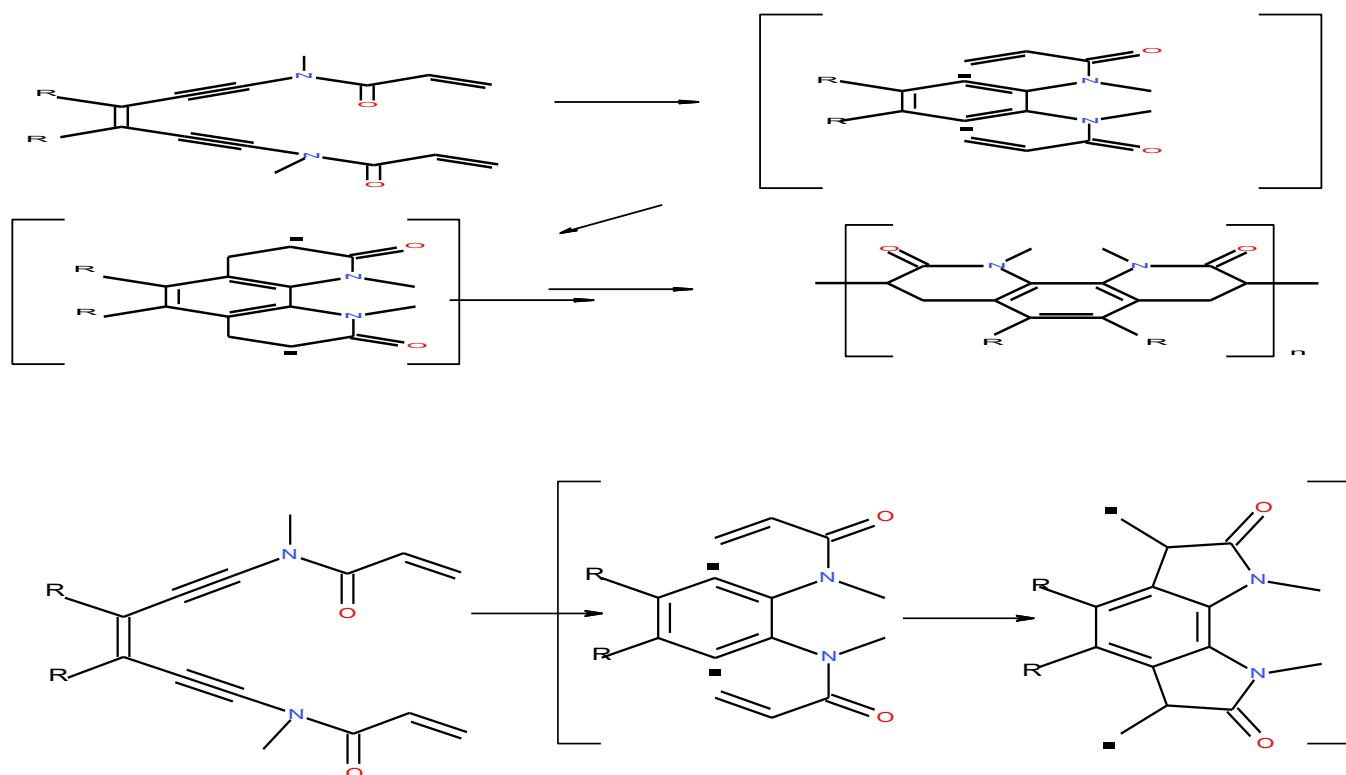
Wang, C., Chen, S., Zhou, H., Gu, J., & Hu, A. (2018). Palladium-catalyzed cycloaromatization polymerization of enediynes. *Chinese Journal of Polymer Science*, 36(2), 237-243.

Prof. Hu is a leading BC polymer authority. He and his colleagues in the above references review BC polymerization mechanism and problems with BC polymer chemistry but the essential diradical mechanism can still explain most of this chemistry.

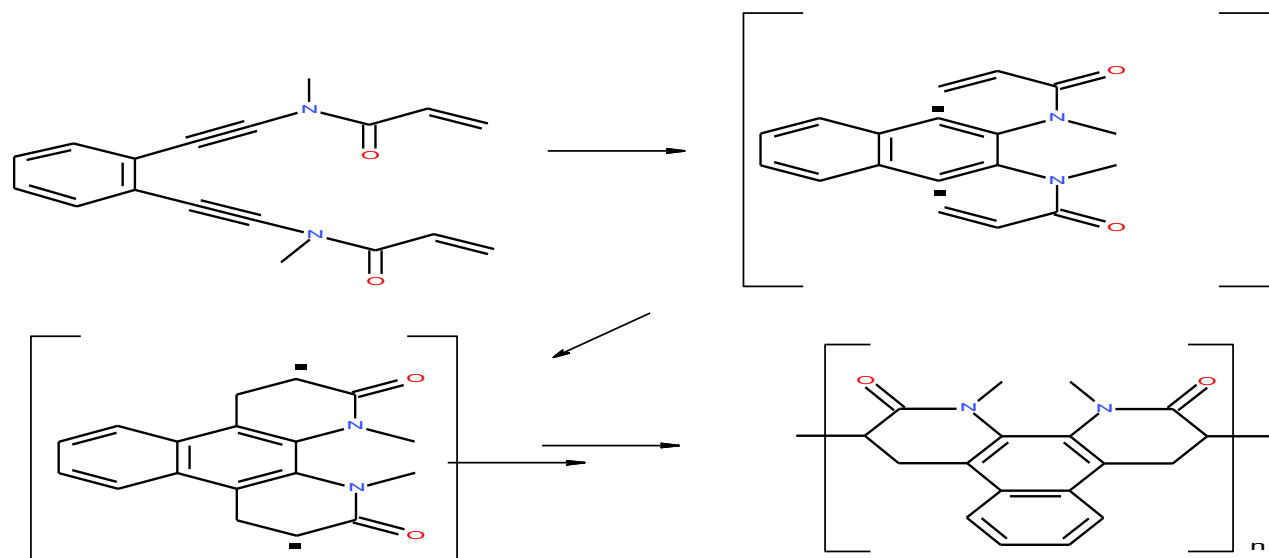


Scheme 1: These are possible polymeric versions. This is the outcome of producing a unsymmetrical diradical and all three(A,B,C) seem possible. Note that ynamides are well known. I want to point out that Baldwin's Rules favors endo-trig.

Wang, X. N., Yeom, H. S., Fang, L. C., He, S., Ma, Z. X., Kedrowski, B. L., & Hsung, R. P. (2013). Ynamides in ring forming transformations. *Accounts of chemical research*, 47(2), 560-578.  
 DeKorver, K. A., Li, H., Lohse, A. G., Hayashi, R., Lu, Z., Zhang, Y., & Hsung, R. P. (2010). Ynamides: a modern functional group for the new millennium. *Chemical reviews*, 110(9), 5064-5106.

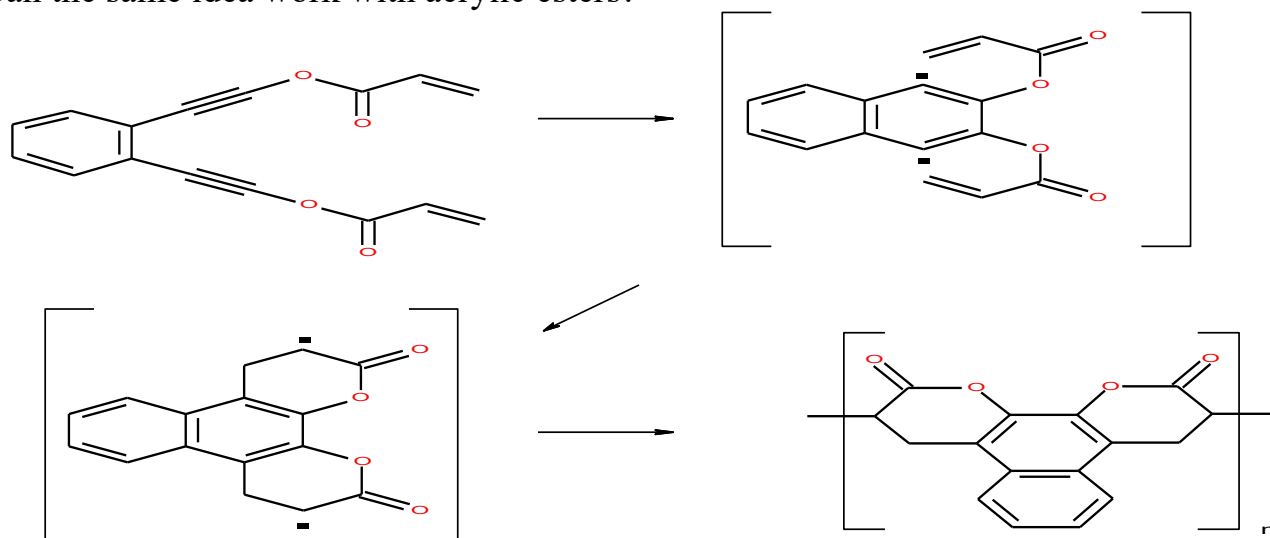


Scheme2: The basic enediyne(endo-trig) symmetrical polymerization. The endo-trig has the advantage of amide stabilization of the generated radical while the exo-trig (shown for clarity) has the intermediate radicals on carbon with no stabilization.



Scheme 3: Symmetrical RM's can result in symmetrical polymers.

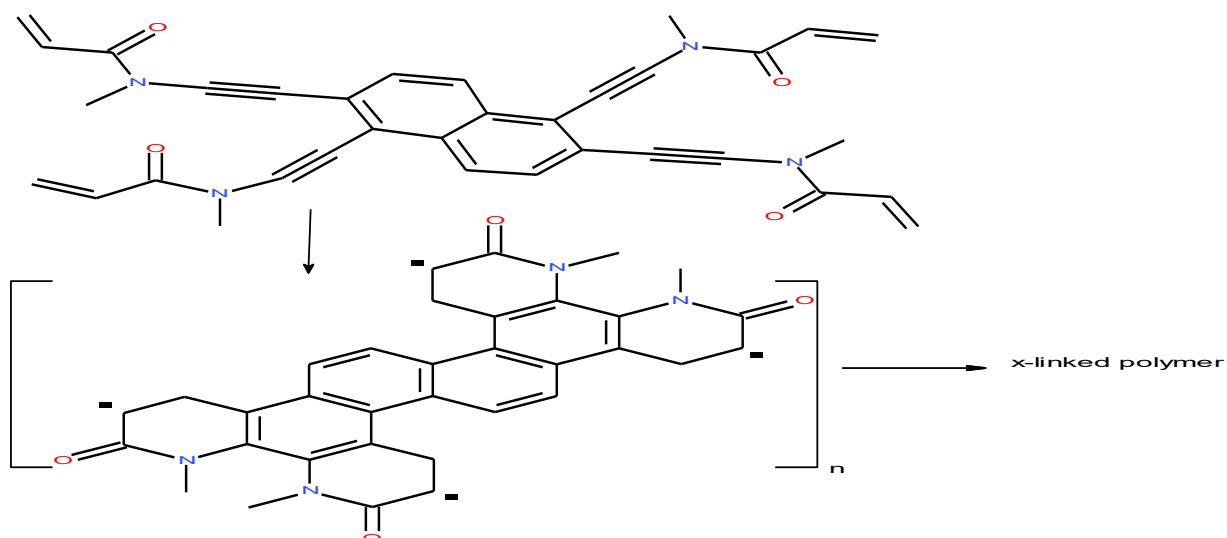
Can the same idea work with acrylic esters?



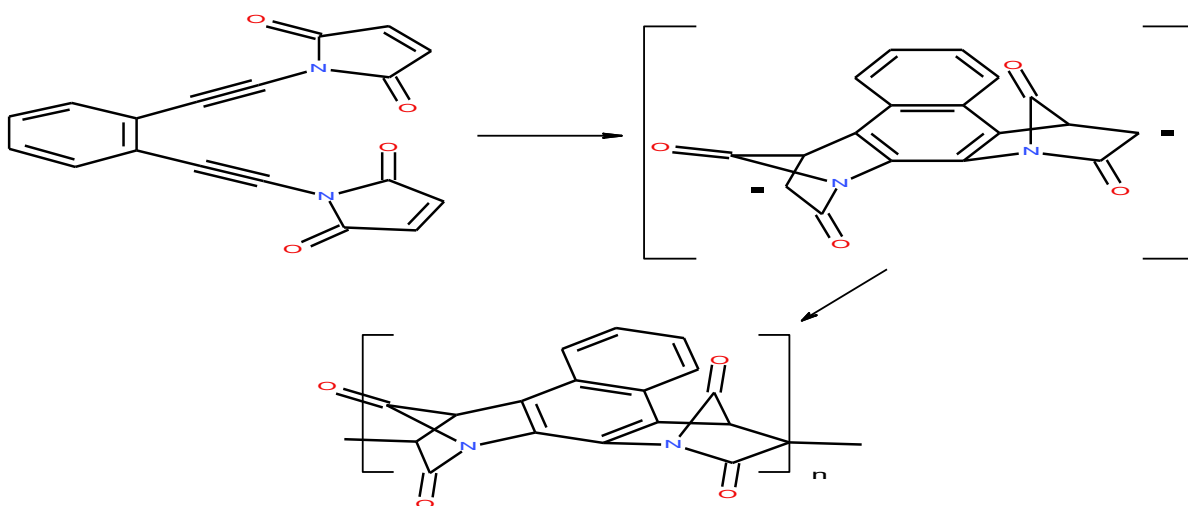
Scheme 4: Here an alkyne alcohol would be the starting compound. Apparently alkyne esters are stable enough to do this chemistry. The following references show how to accomplish their synthesis.

Stang, P. J. (1993). Ynol esters and alkynyl (phenyl) iodonium chemistry. *Russian chemical bulletin*, 42(1), 12-23.

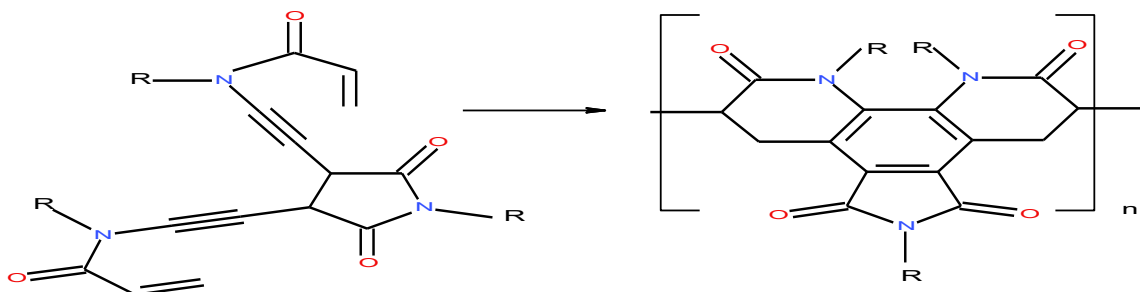
Stang, P. J., Boehshar, M., Wingert, H., & Kitamura, T. (1988). Acetylenic esters. Preparation and characterization of alkynyl carboxylates via polyvalent iodonium species. *Journal of the American Chemical Society*, 110(10), 3272-3278.



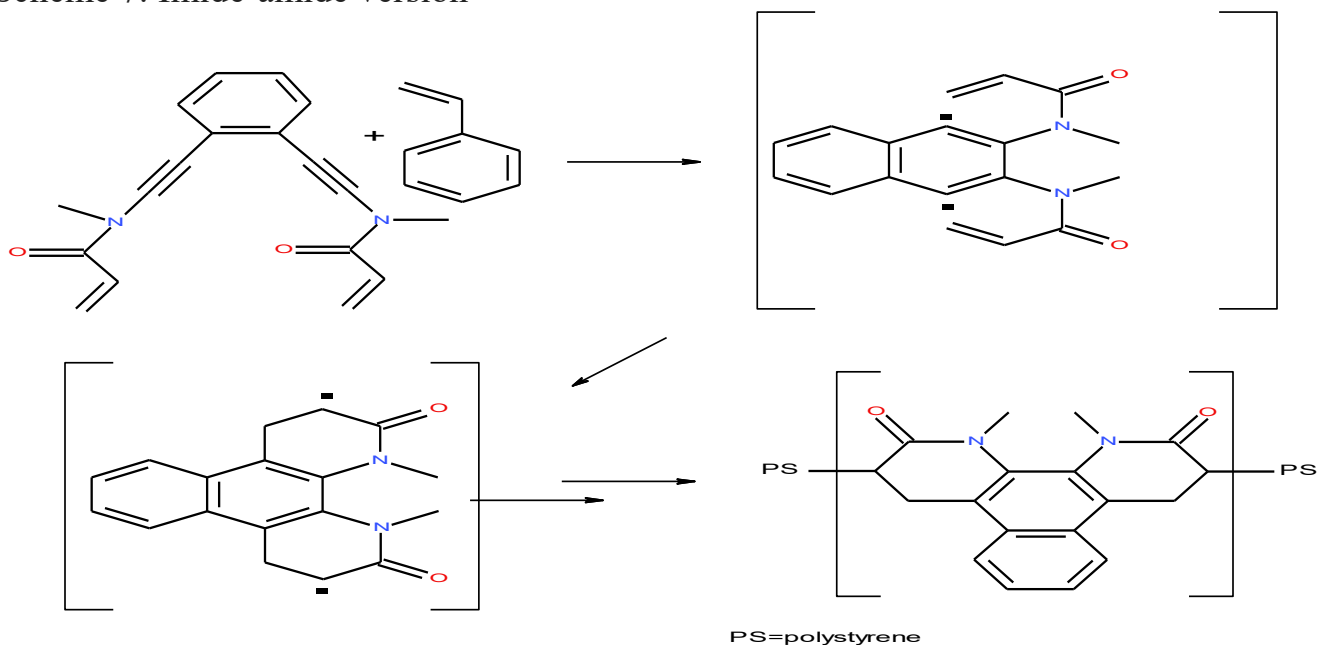
Scheme 5: Example of a x-linked polymer.



Scheme 6: Bicyclic example. Not sure this would work but looks interesting.

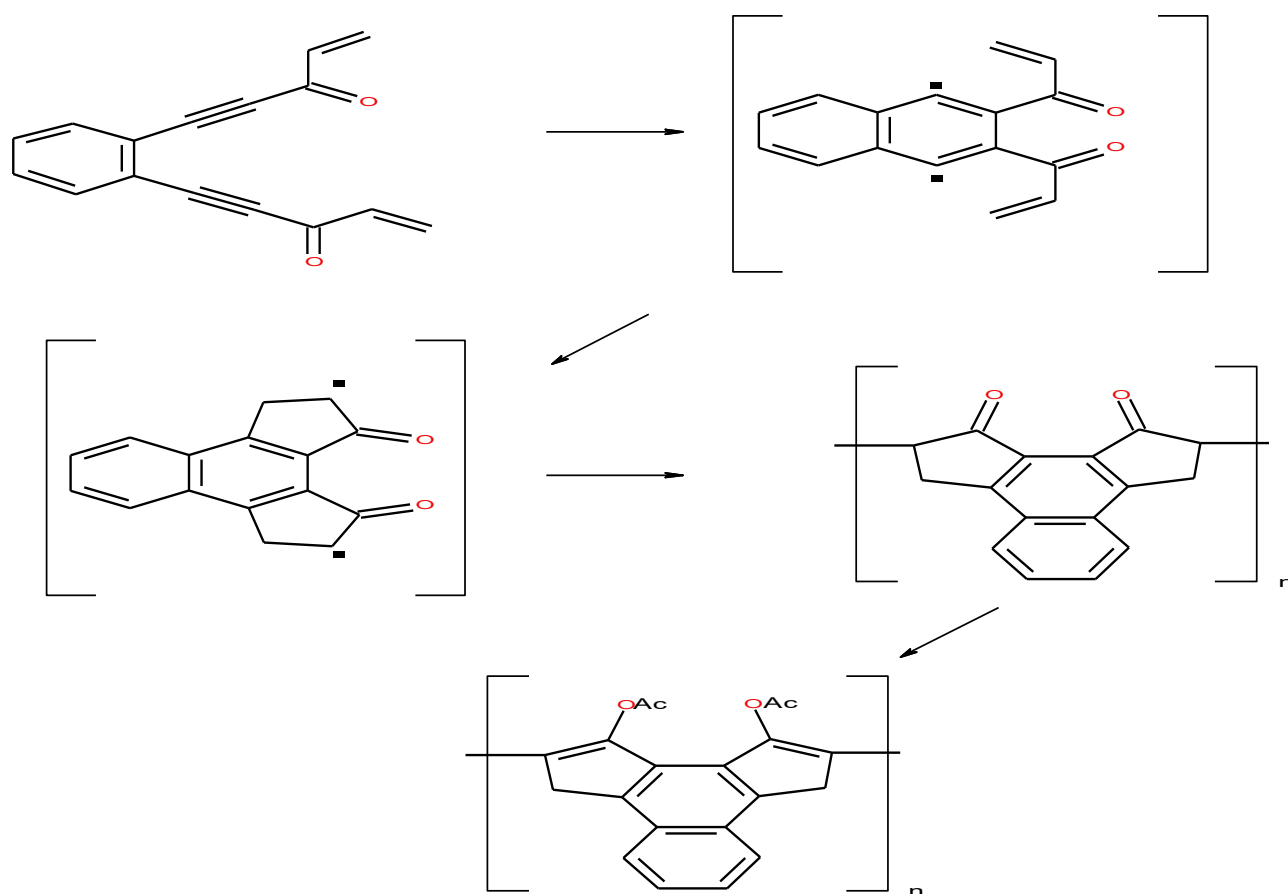


Scheme 7: Imide-amide version

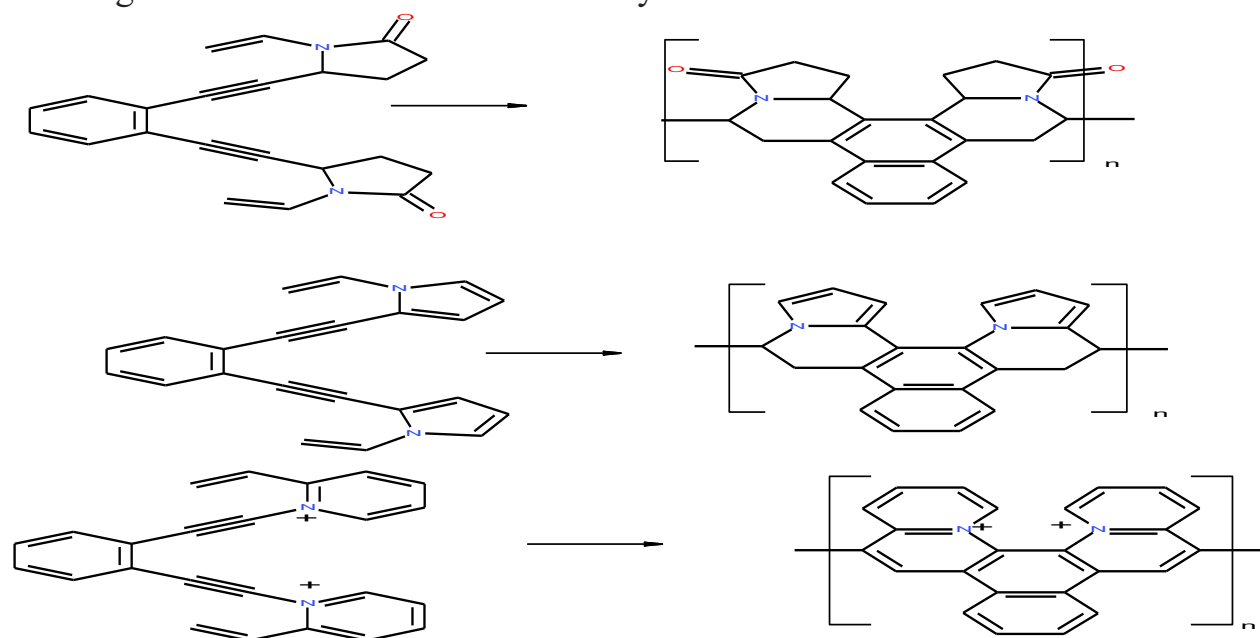


Scheme 8: Example of using this reaction as a free radical initiator.

Should I be wrong about the six-membered rings ( Baldwin's rules), then the following five-membered rings are a possibility? However these are endo-trig and are not favored.

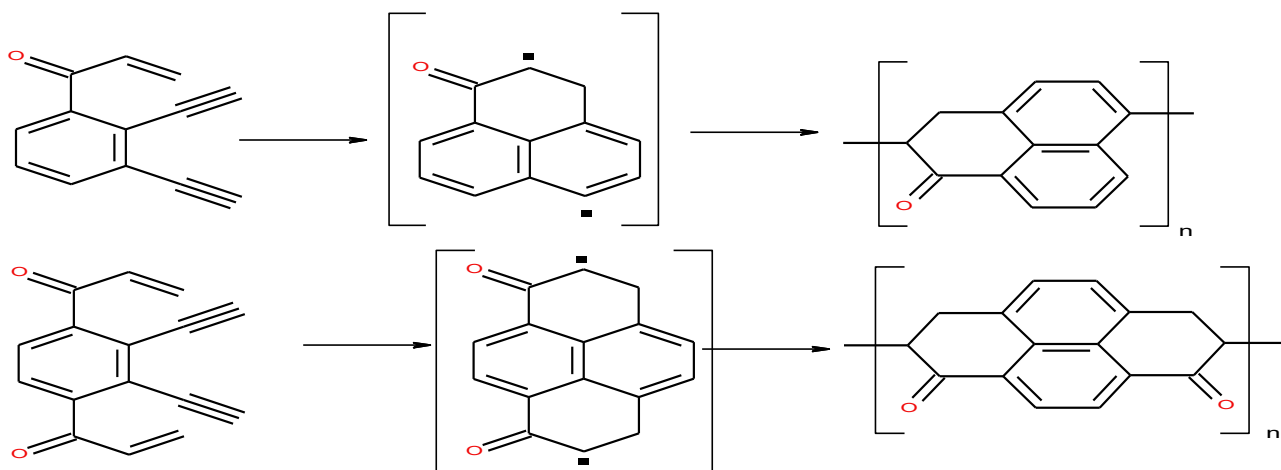


Scheme 9: five-membered version. This then would be an unsaturated polyaromatic. According to Baldwin this is not a favored cyclization.



Scheme 10: Heterocyclic examples. I'm trying to show the versatility of this reaction. Obviously, if polymers are unwanted, then a good source of protons like 1,4-CHD will be needed. The pyridinium containing polymer is depicted after oxidation to the aromatic derivative.

Toriumi, N., Asano, N., Miyamoto, K., Muranaka, A., & Uchiyama, M. (2018). N-Alkynylpyridinium Salts: Highly Electrophilic Alkyne–Pyridine Conjugates as Precursors of Cationic Nitrogen-Embedded Polycyclic Aromatic Hydrocarbons. *Journal of the American Chemical Society*, 140(11), 3858-3862.



Scheme 11: Alternative approach with the receiving group attached to the aromatic ring.

I'm surprised that I was unable to find a reference that claims this chemistry? Its value is that a wide variety of compounds (with 1,4-CHD for example) or polymers are possible. Polyaromatic polymers with the potential of conductivity (semiconductors) with a wide variety of potential applications can also be envisaged.

Thank you for reading this proposal.

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