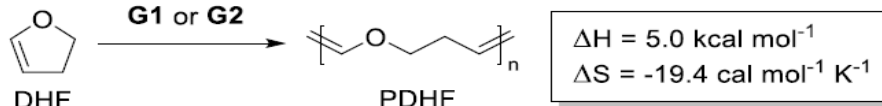


ROMP of Unsaturated Small Cyclics

The following article started me thinking about what other unsaturated small cyclics might undergo ROMP?

Table 1. Romp of 2,3-Dihydrofuran^a



DHF $\xrightarrow{\text{G1 or G2}}$ PDHF

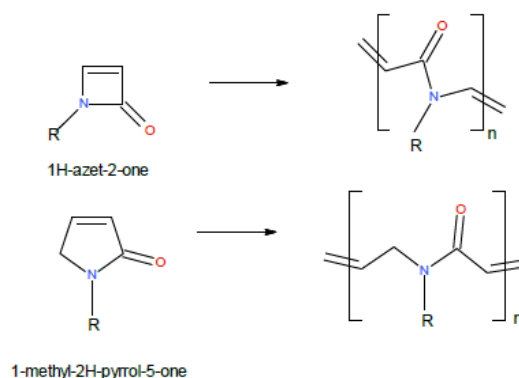
$\Delta H = 5.0 \text{ kcal mol}^{-1}$
 $\Delta S = -19.4 \text{ cal mol}^{-1} \text{ K}^{-1}$

entry	$\frac{[\text{DHF}]_0}{[\text{CTA}]_0} : \frac{[\text{I}]_0}{[\text{I}]_0}$	cat.	temp (°C)	$M_{n,\text{MALLS}}$ (kDa) ^c	\bar{D} ^d
1	2000:1:0	G1	22	34.9	2.66
2	4000:1:0	G1	22	56.3	1.35
3	500:1:0	G2	22	6.0	2.14
4	1000:1:0	G2	22	9.9	1.43
5	2000:1:0	G2	22	30.1	1.70
6	4000:1:0	G2	22	47.4	1.60
7	8000:1:0	G2	22	92.9	1.77
8	10200:1:0	G2	22	127.7	1.35
9	2000:1:0	G2	6	36.0	2.05
10	2000:1:0	G2	40	24.5	1.99
11	1000:1:5	G2	22	5.69	1.80
12	1000:1:10	G2	22	2.83	2.10
13	1000:1:20	G2	22	1.63	1.89
14	1000:1:50	G2	22	0.65	2.31
15	1000:1:100	G2	22	0.29	2.61

^aROMP was performed using neat DHF under an ambient atmosphere for 4 h (using G2) or a N₂ atmosphere for 72 h (using G1), and quenched with basified H₂O₂. ^bInitial equivalents of DHF/Grubbs initiator/ethyl vinyl ether. ^cDetermined by GPC MALLS analysis in THF. ^d M_w/M_n .

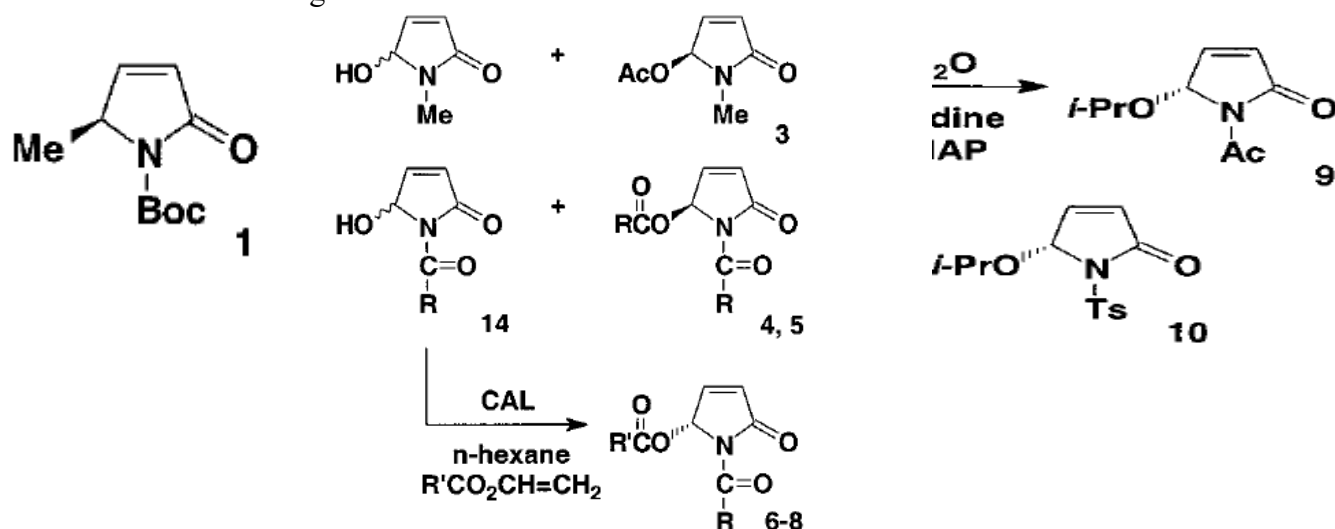
Feist, J. D., & Xia, Y. (2019). Enol ethers are effective monomers for ring-opening metathesis polymerization: Synthesis of degradable and depolymerizable poly(2, 3-dihydrofuran). *Journal of the American Chemical Society*, 142(3), 1186-1189.

First off I admit to being somewhat deficient in ROMP chemistry and learning on the job. There's a mountain of references concerning ROMP and even more about metathesis. So I mean well and please read on.



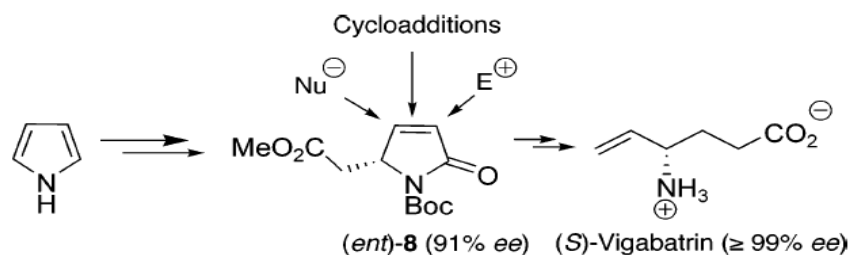
Scheme 1: Would ROMP work with the above monomers?

This then set me searching the literature.



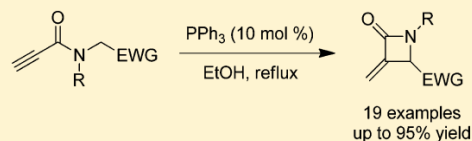
This reference shows routes to all of the above examples.

Cuiper, A. D., Brzostowska, M., Gawronski, J. K., Smeets, W. J., Spek, A. L., Hiemstra, H., ... & Feringa, B. L. (1999). Determination of the Absolute Configuration of 3-Pyrrolidin-2-ones. *Journal of organic chemistry*, 64(7), 2567-2570.

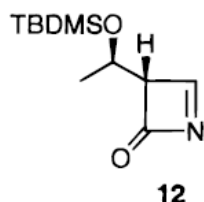


Gheorghe, A., Schulte, M., & Reiser, O. (2006). Synthesis of functionalized pyrrolidin-2-ones and (S)-Vigabatrin from pyrrole. *The Journal of organic chemistry*, 71(5), 2173-2176.

ABSTRACT: We report herein a facile synthesis of α -methylene- β -lactams. Thus, under the catalysis of triphenylphosphine, a number of 2-propiolamidoacetates or α -propiolamido ketones in refluxing ethanol underwent umpolung cyclization to afford the corresponding 4-substituted 3-methyleneazetidin-2-ones in high yields.



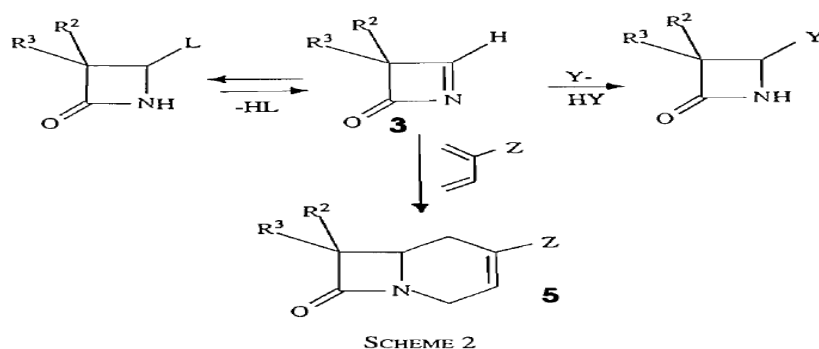
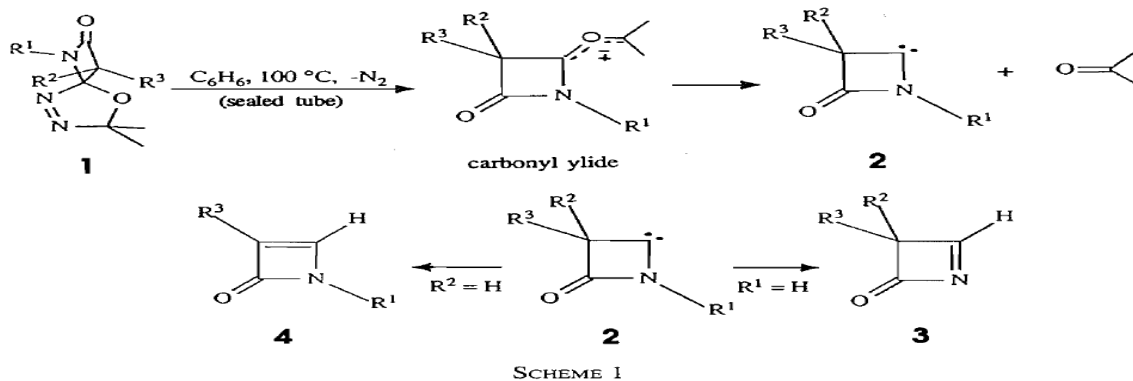
Zhu, L., Xiong, Y., & Li, C. (2015). Synthesis of α -methylene- β -lactams via PPh₃-catalyzed umpolung cyclization of propiolamides. *The Journal of organic chemistry*, 80(1), 628-633.



This is mentioned as a possible reactive intermediate but the unsaturation is in the wrong location.

Kondo, K., Seki, M., Kuroda, T., Yamanaka, T., & Iwasaki, T. (1997). 2-Substituted 2,3-Dihydro-4H-1,3-benzoxazin-4-ones: Novel Auxiliaries for Stereoselective Synthesis of 1- β -Methylcarbapenems. *The Journal of organic chemistry*, 62(9), 2877-2884.

“Azetionones are not stable species: An azetionone of type **4** has been observed at -5°C by spectroscopic methods (**3**) but none has ever been isolated despite attempts by several groups (**4-6**). Azetionones **3** have not been isolated either, but their existence as transients is a facet of postulated mechanisms of nucleophilic substitutions on β -lactams (**7**) bearing a leaving group (L) at C4, Scheme 2, and of the hetero-Diels-Alder reactions, to form **5**, reported by Meyers' group (**8**).”



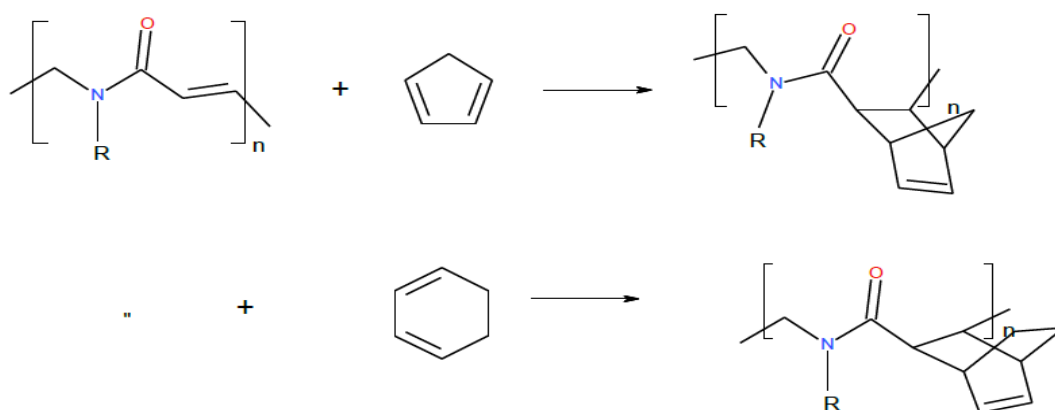
Zoghbi, M., & Warkentin, J. (1992). Azetionone formation is not competitive with intermolecular reactions of a β -lactam-4-ylidene. *Canadian Journal of Chemistry*, 70(11), 2792-2797.

“Azetionone itself is an extremely unstable compound, even at low temperature. Hence,

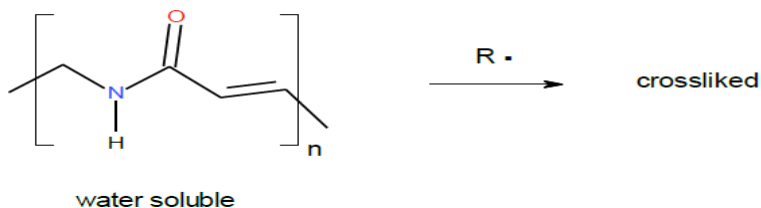
the attempts to obtain this species were not successful.1 The azetinone structure, with four-membered ring, is $\sim 50 \text{ kJ mol}^{-1}$ less stable than its open-ring α -iminoketene isomer.”

Rostkowska, H., Lapinski, L., & Nowak, M. J. (2020). Photochemical Generation of Benzoazetinone by UV Excitation of Matrix-Isolated Precursors: Isatin or Isatoic Anhydride. *The Journal of Physical Chemistry A*, 124(20), 4106-4114.

At this point I was convinced that searching for azetinones was a dead end unless ROMP could be successful at very low temperatures where the azetinones might exist. But the pyrrolidin-2-ones are readily available and I would think large ring versions are also possible. So you would end up with an unsaturated polyamide. I see this polyamide as a polymeric dieneophile that would readily do the Diels-Alder reaction.



Scheme 2: These Diels-Alder reaction along the polymer backbone can then take part in further Metathesis yielding brushes or crosslinked resins.



Scheme 3: This water soluble polymer would be attacked by free radicals. Obviously these polymers, if they exist, would exhibit many other reactions.

Thank you for reading these proposals.

Dr. Robert B. Login rloginconsulting.com