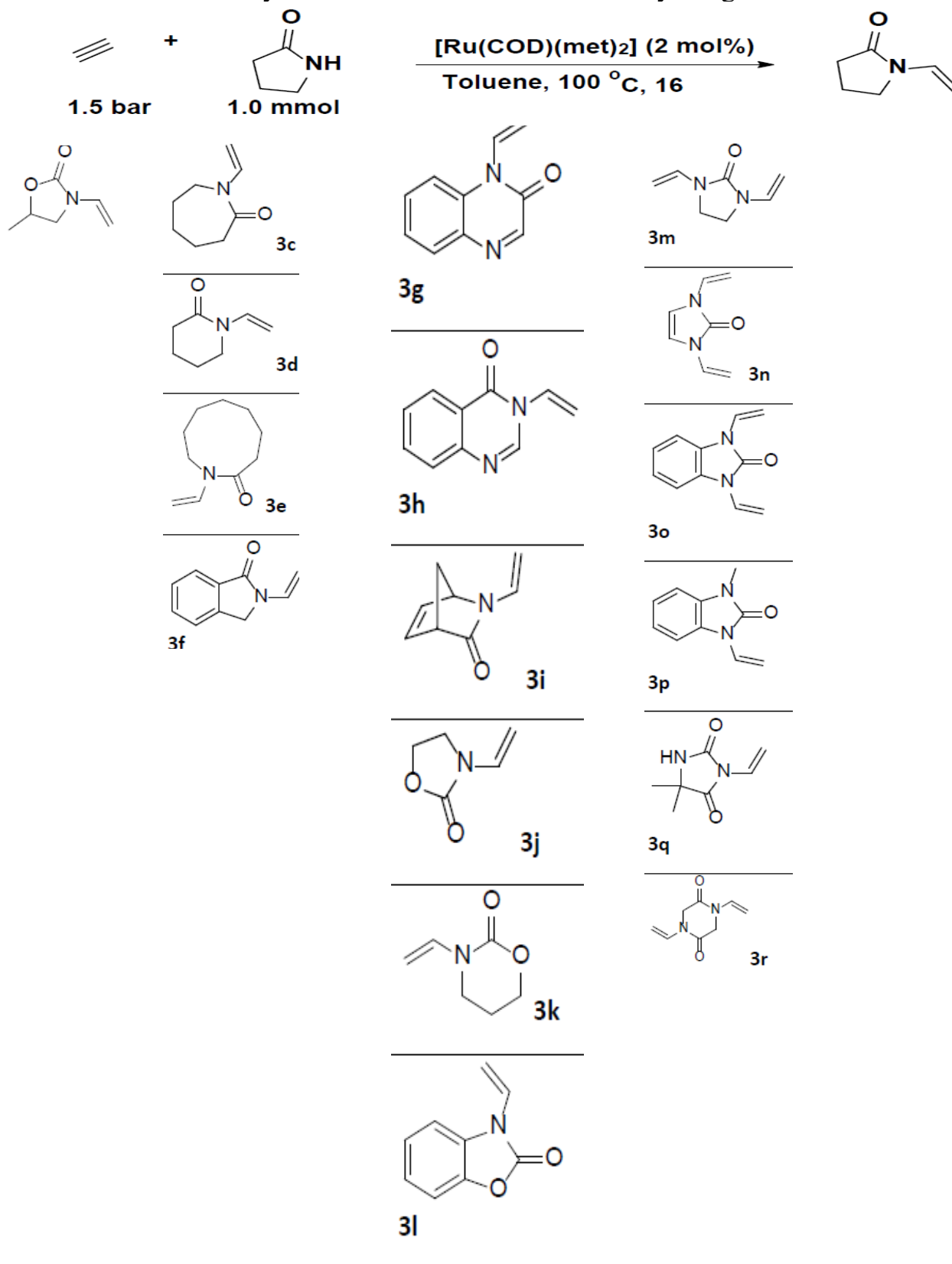


N-Vinyl Lactam Monomers

By: Robert B. Login rloginconsulting.com

If you look at my web page pdf's you will see that over the years I have suggested several new vinyl lactam monomers. What brings me back to this subject was a recent article that covered many such monomers and rekindled my imagination.



The above are all from:

Semina, E., Tuzina, P., Bienewald, F., Hashmi, A. S. K., & Schaub, T. (2020). Ruthenium-catalyzed synthesis of vinylamides at low acetylene pressure. *Chemical Communications*, 56(44), 5977-5980. Can this high yield reaction be scaled up to an industrial scale?

So what other vinyl lactams could be proposed or actually exist?

Use of acetylene to generate vinyl lactams has a long history. A recent review is very interesting:

Yan, L., Chu, B., Zhong, S., Fu, Z., & Cheng, Y. (2020). Synthesis of N-vinyl pyrrolidone by acetylene process in a microreactor. *Chemical Engineering Journal Advances*, 2, 100018.

Although acetylene is the industrial route to vinyl lactams; however, acetylene is not the only route. Acetylene on a commercial large volume scale requires very specialized equipment. Safety is a major consideration, as explosions are very likely and as I understand it, the key to success is to prevent any explosive reactions from propagating through the rest of the reaction mixture. Apparently these are secrets as to how to do this.

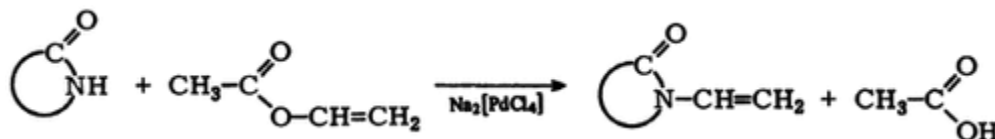
So if you don't use acetylene, how else can you accomplish the synthesis of vinyl lactams?

Transvinylation:

Vinyl acetate can be used to vinylate lactams:

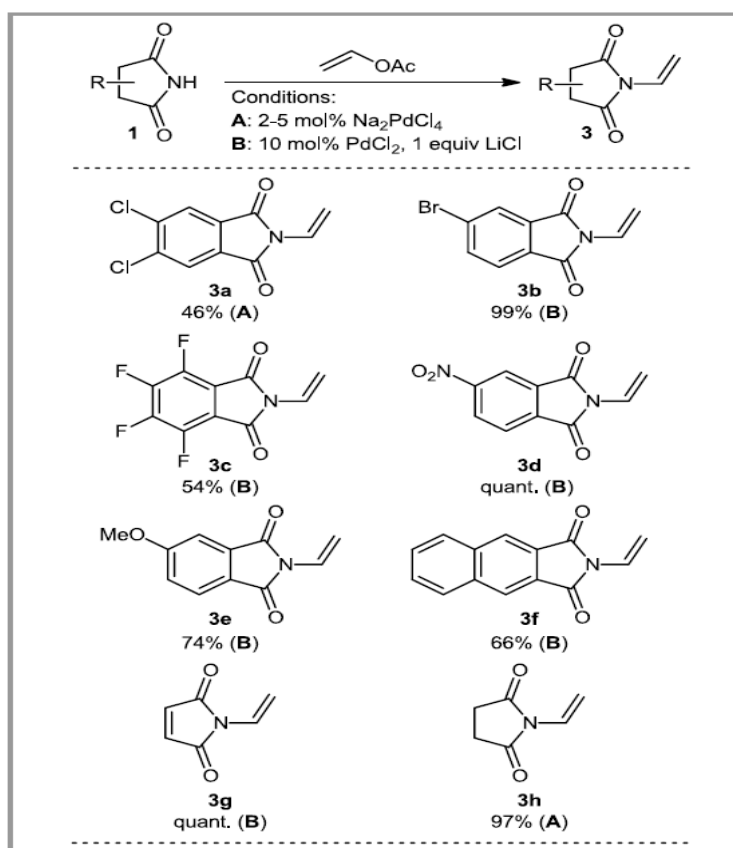
Abstract

A general synthesis of monomeric N-vinylimides and-lactams has been found in the homogeneously catalyzed reaction with vinyl acetate. The reaction proceeds in one step and gives high yields on use of Na_2PdCl_4 as catalyst.



Bayer, E., & Geckeler, K. (1979). Homogeneous Catalytic Vinylation of Cyclic Imides and Lactams for the Synthesis of N-Vinyl Monomers. *Angewandte Chemie International Edition in English*, 18(7), 533-534.

Listemann, M. L., Pierantozzi, R., & Pinschmidt Jr, R. K. (1990). *U.S. Patent No. 4,968,841*. Washington, DC: U.S. Patent and Trademark Office.



Scheme 3 Scope of the vinylation reaction. The reaction conditions used are given in parenthesis after the yield.

Serrano, E., De Nanteuil, F., & Waser, J. (2014). Diester-substituted aminocyclopropanes: synthesis and use in [3+2]-annulation reactions. *Synlett*, 25(ARTICLE), 2285-2288. Although not a lactam, it shows the utility of this reaction. Also from USP 4968841 see:

R. H. Summerville, et al., "Synthesis of N-Vinyl Acetamide and Preparation of Some Polymers and Copolymers," ACS, Polymer Reprints, (1983) 24, pp. 12-13.

S. Takese, et al., "The Reaction of Vinyl Acetate with Fatty Amide", Institute of Chemistry, Coll. of Gen. Education, Osaka Univ., pp. 7-9.

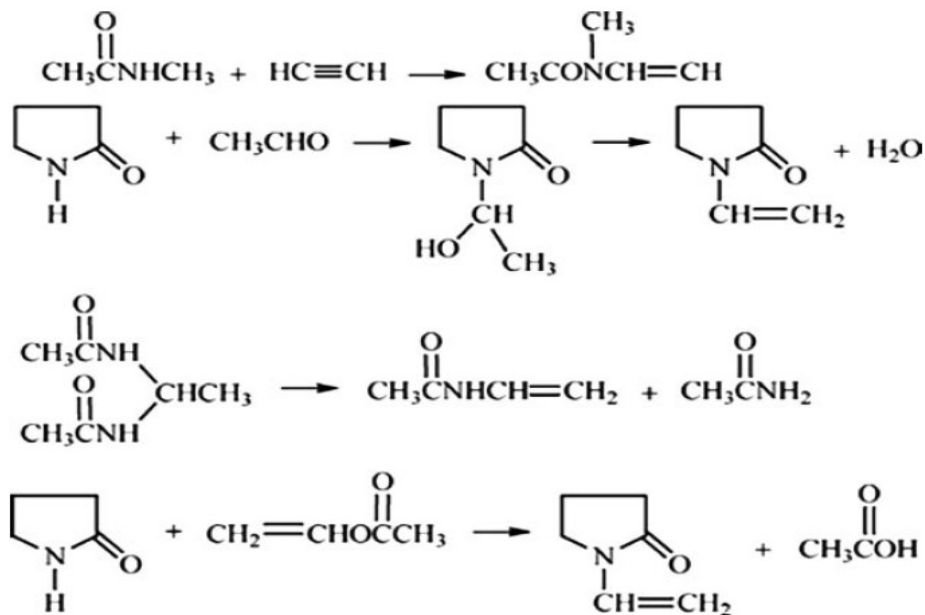
E. Bayer, et al., "Homogeneous Catalytic Vinylation of Cyclic Imides and Lactams for the Synthesis of N-Vinyl Monomers," *Angew. Chem. Int. Ed. Engl.*, (1979) 18(7) pp. 533-534.

There is also dehydration of N-hydroxy ethyl derivatives.

Haus, M. O., Louven, Y., & Palkovits, R. (2019). Extending the chemical product tree: a novel value chain for the production of N-vinyl-2-pyrrolidones from biogenic acids. *Green Chemistry*, 21(23), 6268-6276.

Kirsh, Y. E. (1998). *Water soluble poly-N-vinylamides: synthesis and physicochemical properties*. John Wiley &

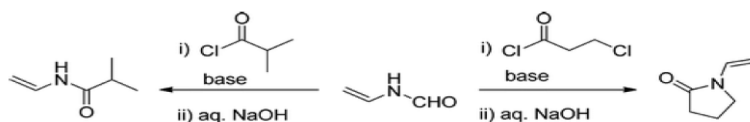
Sons.



Login, R. B. (2002). N-Vinylamide Polymers. *Encyclopedia of Polymer Science and Technology*.

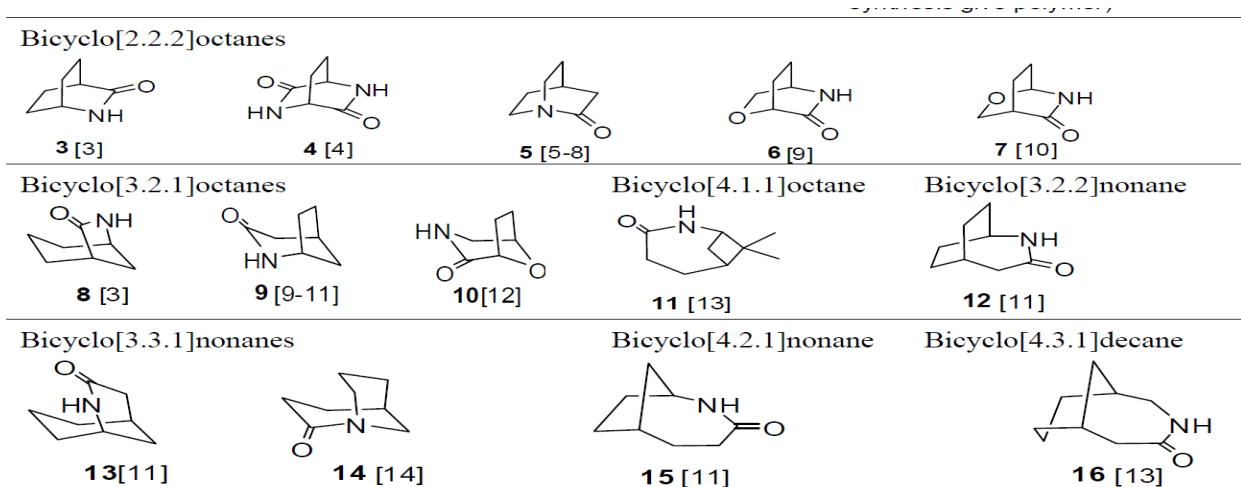
The above is a summary of the most offend employed vinylation methods.

Abstract



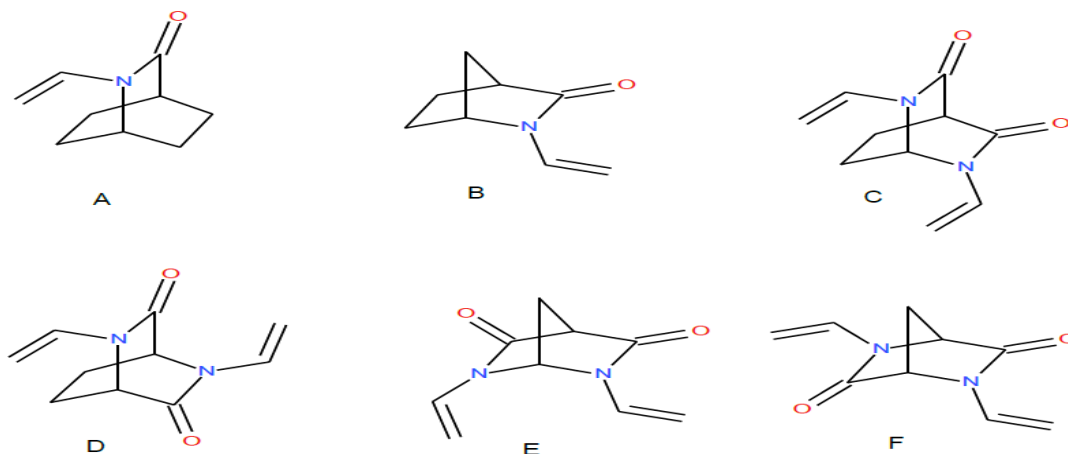
A facile synthesis of *N*-vinylakylamides from commercially available *N*-vinylformamide and corresponding acyl chlorides was developed and exemplified by the preparation of *N*-vinylisobutyramide (NVIBA) and *N*-vinyl-2-pyrrolidinone (NVP) in high yields (80–89%). Both NVIBA and NVP are valuable monomers for water-soluble polymers with an array of applications in personal care, pharmaceutical, agricultural, and industrial products.

Tu, S., & Zhang, C. (2015). Facile preparation of *N*-vinylisobutyramide and *N*-vinyl-2-pyrrolidinone. *Organic Process Research & Development*, 19(12), 2045-2049.



Hall, H. K. (2012). Synthesis and polymerizability of atom-bridged bicyclic monomers. *Polymers*, 4(4), 1674-1686.

The above reference is about ring opening polymerization of the above bicyclics. This led me to think about N-vinyl bicyclic lactams. For example:

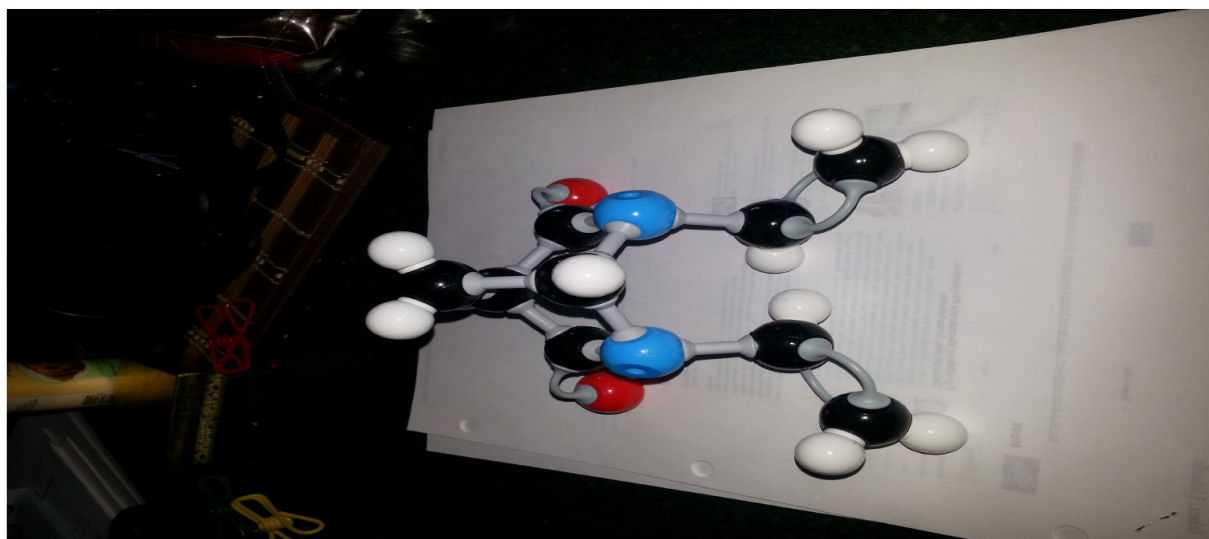


Scheme 1: Possible bicyclic N-vinyl lactams. Many others could be imagined. Synthesis of the starting lactams is covered by references in the above Hall article.

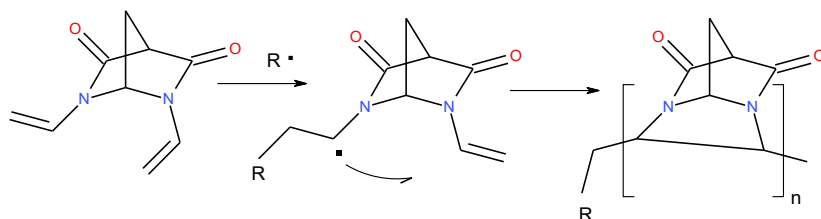
If you want to see practically every possible lactam structure:

Saldívar-González, F. I., Lenci, E., Trabocchi, A., & Medina-Franco, J. L. (2019). Exploring the chemical space and the bioactivity profile of lactams: a chemoinformatic study. *RSC advances*, 9(46), 27105-27116.

These bicyclic N-vinyl lactams have potentially interesting possibilities. Previously in another pdf I illustrated the possibility of Butler cyclopolymerization.



See “Dimerspyrromethanes” and “Polypyrrolodones and Cyclopolymertization” pdf on my web site rloginconsulting.com



This assumes that the nitrogen vinyls are endo and this is likely because the energy barrier here from exo to endo is low. The vinyl groups can twist around to be in an ideal position for cyclopolymerization. I have not built models of the other possibilities from scheme 1 but they too would probably cyclopolymerize.

Bicyclic lactams in polymers would I think contribute rigidity to homo and copolymers. A trivial application would be in spiky hairdos. More importantly copolymers of vinyl lactams have been suggested as DNA, RNA and drug carriers. Possibly bicyclic lactam containing polymers might contribute to this technology?

Thank you for reading these proposals!

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