

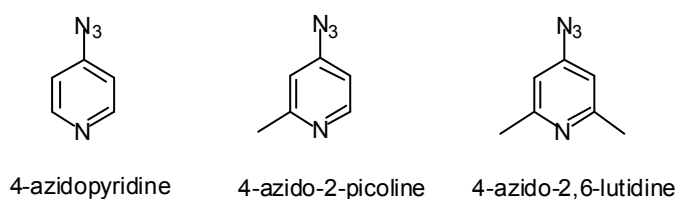
Photochemistry of Self Assembled Monolayers of Azidopyridines on Pt(111)

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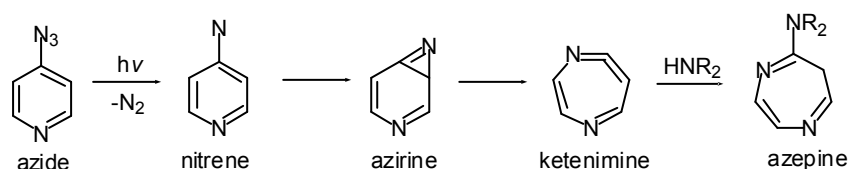
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The study of self assembled monolayers (SAMs) is rapidly growing field of interest as their dense, stable assembly makes them ideal candidates for use in corrosion protection, biochemical and chemical sensing as well as the miniaturization of electronic devices. The majority of studies of SAMs have been focused on large molecular architectures such as long chain alkyl thiols bound to Au, Si and other semiconductor metals. Our focus is the study small molecular architectures, which form SAMs and to investigate their interfacial reactivity. The molecules of interest are a series azidopyridines (AP) (Scheme 1). Irradiation of these molecules in solution results in the loss of molecular nitrogen and formation of a reactive nitrene intermediate, which inserts into the aromatic ring to form an azirine and undergoes ring expansion to give rise a ketenimine, which can be trapped by a variety of nucleophiles (Scheme 2). The characteristic infrared absorption bands of the azidopyridines and their photoproducts allow for easy characterization via reflection absorption infrared spectroscopy (RAIRS). Monolayers of 3- and 4-AP on Pt(111) were prepared in an ultra high vacuum (UHV) chamber and were found to be extremely stable with no surface initiated decomposition of the azide functionality, allowing for the study of their photoreactivity. Photolysis of the SAMs initiated the loss of molecular nitrogen and lead to the first spectroscopic evidence of the formation of an azirine monolayer characterized by an absorption band at 1740cm^{-1} .



Scheme 1



Scheme 2