# FORMATION OF $\alpha$ -ENAMINOKETONES FROM $\alpha$ -AZIDOKETONES: AN ELIMINATION OF MOLECULAR NITROGEN FROM $\alpha$ -AZIDOKETONES

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Abstract:  $\alpha$ -Enaminoketones are readily accessible through reaction of  $\alpha$ -bromoketones with sodium azide followed by an elimination of molecular nitrogen. The reaction is base catalyzed and proceeds under relatively mild conditions. An anionic mechanism is proposed.

 $\alpha$ -Enaminoketones have been interesting synthetic precursors but have not been readily available<sup>1</sup>. A classical approach, reaction of an amine with a 1,2- diketone, suffers from regiospecificity problems<sup>2</sup>. We wish to report a synthesis of  $\alpha$ -enaminoketones by reaction of  $\alpha$ -bromoketones with sodium azide, in the presence of base, which involves a novel loss of molecular nitrogen.

The conversion of an organoazide to an imine has been reported to occur only under heating to  $200^{\circ}C^3$ . We achieved such a conversion under relatively mild conditions with  $\alpha$ -azidoketones. We note yields are improved by the presence of an electron- withdrawing group  $\gamma$ -to the ketone moiety.

#### Scheme I:



On treatment of ethyl 3-bromolevulinate<sup>4</sup> 1 (Scheme I) with excess sodium azide in 60% acetone/ water<sup>5</sup> followed by addition of catalytic triethylamine and subsequent heating to reflux over 5 hours the  $\alpha$ -enaminoketone 2 is generated in 73% yield. If shorter reaction times are used, the  $\alpha$ -azidoketone 3 can be isolated by chromatography The reaction has been generalized to include  $\gamma$ -ketonitriles,  $\gamma$ ketophosphonates, and  $\gamma$ -trifluoromethylketones (Table I). No alkyl migrations are observed.

## Table I:





Our proposed mechanism involves initial displacement of bromide by azide to give the  $\alpha$ -azidoketone as an intermediate. The acidity of the  $\alpha$ -proton makes proton transfer followed by elimination of molecular nitrogen a facile process. A simple tautomerism results in the formation of the enamine.

A nitrene mechanism might also be proposed. However, the alkyl- or acyl- migration product which would be expected in this case is not detected.

The  $\alpha$ -enaminoketones have proven to be useful for the formation of novel heterocycles. Additional applications are in progress.

## **REFERENCES AND NOTES**

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- 5. For best results use 75% THF/ water.
- 6. Satisfactory <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and elemental analysis was obtained for all compounds.

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