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Ceric Ammonium Nitrate (CAN) Mediated Azidoalkoxylation Of Enol Ethers And Olefins.#

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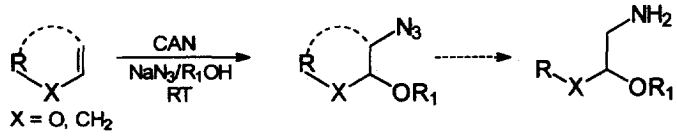
Abstract: The azidoalkoxylation of enol ethers and olefins using ceric ammonium nitrate and sodium azide in presence of various alcohols is described.

Oxidative generation of carbon centered radicals mediated by Ce (IV) salts is well established and in particular the formation of azidonitrates by the reaction of olefins with NaN_3 in presence of CAN is well documented.[1] Various transformations have also been carried out to highlight the potential of this readily available metal as a one electron oxidant.[2] Recently Nishiguchi *et al.*[3] reported a regioselective azidomethoxylation of enol ethers through anodic oxidation to give the corresponding acetals of α-azido carbonyl compounds. Additionally direct conversion of olefins to α-azidoketones has also been reported.[4]

As a continued interest[5] of ours in exploring CAN as a powerful single electron oxidant, we decided to test its efficacy in bringing about azidoalkoxylation of enol ethers and olefins.

Scheme:



A variety of olefins and enol ethers were treated with alcohols in the presence of CAN and sodium azide to yield the azidoalkoxylated products in good to moderate yields (see table). The noteworthy feature of this methodology is that mixed acetals can be readily obtained in synthetically useful yields and it provides one of the easiest routes for the synthesis of amino acetals which are important reagents for the preparation of isoquinolines[6] and other heterocycles. It also allows the azidocarbonyls to be obtained in protected form, which can be readily unmasked to the corresponding carbonyl compounds.

However this reaction did not proceed for electron deficient olefins (entry 6). Also it has been found that the sequence of the addition of the reagents is critical for the success of the reaction and a reversal of the addition of the reagents failed to furnish the desired product. Furthermore the addition of the azido group takes place regioselectively as predicted.[3] A look at the substrates depicted in the table clearly reveals that the azidoalkoxylation reaction works remarkably well with electron rich olefins.

In conclusion, to the best of our knowledge a combination of azide, alcohol and olefin in a single pot reaction to yield the corresponding azidoalkoxy products is the first report of its kind and it constitutes a practical route for the synthesis of amino acetals.

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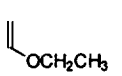
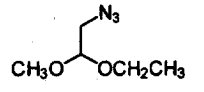
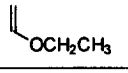
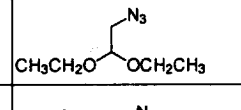
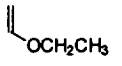
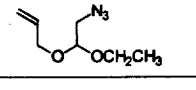
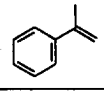
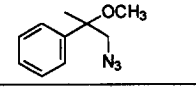
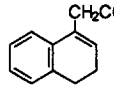
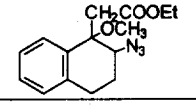
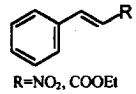
General Procedure:

NaN_3 (0.1 mol) was dissolved in dry acetonitrile to which was added the olefin (0.1 mol) followed by the alcohol (0.5 mol) under an argon atmosphere. Then CAN (0.2 mol) (procured from s.d.fine-chem Ltd./Loba Chemie, India) dissolved in acetonitrile was added to it at 0°C and the reaction mixture was gradually brought to room temperature and left overnight. Work up involved concentration of the reaction mixture under reduced pressure followed by extraction with diethyl ether. The organic layer was washed with water and dried over anhyd. Na_2SO_4 which was further concentrated and the residue chromatographed.

Table:

S.No.	Substrate	Alcohol	Product	Yield (%)
1.		Methyl		60
2.		Ethyl		60
3.		Allyl		55
4.		Methyl		90
5.		Methyl		80
6.	 R=NO_2, COOEt	Methyl	--	--

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