Novel Bicyclic Oxazolines *via* Nitrile Capture of Photochemically Generated Oxyallyl Zwitterions

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Several 4-pyrones bearing 3-alkoxy substituents have been photolysed in acetonitrile to give in two cases novel bicyclic oxazolines, arising from apparent Ritter-type capture of the intermediate oxyallyl zwitterion followed by intramolecular nitrilium trapping by alkoxide.

The photochemistry of 4-pyrones has yielded a variety of novel reactions. Early mechanistic studies showed that rearrangement to isomeric 2-pyrones[1] and trapping by hydroxylic solvent[2] were both significant pathways, with a bicyclic oxyallyl zwitterion serving as the putative intermediate in each case. More recently, we have reported examples of both intermolecular zwitterion capture by MeOH or water[3] and intramolecular capture by pendant alcohols[4] or π nucleophiles[5] which demonstrate the synthetic utility of the chemistry. We report here a new type of trapping reaction in which capture by acetonitrile is followed by cyclization to give novel oxazolines fused to cyclopentenones.

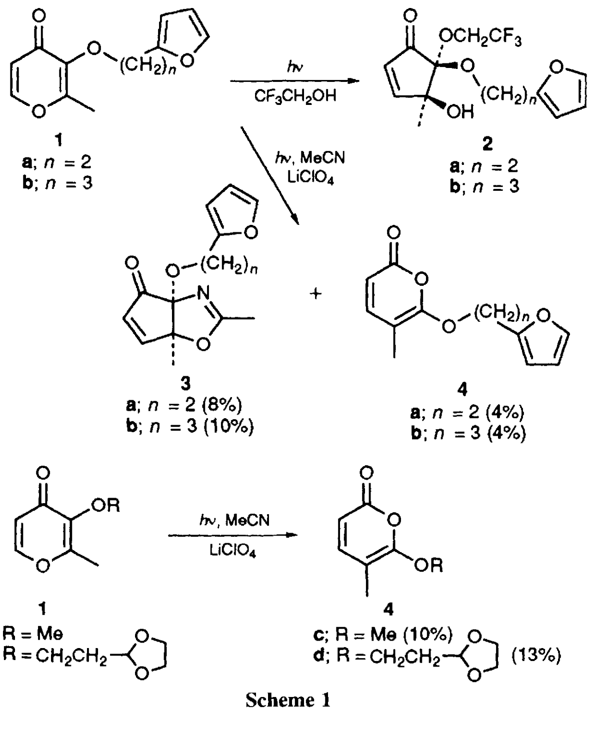
In the course of studying the interception of the zwitterion by pendant 1,3-dienes in concerted [4 + 3] cycloadditions, we had prepared substrates **1a** and **1b**. Under the usual conditions (photolysis in trifluoroethanol), only mixed ketals **2a** and **2b**, arising from solvent capture at the more electrophilic oxyallyl terminus, were obtained (Scheme 1).[6] Solvent studies with a related substrate had shown that acetonitrile containing $LiClO_4$ was comparable to trifluoroethanol in supporting zwitterion chemistry. Thus, we reasoned that use of such a non-hydroxylic solvent system might allow cycloaddition to compete with solvent trapping.

In the event, we found no products of the desired [4 + 3] cycloaddition pathway upon photolysis of **1a**. Two components in the complex reaction mixture could be isolated cleanly, one of which appeared to contain the elements of the 4-pyrone substrate with the ether group intact, along with two additional carbons. Ultimately, the structure was determined to be that of compound **3a**, in which one molecule of acetonitrile had been incorporated. The other isolable product was rearranged 2-pyrone **4a**. Substrate **1b** underwent an analogous conversion to **3b** and **4b**, but **1c** and **1d** failed to yield any solvent adducts.

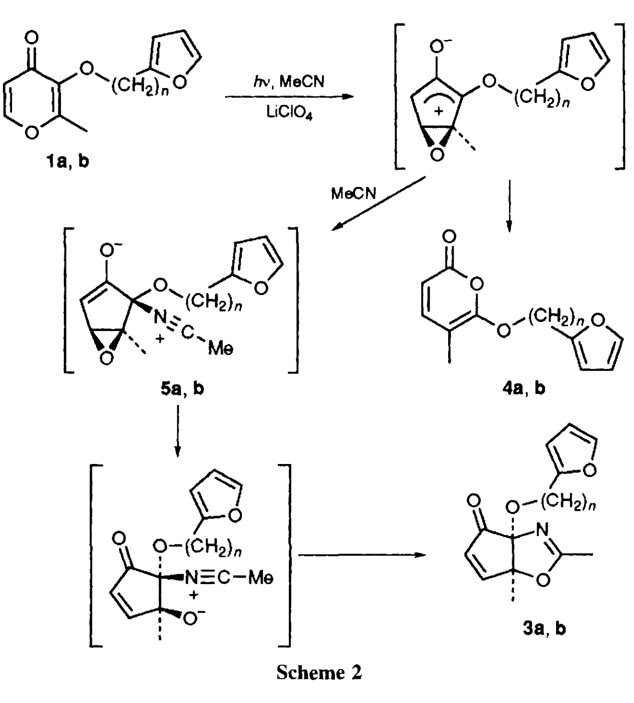
We sssume that oxazolines **3a** and **3b** are derived from nucleophilic attack on the oxyallyl zwitterion by solvent in a Ritter-type reaction[7] to give nitrilium intermediates **5** (Scheme 2). Subsequent fragmentation of the epoxide would produce an internal alkoxide nucleophile which could attack the nitrilium ion and give the observed oxazoline. Importantly, attack of acetonitrile must occur *syn* to the epoxide to permit *cis* ring-fusion of the doubly unsaturated bicyclo[3.3.0]octane skeletons. In most cases where the stereochemistry of solvent capture has been rigorously determined, a *trans* relationship exists between the solvent moiety and the hydroxy group which arose from the epoxide.[2,3] A possible explanation for the low overall mass recovery in these reactions is that the remainder of the material is consumed *via anti* nitrile trapping, with the resultant betaines undergoing decomposition or oligomerization processes in lieu of cyclization.

The presence of an electron releasing ether substituent on one terminus of the oxyallyl intermediate is clearly critical in allowing ionic solvent capture processes to dominate over cycloaddition.[6] Less obvious is the role played by the furan moiety at the end of the side chain. The failure of substrates **1c** and **1d** to give any bicyclic Ritter trapping product is puzzling, but suggests that the furan rings of **1a** and **1b** may facilitate the atypical *syn* delivery of solvent by blocking the anti face of the zwitterion. Results of experiments to further probe this effect will be reported elsewhere.

In summary, the nitrile trapping pathway demonstrates a new type of reactivity by photochemically generated oxyallyl zwitterions, and furnishes structurally novel bicyclic oxazolines.



Scheme 1



Scheme 2

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