The Chemistry of 5-Oxodihydroisoxazoles. Part 23.[1] Photochemical and Thermal Reactions of Isoxazol-5(2*H*)-ones substituted at C-3 or C-4 with Nitrogen, Oxygen or Sulfur

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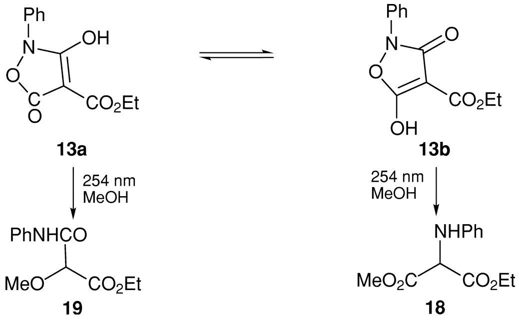
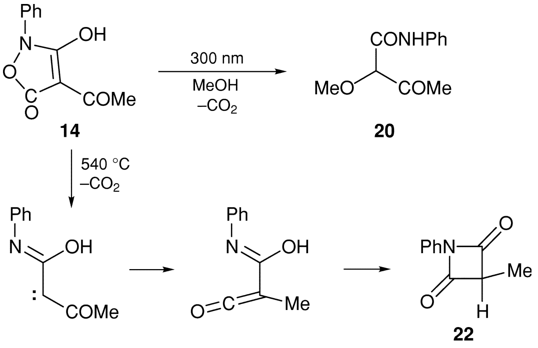
3-Amino- and 3-hydroxy-isoxazol-5(2*H*)-ones can exist as a number of tautomers which give discrete photolysis and pyrolysis products.

Isoxazol-5(2*H*)-ones undergo photochemically or thermally induced loss of CO_2 to form an iminocarbene[1,2] or isomerise to a nitronoketene,[10] and the preferred pathway is greatly influenced by the substituents at the 2-, 3- or 4-position. With a hydroxy group at C-3, a number of tautomers were present, and we have shown that each follows its own decomposition pathway on photolysis.[10] This paper details the synthesis of a number of 3-amino, 3-phenylamino and 3-hydroxyisoxazol-5(2*H*)-ones, and describes the products obtained from them on flash vacuum pyrolysis (fvp) and photolysis. It includes a reinvestigation of the photolysis of 4-phenoxy and thiophenoxy analogues, and details their pyrolysis products.



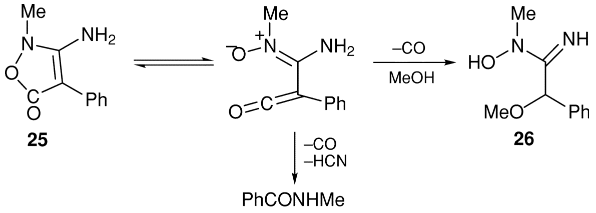
Scheme A

The hydroxy ester **13** underwent photolysis at 254 nm in methanol to give **19** from **13a** and **18** from **13b** (Scheme A), but the acetyl analogue **14** gave the photolysis product **20** and the fvp product **22**, which arise exclusively from the isoxazolone tautomer **14** (Scheme B).



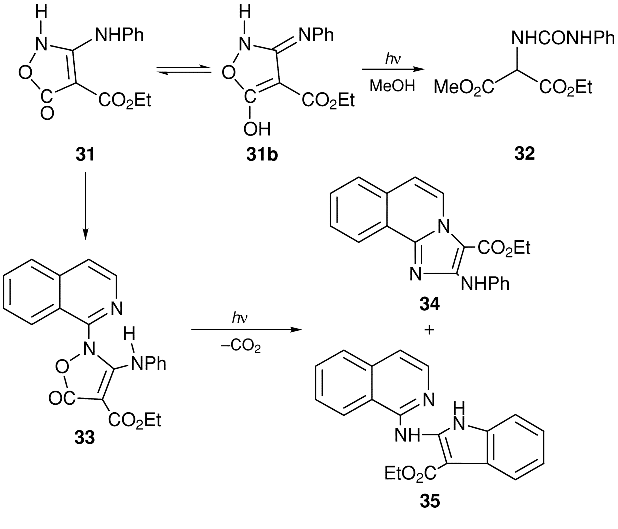
Scheme B

By contrast, the amino compound **25** underwent photolysis totally from the nitonoketene isomer, giving high yields of the amidine **26**, and on fvp gave N-methylbenzamide, which is also postulated to arise from thermal decomposition of the nitronoketene (Scheme C).



Scheme C

The aminoester **31** underwent photolysis from the tautomer **31b** to give **32**, but substitution on N with heteroaryl groups re-established fragmentation by the carbene pathway, giving the imidazole and indole products *e.g.* **34** and **35** (Scheme D).



Scheme D

Techniques used: IR, ^{1}H and ^{13}C NMR, mass spectrometry, flash vacuum pyrolysis

Schemes: 9

References: 26

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