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The Regio- and Stereo-chemistries of the $(2\pi + 2\pi)$ Photocycloaddition of Electron-deficient Ethenes to Isoquinolin-1(2*H*)-one

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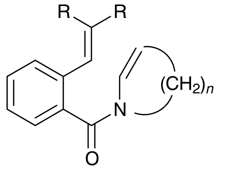
The $(2\pi + 2\pi)$ photocycloaddition of isoquinolin-1(2*H*)-one to electron-deficient ethenes is efficient, regiospecific and highly stereoselective: 254 nm irradiation of the acrylonitrile adduct induces retroadditon and rearrangement to an *N*-vinylisoindolinone with equal efficiencies.

Literature describing the $(2\pi + 2\pi)$ photocycloaddition of ethenes to isoquinolinones is sparse but there does appear to be agreement that the reaction occurs with head-to-tail regioselectivity.[4–10] These cyclobutane derivatives are reported to undergo photochemical cleavage using short-wavelength radiation to give either 2-ethenylbenzamides **1** or starting materials dependent on the adduct structure.[10]



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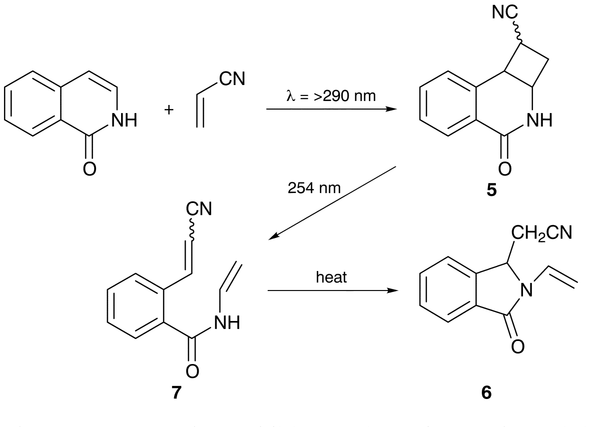
We now report on the regio- and stereo-chemistries of the $(2\pi + 2\pi)$ photocycloaddition reaction, and give the details of the photorearrangement of the cycloadduct **5** of isoquinolinon-1(2*H*)-one and acrylonitrile.

The formation of the *N*-vinylisoindolinone **6** from **5** using 254 nm radiation[11] transpires to be temperature dependent and only becomes a significant process above 35 °C. At lower temperatures, a labile isomer is formed which has spectral data consistent with those of the ring-opened isomer **7**: this then yields **6** by an intramolecular conjugate addition.

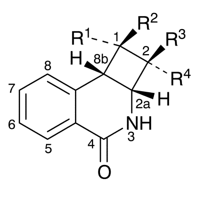


The $(2\pi + 2\pi)$ photoaddition arises from the triplet excited state of isoquinolin-1(2*H*)-one and is most favoured with electron-deficient ethenes. The results for acrylonitrile derivatives as the addends are summarised in Table 1. Significant features of these additions are (i) the regiospecificity derived from polar features in the addends, (ii) the high *exo* stereoselectivity of the cyano group and (iii) the pronounced selectivity for *trans* geometry of the cyano and alkyl or alkoxy substituents on the cyclobutane ring of the adducts regardless of the *cis:trans* ratio of the starting 3-substituted acrylonitriles. The dienophilic ethenes, methyl acrylate, methyl methacrylate and methyl vinyl ketone, also gave $(2\pi + 2\pi)$ photoadducts with isoindolin-1(2*H*)-one with similar yields and selectivities to those observed for the acrylonitriles.

Table 1 The $(2\pi + 2\pi)$ photocycloaddition of substituted acrylonitriles to isoquinolin-1(2*H*)-one

Acrylonitrile derivative	$(2\pi + 2\pi)$ Cycloadducts	Yield (%)
Methacrylonitrile	**16**, **17**[a] respective ratio 9:1	70[b]
But-2-enenitrile (*cis:trans* ratio; 1:3)[d]	**18**, **19**[a] respective ratio 9:1	35[c]
Cis-pent-2-enenitrile	**20**	57[b]
3-Methoxyacrylonitrile (*cis:trans* ratio; 1:2)[d]	**21**[e]	75[b]
3-Ethoxyacrylonitrile (*cis:trans* ratio; 1:2)[d]	**22**	80[b]
2-Chloroacrylonitrile	**23**	45[b]

[a]Structures tentatively assigned from ^{1}H NMR spectra of enriched mixtures with its isomer. The yields of the adducts were not optimised and the values reported are those obtained following purification/separation by flash chromatography[b] and two recrystallisations from methanol[c] at complete conversion of the isoquinolinone. [d]Estimated from ^{1}H NMR spectroscopy. [e]Minor amounts (*ca.* 5%) of an unidentified 1:1 adduct isomer were also formed.



16 R^1 = Me, R^2 = CN, R^3 = R^4 = H
17 R^1 = CN, R^2 = Me, R^3 = R^4 = H
18 R^1 = R^3 = H, R^2 = CN, R^4 = Me
19 R^1 = R^4 = H, R^2 = CN, R^3 = Me
20 R^1 = R^3 = H, R^2 = CN, R^4 = Et
21 R^1 = R^3 = H, R^2 = CN, R^4 = OMe
22 R^1 = R^3 = H, R^2 = CN, R^4 = OEt
23 R^1 = Cl, R^2 = CN, R^3 = R^4 = H

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

References: 16 Tables: 2

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