Photoreactions of α , β -Unsaturated γ , δ -Epoxy Nitriles with Amines. The Novel Photoadditions of Tertiary Amines to the α -Position of the Nitriles

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Direct irradiation of α , β -unsaturated γ , δ -epoxy nitriles (*e.g.* **1**) and tertiary amines gives rise to a novel 1 : 1 α -addition and subsequent retro-Michael reaction leading to α -alkylidenenitriles (*e.g.* **2**).

The photoaddition reaction of α , β -unsaturated ketones and esters with tertiary amines has been reported to give 1:1 β -adducts between carbonyl compounds and amines and α , β -dihydro compounds.^{1,2} These processes are promoted by single electron transfer from the amines to the excited carbonyl compounds. Mariano *et al.* showed the synthetic application of this type of photoadditions using α -trimethylsilylamines to *N*-heterocyclic compounds.³

In earlier studies, we showed the photochemical reactions of α,β -unsaturated γ,δ -epoxy nitriles with 1 equiv. of tertiary amines to give the corresponding divinyl ethers, whose formation probably involves an intermediate generated by photoinduced single electron transfer from the amines to the nitriles.⁴ On the other hand, we performed the photoreaction of nitrile 1⁴ with a high concentration of triethylamine (TEA), involving a new type of α -addition of the amine, to give but-2-enenitrile **2a**. We report here the novel α -photoaddition of tertiary amines to α,β -unsaturated γ,δ -epoxy nitriles (Scheme 1).

Epoxynitrile *E*-1 was irradiated (in TEA as solvent) with a low-pressure mercury lamp through a quartz filter at room temperature (51% conversion) yielding[†] *Z*-1 (6%), **2a** (26%) and reduced compound **3** (13%).[‡] The characteristic signal of **2a** could not be observed in the ¹H NMR spectrum of the crude photoproduct of **1**, which was treated with SiO₂ in CHCl₃, yielding **2a**. The adduct **4** was isolated after basic AlO₃



Scheme 1 Reagents and conditions: i, $\lambda = 254$ nm, Et₃N; ii, SiO₂

chromatography as a mixture of four stereoisomers.§ Under the same reaction conditions (in TEA as solvent) nitrile 5^5 (80% conversion) afforded lactone 6 (10%), 7 (6%), *E*-8 (5%), *Z*-8 (15%), and 9^5 (6%).‡ The lactone 6 was formed by cyclization of compound 10 and subsequent hydrolysis.¶

The photoreactions of E-1 were examined in acetonitrile containing various concentrations of TEA, and the results are summarized in Table 1. In the high concentration range (30–40



Table 1 Irradiation of E-1 (0.0564 mol dm⁻³) in the presence of varying TEA concentrations

	Et ₃ N/mol dm ⁻³ (equiv.)	Conversion (%)	Yield	μ	
			Z-1	2a	3
	0.282(5)	80	10	8	20 ⁶
	0.564(10)	89	4	18	19 ^b
	1.13 (20)	87	4	30	21 ^b
	1.69 (30)	95	1	45	13 ^b
	2.26 (40)	89	2	45	10^{b}
	neat	51	6	26	13 ^c

^a Yields based on converted starting material, determined by ¹H NMR analysis using bis(trimethylsilyl)acetylene as internal standard, after stirring the reaction mixture with SiO₂ in CHCl₃ for 2 h. ^b Solutions irradiated for 1.5 h in acetonitrile. ^c Solution irradiated for 1.5 h in TEA as solvent.

 Table 2 Preparative photochemical reactions of 1 in the presence of 30 equiv. tertiary amines in acetonitrile



 Amine	Conversion (%)	Products [Yields (%)]"
EtNMe ₂ Et ₂ NMe Pr ₃ N	91 94 76	2a [11], 2b [19], 3 [19] 2a [22], 2b [13], 3 [20] 2c [12], 3 [28]
-N	81	2b [2], 3 [20]
 -N	74	2b [5], 3 [4]

^a Isolated yields after SiO₂ flash-chromatography.

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equiv.) of TEA the yield of **2a** was increased. Furthermore, **1** was irradiated in the presence of 30 equiv. of other tertiary amines (*N*,*N*-dimethylethylamine, *N*-methyldiethylamine, tripropylamine, 1-methylpyrrolidine and 1-methylpiperidine) in acetonitrile, and the results are summarized in Table 2. The *N*-methyl and *N*-ethyl substituents show nearly the same reactivity for the addition reaction. However, addition of the α -carbon atom in cyclic amine to the nitrile **1** was not observed. The reactions of **1** with secondary and primary amines were also performed under the same conditions and gave no α -adduct.

A probable reaction mechanism for the formation of α -alkylidenenitriles and acetonitriles may be rationalized in terms of a single electron transfer from tertiary amines to the excited epoxynitriles. The resulting ion-radical intermediates (*e.g.* **A**) are transformed to the reduced compound (*e.g.* **3**) and the adducts (*e.g.* **4**) via biradical intermediates (*e.g.* **B**), in a manner similar to the reaction of enones and tertiary amines,² followed by acid-catalysed retro-Michael reaction leading to α -alkylidenenitriles **2**.

The present work has demonstrated that the photoreactions of α,β -unsaturated γ,δ -epoxy nitriles 1 and 5 with tertiary amines afforded the novel 1:1 α -adducts between nitriles and amines.

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Footnotes

[†] Yields of photoreactions throughout the paper are based on converted starting material.

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‡ All new compounds exhibited IR, NMR and mass spectra which were consistent with the assigned structures, and gave satisfactory elemental analyses or high-resolution mass spectra. Selected NMR data: for **2a**: δ_H (CDCl₃, 270 MHz) 2.12 (3H, d), 6.09 (1H, br s) and 6.46 (1H, q); δ_C 17.5 (q), 69.1, 115.7, 119.0, 130.8 (4s), 132.5 and 139.3 (2d). For **3**: δ_H 3.04 (2H, br s) and 5.72 (1H, d); δ_C 25.7 (t), 69.1, 127.7 (2s) and 131.1 (d). For **6**: δ_H 1.19 (3H, d), 6.35 (1H, s) and 65.9 (s). For *E*-7: δ_H 3.32 (2H, d) and 5.86 (1H, t); δ_C 73.8 (s) and 112.6 (d). For **Z**-**8**: δ_H 3.49 (1H, dd), 3.71 (1H, dd) and 5.43 (1H, t); δ_C 74.2 (s) and 113.6 (d).

§ The characteristic signals for 4 were observed in the ^{13}C NMR spectrum at δ_C 43–47 (d) and 55–56 (d) due to C-CN and C-NEt_2, respectively.

¶ The photochemical reaction of 5 in acetonitrile with 1 equiv. of TEA gave the products formed by a $C(\gamma)$, $C(\delta)$ -bond cleavage.⁴ However, on reaction in high concentration of TEA, 5 undergoes a $C(\gamma)$, Orather than a $C(\gamma)$, $C(\delta)$ -bond cleavage leading to 6–9. Both processes may occur competitively after single electron transfer from TEA to excited 5 and depend on the concentration of TEA.

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