

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

Keitaro Ishii,* Masashi Kotera and Masanori Sakamoto

Meiji College of Pharmacy, 1-35-23 Nozawa, Setagaya-ku, Tokyo 154, Japan

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 **1** 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).

Epoxy nitrile **E-1** was irradiated (in TEA as solvent) with a low-pressure mercury lamp through a quartz filter at room temperature (51% conversion) yielding \dagger **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

chromatography as a mixture of four stereoisomers.[§] Under the same reaction conditions (in TEA as solvent) nitrile **5**[§] (80% conversion) afforded lactone **6** (10%), **7** (6%), *E-8* (5%), *Z-8* (15%), and **9**[§] (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

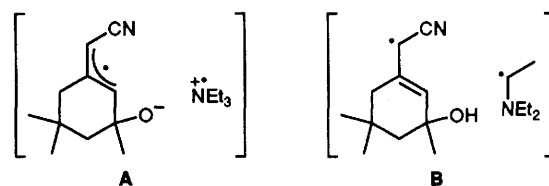
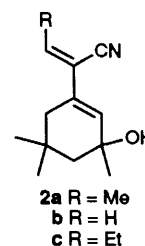


Table 1 Irradiation of *E-1* (0.0564 mol dm⁻³) in the presence of varying TEA concentrations

Et ₃ N/mol dm ⁻³ (equiv.)	Conversion (%)	Yields (%) ^a		
		Z-1	2a	3
0.282 (5)	80	10	8	20 ^b
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

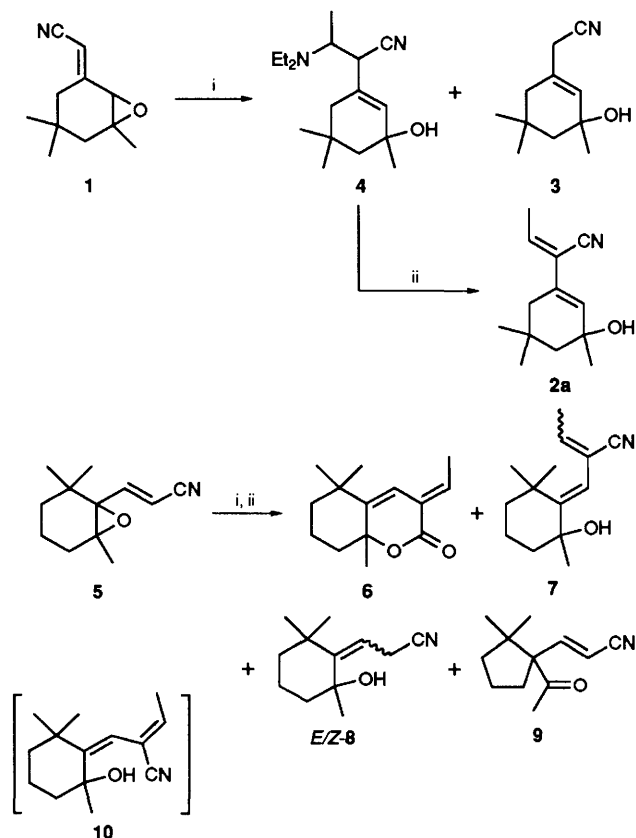
^a Yields based on converted starting material, determined by ¹H NMR analysis using bis(trimethylsilyl)acetylene as internal standard, after stirring the reaction mixture with SiO₂ in CHCl₃ for 2 h. ^b Solutions irradiated for 1.5 h in acetonitrile. ^c Solution irradiated for 1.5 h in TEA as solvent.

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



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

^a Isolated yields after SiO₂ flash-chromatography.



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

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 epoxy nitriles. 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.

Received, 21st July 1994; Com. 4/04467C

Footnotes

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

‡ 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 6.91 (1H, qd); δ_{C} 13.8 (q), 83.7 (s), 114.0 (d), 124.1 (s), 135.5 (d), 149.3 (s) and 165.9 (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 ¹³C NMR spectrum at δ_{C} 43–47 (d) and 55–56 (d) due to C-CN and C-NEt₂, respectively.

¶ The photochemical reaction of **5** in acetonitrile with 1 equiv. of TEA gave the products formed by a C(γ), C(δ)-bond cleavage.⁴ However, on reaction in high concentration of TEA, **5** undergoes a C(γ), O- rather than a C(γ), C(δ)-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.

References

- 1 R. C. Cookson, J. Hudec and N. A. Mirza, *J. Chem. Soc., Chem. Commun.*, 1968, 180.
- 2 N. J. Pienta and J. E. McKimmey, *J. Am. Chem. Soc.*, 1982, **104**, 5501; D. W. Smith and N. J. Pienta, *Tetrahedron Lett.*, 1984, **25**, 915; N. J. Pienta, *J. Am. Chem. Soc.*, 1984, **106**, 2704.
- 3 Y. T. Jeon, C.-P. Lee and P. S. Mariano, *J. Am. Chem. Soc.*, 1991, **113**, 8847; U. C. Yoon and P. S. Mariano, *Acc. Chem. Res.*, 1992, **25**, 233.
- 4 K. Ishii, D. Gong, R. Asai and M. Sakamoto, *J. Chem. Soc., Perkin Trans. 1*, 1990, 855.
- 5 K. Ishii, M. Abe and M. Sakamoto, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1937.