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Novel photoadditions of tertiary amines to the α-position of α,β-unsaturated γ,δ-epoxy nitriles

Keitaro Ishii,* Satoshi Hakamada, Mayumi Nagano, Masahiro Noji, Shigeo Sugiyama, Masashi Kotera and Masanori Sakamoto

Meiji Pharmaceutical University, 2-522-1 Noshio, Kiyose-shi, Tokyo 204-8588, Japan.
E-mail: ishiikei@my-pharm.ac.jp; Fax: +81 (0)424 958783; Tel: +81 (0)424 958783

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The photoreactions of α,β-unsaturated γ,δ-epoxy nitriles **1**, **2**, **13** and **16** with triethylamine give rise to novel 1 : 1 α-adducts (*e.g.*, **5**) efficiently. After treatment with silica gel, the adducts undergo retro-Michael reaction leading to the corresponding α-alkylidenenitrile derivatives (*e.g.*, **3**). The epoxy nitrile **1** also reacts with various tertiary amines to afford α-adducts. The reaction of **1** and the silylamine **24** gives mainly methylene derivative **22** and silylated compound **25** after treatment with silica gel. The reaction may proceed *via* single- electron-transfer from the amine to the excited epoxy nitrile.

Introduction

Photoinduced electron-transfer reactions have received considerable interest recently in the discovery of new and synthetically useful chemical reactions.[1] For example, the photoadditions of tertiary amines to α,β-unsaturated ketones and esters have been reported to afford 1 : 1 β -adducts between carbonyl compounds and amines and reduced compounds.[2] Mariano *et al.* conducted intensive studies on the photoaddition using α-trimethylsilylamine and on synthetic applications of the photoaddition to *N*-heterocyclic compounds.[3,4]

In a previous communication,[5] we have shown that direct irradiation of α,β-unsaturated γ,δ-epoxy nitrile **1**[6] with triethylamine (TEA) undergoes novel 1 : 1 α-addition and subsequent retro-Michael reaction leading to α-alkylidenenitrile **3**. Similarly, the reaction of **2**[7] gives lactone **6** and α-alkylidenenitrile **7** (Scheme 1). In this paper we describe the details of the photoreactions of the epoxy nitriles **1** and **2** with TEA, reactions of **1** with various tertiary amines, and studies on the scope and limitation of the addition for epoxy compounds. Furthermore, the addition of [(trimethylsilyl)-methyl]diethylamine (TMSA) **24** to the epoxy nitrile **1** is also investigated.

Results and discussion

Photoadditions of epoxy nitriles with TEA

Preparative irradiation of nitrile 1 in TEA. The nitrile (*E*)-**1** was irradiated in TEA with a low-pressure mercury lamp through a quartz filter (λ = 254 nm) at RT (conversion 51%) and subsequent silica gel column chromatography yielded (*Z*)-**1** (6%), α-alkylidenenitrile **3** (26%) and reduced compound **4** (13%) (Scheme 1).† The structure of product **3** was deduced from the H–H and C–H COSY, phase-sensitive NOESY, and HMBC spectra. In the HMBC spectrum of **3**, the crosspeaks between H-3 and C(2) (^2J), between H-3 and C(1) (^3J) and between H-4 and C(2) (^3J) are observed. The appearance of the crosspeak between H-3 and H-6′ in the NOESY spectrum indicates *Z* orientation at the C(2) double bond.

The characteristic signals of **3** could not be observed in the ^{1}H NMR spectrum of the crude photoproduct of **1**. The TEA-adduct **5** was separated after basic aluminium oxide chromatography as a mixture of four diastereomers, which were treated with silica gel leading to **3** quantitatively. The result

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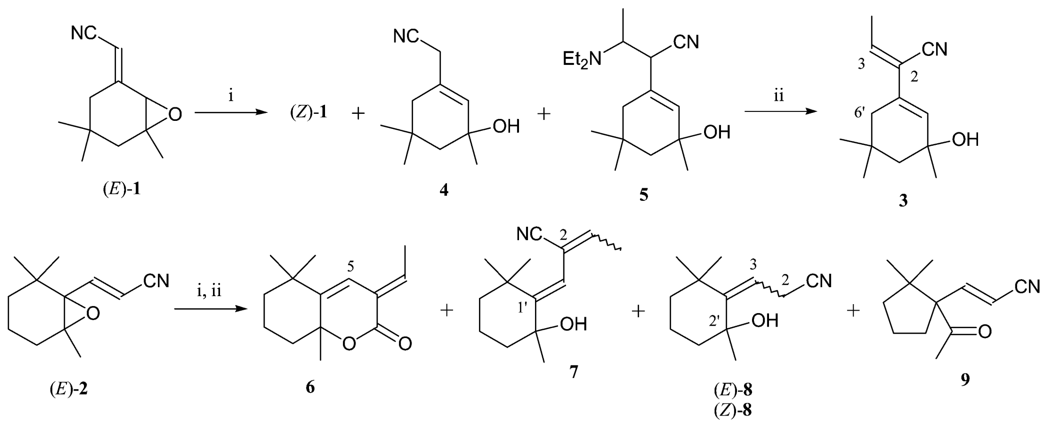
† Yields for compounds throughout the rest of the paper are based on converted starting material.



Scheme 1 *Reagents and conditions*: i, λ = 254 nm, Et_3N, RT; ii, silica gel.

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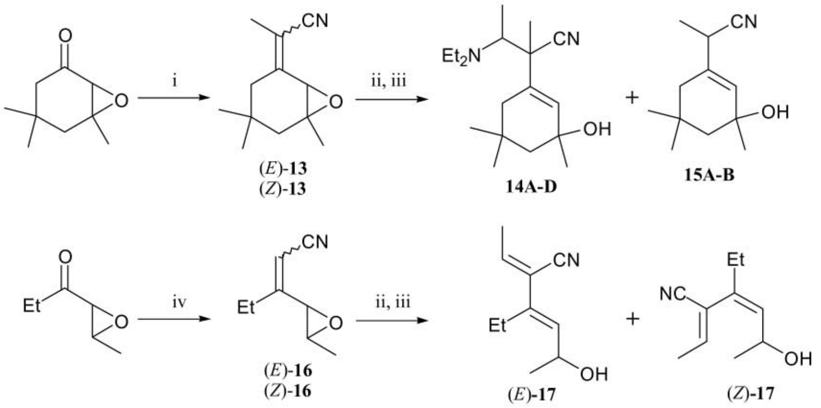

Scheme 2 *Reagents and conditions*: i, $(EtO)_2P(O)CH(Me)CN$, NaH, DMF; ii, λ = 254 nm, Et_3N, MeCN, RT; iii, silica gel; iv, $(EtO)_2P(O)CH_2CN$, NaH, DMF.

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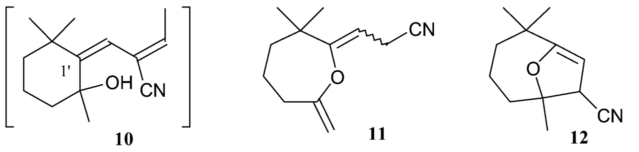
shows that **5** is transformed by acid-catalyzed retro-Michael reaction to the α-alkylidenenitrile **3**.

Preparative irradiation of nitrile 13 with TEA. As the TEA-adduct **5** could not be separated in pure form, we attempted to obtain the TEA-adduct **14**, stable to silica gel. The epoxy nitrile **13** was prepared from isophorone oxide in 85% yield ($E : Z \approx 2 : 3$) by the Horner–Emmons reaction. Preparative irradiation of **13** and TEA (30 equiv.) in acetonitrile with a low-pressure mercury lamp through a quartz filter (λ = 254 nm) at RT (conversion 65%) gave four adducts **14A–D** (20%) and two reduced compounds **15A–B** (16%) (Scheme 2).† One of the adducts **14A** was separated in *ca.* 80% purity and the structure was assured by its spectral data (see Experimental section).

Preparative irradiation of nitrile 2 in TEA. The nitrile (E)-**2** was irradiated in TEA with a low-pressure mercury lamp through a quartz filter (λ = 254 nm) at RT (conversion 80%) and subsequent silica gel chromatography afforded lactone **6** (10%), α-alkylidenenitrile **7** (6%), reduced compounds (E)-**8** (5%) and (Z)-**8** (15%) and ketone **9**[7] (6%) (Scheme 1).†

The structures of **6**–**8** were determined on the basis of spectral data. In particular, the ^{13}C NMR spectrum of **6** shows a characteristic signal at δ_C 165.9 due to the δ-lactone moiety, which is also evidenced by the IR band at 1720 cm^{-1}. As characteristic signals for the ethylidene moiety of **6**, the ^1H NMR spectrum shows a doublet at δ 1.91 and a quartet-doublet at δ 6.91, the ^{13}C NMR spectrum has a quartet at δ_C 13.8 and a doublet at δ_C 135.5. Furthermore, the (E/Z)-configuration at the ethylidene moiety was established by the significant NOE enhancement (6.9%) between 5-H and Me in the ethylidene group. The lactone **6** was presumably formed by cyclization of α-alkylidenenitrile **10** (Fig. 1) possessing the (Z)-configuration of the exocyclic double bond at C(1′) and by subsequent hydrolysis with silica gel.



10 **11** **12**

Fig. 1

Compound **7** could not be isolated in pure form, but the structure could be presumed by the spectral data of a 1 : 4 mixture of **7** and (Z)-**8**. The ^1H NMR spectrum of **7** shows a double doublet at δ 2.03 and a quartet-doublet at δ 6.23; the ^{13}C NMR spectrum has a quartet at δ_C 17.0 and a doublet at δ_C 143.2 due to the ethylidene moiety and two singlets at δ_C 115.5 and 118.2 due to C(1) and C(2). After treatment of **7** with silica gel, the formation of lactone **6** was not observed. Therefore, the (E/Z)-configuration of the exocyclic double bond at C(1′) should be E. However, the (E/Z)-configuration at C(2) for **7** could not be determined.

The (E/Z)-configuration of **8** was deduced from the chemical shift for 2-H_2 and 3-H in the ^1H NMR spectrum; the signals for 2-H_2 (δ 3.49 and 3.71) for (Z)-**8** and for 3-H (δ 5.86) for (E)-**8** appear at lower field than those for (E)-**8** (δ 3.32) and for (Z)-**8** (δ 5.43), respectively, due to the deshielding effects of the hydroxy group at C(2′).

The mechanism for the formation of the ketone **9** in TEA solution is not yet clear, because **9** has been afforded by triplet sensitization reaction of **2** in earlier studies.[6,7]

We could not isolate the nitriles **11** and **12** (Fig. 1), which are mainly formed in the photoreaction of **2** in the presence of TEA (1 equiv.) in acetonitrile.[6] In the case of the photoreaction of **2** in TEA solution, the formation of **11** and **12** is suppressed because the SET process from TEA to the excited state **2*** occurs (presumably) faster than the C(γ)–C(δ) bond cleavage.

Preparative irradiation of nitrile 16 with TEA. The nitrile **16** was prepared from *trans*-4,5-epoxyhexan-3-one in 49% yield ($E : Z \approx 9 : 2$) by the Horner–Emmons reaction. A solution of the nitrile **16** ($E : Z \approx 3 : 2$) and TEA (30 equiv.) in acetonitrile was irradiated with a low-pressure mercury lamp through a quartz filter (λ = 254 nm) at RT (conversion 92%) and subsequent silica gel column chromatography yielded α-alkylidenenitriles (E)-**17** (14%) and (Z)-**17** (12%).† The reduced compound could not be observed.

The (E/Z)-configuration at C-3 for **17** was deduced from the chemical shift for 3-CH_2CH_3 in the ^{13}C NMR spectrum; the signal (δ_C 20.7) for (E)-**17** appears at lower field than that for (Z)-**17** (δ_C 29.4) due to the steric interactions between 3-Et and 4-CH(OH)Me. Furthermore, the (E/Z)-configuration at C-3 was established by the significant NOE enhancements between 3-CH_2CH_3 and 5-H (8.5%) for (E)-**17** and between 3-CH_2CH_3 and 4-H (3.5%) for (Z)-**17**. The (Z)-configuration at the ethylidene moiety was determined also by the significant NOE enhancements between 3-CH_2CH_3 and 2-CH in the ethylidene group (6.6%) for (E)-**17** and between 5-H and 2-CH (2.2%) for Z-**17**.

In the order to test the viability of the reaction, epoxy ketones **18**[8] and **19**‡ and epoxy nitrile **20**[10] (Fig. 2) were irradiated in the presence of TEA (30 equiv.) under the same reaction conditions. However, the TEA-adduct or α-alkylidenenitrile derivative could not be obtained.

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‡ The irradiations of α,β-epoxy ketones in acetonitrile in the presence of 5 equiv. of Et_3N afford the corresponding β-hydroxy ketones.[9]

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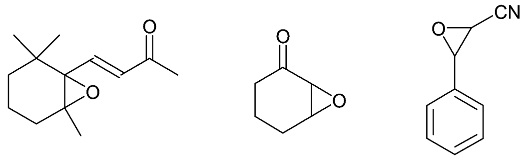
Table 1 Analytical irradiations of **1** with TEA[a]

Entry	Concentration of TEA (mol dm^{-3}) [equiv.]	Solvent	Conversion (%)	Yields (%)†[b] **3**	Yields (%)†[b] **4**
1	0.056 [1]	MeCN	56	trace	5 ⟨6⟩[c]
2	0.282 [5]	MeCN	72	8	23 ⟨3⟩
3	0.564 [10]	MeCN	85	19	20
4	1.13 [20]	MeCN	84	31	22
5	1.69 [30]	MeCN	95	45	14
6	2.26 [40]	MeCN	87	46	10
7	neat	—	49	27	14
8[de]	0.564 [10]	MeCN	99	43	7
9[d]	1.69 [30]	PrCN	51	36	12
10[d]	1.69 [30]	Hexane	36	22	6

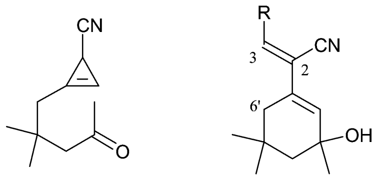
[a] A 0.0564 mol dm^{-3} solution of **1** (E/Z = 2 : 1) in solvent was irradiated for 1.5 h at RT. [b] The yields were determined by ^{1}H NMR analysis using bis(trimethylsilyl)acetylene as internal standard, after stirring of the reaction mixture with silica gel in $CHCl_3$ for 2 h at RT. [c] Values in angle brackets are yields the of cyclopropene **21**. [d] Irradiation for 1 h. [e] With 5 equiv. of Pr^iNH_2.



18 **19** **20**

Fig. 2

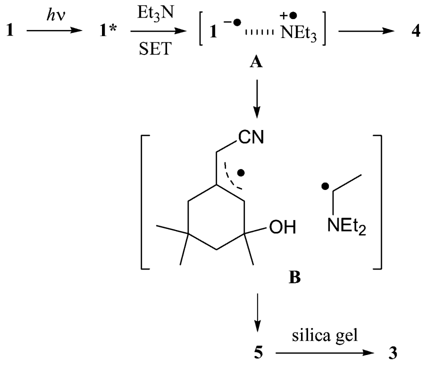
Analytical irradiations of 1 with TEA. Photoreactions of nitrile **1** ($E/Z = 2 : 1$) in acetonitrile containing varying amounts of TEA (1, 5, 10, 20, 30 and 40 equiv.) or in TEA were performed, and results are shown in Table 1. The yield of **3** increased with increasing TEA concentration up to 40 equiv. In the low concentration range of TEA (entries 1 and 2) the cyclopropene **21**[6] (Fig. 3) was also formed. For the formation of **3** a high concentration of TEA is required. The results may suggest that TEA functions partially as a base in the reaction. Thus, isopropylamine (5 equiv.), possessing low electron donating character, was added to the solution of **1** and TEA (10 equiv.) in acetonitrile and the solution was irradiated. The yield of **3** (43%†; entry 8) was similar to that for the reaction using 30 equiv. of TEA (Entry 5). As the polarity of solvent decreases, the conversion and the yield of **3** decrease (entries 5, 9 and 10). These results may indicate that a single-electron transfer (SET) from TEA to the excited epoxy nitrile **1*** occurs (Scheme 3). The resulting ion-radical intermediates (*e.g.*, **A**) are transformed into the reduced compound **4** and the adduct **5** *via* biradical intermediates (*e.g.*, **B**) in a manner similar to the reaction of enones and tertiary amines.[2] Direct irradiation of α,β-unsaturated γ,δ-epoxy nitriles and ketones (*e.g.*, **2** and **18**) (λ = 254 nm) in acetonitrile gave mainly the C(γ)–C(δ) bond-cleaved products (*e.g.*, **12**) and the cyclopropene (*e.g.*, **21**) *via* the carbene intermediate.[7,8] Therefore, in the low concentration range of TEA these compounds are formed faster than are the SET products (*e.g.*, **4** and **5**).



21 **22** R=H **23** R=Et

Fig. 3

Photoadditions of nitrile 1 with various amines



Scheme 3

The results of the photoreactions of the nitriles **1**, **2** and **16** with TEA prompted us to investigate the reactions of nitrile **1** and other amines. The nitrile **1** was irradiated in the presence of 30 equiv. of tertiary amines (dimethylethylamine, methyldiethyl amine, tripropylamine, ethyldiisopropylamine, diethylethanolamine, 1-methylpyrrolidine, 1-methylpiperidine, tetramethylmethanediamine and tetramethylethylenediamine), and the results are summarized in Table 2. The reactivity for the addition reaction decreases in the order *N*–Me ≈ *N*–Et > *N*–Pr > *N*–Pr^i substituents owing (presumably) to the steric hindrance of the α-carbon atom (entries 1–4). The α-carbon atom in cyclic amines and in diamines has no reactivity (entries 6–9). Furthermore, the reactions of **1** with a secondary amine (diethylamine) and a primary amine (butylamine) were also performed under the same reaction conditions. However, the corresponding adducts could not be observed.

The structures of the α-alkylidenenitriles **22** and **23** (Fig. 3) were determined on the basis of their spectral data. In particular, the (*Z*)-orientation at the C(2) double bond in **23** was determined by comparison of the ^{1}H NMR chemical shifts of H-3 (δ 6.38) and H_2-6′ (δ 1.86 and 2.00) with those of **3** (δ 6.46 for H-3 and δ 1.87 and 1.98 for H_2-6′).

Photoaddition of nitrile 1 with TMSA 24

Preparative irradiation. Since the reactions of the nitrile **1** and tertiary amine had given the α -adducts in moderate yields, the photoreaction of **1** and TMSA **24**,[11] which is known as a stronger electron donor than TEA,§ was investigated. A solution of the nitrile **1** ($E : Z = 2 : 1$) and **24** (10 equiv.) in acetonitrile was irradiated with a low-pressure mercury lamp through a quartz filter (λ = 254 nm) at RT (conversion 100%) and subsequent silica gel column chromatography yielded **3** (6%), **4** (23%), **22** (12%) and silylated compound **25** (21%) (Scheme 4).†

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§ Oxidation potentials of TMSA **24** and TEA are 0.57 V and 0.89 V *vs.* SCE, respectively.[12]

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Table 2 Irradiations of **1** with various tertiary amines[a]

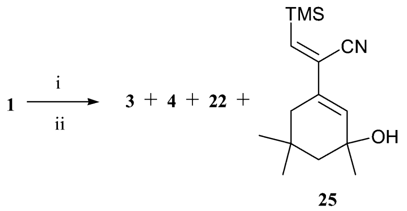
Entry	Amine	Irradiation Time (h)	Conversion (%)	Yields (%)† [b]			
				3	**22**	**23**	**4**
1	$EtNMe_2$	4.5	91	11	19	—	19
2	Et_2NMe	5	94	22	13	—	20
3	Pr_3N	3	76	—	—	12	28
4	Pr^i_2NEt	5	69	28	—	—	17
5	$Et_2N(CH_2)_2OH$	6.5	89	41	—	—	10
6	1-Methylpyrrolidine	3.5	81	—	2	—	20
7	1-Methylpiperidine	7	74	—	5	—	4
8	$Me_2NCH_2NMe_2$	2.5	90	—	1	—	16
9	$Me_2N(CH_2)_2NMe_2$	2.5	100	—	8	—	22

[a] A 0.0564 mol dm^{-3} solution of **1** (*E*/*Z* = 2 : 1) in acetonitrile was irradiated (λ = 254 nm) with 30 equiv. of amine at RT. [b] Isolated yields after silica gel flash-chromatography.

Table 3 Irradiations of **1** with various concentrations of TMSA **24** in various solvents[a]

Entry	Concentration of TMSA (mol dm^{-3}) [equiv.]	Solvent	Conversion (%)	Yields (%)† [b]			
				3	**22**	**25**	**4**
1	−0.175 [5]	MeCN	41	3	7	10	8
2	0.350 [10]	MeCN	58	5	9	19	11
3	0.525 [15]	MeCN	51	8	10	20	8
4	−1.05 [30]	MeCN	53	4	6	12	5
5	0.350 [10]	0.1%MeOH–MeCN	60	8	13	19	7
6	0.350 [10]	0.7%MeOH–MeCN	89	5	11	11	8
7	0.350 [10]	1.4%MeOH–MeCN	81	5	11	10	7
8	0.350 [10]	10%MeOH–MeCN	74	4	8	1	6

[a] A 0.035 mol dm^{-3} solution of **1** (*E*/*Z* = 2 : 1) was irradiated (λ = 254 nm) for 0.5 h at RT. [b] The yields were determined by GLC analysis using octadecane as an internal standard, after stirring of the reaction mixture with silica gel in $CHCl_3$ for 2 h at RT.



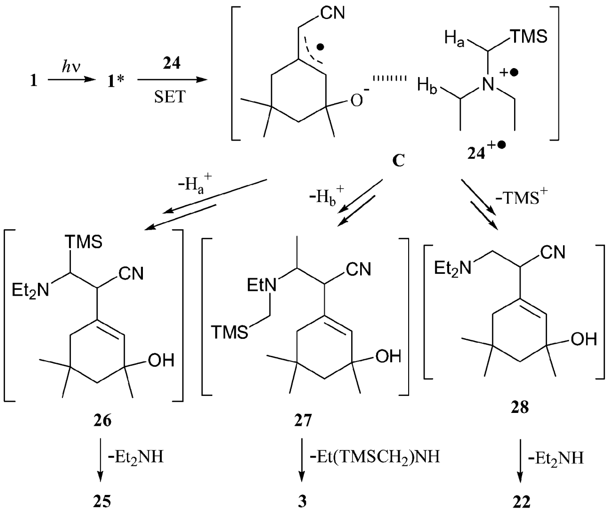
Scheme 4 *Reagents and conditions* : i, λ = 254 nm, Et_2NCH_2TMS **24**, MeCN, RT; ii, silica gel, $CHCl_3$, RT.

The structure of product **25** was determined on the basis of its spectral data. In particular, the (*Z*)-orientation at the C(2) double bond was determined by comparison of the ^1H NMR chemical shifts of H-3 (δ 6.57) and H_2-6′ (δ 1.85 and 2.03) with those of **3**.

We also confirmed the reaction of epoxy ketones **18**[8] and **19** and epoxy nitrile **20**[10] (Fig. 2) in the presence of 10 equiv. of TMSA **24** under the same reaction conditions. However, the TMSA-adducts could not be detected.

Analytical irradiations

Photoreactions of nitrile **1** (*E*/*Z* = 2 : 1) in acetonitrile containing varying amounts of TMSA **24** (5, 10, 15 and 30 equiv.) (entries 1–4) and containing MeOH and **24** (entries 5–8) were performed, and results are shown in Table 3. The yield of **3**, **22** and **25** increased with increasing TMSA **24** concentration up to 0.525 mol dm^{-3}. The yield of **25** decreased with increasing MeOH concentration. The probable reaction mechanism for the formation of α-alkylidenenitriles **3**, **22** and **25** outlined in Scheme 5 appears to rationalize these results. SET between the excited nitrile **1*** and TMSA **24** results in generation of the radical-ion-pair (*e.g.*, **C**). The resulting cation radical $24^{+\bullet}$ undergoes α-deprotonation (H_a^+ and H_b^+) and nucleophile-assisted desilylation[4] leading to the adducts **26** and **27** and **28**, respectively. Finally, retro-Michael reaction gives the respective olefins **25**, **3** and **22**. Compound **25** is preferentially formed in less polar aprotic solvents rather than in polar protic solvents. The results may show that the deprotonation of H_a^+ in **C** occurs favorably in a solvent cage (contact-ion-pair).[4]



Scheme 5

In conclusion, the photoreactions of α,β-unsaturated γ,δ-epoxy nitriles **1**, **2**, **13** and **16** with TEA afford novel 1 : 1 α-adducts between the nitriles and TEA, and subsequent retro-Michael reaction gives α-alkylidenenitriles (*e.g.*, **3**). The nitrile **1** also reacts with various tertiary amines and TMSA **24**. The reaction is peculiar to α,β-unsaturated γ,δ-epoxy nitriles and may proceed *via* SET from the amine to the excited nitrile.

Experimental

Mps and bps are uncorrected. Mps were measured with a Yanaco MP-3 apparatus and bps were measured with a Büchi

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Kugel Rohr GKR-50 apparatus. UV spectra were recorded on a Hitachi 124 spectrometer and IR spectra on a Hitachi 215 spectrometer. NMR spectra were obtained with a JEOL JNM-EX270 (270 MHz; EX) or a JEOL JNM-GX400 (400 MHz; GX) spectrometer for samples in $CDCl_3$ solution using tetramethylsilane as internal standard, and *J*-values are given in Hz. Mass spectra (MS) and high-resolution MS (HRMS) were taken on a JEOL JMS-DX302 spectrometer. GLC was carried out on a Shimadzu GC-14A instrument (flame ionization detection) and a 30 m × 0.25 mm column of Rascot OV-1 was used. Column chromatography was performed with Nacalai silica gel 60 [230–400 mesh (SiO_2)] or Merck aluminium oxide 90(basic) [70–230 mesh, activity III (Al_2O_3)].

An Eikosha 60 W low-pressure mercury lamp was used for irradiation. The photolysis solutions were purged with argon both before and during irradiation.

Photoadditions of nitriles with triethylamine (TEA)

Preparative irradiation of nitrile 1 in TEA. A solution of (*E*)-**1**[6] (700 mg, 3.99 mmol) in TEA (70 cm^3) was irradiated with a low-pressure mercury lamp in a quartz test tube (conversion 51%) for 7 h at RT. After removal of the solvent, flash chromatography [SiO_2; hexane–ethyl acetate (4 : 1)] of the residue afforded (*Z*)-**1**[6] (21.7 mg, 6%), α-alkylidenenitrile **3** (110 mg, 26%) and the alcohol **4** (48.2 mg, 13%).†

2-(3-Hydroxy-3,5,5-trimethylcyclohex-1-enyl)isocrotononitrile **3**, bp 130 °C at 0.22 mmHg (Found: M^+, 205.1468. $C_{13}H_{19}NO$ requires *M*, 205.1466); λ_{max} (EtOH)/nm 245 (ε/dm^3 mol^{-1} cm^{-1} 5000); ν_{max} (film)/cm^{-1} 3420 (O–H) and 2190 ($C\equiv N$); δ_H (EX) 1.02 and 1.05 (6 H, 2 s, 2 × 5′ CH_3), 1.34 (3 H, s, 3′-CH_3), 1.56 (1 H, d, *J* 14.2, 4′-H), 1.72 (1 H, dd, *J* 14.2 and 1.0, 4′-H), 1.72–1.82 (1 H, br s, OH), 1.87 and 1.98 (2 H, each d, *J* 16.5, 6′-H_2), 2.12 (3 H, d, *J* 7.3, 4-H_3), 6.09 (1 H, br s, 2′-H) and 6.46 (1 H, q, *J* 7.3, 3-H); δ_C (EX) 17.5 (q, C-4), 27.8 and 30.8 (2 q, 2 × 5′-CH_3), 30.1 (s, C-5′), 31.2 (q, 3′-CH_3), 38.8 (t, C-6′), 50.0 (t, C-4′), 69.1 (s, C-3′), 115.7 (s, C-1), 119.0 (s, C-2), 130.8 (s, C-1′), 132.5 (d, C-2′) and 139.9 (d, C-3); *m*/*z* 205 (M^+, 25%), 190 (100), 163 (17), 148 (19), 139 (17), 134 (11) and 120 (13).

(3-Hydroxy-3,5,5-trimethylcyclohex-1-enyl)acetonitrile **4**, bp 110 °C at 0.3 mmHg (Found: M^+, 179.1333. $C_{11}H_{17}NO$ requires *M*, 179.1311); ν_{max} (film)/cm^{-1} 3420 (O–H) and 2240 ($C\equiv N$); δ_H (EX) 1.00 and 1.06 (6 H, 2 s, 2 × 5′-CH_3), 1.30 (3 H, s, 3′-CH_3), 1.53 and 1.68 (2 H, each d, *J* 14.2, 4′-H_2), 1.65–1.75 (1 H, br s,OH), 1.76–1.90 (2 H, m, 6′-H_2), 3.04 (2 H, br s, 2-H_2) and 5.72 (1 H, d, *J* 1.0, 2′-H); δ_C (EX) 25. 7 (t, C-2), 27.7, 30.7 and 31.1 (3 q, 2 × 5′-CH_3 and 3′-CH_3), 30.4 (s, C-5′), 42.1 (t, C-6′), 49.6 (t, C-4′), 69.1 (s, C-3′), 117.7 (s, C-1), 127.7 (s, C-1′), and 131.1 (d, C-2′); *m*/*z* 179 (M^+, 3%), 164 (100), 139 (36), 123 (27), 100 (20) and 43 (28).

Isolation of TEA-adduct 5. A solution of **1** (1.16 g, 6.56 mmol) in TEA (116 cm_3) was irradiated with a low-pressure mercury lamp in a quartz test-tube (conversion 61%) for 8 h at RT. After removal of the solvent, chromatography [Al_2O_3; hexane–ethyl acetate (2 : 1)] of the residue gave a mixture of four stereoisomers of compound **5** (635 mg, 57%).†

3-(Diethylamino)-2-(3-hydroxy-3,5,5-trimethylcyclohex-1-enyl)butyronitrile **5**, an oil (Found: M^+, 278.2377. $C_{17}H_{30}N_2O$ requires *M*, 278.2358); ν_{max} (film)/cm^{-1} 3410 (O–H) and 2230 ($C\equiv N$); δ_H (EX) *inter alia* 2.33–2.67 (4 H, m, 2 × NC*H*$_2$), 3.01–3.27 (2 H, m, 2- and 3-H) and 5.59 and 5.65 (1 H, 2 br s, 2′-H); δ_C (EX) *inter alia* 39.6, 39.7, 40.2 and 40.6 (4 t, C-6′), 43.4, 43.5, 46.3 and 46.6 (4 d, C-2), 55.18, 55.22 and 55.5 (3 d, C-3), 69.1 and 69.2 (2 s, C-3′), 119.96 and 120.03 (2 s, C-1), 131.3, 131.4, 131.89 and 131.95 (4 s, C-1′) and 131.8, 133.0 and 133.1 (3 d, C-2′).

Transformation of 5 into 3. A solution of **5** (51.9 mg, 0.187 mmol) in chloroform (10 cm^3) was stirred in the presence of SiO_2 (1.0 g) for 2 h at RT. After filtration, ^1H NMR analysis of the reaction mixture showed that **5** was converted to α-alkylidenenitrile **3** quantitatively.

Preparation of nitrile 13. Diethyl (1-cyanoethyl)phosphonate (7.64 g, 40.0 mmol) was added dropwise to a suspension of 60% NaH (1.60 g, 40.0 mmol) in dry DMF (56 cm^3) at RT. After stirring of the mixture for 20 min at RT, isophorone oxide (5.53 g, 35.9 mmol) was added dropwise and stirring was continued at −50 °C for 20 min and for 30 min at RT; ice–water (53 cm^3) was then added to the mixture, and the organic phase was extracted with diethyl ether. The continued extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*, giving a residue, which was subjected to flash chromatography [SiO_2; hexane–ethyl acetate (9 : 1)] to afford the nitriles (*E*)-**13** (2.18 g, 32%) and (*Z*)-**13** (3.65 g, 53%).

(*E*)-2-[4,4,6-Trimethyl-7-oxabicyclo[4.1.0]heptan-2-ylidene] propiononitrile (*E*)-**13**, bp 85 °C at 0.25 mmHg (Found : C, 75.22; H, 8.99; N, 7.31. $C_{12}H_{17}NO$ requires C, 75.35; H, 8.96; N, 7.32%); ν_{max} (film)/cm^{-1} 2210 ($C\equiv N$); δ_H (EX) 0.83, 0.97 and 1.39 (9 H, 3 s, 2 × 4′-CH_3 and 6′-CH_3), 1.58 (1 H, dd, *J* 15 and 1, 1- or 5′- H), 1.87 (1 H, d, *J* 15.2, 5′-H), 2.08–2.10 (3 H, m with t character, *J* 1, 3-H_3), 2.24–2.26 (2 H, m, 3′-H_2) and 3.50 (1 H, s, 5′- or 1′- 1′-H); δ_C (EX) 15.4, 24.7, 27.2 and 30.2 (4 q, 4 × CH_3), 32.3 (s, C-4′), 41.1 and 42.9 (2 t, C-3′ and C-5′), 56.8 (d, C-1′), 61.8 (s, C-6′), 108.3 (s, C-2), 119.0 (s, C-1) and 151.8 (s, C-2′); *m*/*z* 191 (M^+, 100%), 176 (57), 148 (36), 135 (68), 118 (24), 107 (31) and 91 (21).

(*Z*)-2-[4,4,6-Trimethyl-7-oxabicyclo[4.1.0]heptan-2-ylidene] propiononitrile (*Z*)-**13**, bp 140 °C at 0.9 mmHg (Found : M^+, 191.1312. $C_{12}H_{17}NO$ requires *M*, 191.1310); ν_{max} (film)/cm^{-1} 2210 ($C\equiv N$); δ_H (EX) 0.79, 0.98 and 1.40 (9 H, 3 s,2 × 4′-CH_3 and 6′-CH_3), 1.58 (1 H, d, *J* 15, 5′-H), 1.88 (1 H, d, *J* 15, 5′-H), 1.97 (3 H, s, 3-H_3), 2.03 (2 H, br s, 3′-H_2) and 3.81 (1 H, s, 1′-H); δ_C (EX) 16.4, 24.6, 27.0 and 30.7 (4 q, 4 × CH_3), 32.5 (s, C-4′), 36.6 and 42.9 (2 t, C-3′ and C-5′), 60.6 (d, C-1′), 61.7 (s, C-6′), 107.9 (s, C-2), 118.9 (s, C-1) and 152.9 (s, C-2′); *m*/*z* 191 (M^+, 100%), 176 (48), 148 (32), 135 (64), 118 (23), 107 (31) and 91 (17).

Preparative irradiation of nitrile 13 with TEA. A solution of **13** (*E* : *Z* = 1 : 2) (736 mg, 3.85 mmol) and TEA (11.7 g, 11.6 mmol) in acetonitrile (100 cm^3) was irradiated with a low-pressure mercury lamp in a quartz-test-tube (conversion 65%) for 2.5 h at RT. After removal of the solvent, flash chromatography [SiO_2; hexane–ethyl acetate (4 : 1 ⟶ 1 : 1)] of the residue afforded adducts **14** (a mixture of four diastereomers, 142 mg, 20%), alcohols **15** [a mixture of two diastereomers (1 : 1), 77.7 mg, 16%]† and intractable materials (mainly polymers). Further purification of **14** and **15** by flash chromatography [SiO_2; cyclohexane–ethyl acetate (3 : 2)] gave **14A** (contaminated with *ca.* 20% of **14B**) from **14**, and **15A** (contaminated with *ca.* 20% of **15B**) and **15B** (contaminated with *ca.* 30% of **15A**) from **15**.

3-(Diethylamino)-2-(3-hydroxy-3,5,5-trimethylcyclohex-1-enyl)-2-methylbutyronitrile **14A** (contaminated with *ca.* 20% of **14B**), an oil (Found : $M^+ - CH_3$, 277.2275. $C_{18}H_{32}N_2O - CH_3$ requires *M*/*Z*, 277.2280); ν_{max} (film)/cm^{-1} 3460 (O–H) and 2220 ($C\equiv N$); δ_H (EX) 0.99–1.06 (15 H, m, 4 × CH_3 and 4-H_3), 1.30 and 1.50 (6 H, 2 s, 2 × CH_3), 1.51–1.90 (5 H, m, OH, 4′-H_2 and 6′-H_2), 2.36–2.49 (2 H, m, 2 × NC*H*), 2.36–2.49 (3 H, m, 2 × NC*H* and 3-H) and 5.96–5.98 (1 H, m, 2′-H); δ_C (EX) 10.5, 14.1, 22.9, 27.0, 30.9 and 31.5 (7 q, 2 q at δ_C 14.1, 7 × CH_3), 30.3 (s, C-5′), 37.8 and 44.3 (3 t, 2 t at δ_C 44.3, 2 × NCH_2 and C-6′), 49.8 (t, C-4′), 49.2 (s, C-2), 58.7 (d, C-3), 69.1 (s, C-3′), 122.8 (s, C-1), 129.9 (d, C-2′) and 135.6 (s, C-1′); *m*/*z* 277 (M^+ − 15, 0.7%), 191 (0.7), 178 (16), 175 (15), 160 (15), 132 (11), 100 (100), 84 (11) and 56 (12).

2-(3-Hydroxy-3,5,5-trimethylcyclohex-1-enyl)-2-methylpropiononitrile **15A** (contaminated with *ca.* 20% of **15B**), bp 110 °C

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at 0.35 mmHg (Found : M^+, 193.1470. $C_{12}H_{19}NO$ requires *M*, 193.1467); ν_{max} (film)/cm^{-1} 3520 (O–H) and 2230 (C≡N); δ_H (EX) 1.01, 1.06 and 1.30 (9 H, 3 s, 3′-CH_3 and 2 × 5′-CH_3), 1.42 (3 H, d, *J* 7.3, 3-H_3), 1.53 (1 H, d, *J* 14, 4′-H), 1.62 (1 H, br s, OH), 1.68 (1 H, dt, *J* 14 and 1.1, 4′-H), 1.83 (1 H, dd, *J* 16.5 and 1.8, 6′-H), 1.89 (1 H, d, *J* 16.5, 6′-H), 3.22 (1 H, q, *J* 7.3, 2-H) and 5.68 (1 H, dd, *J* 1.8 and 1.1, 2′-H); δ_C (EX) 17.3, 27.4, 30.6 and 31.1 (4 q, 4 × CH_3), 30.4 (s, C-5′), 32.6 (d, C-2), 40.1 (t, C-6′), 49.9 (d, C-4′), 69.1 (s, C-3′), 120.9 (s, C-1), 129.8 (d, C-2′) and 133.4 (s, C-1′); *m*/*z* 193 (M^+, 2%), 178 (100), 160 (24), 139 (40), 106 (15), 91 (18) and 77 (12).

2-(3-Hydroxy-3,5,5-trimethylcyclohex-1-enyl)-2-methylpropiononitrile **15B** (contaminated with *ca.* 30% of **15A**), an oil; δ_H (EX) 1.01, 1.05 and 1.30 (9 H, 3 s, 3′-CH_3 and 2 × 5′-CH_3), 1.42 (3 H, d, *J* 7.3, 3-H_3), 1.55 (1 H, d, *J* 13.9, 4′-H), 1.69 (1 H, br s, OH), 1.68 (1 H, dd, *J* 13.5 and 1.1, 4′-H), 1.82 and 1.89 (2 H, each d, *J* 16.9, 6′-H_2), 3.24 (1 H, q, *J* 7.3, 2-H) and 5.67–5.69 (1 H, m, 2′-H); δ_C (EX) 17.4, 27.5, 30.6 and 31.1 (4 q, 4 × CH_3), 30.4 (s, C-5′), 32.6 (d, C-2), 40.0 (t, C-6′), 49.9 (d, C-4′), 69.1 (s, C-3′), 120.8 (s, C-1), 129.8 (d, C-2′) and 133.3 (s, C-1′).

Preparative irradiation of nitrile 2 in TEA. A solution of (*E*)-**2**[7] (1.22 g, 6.39 mmol) in TEA (122 cm^3) was irradiated with a low-pressure mercury lamp in a quartz test-tube (conversion 80%) for 50 h at RT. After removal of the solvent, flash chromatography [SiO_2; hexane–ethyl acetate (4 : 1)] of the residue afforded lactone **6** (110 mg, 10%), α -alkylidenenitrile **7** (63.0 mg, 6%), alcohols (*E*)-**8** (54.0 mg, 5%) and (*Z*)-**8** (147 mg, 15%) and ketone **9**[7] (58.2 mg, 6%).†

4-(*E*)-Ethylidene-1,7,7-trimethyl-2-oxabicyclo[4.4.0]dec-5-en-3-one **6**, bp 125 °C at 0.2 mmHg (Found : M^+, 220.1460. $C_{14}H_{20}O_2$ requires *M*, 220.1463); ν_{max} (film)/cm^{-1} 1720 (C=O); δ_H (EX) 1.18, 1.26 and 1.56 (9 H, 3 s, 1-CH_3 and 2 × 7-CH_3), 1.39–2.08 (6 H, m, 8-, 9-and 10-H_2), 1.91 (3 H, d, *J* 7.6, 4 = CHC*H*$_3$), 6.35 (1 H, s, 5-H) and 6.91 (1 H, qd, *J* 7.6 and 1.0, 4 = C*H*); δ_C (EX) 13.8 (q, 4 = CH*C*H$_3$), 19.1 (t, C-9), 29.5, 29.8 and 30.9 (3 q, 3 × CH_3), 36.3 (s, C-7), 39.5 and 39.9 (2 t, C-8 and C-10), 83.7 (s, C-1), 114.0 (d, C-5), 124.1 (s, C-4), 135.5 (d, 4 = CH), 149.3 (s, C-6) and 165.9 (s, C-3); *m*/*z* 220 (M^+, 89%), 205 (43), 180 (22), 150 (100), 100 (47) and 96 (18).

2-[(*E*)-2-Hydroxy-2,6,6-trimethylcyclohexylidenemethyl]but-2-enenitrile **7** [contaminated with *ca.* 80% of (*Z*)-**8**], an oil; δ_H (EX) *inter alia* 2.03 (3 H, dd, *J* 7.3 and 1.3, 4-H_3), 5.87 (1 H, br s, 2-CH=C) and 6.23 (1 H, qd, *J* 7.3 and 1.7, 3-H); δ_C (EX) *inter alia* 17.0 (q, C-4), 74.3 (s, C-2′), 115.5 and 118.2 (2 s, C-1 and C-2), 116.7 (d, 2-*C*H=C), 143.2 (d, C-3) and 157.2 (s, C-1′).

3-[(*E*)-2-Hydroxy-2,6,6-trimethylcyclohexylidene]propiononitrile (*E*)-**8**, bp 120 °C at 0.1 mmHg (Found: M^+, 193.1458. $C_{12}H_{19}NO$ requires *M*, 193.1467); ν_{max} (film)/cm^{-1} 3430 (O–H) and 2240 (C≡N); δ_H (EX) 1.22, 1.29 and 1.39 (9 H, 3 s, 2′-CH_3 and 2 × 6′-CH_3), 1.39–1.82 (7 H, m, 3′-, 4′- and 5′-H_2 and OH), 3.32 (2 H, d, *J* 7.3, 2-H_2) and 5.86 (1 H, t, *J* 7.3, 3-H); δ_C (EX) 18.1 and 18.2 (2 t, C-2 and C-4′), 29.6, 30.7 and 31.4 (3 q, 2 × 6′-CH_3 and 2′-CH_3), 36.2 (s, C-6′), 39.1 and 40.9 (2 t, C-3′ and C-5′), 73.8 (s, C-2′), 112.6 (d, C-3), 118.9 (s, C-1) and 156.3 (d, C-1′); *m*/*z* 193 (M^+, 10%), 178 (70), 160 (20), 153 (100), 135 (37), 108 (36), 100 (44), 95 (30) and 43 (33).

3-[(*Z*)-2-Hydroxy-2,6,6-trimethylcyclohexylidene]propiononitrile (*Z*)-**8**, bp 120 °C at 0.15 mmHg (Found: M^+, 193.1468. $C_{12}H_{19}NO$ requires *M*, 193.1467); ν_{max} (film)/cm^{-1} 3420 (O–H) and 2240 (C≡N); δ_H (EX) 1.09 and 1.16 (6 H, 2 s, 2 × 6′-CH_3), 1.44 (3 H, s, 2′-CH_3), 1.40–1.89 (7 H, m, 3′-, 4′- and 5′-H_2 and OH), 3.49 (1 H, dd, *J* 18.1 and 7.6, 2-H), 3.71 (1 H, dd, *J* 18.1 and 6.9, 2-H) and 5.43 (1 H, m with t-character, *J* 7, 3-H); δ_C (EX) 18.1 and 19.2 (2 t, C-2 and C-4′), 29.2, 31.4 and 31.9 (3 q, 2 × 6′-CH_3 and 2′-CH_3), 37.5 (s, C-6′), 39.6 and 43.9 (2 t, C-3′ and C-5′), 74.2 (s, C-2′), 113.6 (d, C-3), 120.2 (s, C-1) and 156.3 (d, C-1′); *m*/*z* 193 (M^+, 20%), 178 (100), 160 (61), 153 (90), 119 (39), 95 (49), 81 (40) and 43 (90).

Irradiations of (*E*)-1 in acetonitrile containing varying amounts of TEA. Aliquots of a 0.0564 mol dm^{-3} solution of nitrile (*E*)-**1** in acetonitrile in the presence of TEA (1, 5, 10, 20, 30 and 40 equiv.) or in TEA were irradiated in quartz test-tubes under argon for 1.5 h at RT. Yields were determined by ^{1}H NMR (GX) analysis using bis(trimethylsilyl)acetylene as internal standard, after stirring of the reaction mixture with SiO_2 in $CHCl_3$ for 2 h at RT, and results are shown in Table 1.

Preparation of nitrile 16. Diethyl cyanomethylphosphonate (3.24 g, 18.3 mmol) was added dropwise to a suspension of 60% NaH (0.73 g, 18.3 mmol) in dry DMF (20 cm^3) at 0 °C. After stirring of the mixture for 20 min at 0 °C, a solution of *trans*-4,5-epoxyhexan-3-one (1.90 g, 16.7 mmol) in DMF (6 cm^3) was added dropwise. After stirring of the mixture for 2 h at RT, ice–water (24 cm^3) was then added to the mixture, the organic phase was extracted with diethyl ether, and the combined extracts were subjected to the same work-up as used for the synthesis of **13**. Flash chromatography [SiO_2; hexane–benzene–ethyl acetate (15 : 5 : 1)] afforded the nitriles (*E*)-**16** (875 mg, 40%) and (*Z*)-**16** (195 mg, 9%). (*E*,4*R*S,5*R*S)-3-Ethyl-4,5-epoxyhex-2-enenitrile (*E*)-**16**, bp 80 °C at 1 mmHg (Found: M^+, 137.0844. $C_8H_{11}NO$ requires *M*, 137.0840); ν_{max} ($CHCl_3$)/cm^{-1} 2220 (C≡N) and 1620 (C=C); δ_H (GX) 1.17 (3 H, t, *J* 7.7, 3-CH_2C*H*$_3$), 1.40 (3 H, d, *J* 5.1, 6-H_3), 2.40 (1 H, dd, *J* 17 and 7.7, 3-CH), 2.53 (1 H, dd, *J* 17 and 7.7, 3-CH), 2.80 (1 H, qd, *J* 5.1 and 1.8, 5-H), 3.14–3.15 (1 H, m with d-character, *J* 1, 4-H) and 5.33 (1 H, s, 2-H); δ_C (EX) 12.9 and 17.7 (2 q, 2 × CH_3), 25.5 (t, 3-CH_2), 58.5 and 58.6 (2 d, C-4 and C-5), 93.8 (s, C-2), 116.4 (s, C-1) and 165.4 (s, C-3); *m*/*z* 137 (M^+, 21%), 122 (100), 108 (21), 94 (76), 79 (28) and 66 (69). (*Z*,4*R*S,5*R*S)-3-Ethyl-4,5-epoxyhex-2-enenitrile (*Z*)-**16** [contaminated with *ca.* 20% of (*E*)-**16**], an oil; δ_H (GX) 1.07 (3 H, t, *J* 7.3, 3-CH_2C*H*$_3$), 1.43 (3 H, d, *J* 5.1, 6-H_3), 1.98 (1 H, dqd, *J* 17, 7.3 and 2, 3-CH), 2.13 (1 H, dqd, *J* 17, 7.3 and 1.8, 3-CH), 3.09 (1 H, qd, *J* 5.1 and 2.2, 5-H), 3.64–3.65 (1 H, m with d-character, *J* 1, 4-H) and 5.32 (1 H, s, 2-H); δ_C (EX) 11.6 and 17.6 (2 q, 2 × CH_3), 23.6 (t, 3-CH_2), 54.8 and 58.4 (2 d, C-4 and C-5), 96.5 (s, C-2), 116.1 (s, C-1) and 165.5 (s, C-3).

Preparative irradiation of nitrile 16 with TEA. A solution of **16** (*E* : *Z* = 3 : 2) (1.10 g, 8.02 mmol) and TEA (24.3 g, 241 mmol) in acetonitrile (76.5 cm^3) was irradiated with a low-pressure mercury lamp in a quartz test-tube (conversion 92%) for 7 h at RT. After removal of the solvent, a solution of the residue in $CHCl_3$ (110 cm^3) was stirred in the presence of SiO_2 (22 g) for 2 h at RT. After filtration, the filtrate was evaporated to give a residue, which was subjected to flash chromatography [SiO_2; hexane–ethyl acetate (4 : 1)] to afford (*E*)-**17** (165 mg, 14%), (*Z*)-**17** (145 mg, 12%) and intractable materials (mainly polymers).† (*E*)-3-Ethyl-2-[(*Z*)-ethylidene]-5-hydroxyhex-3-enenitrile (*E*)-**17** [contaminated with *ca.* 45% of (*Z*)-**17**], an oil; δ_H (GX) 1.03 (3 H, t, *J* 7.3, 3-CH_2C*H*$_3$), 1.32 (3 H, d, *J* 6.3, 6-H_3), 1.91 (1 H, br s, OH), 2.10 (3 H, d, *J* 7.1, 2-CHC*H*$_3$), 2.30 and 2.37 (2 H, each dq, *J* 14.3 and 7.3, 3-CH_2), 4.66 (1 H, dq, *J* 8.6 and 6.3, 5-H), 5.88 (1 H, d, *J* 8.6, 4-H) and 6.50 (1 H, q, *J* 7.1, 2-CH); δ_C (GX) 13.7, 17.6 and 23.8 (3 q, 3 × CH_3), 20.7 (t, 3-CH_2), 64.5 (d, C-5), 116.0 and 118.4 (2 s, C-2 and C-1), 134.6 (d, C-4), 136.2 (s, C-3) and 140.4 (d, 2-CH). (*Z*)-3-Ethyl-2-[(*Z*)-ethylidene]-5-hydroxyhex-3-enenitrile (*Z*)-**17**, an oil (Found: M^+, 165.1154. $C_{10}H_{15}NO$ requires *M*, 165.1083); ν_{max} ($CHCl_3$)/cm^{-1} 3370 (C–O) and 2180 (C≡N); δ_H (GX) 1.03 (3 H, t, *J* 7.6, 3-CH_2C*H*$_3$), 1.29 (3 H, d, *J* 6.4, 6-H_3), 1.58 (1 H, br s, OH), 2.11 (3 H, d, *J* 7.0, 2-CHC*H*$_3$), 2.23 (2 H, qd, *J* 7.6 and 1.2, 3-CH_2), 4.52 (1 H, dq, *J* 9.2 and 6.4, 5-H), 5.45 (1 H, d, *J* 9.2, 4-H) and 6.38 (1 H, q, *J* 7.0, 2-CH); δ_C (GX) 12.5, 17.4 and 23.7 (3 q, 3 × CH_3), 29.4 (t, 3-CH_2), 64.8 (d, C-5), 114.7 and 116.5 (2 s, C-2 and C-1), 133.1 (d, C-4), 137.4 (s, C-3) and 146.0 (d, 2-CH); *m*/*z* 165 (M^+, 13%), 151 (41), 147 (9), 136 (33), 123 (100), 108 (30), 95 (25) and 77 (23).

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Photoadditions of nitrile 1 with various amines

By analogy with the photoreaction of **16** with TEA, the nitrile **1** was irradiated with 30 equiv. of an amine in acetonitrile, affording the corresponding adducts. The results are summarized in Table 2.

2-(3-Hydroxy-3,5,5-trimethylcyclohex-1-enyl)acrylonitrile **22**, bp 150 °C at 0.3 mmHg (decomposition) (Found: M^+, 191.1309. $C_{12}H_{17}NO$ requires *M*, 191.1310); ν_{max} ($CHCl_3$)/cm^{-1} 3590, 3470 (O–H) and 2220 (C≡N); δ_H (EX) 1.03 and 1.06 (6 H, 2 s, 2 × 5′-CH_3), 1.36 (3 H, s, 3′-CH_3), 1.57 and 1.73 (2 H, each d, *J* 14.2, 4′-H_2), 1.66 (1 H, br s, OH), 1.87 (1 H, dd, *J* 16.5 and 2, 6′-H), 2.01 (1 H, d, *J* 16.5, 6′-H), 5.88 and 5.93 (2 H, each s, 3-H_2) and 6.22 (1 H, br s, 2′-H); δ_C (EX) 27.8, 30.9 and 31.1 (3 q, 3 × CH_3), 30.1 (s, C-5′), 38.0 (t, C-6′), 49.5 (t, C-4′), 69.1 (s, C-3′), 117.1 (s, C-1), 124.6 (s, C-2), 126.9 (t, C-3), 130.8 (s, C-1′) and 135.3 (d, C-2′); *m*/*z* 191 (M^+, 38%), 176 (100), 149 (27), 139 (41), 134 (29), 120 (26) and 106 (23).

(*Z*)-2-(3-Hydroxy-3,5,5-trimethylcyclohex-1-enyl)pent-2-enenitrile **23**, bp 130 °C at 0.15 mmHg (Found: M^+, 219.1620. $C_{14}H_{21}NO$ requires *M*, 219.1623); ν_{max} (film)/cm^{-1} 3410 (O–H) and 2220 (C≡N); δ_H (EX) 1.02 and 1.06 (6 H, 2 s, 2 × 5′-CH_3), 1.12 (3 H, t, *J* 7.6, 5-H_3), 1.34 (3 H, s, 3′-CH_3), 1.56 (1 H, d, *J* 14.2, 4′-H), 1.72 (1 H, m with dt-character, *J* 14.2 and 1, 4′-H), 1.75 (1 H, br s, OH), 1.86 (1 H, dd, *J* 16.5 and 1.7, 6′-H), 2.00 (1 H, m with dt-character, *J* 16.5 and 1, 6′-H), 2.50 (2 H, quintet, *J* 7.6, 4-H_2), 6.09 (1 H, br s, 2′-H) and 6.38 (1 H, t, *J* 7.6, 3-H); δ_C (EX) 13.2 (q, C-5), 25.3 (t, C-4), 27.9, 30.9 and 31.3 (3 q, 3 × CH_3), 30.1 (s, C-5′), 38.8 (t, C-6′), 49.6 (t, C-4′), 69.1 (s, C-3′), 115.7 and 117.3 (2 s, C-1 and C-2), 130.8 (s, C-1′), 132.8 (d, C-2′) and 146.5 (d, C-3); *m*/*z* 219 (M^+, 31%), 204 (100), 177 (16), 148 (9), 139 (20) and 134 (10).

Photoaddition of nitrile 1 with TMSA 24

Preparative irradiation. A solution of **1** (*E* : *Z* = 2 : 1) (470 mg, 2.65 mmol) and TMSA **24** (4.22 g, 26.5 mmol) in acetonitrile (71.6 cm^3) was irradiated with a low-pressure mercury lamp in a quartz test-tube (conversion 100%) for 4 h at RT. After removal of the solvent, a solution of the residue in $CHCl_3$ (97 cm^3) was stirred in the presence of silica gel (1.9 g) for 2 h at RT. After filtration, the filtrate was evaporated to give the residue, which was subjected to flash chromatography [SiO_2; benzene–ethyl acetate (9 : 1)] to afford **3** (6%), **4** (23%), **22** (12%) and **25** (21%).†

(*Z*)-2-(3-Hydroxy-3,5,5-trimethylcyclohex-1-enyl)-3-(trimethylsilyl)acrylonitrile **25**, mp 87–89 °C (Found: M^+, 263.1696. $C_{15}H_{25}NOSi$ requires *M*, 263.1705); ν_{max} (film)/cm^{-1} 3440 (O–H) and 2220 (C≡N); δ_H (EX) 0.29 [9 H, s, Si(CH_3)$_3$], 1.04 and 1.06 (6 H, 2 s, 2 × 5′-CH_3), 1.36 (3 H, s, 3′-CH_3), 1.56 and 1.73 (2 H, each d, *J* 14.2, 4′-H_2), 1.70 (1 H, br s, OH), 1.85 (1 H, dd, *J* 16.5 and 2.0, 6′-H), 2.03 (1 H, m with d-character, *J* 16.5, 6′-H), 6.24 (1 H, br s, 2′-H) and 6.57 (1 H, s, 3-H); δ_C (EX) −1.38 [3 q, Si(CH_3)$_3$], 27.9, 30.2 and 30.9 (3 q, 3 × CH_3), 30.2 (s, C-5′), 38.4 (t, C-6′), 49.6 (t, C-4′), 69.3 (s, C-3′), 117.2 (s, C-1), 129.6 and 130.8 (2 s, C-2 and C-1′), 134.4 (d, C-2′) and 145.5 (d, C-3); *m*/*z* 263 (M^+, 7%), 248 (18), 145 (86), 130 (100), 203 (17), 139 (24), 84 (16) and 73 (62).

Irradiations with various concentrations of TMSA 24 in various solvents. Aliquots of a 0.0564 mol dm^{-3} solution of nitrile **1** (*E*/*Z* = 2 : 1) in acetonitrile containing varying amounts of TMSA **24** (5, 10, 15 and 30 equiv.) and MeOH were irradiated in quartz test-tubes under argon for 0.5 h at RT. Yields were determined by GLC analysis using octadecane as internal standard, after stirring of reaction mixture with SiO_2 in $CHCl_3$ for 2 h at RT, and results are shown in Table 3.

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References

1 G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401; J. Mattay, *Synthesis*, 1989, 233; J. Mattay and M. Vondenhof, *Top. Curr. Chem.*, 1991, **159**, 219; A. Albini, E. Fasani and M. Mella, *Top. Curr. Chem.*, 1993, **168**, 143; G. Pandey, *Top. Curr. Chem.*, 1993, **168**, 175; F. Müller and J. Mattay, *Chem. Rev.*, 1993, **93**, 99; J. Cossy, *Bull. Soc. Chim. Fr.*, 1994, **131**, 344; U. C. Yoon, P. S. Mariano, R. S. Givens and B. W. Atwater, in *Advances in Electron Transfer Chemistry*, ed. P. S. Mariano, JAI Press, Stamford, 1994, vol. 4, p. 117; F. D. Lewis, in *Advances in Electron Transfer Chemistry*, ed. P. S. Mariano, JAI Press, Stamford, 1996, vol. 5, p. 1; J. Cossy and J. P. Pete, in *Advances in Electron Transfer Chemistry*, ed. P. S. Mariano, JAI Press, Stamford, 1996, vol. 5, p. 141.

2 R. C. Cookson, J. Hudec and N. A. Mirza, *Chem. Commun.*, 1968, 180; 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; S. Bertrand, N. Hoffmann, S. Humbel and J. P. Pete, *J. Org. Chem.*, 2000, **65**, 8690.

3 Y. T. Jeon, C.-P. Lee and P. S. Mariano, *J. Am. Chem. Soc.*, 1991, **113**, 8847.

4 U. C. Yoon and P. S. Mariano, *Acc. Chem. Res.*, 1992, **25**, 233.

5 K. Ishii, M. Kotera and M. Sakamoto, *J. Chem. Soc., Chem. Commun.*, 1994, 2465.

6 K. Ishii, D. Gong, R. Asai and M. Sakamoto, *J. Chem. Soc., Perkin Trans. 1*, 1990, 855.

7 K. Ishii, M. Abe and M. Sakamoto, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1937.

8 B. Frei, H. Eichenberger, B. von Wartburg, H. R. Wolf and O. Jeger, *Helv. Chim. Acta*, 1977, **60**, 2968.

9 J. Cossy, A. Bouzide, S. Ibhi and P. Aclinou, *Tetrahedron*, 1991, **47**, 7775.

10 A. Jończyk, M. Fedoryński and M. Mąkosza, *Tetrahedron Lett.*, 1972, 2395.

11 E. Hasegawa, M. A. Brumfield and P. S. Mariano, *J. Org. Chem.*, 1988, **53**, 5435.

12 E. Hasegawa, K. Ishiyama, T. Fujita, T. Kato and T. Abe, *J. Org. Chem.*, 1997, **62**, 2396.