

1,3-Dipolar cycloadditions of photoinduced carbonyl ylides. Part 2.¹ Photoreactions of α,β -unsaturated γ,δ -epoxy dinitriles and ethyl vinyl ether

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Photoinduced carbonyl ylides **B**, **C**, **E** and **F** from the α,β -unsaturated γ,δ -epoxy dinitriles **2**, **3**, **5** and **6**, respectively, undergo 1,3-dipolar cycloaddition with ethyl vinyl ether, leading to the tetrahydrofuran system. The cycloaddition proceeds with high regioselectivity affording predominantly the *exo*-adduct. However, the ylide from the mononitrile **1** and dinitrile **4** gives little or no adduct. The observed regioselectivity and the difference of the reactivity in these cycloadditions can be nicely accommodated in terms of semiempirical AM1 calculations. The reactivity of the cycloaddition depends on the LUMO energy level and the C(γ),C(δ) distance of the ylide.

Introduction

Photochemical reactions of α,β -unsaturated γ,δ -epoxy nitriles have been investigated systematically.^{2,3} These studies have revealed that epoxy nitriles generate carbonyl ylides more efficiently than the corresponding epoxy enones.⁴ We have reported new methodology for the syntheses of spiroacetals *via* the carbonyl ylide intermediates³ and we became interested in extending the carbonyl ylide chemistry to 1,3-dipolar cycloadditions. The carbonyl ylides used for 1,3-dipolar cycloaddition have been generated by the heating of oxiranes bearing an adjacent electron withdrawing group,⁵ by treatment of an α -diazo carbonyl compound with copper(II)^{6a} or rhodium(II) acetate,^{6b} by treatment of chloromethyl trimethylsilylmethyl ether with CsF^{7a} and iodohydrin silyl ether with SmI₂,^{7b} or by irradiation of oxiranes possessing adjacent phenyl groups.⁸

In a previous communication,¹ we have shown that simple carbonyl ylides (having no phenyl group) generated from epoxy dinitriles photochemically afford 1,3-dipolar cycloadducts with enol ethers. In this paper we describe the details of the preparation of the nitrile **1** and the dinitriles **2–6**, the photoreactions of **1–6** with ethyl vinyl ether (EVE) (Fig. 1) and consideration of the regioselectivity and the difference of the reactivity in these cycloadditions on the basis of semiempirical AM1 calculations.

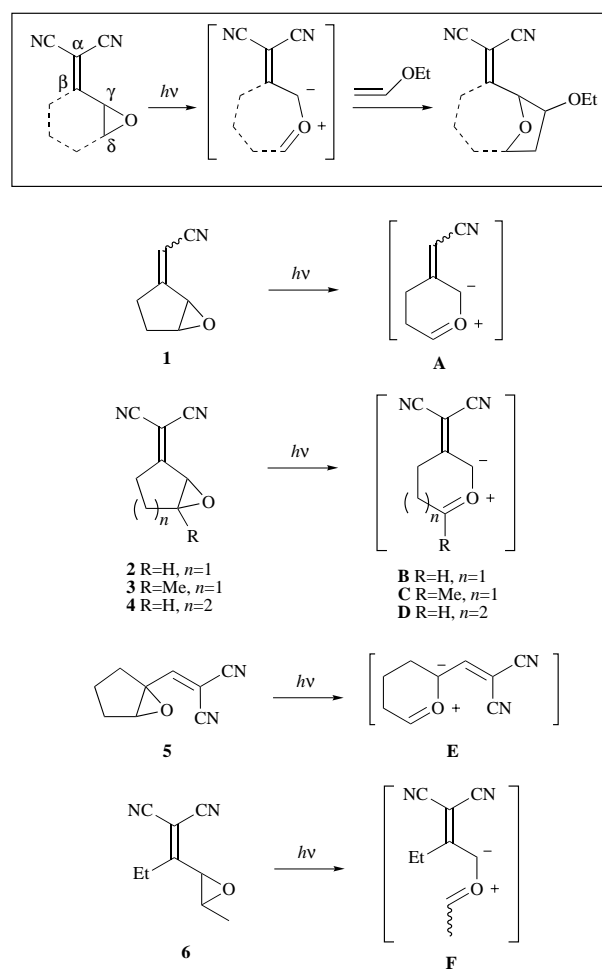
Results and discussion

Preparation of the nitrile **1** and the dinitriles **2–6**

The mononitrile **1** was prepared from the epoxy ketone **7**⁹ in 84% yield (*E:Z* = 2:1) by the Horner–Emmons reactions. The dinitrile **2** was obtained by Knoevenagel condensation¹⁰ from **7** in 76% yield. In a similar manner, the dinitriles **3–6** were prepared from the corresponding epoxy ketones **8**,^{9,11} **9**,¹¹ **10**¹² and **11**¹³ in 79, 75, 35 and 35% yields, respectively (Scheme 1). The structures of **1–6** were deduced from the spectral data. In particular, the ¹³C NMR spectra of the dinitriles **2–6** show two signals at 84.5–89.2 and 163.3–183.9 ppm due to the carbon atoms positioned α and β , respectively, to the dicyano group.

Photochemical reactions of the mononitrile **1** and the dinitrile **2** with EVE

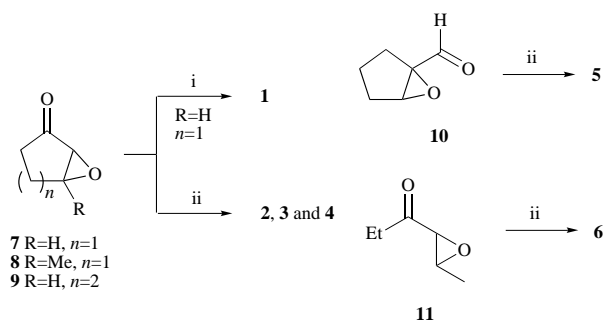
Preparative irradiation of **1** and EVE (10 equiv.) in acetonitrile with a low-pressure mercury lamp through a quartz filter (λ 254



nm) at 0 °C failed to give a cycloadduct but, instead, gave α,β -unsaturated ketone **12** (33%[‡]); this is probably formed by the C(γ),O bond cleavage of the oxirane leading to intermediate **G** followed by a δ -H-shift to the α position. In order to trap the carbonyl ylide **A**, the mononitrile **1** was irradiated (λ 254 nm) in MeOH at 0 °C giving solely **12** (38%[‡]); the methanol

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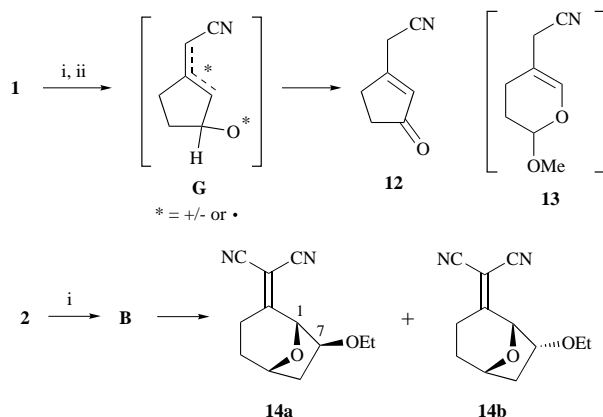
[‡] Yields for compounds throughout the rest of the paper are based on converted starting material.



Scheme 1 Reagents and conditions: i, (EtO)₂P(O)CH₂CN, NaH, DMF, -50 °C; ii, malononitrile, AcNH₄, AcOH, benzene, room temperature

adduct **13**, a product trapping the ylide,^{2b} could not be detected (Scheme 2). The results may indicate either that the carbonyl ylide **A** is not produced in this reaction or that the adduct **13** is decomposed by hydrolysis and polymerization.

In contrast, preparative irradiation of the dinitrile **2** and EVE (100 equiv.) under the same conditions as the reaction of **1** afforded regioselectively the 7-ethoxy substituted *exo*-**14a** (36%) and the *endo*-adduct **14b** (8%), but no 6-substituted isomer (Scheme 2).[‡] The structures of the photoadducts were deduced



Scheme 2 Reagents and conditions: i, $\lambda = 254$ nm, MeCN, EVE; ii, $\lambda = 254$ nm, MeOH

on the basis of their spectral data. The molecular ion peak in the mass spectrum (MS) indicates the presence of the 1:1 adducts of the carbonyl ylide **B** and EVE and the ¹³C NMR spectra show three doublets at 75.0, 80.9 and 82.7 ppm for **14a** and at 74.7, 77.5 and 80.4 ppm for **14b** due to C-1, C-5 or C-7, respectively. In particular, the *exo* and *endo* configuration of **14** are determined by means of the coupling constant of 1-H in the ¹H NMR spectra; they show a singlet for *exo* and a doublet (J 6.6 Hz) for *endo*. The coupling constant is nearly the same as those calculated by the Karplus equation¹⁴ from the dihedral angle of H-C(1)-C(7)-H [96° (*exo*) and 23° (*endo*)] in the stable conformation of **14** obtained from the MM2 force-field calculations.[§] The reactivity of the cycloaddition between the mononitrile **1** and the dinitrile **2** will be discussed later in this paper.

The photoreactions of **2** have been studied in the presence of varying EVE concentrations (100–3 equiv. of **2**). The total yield of the adducts **14a** and **b** does not clearly change in the 100–10 equiv. concentration range (36–44%) but decreases at an EVE concentration of <5 equiv. The results are summarized in Table 1.

Photochemical reactions of various dinitriles 3–6 with EVE

Since the reaction of the carbonyl ylide **B** and EVE had given the cycloadduct **14** in moderate yield, the cycloaddition of the

Table 1 Irradiation of **2** with various concentrations of EVE^a

Entry	Concentration of EVE $c/\text{mol cm}^{-3}$ (equiv.)	Conversion (%)	Yields (%) ^{‡,b}	
			14a (<i>exo</i>)	14b (<i>endo</i>)
1	3.50 (100)	98	23	7
2	1.75 (50)	99	28	8
3	1.05 (30)	99	29	9
4	0.35 (10)	98	33	9
5	0.175 (5)	100	20	6
6	0.105 (3)	100	13	3

^a A 0.035 mol cm⁻³ solution of **2** in acetonitrile was irradiated for 4 h at 0 °C. ^b Yields and conversions were determined by GLC analysis.

Table 2 Photoreactions of the dinitriles 2–6 with EVE^a

Dinitrile	Irradiation time (h)	Conversion (%)	Yields (%) ^{‡,b}	
			14a (36) and 14b (8)	15a (25) and 15b (7)
2 ^c	6	95	14a (36) and 14b (8)	
3	7	79	15a (25) and 15b (7)	
4	6	84	16 (2)	
5	4	100	17 (8) and 18 (6)	
6	4	83	19a (13), 19b (9), 19c (25), 19d (6) and 20 (1)	

^a A 0.035 mol cm⁻³ solution of dinitrile in acetonitrile with 10 equiv. of EVE was irradiated at 0 °C. ^b Isolated yield. ^c With 100 equiv. of EVE.

carbonyl ylides **C–F** generated from the dinitriles **3–6** and EVE were studied under the conditions of entry 4 in Table 1 and afforded the adducts **15–20** (Scheme 3). The results are summarized in Table 2.

The yields of the cycloadducts derived from the 7-membered carbonyl ylide **D** drastically decreased in comparison with those from the 6-membered carbonyl ylides **B** and **C**, the reactivities of which are discussed later in this paper.

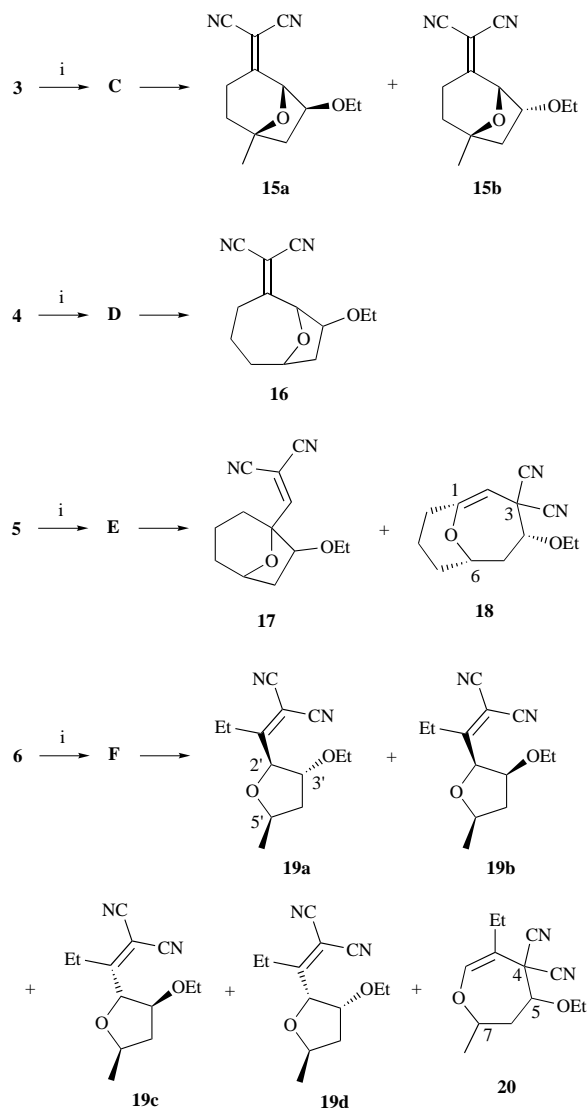
The structure of the adducts **15** and **16** was determined on the basis of the spectral data. In particular, the ¹³C NMR spectra of **15** and **16** show three characteristic signals at 78.6–83.6 ppm due to the carbon atoms adjacent to the bridgehead oxygen and to the ethoxy group. The assignment of the *exo* and *endo* configuration of **15** is made by the coupling constant of 1-H in the ¹H NMR spectra in the same manner as described for **14**.

The cycloaddition of the carbonyl ylide **E** and EVE gave the 3 + 2-adduct **17** and the 5 + 2-adduct **18**, which is produced by bond formation at the α - and δ -positions in **E** owing to the flexibility of its C(β),C(γ) bond. The structures of **17** and **18** were inferred from their spectral characteristics. The stereochemistry of **17** could not be determined by the NOE experiment. In its MS the molecular ion peak of **18** shows a peak for a 1:1 adduct of the carbonyl ylide **E** and EVE. The ¹H NMR spectrum of **18** shows a doublet at 5.23 ppm due to the olefinic proton and the ¹³C NMR spectrum two singlets at 161.7 (C-1) and 40.4 ppm (C-3) and three doublets at 104.5 (C-2), 80.4 (C-4) and 77.9 ppm (C-6). Furthermore, the stereochemistry (4*R**,6*R**) of **18** was established by the significant NOE enhancement (5.5%) between 4-H and 6-H (Fig. 2), whose location in the stable conformation obtained from MM2 force-field calculation is close (0.27 nm).

The photoreaction of the dinitrile **6** and EVE afforded, *via* acyclic carbonyl ylide **F**, the 5 + 2-adduct **20** and all the possible 3'-ethoxy substituted 3 + 2-adducts **19a–d** in spite of the *trans* configuration of the epoxy ring in **6**. The results suggest that the cycloaddition may occur stepwise and/or *via* the ylide intermediates in two conformations (*exo-exo* **F1** and *exo-endo* **F2**; Fig. 3).

As characteristic signals for **19a–c**, the ¹³C NMR spectra have three doublets at 75.7–85.8 ppm due to C-2', C-3' and C-5'. The stereochemistry at C-2', C-3' and C-5' in **19a–c** was assigned as 2'*R**,3'*S**,5'*S** for **a**, 2'*R**,3'*R**,5'*S** for **b** and

[§] CAChe system, Tektronix Corp. version 3.0 (Beaverton, Oregon, USA).



Scheme 3 Reagents and conditions: i, $\lambda = 254$ nm, MeCN, EVE

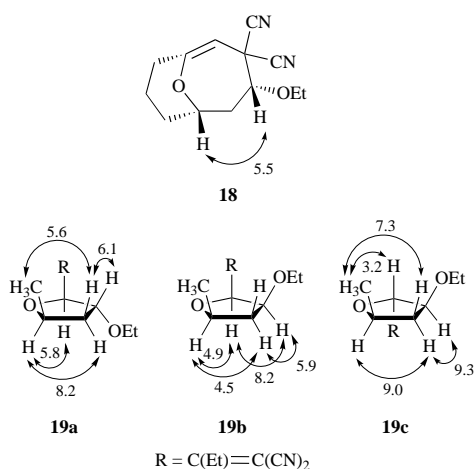


Fig. 2 NOE enhancement (%)

$2'R^*,3'S^*,5'R^*$ for **c** by using the characteristic NOE enhancements between $2'-, 3'-, 4'-, 5'-H$ and $5'-Me$. The results of these experiments are shown in Fig. 3. The stereochemistry of **19d** was deduced from a comparison of the 1H NMR and H-H COSY spectral data of a mixture of **19c** and **19d** with those of **19a-c** and may be assigned as $2'R^*,3'R^*,5'R^*$. Concerning the structure of **20**, a singlet (6.45 ppm) in the 1H NMR spectrum and a singlet (113.1, 113.3 or 114.6 ppm) and a doublet (148.5 ppm) in the ^{13}C NMR spectrum are characteristic of an enol

Table 3 LUMO energies and $C(\gamma),C(\delta)$ -distance for carbonyl ylides

Carbonyl ylide	LUMO energy (eV)	Energy separation ^a ($\Delta E/eV$)	$C(\gamma),C(\delta)$ -distance (nm)	Yield of 3 + 2-adducts (%)
A	-1.13	8.23	0.229	0
B	-1.79	7.56	0.232	44
C	-1.77	7.58	0.232	32
D	-1.68	7.68	0.240	2
F	-1.53	7.82	0.231	53

^a LUMO(ylide) – HOMO(EVE; -9.36 eV).

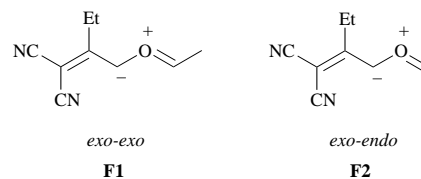


Fig. 3

ether moiety. Furthermore, the ^{13}C NMR spectrum shows a singlet at 45.0 ppm for C-4 and two doublets at 74.3 and 77.6 ppm for C-7 and C-5, respectively, which are assigned from the C-H COSY spectrum.

Frontier-MO explanation of the reactivity of the cycloaddition

The dinitriles and EVE undergo regioselectively 1,3-dipolar cycloaddition leading preferably to the *exo*-adducts. The results of the cycloaddition would suggest that the reactivity depends on the structure of the ylide. Therefore, the reactivity and the regioselectivity of the cycloaddition of the ylides **A-D** and **F** and EVE were studied by frontier-MO calculations using the semiempirical AM1 calculations.[¶] The calculated results are summarized in Table 3. According to the calculations the reactivity of the cycloaddition would be controlled by two factors. The first one is the energy gap of LUMO (carbonyl ylide) – HOMO (EVE) and the second one is the distance of the reactive centre carbon atoms,¹⁶ $C(\gamma)$ and $C(\delta)$, in the ylide.

The two cyano groups in **B** lower the LUMO energy level, and hence the LUMO (**B**) – HOMO (EVE) energy gap is smaller than the LUMO (**A**) – HOMO (EVE) ($\Delta E = 8.23$ eV). The LUMO (**C** and **F**) – HOMO (EVE) energy gap (7.58 and 7.82 eV) is similar to that in the case of **B**. Consequently, the 1,3-dipolar cycloadditions of dinitriles **2**, **3** and **6** with EVE are more favourable than that of the mononitrile **1**. Although the energy gap in the 7-membered carbonyl ylides **D** is nearly the same as that in **B**, **C** and **F**, a little of the adduct was produced. The difference of reactivity could be rationalized in terms of the distance of the reactive centre carbon atoms, $C(\gamma)$ and $C(\delta)$, in the carbonyl ylides; the length in **D** (0.240 nm) is longer than those in **B**, **C** and **F** (0.231–0.232 nm). Consequently, the results indicate that it would be unfavourable for the LUMO of **D** to overlap with the HOMO of EVE.

The high regioselectivity and the preferred formation of the *exo*-adduct can be explained by the coefficients of the LUMO (ylide) and the HOMO (EVE). The preferred regioisomer will be that in which the atoms bearing larger coefficients of the interacting frontier orbitals overlap;¹⁷ $C(\delta)$ in the LUMO of the ylide and the terminal carbon atom in the HOMO of EVE interact. The dominant formation of the *exo*-adduct may be rationalized in terms of steric hindrance and the unfavourable secondary orbital interaction between the coefficient at $C(\beta)$ of the LUMO (ylide) and that of oxygen atom of the HOMO (EVE) in the *endo* transition state. The interaction of the LUMO of **B** and the HOMO of EVE is depicted in Fig. 4.

¶ CAChe MOPAC version 94. All orbital energies were obtained from AM1 optimized geometries.

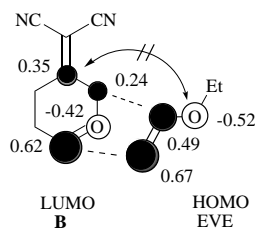


Fig. 4 Coefficients of LUMO (**B**) and HOMO (EVE)

Semiempirical AM1 calculations of the transition states of *exo*- and *endo*-addition of **B** and EVE were also performed. The results show that the transition state of *exo* is more stable than that of *endo* ($\Delta\Delta H_f^\ddagger = 1.1 \text{ kcal mol}^{-1}$), and thus the *exo*-addition proceeds more smoothly.

In summary, the carbonyl ylides **B–F** generated photochemically from the epoxy dinitriles **2–6** and EVE undergo regioselectively 1,3-dipolar cycloaddition leading predominantly to the corresponding *exo*-adduct. It can be suggested according to the semiempirical AM1 calculations that the reactivity of the cycloaddition depends on the LUMO energy level and the $C(\gamma), C(\delta)$ distance of the ylide.

Experimental

Mps and bps are uncorrected. Mps were measured with a Yanaco MP-3 apparatus and bps were measured with a Büchi 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 in CDCl_3 solutions using tetramethylsilane as an 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) using a column $30 \text{ m} \times 0.25 \text{ mm}$ (Rascot OV-1). Column chromatography was performed with either Nakarai silica gel 60 [230–400 mesh (SiO_2 , A)] or Kanto silica gel [100–200 mesh (SiO_2 , B)].

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

Epoxy nitrile 1

Preparation of 1. Diethyl cyanomethylphosphonate (5.42 g, 25.9 mmol) was added dropwise to a suspension of NaH (60%; 1.22 g, 30.5 mmol) in dry DMF (45 cm^3) at room temperature. After the mixture had been stirred for 20 min, the epoxy ketone **7**⁸ (2.50 g, 25.5 mmol) was added dropwise to it and stirring was continued for 3 h at -50°C . Ice–water was then added to the mixture and the organic phase was extracted with diethyl ether. The ethereal extracts were washed with brine, dried (MgSO_4) and concentrated *in vacuo*, giving a residue that was subjected to flash chromatography [SiO_2 , A; CH_2Cl_2 –hexane (5:1)] to afford the epoxy nitrile (*E/Z*)-**1** (*E/Z* = 2:1, 2.59 g, 84%).

(*E/Z*)-6-Oxabicyclo[3.1.0]hexan-2-ylideneacetonitrile (*E/Z*)-**1**, bp 120°C at 0.15 mmHg (Found: M^+ , 121.0520. $\text{C}_7\text{H}_7\text{NO}$ requires M , 121.0528); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2222 (C≡N) and 1648 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.81–1.98, 2.17–2.40 and 2.62–2.74 (4 H, 3 m, 2 CH_2), 3.71 (1 H, d, J 2.6, 1-H for *E*), 3.88–3.90 (1 H, m, 5-H), 4.06 (1 H, d, J 2.6, 1-H for *Z*), 5.41–5.42 (1 H, m, HCCN for *Z*) and 5.59–5.61 (1 H, m, HCCN for *E*); δ_{C} for *E* (EX) 26.1 and 26.2 (2 t, 2 CH_2), 57.8 and 60.6 (2 d, C-1 and -5), 95.4 (d, CHCN), 116.0 (s, CN) and 166.5 (s, C-2); δ_{C} for *Z* (EX) 26.2 and 27.1 (2 t, 2 CH_2), 56.4 and 60.2 (2 d, C-1 and -5), 95.5 (d, CHCN), 115.9 (s, CN) and 166.4 (s, C-2); m/z 121 (M^+ , 23%), 93 (24) and 66 (100).

Photoreaction of mononitrile (*E/Z*)-1 and EVE

A solution of (*E/Z*)-**1** (*E/Z* = 2:1; 492 mg, 4.06 mmol) in dry acetonitrile (110 cm^3) with EVE (2.93 g, 40.6 mmol) was irradiated with a low-pressure mercury lamp in a quartz test tube (conversion 35%) for 3.5 h at 0°C . After removal of the solvent, flash chromatography [SiO_2 , A; hexane–ethyl acetate (1:1→1:4)] afforded the enone **12** (56.8 mg, 33%) and intractable material (mainly polymers).

3-Cyanomethylcyclopent-2-enone **12**, an oil (Found: M^+ , 121.0533. $\text{C}_7\text{H}_7\text{NO}$ requires M , 121.0528); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 2260 (C≡N), 1717 (C=O) and 1630 (C=C); $\delta_{\text{H}}(\text{EX})$ 2.51–2.54 and 2.70–2.73 (4 H, 2 m, 2 CH_2), 3.54 (2 H, br s, CH_2CN) and 6.28 (1 H, quintet, J 1.7, 2-H); $\delta_{\text{C}}(\text{EX})$ 21.9, 30.8 and 35.6 (3 t, 3 CH_2), 115.2 (s, CN), 132.8 (d, C-2), 167.8 (s, C-3) and 207.6 (s, C-1); m/z 121 (M^+ , 100%), 81 (39), 66 (36) and 53 (49).

Photoreaction of 1 in methanol

A solution of (*E/Z*)-**1** (*E/Z* = 2:1; 466 mg, 3.85 mmol) in MeOH (110 cm^3) was irradiated with a low-pressure mercury lamp in a quartz test tube (conversion 34%) for 2.5 h at 0°C . After removal of the solvent, flash chromatography [SiO_2 , A; hexane–ethyl acetate (1:1→1:4)] of the residue afforded the enone **12** (59.5 mg, 38%) and intractable material (mainly polymers).

Epoxy dinitriles 2–6

Typical procedure for preparation. A suspension of the epoxy ketone **7** (2.61 g, 26.6 mmol), malononitrile (1.76 g, 26.6 mmol), ammonium acetate (411 mg, 5.33 mmol) and acetic acid (1.62 g, 26.7 mmol) in benzene (10 cm^3) was stirred for 3 h at room temperature. The reaction mixture was extracted with ether, after which the extracts were combined, washed with sat. aqueous NaHCO_3 and subjected to the same work-up as used for synthesis of **1**. Flash chromatography [SiO_2 , A; hexane–ethyl acetate (1:1)] of the residue gave the dinitrile **2** (2.97 g, 76%). By analogy with the synthesis of **2**, the epoxy compounds **8**,^{9,11} **9**,¹¹ **10**¹² and **11**¹³ afforded the corresponding dinitriles **3** (79%), **4** (75%), **5** (35%) and **6** (35%), respectively.

6-Oxabicyclo[3.1.0]hexan-2-ylidenemalononitrile **2**, mp 51 – 53°C ; bp 105°C at 0.20 mmHg (Found: C, 65.64; H, 4.26; N, 19.15. $\text{C}_8\text{H}_8\text{N}_2\text{O}$ requires C, 65.75; H, 4.14; N, 19.17%); $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$ 245 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 18 400); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2240 (C≡N) and 1625 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.99–2.11 (1 H, m, 4-H), 2.37 (1 H, dd, J 14 and 9, 4-H), 2.47–2.60 (1 H, m, 3-H), 2.86 (1 H, dd, J 19 and 9, 3-H), 4.09 (1 H, br s, 5-H) and 4.13 (1 H, d, J 2.3, 1-H); $\delta_{\text{C}}(\text{EX})$ 26.0 and 28.4 (2 t, 2 CH_2), 56.7 and 62.0 (2 d, C-1 and -5), 85.4 [s, $\text{C}(\text{CN})_2$], 110.8 and 110.9 (2 s, 2 CN) and 182.7 (s, C-2); m/z 146 (M^+ , 49%), 131 (20), 118 (21) and 91 (100).

5-Methyl-6-oxabicyclo[3.1.0]hexan-2-ylidenemalononitrile **3**, mp 79 – 82°C (hexane–ethyl acetate) (Found: C, 67.30; H, 5.07; N, 17.38. $\text{C}_9\text{H}_8\text{N}_2\text{O}$ requires C, 67.49; H, 5.03; N, 17.49%); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 2240 (C≡N) and 1625 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.64 (3 H, s, CH_3), 1.98 (1 H, br dt, J 14 and 8, 4-H), 2.28 (1 H, br dd, J 14 and 8, 4-H), 2.57 (1 H, dt, J 18.8 and 8.2, 3-H), 2.84 (1 H, br dd, J 19 and 8, 3-H) and 3.93 (1 H, s, 1-H); $\delta_{\text{C}}(\text{EX})$ 17.7 (q, CH_3), 29.8 and 30.4 (2 t, 2 CH_2), 62.4 (d, C-1), 70.6 (s, C-5), 84.5 [s, $\text{C}(\text{CN})_2$], 110.9 and 111.0 (2 s, 2 CN) and 183.9 (s, C-2); m/z 160 (M^+ , 100%), 145 (46), 131 (47) and 104 (41).

7-Oxabicyclo[4.1.0]heptan-2-ylidenemalononitrile **4**, bp 135°C at 0.35 mmHg (Found: M^+ , 160.0636. $\text{C}_9\text{H}_8\text{N}_2\text{O}$ requires M , 160.0637); $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 2236 (C≡N) and 1592 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.55–1.69, 1.74–2.00 and 2.18–2.29 (4 H, 3 m, 2 CH_2), 2.50 (1 H, ddd, J 17.2, 8.9 and 5.0, 3-H), 2.79 (1 H, ddd, J 17.2, 7.3 and 4.3, 3-H), 3.70 (1 H, m, 6-H) and 3.94 (1 H, d, J 4.0, 1-H); $\delta_{\text{C}}(\text{EX})$ 18.4, 22.6 and 29.1 (3 t, 3 CH_2), 51.5 and 57.0 (2 d, C-1 and -6), 88.3 [s, $\text{C}(\text{CN})_2$], 110.7 and 110.9 (2 s, 2 CN) and 176.6 (s, C-2); m/z 160 (M^+ , 83%), 131 (70), 104 (62) and 41 (100).

2-Cyano-3-(6'-oxabicyclo[3.1.0]hexan-1'-yl)acrylonitrile **5**,

bp 135 °C at 2.0 mmHg (Found: M^+ , 160.0634. $C_9H_8N_2O$ requires M , 160.0637); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2238 (C≡N) and 1610 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.48–1.88, 2.04–2.20 and 2.25–2.33 (6 H, 3 m, 3 CH_2), 3.75 (1 H, s, 5'-H) and 7.23 (1 H, s, 3-H); $\delta_{\text{C}}(\text{EX})$ 19.3, 27.5 and 28.8 (3 t, 3 CH_2), 64.9 (s, C-1'), 68.6 (d, C-5'), 89.2 (s, C-2), 110.5 and 112.3 (2 s, 2 CN) and 163.3 (d, C-3); m/z 160 (M^+ , 33%), 131 (56), 104 (45) and 55 (100).

(*trans*)-2,3-Epoxy-1-ethylbutylidenemalononitrile **6**, bp 105 °C at 0.5 mmHg (Found: M^+ , 162.0794. $C_9H_{10}N_2O$ requires M , 162.0793); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2225 (C≡N) and 1590 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.20 (3 H, t, J 7.6, CH_2CH_3), 1.50 (3 H, d, J 5.0, 4- H_2), 2.22 and 2.51 (2 H, each dq, J 12.5 and 7.6, CH_2CH_3), 3.15 (1 H, qd, J 5.0 and 1.7, 3-H) and 3.68 (1 H, d, J 1.7, 2-H); $\delta_{\text{C}}(\text{EX})$ 13.2 and 17.5 (2q, 2 CH_3), 24.8 (t, CH_2), 56.6 and 57.7 (2 d, C-2 and -3), 86.2 [s, $\text{C}(\text{CN})_2$], 110.9 and 111.1 (2 s, 2 CN) and 181.9 (s, C-1); m/z 162 (M^+ , 83%), 147 (100), 119 (56) and 107 (36).

Photoreaction of the dinitrile **2** and EVE

A solution of **2** (265 mg, 1.81 mmol) in dry acetonitrile (35 cm^3) with EVE (13.1 g, 182 mmol) was irradiated with a low-pressure mercury lamp in a quartz test tube (conversion 95%) for 6 h at 0 °C. After removal of the solvent, flash chromatography [SiO_2 A; CH_2Cl_2 -hexane (2:1→5:1)] to afford the *exo*-adduct **14a** (133 mg, 36%), *endo*-adduct **14b** (28.6 mg, 8%) and intractable material (mainly polymers).

(1*R**,5*S**,7*S**)-7-Ethoxy-8-oxabicyclo[3.2.1]octan-2-ylidene-malononitrile (1*R**,5*S**,7*S**)-**14a**, an oil (Found: M^+ , 218.1054. $C_{12}H_{14}N_2O_2$ requires M , 218.1055); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2236 (C≡N) and 1604 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.24 (3 H, t, J 6.9, CH_3), 1.66–1.74, 2.05–2.18, 2.21–2.26, 2.34–2.48 and 2.90–2.98 (6 H, 5 m, 3- H_2 , 4- H_2 and 6- H_2), 3.47 and 3.57 (2 H, each dq, J 8.9 and 6.9, CH_2CH_3), 3.93–3.97 (1 H, m, 7-H), 4.74 (1 H, br s, 5-H) and 5.03 (1 H, s, 1-H); $\delta_{\text{C}}(\text{EX})$ 15.1 (q, CH_3), 25.6, 30.7 and 37.4 (3 t, C-3, -4 and -6), 65.8 (t, CH_2CH_3), 75.0 (d, C-5), 80.9 (d, C-1), 82.7 (d, C-7), 83.4 [s, $\text{C}(\text{CN})_2$], 110.2 and 110.7 (2 s, 2 CN) and 176.5 (s, C-2); m/z 218 (M^+ , 22%), 146 (100), 118 (28) and 91 (32).

(1*R**,5*S**,7*R**)-7-Ethoxy-8-oxabicyclo[3.2.1]octan-2-ylidene-malononitrile (1*R**,5*S**,7*R**)-**14b**, an oil (Found: M^+ , 218.1057. $C_{12}H_{14}N_2O_2$ requires M , 218.1055); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2236 (C≡N), 2218 (C≡N) and 1609 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.17 (3 H, t, J 6.9, CH_3), 1.73 (1 H, ddd, J 13.5, 4.0 and 1.0, 6-H), 1.80–1.87, 2.11–2.24 and 2.91–2.97 (4 H, 3 m, 3- H_2 and 4- H_2), 2.58 (1 H, ddd, J 13.5, 10.2 and 7.6, 6-H), 3.46 and 3.55 (2 H, each dq, J 9.2 and 6.9, CH_2CH_3), 4.37 (1 H, ddd, J 10.2, 6.6 and 4.0, 7-H), 4.46–4.50 (1 H, m, 5-H) and 5.08 (1 H, d, J 6.6, 1-H); $\delta_{\text{C}}(\text{EX})$ 15.3 (q, CH_3), 25.9 and 31.8 (2 t, C-3 and -4), 34.8 (t, C-6), 67.1 (t, CH_2CH_3), 74.7 (d, C-5), 77.5 (d, C-1), 80.4 (d, C-7), 84.8 [s, $\text{C}(\text{CN})_2$], 110.9 and 111.0 (2 s, 2 CN) and 178.0 (s, C-2); m/z 218 (M^+ , 32%), 146 (100), 118 (21) and 91 (26).

Analytical irradiation of **2** containing varying amounts of EVE

Aliquots of a 0.035 mol cm^{-3} solution of **2** in acetonitrile containing EVE (3.5, 2.63, 1.75, 1.05, 0.35, 0.175 and 0.105 mol cm^{-3}) were irradiated in quartz test-tubes under argon for 4 h at 0 °C. Yields and conversions were determined by GLC analysis using octadecane as an internal standard. The results are shown in Table 1.

Photoreaction of the dinitriles **3–6** and EVE

By analogy with the photolysis of **2**, the dinitriles **3**, **4**, **5** and **6** were irradiated with 10 equiv. EVE, affording the corresponding adducts. The results are summarized in Table 2.

(1*R**,5*S**,7*S**)-7-Ethoxy-5-methyl-8-oxabicyclo[3.2.1]octan-2-ylidene-malononitrile (1*R**,5*S**,7*S**)-**15a**, bp 140 °C at 0.2 mmHg (Found: M^+ , 232.1207. $C_{13}H_{16}N_2O_2$ requires M , 232.1212); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2220 (C≡N) and 1595 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.23 (3 H, t, J 6.9, CH_2CH_3), 1.47 (3 H, s, 5- CH_3), 1.73–1.95 and 2.35–2.52 (5 H, 2 m, 3- H_2 , 4- H_2 and 6- H_2), 2.96 (1 H, ddt, J 17.5, 6.3 and 1.7, 3-H), 3.44 and 3.55 (2 H, each dq, J 8.9 and 6.9,

CH_2CH_3), 3.93 (1 H, dd, J 7 and 3, 7-H) and 5.02 (1 H, s, 1-H); $\delta_{\text{C}}(\text{EX})$ 15.1 and 25.3 (2 q, 2 CH_3), 26.9, 36.7 and 43.6 (3 t, C-3, -4 and -6), 65.6 (t, CH_2CH_3), 81.6 (s, C-5), 81.8 and 83.6 (2 d, C-1 and -7), 83.1 [s, $\text{C}(\text{CN})_2$], 110.3 and 110.8 (2 s, 2 CN) and 176.4 (s, C-2); m/z 232 (M^+ , 6%), 160 (100), 145 (10) and 43 (11).

(1*R**,5*S**,7*R**)-7-Ethoxy-5-methyl-8-oxabicyclo[3.2.1]octan-2-ylidene-malononitrile (1*R**,5*S**,7*R**)-**15b**, an oil (Found: M^+ , 232.1203. $C_{13}H_{16}N_2O_2$ requires M , 232.1212); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2225 (C≡N) and 1600 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.16 (3 H, t, J 6.9, CH_2CH_3), 1.35 (3 H, s, 5- CH_3), 1.84–2.00 (3 H, m, 4- H_2 and 6-H), 2.21 (1 H, ddd, J 13.5, 10.2 and 1.0, 6-H), 2.92–2.98 (2 H, m, 3- H_2), 3.44 and 3.52 (2 H, each dq, J 9.2 and 6.9, CH_2CH_3), 4.40 (1 H, ddd, J 10.2, 6.6 and 4.0, 7-H) and 5.10 (1 H, d, J 6.6, 1-H); $\delta_{\text{C}}(\text{EX})$ 15.3 and 26.0 (2 q, 2 CH_3), 27.3, 37.8 and 41.0 (3 t, C-3, -4 and -6), 66.9 (t, CH_2CH_3), 78.6 and 80.7 (2 d, C-1 and -7), 80.7 (s, C-5), 84.7 [s, $\text{C}(\text{CN})_2$], 110.9 and 111.1 (2 s, 2 CN) and 177.9 (s, C-2); m/z 232 (M^+ , 6%), 160 (100), 145 (10) and 43 (12).

8-Ethoxy-9-oxabicyclo[4.2.1]nonan-2-ylidene-malononitrile **16**, an oil (Found: M^+ , 232.1216. $C_{13}H_{16}N_2O_2$ requires M , 232.1212); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2234 (C≡N) and 1592 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.21 (3 H, t, J 7.3, CH_3), 1.59–1.67 and 1.82–2.04 (5 H, 2 m, 4- H_2 , 5- H_2 and 7-H), 2.52 (1 H, dt, J 13.5 and 9, 7-H), 2.57–2.72 (1 H, m, 3-H), 2.96–3.07 (1 H, m with d-character, J 15, 3-H), 3.52 and 3.61 (2 H, each dq, J 9.2 and 7.3, CH_2CH_3), 4.45 (1 H, td, J 9 and 3, 8-H), 4.65–4.71 (1 H, m, 6-H) and 5.21 (1 H, d, J 9, 1-H); $\delta_{\text{C}}(\text{EX})$ 15.1 (q, CH_3), 20.8, 35.0, 35.6 and 35.7 (4 t, C-3, -4, -5 and -7), 67.2 (t, CH_2CH_3), 80.3, 81.0 and 82.3 (3 d, C-1, -6 and -8), 84.1 [s, $\text{C}(\text{CN})_2$], 111.7 and 111.8 (2 s, 2 CN) and 187.1 (s, C-2); m/z 232 (M^+ , 78%), 203 (37), 175 (34) and 160 (100).

2-Cyano-3-(7'-ethoxy-8'-oxabicyclo[3.2.1]octanyl)acrylonitrile **17**, an oil (Found: M^+ , 232.1215. $C_{13}H_{16}N_2O_2$ requires M , 232.1212); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2250 (C≡N) and 1620 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.18 (3 H, t, J 6.9, CH_3), 1.23–1.36 and 1.53–1.82 (6 H, 2 m, 3 CH_2), 2.10–2.15 (2 H, m, 6'- H_2), 3.34 and 3.54 (2 H, each dq, J 8.9 and 6.9, CH_2CH_3), 4.18 (1 H, dd, J 6 and 4, 7'-H), 4.65–4.67 (1 H, m, 5'-H) and 7.25 (1 H, s, 3-H); $\delta_{\text{C}}(\text{EX})$ 15.0 (q, CH_3), 16.8, 28.5 and 32.8 (3 t, C-2', -3' and -4'), 38.1 (t, C-6'), 64.8 (t, CH_2CH_3), 75.8 (d, C-5'), 82.7 (d, C-7'), 86.1 and 88.5 (2 s, C-2 and -1'), 111.2 and 112.8 (2 s, 2 CN) and 167.3 (d, C-3); m/z 232 (M^+ , 36%), 160 (100), 134 (38), 121 (57) and 55 (43).

(4*R**,6*S**)-4-Ethoxy-10-oxabicyclo[4.3.1]dec-1-ene-3,3-dicarbonitrile (4*R**,6*S**)-**18**, an oil (Found: M^+ , 232.1205. $C_{13}H_{16}N_2O_2$ requires M , 232.1212); $\delta_{\text{H}}(\text{EX})$ 1.30 (3 H, t, J 6.9, CH_3), 1.53–1.59, 1.89–2.06, 2.08–2.19 and 2.25–2.32 (7 H, 4 m, 5-H, 7-, 8- and 9- H_2), 2.40 (1 H, dt, J 14.8 and 10, 5-H), 3.73 and 3.87 (2 H, each dq, J 9.2 and 6.9, CH_2CH_3), 4.36 (1 H, dd, J 10 and 2, 4-H), 4.47–4.55 (1 H, m, 6-H) and 5.23 (1 H, d, J 1.0, 2-H); $\delta_{\text{C}}(\text{EX})$ 15.0 (q, CH_3), 25.0, 26.7, 30.3 and 32.4 (4 t, C-5, -7, -8 and -9), 40.4 (s, C-3), 67.6 (t, CH_2CH_3), 77.9 and 80.4 (2 d, C-4 and -6), 104.5 (d, C-2), 114.1 and 115.5 (2 s, 2 CN) and 161.7 (s, C-1); m/z 232 (M^+ , 23%), 160 (100), 134 (46), 121 (81) and 55 (51).

(2'*R**,3'*S**,5'*S**)-2-Cyano-3-(3'-ethoxy-5'-methyltetrahydrofuran-2'-yl)pent-2-enenitrile (2'*R**,3'*S**,5'*S**)-**19a**, an oil (Found: M^+ , 234.1372. $C_{13}H_{18}N_2O_2$ requires M , 234.1368); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2225 (C≡N) and 1595 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.22 (3 H, t, J 7, OCH_2CH_3), 1.25 (3 H, t, J 8, 5- H_3), 1.37 (3 H, d, J 6, 5'- CH_3), 1.67 (1 H, ddd, J 13.2, 9.9 and 6.9, 4'-H), 2.15 (1 H, ddd, J 13.2, 6 and 2, 4'-H), 2.53 and 2.57 (2 H, each dq, J 12.5 and 8, 4- H_2), 3.46 and 3.53 (2 H, each dq, J 8.9 and 7, OCH_2CH_2), 3.85 (1 H, ddd, J 6.9, 4.3 and 2, 3'-H), 4.30 (1 H, m with d-quintet-character, J 9.9 and 6, 5'-H) and 4.67 (1 H, d, J 4.3, 2'-H); $\delta_{\text{C}}(\text{EX})$ 13.1, 15.3 and 19.4 (3 q, 3 CH_3), 27.2 and 40.5 (2 t, C-4 and -4'), 65.7 (t, OCH_2CH_3), 76.7, 85.6 and 85.8 (3 d, C-2', -3' and -5'), 85.0 (s, C-2), 111.2 and 111.9 (2 s, 2 CN) and 183.7 (s, C-3); m/z 234 (M^+ , 3%), 192 (58), 136 (58), 99 (100) and 85 (45).

(2'*R**,3'*R**,5'*S**)-2-Cyano-3-(3'-ethoxy-5'-methyltetrahydrofuran-2'-yl)pent-2-enitrile (2'*R**,3'*R**,5'*S**)-**19b**, an oil (Found: M^+ , 234.1370. $C_{13}H_{18}N_2O_2$ requires M , 234.1368); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2225 (C \equiv N) and 1590 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.13 (3 H, t, J 6.9, OCH_2CH_3), 1.21 (3 H, t, J 7.6, 5-H₃), 1.39 (3 H, d, J 5.9, 5'-CH₃), 1.65 (1 H, ddd, J 13.2, 7.6 and 4.0, 4'-H), 2.36 (1 H, dt, J 13.2 and 6.6, 4'-H), 2.61 and 2.69 (2 H, each dq, J 12.5 and 7.6, 4-H₂), 3.30 and 3.49 (2 H, each dq, J 9.2 and 6.9, OCH_2CH_3), 4.09 (1 H, m with d-quintet-character, J 7.6 and 6, 5'-H), 4.36 (1 H, td, J 6 and 4.0, 3'-H) and 4.81 (1 H, d, J 5.6, 2'-H); $\delta_{\text{C}}(\text{EX})$ 13.0, 15.0 and 20.9 (3 q, 3 CH₃), 27.9 and 39.9 (2 t, C-4 and -4'), 65.4 (t, OCH_2CH_3), 75.7, 81.9 and 83.4 (3 d, C-2', -3' and -5'), 84.4 (s, C-2), 111.6 and 111.8 (2 s, 2 CN) and 186.6 (s, C-3); m/z 234 (M^+ , 5%), 192 (61), 136 (56), 99 (100) and 85 (44).

(2'*R**,3'*S**,5'*R**)-2-Cyano-3-(3'-ethoxy-5'-methyltetrahydrofuran-2'-yl)pent-2-enitrile (2'*R**,3'*S**,5'*R**)-**19c** (contaminated with ca. 20% **18d**), an oil (Found: M^+ , 234.1373. $C_{13}H_{18}N_2O_2$ requires M , 234.1368); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2220 (C \equiv N) and 1595 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.22 (3 H, t, J 6.9, OCH_2CH_3), 1.25 (3 H, t, J 7.6, 5-H₃), 1.35 (3 H, d, J 6.3, 5'-CH₃), 1.75 (1 H, ddd, J 12.2, 8.3 and 7.3, 4'-H), 2.41 (1 H, dt, J 12.2 and 6, 4'-H), 2.48–2.63 (2 H, m, 4-H₂), 3.45 and 3.56 (2 H, each dq, J 9.2 and 6.9, OCH_2CH_3), 3.91 (1 H, q, J 7, 3'-H), 4.45 (1 H, d-quintet, J 8.3 and 6, 5'-H) and 4.75 (1 H, d, J 6.6, 2'-H); $\delta_{\text{C}}(\text{EX})$ 13.1, 15.3 and 21.4 (3 q, 3 CH₃), 26.9 and 39.8 (2 t, C-4 and -4'), 65.9 (t, OCH_2CH_3), 76.5, 83.5 and 84.8 (3 d, C-2', -3' and -5'), 84.4 (s, C-2), 111.4 and 112.2 (2 s, 2 CN) and 185.7 (s, C-3); m/z 234 (M^+ , 3%), 192 (58), 136 (54), 99 (100) and 85 (43).

(2'*R**,3'*R**,5'*R**)-2-Cyano-3-(3'-ethoxy-5'-methyltetrahydrofuran-2'-yl)pent-2-enitrile (2'*R**,3'*R**,5'*R**)-**19d** (contaminated with ca. 80% **19c**), $\delta_{\text{H}}(\text{EX})$ 1.14 (3 H, t, J 6.9, OCH_2CH_3), 1.51–1.62 (1 H, m, 4'-H), 2.23–2.29 (1 H, m with dd-character, J 13 and 5, 4'-H), 3.31 (1 H, dq, J 9.2 and 6.9, OCH_2CH_3), 4.34–4.39 (1 H, m, 3'-H) and 5.04 (1 H, d, J 5.0, 2'-H).

5-Ethoxy-3-ethyl-7-methyl-4,5,6,7-tetrahydrooxepine-4,4-dicarbonitrile **20**, an oil (Found: M^+ , 234.1368. $C_{13}H_{18}N_2O_2$ requires M , 234.1368); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2240 (C \equiv N) and 1645 (C=C); $\delta_{\text{H}}(\text{EX})$ 1.21 (3 H, t, J 7.6, 3- CH_2CH_3), 1.26 (3 H, t, J 6.9, OCH_2CH_3), 1.31 (3 H, d, J 6.3, 7-CH₃), 2.15–2.48 (4 H, m, 6-H₂ and 3- CH_2CH_3), 3.74 (2 H, q, J 6.9, OCH_2CH_3), 4.09 (1 H, dd, J 7.9 and 5.0, 5-H), 4.10–4.23 (1 H, m, 7-H) and 6.45 (1 H, s, 2-H); $\delta_{\text{C}}(\text{EX})$ 13.8, 15.2 and 21.9 (3 q, 3 CH₃), 26.0 and 40.8 (2 t, C-6 and 3- CH_2CH_3), 45.0 (s, C-4), 67.5 (t, OCH_2CH_3), 74.3 (d, C-7), 77.6 (d, C-5), 113.1, 113.3 and 114.6 (3 s, 2 CN and C-3) and 148.5 (d, C-2); m/z 234 (M^+ , 4%), 192 (52), 136 (76), 99 (100) and 85 (56).

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