1,3-DIPOLAR CYCLOADDITIONS OF PHOTOINDUCED CARBONYL YLIDES. PART 3:[1] PHOTOREACTIONS OF α,β-UNSATURATED γ,δ-EPOXY DINITRILE, α-CYANO ESTER, AND DIESTER WITH VARIOUS DIPOLAROPHILES

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Abstract- Photoinduced carbonyl ylide (**A**) from α,β-unsaturated γ,δ-epoxy dinitrile (**1**) undergoes 1,3-dipolar cycloaddition with enol ethers, leading to tetrahydrofuran system with high regioselectivity in moderate yield. However, The cycloadditions of **A** with nonactivated and electron-deficient olefins and with C=N containing dipolarophiles gave the corresponding adducts slightly. The reactivity for the cycloaddition of α-cyano ester (**8**) and diester (**9**) with ethyl vinyl ether decreases.

Introduction

The 1,3-dipolar cycloaddition of a carbonyl ylide with a dipolarophile is an important and useful strategy for tetrahydrofuran formation.[2] In earlier studies[1] we have shown that the carbonyl ylide (**A**) photoinduced (λ = 254 nm) from epoxy dinitrile (**1**) regioselectively undergoes 1,3-dipolar cycloaddition with ethyl vinyl ether (EVE) leading to the *exo*-adduct (**2**) predominantly (Figure 1). In a similar manner, the carbonyl ylides generated from epoxy dinitriles (**3**)-(**5**) (Figure 1) photochemically react with EVE to give the corresponding cycloadducts. However, the ylide from mononitrile (**6**) and the seven-membered ylide from dinitrile (**7**) give little or no adduct. The reactivity of the cycloaddition depends on the LUMO energy level and the C(γ), C(δ) distance of the ylide. Consequently, we are interested in probing the scope and limitation of the cycloaddition for the formation of tetrahydro-furan system. In this paper, we report on the 1,3-dipolar cycloaddtions of the carbonyl ylide (**A**)

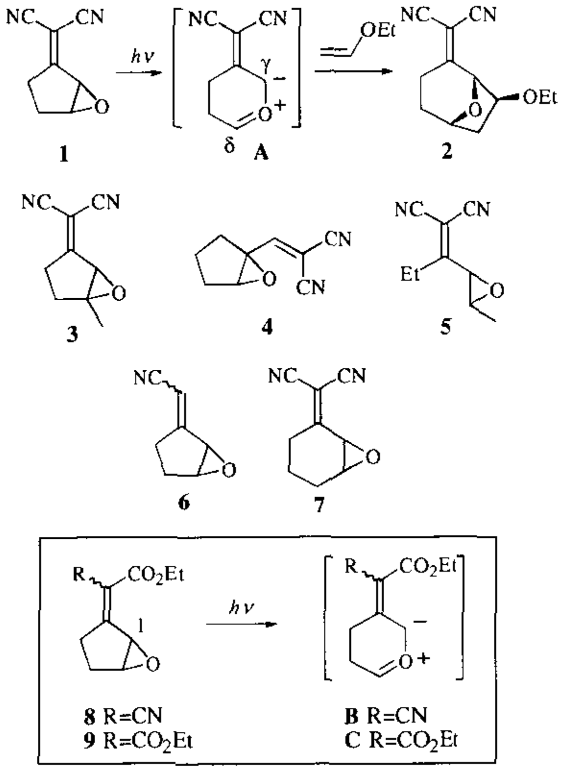
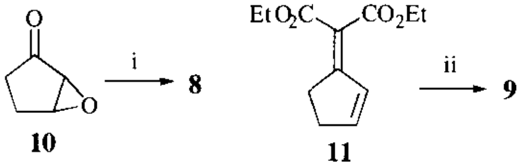


Figure 1

with the other enol ethers, nonactivated and electron-deficient olefins, and C=N containing dipolarophiles. Furthermore, photoreactions of epoxy α-cyano ester (**8**) and diester (**9**) with EVE are studied.

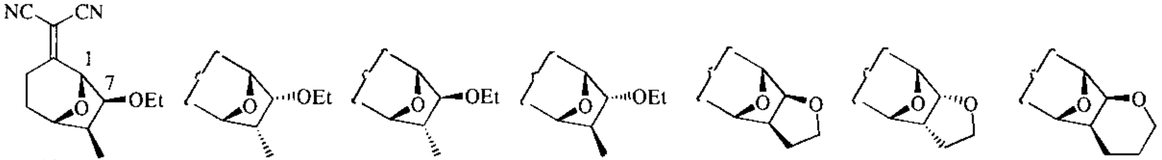
Results and Discussion

The epoxy α-cyano ester (**8**) was prepared from epoxy ketone (**10**)[3] and ethyl cyanoacetate by Knoevenagel condensation[4] in 56 % yield (*E*:*Z* = 3:4). The compound (**9**) was obtained by epoxidation of diester (**11**)[5] with *m*-chloroperbenzoic acid in 37 % yield (Scheme 1). The structures of **8** and **9** were determined from the spectral data. In particular, the *E* and *Z* configuration of **8** was assigned by a comparison of the chemical shift of H-1 in the ^{1}H NMR spectra (δ 4.18 for *E* and 4.96 for *Z*) with those of **1** (δ 4.13)[1] and **9** (δ 4.38) (see EXPERIMENTAL).



Scheme 1 *Reagents and conditions*: i, ethyl cyanoacetate, AcNH$_4$, AcOH, benzene, 80 °C; ii, *m*-CPBA, dichloromethane, rt

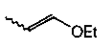
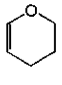
Preparative irradiation of the dinitrile (**1**) and 10 equiv. of enol ethers (ethyl 1-propenyl ether, 2,3-dihydrofuran, and 3,4-dihydro-2*H*-pyran) in acetonitrile with a low-pressure mercury lamp through a quartz filter (λ = 254 nm) at 0 °C afforded the corresponding adducts (**12**)-(**14**) (Figure 2). The results are summarized in Table 1. The reactions proceed with high regioselectivity and preferred formation of *exo*- adduct, which can be rationalized in terms of the interaction between the coefficients of LUMO (**A**) and HOMO (enol ether) for thermal cycloaddition as discussed in the earlier report.[1]



12a **12b** **12c** **12d** **13a** **13b** **14**

Figure 2

Table 1 Photoreactions of the nitrile (**1**) with enol ethers[a]

Enol ether	Irradiation Time (h)	Conversion (%)	Yields (%)[b]
	6	94	**12a** (19), **12b** (10), **12c** (3), and **12d** (1)
	2.5	97	**13a** (21) and **13b** (5)
	7	98	**14** (7)

[a] A 0.035 mol L^{-1} solution of **1** in acetonitrile with 10 equiv. of enol ether was irradiated at 0 °C. [b] Isolated yield.[6]

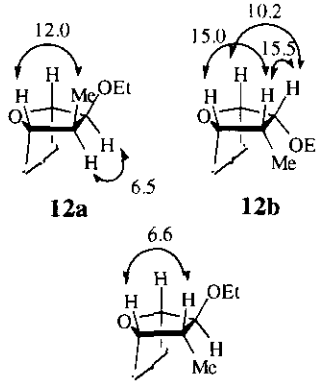


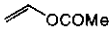
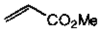
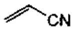
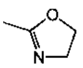
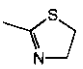
Figure 3 NOE enhancement (%) of **12a-c**

Although ethyl 1-propenyl ether was *trans* rich (*E*:*Z* = 3:1) and the *E*/*Z*-isomerization could not be observed under these reaction conditions, the *cis*-adducts (**12a**) and (**12b**) were predominantly obtained. The results may show that the activation energy for the addition of the *Z* ether and **A** is smaller than that for the *E* ether and **A**.[7]

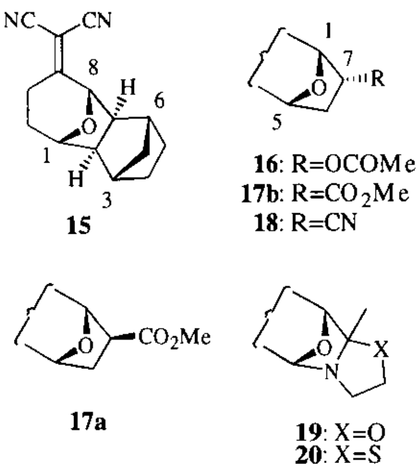
The structures of the adducts (**12**)-(**14**) were inferred from their spectral data. The assignment of the *exo* and *endo* configuration of **12-14** is made by the coupling constant of H-1 in the ^{1}H NMR spectra in the same manner as described in the previous report.[1] As characteristic signals for **12a-d**, the ^{13}C NMR spectra have three doublets at 78.7-89.9 ppm due to C-1, C-5, and C-7 and a doublet at 37.7-45.0 ppm due to C-6. The stereochemistry at C-1, C-5, C-6, and C-7 in **12a-c** was assigned as *rel*-(1*R*,5*S*,6*S*,7*S*) for **a**, *rel*-(1*R*,5*S*,6*R*,7*R*) for **b**, and *rel*-(1*R*,5*S*,6*R*,7*S*) for **c** by using the characteristic NOE enhancements between H-5, H-6, H-7, and Me-6. These results are shown in Figure 3. The stereochemistry of **12d** was deduced from a comparison of the ^{1}H and ^{13}C NMR and H-H and C-H COSY spectral data of a mixture of **12b** and **12d** with those of **12a-c** and may be assigned as *rel*-(1*R*,5*S*,6*S*,7*R*).

Since the reaction of the carbonyl ylide (**A**) and enol ethers had given the cycloadducts in moderate yield, the cycloadditions of the ylide (**A**) with bicyclo[2.2.1]hept-2-ene, vinyl acetate, methyl acrylate, acrylonitrile, 2-methyl-2-oxazoline, and 2-methyl-2-thiazoline were studied under the same conditions as described in Table 1 and afforded the adducts (**15**)-(**20**) (Figure 4). The results are summarized in Table 2. The structure of the cycloadduct (**15**) was determined on the basis of the spectral data (MS, ^{1}H and ^{13}C NMR, and H-H and C-H COSY spectra). The stereochemistry *rel*-(1*R*,2*S*,3R,6S,7*R*,8*R*) in **15** was established by the NOESY spectrum; there are crosspeaks between H-1 and H-3, between H-6 and H-8, and between H-2 or H-7 and H-4 or H-5.

Table 2 Photoreactions of the nitrile (**1**) with other dipolarophiles[a]

Dipolarophile	Irradiation time (h)	Conversion (%)	Yields (%)[b]
	2.5	70	**15** (4)
	3.5	93	**16** (1)
	6	68	**17a** (4) and **17b** (2)
	5	96	**18** (1)
	3.5	100	**19** (10)
	6	100	**20** (8)

[a] A 0.035 mol L^{-1} solution of **1** in acetonitrile with 10 equiv. of dipolarophile was irradiated at 0 °C. [b] Isolated yield.[6]



15

16: R=OCOMe
17b: R=CO_2Me
18: R=CN

17a

19: X=O
20: X=S

Figure 4

The yield of the cycloaddition of **A** and vinyl acetate decreases in comparison with that of **A** and enol ethers. The difference of the reactivity can be explained by the energy gap of LUMO (**A**)-HOMO (dipolarophile); the energy gap for vinyl acetate (ΔE = 8.11 eV) is larger than that for EVE (ΔE = 7.56 eV).[8,9] On the other hand, the cycloadditions of **A** with methyl acrylate and with acrylonitrile afford the head-head adducts (**17**) and (**18**). On the basis of the frontier MO consideration,[10] the regiochemistry of the adduct in thermal process ought to be head-tail type predominantly.[11] The mechanism for the formation of **17** and **18** is not yet clear.

The stereo- and regiochemistry of **16**-**20** was determined by mean of the ^{1}H and ^{13}C NMR spectra and/or H-H and C-H COSY spectra. In particular, the H-H COSY spectrum of **17b** has crosspeaks between H-1 and H-7 and between H-5 and H-6.

However, the photoreactions of **1** with 1-methylcyclopentene, cyclohexene, isoprene, allyl acetate, dimethyl acetylenedicarboxylate, and 2-cyclopentenone gave no cycloadduct.

The epoxy dinitriles and EVE undergo regioselectively 1,3-dipolar cycloaddition leading to the adducts. Consequently, the reactions of the epoxy cyanoacetate (**8**) and the epoxy diester (**9**) were also studied in the presence of EVE. These compounds bear one or two ester functions in place of the cyano group of **1**. Preparative irradiation of **8** and EVE (10 equiv.) under the same conditions as described in Table 1 gave adducts ((*E*/*Z*)-**21**) in 2 % yield.[6] The reaction of **9** with EVE, however, failed to afford a cycloadduct but, instead, gave α,β-unsaturated ketone (**22**) (74%)[6] (Scheme 2), whose analogue was also isolated in the reaction of epoxy mononitrile (**6**) and EVE.[1]

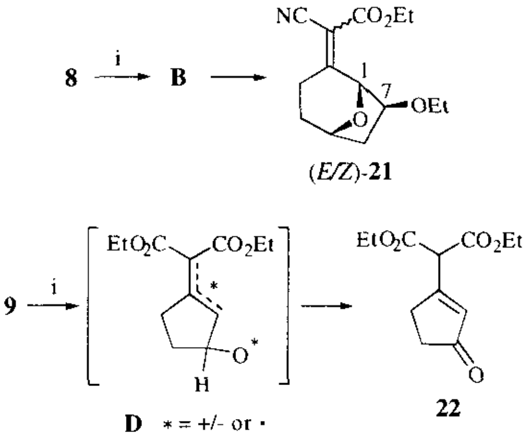
The decrease of the reactivity in the cycloaddition of the carbonyl ylides (**B**) and (**C**) with EVE could be explained by the LUMO (ylide)-HOMO (EVE) energy gap (Table 3); the yield of adducts increases as the energy gap decreases.

The structures of **21** and **22** were determined from a comparison of the spectral date with those of the analogous compounds described in ref. 1.

Table 3 LUMO energies for carbonyl ylides (**A**), (**B**) and (**C**)

Carbonyl ylide	LUMO energy (eV)	Energy separation[a] (ΔE/eV)	Yields of adducts (%)[b]
A[c]	-1.79	7.56	44
B	-1.72	7.64	2
C	-1.56	7.80	0

[a] LUMO (ylide) – HOMO (EVE; -9.36 eV).
[b] Isolated yield.[6] [c] Ref. 1.



Scheme 2 *Reagents and conditions*: i, λ=254 nm, MeCN, EVE

In summary, the carbonyl ylide (**A**) generated photochemically from **1** and enol ethers undergo regioselectively 1,3-dipolar cycloaddition leading to tetrahydrofuran system in moderate yield. The cycloadditions of **A** with nonactivated and electron deficient olefins and with C=N dipolarophiles afforded the corresponding adducts slightly. The decrease of the reactivity for the cycloaddition of **8** and **9** with EVE can be explained by the higher LUMO level in the ylides (**B**) and (**C**) than that in **A**.

EXPERIMENTAL

General Procedures

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 spectrophotometer and IR spectra on a Hitachi 215 spectrophotometer. NMR spectra were obtained with a JEOL JNM-EX270 (270 MHz; EX), a JEOL JNM-GX400 (400 MHz; GX), or a JEOL JNM-LA500 (500 MHz; LA) spectrometer in $CDCl_3$ solutions using tetramethylsilane as an internal standard and *J* values are given in Hz. MS and HRMS were taken on a JEOL JMS-DX302 spectrometer. Column chromatography was performed with Nakarai silica gel 60 (230-400 mesh). An Eikosha 60 W low-pressure mercury lamp was used for irradiation. The photolysis solutions were purged with argon both before and during irradiation.

Preparation of epoxy cyanoacetate (8) and epoxy diester (9)

Preparation of 8. A suspension of the epoxy ketone (**10**)[3] (1.00 g, 10.2 mmol), ethyl cyanoacetate (1.15 g, 10.2 mmol), ammonium acetate (157 mg, 2.04 mmol), and acetic acid (0.61 g, 10.2 mmol) in benzene (4 mL) was placed in a flask fitted with a water separator and refluxed for 4 h. After cooling the reaction mixture, sat. aqueous sodium bicarbonate (5 mL) was added. The reaction mixture was extracted with ether, the extracts were washed with brine, dried over magnesium sulfate, and concentrated *in vacuo* giving a residue that was subjected to flash chromatography [hexane-ethyl acetate (2:1)] to afford the epoxy cyanoacetate ((*E*)-**8**) (470 mg, 24%) and ((*Z*)-**8**) (631 mg, 32%).

(*E*)-Ethyl 6-oxabicyclo[3.1.0]hexan-2-ylidenecyanoacetate ((*E*)-**8**) [contaminated with *ca.* 30% of (*Z*)-**8**], an oil; ^{1}H NMR δ (EX): 1.36 (3H, t, *J*=7.3, CH_3), 1.90-2.09 (1H, m, H-4), 2.22-2.45 (2H, m, H-3, H-4), 3.39 (1H, m with dd-character, *J*=20, 9, H-3), 3.98-4.00 (1H, m, H-5), 4.18 (1H, d, *J*=2.3, H-1), 4.30 (2H, q, *J*=7.3, $OC\underline{H}_2CH_3$); ^{13}C NMR δ (EX): 14.1 (q, CH_3), 26.6, 27.5 (2t, C-3, C-4), 58.7, 60.5 (2d, C-1, C-5), 62.2 (t, $O\underline{C}H_2CH_3$), 105.0 (s, $\underline{C}CO_2Et$), 114.5 (s, CN), 161.1, 177.1 (2s, C-2, CO).

(*Z*)-Ethyl 6-oxabicyclo[3.1.0]hexan-2-ylidenecyanoacetate ((*Z*)-**8**), bp 160 °C at 0.4 mmHg; ^{1}H NMR δ (EX): 1.38 (3H, t, *J*=7.3, CH_3), 1.88-2.01 (1H, m, H-4), 2.28 (1H, m with dd-character, *J*=14, 7, H-4), 2.54 (1H, dt, *J*=18.8, 8.3, H-3), 2.83 (1H, ddd, *J*=18.8, 9, 1, H-3), 3.98-4.00 (1H, m, H-5), 4.34 (2H, q, *J*=7.3, $OC\underline{H}_2CH_3$), 4.96 (1H, d, *J*=2.6, H-1); ^{13}C NMR δ (EX): 14.1 (q, CH_3), 25.2, 29.4 (2t, C-3, C-4), 54.6, 61.8 (2d, C-1, C-5), 62.3 (t, $O\underline{C}H_2CH_3$), 106.5 (s, $\underline{C}CO_2Et$), 114.5 (s, CN), 160.9, 176.7 (2s, C-2, CO). IR ν_{max} film cm^{-1}: 2220 (C≡N), 1720 (C=O), 1630 (C=C). MS *m/z*: 193 (M^+, 2%), 165 (62), 148

(42), 137 (100), 123 (70). HRMS *m/z*: Calcd for $C_{10}H_{11}NO_3$, 193.0739. Found: 193.0738 (M^+).

Preparation of 9. To a solution of the diester (**11**)[5] (8.13 g, 36.3 mmol) in 0.5 mol L^{-1} aqueous sodium bicarbonate (190 mL) and dichloromethane (270 mL) was added dropwise a solution of *m*-chloroperbenzoic acid (80%; 11.2 g, 51.9 mmol) in dichloromethane (190 mL) at 0 °C. The reaction mixture was stirred for 24 h at rt and extracted with dichloromethane, after which the extracts were combined, washed with 10% aqueous sodium thiosulfate, and subjected to the same work-up as used for synthesis of **8**. Flash chromatography [hexane-ethyl acetate (2:1)] of the residue gave the epoxy diester (**9**) (3.19 g, 37%).

Diethyl 6-oxabicyclo[3.1.0]hexan-2-ylidenemalonate (**9**), bp 130 °C at 0.15 mmHg; ^{1}H NMR δ (GX): 1.30 and 1.33 (6H, each t, *J*=7.0, $2CH_3$), 1.83-1.88 (1H, m, H-4), 2.20 (1H, ddd, *J*=14.0, 8.6, 0.5, H-4), 2.35 (1H, dt, *J*=18.6, 8.6, H-3), 2.80 (1H, ddd, *J*=18.6, 9.4, 1, H-3), 3.85 (1H, dd, *J*=2.4, 1.6, H-5), 4.20-4.34 (4H, m, $2OC\underline{H}_2CH_3$), 4.38 (1H, d, *J*=2.4, H-1); ^{13}C NMR δ (EX): 14.1 (2q, $2CH_3$), 26.1, 26.4 (2t, C-3, C-4), 56.1, 60.2 (2d, C-1, C-5), 61.2, 61.5 (2t, $2O\underline{C}H_2CH_3$), 125.9 [s, $\underline{C}(CO_2Et)_2$], 160.2, 164.6, 164.7 (3s, C-2, 2CO). IR ν_{max} film cm^{-1}: 1720 (C=O), 1655 (C=C); MS *m/z*: 240 (M^+, 1%), 212 (27), 195 (39), 166 (100), 138 (83), 124 (26). HRMS *m/z*: Calcd for $C_{12}H_{16}O_5$, 240.0997. Found: 240.0993 (M^+).

Photoreaction of dinitriles (1) with various dipolarophiles

A 0.035 mol L^{-1} solution of **1** in dry acetonitrile with 10 equiv. dipolarophile was irradiated with a low-pressure mercury lamp in a quartz test tube at 0 °C. After removal of the solvent, flash chromatography afforded the adduct and intractable material (mainly polymers). Yields and conversion were determined by ^{1}H NMR analysis of the chromatographic fractions. The results summarized in Tables 1 and 2.

With ethyl 1-propenyl ether. *rel*-(1*R*,5*S*,6*S*,7*S*)-7-Ethoxy-6-methyl-8-oxabicyclo[3.2.1]octan-2-ylidenemalononitrile (*rel*-(1*R*,5*S*,6*S*,7*S*)-**12a**), mp 47-48.5 °C (hexane-ethyl acetate); ^{1}H NMR δ (GX): 1.15 (3H, d, *J*=7.3, CH_3-6), 1.24 (3H, t, *J*=7.1, $CH_2C\underline{H}_3$), 1.73-1.79, 2.06-2.14, 2.42-2.51 (4H, 3m, H-3, 2H-4, H-6), 2.94 (1H, ddd, *J*=17.6, 6.8, 1.2, H-3), 3.43, 3.64 (2H, each dq, *J*=9.0, 7.1, $C\underline{H}_2CH_3$), 3.79 (1H, d, *J*=7.6, H-7), 4.20 (1H, br d, *J*=3.4, H-5), 5.01 (1H, s, H-1); ^{13}C NMR δ (EX): 14.0, 15.0 (2q, $2CH_3$), 25.8, 30.2 (2t, C-3, C-4), 41.6 (d, C-6), 66.9 (t, $\underline{C}H_2CH_3$), 82.4, 82.9, 83.9 (3d, C-1, C-5, C-7), 83.2 [s, $\underline{C}(CN)_2$], 110.3, 110.7 (2s, 2CN), 177.4 (s, C-2). IR ν_{max} $CHCl_3$ cm^{-1}: 2236 (C≡N), 1601 (C=C). MS *m/z*: 232 (M^+, 53%), 146 (100), 91 (22), 87 (27), 59 (22). HRMS *m/z*: Calcd for $C_{13}H_{16}N_2O_2$, 232.1212. Found: 232.1213 (M^+).

rel-(1*R*,5*S*,6*R*,7*R*)-7-Ethoxy-6-methyl-8-oxabicyclo[3.2.1]octan-2-ylidenemalononitrile (*rel*-(1*R*,5*S*,6*R*, 7*R*)-**12b**) (contaminated with *ca.* 15% of **12d**), crystals; ^{1}H NMR δ (GX) 1.03 (3H, d, *J*=7.6, CH_3-6), 1.15 (3H, t, *J*=7.1, $CH_2C\underline{H}_3$), 1.88-1.95, 2.02-2.13 (2H, 2 m, 2H-4), 2.62 (1H, d-quintet, *J*=10.0, 7, H-6), 2.83-2.87 (2H, m, 2H-3), 3.46, 3.56 (2H, each dq, *J*=9.3, 7.1, $C\underline{H}_2CH_3$), 4.24-4.29 (2H, m, H-5, H-7), 5.16 (1H, d, *J*=6.8, H-1); ^{13}C NMR δ (EX) 9.0 (q, CH_3-6), 15.2 (q, $CH_2\underline{C}H_3$), 26.0, 26.5 (2t, C-3, C-4), 37.7 (d, C-6), 67.8 (t, $\underline{C}H_2CH_3$), 78.0, 78.6, 80.4 (3d, C-1, C-5, C-7), 84.1 [s, $\underline{C}(CN)_2$], 111.0, 111.0 (2s, 2CN), 179.2 (s, C-2). IR ν_{max} $CHCl_3$ cm^{-1}: 2236 (C≡N), 1601 (C=C). MS *m/z*: 232 (M^+, 45%), 146 (100), 91 (24), 87 (29), 59 (25). HRMS *m/z*: Calcd for $C_{13}H_{16}N_2O_2$, 232.1212. Found: 232.1212 (M^+).

rel-(1*R*,5*S*,6*R*,7*S*)-7-Ethoxy-6-methyl-8-oxabicyclo[3.2.1]octan-2-ylidenemalononitrile (*rel*-(1*R*,5*S*,6*R*,7*S*)-**12c**), mp 62-65 °C (hexane-ethyl acetate); ^{1}H NMR δ (GX): 1.23 (3H, d, *J*=7.3, CH_3-6), 1.25 (3H, t, *J*=7.1, $CH_2C\underline{H}_3$), 1.89 (1H, dd, *J*=14.2, 7.8, H-4), 2.04-2.13 (1H, m, H-4), 2.38 (1H, ddd, *J*=18, 11, 8, H-3), 2.55 (1H, quintet-d, *J*=7.3, 4.4, H-6), 2.92-2.98 (1H, m, H-3), 3.44-3.52 (2H, m, H-7, $C\underline{H}_2CH_3$), 3.56 (1H, dq. *J*=9.0, 7.1, $C\underline{H}_2CH_3$), 4.44-4.47 (1H, m, H-5), 4.94 (1H, s, H-1); ^{13}C NMR δ (EX): 13.2, 15.2 (2q, 2CH_3), 25.8, 26.2 (2t, C-3, C-4), 45.0 (d, C-6), 66.2 (t, $\underline{C}H_2CH_3$), 78.4, 81.4, 89.9 (3d, C-1, C-5, C-7), 83.0 [s, $\underline{C}(CN)_2$], 110.3, 110.7 (2s, 2CN), 177.0 (s, C-2). IR ν_{max} $CHCl_3$ cm^{-1}: 2236 (C≡N), 1600 (C=C). MS *m/z*: 232 (M$^+$, 16%), 146 (100), 91 (30). HRMS *m/z*: Calcd for $C_{13}H_{16}N_2O_2$, 232.1212. Found: 232.1212 (M$^+$).

rel-(1*R*,5*S*,6*S*,7*R*)-7-Ethoxy-6-methyl-8-oxabicyclo[3.2.1]octan-2-ylidenemalononitrile (*rel*-(1*R*,5*S*,6*S*,7*R*)-**12d**) (contaminated with *ca.* 85% of **12b**), an oil; ^{1}H NMR δ (GX): 1.29 (3H, d, *J*=7.1, CH_3-6), 3.87 (1H, dd, *J*=6.5, 3.6, H-7), 3.97-3.99 (1H, m, H-5), 5.13 (1H, d, *J*=6.5, H-1); ^{13}C NMR δ (EX): 20.7 (q, CH_3-6), 26.2, 31.1 (2t, C-3, C-4), 42.7 (d, C-6), 67.0 (t, $\underline{C}H_2CH_3$), 78.7, 82.0, 88.5 (3d, C-1, C-5, C-7), 178.0 (s, C-2).

With 2,3-dihydrofuran. *rel*-(1*R*,2*S*,6*S*,7*S*)-3,11-Dioxatricyclo[5.3.1.0^{2,6}]undecan-10-ylidenemalononitrile (*rel*-(1*R*,2*S*,6*S*,7*S*)-**13a**), an oil; ^{1}H NMR δ (GX): 1.81-1.95, 2.04-2.13, 2.22-2.30 (4H, 3 m, 2H-5, 2H-8), 2.37-2.46 (1H, m with ddd-character, *J*=17, 11, 7, H-9), 2.83-2.89 (1H, m, H-6), 2.94 (1H, ddd, *J*=17, 6, 0.7, H-9), 3.79 (1H, dt, *J*=8.3, 6, H-4), 3.98 (1H, dt, *J*=8.3, 6.8, H-4), 4.39 (1H, m with d-character, *J*=3.7, H-7), 4.47 (1H, d, *J*=6.6, H-2), 5.02 (1H, d, *J*=1.2, H-1); ^{13}C NMR δ (GX): 26.2, 31.0, 33.4 (3t, C-5, C-8, C-9), 47.7 (d, C-6), 69.9 (t, C-4), 82.2 (d, C-7), 83.1 (d, C-1), 84.0 [s, $\underline{C}(CN)_2$], 85.8 (d, C-2), 110.2, 110.8 (2s, 2CN), 175.1 (s, C-10). IR ν_{max} film cm^{-1}: 2238 (C≡N), 1605 (C=C). MS *m/z*: 216 (M$^+$, 50%), 146 (100), 118 (24), 91 (28), 71 (26). HRMS *m/z*: Calcd for $C_{12}H_{12}N_2O_2$, 216.0899. Found: 216.0893 (M$^+$).

rel-(1*R*,2*R*,6*R*,7*S*)-3,11-Dioxatricyclo[5.3.1.0^{2,6}]undecan-10-ylidenemalononitrile (*rel*-(1*R*,2*R*,6*R*,7*S*)-**13b**), mp 101.5-104 °C (hexane-ethyl acetate); ^{1}H NMR δ (GX): 1.71-1.80 (1H, m, H-5), 1.91 (1H, ddd, *J*=14.2, 7.8, 2.0, H-8), 1.96-2.05 (1H, m, H-5), 2.24 (1H, dtd, *J*=14.2, 8.5, 5.9, H-8), 2.77 (1H, dd, *J*=18, 9, H-9), 2.86 (1H, ddd, *J*=18, 8.5, 2.9, H-9), 3.26 (1H, tt, *J*=9, 7, H-6), 4.01 (1H, td; *J*=9.5, 7.1, H-4), 4.26 (1H, m with td-character, *J*=9, 2.9, H-4), 4.41-4.45 (1H, m with t-character, *J*=7 , H-7), 4.88 (1H, dd, *J*=9, 6.8, H-2), 5.09 (1H, d, *J*=6.8, H-1); ^{13}C NMR δ (GX): 24.4, 25.3, 26.0 (3t, C-5, C-8, C-9), 47.5 (d, C-6), 74.6 (t, C-4), 75.4 (d, C-7), 78.0 (d, C-1), 84.7 [s, $\underline{C}(CN)_2$], 86.7 (d, C-2), 110.7, 111.0 (2s, 2CN), 177.8 (s, C-10). IR ν_{max} $CHCl_3$ cm^{-1}: 2240 (C≡N), 1604 (C=C). MS *m/z*: 216 (M$^+$, 42%), 146 (100), 118 (22), 91 (34) and 71 (33). HRMS *m/z*: Calcd for $C_{12}H_{12}N_2O_2$, 216.0899. Found: 216.0893 (M$^+$).

With 3,4-dihydro-2*H*-pyran. *rel*-(1*R*,2*S*,7*S*,8*S*)-3,12-Dioxatricyclo[6.3.1.0^{2,7}]dodecan-11-ylidenemalononitrile (*rel*-(1*R*,2*S*,7*S*,8*S*)-**14**), an oil; ^{1}H NMR δ (EX): 1.47-1.95, 2.05-2.30 (7H, 3m, 2H-5, 2H-6, H-7, 2H-9), 2.41 (1H, ddd, *J*=16.8, 11.2, 7.6, H-10), 2.91-3.00 (1H, m with ddd-character, *J*=16.8, 6.3, 1.7, H-10), 3.54 (1H, ddd, *J*=11.2, 8.6, 5.3, H-4), 3.86-3.98 (2H, m, H-4, H-8), 4.27 (1H, d, *J*=3.6, H-2), 5.00 (1H, s, H-1); ^{13}C NMR δ (EX) 20.3, 20.5, 26.2, 31.4 (4t, C-5, C-6, C-9, C-10), 43.6 (d, C-7), 62.4 (t, C-4), 79.5 (d, C-8), 81.6 (d, C-2), 82.9 (d, C-1), 84.0 [s, $\underline{C}(CN)_2$], 110.3, 110.8 (2s, 2CN), 175.7 (s, C-11).

IR ν_{max} film cm^{-1}: 2236 (C≡N), 2220 (C≡N), 1607 (C=C). MS *m/z*: 230 (M$^+$, 46%), 182 (27), 146 (100), 110 (20), 91 (20), 85 (50). HRMS *m/z*: Calcd for $C_{13}H_{14}N_2O_2$, 230.1055. Found: 230.1057 (M$^+$).

With bicyclo[2.2.1]hept-2-ene. *rel*-(1*R*,2*S*,3R,6S,7*R*,8*R*)-13-Oxatetracyclo[6.3.1.1^{3,6}.0^{2,7}]tridecan-9-ylidenemalononitrile (*rel*-(1*R*,2*S*,3R,6S,7*R*,8*R*)-**15**), mp 87-92 °C (hexane-diethyl ether); ^{1}H NMR δ (LA): 1.03 (1H, td, *J*=10.1, 1.5, H-12), 1.17-1.21 (2H, m, H-4, H-5), 1.47-1.53 (2H, m, H-4, H-5), 1.80 (1H, ddd, *J*=13.4, 7.3, 0.9, H-11), 1.90 (1H, d-quintet, *J*=10.1, 2.1, H-12), 1.94 (1H, d, *J*=7, H-7), 2.00-2.08 (1H, m, H-11), 2.07 (1H, d, *J*=7, H-2), 2.27 (1H, br s, H-3), 2.34 (1H, br s, H-6), 2.58 (1H, ddd, *J*=16.8, 11, 7.3, H-10), 2.80-2.86 (1H, m with ddd-character, *J*=16.8, 6.4, 1.5, H-10), 4.20 (1H, d, *J*=4.0, H-1), 4.81 (1H, s, H-8); ^{13}C NMR δ (LA): 25.6 (t, C-10), 28.4, 28.6 (2t, C-4, C-5), 32.7 (t, C-11), 34.0 (t, C-12), 40.6 (d, C-3), 41.2 (d, C-6), 51.3 (d, C-2), 52.7 (d, C-7), 80.1 (d, C-1), 81.4 (d, C-8), 81.5 [s, $\underline{C}(CN)_2$], 110.6, 111.0 (2s, 2CN), 178.7 (s, C-9). IR ν_{max} $CHCl_3$ cm^{-1}: 2225 (C≡N), 1600 (C=C). MS *m/z*: 240 (M$^+$, 81%), 211 (18), 121 (100), 79 (20), 67 (22). *Anal.* Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.89; H, 6.77; N, 11.57.

With vinyl acetate. *rel*-(1*R*,5*S*,7*R*)-2-Dicyanomethyliden-8-oxabicyclo[3.2.1]octan-7-yl acetate (*rel*-(1*R*,5*S*,7*R*)-**16**), an oil (contaminated with *ca.* 20% unknown compounds); ^{1}H NMR δ (LA): 1.77 (1H, ddd, *J*=14.0, 4.0, 0.9, H-4), 1.87 (1H, dd, *J*=14.0, 8, H-4), 2.18-2.26, 2.74-2.83 (3H, 2m, H-3, 2H-6), 3.01 (1H, m with ddd-character, *J*=17.4, 6.4, 1.5, H-3), 4.52-4.56 (1H, m, H-5), 5.22 (1H, d, *J*=6.7, H-1), 5.37 (1H, ddd, *J*=10.7, 6.7, 4.0, H-7); ^{13}C NMR δ (LA): 20.7 (q, CH_3), 25.5, 31.5, 34.2 (3t, C-3, C-4, C-6), 73.9, 74.5, 76.6 (3d, C-1, C-5, C-7), 85.8 [s, $\underline{C}(CN)_2$], 110.2, 110.8 (2s, 2CN), 169.9, 175.2 (2s, C-2, CO).

With methyl acrylate. *rel*-(1*R*,5*R*,7*R*)-Methyl 2-dicyanomethylidene-8-oxabicyclo[3.2.1]octane-7-carboxylate (*rel*-(1*R*,5*R*,7*R*)-**17a**), mp 68-70 °C (hexane-ethyl acetate); ^{1}H NMR δ (EX): 1.77-1.86, 2.09-2.23, 2.48-2.69, 2.90-3.03 (7H, 4m, 2H-3, 2H-4, 2H-6, H-7), 3.78 (3H, s, CH_3), 4.67-4.72 (1H, m, H-5), 5.41 (1H, s, H-1); ^{13}C NMR δ (EX): 25.0, 31.7, 31.8 (3t, C-3, C-4, C-6), 47.9 (d, C-7), 53.0 (q, CH_3), 75.5 (d, C-5), 78.8 (d, C-1), 83.5 [s, $\underline{C}(CN)_2$], 110.1, 110.7 (2s, 2CN), 171.9, 176.3 (2s, C-2, CO). IR ν_{max} $CHCl_3$ cm^{-1}: 2238 (C≡N), 1741 (C=O), 1609 (C=C). MS *m/z*: 232 (M$^+$, 100%), 203 (87), 172 (51), 171 (56), 143 (86), 113 (70). HRMS *m/z*: Calcd for $C_{12}H_{12}N_2O_3$, 232.0848. Found: 232.0846 (M$^+$).

rel-(1*R*,5*R*,7*S*)-Methyl 2-dicyanomethylidene-8-oxabicyclo[3.2.1]octane-7-carboxylate (*rel*-(1*R*,5*R*,7*S*)-**17b**), mp 79.5-82 °C (hexane-ethyl acetate); ^{1}H NMR δ (GX): 1.87 (1H, dd, *J*=13.7, 7.6, H-4), 2.12-2.21 (1H, m, H-4), 2.29 (1H, ddd, *J*=13, 6.6, 1.5, H-6), 2.47 (1H, m with td-character, *J*=13, 7.8, H-6), 2.69 (1 H, ddd, *J*=17.6, 11.5, 7.6, 3-H), 2.92 (1H, m with ddd-character, *J*=17.6, 6.6, 1.5, H-3), 3.58 (1H, ddd, *J*=12.0, 7.3, 6.6, H-7), 3.74 (3H, s, CH_3), 4.61-4.63 (1H, m, H-5), 5.28 (1H, d, *J*=7.3, H-1); ^{13}C NMR δ (GX): 25.1, 29.9, 32.2 (3t, C-3, C-4, C-6), 48.8 (d, C-7), 52.6 (q, CH_3), 75.5 (d, C-5), 77.4 (d, C-1), 85.0 [s, $\underline{C}(CN)_2$], 110.3, 110.7 (2s, 2CN), 170.3, 175.7 (2s, C-2, CO). IR ν_{max} $CHCl_3$ cm^{-1}: 2240 (C≡N), 1740 (C=O), 1606 (C=C). MS *m/z*: 232 (M$^+$, 48%), 200 (92), 172 (100), 171 (46), 143 (83), 113 (45). HRMS *m/z*: Calcd for $C_{12}H_{12}N_2O_3$, 232.0848. Found: 232.0844 (M$^+$).

With acrylonitrile. *rel*-(1*R*,5*R*,7*R*)-7-Cyano-8-oxabicyclo[3.2.1]octan-2-ylidenemalononitrile (*rel*-(1*R*, 5*R*,7*R*)-**18**), an oil; ^{1}H NMR δ (LA): 1.91 (1H, dd, *J*=13.7, 7, H-4), 2.18 (1H, ddd, *J*=13.4, 5.8, 1.5, H-6), 2.18-2.26 (1H, m, H-4), 2.73 (1H, dddd, *J*=13.4, 12.5, 7.3, 0.9, H-6), 2.81 (1H, ddd, *J*=18.0, 11, 7, H-3), 3.09 (1H, ddq, *J*=18.0, 6.4, 1.5, H-3), 3.45 (1H, ddd, *J*=12.5, 7.0, 5.8, H-7), 4.68-4.71 (1H, m, H-5), 5.32 (1H, dd, *J*=7.0, 1, H-1); ^{13}C NMR δ (LA): 24.6 (t, C-3), 31.5 (t, C-4), 31.9 (d, C-7), 32.9 (t, C-6), 75.4 (d, C-5), 77.0 (d, C-1), 86.7 [s, $\underline{\mathrm{C}}\mathrm{(CN)_2}$], 109.9, 110.1, 116.8 (3s, 3CN), 172.2 (s, C-2). IR ν_{max} $\mathrm{CHCl_3}$ cm^{-1}: 2220 (C≡N), 1600 (C=C). MS *m/z*: 199 (M$^+$, 100%), 170 (60), 146 (87), 91 (40), 80 (73). HRMS *m/z*: Calcd for $\mathrm{C_{11}H_9N_3O}$, 199.0745. Found: 199.0741 (M$^+$).

With 2-methyl-2-oxazoline. *rel*-(1*R*,2*R*,6*S*,7*S*)-6-Methyl-5,11-dioxa-2-azatricyclo[5.3.1.0^{2,6}]undecan-8-ylidenemalononitrile (*rel*-(1*R*,2*R*,6*S*,7*S*)-**19**), mp 43-45.5 ℃ (hexane-ethyl acetate); ^{1}H NMR δ (GX): 1.33 (3H, s, $\mathrm{CH_3}$), 1.97-2.01 (2H, m, 2H-10), 2.81-2.98 (2H, m, 2H-9), 3.21-3.34 (2H, m, 2H-3), 3.76 (1H, ddd, *J*=10.7, 7.6, 5.6, H-4), 3.93-3.98 (1H, m, H-4), 4.91 (1H, s, H-1), 5.04 (1H, s, H-7); ^{13}C NMR δ (GX): 19.4 (q, $\mathrm{CH_3}$), 24.9, 31.6 (2t, C-9, C-10), 54.5 (t, C-3), 66.4 (t, C-4), 84.3 (d, C-7), 85.9 [s, $\underline{\mathrm{C}}\mathrm{(CN)_2}$], 96.9 (d, C-1), 104.0 (s, C-6), 110.3, 110.6 (2s, 2CN), 174.6 (s, C-8). IR ν_{max} $\mathrm{CHCl_3}$ cm^{-1}: 2250 (C≡N), 2220 (C≡N), 1603 (C=C). MS *m/z*: 231 (M$^+$, 4%), 112 (100), 86 (23) and 43 (17). HRMS *m/z*: Calcd for $\mathrm{C_{12}H_{13}N_3O_2}$, 231.1008. Found: 231.1009 (M$^+$).

With 2-methyl-2-thiazoline. 6-Methyl-11-oxa-5-thia-2-azatricyclo[5.3.1.0^{2,6}]undecan-8-ylidenemalononitrile (**20**), mp 125-128 °C (decomposition); ^{1}H NMR δ (EX): 1.50 (3H, s, $\mathrm{CH_3}$), 1.89-2.05 (2H, m, 2H-10), 2.79-3.22 (5H, m, H-3, 2H-4, 2H-9), 3.64-3.68 (1H, m with d-character, *J*=12, 3-H), 4.79 (1H, s, H-1) and 5.21 (1H, s, H-7); ^{13}C NMR δ (EX): 23.4 (q, $\mathrm{CH_3}$), 25.0, 32.0, 35.5 (3t, C-4, C-9, C-10), 58.8 (t, C-3), 85.2 (s, C-6), 86.0 [s, $\underline{\mathrm{C}}\mathrm{(CN)_2}$], 86.0 (d, C-7), 94.8 (d, C-1), 110.3, 110.6 (2s, 2CN), 175.8 (s, C-8). IR ν_{max} $\mathrm{CHCl_3}$ cm^{-1}: 2240 (C≡N), 1601 (C=C). MS *m/z*: 247 (M$^+$, 100%), 172 (22), 158 (20), 128 (80), 61 (47). HRMS *m/z*: Calcd for $\mathrm{C_{12}H_{13}N_3OS}$, 247.0779. Found: 247.0785 (M$^+$).

Photoreaction of epoxy cyanoester (8) and epoxy diester (9) with EVE

Photoreaction of 8 and EVE. A solution of (*E/Z*)-**8** (*E/Z*=3:4; 3.00 g, 15.5 mmol) in dry acetonitrile (430 mL) with EVE (11.2 g, 155 mmol) was irradiated with a low-pressure mercury lamp in a quartz test tube (conversion 94 %) for 2.5 h at 0 °C. After removal of the solvent, flash chromatography [hexane-ethyl acetate (2:1→1:1)] afforded the adduct ((*E/Z*)-**21**) (81 mg, 2%[6]) and intractable material (mainly polymers).

(*E/Z*)-*rel*-(1*R*,5S,7*S*)-Ethyl 7-ethoxy-8-oxabicyclo[3.2.1]octan-2-ylidenecyanoacetate ((*E/Z*)-*rel*-(1*R*,5S, 7*S*)-**21**) (*E*:*Z*=3:4 mixture), bp 130 °C at 0.13 mmHg; ^{1}H NMR δ (LA) for *E*: 1.24 (3H, t, *J*=7.0, 7-$\mathrm{OCH_2C\underline{H}_3}$), 1.36 (3H, t, *J*=7.0, $\mathrm{CO_2CH_2C\underline{H}_3}$), 1.58 (1H, m with dd-character, *J*=13.7, 7.6, H-4), 1.99-2.07 (1H, m, H-4), 2.11-2.27 (2H, m, 2H-6), 2.35 (1H, ddd, *J*=18.3, 11.0, 7.6, H-3), 3.46, 3.65 (2H, each dq, *J*=9.2, 7.0, 7-$\mathrm{OC\underline{H}_2CH_3}$), 3.66-3.72 (1H, m, H-3), 3.94-3.99 (1H, m with td-character, *J*=8, 3, H-7), 4.27-4.34 (2H, m, $\mathrm{CO_2C\underline{H}_2CH_3}$), 4.66-4.72 (1H, m, H-5), 5.11 (1H, s, H-1); ^{13}C NMR δ (LA) for *E*: 14.1 (q, $\mathrm{CO_2CH_2\underline{C}H_3}$), 15.2 (q, $\mathrm{OCH_2\underline{C}H_3}$), 22.9 (t, C-3), 30.1 (t, C-4), 37.5 (t, C-6), 62.1 (t, $\mathrm{CO_2\underline{C}H_2CH_3}$), 65.7 (t, $\mathrm{O\underline{C}H_2CH_3}$), 75.2 (d, C-5), 82.5 (d, C-1), 83.6 (d, C-7), 102.7 (s, $\mathrm{\underline{C}CO_2Et}$), 114.0 (s, CN), 161.4, 171.7 (2s, C-2, CO); ^{1}H NMR δ (LA) for *Z*: 1.23 (3H, t, *J*=7.0, 7-$\mathrm{OCH_2C\underline{H}_3}$), 1.36 (3H, t, *J*=7.0, $\mathrm{CO_2CH_2C\underline{H}_3}$), 1.65 (1H, m with dd-character, *J*=13.4, 7.6, H-4), 2.11-2.20 (1H, m, H-4), 2.11-2.27 (2H, m, 2H-6), 2.44 (1H, ddd, *J*=17.4, 10.7, 7.3, H-3), 2.91-2.98 (1H, m with ddd-character, *J*=17.4, 6.7, 1.5, H-3), 3.46, 3.74 (2H, each dq, *J*=9, 7.0, 7-$\mathrm{OC\underline{H}_2CH_3}$), 3.94-3.99 (1H, m with td-character, *J*=8, 3, H-7), 4.27-4.34 (2H, m, $CO_2C\underline{H}_2CH_3$), 4.66-4.72 (1H, m, H-5), 5.96 (1H, s, H-1); ^{13}C NMR δ (LA) for *Z*: 14.1 (q, $CO_2CH_2\underline{C}H_3$), 15.3 (q, $OCH_2\underline{C}H_3$), 26.5 (t, C-3), 30.9 (t, C-4), 37.8 (t, C-6), 62.3 (t, $CO_2\underline{C}H_2CH_3$), 65.4 (t, $O\underline{C}H_2CH_3$), 74.5 (d, C-5), 78.8 (d, C-1), 83.1 (d, C-7), 103.5 (s, $\underline{C}CO_2Et$), 114.5 (s, CN), 161.0, 171.7 (2s, C-2, CO). IR ν_{max} film cm^{-1}: 2220 (C≡N), 1720 (C=O), 1600 (C=C). MS *m/z*: 265 (M^+, 23%), 193 (33), 165 (90), 137 (100), 123 (45), 73 (44), 43 (63). HRMS *m/z*: Calcd for $C_{14}H_{19}NO_4$, 265.1314. Found: 265.1311 (M^+).

Photoreaction of 9 and EVE. A solution of **9** (925 mg, 3.85 mmol) in dry acetonitrile (106 mL) with EVE (2.78 g, 38.5 mmol) was irradiated with a low-pressure mercury lamp in a quartz test tube (conversion 69 %) for 3.5 h at 0 °C. After removal of the solvent, flash chromatography [hexane-ethyl acetate (2:1)] afforded the enone (**22**) (469 mg, 74%[6]).

Diethyl 3-oxo-1-cyclopentenylmalonate (**22**), bp 118 °C at 0.23 mmHg; ^1H NMR δ (EX): 1.31 (6H, 2t, *J*= 7, $2CH_3$), 2.46-2.50, 2.78-2.83 (4H, 2m, 2H-4, 2H-5), 4.26, 4.27 (4H, each q, *J*=7, $2OC\underline{H}_2CH_3$), 4.51 [1H, s, $C\underline{H}(CO_2Et)_2$], 6.22-6.25 (1H, m with td-character, *J*=2, 1, H-2); ^{13}C NMR δ (EX): 14.0 (2q, $2CH_3$), 30.4, 35.4 (2t, C-4, C-5), 55.7 [d, $\underline{C}H(CO_2Et)_2$], 62.4 (2t, $2O\underline{C}H_2CH_3$), 133.9 (d, C-2), 165.9, 169.8 (3s, C-1, $2CO_2$), 208.8 (s, C-3). IR ν_{max} film cm^{-1}: 1730 (C=O), 1710 (C=C), 1615 (C=C). MS *m/z*: 240 (M^+, 100%), 195 (36), 194 (75), 139 (90), 138 (46), 122 (29), 110 (28). HRMS *m/z*: Calcd for $C_{12}H_{16}O_5$, 240.0997. Found: 240.0999 (M^+).

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6. Yields for compounds are based on converted starting material.
7. The semiempirical AM1 calculations[8, 9] of the transition states for *exo* cycloaddition of *E* and *Z* ethyl 1-propenyl ethers and the ylide **A** show that the activation enthalpy for the *Z* ether is smaller than that for the *E* ether ($\Delta\Delta H_f^{\ddagger}$ = 2.1 kcal mol^{-1}).
8. CAChe MOPAC version 94. All orbital energies were obtained from AM1 optimized geometries.
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11. In the case of the cycloaddition of **A** and methyl acrylate (MA), the interaction between LUMO (MA) and HOMO (**A**) (ΔE = 8.09 eV) is more favorable than that of the LUMO (**A**) and next-highest occupied MO (MA) (ΔE = 9.14 eV) according to the AM1 calculations.[8] The inter-action of the LUMO of MA and the HOMO of **A** is depicted in Figure 5.

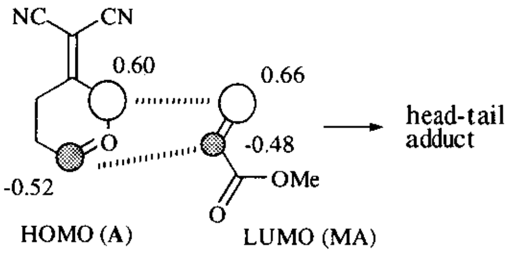

Figure 5 Coefficients of HOMO (**A**) and LUMO (MA)

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