Photochemical Reactions of α,β-Unsaturated γ,δ-Epoxy Ketones and Nitriles in the Presence of Amine

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Direct irradiation (λ 254 nm) of the α,β-unsaturated γ,δ-epoxy ketone (1) and nitrile (2) in acetonitrile in the presence of aliphatic amines gave the divinyl ethers (5) and (11), respectively, as the main products, whose formation was shown to depend on solvent polarity and ionization potential of amines. On the other hand, when compounds (1) and (2) were irradiated in various alcohols in the presence of an amine they afforded the corresponding ketals (14)–(19) and (21) in 85–21% yield. Photochemical reactions of ketone (3) and nitrile (4) in methanol, were also studied.

Photochemical reactions of α,β-unsaturated γ,δ-epoxy ketones [1,2] and nitrile (2)[3] have been investigated systematically. Studies have revealed that, in general, on triplet sensitization, these compounds undergo product formation *via* C(γ),O-bond cleavage and/or (*E/Z*)-isomerization, whereas selective π,π*-excitation causes reactions leading to carbonyl ylide and carbene intermediates. There has been growing interest in the photochemistry of carbonyl and cyano compounds in the presence of amines.[4,5] However, relatively few reports have dealt with the photoreactions of aliphatic carbonyl compounds.[5] We report here the photochemistry of (1) and (2) in the presence of aliphatic amines in various solvents and a study on the photochemistry of γ,δ-epoxy α-enone (3)[1] and α-enenitrile (4) in MeOH.

Results and Discussion

Photochemical Reactions of Compounds (1) and (2) in Acetonitrile.—Preparative irradiation of (1). Irradiation of the γ,δ-epoxy α-enone (1) in the presence of 1 equivalent of *N,N*-dimethylcyclohexylamine (DMCA) in acetonitrile at room temperature (98% conversion) gave the following products:†
(5)[6] (40%), (6)[1] (3%), (7)[1] (7%), (8)[1] (3%), (9)[1] (6%), and (10)[1] (3%). However, on direct irradiation of (1) the divinyl ether (5)‡ was obtained in small yield (3%).[6]

Preparative irradiation of (2). Similarly, irradiation of the nitrile (2) in the presence of triethylamine (TEA) gave the divinyl ether (11) (29%), the enol ether (12)[3] (9%), and the cyclopropene (13)[3] (7%). Compound (11) could be detected neither on direct irradiation nor on triplet sensitization of (2).[3] The structure of (11) was determined from a comparison of its spectral data with those of compound (5). The ^{1}H NMR spectrum shows two singlets at 4.15 and 4.43 ppm due to the methylene protons, and a triplet at 5.09 ppm due to the alkene hydrogen.

Analytical irradiation of compounds (1) and (2). The photoreactions of (1) and (2) (λ 254 nm) were studied in the presence of 1 equivalent of various amines {cyclohexylamine (CHA), $Bu^t NH_2$, diethylamine (DEA), DMCA, TEA, and 1,4-diazabicyclo[2.2.2]octane (DABCO)} in various solvents [pentane, tetrahydrofuran (THF), CH_2Cl_2, MeCN, and MeOH]. The results are summarized in Table 1. The divinyl ether (11) was formed in polar solvents and in the presence of amines with lower ionization potential, but was not formed in MeOH, probably owing to the trapping of the carbonyl ylide (2a) (Scheme 1) and/or interaction between the amine and MeOH, which suppress the electron transfer process.[8] The formation of (5) was also observed under the same reaction conditions.

(1) R = COMe
(2) R = CN

(3)

E,Z-(4)

(5)

(6)

(7)

(8)

(9)

(10)
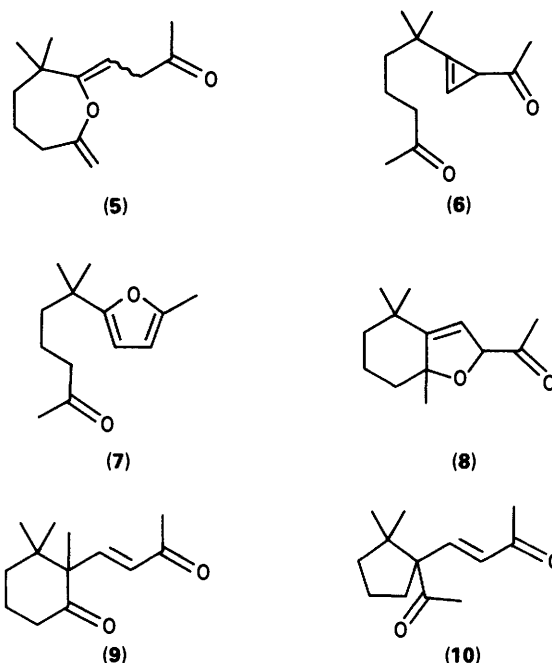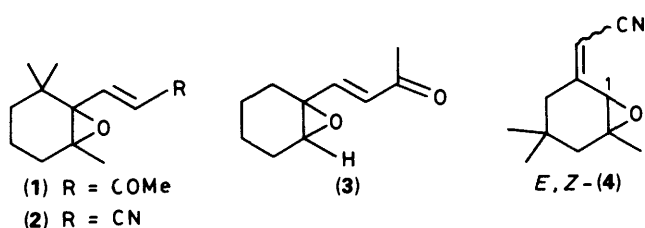
Furthermore, the irradiation of (2) was examined with various concentrations of TEA in acetonitrile. The yields of (11) and (12) clearly depend upon TEA concentration. The results are summarized in Table 2. The yield of (11) increased with increasing TEA concentration, where that of (12) decreased.
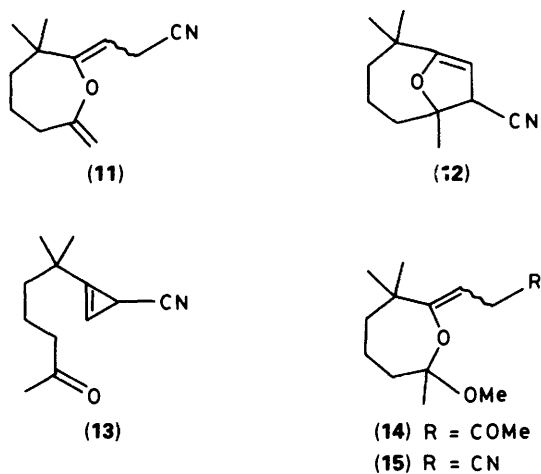
A reaction mechanism for the transformation (1) ——→ (5) and

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† Yields throughout the paper are based on converted starting material.
‡ On thermolysis (585 °C), enone (1) undergoes a [1,5]-homosigmatropic H-shift leading to (5) in 78% yield.[7]

Table 1. Photochemical reactions of (1) and (2).

Substrate	Amine	Solvent	Conversion (%)	Products (%)[a]				
				(5)	(11)	(12)	(13)	(15)
(1)	Bu^{t}NH$_2$ (8.83)[b]	MeCN (0.46)[e]	64	—				
	DEA (8.51)[b]	MeCN	65	10				
	DMCA (8.09)[c]	MeCN	64	42				
	TEA (7.84)[b]	MeCN	63	38				
(2)	CHA (8.86)[b]	MeCN	66		—	—	7	—
	Bu^{t}NH$_2$	MeCN	75		—	5	3	—
	DEA	MeCN	52		—	6	6	—
	DMCA	MeCN	72		25	12	3	—
	TEA	MeCN	63		26	29	7	—
	DABCO (7.52)[d]	MeCN	63		12	8	trace	—
	TEA	Pentane (0.01)	18		—	38	29	—
	TEA	THF (0.21)	52		—	53	11	—
	TEA	CH$_2$Cl$_2$ (0.31)	75		5	4	—	—
	TEA	MeOH (0.76)	83		—	—	6	92

[a] The yields are based on converted starting material and determined by ^{1}H NMR analysis of the reaction mixture using bis(trimethylsilyl)acetylene as an internal standard, in this and in Table 3. [b] Ionization potential given in parentheses, units eV, ref. 9. [c] Ref. 10. [d] Ref. 11. [e] E_T^N-Values given in parentheses, ref. 12.

(11)

(12)

(13)

(14) R = COMe
(15) R = CN

Scheme 1.

(2) ⟶ (11) is not yet clear. We assumed that the formation of the divinyl ether (11) involved the intermediate (2b) [probably

Table 2. Irradiation of (2) with various concentration of TEA.[a]

[TEA]/mM	Yields (%)[b]	
	(11)	(12)
0	—	93
5.2	14	71
15.7	28	68
52.3	30	48
104.7	35	33

[a] A 52.3mM solution of (2) in acetonitrile was irradiated and the conversions were 26–30%. [b] Yields are based on converted starting material, and were determined by GLC analysis using nonadecane as an internal standard.
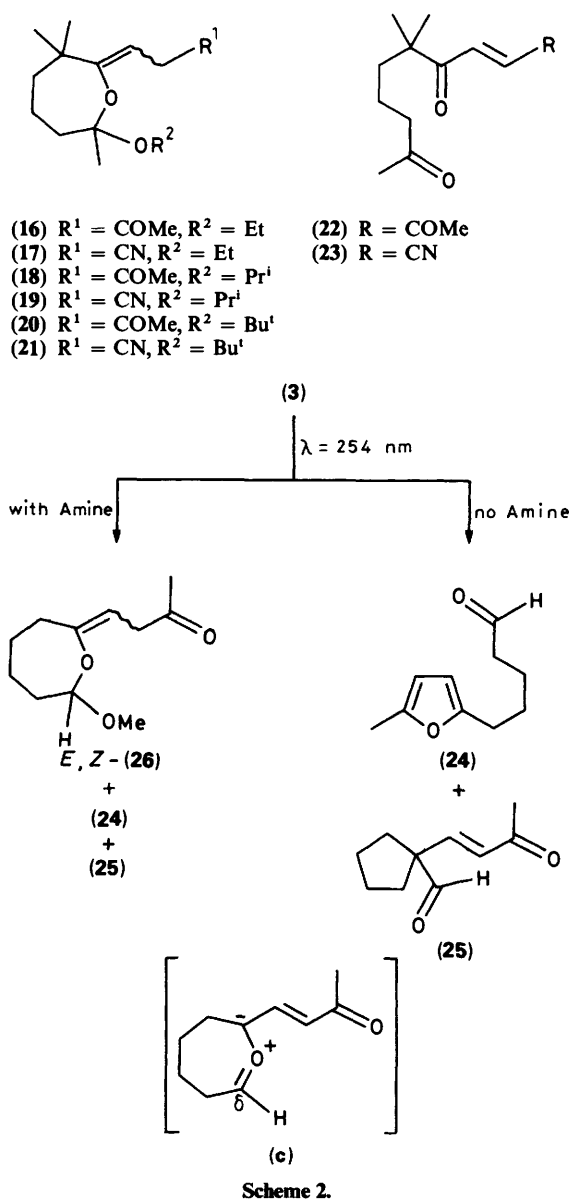
resulting from electron transfer from the amine to the carbonyl ylide (2a)]. Compound (12) is competitively formed via the carbonyl ylide (2a) directly.[3] In general, the irradiation of enones with amine gave the 1:1 adduct and/or reduced products.[5] However, on irradiation of compounds (1) and (2) those compounds could not be observed.

As the photolysis of (2) in MeOH afforded the ketal (15) in good yield (Table 1), the photochemical reactions of enones (1) and (3) and nitriles (2) and (4) were investigated in alcohol in the presence of amine.

Photochemical Reaction of Compounds (1) *and* (2) *in Alcohol.*—A 52mM solution of (2) and TEA (1 equiv.) in MeOH was irradiated in a quartz test-tube with a low-pressure mercury lamp (85% conversion). The ketal (15)[3] and the cyclopropene (13)[3] were formed in 85% and 5% yield, respectively. Similarly, the epoxides (1) and (2) were irradiated in the presence of TEA (1 equiv.) in MeOH, EtOH, Pr^{i}OH, and Bu^{t}OH. The results are summarized in Table 3, and they show that the ketals (14)–(21) are formed in higher yields in the presence of TEA. Addition of K$_2$CO$_3$, instead of amine, increased the yield of (15) but not so efficiently. The yields of the ketals (14)–(21) decrease in the order MeOH > EtOH > Pr^{i}OH > Bu^{t}OH, whereas the yield of (12) increases, owing to the nucleophilicity of the alcohol.

The structure of ketals (16)–(19) and (21) was deduced from a comparison of their ^{1}H NMR and mass spectral data with those of compounds (14)[6] and (15).[3]

Photoreaction of (2) in EtOH containing varying amounts of TEA (0.1–1.6 equiv.) gave the ketal (17) in 77–86% yield.
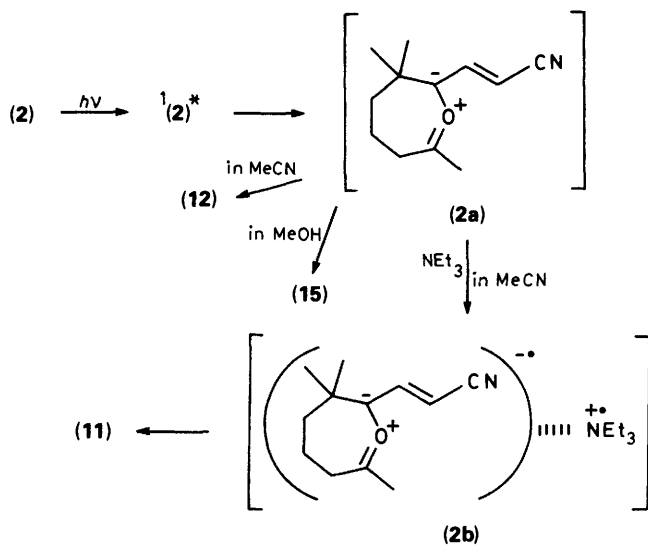
Table 3. Formation of ketals from (1) and (2) in alcohols with 1 equiv. TEA.

Substrate	Alcohol	Conversion (%)	Yields (%)		
			Ketal	Ketone	(12)
(1)	MeOH	90 [73][a]	(14) 62 [—]	(22) — [24]	
	EtOH	81 [77]	(16) 55 [—]	— [35]	
	Pr^{i}OH	88 [67]	(18) 48 [—]	9 [30]	
	Bu^{t}OH	79 [68]	(20) trace [—]	21 [25]	
(2)	MeOH	85 [89] ⟨90⟩[b]	(15) 85 [40] ⟨65⟩	(23) — [—] ⟨—⟩	— [—] ⟨—⟩
	EtOH	88 [92]	(17) 71 [—]	— [47]	— [—]
	Pr^{i}OH	93 [88]	(19) 58 [—]	6 [56]	4 [3]
	Bu^{t}OH	82 [76]	(21) 21 [—]	27 [50]	12 [19]

[a] Values in square brackets are yields in the absence of TEA. [b] Values in angle brackets are yields in the presence of 1 equivalent of K_2CO_3.

(16) R^1 = COMe, R^2 = Et
(17) R^1 = CN, R^2 = Et
(18) R^1 = COMe, R^2 = Pr^i
(19) R^1 = CN, R^2 = Pr^i
(20) R^1 = COMe, R^2 = Bu^t
(21) R^1 = CN, R^2 = Bu^t

(22) R = COMe
(23) R = CN

(3)

λ = 254 nm

with Amine

no Amine

E, Z - (26)
+
(24)
+
(25)

(24)

(25)

(c)

Scheme 2.

Furthermore when compound (2) was irradiated in MeOH in the presence of 1 equivalent of each of various amines (CHA, Bu^{t}NH$_2$, DEA, and DABCO), the ketal (15) was afforded in 81–91% yield, showing that in contrast to the photolysis in acetonitrile, the yield of the ketal did not depend on the ionization potential and the concentration of amine. From these

results, we postulate that on π,π^*-excitation the epoxides (1) and (2) undergo C(γ),C(δ)-bond cleavage of the oxirane leading to the carbonyl ylide, followed by addition of alcohol to give the ketals (14)–(21). The addition of amine * stabilises ketals, which are easily hydrolyzed with a trace of acid leading to the carbonyl derivatives (22) and (23).

Photochemical Reactions of Epoxy Enone (3).—In contrast to the photolyses of enone (1), direct irradiation of the compound (3) in pentane or in acetonitrile did not afford products arising from C(γ),C(δ)-bond cleavage, because of instability of the carbonyl ylide (c) possessing no methyl group in the δ-position.[1] We investigated trapping of the carbonyl ylide (c) in MeOH in the presence of amine.

Irradiation of epoxy enone (3) (low pressure mercury lamp, quartz filter, under argon) in MeOH, (as a carbonyl ylide trapping agent), in the absence of amine, at room temperature (71% conversion) did not afford the products arising from the ylide (c), but gave only the known cyclopentane (24)[1] (11%) and furan (25)[1] (25%). However, the photolysis of a 72mM solution of (3) in the presence of DMCA (1 equiv.) in MeOH under the same conditions (93% conversion) gave the acetals E-(26) (9%) and Z-(26) (6%), (24) (5%), and (25) (18%).

The structure of compound Z-(26) was deduced from the spectral data. The acetal moiety is evidenced by the double doublet (J 4.9 and 1.5 Hz) in the ^1H NMR spectrum at 4.90 ppm as well as by the doublet in the ^{13}C NMR spectrum at 97.8 ppm. Compound E-(26) could not be isolated in pure form. The structure was derived by comparison of the ^1H NMR spectrum [1:1 mixture of E-(26) and (24)] with that of compound Z-(26). The alkene proton in the enol ether moiety of Z-(26) shows a triplet (4.55 ppm) at higher field than that of (26) shows a triplet (4.55 ppm) at higher field than that of E-(26) (5.10 ppm) in the ^1H NMR spectrum, indicating a (Z)-configuration, which is also evidenced by comparison of the chemical shift (3.18 ppm) due to the methylene protons positioned α to the carbonyl group for Z-(26) with that of E-(26) (3.05 ppm). Thus, the configuration of the alkene in E-(26) is *trans*.

Photochemical Reaction of the Epoxy Enenitrile (4).—We studied the photochemistry of nitrile (4) possessing no alkyl substituent γ to the cyano group and an exocyclic double bond.

Preparation of the nitrile (4). The nitriles E-(4) and Z-(4) were prepared from the 1:1 mixture of dienenitriles E-(27) and Z-(27)[13] in 30% and 23% yields by epoxidation with *m*-chloroperbenzoic acid (*m*-CPBA), respectively. The structure of E-(4) and Z-(4) was determined from the spectral data. In particular, the ^1H NMR spectra for E-(4) and Z-(4) show a

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* The hydrogen bonding interaction between amine and alcohol[8] presumably also influences formation of the ketals.
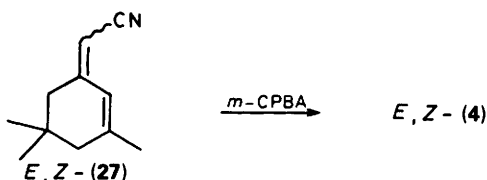
Scheme 3.

singlet at 3.26 and 3.77 ppm due to 1-H, and a doublet (J 1.8 Hz) at 5.55 and 5.37 ppm due to the protons positioned α to the cyano group, respectively.

Irradiation of the nitrile Z-(4) in MeOH. The photolysis of a 56mM solution of epoxy enenitrile Z-(4) in the presence of TEA (1 equiv.) in MeOH (low pressure mercury lamp, quartz filter, under argon) at room temperature (74% conversion), and the subsequent chromatography on SiO_2 gave the ketals *E*-(28) (12%), *Z*-(28) (17%) and (29) (12%), the cyclopropene (30) (9%), the aldehyde (31) (3%), and *E*-(4) (32%). The aldehyde (31) could not be detected by the ^{1}H NMR spectrum of the crude photoproducts. The ketal (29) was treated with SiO_2 leading to aldehyde (31), whose formation could not be observed on heating (29) (60 °C). On further irradiation in the presence of TEA (1 equiv.) the *E*-isomer *E*-(28) leads to the *Z*-isomer *Z*-(28) only. We assumed that π,π^*-excitation of *Z*-(4) shows C(γ),C(δ)-bond cleavage to the carbonyl ylide (d) and the carbene (e) intermediates similar to those obtained from (2).[3] By a known process,[1,2,3] the carbene (e) undergoes addition to the adjacent double bond to furnish the cyclopropene (30). The carbonyl ylide (d) undergoes a direct 1,5-addition of MeOH to give the ketal (29), which presumably leads to the aldehyde (31) by an acid catalyzed [1,3]-sigmatropic shift. An analogous reaction sequence to (29) ⟶ (31) was observed on photolysis of (32) [(f) ⟶ (33)].[14] In the case of *Z*-(4), the formation of (28) by 1,3-addition of MeOH to the carbonyl ylide (d) was also observed,* presumably owing to partial overlap of the π-orbitals of C(β) and C(γ) in the carbonyl ylide (d); Dreiding models show that their planarization is inhibited by four sp^2-orbitals at the centre of the seven-membered ring.
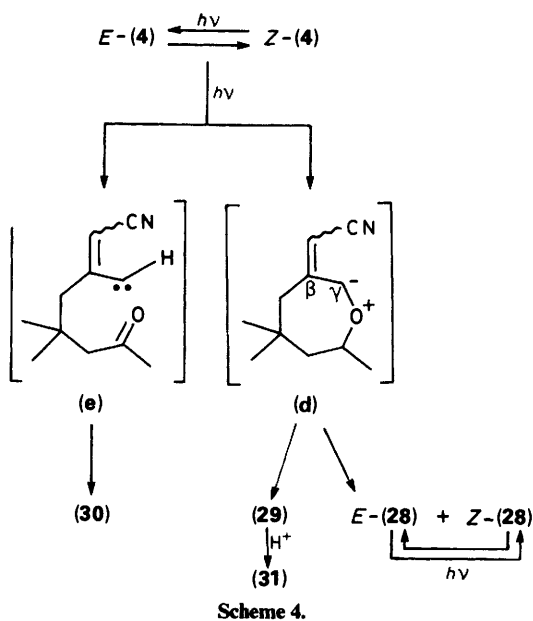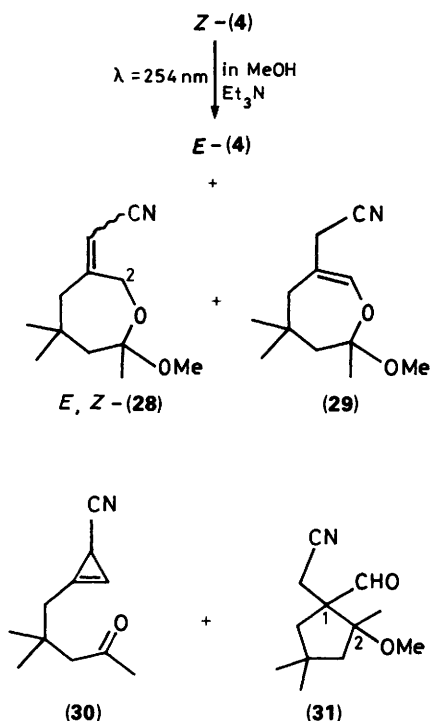
Scheme 4.

The structural features of compounds *E*- and *Z*-(28) were determined from their spectra. In particular, the ^{1}H NMR spectra show a doublet with m-character at 5.20 ppm and a broad singlet at 5.11 ppm due to the olefinic proton, and signals at 3.96 and 4.36 ppm and at 4.33 and 4.52 ppm due to 2-H. These chemical shifts indicate that the configuration of compounds *E*-(28) and *Z*-(28) are *trans* and *cis*, respectively. The ketal moiety of *E*-(28) and *Z*-(28) produces singlets at 101.8 and 101.9 ppm in the ^{13}C NMR spectra, respectively.

The structure of the compound (29) was determined from the ^{1}H NMR spectrum of a mixture of the photoproducts [contaminated with *ca.* 60% *E*-(4), *Z*-(28), and (31)] showing a singlet at 2.93 ppm and a broad singlet at 6.07 ppm due to the acetonitrile and the enol ether moiety, respectively.

The structure of cyclopropene (30) was also deduced from its spectral data. Characteristic signals, in ^{1}H NMR spectrum were two doublets (J 1.5 Hz) at 1.83 and 6.57 ppm, the ^{13}C NMR spectrum had two doublets at 3.4 and 95.9 ppm and a singlet at 123.3 ppm due to the cyclopropene moiety, which was also evidenced by the IR band at 1 780 cm^{-1}.

The spectral evidence for aldehyde (31) includes an IR band at 1 715 cm^{-1} and a singlet at 9.69 ppm in the ^{1}H NMR spectrum indicating an aldehyde moiety. The ^{13}C NMR spectrum showed two singlets at 64.0 and 85.7 ppm due to C-1 and C-2, respectively. Only one stereoisomer of the aldehyde (31) was isolated, and the configuration of the side-chains could not be assigned.

In conclusion, our investigation shows that direct irradiation (λ 254 nm) of the ketone (1) and nitrile (2) in acetonitrile in the presence of aliphatic amines gave the divinyl ethers (5) and (11) as main products, whose formation was observed in a polar solvent and in the presence of amine with lower ionization potential. On the other hand, when compounds (1), (2), (3), and (4) were irradiated in alcohol in the presence of amine, they afforded the corresponding ketals or acetals in moderate yields.

Experimental

B.p.s are uncorrected and were measured with a Büchi Kugel Rohr GKR-50 apparatus. UV spectra were recorded on a

* The 1,3-adduct of MeOH was also obtained on the photolysis of 3-(1,2-epoxy-2-methylpropyl)-5,5-dimethycyclohex-1-2-enone.[15]

Scheme 5.
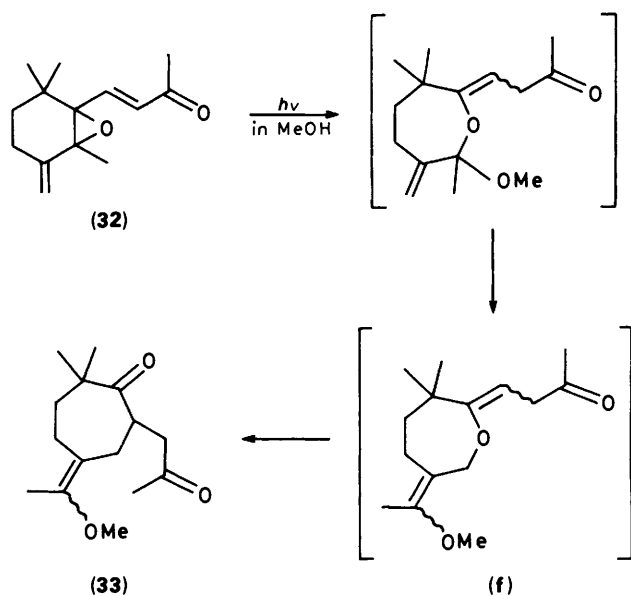
Hitachi 124 spectrometer and IR spectra on a Hitachi 215 spectrometer. ^{1}H NMR spectra were obtained with a JEOL PMX-60, a JEOL PS-100 or a JEOL GX-400 spectrometer and ^{13}C NMR spectra were run on a JEOL GX-400 spectrometer using tetramethylsilane as internal standard. Mass spectra were taken on a JEOL JMS-D300 spectrometer. GLC was carried out on a JEOL JGC-1100 instrument (flame ionization detection) and a column used was 3 m × 3 mm of 5% OV-17 on Chromosorb W. Column chromatography was performed with Kanto silica gel, 100–200 mesh (SiO_2 A), Nacalai silica gel 60, 230–400 mesh (SiO_2 B), or Merck aluminium oxide 90 basic, activity III, 70–230 mesh (Al_2O_3).

A Eikosha 60 W low pressure mercury lamp was used as irradiation source. All solvents used for photolyses were spectroscopic grade. 1,4-Diazabicyclo[2.2.2]octane (DABCO) from Tokyo Kasei was used as received, each of the other amines (the highest grade available commercially) was distilled over KOH prior to use.

Photochemical Reactions of Compounds **(1)** *and* **(2)** *in Acetonitrile.—Preparative irradiation of* **(1)**. A solution of epoxy enone **(1)**[1] (4.00 g, 19.2 mmol) in the presence of *N,N*-dimethylcyclohexylamine (DMCA) (2.44 g, 19.2 mmol) in acetonitrile (400 ml) under argon was irradiated through a quartz filter (98% conversion) for 2 h at room temperature. After removal of the solvent, chromatography [SiO_2 B, hexane–ethyl acetate (4:1)] of the residue yielded several fractions; the following product distribution was determined from ^{1}H NMR analysis: **(5)**[6] (1.55 g, 40%), **(6)**[1] (108 mg, 3%), **(7)**[1] (266 mg, 7%), **(8)**[1] (127 mg, 3%), **(9)**[1] (229 mg, 6%), and **(10)**[1] (127 mg, 3%).

Preparative irradiation of **(2)**. A solution of epoxy enenitrile **(2)**[3] (1.70 g, 8.90 mmol) and triethylamine (TEA) (899 mg, 8.90 mmol) in acetonitrile (170 ml) was irradiated for 2.75 h in the same manner as described above (81% conversion). Chromatography [SiO_2 B, hexane–ether (4:1)] gave **(11)** (393 mg, 29%), **(12)**[3] (118 mg, 9%), **(13)**[3] (98.1 mg, 7%), and unknown compounds (557 mg).

3-(7',7'-Dimethyl-3'-methylene-2'-oxacycloheptylidene)propanonitrile **(11)** had b.p. 80 °C at 0.4 mmHg (decomp.) (Found: M^+, 191.1309. $C_{12}H_{17}NO$ requires *M*, 191.1310); ν_{max}(film) 2 250 (C≡N), 1 660 (C=C), and 1 640 cm^{-1} (C=C); δ_H(100 MHz; $CDCl_3$) 1.19 (6 H, s, 7'-Me$_2$), 1.2–1.9 (4 H, m, 5'- and 6'-H$_2$), 2.16–2.34 (2 H, m, 4'-H$_2$), 3.19 (2 H, d, *J* 7 Hz, 2-H$_2$), 4.15 and 4.43 (2 H, 2 × s, 3' = CH$_2$), and 5.09 (1 H, t, *J* 7 Hz, 3-H);

δ_C($CDCl_3$) 13.8 and 24.1 (2 × t, C-2 and C-5'), 26.6 (2 × q, 2 × Me), 31.1 and 42.2 (2 × t, C-4' and C-6'), 39.0 (s, C-7'), 89.5 (t, 3'=CH$_2$), 101.1 (d, C-3), 118.5 (s, C-1), and 160.8 and 162.9 (2 × s, C-1' and C-3'); *m/z* 191 (M^+, 4%), 109 (16), 69 (21), and 43 (100).

Analytical Irradiation of Compounds **(1)** *and* **(2)**.—*Irradiation of* **(1)** *and* **(2)** *in the presence of various amines in various solvents*. Solutions of **(1)** (48mM) and **(2)** (52mM) in solvent [pentane, tetrahydrofuran (THF), CH_2Cl_2, MeCN, or MeOH] with 1 equivalent of amine [cyclohexylamine (CHA), Bu^{t}NH$_2$, diethylamine (DEA), DMCA, TEA, or DABCO] were irradiated for 3 h in a merry-go-round apparatus under argon at room temperature. The yields were determined by ^{1}H NMR (60 MHz) analysis of the reaction mixture using bis(trimethylsilyl)acetylene as an internal standard, the results are shown in Table 1.

Determination of the yield of **(11)** *and* **(12)** *as function of the TEA concentration*. To aliquots of a 52.3mM acetonitrile (3 ml) solution of **(2)** and nonadecane as an internal standard for GLC (180 °C) analysis definite amounts of TEA were added, and the solutions were degassed by three freeze-pump-thaw cycles and irradiated in a merry-go-round apparatus. Yields of **(11)**, **(12)**, and converted **(2)** were determined by GLC analysis, the results are shown in Table 2.

Photochemical Reactions of Compounds **(1)** *and* **(2)** *in Alcohol.—Irradiation of* **(1)** *and* **(2)** *in the presence of TEA in various alcohols*. Aliquots of a 48mM solution of epoxy enone **(1)** in alcohol (MeOH, EtOH, Pr^{i}OH, or Bu^{t}OH) containing TEA (1 equiv.) or nothing were irradiated in quartz test-tubes under argon for 1.5 h at room temperature. Aliquots of a 0.052M solution of epoxy enenitrile **(2)** containing TEA (1 equiv.), K_2CO_3, or nothing were irradiated in the same conditions as described above. Yields were determined by ^{1}H NMR analysis of the reaction mixture using bis(trimethylsilyl)acetylene as an internal standard, the results are shown in Table 3. The analytical samples were purified by chromatography [Al_2O_3; hexane–ethyl acetate (4:1)].

Irradiation of **(2)** *in EtOH containing varying amounts of TEA*. Analogous irradiation of **(2)** (53mM) in EtOH in the presence of TEA (0.1, 0.2, 0.4, 0.8, and 1.6 equiv.) for 1 h gave the ketal **(17)** in 77, 80, 85, 81, and 86% yields, respectively. The determination of the yields was as described above.

Irradiation of **(2)** *in MeOH in the presence of various amines*. Analogous irradiation of **(2)** (53mM) in MeOH in the presence of 1 equivalent of amine (CHA, Bu^{t}NH$_2$, DEA, and TEA) afforded the ketal **(15)** in 82, 81, 85, 82, and 91% yields, respectively.

4-(3'-Ethoxy-3',7',7'-trimethyl-2'-oxacycloheptylidene)butan-2-one **(16)** (*ca.* 70% pure), an oil; δ_H(400 MHz; $CDCl_3$) 1.08, 1.15, and 1.49 (9 H, 3 × s, 3'-Me and 7'-Me$_2$), 1.21 (3 H, t, *J* 7.0 Hz, OCH$_2$C*H*$_3$), 1.2–1.85 (6 H, m, 3 × CH$_2$), 2.14 (3 H, s, 1-H$_3$), 3.26 and 3.29 (2 H, each dd, *J* 18 and 6.7 Hz, 3-H$_2$), 3.66 and 3.82 (2 H, each dq, *J* 8.9 and 7.0 Hz, OCH$_2$), and 5.18 (1 H, t, *J* 6.7 Hz, 4-H); *m/z* 254 (M^+, 0.3%), 209 (4), and 123 (100).

3-(3'-Ethoxy-3',7',7'-trimethyl-2'-oxacycloheptylidene)propanonitrile **(17)** (*ca.* 80% pure), an oil; δ_H(400 MHz; $CDCl_3$) 1.06, 1.12, and 1.51 (9 H, 3 × s, 3'-Me and 7'-Me$_2$), 1.21 (3 H, t, *J* 7.0 Hz, OCH$_2$C*H*$_3$), 1.2–1.85 (6 H, m, 3 × CH$_2$), 3.20 and 3.22 (2 H, each dd, *J* 18 and 6.7 Hz, 2-H$_2$), 3.66 and 3.76 (2 H, each dq, *J* 9 and 7.0 Hz, OCH$_2$), and 5.00 (1 H, t, *J* 6.7 Hz, 3-H); *m/z* 237 (M^+, 2%), 192 (7), and 112 (100).

4-(3'-Isopropyl-3',7',7'-trimethyl-2'-oxacycloheptylidene)butan-2-one **(18)** (*ca.* 90% pure), an oil; δ_H(100 MHz; $CDCl_3$) 1.07 and 1.41 (9 H, 3 × s, 2 × s at 1.07, 3'-Me and 7'-Me$_2$), 1.12 and 1.22 [6 H, each d, *J* 7 Hz, OCH(C*H*$_3$)$_2$], 1.2–1.85 (6 H, m, 3 × CH$_2$), 2.07 (3 H, s, 1-H$_3$), 3.11 and 3.35 (2 H, each dd, *J* 18

and 7.5 Hz, 3-H$_2$), 4.15 (1 H, septet, J 7 Hz, OCH), and 5.07 (1 H, t, J 7.5 Hz, 4-H); m/z 268 (M^+, 0.4%), 209 (5), 123 (35), and 43 (100).

3-(3'-Isopropyl-3',7',7'-trimethyl-2'-oxacycloheptylidene)-propanonitrile (19) [contaminated with *ca.* 10% of (2)], an oil; δ_H(100 MHz; CDCl$_3$) 1.03, 1.06, and 1.44 (9 H, 3 × s, 3'-Me and 7'-Me$_2$), 1.11 and 1.19 [6 H, each d, J 7 Hz, OCH(CH_3)$_2$], 1.2–1.85 (6 H, m, 3 × CH$_2$), 3.21 (2 H, d, J 7.5 Hz, 2-H$_2$), 4.07 (1 H, septet, J 7 Hz, OCH), and 4.93 (1 H, t, J 7.5 Hz, 3-H); m/z 251 (M^+, 1%), 192 (22), and 84 (100).

3-(3'-t-Butyl-3',7',7'-trimethyl-2'-oxacycloheptylidene)-propanonitrile (21) (*ca.* 70% pure), an oil; δ_H(100 MHz; CDCl$_3$) 1.06, 1.10, and 1.41 (9 H, 3 × s, 3'-Me and 7'-Me$_2$), 1.31 (9 H, s, OBu^t), 1.2–1.85 (6 H, m, 3 × CH$_2$), 3.20 (2 H, d, J 7.5 Hz, 2-H$_2$), and 4.90 (1 H, t, J 7.5 Hz, 3-H); m/z 265 (M^+, 0.2%), 209 (5), 192 (23), 84 (78), and 57 (100).

Photochemical Reactions of Epoxy Enone (3) in MeOH.—*In the absence of amine.* A solution of epoxy enone (3)[1] (633 mg, 3.81 mmol) in MeOH (60 ml) was irradiated under argon through a quartz filter (71% conversion) for 6.5 h at room temperature. After removal of the solvent, chromatography [SiO$_2$ B, hexane–ethyl acetate (2:1)] of the residue yielded several fractions; the following product distribution was determined from ^{1}H NMR analysis: (24)[1] (47.8 mg, 11%) and (25)[1] (109.8 mg, 25%).

In the presence of amine. A solution of (3) (600 mg, 3.61 mmol) in the presence of DMCA (495 mg, 3.61 mmol) in MeOH (50 ml) was irradiated for 4 h under the same conditions as described above (93% conversion). Chromatography [SiO$_2$ B, hexane–ethyl acetate (4:1)] of the reaction mixture gave E-(26) (59.8 mg, 9%), Z-(26) (37.9 mg, 6%), (24) (28.0 mg, 5%), and (25) (99.3 mg, 18%).

(E)-4-(3'-Methoxy-2'-oxacycloheptylidene)butan-2-one E-(26) [contaminated with *ca.* 50% of (24)], an oil; δ_H(400 MHz; CDCl$_3$) 3.05 (2 H, d, J 7.7 Hz, 3-H$_2$), 3.45 (3 H, s, OMe), 4.73 (1 H, dd, J 7.2 and 2.5 Hz, 3'-H), and 5.10 (1 H, t, J 7.7 Hz, 4-H).

(Z)-4-(3'-Methoxy-2'-oxacycloheptylidene)butan-2-one Z-(26) (Found: M^+, 198.1275. C$_{11}$H$_{18}$O$_3$ requires M, 198.1257); ν_{max}(film) 1 715 (C=O) and 1 655 cm^{-1} (C=C); δ_H(400 MHz; CDCl$_3$) 1.40–1.95 (6 H, m, 3 × CH$_2$), 2.15 (3 H, s, 1-H$_3$), 2.23–2.49 (2 H, m, 7'-H$_2$), 3.18 (2 H, d, J 7.0 Hz, 3-H$_2$), 3.43 (3 H, s, OMe), 4.55 (1 H, t, J 7.0 Hz, 4-H), and 4.90 (1 H, dd, J 4.9 and 1.5 Hz, 3'-H); δ_C(CDCl$_3$) 23.8, 27.9, 34.2, 35.2, and 40.4 (5 × t, 5 × CH$_2$), 29.2 (q, C-1), 55.8 (q, OMe), 97.8 (d, C-3'), 103.6 (d, C-4), 155.5 (s, C-1'), and 207.9 (s, C-2); m/z 198 (M^+, 2%), 166 (11), 95 (68), 84 (97), and 55 (100).

Preparation of the Epoxy Enenitriles E-(4) and Z-(4).—A mixture of the dienenitriles E and Z-(27)[13] (1:1; 5.01 g, 31.1 mmol) in CH$_2$Cl$_2$ (133 ml) and aqueous NaHCO$_3$ (0.5M, 87 ml) was cooled to 0 °C, and a solution of *m*-chloroperbenzoic acid (80%; 9.52 g, 44.1 mmol) in CH$_2$Cl$_2$ (62 ml) was added dropwise with stirring. The mixture was stirred for 1 h at 0 °C, then for 48 h at room temperature. The organic phase was then separated, and worked up. The residue was chromatographed [SiO$_2$ B; hexane–ethyl acetate (4:1)] to afford recovered E and Z-(27) (1:1 mixture; 802 mg, 16%), E-(4) (1.68 g, 30%), and Z-(4) (1.28 g, 23%).

(E)-4,4,6-Trimethyl-7-oxabicyclo[4.1.0]hept-2-ylidenaceto-nitrile E-(4) had b.p. 110 °C at 0.4 mmHg (Found: M^+, 177.1173. C$_{11}$H$_{15}$NO requires M, 177.1154); λ_{max}(CHCl$_3$) 242 nm (ε 6 700); ν_{max}(film) 2 220 (C≡N) and 1 630 cm^{-1} (C=C); δ_H(400 MHz; CDCl$_3$) 0.84, 1.01, and 1.39 (9 H, 3 × s, 3 × Me), 1.60 (1 H, dd, J 15.0 and 1.8 Hz, 5-H), 1.89 (1 H, d, J 15.0 Hz, 5-H), 2.21 and 2.31 (2 H, each d with m-character, J 14.0 Hz, 3-H$_2$), 3.26 (1 H, s, 1-H), and 5.55 (1 H, d, J 1.8 Hz, HCCN); δ_C(CDCl$_3$) 24.4, 26.8, and 30.5 (3 × q, 3 × Me), 32.9 (s, C-4),

39.5 and 43.0 (2 × t, C-3 and C-5), 61.2 (d, C-1), 62.3 (s, C-6), 98.0 (d, HCCN), 115.9 (s, CN), and 161.7 (s, C-2); m/z 177 (M^+, 27%), 162 (34), and 43 (100).

(Z)-4,4,6-Trimethyl-7-oxabicyclo[4.1.0]hept-2-ylidenaceto-nitrile Z-(4), b.p. 100 °C at 0.3 mmHg (Found: M^+, 177.1161. C$_{11}$H$_{15}$NO requires M, 177.1154); λ_{max}(CHCl$_3$) 242 nm (ε 4 500); ν_{max}(film) 2 220 (C≡N) and 1 630 cm^{-1} (C=C); δ_H(400 MHz; CDCl$_3$) 0.80, 0.96, and 1.42 (9 H, 3 × s, 3 × Me), 1.60 (1 H, dd, J 15.0 and 2.1 Hz, 5-H), 1.89 (1 H, d, J 15.0 Hz, 5-H), 1.75 and 2.30 (2 H, each d with m-character, J 13.5 Hz, 3-H$_2$), 3.77 (1 H, s, 1-H), and 5.37 (1 H, d, J 1.8 Hz, HCCN); δ_C(CDCl$_3$) 24.5, 27.1, and 30.5 (3 × q, 3 × Me), 32.7 (s, C-4), 42.0 and 42.8 (2 × t, C-3 and C-5), 58.8 (d, C-1), 62.2 (s, C-6), 98.1 (d, HCCN), 115.8 (s, CN), and 161.7 (s, C-2); m/z 177 (M^+, 47%), 162 (52), and 43 (100).

Photochemical Reaction of Epoxy Enenitrile Z-(4).—A solution of epoxy enenitrile Z-(4) (1.18 g, 6.64 mmol) in the presence of TEA (671 mg, 6.64 mmol) in MeOH (118 ml) was irradiated under argon through a quartz filter (74% conversion) for 2 h at room temperature. After removal of the solvent, chromatography [SiO$_2$ B, hexane–ethyl acetate (4:1)] of the residue yielded several fractions; the following product distribution was determined from ^{1}H NMR analysis: E-(4) (276 mg, 32%), E-(28) (128 mg, 12%), Z-(28) (171 mg, 17%), (29) (118 mg, 12%), (30) (79.0 mg, 9%), and (31) (34.6 mg, 3%).

(E)-4-Methoxy-4,6,6-trimethyl-3-oxacycloheptylidenaceto-nitrile E-(28) had b.p. 90 °C at 0.3 mmHg (Found: M^+, 209.1381. C$_{12}$H$_{19}$NO$_2$ requires M, 209.1413); λ_{max}(EtOH) 222 nm (ε 10100); ν_{max}(film) 2 220 (C≡N) and 1 625 cm^{-1} (C=C); δ_H(400 MHz; CDCl$_3$) 1.05, 1.15, and 1.38 (9 H, 3 × s, 3 × Me), 1.70 and 1.77 (2 H, each d, J 15.4 Hz, 5-H$_2$), 2.35 and 2.74 (2 H, each d, J 13.1 Hz, 7-H$_2$), 3.17 (3 H, s, OMe), 3.96 (1 H, dd, J 15.3 and 0.9 Hz, 2-H), 4.36 (1 H, d with d-character, J 15.3 Hz, 2-H), and 5.20 (1 H, d with m-character, J 0.9 Hz, HCCN); δ_C(CDCl$_3$) 23.9, 27.8, and 32.2 (3 × q, 3 × Me), 33.6 (s, C-6), 46.4 and 50.6 (2 × t, C-5 and C-7), 47.7 (q, OMe), 64.3 (t, C-2), 95.6 (d, HCCN), 101.8 (s, C-4), 116.6 (s, CN), and 164.5 (s, C-1); m/z 209 (M^+, 1%), 194 (13), 178 (22), and 43 (100).

(Z)-4-Methoxy-4,6,6-trimethyl-3-oxacycloheptylidenaceto-nitrile, Z-(28) (*ca.* 80% pure), b.p. 110 °C at 0.2 mmHg (Found: M^+, 209.1445. C$_{12}$H$_{19}$NO$_2$ requires M, 209.1413); ν_{max}(film) 2 220 (C≡N) and 1 625 cm^{-1} (C=C); δ_H(400 MHz; CDCl$_3$) 0.94, 1.13, and 1.41 (9 H, 3 × s, 3 × Me), 1.62 and 1.67 (2 H, each d, J 15.3 Hz, 5-H$_2$), 2.07 and 2.63 (2 H, each d, J 12.7 Hz, 7-H$_2$), 3.20 (3 H, s, OMe), 4.33 (1 H, dd, J 17.1 and 1.8 Hz, 2-H), 4.52 (1 H, br d, J 17.1 Hz, 2-H), and 5.11 (1 H, br s, $w_{\frac{1}{2}}$ 4.5 Hz, HCCN); δ_C(CDCl$_3$) 23.5, 29.4, and 31.4 (3 × q, 3 × Me), 33.0 (s, C-6), 47.6 and 49.9 (2 × t, C-5 and C-7), 47.8 (q, OMe), 62.4 (t, C-2), 93.4 (d, HCCN), 101.9 (s, C-4), 115.6 (s, CN), and 166.3 (s, C-1); m/z 209 (M^+, 4%), 194 (24), 178 (42), and 43 (100).

4-Methoxy-4,6,6-trimethyl-3-oxa-1-cycloheptenylaceto-nitrile (29) [contaminated with ca. 60% E-(4), Z-(28), and (31)]; δ_H(60 MHz; CDCl$_3$) 2.93 (2 H, s, H$_2$CCN), 3.20 (3 H, s, OMe), and 6.07 (1 H, br s, 2-H).

1-(2',2'-Dimethyl-4'-oxopentyl)cyclopropene-3-carbonitrile (30), b.p. 105 °C at 0.2 mmHg (Found: M^+, 177.1162. C$_{11}$H$_{15}$NO requires M, 177.1154); ν_{max}(film) 3 120 (cyclopro-pene), 2 210 (C≡N), 1 780 (C=C in cyclopropene), and 1 710 cm^{-1} (C=O); δ_H(400 MHz; CDCl$_3$) 1.12 and 1.13 (6 H, 2 × s, 2'-Me$_2$), 1.83 (1 H, d, J 1.5 Hz, 3-H), 2.14 (3 H, s, 5'-H$_3$), 2.47 (2 H, s, 3'-H$_2$), 2.74 (2 H, s with m-character, 1'-H$_2$), and 6.57 (1 H, d, J 1.5 Hz, 2-H); δ_C(CDCl$_3$) 3.4 (d, C-3), 27.6 (2 × q, 2 × Me), 32.0 (q, C-5'), 33.6 (s, C-2'), 36.4 and 52.9 (2 × t, C-1' and C-3'), 95.9 (d, C-2), 114.1 (s, CN), 123.3 (s, C-1), and 207.6 (s, C-4'); m/z 177 (M^+, 16%), 162 (35), 134 (50), and 43 (100).

1-Formyl-2-methoxy-2,4,4-trimethylcyclopentylacetonitrile (31), b.p. 100 °C at 0.2 mmHg (Found: C, 68.64; H, 9.31; N, 6.44.

$C_{12}H_{19}NO_2$ requires C, 68.86; H, 9.15; N, 6.69%); ν_{max}(film) 2 230 (C≡N) and 1 715 cm⁻¹ (C=O); δ_H(400 MHz, CDCl₃) 1.17, 1.18, and 1.19 (9 H, 3 × s, 3 × Me), 1.59 and 2.15 (2 H, each d, J 14.7 Hz, 3- or 5-H₂), 1.92 and 2.05 (2 H, each d, J 14.3 Hz, 3- or 5-H₂), 2.68 and 2.74 (2 H, each d, J 16.8 Hz, H₂CCN), 3.18 (3 H, s, OMe), and 9.69 (1 H, s, CHO); δ_C(CDCl₃) 17.4 (t, H₂CCN), 18.0, 32.1, and 32.2 (3 × q, 3 × Me), 36.0 (s, C-4), 46.8 and 48.6 (2 × t, C-3 and C-5), 48.8 (q, OMe), 64.0 (s, C-1), 85.7 (s, C-2), 118.5 (s, CN), and 200.6 (d, CHO); m/z 194 ($M^+ - 15$, 0.6%), 177 (0.3), 113 (100), and 99 (44).

Photochemical Reaction of the Compound E-(28).—A solution of E-(**28**) (84.0 mg, 0.402 mmol) and TEA (40.6 mg, 0.402 mmol) in MeOH (8.4 ml) was irradiated under argon through a quartz filter (64% conversion) for 12.8 h at room temperature. After the solvent had been removed, the mixture was chromatographed [SiO₂ A; hexane–ethyl acetate (9:1)] to yield the Z-isomer Z-(**28**) (30.0 mg, 56%).

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