

Photochemical Reactions of Nitrile Compounds. Part 2.¹ Photochemistry of an α,β -Unsaturated γ,δ -Epoxy Nitrile and an γ,δ -Cyclopropyl Nitrile

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Direct irradiation (λ 254 nm) of the α,β -unsaturated γ,δ -epoxy nitrile (**1**) led selectively to the products (**13**)—(**19**) arising from a carbonyl ylide or a carbene intermediate. However, products of an (*E/Z*)-isomerization and a transformation *via* C(γ)–O bond cleavage of the oxirane, which are triplet processes, were not observed. On singlet excitation (λ 254 nm), the α,β -unsaturated γ,δ -cyclopropyl nitrile (**4**) afforded (**38**) as the main product along with (**39**) whereas, on triplet excitation of (**4**) (*E/Z*)-isomerization was the main process observed. Acid-catalysed rearrangements of compounds (**1**) and (**8**) were also studied.

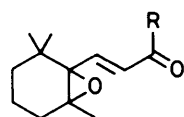
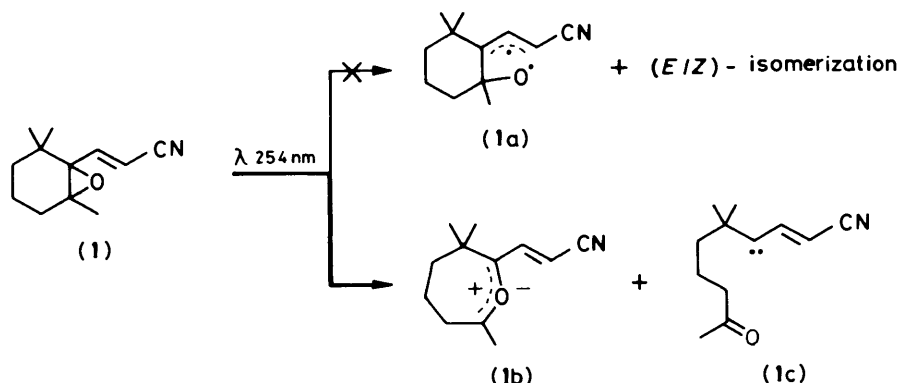
Photochemical reactions of γ,δ -epoxy enones have been widely investigated.^{2,3} In a previous communication,¹ we showed that the epoxy nitrile (**1**) gives rise to selective cleavage of the C(γ)–C(δ) bond of the oxirane followed by product formation *via* the carbonyl ylide (**1b**) and the carbene intermediate (**1c**). However, (*E/Z*)-isomerization of the side chain and transformation *via* C(γ)–O bond cleavage of the oxirane do not occur as observed on ¹ π,π^* -excitation (λ 254 nm) of γ,δ -epoxy α -enones of type (**2**)² and the corresponding ester (**3**).⁴

By replacement of the carbonyl group in the γ,δ -epoxy enone (**2**) by a cyano group, on ¹ π,π^* -excitation of (**1**) the isomerization *via* C(γ)–O cleavage is clearly avoided. Here we describe the details of the photochemistry and acid-catalysed reaction of (**1**), and also a study of the photochemistry of γ,δ -cyclopropyl α -enenitrile (**4**), which bears a cyano group in place of the methyl ketone function of (**5**).⁵

(**6**)⁶ in 81% yield by epoxidation with *m*-chloroperbenzoic acid (*m*-CPBA). Wittig–Horner reaction of the aldehyde (**7**)⁷ gave the cyclopropyl enenitrile (**4**) in 58% yield.

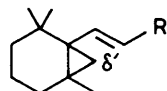
Photochemical Reactions of Compound (1).—On triplet sensitization, compound (**1**) in acetone ($\lambda > 280$ nm) selectively undergoes (*E/Z*)-isomerization of the side chain and C(γ)–O cleavage of the oxirane leading to intermediate (**1a**), followed by stabilization to compound (**9**) and by a [1,2]-alkyl shift to products (**10**), (**11**), and (**12**). Similar types of photoproducts were formed on triplet sensitization of the corresponding γ,δ -epoxy α -enones^{2,3} and the corresponding esters.⁴

By contrast, π,π^* -excitation of (**1**) in pentane (λ 254 nm) shows C(γ)–C(δ) cleavage to the carbonyl ylide (**1b**) and the carbene (**1c**); intermediates similar to those obtained from (**2**) and (**3**). By a known process, the carbonyl ylide (**1b**) undergoes



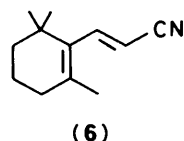
(2) R = Me

(3) R = OMe

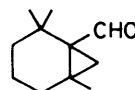


(4) R = CN

(5) R = COMe



(6)



(7)



Results and Discussion

Preparation of the Epoxy Enenitrile (1) and Cyclopropyl Enenitrile (4).—The nitrile (**1**) was prepared from dienitrile

Scheme 2. Reagents: i, *m*-CPBA; ii, (EtO)₂P(O)CH₂CN

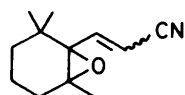
Table. Results of the photolyses of compound (1)

Solvent	λ /nm	Conversion/%	Product distribution/% ^a															
			(8)	(9) ^b	(10)	(11)	(12)	(13) ^b	(14)	(15) ^c	(16) ^{b,d}	(17) ^b	(18)	(19) ^c	(20) ^b	(21)		
Acetone	>280	88	10	21	8	21	15											
Pentane	254	86						6	23	8	5	10	18	2				
MeCN	254	81						51	4	5		11	8					
MeOH	254	83											8	Trace		7		49

^a Yields are based on converted starting material, and were determined after chromatography on SiO₂ by ¹H n.m.r. spectroscopy of the fractions.

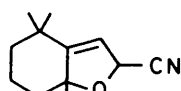
^b Only a single stereoisomer was detected, and the configuration could not be assigned. ^c The mixture (15) and (19) (8:2) could not be separated.

^d Compound (16) could be isolated as the 2,4-dinitrophenylhydrazone derivative (27).

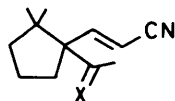


(1) E

(8) Z

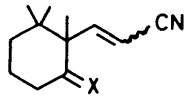


(9)



(10) X = O

(23) X = R



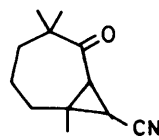
(11) E; X = O

(12) Z; X = O

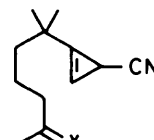
(24) E; X = R

from C(γ)-O bond cleavage, because of the low lying n,π^* -state of the cyano groups.¹¹

On photolysis of (1) in acetonitrile, however, the yield of the photoproduct (13) via the carbonyl ylide (1b) increased substantially, since the carbonyl ylide presumably becomes stabilized in a polar solvent.¹²

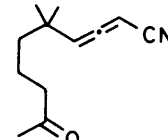


(17)



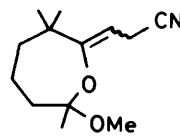
(18) X = O

(29) X = R

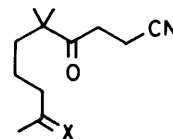


(19)

electrocyclization⁸ to give the enol ether (13), and by a [1,4]-H shift to form intermediate enol ether (22),* which presumably leads to the methyl ketones (14), (15), and (16) by a [1,3]-sigmatropic rearrangement.⁴ On further irradiation, (13) is isomerized to the bicyclic ketone (17) by a [1,3]-sigmatropic rearrangement.^{4,9} The carbene intermediate (1c) undergoes

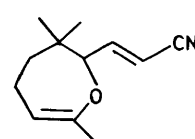


(20)

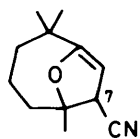


(21) X = O

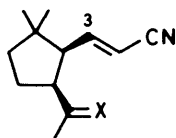
(30) X = R



(22)

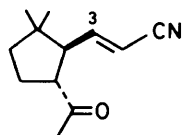


(13)

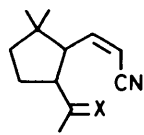


(14) X = O

(26) X = R

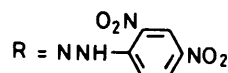


(15)



(16) X = O

(27) X = R

R = NNH-C₆H₃(NO₂)₂

By contrast, the photolysis of (1) in methanol afforded the acetal (20) and diketone (21) as the main products; (21) being formed by hydrolysis of (20). Since, in the presence of methanol, the ylide (1b) is rapidly quenched, the formation of the products (13)—(17) via the ylide (1b) could not be affirmed.

Structure of the Photoproducts.—As analogues of most of the products obtained here have already been described by Jeger and co-workers,^{2,3,4} only the relevant spectral data are discussed herein; full data and assignment of the n.m.r. signals are presented in the Experimental part.

cis-Epoxy enenitrile (8). The structure of (8) was determined from a comparison of its spectral data with those of compound (1). In the ¹H n.m.r. spectrum, two doublets at 5.53 and 6.59 p.p.m. show the characteristic *cis*-coupling constant of 12 Hz.

The dihydrofuran (9). The characteristic signals in the ¹H n.m.r. spectrum of (9) were the two doublets at 5.17 and 5.30 p.p.m. (*J* 2 Hz) due to the proton positioned α to the cyano group and the alkenic proton, and in the ¹³C n.m.r. spectrum two doublets at 69.2 and 112.1 p.p.m. and two singlets at 90.4 and 158.8 p.p.m. due to the carbon atoms of the dihydrofuran ring. The i.r. band due to cyano group was not observed, because the band of α -O-substituted nitriles is absent.¹³

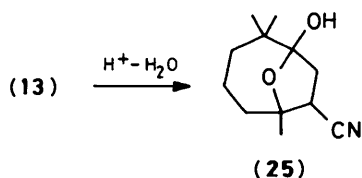
addition to the adjacent double bond to furnish the cyclopropene (18), and a [1,2]-H shift to give the allene (19).^{2,10}

However, in contrast to the photolyses of (2) and (3), irradiation of the nitrile (1) (λ 254 nm) did not afford products arising

* The formation of (22) by a [1,3]-homosigmatropic hydrogen shift may be excluded.

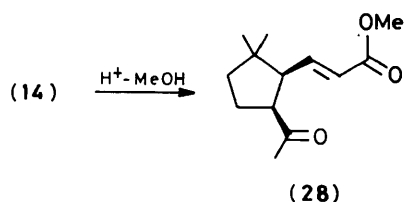
The methyl ketone (10), and cyclohexanones (11) and (12). In particular, an i.r. band at 1700 cm^{-1} and a singlet (2.12 p.p.m.) in the ^1H n.m.r. spectrum of (10) are characteristic of the methyl ketone moiety. An i.r. band in the spectra of (11) and (12) at 1705 cm^{-1} indicated a saturated carbonyl group. Significant signals in the ^1H n.m.r. spectra of (11) and (12) were the multiplets at δ 2.32–2.50 and δ 2.40–2.60 due to the CH_2 group in the position α to the carbonyl group, respectively. The n.m.r. spectra indicated that the enenitrile moiety was intact in (10), (11), and (12). Further evidence for the structures of (10) and (11) was obtained by reaction with 2,4-dinitrophenylhydrazine which afforded the hydrazones (23) (55%) and (24) (35%), respectively.

The dihydrofuran (13). The significant signals in the ^1H n.m.r. spectrum were a doublet (J 2 Hz) at 3.90 p.p.m. due to 7-H and a doublet (J 2 Hz) at 4.95 p.p.m. due to 8-H of the enol ether moiety, which is also evidenced by the i.r. band at 1630 cm^{-1} . Furthermore, compound (13) was hydrolysed with toluene-*p*-sulphonic acid in tetrahydrofuran–water leading to the alcohol (25) (35%). A similar type of compound was recently isolated from the photolysis of (2).¹⁴



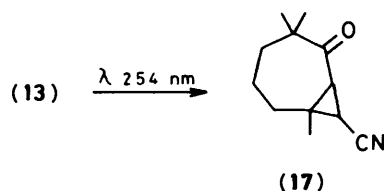
Scheme 3.

Methyl ketones (14), (15), and (16). Compounds (15) and (16) could not be isolated in pure form, but the structure of (15) could be determined from the spectral data of an 8:2 mixture of (15) and (19), and that of (16) from its pure 2,4-dinitrophenylhydrazone derivative (27) (63%). In particular, the ^1H n.m.r. spectra of compounds (14), (15), and (27) show singlets at 2.15, 2.09, and 2.08 p.p.m. respectively due to the methyl ketone or the methyl hydrazone side-chain, and double doublets at δ 6.55 (J 16 and 9 Hz), δ 6.53 (J 16.6 and 11.2 Hz), and a triplet at δ 6.32 (J 11 Hz) due to 3-H. The configuration of compound (14) was determined by its methanolysis to the known methyl ester (28)⁴ (56%), in which the methyl ketone and the enenitrile side-chains are *cis*-disposed. Thus, the configuration of the side-chains in (15) is *trans*. Further evidence for the structure of (14) was obtained from its reaction with 2,4-dinitrophenylhydrazine which led to (26) (60%). The configuration of the side-chains in (16) could not be assigned.



Scheme 4.

The bicyclo[5.1.0]octan-2-one (17). The structure of this compound was deduced from the fact that it was formed on photolysis of (13) via a [1,3]-sigmatropic rearrangement.⁴ In particular, the ^{13}C n.m.r. spectrum showed two doublets at 20.3 and 41.0 p.p.m. and a singlet at 28.7 p.p.m. due to the cyclopropyl moiety, and a singlet at 48.4 p.p.m. due to the carbon



Scheme 5.

atom bearing the geminal methyl groups, which is in α -position to a C=O group.

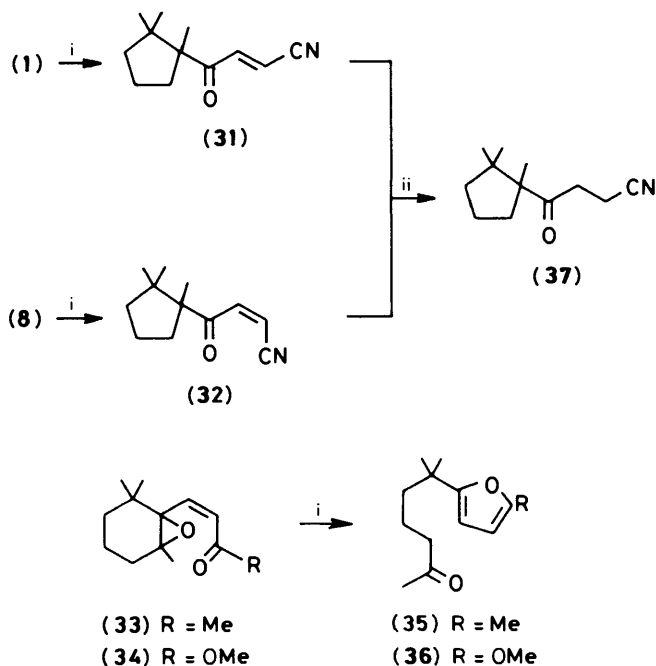
The cyclopropene (18). As characteristic signals, the ^1H n.m.r. spectrum showed two doublets (J 2 Hz) at 1.85 and 6.42 p.p.m., and the ^{13}C n.m.r. spectrum had two doublets at 2.3 and 92.5 p.p.m. and a singlet at 122.0 or 123.3 p.p.m. due to the cyclopropene moiety, which was also evidenced by the i.r. band at 1785 cm^{-1} . Furthermore, compound (18) was treated with 2,4-dinitrophenylhydrazine leading to (29) (50%).

The allene (19). This compound could not be isolated in pure form. Evidence for the structure stemmed from the ^1H n.m.r. spectrum of an 8:2 mixture of (15) and (19) showing two doublets (J 6.4 Hz) at 5.28 and 5.66 p.p.m. and an i.r. band at 1960 cm^{-1} , which are characteristic for the allene moiety.

The acetal (20). Most of the structural evidence stemmed from the ^1H n.m.r. spectrum. In particular, a singlet at 3.07 and a triplet (J 7 Hz) at 4.94 p.p.m. are characteristic of the methoxy group and for the alkene hydrogen, respectively.

The diketone (21). The two carbonyl groups were evidenced by the i.r. band at 1710 cm^{-1} and two singlets at 208.1 and 211.1 p.p.m. in the ^{13}C n.m.r. spectrum. Further evidence for the structure of (21) was obtained from its reaction with 2,4-dinitrophenylhydrazine which gave the monohydrazone (30) (30%).

Acid-catalysed Rearrangements of Compounds (1) and (8).—On treatment with $\text{BF}_3\text{-OEt}_2$, the epoxy nitriles (1) and (8) undergo isomerization to compounds (31) (97%) and (32) (47%), respectively. This type of isomerization is also observed

Scheme 6. Reagents: i, $\text{BF}_3\text{-OEt}_2$; ii, Pd-C-H_2

during the acid-catalysed rearrangement of (2)² and (3),⁴ but (33) and (34), the *cis* derivatives of (2) and (3), isomerize to the furans (35) and (36), respectively. In the case of (32), however, the same rearrangement observed for (31) occurred as evidenced by the absence of the CO function.

The spectral evidence for (31) includes an i.r. band at 1 690 cm⁻¹ and two doublets at 6.34 and 7.26 p.p.m. (*J* 16 Hz) in the ¹H n.m.r. spectrum indicating a *trans*-enone moiety; for (32) an i.r. band at 1 695 cm⁻¹ and two doublets at 5.70 and 7.80 p.p.m. (*J* 11 Hz) in the ¹H n.m.r. spectrum, indicating a *cis*-enone moiety. Moreover, compounds (31) and (32) were converted to the same oxo nitrile (37) (79 and 57%, respectively) by reduction with Pd-C-H₂.

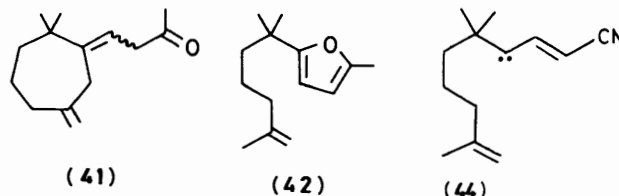
Photochemical Reactions of Compound (4).—The photolysis of a 0.053M solution of the cyclopropyl enenitrile (4) in pentane with a low pressure mercury lamp through a quartz filter (λ 254 nm) under argon at room temperature (100% conversion) gave the cycloheptane (38) (46%),† the cyclopropene (39) (18%), and unknown compounds (26%).

Triplet sensitization of a 0.053M solution of (4) with benzophenone in acetonitrile with a high pressure mercury lamp through a Pyrex filter (λ > 280 nm; 71% conversion) gave compound (40) (21%) † and unknown compounds (30%).

π,π*-Excitation of compound (4) shows C(γ)-C(δ) cleavage to give the cycloheptane (38) by a [1,3]-homosigmatropic rearrangement, and to the cyclopropene (39) via a carbene intermediate (44).¹⁵ Whereas on triplet sensitization, compound (4) undergoes mainly (*E/Z*)-isomerization, the formation of the compounds (38) and (39) could not be observed. In contrast to the photochemistry of the cyclopropyl enone (5), which produces mainly the diene (41) via δ'-H abstraction with carbonyl group and furan (42) via a carbene intermediate,⁵ the formation of the analogous products (41) and (42) from the photolysis of (4), is hindered, because of the absence of the carbonyl group.

The structure of compound (38) was deduced from the spectral data. In particular, the ¹H n.m.r. spectrum showed a doublet at 5.28 p.p.m. (*J* 16 Hz) and a double doublet at 6.67 p.p.m. (*J* 16 and 10 Hz) due to the acrylonitrile moiety, and two singlets at 4.70 and 4.73 p.p.m. due to the methylene group, which is also evidenced in the ¹³C n.m.r. spectrum by a triplet at 112.2 p.p.m. The structure of (39) was confirmed by comparison of the spectral data with that of (18). Instead of the carbonyl

group, the methylene group gave rise to two singlets at 4.67 and 4.71 p.p.m. in the ¹H n.m.r. spectrum. Compound (40) could not be isolated in pure form, but its structure was determined from the n.m.r. spectrum of a 6:3 mixture of (4) and (40). In the ¹H n.m.r. spectrum two doublets at 5.48 and 6.66 p.p.m. showed the characteristic *cis* coupling constant (*J* 11.3 Hz), and in the ¹³C n.m.r. spectrum a triplet at 17.5 p.p.m. indicated the CH₂ group of the cyclopropane ring.



The thermolysis of (4) however led to the cycloheptane (43) (73%) † by a [1,5]-homosigmatropic rearrangement.¹⁶ The ¹H n.m.r. spectrum showed characteristic signals: a doublet (*J* 6.7 Hz) at 3.14 p.p.m. due to the 2-H₂ and two singlets at 4.65 and 4.73 p.p.m. due to the methylene group.

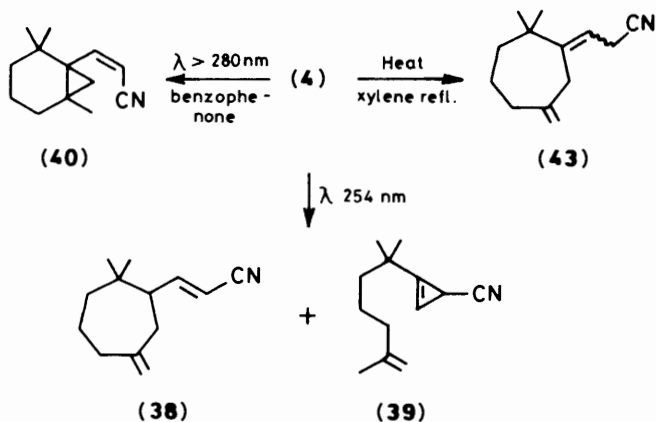
In conclusion, our investigation shows that on direct irradiation (λ 254 nm) of compounds (1) and (4), which bear a cyano group in place of the methyl ketone function of (2) and (5) respectively, the triplet processes are clearly avoided.

Experimental

M.p.s and b.p.s are uncorrected. M.p.s were measured with a Yanaco MP-3 apparatus and b.p.s were measured with Büchi Kugelrohr GKR-50 apparatus. U.v. spectra were recorded on a Hitachi 124 spectrometer and i.r. spectra on a Hitachi 215 spectrometer. ¹H n.m.r. spectra were obtained with a JEOL PMX-60, a JEOL PS-100, or a JEOL GX-400 spectrometer and ¹³C n.m.r. spectra were run on a JEOL FX-60 or a JEOL GX-400 spectrometer using tetramethylsilane as the internal standard. Mass spectra were taken on a JEOL JMS-D300 spectrometer. G.l.c. was carried out on a JEOL JGC-1100 instrument (flame ionization detection) and the column used was 3 m × 3 mm of 5% OV-17 on Chromosorb W. Column chromatography was performed with Kanto silica gel, 80–100 mesh (SiO₂ A), or Merck silica gel 60, 230–400 mesh (SiO₂ B).

A Riko 100 W (lamp A) and 400 W (lamp B) high pressure mercury lamp and an Eikosha 60 W low pressure mercury lamp (lamp C) were used as the irradiation sources. Primed locants in the n.m.r. data refer to ring protons or carbon atoms.

Preparation of the Epoxy Enenitrile (1).—A mixture of the dienitrile (6)⁶ (275 mg, 1.57 mmol) in CH₂Cl₂ (6 ml) and aqueous NaHCO₃ (0.5M; 3 ml) was cooled to 0 °C, and a solution of *m*-chloroperbenzoic acid (80%; 344 mg, 1.60 mmol) in CH₂Cl₂ (4.0 ml) was added dropwise with stirring. The mixture was stirred for 2 h at 0 °C, then for 2 h at room temperature. The organic phase was then separated, and worked up. The residue was chromatographed [SiO₂ A; hexane-ether (4:1)] to afford (*E*)-3-(1,2-epoxy-2,6,6-trimethylcyclohexyl)propenenitrile (1) (243 mg, 81%) which had b.p. 100 °C at 0.2 mmHg (Found: C, 75.05; H, 9.1; N, 7.2. C₁₂H₁₇NO requires C, 75.35; H, 8.96; N, 7.32%); λ_{max}(EtOH) 222 nm (ε 10 700); ν_{max}(film) 2 220 (C≡N) and 1 630 cm⁻¹ (C=C); δ_H (100 MHz; CDCl₃) 0.91, 1.11, and 1.14 (9 H, 3 × s, 3 × Me), 1.10–2.05 (6 H, m, 3 × CH₂), 5.53 (1 H, d, *J* 16 Hz, 2-H), and 6.94 (1 H, d, *J* 16 Hz, 3-H); δ_C(CDCl₃) 16.8 (t, C-4'), 20.4 and 25.7 (3 × q, 2 × q at 25.7, 3 × Me), 29.8 (t, C-3'), 33.5 (s, C-6'), 35.6 (t, C-5'), 66.5 and 70.9 (2 × s, C-1' and C-2'), 102.8 (d, C-2), 117.2 (s, C-1), and 150.9 (d, C-3); *m/z* 191 (*M*⁺) and 43 (*M*⁺ - 148, 100%).



Scheme 7.

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

Preparation of the Cyclopropyl Enenitrile (4).—To a suspension of NaH [1.16 g, 48.3 mmol; prepared from an NaH dispersion (50%, 2.32 g) by washing it twice with pentane (30 ml)] in dry dimethylformamide (85 ml) was added dropwise diethyl cyanomethylphosphonate (7.09 g, 40.1 mmol) at room temperature. After the mixture had been stirred at room temperature for 20 min, 2,2,6-trimethylbicyclo[4.1.0]heptanecarbaldehyde (**7**)⁷ (4.79 g, 28.9 mmol) was added at 0 °C and stirring was continued at room temperature for 2 h. Ice-water (85 ml) was then added to the mixture and the organic phase was extracted with Et₂O and worked up. The residue was chromatographed (SiO₂, A; benzene) to afford (E)-3-(2',2',6'-trimethylbicyclo[4.1.0]heptyl)propenenitrile (**4**), (3.17 g, 58%), b.p. 70 °C at 0.15 mmHg (Found: *M*⁺, 189.1517. C₁₃H₁₉N requires *M*, 189.1517); λ_{max}(EtOH) 237 nm (ε 6 200); ν_{max}(film) 2 220 (C≡N) and 1 620 cm⁻¹ (C=C); δ_H (100 MHz; CDCl₃) 0.48 and 0.67 (2 H, 2 × d, *J* 5 Hz, 7'-H₂), 0.86, 0.98, and 1.10 (9 H, 3 × s, 3 × Me), 1.1—1.8 (6 H, m, 3 × CH₂), 5.26 (1 H, d, *J* 16 Hz, 2-H), and 7.00 (1 H, d, *J* 16 Hz, 3-H); δ_C(CDCl₃) 17.4 (t, C-7'), 20.2 (t, C-4'), 23.5, 26.6, and 28.8 (3 × q, 3 × Me), 24.0 (s, C-6'), 29.6 (t, C-5'), 32.0 and 38.6 (2 × s, C-1' and C-2'), 36.0 (t, C-3'), 101.6 (d, C-2), 117.8 (s, C-1), and 158.3 (d, C-3); *m/z* 189 (*M*⁺) and 174 (*M*⁺ - 15, 100%).

Photochemical Reactions of the Epoxy Enenitrile (1).—In acetone (λ > 280 nm). A solution of the epoxy enenitrile (**1**) (973 mg, 5.09 mmol) in acetone (125 ml) was irradiated under argon through a Pyrex filter (lamp A; 88% conversion) for 25 h at room temperature. After the solvent had been removed, chromatography [SiO₂, A; hexane-ether (4:1)] of the residue yielded several fractions; the following product distribution was determined from ¹H n.m.r. analysis: * (**8**) (89 mg, 10%), (**9**) (175 mg, 21%), (**10**) (65 mg, 8%), (**11**) (181 mg, 21%), and (**12**) (129 mg, 15%).

(Z)-3-(1',2'-Epoxy-2',6',6'-trimethylcyclohexyl)propenenitrile (**8**) had m.p. 57.5—58.5 °C (Found: C, 75.1; H, 9.05; N, 7.3. C₁₂H₁₇NO requires C, 75.35; H, 8.96; N, 7.32%); ν_{max}(film) 2 220 (C≡N) and 1 625 cm⁻¹ (C=C); δ_H (100 MHz; CDCl₃) 1.05, 1.10, and 1.25 (9 H, 3 × s, 3 × Me), 1.20—2.08 (6 H, m, 3 × CH₂), 5.53 (1 H, d, *J* 12 Hz, 2-H), and 6.59 (1 H, d, *J* 12 Hz, 3-H); δ_C(CDCl₃) 16.8 (t, C-4'), 21.4, 25.5, and 25.8 (3 × q, 3 × Me), 29.5 (t, C-3'), 34.2 (s, C-6'), 35.2 (t, C-5'), 64.9 and 70.6 (2 × s, C-1' and C-2'), 102.3 (d, C-2), 116.1 (s, C-1), and 149.6 (d, C-3); *m/z* 191 (*M*⁺) and 43 (*M*⁺ - 148, 100%).

2,2,6-Trimethyl-7-oxabicyclo[4.3.0]nona-1(9)-ene-8-carbonitrile (**9**) had b.p. 100 °C at 0.04 mmHg; ν_{max}(film) 1 645 cm⁻¹ (C=C); δ_H (100 MHz; CDCl₃) 1.11, 1.17, and 1.52 (9 H, 3 × s, 3 × Me), 1.20—2.05 (6 H, m, 3 × CH₂), and 5.17 and 5.30 (2 H, each d, *J* 2 Hz, 8- and 9-H); δ_C(CDCl₃) 20.1 (t, C-4), 25.5, 25.8, and 30.3 (3 × q, 3 × Me), 35.1 (s, C-2), 40.9 (2 × t, C-3 and C-5), 69.2 (d, C-8), 90.4 (s, C-6), 112.1 (d, C-9), 118.7 (s, CN), and 158.8 (s, C-1); *m/z* 191 (*M*⁺) and 176 (*M*⁺ - 15, 100%).

(E)-3-(1'-Acetyl-2',2'-dimethylcyclopentyl)propenenitrile (**10**) had b.p. 110 °C at 0.15 mmHg; ν_{max}(film) 2 225 (C≡N), 1 700 (C=O), and 1 625 cm⁻¹ (C=C); δ_H (100 MHz; CDCl₃) 0.99 and 1.02 (6 H, 2 × s, 2 × Me), 1.4—2.5 (6 H, m, 3 × CH₂), 2.12 (3 H, s, MeCO), 5.30 (1 H, d, *J* 17 Hz, 2-H), and 7.03 (1 H, d, *J* 17 Hz, 3-H); δ_C(CDCl₃) 19.9 (t, C-4'), 24.9 and 30.5 (3 × q, 2 × q at 24.9, 3 × Me), 29.7 (t, C-5'), 39.3 (t, C-3'), 47.1 (s, C-2'), 67.8 (s, C-1'), 100.4 (d, C-2), 117.1 (s, C-1), 156.2 (d, C-3), and 207.5 (s, CO); *m/z* 191 (*M*⁺), 149 (*M*⁺ - 42), and 43 (*M*⁺ - 148, 100%).

(E)-3-(1',2',2'-Trimethyl-6'-oxocyclohexyl)propenenitrile (**11**) had m.p. 37—38 °C; ν_{max}(CHCl₃) 2 225 (C≡N), 1 705 (C=O),

and 1 615 cm⁻¹ (C=C); δ_H (100 MHz; CDCl₃) 0.91, 0.97, and 1.21 (9 H, 3 × s, 3 × Me), 1.59—2.02 (4 H, m, 3'-H₂ and 4'-H₂), 2.32—2.50 (2 H, m, 5'-H₂), 5.29 (1 H, d, *J* 17 Hz, 2-H), and 7.16 (1 H, d, *J* 17 Hz, 3-H); *m/z* 191 (*M*⁺) and 123 (*M*⁺ - 68, 100%).

(Z)-3-(1',2',2'-Trimethyl-6'-oxocyclohexyl)propenenitrile (**12**) had b.p. 120 °C at 0.1 mmHg (Found: C, 75.55, H, 9.2; N, 6.95. C₁₂H₁₇NO requires C, 75.35; H, 8.96; N, 7.32%); λ_{max}(EtOH) 216 (ε 7 128) and 294 nm (203); ν_{max}(film) 2 215 (C≡N) and 1 705 cm⁻¹ (C=O); δ_H (100 MHz; CDCl₃) 1.00 and 1.54 (9 H, 3 × s, 2 × s at 1.00, 3 × Me), 1.58—2.04 (4 H, m, 3'-H₂ and 4'-H₂), 2.40—2.60 (2 H, m, 5'-H₂), 5.55 (1 H, d, *J* 12 Hz, 2-H), and 6.82 (1 H, d, *J* 12 Hz, 3-H); δ_C(CDCl₃) 16.6, 24.1, and 24.5 (3 × q, 3 × Me), 22.1 (t, C-4'), 35.4 and 37.0 (2 × t, C-3' and C-5'), 42.0 (s, C-2'), 59.7 (s, C-1'), 100.3 (d, C-2), 115.9 (s, C-1), 154.1 (d, C-3), and 210.8 (s, C-6'); *m/z* 191 (*M*⁺) and 123 (*M*⁺ - 68, 100%).

In pentane (λ 254 nm). A solution of the epoxy enenitrile (**1**) (1.77 g, 9.27 mmol) in pentane (200 ml) was irradiated under argon through a quartz filter (lamp C; 86% conversion) for 8 h at room temperature. After the solvent had been removed, chromatography [SiO₂, A; hexane-ether (4:1)] of the residue yielded several fractions. The following product distribution was determined from ¹H n.m.r. analysis: * (**13**) (90 mg, 6%), (**14**) (349 mg, 23%), (**15**) (117 mg, 8%), (**16**) (73 mg, 5%), (**17**) (152 mg, 10%), (**18**) (272 mg, 18%), and (**19**) (31 mg, 2%).

2,2,6-Trimethyl-9-oxabicyclo[4.2.1]non-1(8)-ene-7-carbonitrile (**13**) (ca. 90% pure) had b.p. 75 °C at 0.1 mmHg; ν_{max}(film) 2 240 (C≡N) and 1 635 cm⁻¹ (C=C); δ_H (100 MHz; CDCl₃) 1.04, 1.16, and 1.55 (9 H, 3 × s, 3 × Me), 1.1—2.1 (6 H, m, 3 × CH₂), 3.90 (1 H, d, *J* 2 Hz, 7-H), and 4.95 (1 H, d, *J* 2 Hz, 8-H); δ_C(CDCl₃) 20.1 (t, C-4), 25.5, 25.8, and 30.3 (3 × q, 3 × Me), 35.1 (s, C-2), 40.9 (2 × t, C-3 and C-5), 69.2 (d, C-7), 90.4 (s, C-6), 112.1 (d, C-8), 118.7 (s, CN), and 158.8 (s, C-1); *m/z* 191 (*M*⁺) and 43 (*M*⁺ - 148, 100%).

(E)-3-[(1'RS)-5'-Acetyl-2',2'-dimethylcyclopentyl]propenenitrile (**14**) had b.p. 130 °C at 0.07 mmHg; λ_{max}(EtOH) 221 (ε 8 200) and 276 nm (47); ν_{max}(film) 2 230 (C≡N), 1 715 (C=O), and 1 635 cm⁻¹ (C=C); δ_H (100 MHz; CDCl₃) 0.89 and 1.03 (6 H, 2 × s, 2'-Me₂), 1.44—2.32 (4 H, m, 2 × CH₂), 2.15 (3 H, s, MeCO), 2.55 (1 H, dd with t-character, *J* 9 Hz, 1'-H), 2.83—3.13 (1 H, m, 5'-H), 5.35 (1 H, d, *J* 16 Hz, 2-H), and 6.55 (1 H, dd, *J* 16 and 9 Hz, 3-H); δ_C(CDCl₃) 22.6, 27.4, and 29.6 (3 × q, 3 × Me), 26.5 and 40.6 (2 × t, C-3' and C-4'), 44.4 (s, C-2'), 55.6 (2 × d, C-1' and C-5'), 101.6 (d, C-2), 117.1 (s, C-1), 154.8 (d, C-3), and 208.4 (s, CO); *m/z* 191 (*M*⁺), 148 (*M*⁺ - 43), 122 (*M*⁺ - 69), and 43 (*M*⁺ - 148, 100%).

(E)-3-[(1'RS)-5'-Acetyl-2',2'-dimethylcyclopentyl]propenenitrile (**15**) [contaminated with ca. 20% of (**19**)], an oil, had ν_{max}(film) 2 225 (C≡N), 1 710 (C=O), and 1 630 cm⁻¹ (C=C); δ_H (400 MHz; CDCl₃) 0.93 and 1.06 (6 H, 2 × s, 2'-Me₂), 2.09 (3 H, s, MeCO), 2.17—2.27 (1 H, m, 5'-H), 2.54 (1 H, dd, *J* 11.2 and 8 Hz, 1'-H), 5.33 (1 H, d, *J* 16.6 Hz, 2-H), and 6.53 (1 H, dd, *J* 16.6 and 11.2 Hz, 3-H).

3,3,7-Trimethyl-2-oxobicyclo[5.1.0]octane-8-carbonitrile (**17**) had m.p. 127—128 °C (Found: C, 75.25; H, 9.1; N, 7.3. C₁₂H₁₇NO requires C, 75.35; H, 8.96; N, 7.32%); λ_{max}(EtOH) 281 nm (ε 83); ν_{max}(CHCl₃) 2 240 (C≡N) and 1 710 cm⁻¹ (C=O); δ_H (100 MHz; CDCl₃) 0.99, 1.11, and 1.17 (9 H, 3 × s, 3 × Me), 1.36—2.20 (6 H, m, 3 × CH₂), and 2.18 and 2.58 (2 H, each d, *J* 8 Hz, 1-H and 8-H); δ_C(CDCl₃) 19.2, 22.5, and 28.7 (3 × q, 3 × Me), 20.3 (d, C-8), 23.4, 33.7, and 40.4 (3 × t, 3 × CH₂), 28.7 (s, overlapping with q, C-7), 41.0 (d, C-1), 48.4 (s, C-3), 117.4 (s, CN), and 203.4 (s, C-2); *m/z* 191 (*M*⁺), 176 (*M*⁺ - 15), and 55 (*M*⁺ - 136, 100%).

1-(1',1'-Dimethyl-5'-oxohexyl)cyclopropene-3-carbonitrile (**18**) had b.p. 120 °C at 0.1 mmHg; ν_{max}(film) 3 140 (cyclopropene), 2 230 (C≡N), 1 785 (C=C in cyclopropene), and 1 720 cm⁻¹ (C=O); δ_H (100 MHz; CDCl₃) 1.26 (6 H, s, 1-Me₂),

1.43—1.60 (4 H, m, 2-H₂ and 3-H₂), 1.85 (1 H, d, *J* 2 Hz, cyclopropene 2-H), 2.14 (3 H, s, 6-H₃), 2.37—2.53 (2 H, m with t-character, 4-H₂), and 6.42 (1 H, d, *J* 2 Hz, cyclopropene 2-H); $\delta_{\text{C}}(\text{CDCl}_3)$ 2.3 (d, cyclopropene C-3), 18.9 (t, C-3), 25.4 and 29.9 (3 \times q, 2 \times q at 25.4, 3 \times Me), 34.5 (s, C-1), 39.7 and 43.6 (2 \times t, C-2 and C-4), 92.5 (d, cyclopropene C-2), 122.0 and 123.3 (2 \times s, cyclopropene C-1 and CN), and 208.2 (s, C-5); *m/z* 191 (*M*⁺), 176 (*M*⁺ - 15), 148 (*M*⁺ - 43), and 43 (*M*⁺ - 148, 100%).

5,5-Dimethyl-9-oxodeca-2,3-dienitrile (19) [contaminated with ca. 80% (15)], an oil, had $\nu_{\text{max.}}$ (film) 2 225 (C≡N), 1 960 (C=C=C), and 1 710 cm⁻¹ (C=O); δ_{H} (400 MHz; CDCl₃) 2.13 (3 H, s, 10-H₃), 2.44 (2 H, t, *J* 7.3 Hz, 8-H₂), and 5.28 and 5.66 (2 H, each d, *J* 6.4 Hz, 2-H and 3-H).

In acetonitrile (λ 254 nm). A solution of the nitrile (1) (300 mg, 1.57 mmol) in acetonitrile (25 ml) was irradiated under argon through a quartz filter (lamp C; 81% conversion) for 2.5 h at room temperature. After the solvent had been removed, the residual oil was chromatographed [SiO₂ B; hexane-ethyl acetate (4:1)-hexane-ethyl acetate (4:1)]. The following product distribution was determined from the ¹H n.m.r. spectrum of the mixed fraction.* (13) (124 mg, 51%), (14) (8 mg, 4%), (15) (12 mg, 5%), (17) (26 mg, 11%), and (18) (19 mg, 8%).

In methanol (λ 254 nm). A solution of the nitrile (1) (626 mg, 3.28 mmol) in methanol (60 ml) was irradiated under argon through a quartz filter (lamp C; 83% conversion) for 2.5 h at room temperature. After the solvent had been removed, the residual oil was chromatographed [SiO₂ B; hexane-ethyl acetate (4:1)]. The following product distribution was determined from the ¹H n.m.r. spectrum of the mixed fraction.* (18) (43 mg, 8%), (19) (trace), (20) (38 mg, 7%), and (21) (256 mg, 49%).

3-(3-Methoxy-3,7,7-trimethyl-2-oxacycloheptylidene)propanenitrile (20) had b.p. 100 °C at 0.15 mmHg (Found: *M*⁺, 223.1576. C₁₃H₂₁NO₂ requires *M*, 223.1572); $\nu_{\text{max.}}$ (film) 2 245 (C≡N) and 1 658 cm⁻¹ (C=C); δ_{H} (100 MHz; CCl₄) 1.06, 1.12, and 1.47 (9 H, 3 \times s, 3 \times Me), 1.20—1.80 (6 H, m, 3 \times CH₂), 3.07 (2 H, d, *J* 7 Hz, 2-H₂), 3.40 (3 H, s, OMe), and 4.94 (1 H, t, *J* 7 Hz, 3-H); *m/z* 223 (*M*⁺), 192 (*M*⁺ - 31), and 98 (*M*⁺ - 125, 100%).

5,5-Dimethyl-4,9-dioxodecanenitrile (21) had b.p. 150 °C at 0.3 mmHg (Found: *M*⁺, 209.1434. C₁₂H₁₉NO₂ requires *M*, 209.1416); $\nu_{\text{max.}}$ (CHCl₃) 2 250 (C≡N) and 1 710 cm⁻¹ (C=O); δ_{H} (400 MHz; CDCl₃) 1.50 (6 H, s, 5-Me₂), 1.37—1.53 (4 H, m, 6-H₂ and 7-H₂), 2.13 (3 H, s, 10-H₃), 2.43 (2 H, t, *J* 6.7 Hz, 8-H₂), and 2.59 and 2.90 (4 H, each t, *J* 7.3 Hz, 2-H₂ and 3-H₂); $\delta_{\text{C}}(\text{CDCl}_3)$ 11.8 (t, C-2), 18.7 (t, C-7), 24.1 (2 \times q, 5-Me₂), 29.9 (q, C-10), 32.8 and 39.1 (2 \times t, C-3 and C-6), 43.4 (t, C-8), 47.3 (s, C-5), 119.2 (s, C-1), and 208.1 and 211.1 (2 \times s, C-4 and C-9); *m/z* 209 (*M*⁺) and 43 (*M*⁺ - 166, 100%).

Photochemical Reaction of the Dihydrofuran (13).—A solution of the dihydrofuran (13) (30 mg, 0.157 mmol) in pentane (3.0 ml) was irradiated under argon through a quartz filter (lamp C; 68% conversion) for 1 h at room temperature. The yield of the product (17)* as estimated by g.l.c. (*T* 180 °C) analysis using nonadecane as an internal standard was (45%).

Formation of Hydrazone Derivatives.—*The methyl ketone (10).* To a solution of 2,4-dinitrophenylhydrazine (32.4 mg, 0.164 mmol) in ethanol (2.6 ml) and 2 drops of concentrated HCl was added the methyl ketone (10) (31 mg, 0.164 mmol) at room temperature. After 15 min, the volume of the solution was reduced by half, and the remainder was filtered. Recrystallization from ethanol afforded (E)-3-[1'-[1'-(2'',4''-dinitro-

phenylhydrazono)ethyl]-2',2'-dimethylcyclopentyl]propenenitrile (23), (34 mg, 55%), m.p. 209.5—211.5 °C (Found: C, 58.1; H, 5.65; N, 19.15. C₁₈H₂₁N₅O₄ requires C, 58.21; H, 5.70; N, 18.86%); $\lambda_{\text{max.}}$ (CHCl₃) 247 (ϵ 10 200) and 362 nm (18 900); $\nu_{\text{max.}}$ (CHCl₃) 3 330 (N-H), 2 230 (C≡N), and 1 620 cm⁻¹ (C=N); δ_{H} (60 MHz; CDCl₃) 0.98 and 1.18 (6 H, 2 \times s, 2'-Me₂), 1.4—2.8 (6 H, m, 3 \times CH₂), 2.07 (3 H, s, 2''-H₃), 5.27 (1 H, d, *J* 17 Hz, 2-H), 7.10 (1 H, d, *J* 17 Hz, 3-H), 7.87 (1 H, d, *J* 9 Hz, 6'''-ArH), 8.35 (1 H, dd, *J* 9 and 2 Hz, 5'''-ArH), 9.13 (1 H, d, *J* 2 Hz, 3'''-ArH), and 11.09 (1 H, s, ω 5 Hz, NH); *m/z* 371 (*M*⁺), 354 (*M*⁺ - 15), and 302 (*M*⁺ - 69, 100%).

The ketone (11). Analogous treatment of the ketone (11) (51.1 mg, 0.268 mmol) yielded (E)-3-[6'-(2'',4''-dinitrophenylhydrazono)-1',2',2'-trimethylcyclohexyl]propenenitrile (24) (35 mg, 35%), m.p. 165.5—168.5 °C (Found: C, 58.05; H, 5.65; N, 18.95. C₁₈H₂₁N₅O₄ requires C, 58.21; H, 5.70; N, 18.86%); $\lambda_{\text{max.}}$ (CHCl₃) 250 (ϵ 10 100) and 354 nm (15 100); $\nu_{\text{max.}}$ (CHCl₃) 3 330 (N-H), 2 230 (C≡N), and 1 625 cm⁻¹ (C=N); δ_{H} (60 MHz; CDCl₃) 0.93, 1.04, and 1.36 (9 H, 3 \times s, 3 \times Me), 1.5—2.1 (4 H, m, 3'-H₂ and 4'-H₂), 2.37—2.73 (2 H, m, 5'-H₂), 5.32 (1 H, d, *J* 17 Hz, 2-H), 7.25 (1 H, d, *J* 17 Hz, 3-H), 7.82 (1 H, d, *J* 9 Hz, 6''-ArH), 8.33 (1 H, dd, *J* 9 and 2 Hz, 5''-ArH), 9.08 (1 H, d, *J* 2 Hz, 3''-ArH), and 11.20 (1 H, s, ω 4 Hz, NH); $\delta_{\text{C}}(\text{CDCl}_3)$ 17.8, 24.5, and 24.7 (3 \times q, 3 \times Me), 20.5 and 22.8 (2 \times t, C-4' and C-5'), 35.9 (t, C-3'), 39.2 (s, C-2'), 53.2 (s, C-1'), 100.0 (d, C-2), 116.3 (d, C-6'), 117.5 (s, C-1), 123.3 (d, C-3'), 129.4 (s, C-2''), 130.2 (d, C-5'), 138.1 (s, C-4''), 145.2 (s, C-1''), 158.4 (d, C-3), and 161.4 (s, C-6'); *m/z* 371 (*M*⁺) and 69 (*M*⁺ - 302, 100%).

The methyl ketone (14). Analogous treatment of the methyl ketone (14) (73.8 mg, 0.386 mmol) gave (E)-1'(RS,5'RS)-3-{5'-[1''-(2''',4'''-dinitrophenylhydrazono)ethyl]-2',2'-dimethylcyclopentyl}propenenitrile (26) (86 mg, 60%), m.p. 134—137 °C (Found: C, 58.45; H, 5.55; N, 19.05. C₁₈H₂₁N₅O₄ requires C, 58.21; H, 5.70; N, 18.86%); $\nu_{\text{max.}}$ (CHCl₃) 3 320 (N-H), 2 220 (C≡N), and 1 620 cm⁻¹ (C=N); δ_{H} (400 MHz; CDCl₃) 0.94 and 1.11 (6 H, 2 \times s, 2'-Me₂), 1.69 (2 H, t, *J* 7 Hz, 3'-H₂), 1.78 (1 H, dq, *J* 13 and 7 Hz, 4'-H), 2.05 (3 H, s, 2''-H₃), 2.18 (1 H, ddt, *J* 13, 10, and 7 Hz, 4'-H), 2.53 (1 H, dd with t-character, *J* 10 and 9 Hz, 1'-H), 3.05 (1 H, dt, *J* 10 and 7 Hz, 5'-H), 5.38 (1 H, d, *J* 16 Hz, 2-H), 6.64 (1 H, dd, *J* 16 and 9 Hz, 3-H), 7.86 (1 H, d, *J* 9 Hz, 6'''-ArH), 8.31 (1 H, dd, *J* 9 and 2.5 Hz, 5'''-ArH), 9.12 (1 H, d, *J* 2.5 Hz, 3'''-ArH), and 11.03 (1 H, s, NH); *m/z* 371 (*M*⁺), 354 (*M*⁺ - 15), 325 (*M*⁺ - 46), and 132 (*M*⁺ - 239, 100%).

The methyl ketone (16). Analogous treatment of the methyl ketone (16) (70%; 56 mg, 0.293 mmol) afforded (Z)-3-{5'-[1''-(2''',4'''-dinitrophenylhydrazono)ethyl]-2',2'-dimethylcyclopentyl}propenenitrile (27) (68 mg, 63%), m.p. 182—184 °C (Found: C, 58.35; H, 5.65; N, 19.1. C₁₈H₂₁N₅O₄ requires C, 58.21; H, 5.70; N, 18.86%); $\lambda_{\text{max.}}$ (CHCl₃) 241 (ϵ 11 600) and 364 nm (21 300); $\nu_{\text{max.}}$ (CHCl₃) 3 330 (N-H), 2 230 (C≡N), and 1 625 cm⁻¹ (C=N); δ_{H} (100 MHz; CDCl₃) 0.97 and 1.16 (6 H, 2 \times s, 2'-Me₂), 1.52—2.30 (4 H, m, 2 \times CH₂), 2.08 (3 H, s, 2''-H₃), 2.80—3.25 (2 H, m, 1'-H and 5'-H), 5.39 (1 H, d, *J* 11 Hz, 2-H), 6.32 (1 H, t, *J* 11 Hz, 3-H), 8.01 (1 H, d, *J* 10 Hz, 6'''-ArH), 8.27 (1 H, dd, *J* 10 and 2 Hz, 5'''-ArH), 9.05 (1 H, d, *J* 2 Hz, 3'''-ArH), and 11.02 (1 H, s, NH); $\delta_{\text{C}}(\text{CDCl}_3)$ 15.0, 22.9, and 28.1 (3 \times q, 3 \times Me), 28.2 and 40.7 (2 \times t, C-3' and C-4'), 45.3 (s, C-2'), 52.5 and 55.1 (2 \times d, C-1' and C-5'), 101.4 (d, C-2), 116.4 (s, C-1), 117.0 (d, C-6'''), 123.4 (d, C-3'''), 129.3 (s, C-2'''), 130.1 (d, C-5'''), 138.0 (s, C-4'''), 145.1 (s, C-1'''), 154.9 (d, C-3), and 157.7 (s, C-1''); *m/z* 371 (*M*⁺), 325 (*M*⁺ - 46), and 132 (*M*⁺ - 239, 100%).

The cyclopropene (18). Analogous treatment of the cyclopropene (18) (42 mg, 0.220 mmol) yielded 2-[5'-(2'',4''-dinitrophenylhydrazono)-1',1'-dimethylhexyl]cyclopropenecarbonitrile (29) (41 mg, 50%), m.p. 86—88 °C (Found: C, 58.0; H, 5.7; N, 18.9. C₁₈H₂₁N₅O₄ requires C, 58.21; H, 5.70; N, 18.86%); $\nu_{\text{max.}}$ (CHCl₃) 3 360 (N-H), 3 140 (cyclopropene), 2 260

* As † on p. 1940.

(C≡N), 1 800 (C=C in cyclopropene), and 1 630 cm⁻¹ (C=N); δ_H (60 MHz; CDCl₃) 1.28 (6 H, s, 1'-Me₂), 1.5—2.7 (6 H, m, 3 × CH₂), 1.87 (1 H, d, *J* 2 Hz, 1-H), 2.07 (3 H, s, 6'-H₃), 6.45 (1 H, d, *J* 2 Hz, 3-H), 7.93 (1 H, d, *J* 9 Hz, 6''-ArH), 8.31 (1 H, dd, *J* 9 and 2 Hz, 5''-ArH), 9.11 (1 H, d, *J* 2 Hz, 3''-ArH), and 11.02 (1 H, s, w_{1/2} 5 Hz, NH); *m/z* 371 (*M*⁺), 354 (*M*⁺ - 15), and 41 (*M*⁺ - 330, 100%).

The diketone (21). Analogous treatment of the diketone (21) (358 mg, 1.71 mmol) and 2,4-dinitrophenylhydrazine (674 mg, 3.40 mmol) gave 9-(2',4'-dinitrophenylhydrazono)-5,5-dimethyl-4-oxodecanonitrile (30) (202 mg, 30%), m.p. 98—100 °C (Found: C, 55.7; H, 5.95; N, 17.95. C₁₈H₂₃N₅O₅ requires C, 55.52; H, 5.95; N, 17.99%); ν_{max}(CHCl₃) 3 340 (N-H), 2 260 (C≡N), 1 710 (C=O), and 1 620 cm⁻¹ (C=N); δ_H (400 MHz; CDCl₃) 1.21 (6 H, s, 5-Me₂), 1.52—1.64 (4 H, m, 6-H₂ and 7-H₂), 2.05 (3 H, s, 10-H₃), 2.42 and 2.88 (4 H, each t, *J* 7.0 Hz, 2-H₂ and 3-H₂), 2.59 (2 H, t, *J* 6.6 Hz, 8-H₂), 7.93 (1 H, d, *J* 9.5 Hz, 6'-ArH), 8.29 (1 H, dd, *J* 9.5 and 2.6 Hz, 5'-ArH), 9.09 (1 H, d, *J* 2.6 Hz, 3'-ArH), and 11.01 (1 H, s, NH); δ_C(CDCl₃) 11.9 (t, C-2), 16.0 (q, C-10), 21.2 (t, C-7), 24.4 (2 × q, 5-Me₂), 33.1 and 39.3 (3 × t, 2 × t at 39.3, C-3, C-6, and C-8), 47.3 (s, C-5), 116.5 (d, C-6'), 119.2 (s, C-1), 123.4 (d, C-3'), 129.1 (s, C-2'), 130.0 (d, C-5'), 137.8 (s, C-4'), 145.2 (s, C-1'), 157.3 (s, C-9), and 210.9 (s, C-4); *m/z* 389 (*M*⁺) and 41 (*M*⁺ - 348, 100%).

Additional Experiments.—Hydrolysis of the dihydrofuran (13). A solution of the dihydrofuran (13) (70 mg, 0.37 mmol) and toluene-*p*-sulphonic acid (*ca.* 7 mg) in THF (4 ml) and water (1.3 ml) was refluxed for 3 h. The cooled reaction mixture was then extracted with ether, and the organic layer was washed with saturated aqueous NaHCO₃ and worked up. Subsequent chromatography of the mixture [SiO₂ A; hexane-ethyl acetate (3:1)] afforded 1-hydroxy-2,2,6-trimethyl-9-oxabicyclo[4.2.1]nonane-7-carbonitrile (25), (27 mg, 35%), m.p. 108—109 °C (Found: C, 68.55; H, 9.4; N, 6.55. C₁₂H₁₉NO₂ requires C, 68.86; H, 9.15; N, 6.69%); ν_{max}(CHCl₃) 3 590 (OH) and 2 250 cm⁻¹ (C≡N); δ_H (400 MHz; CDCl₃) 0.93, 1.06, and 1.47 (9 H, 3 × s, 3 × Me), 1.27—1.35 and 1.41—1.81 (6 H, 2 × m, 3-H₂, 4-H₂, and 5-H₂), 2.24 (1 H, dd, *J* 13.7 and 8.5 Hz, 8-H), 2.47 (1 H, dd, *J* 13.7 and 11.7 Hz, 8-H), 2.36—2.65 (1 H, br, OH), and 2.97 (1 H, dd, *J* 11.7 and 8.5 Hz, 7-H); δ_C(CDCl₃) 20.3 (t, C-4), 21.1, 25.0, and 27.6 (3 × q, 3 × Me), 37.7, 38.0, and 41.3 (3 × t, C-3, C-5, and C-8), 39.7 (d, C-7), 40.5 (s, C-2), 82.9 (s, C-6), 109.5 (s, C-1), and 118.9 (s, CN); *m/z* 209 (*M*⁺) and 69 (*M*⁺ - 140, 100%).

Methanolysis of (14). A solution of (14) (27.5 mg, 0.144 mmol) in methanol (1 ml) with 2 drops of concentrated H₂SO₄ was heated under reflux for 12 h. After work-up of the reaction mixture, chromatography [SiO₂ A; hexane-ether (4:1)] yielded compound (28)⁴ (18 mg, 56%).

Hydrolysis of the acetal (20). A solution of (20) (89 mg, 0.34 mmol) and oxalic acid (20 mg, 0.16 mmol) in dioxane (3 ml) and water (1.5 ml) was stirred for 10 h at room temperature. After work-up, the diketone (21) was afforded quantitatively.

Acid-catalysed Rearrangements of Compounds (1) and (8).—

Reaction of (1) with BF₃-OEt₂. To a solution of the epoxy enenitrile (1) (300 mg, 1.57 mmol) in dry benzene (57 ml) was added slowly a solution of boron trifluoride-diethyl ether (95%; 0.11 ml, 0.89 mmol) in dry benzene (16 ml) at ambient temperature. After the reaction had been stirred for 1 h, work-up and subsequent chromatography [SiO₂ A; hexane-ether (4:1)] yielded (E)-4-oxo-4-(1',2',2'-trimethylcyclopentyl)but-2-enonitrile (31), (292 mg, 97%), b.p. 100 °C at 0.3 mmHg (Found: C, 74.85; H, 9.15; N, 7.25. C₁₂H₁₇NO requires C, 75.35; H, 8.96; N, 7.32%); ν_{max}(film) 2 230 (C=N), 1 690 (C=O), and 1 610 cm⁻¹ (C=C); δ_H (400 MHz; CDCl₃) 0.85, 1.08, and 1.18 (9 H, 3 × s, 3 × Me), 1.48—1.55, 1.64—1.77, and 2.37—2.44 (6 H, 3 × m,

3 × CH₂), 6.34 (1 H, d, *J* 16 Hz, 2-H), and 7.26 (1 H, d, *J* 16 Hz, 3-H); δ_C(CDCl₃) 19.7 (t, C-4'), 19.9, 24.4, and 25.4 (3 × q, 3 × Me), 34.3 and 40.4 (2 × t, C-3' and C-5'), 44.6 (s, C-2'), 59.1 (s, C-1'), 109.8 (d, C-2), 116.6 (s, C-1), 143.0 (d, C-3), and 200.6 (s, C-4); *m/z* 191 (*M*⁺) and 69 (*M*⁺ - 122, 100%).

Reaction of (8) with BF₃-OEt₂. Analogous treatment of (8) (100 mg, 0.524 mmol) with boron trifluoride-diethyl ether (95%; 0.04 ml, 0.31 mmol) for 2 h, yielded recovered (8) (11 mg, 11%) and (Z)-4-oxo-4-(1',2',2'-trimethylcyclopentyl)but-2-enonitrile (32), (33 mg, 33%), b.p. 110 °C at 0.05 mmHg; ν_{max}(film) 2 225 (C≡N), 1 695 (C=O), and 1 605 cm⁻¹ (C=C); δ_H (100 MHz; CDCl₃) 0.91, 1.10, and 1.20 (9 H, 3 × s, 3 × Me), 1.35—1.92 and 2.20—2.60 (6 H, 2 × m, 3 × CH₂), 5.70 (1 H, d, *J* 11 Hz, 2-H), and 7.08 (1 H, d, *J* 11 Hz, 3-H); δ_C(CDCl₃) 19.7 (t, C-4'), 20.1, 24.4, and 25.4 (3 × q, 3 × Me), 34.3 and 40.3 (2 × t, C-3' and C-5'), 44.6 (s, C-2'), 59.2 (s, C-1'), 107.0 (d, C-2), 115.6 (s, C-1), 143.1 (d, C-3), and 201.1 (s, C-4); *m/z* 191 (*M*⁺) and 69 (*M*⁺ - 122, 100%).

Catalytic Hydrogenations of Compounds (31) and (32).—(a) A suspension of Pd-C (5%; 4.4 mg) in ethanol (1.4 ml) was stirred under H₂ for 1 h, and a solution of (31) (52 mg, 0.27 mmol) in ethanol (0.5 ml) was added. The mixture was stirred under H₂ for 48 h, filtered through Celite and the solvent was evaporated. Chromatography [SiO₂ A; hexane-ether (4:1)] of the residue gave (37) (41 mg, 79%).

(b) Hydrogenation of (32) (16 mg, 0.084 mmol) according to procedure (a) for 48 h afforded, after chromatography, 4-oxo-4-(1',2',2'-trimethylcyclopentyl)butanonitrile (37), (9.2 mg, 57%), b.p. 120 °C at 0.15 mmHg; ν_{max}(film) 2 240 (C≡N) and 1 700 cm⁻¹ (C=O); δ_H (100 MHz; CDCl₃) 0.88, 1.11, and 1.18 (9 H, 3 × s, 3 × Me), 1.35—1.86, 2.14—2.64, and 2.71—2.94 (10 H, 3 × m, 5 × CH₂); *m/z* 193 (*M*⁺) and 111 (*M*⁺ - 82, 100%).

Photochemical Reactions of the Cyclopropyl Enenitrile (4).—*In pentane* (λ 254 nm). A solution of (4) (1.61 g, 8.52 mmol) in pentane (160 ml) was irradiated under argon through a quartz filter (lamp C, 100% conversion) for 22 h at room temperature. After removal of the solvent, chromatography [SiO₂ A; hexane-ether (8:1)] of the residue yielded several fractions. The following product distribution was determined by ¹H n.m.r. analysis.* (38) (740 mg, 46%), (39) (283 mg, 18%), and unknown compounds (413 mg, 26%).

(E)-3-(2',2'-Dimethyl-6-methylenecycloheptyl)propenenitrile (38) had b.p. 65 °C at 0.15 mmHg (Found: C, 82.35; H, 10.3; N, 7.35. C₁₃H₁₉N requires C, 82.48; H, 10.12; N, 7.40%); ν_{max}(film) 2 220 (C≡N) and 1 625 cm⁻¹ (C=C); δ_H (400 MHz; CDCl₃) 0.86 and 0.91 (6 H, 2 × s, 2 × Me), 1.36—1.62 (4 H, m, 3'-H₂ and 4'-H₂), 2.11 (1 H, dt, *J* 10 and 2.5 Hz, 1'-H), 2.18—2.37 (4 H, m, 5'-H₂ and 7'-H₂), 4.70 and 4.73 (2 H, 2 × s, w_{1/2} 4.7 Hz, =CH₂), 5.28 (1 H, d, *J* 16 Hz, 2-H), and 6.67 (1 H, dd, *J* 16 and 10 Hz, 3-H); δ_C(CDCl₃) 21.8 (t, C-4'), 23.7 and 29.9 (2 × q, 2 × Me), 36.1 (s, C-2'), 36.2, 36.9, and 42.1 (3 × t, C-3', C-5', and C-7'), 53.3 (d, C-1'), 99.1 (d, C-2), 112.2 (t, =CH₂), 117.5 (s, C-1), 148.2 (s, C-6'), and 158.4 (d, C-3); *m/z* 189 (*M*⁺) and 94 (*M*⁺ - 95, 100%).

1-(1',1',5'-Trimethylhex-5'-enyl)cyclopropene-3-carbonitrile (39) had b.p. 90 °C at 0.5 mmHg (Found: *M*⁺, 189.1515. C₁₃H₁₉N requires *M*, 189.1517); ν_{max}(film) 3 160 (cyclopropene), 3 080 (methylene), 2 250 (C≡N), 1 785 (C=C in cyclopropene), and 1 650 cm⁻¹ (C=C); δ_H (400 MHz; CDCl₃) 1.23 (6 H, s, 1'-Me₂), 1.45—1.60 (4 H, m, 2'-H₂ and 3'-H₂), 1.70 (3 H, s, 5'-Me), 1.83 (1 H, d, *J* 1.8 Hz, 1-H), 2.01 (2 H, t, *J* 7.5 Hz, 4'-H₂), 4.67 and 4.71 (2 H, 2 × s, w_{1/2} 6 Hz, 6'-H₂), and 6.38 (1 H, d, *J* 1.8 Hz, 3-H); δ_C(CDCl₃) 2.3 (d, C-1'), 22.2 (q, 5'-Me), 22.5 (t, C-3'),

* As † on p. 1940.

25.4 and 25.5 (2 × q, 1'-Me₂), 34.4 (s, C-1'), 37.9 and 39.9 (2 × t, C-2' and C-4'), 92.1 (d, C-3), 110.1 (t, C-6'), 122.3 and 123.5 (2 × s, C-2 and CN), and 145.3 (s, C-5').

Triplet excitation ($\lambda > 280$ nm; benzophenone). A solution of (4) (500 mg, 2.64 mmol) and benzophenone (2.40 g, 13.2 mmol) in acetonitrile (50 ml) was irradiated under argon through a Pyrex filter (lamp B; 71% conversion) for 6 h at room temperature. After the solvent had been removed, the mixture was chromatographed [SiO₂ A; hexane-ether (9:1)] to yield (40) (77 mg, 21%* and compounds of unknown structure (106 mg, 30%). (Z)-3-(2',2',6'-Trimethylbicyclo[4.1.0]heptyl)propanonitrile (40) [contaminated with 67% of (4)], an oil; δ_{H} (400 MHz; CDCl₃) 0.86 and 0.88 (2 H, 2 × d, *J* 5.8 Hz, 7'-H₂), 1.00, 1.01, and 1.05 (9 H, 3 × s, 3 × Me), 5.48 (1 H, d, *J* 11.3 Hz, 2-H), and 6.66 (1 H, d, *J* 11.3 Hz, 3-H); δ_{C} (CDCl₃) 17.5 (t, C-7'), 22.0 (s, C-6'), 22.1 (t, C-4'), 24.1 26.3, and 29.0 (3 × q, 3 × Me), 29.6 (t, C-5'), 33.3 and 36.6 (2 × s, C-1' and C-2'), 35.8 (t, C-6'), 102.2 (d, C-2), 116.7 (s, C-1), and 157.2 (d, C-3).

Thermolysis of Compound (4).—A solution of (4) (213 mg, 1.12 mmol) in xylene (25 ml) was refluxed for 30 min (74% conversion). After the solvent had been removed, chromatography [SiO₂ A; hexane-ether (8:1)] of the residue afforded 3-(2',2'-dimethyl-6'-methyleneheptan-2-ylidene)propanonitrile (43) (115 mg, 73%*), b.p. 115 °C at 0.3 mmHg (Found: *M*⁺, 189.1523. C₁₃H₁₉N requires *M*, 189.1517); ν_{max} (film) 3 080 (methylene), 2 250 (C≡N), and 1 645 cm⁻¹ (C=C); δ_{H} (400 MHz; CDCl₃) 1.07 (6 H, s, 2 × Me), 1.40—1.46 and 1.55—1.58 (4 H, 2 × m, 3'-H₂ and 4'-H₂), 2.21 (2 H, t, *J* 5.8 Hz, 5'-H₂), 2.90 (2 H, s, 7'-H₂), 3.14 (2 H, d, *J* 6.7 Hz, 2-H₂), 4.65 and 4.73 (2 H, 2 × s, 6'=CH₂), and 5.31 (1 H, t, *J* 6.7 Hz, 3-H); δ_{C} (CDCl₃) 16.4 and 23.3 (2 × t, C-2 and C-4'), 28.6 (2 × q, 2 × Me), 35.3, 37.9, and 42.0 (3 × t, C-3', C-5', and C-7'), 39.7 (s, C-2'), 110.7 (t, 6'=CH₂), 112.5 (d, C-3), 118.8 (s, C-1), and 147.2 and 150.8 (2 × s, C-1' and C-6').

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