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THE PHOTOCHEMISTRY OF α-OXIMINO KETONES

2-OXIMINOCYCLODODECANONE[1]

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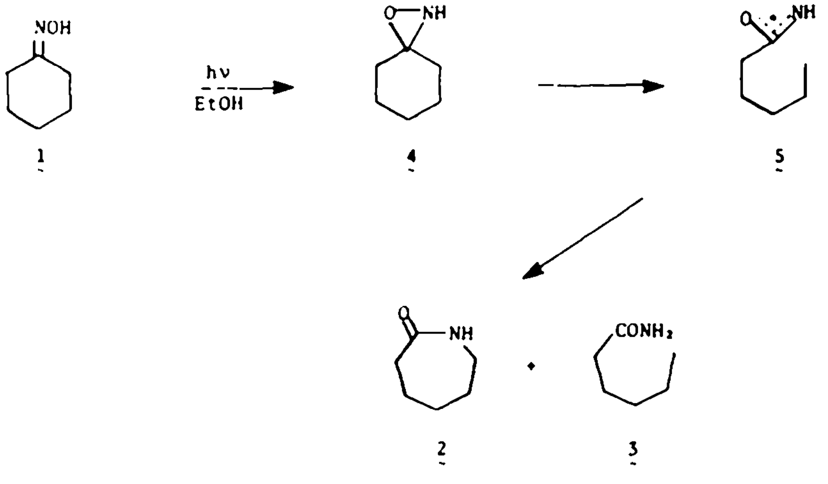
Abstract—Irradiation of (*E*)-2-oximinocyclododecanone (**12**) in methanol with a medium pressure mercury lamp gives (*Z*)-2-oximinocyclododecanone (**13**), 12-hydroxybicyclo[8.2.0]dodecan-11-one oxime (**14**), (2-oxocyclodecane) acetonitrile (**17**), and methyl 10-undecenoate (**18**). The nitrile **17** has been shown to be formed from the oxime **14** on irradiation of the latter in methanol or on treatment with acetic anhydride in pyridine. It is proposed that the ester **18** arises, like oxime **14**, via γ-H-abstraction by the O atom of the CO group of the α-oximino ketone **12**, and that the primary photochemical processes under the conditions used are limited to geometrical isomerization about the C=N bond and such γ-H-abstraction.

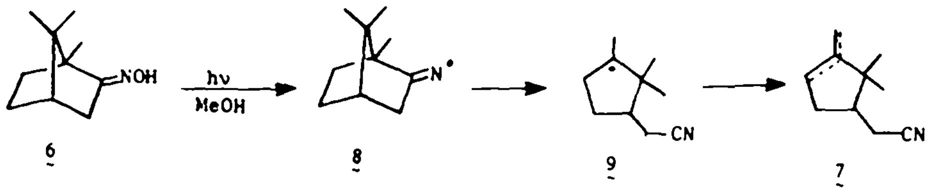
The photochemistry of oximes has been studied extensively. In non-polar solvents, *syn-anti* isomerization at the C=N bond is the major reaction pathway, while in hydroxylic solvents α-C–C bond cleavage occurs in addition. Thus, Just *et al.*[2] have found that cyclohexanone oxime (**1**) gives caprolactam (**2**) as the major product on irradiation in methanol (photo-Beckmann rearrangement), and hexanoamide (**3**) as the major product on irradiation in isopropyl alcohol; in both cases these were accompanied by small amounts of cyclohexanone. The reactions were found to be regioselective with cleavage of α-substituted cyclohexanones occurring mainly at the more highly substituted α-C atom.[2,3] It has been proposed[2] that the cleavage reaction involves conversion of the oxime to the oxaziridine (**4**) followed by homolytic cleavage to give the diradical **5** (Scheme 1). Recent results[4] suggest that the intermediate oxaziridines may also undergo heterolytic cleavage if a relatively stable carbonium ion can be formed thereby. These intermediates can also account for the formation of the parent ketones, since it has been observed that oxaziridines decompose in hydroxylic solvent to give carbonyl compounds and ammonia.[5]

Another type of primary photochemical process is evidently involved in the case of certain cyclic ketoximes,[6] as exemplified by camphor oxime (**6**) which gives unsaturated nitriles (**7**) together with the parent ketone. The formation of the former has been interpreted in terms of an initial N–O cleavage to give the iminyl radical **8** which then undergoes α-cleavage to give **9** (Scheme 2). It may be noted that although the latter reaction is analogous to the α-cleavage of excited ketones, ketoximes themselves do not undergo photochemical α-cleavage, since the photolysis of enantiomers of ketoximes with an α chiral carbon does not result in racemization.[2a] Acylation or alkylation of the O atom of oximes facilitates photochemical N–O cleavage.[7]

The photochemistry of α-oximino ketones (α-keto oximes) and their O-substituted derivatives has received little attention until recently,[8] when Baas and Cerfontain carried out extensive investigations in this area.[9] They have found that these, like simple oximes, can undergo both *syn-anti* isomerization and N–O bond cleavage, although products derived from oxaziridine formation have not been observed. In addition cyclobutanol formation can occur via γ-H-abstraction by the



Scheme 1.



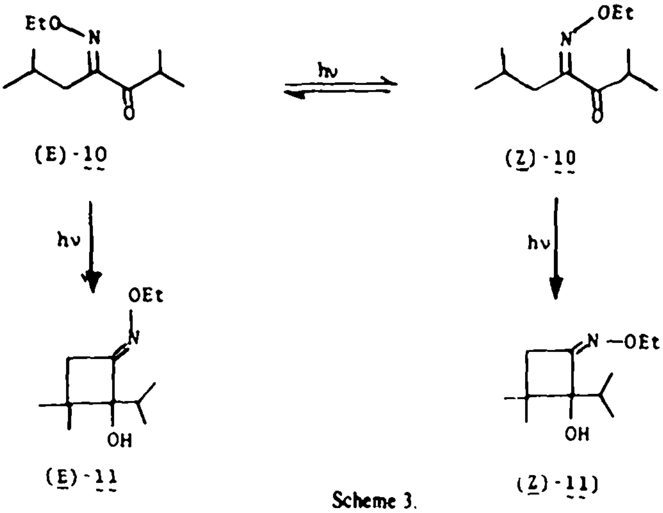
Scheme 2.

oxygen of the CO group, as in the photochemistry of simple ketones; thus 4-ethoxyimino-2,6-dimethylheptan-3-one (**10**) undergoes *syn-anti* isomerization and cyclization to the stereoisomeric cyclobutanols **11** (Scheme 3).[10] The inclusion of the ethoxyimino function in the cyclobutane ring and the absence of Norrish type II elimination products parallels the photochemistry of α-diketones.[11]

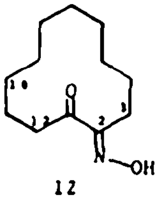
Our own interest in this area was stimulated by the report of Stojiljković and Tasovac[12] that the irradiation of (*E*)-2-oximinocyclododecanone (**12**) in methanolic solution through quartz with a low-pressure mercury lamp[13] gives after 45 hr a mixture of **12** and compounds **13**–**16**. The reported formation of **15** is of particular interest in that this has the potential of providing a route for the conversion of even-numbered into odd-numbered cycloalkanones. We have examined the photochemistry of 2-oximinocyclododecanone in methanolic solution in quartz with a Hanovia 450-W medium-pressure mercury lamp and have obtained results that differ in some respects from those previously reported. Irradiation for 4–12 hr gave products to which we assign structures **13**, **14**, **17**, and **18** (Scheme 4).

Geometrical isomerization

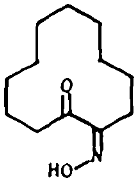
Formation of **13**. Compound **13** was isolated in 20% yield as an amorphous solid after irradiation of **12** for 4 hr. Attempted crystallization of **13** gave crystals of **12**, to which **13** also reverted slowly on standing. Its spectroscopic properties [λ_{max} 2.85–3.10, 5.93 μ; $^{H}\delta$ 1.37–1.93 (br s, 16H) 2.60 (br s, 2H) 2.80–3.00 (m, 2H), 8.50 (br s, 1H)] showed it to be an α-oximino ketone and the relationship of these to the spectra of **12** (*vide infra*) and the ready conversion of **13** to the latter confirmed that **12** and **13** are geometrical isomers of 2-oximinocyclododecanone, as previously proposed.[12] The configurations shown are assigned on the basis of the following considerations.



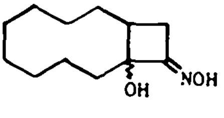
Scheme 3.



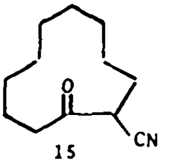
12



13



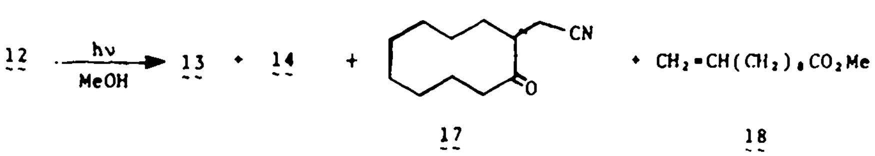
14



15

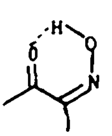
$NC(CH_2)_{10}CO_2H$

16



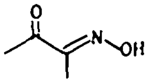
Scheme 4.

The earlier workers[12] assigned the (*E*)-*s-trans* configuration and conformation to **12** because of their observation of a large bathochromic shift of its UV maximum in basic medium.[15] However, it is to be expected that this criterion of configuration will only be valid for α-oximino ketones with *s-cis* conformations, where the OH group in the *Z* isomer (**19a**) is H-bonded to the CO oxygen, while that in the *E* isomer (**19b**) is not. In the case of *s-trans* conformations, where there is no intramolecular H-bonding in either the *Z* (**19c**) or *E* (**19d**) isomer, both isomers would be expected to show similar bathochromic shifts, as was indeed observed in the present case.[16] Their IR spectra, while differing slightly in the "finger-print" region, are very similar, indicating that they are not the (Z)-*s-cis* and (E)-*s-cis* isomer pair of types **19a** and **19b** since H-bonding in the former would lead to significant differences in their CO stretching frequencies.[17] The similarity of the IR spectra indicates furthermore that they are the (*Z*)-*s-trans* and (*E*)-*s-trans* isomer pair of types **19c** and **19d**, since appreciable differences would be expected if one were of type **19b** and the other of type **19c** or **19d**. A more marked difference could be detected in the ^{1}H NMR spectra of the isomers, that of **12** showing a four-proton multiplet at $\delta \sim 2.80$ ppm that can be interpreted as arising from the overlap of two two-proton triplets at $\delta \sim 2.75$ and ~ 2.85 ppm, and that of **13** showing two corresponding two-proton triplets at δ 2.53 and 2.83 ppm. These signals are undoubtedly attributable to the C-3 and C-12 methylene proton of **12** and **13**. It is known for simple oximes that the *syn*-α-methylene protons are deshielded relative to the *anti*-α-methylene protons.[18] The magnitude of this effect in the case of cyclohexanone oxime is $\Delta\delta$ 0.26 ppm. Thus the relationship of the ^{1}H NMR spectra of **12** and **13** can be interpreted in terms of these structures if the triplet at δ 2.53 ppm in the spectrum of the latter is assigned to the C-3 protons. Definitive differentiation between **12** and **13** could be made from their ^{13}C NMR spectra. Comparison with the spectra of simple cyclic ketones[19] and ketoximes[20] readily permits assignment of signals in the spectrum of **13** at δ 30.6 and 43.4 to C-3 and C-12, respectively. In the spectrum of **12** the C-13 signal must be one of those with $\delta \leq 26.3$ ppm while that of C-12 occurs at δ 38.4 ppm. It is known that the *syn*-α-methylene carbon is shielded relative to the *anti*-α-methylene carbon,[20] and thus the relationship of the chemical shifts of the C-3 signals of **12** and **13** establishes their stereochemical relationship to be that depicted. It is of interest that the effect of the change of stereochemistry in the ^{13}C spectrum is the opposite of that in the ^{1}H spectrum; presumably the predominant factor in the former is the γ-effect of the OH oxygen atom. It is also of interest that there is a considerable downfield shift of the C-12 signal of **13** relative to that of **12**, perhaps due to a δ-effect[21] between this carbon and the OH oxygen atom. Models indicate that there is a considerable steric interaction between this oxygen and the C-12 methylene group, a circumstance that may also account for the facile and complete reversion of **13** to **12**.



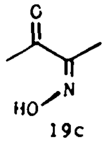
19a

(Z)-s-cis



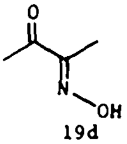
19b

(E)-s-cis



19c

(Z)-s-trans

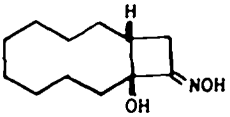


19d

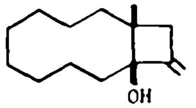
(E)-s-trans

Cyclization to a cyclobutanol

Formation of **14** *and its conversion to* **17**. Irradiation of **12** for 6 hr led to a mixture containing **12**, **13**, and a second major photoproduct that was obtained in 25–40% yield. This corresponds in properties to the cyclobutanol **14** obtained by Stojiljković and Tasovac.[12] We assign to it the *cis*-fused structure **14a** based on analogy with the assignment of the *cis*-fused structure **20** to the cyclobutanol formed on photolysis of 2-methylenecyclododecanone,[22] since the steric considerations underlying the latter assignment apply also in the case of **14**. The formation of a single cyclobutanol via abstraction by the excited CO group of a γ-H atom at C-4 in **12** is analogous to previous observations with α-oximino ketones and α-diketones (*vide supra*). The absence of a cyclobutanol derived from γ-H-abstraction from C-10 can be interpreted in terms of a less favorable entropy factor as in the case of α-diketones.[23]



14a



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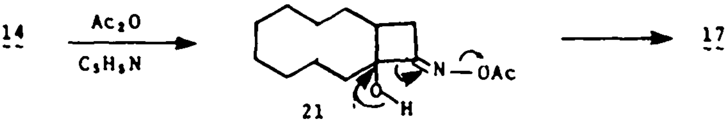
Treatment of **14** with acetic anhydride and pyridine gave a complex mixture whose major constituent was the γ-cyano ketone **17** (Scheme 5), which we had previously found to be a constituent of the photolysate from **12** (*vide infra*). This process is considered to involve a second order Beckmann fragmentation of **21**, the acetyl derivative of **14**, which is facilitated by the relief of strain in the cyclobutane ring (Scheme 5). The formation of analogous γ-keto nitriles has been observed in the photolysis or thermolysis of certain steroidal α-hydroxy



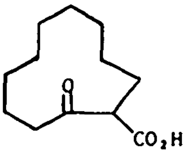
Scheme 5.

C-6 oxime acetates[24] and the photolysis of the acetate of 3-oximino-2-pentanone.[9]

As mentioned earlier we first isolated 17 from the photolysate from 12; it was obtained in 5% yield after irradiation for 12 hr. Its structure was assigned on the basis of the presence of nitrile and ketonic CO stretching bands in its IR spectrum at 4.45 and 5.86 μ, respectively, and its independent synthesis by the route shown in Scheme 6. Treatment of cyclodecanone with sodium hydride and dimethyl carbonate gave 2-carbomethoxycyclodecanone (22a), which exists in equilibrium with its enol tautomer 22b, as shown by the complexity of its IR spectrum (bands at 5.75, 5.88, 6.08, and 6.24 μ) and the presence of two OMe signals (δ 3.67 and 3.80 ppm) and an enolic proton signal (δ 12.93 ppm) in its ^{1}H NMR spectrum. Generation of the enolate ion of 22 with sodium hydride followed by reaction with chloroacetonitrile gave the alkylation product 23. This on hydrolysis and decarboxylation with aqueous methanolic potassium hydroxide at room temperature gave 17, which was shown to be identical with the keto nitrile obtained from the photolysis of 12 and from treatment of 14 with acetic anhydride and pyridine.

The formation of 17 from 14 suggested that the former might be a secondary product in the photolysis of 12 resulting from photolysis of the primary product 14. That this is indeed the case is also suggested by the observation that photolysis of 14 under analogous conditions leads to a more rapid consumption of 14 than of 12 and gives a product mixture from which 17 was isolated in 22% yield by chromatography on silica gel. Some 17 may be formed from 14 during chromatography, since prolonged exposure of 14 to silica gel was found to give 17, nevertheless it appears that 17 is also formed from 14 photochemically and represents a secondary product in the photolysis of 12.

We obtained no evidence for the formation of a second keto nitrile corresponding to the product 15 reported by Stojiljković and Tasovac.[12] It is noteworthy that these workers hydrolyzed the product to which they assigned structure 15 and obtained a product that they considered to be the β-keto acid 24, but did not report that it underwent ready decarboxylation, as might have been expected.[25] Hydrolysis of the γ-keto nitrile 17 with ethanolic potassium hydroxide followed by acidification gave the γ-keto acid 25, as shown by its spectra (Experimental) and its independent synthesis by a route analogous to that used for the independent synthesis of 17 via 26 (Scheme 7). As expected for a γ-keto acid 25



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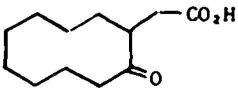

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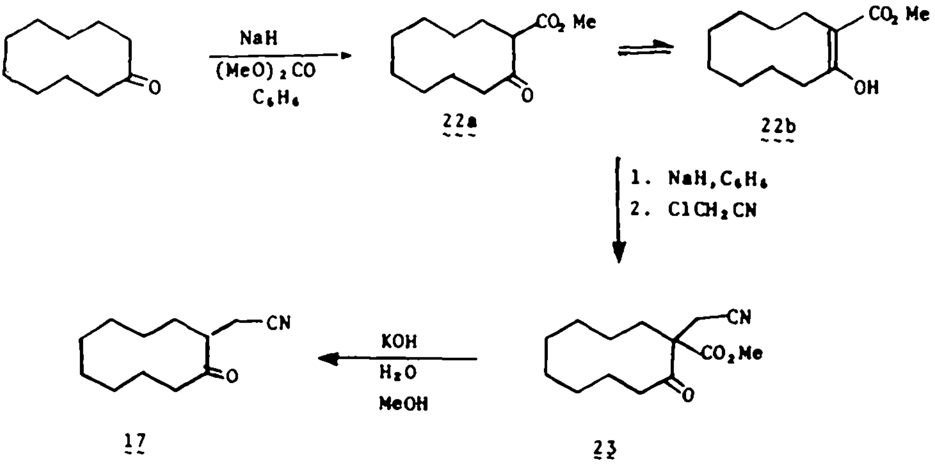
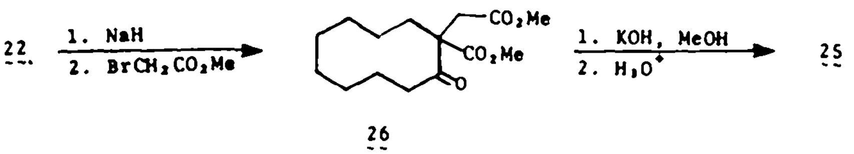


Scheme 6.



Scheme 7.

does not undergo ready decarboxylation. Although our photolysis conditions were different from those of the earlier workers,[12] it seems not unlikely that the keto nitrile obtained by them was in fact **17**.

Ring cleavage

Formation of **18**. Photolysis of **12** gave a fourth product, which was isolated in 13% yield after irradiation for 12 hr. Peaks at 6.04, 10.05 and 10.95 μ in its IR spectrum and signals at δ 4.8–5.1 (m, 2H) and 5.5–6.0 ppm (m, 1H) showed that it had a terminal olefinic group. These spectra also showed the presence of a carbomethoxy group [λ_{max} 5.74 μ; δ 3.67 ppm (s, 3H)]. The presence of these functional groups suggested that this product was either methyl 10-undecenoate (**18**) or methyl 9-decenoate (**27**). Its mass spectrum showed a peak at *m/e* 166 that favored assignment of the former structure since it corresponds to the loss of the elements of methanol from its molecular ion; however, it could not be excluded that the *m/e* 166 peak arose from loss of water from the molecular ion of **27**.[26] Spectroscopic and VPC comparison of the product with authentic samples of both **18** and **27** showed that it had the former structure.

The formation of **18**, like **14**, can be interpreted in terms of a Norrish type II process involving the CO group of **12** (Scheme 8). Thus the diradical intermediate **28** can either undergo cyclization to give **14** or fragmentation to give **29**. Dehydration of this to the acyl cyanide **30** followed by methanolysis could then give **18**. The postulated Norrish type II elimination process (**28** → **29**) is seldom observed with α-diketones because geometrical factors favor cyclobutanol formation (**28** → **14**). However, analogous processes have been observed in the case of α-keto esters.[27] Methanolysis of **30** to **18** is expected to be ready.[28]

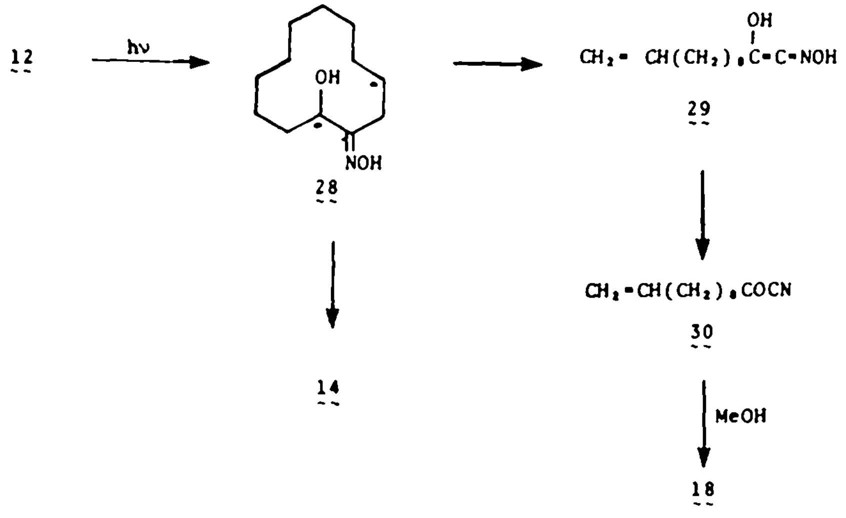
A possible alternative route to **18** could involve cycloreversion of **14** to **29**. However, our failure to observe **18** among the products of photolysis or thermolysis of **14** excludes this possibility.

DISCUSSION

As described earlier, three types of primary process have been observed or postulated in the photolysis of simple oximes (i) *anti-syn* isomerization (ii) isomerization to an oxaziridine, and (iii) cleavage of the N–O bond to give an imino radical. In the case of α-oximino ketones, the formation of cyclobutanols indicates that a fourth primary process can occur—the abstraction of a γ-H atom by the CO oxygen atom. The products that we have observed to be formed on irradiation of (*E*)-2-oximinocyclododecanone in methanol with a medium-pressure mercury lamp are considered to arise via the first (**13**) or fourth (**14**, **17** and **18**) of these primary processes. As in the case of previous studies of the irradiation of α-oximino ketones no products attributable to oxaziridine formation were observed. This may reflect an enhanced barrier to cyclization relative to simple oximes because of delocalization in the α-oximino ketone grouping or differences in the excited states of the oximes and α-oximino ketones. The third primary process, N–O cleavage, has been observed to occur in the case of other α-oximino ketones and indeed Stojiljković and Tasovac[12] have observed the formation of a product—11-cyanoundecanoic acid (**16**)—in their photolysis of **12** whose formation is attributable to N–O bond cleavage. However, their irradiation was carried out with a low-pressure mercury lamp, suggesting that the occurrence of N–O bond cleavage involves the intermediacy of an excited state of the α-oximino ketone of higher energy than that involved in geometrical isomerization and isomerization via γ-H-abstraction.[10] This is in accord with the observations of Baas and Cerfontain that the rate of photodecomposition of the ethers of α-oximino ketones via N–O bond cleavage relative to that of photoisomerization is slow upon irradiation at λ313 or 366 nm but fast upon irradiation at 254 nm.[9]

EXPERIMENTAL

M.ps were determined on a calibrated Thomas–Kofler micro hot stage apparatus. The IR spectra were taken in $CHCl_3$ soln, the ^1H and ^{13}C NMR spectra in $CDCl_3$ soln, and the UV spectra in MeOH soln. Preparative tlc was carried out on 2 mm 20 × 20 cm Sil G-100 UV_{254} silica gel plates and column chromatography on silica gel 60 0.05–2 mm/70–270 mesh ASTM, both from Brinkmann Industries, Ltd.; unless otherwise stated the amount of silica gel used in the latter was 40 : 1 w/w, and the solvent was $CHCl_3$. Vapor phase chromoatographic analyses were carried out



Scheme 8.

on a Varian Aerograph series 2740 gas chromatograph with a hydrogen flame-ionization detector and either a 6 ft × 2 mm i.d. 5% Carbowax 20 M glass column or a 6 ft × 2 mm i.d. 3% OV101 on Chromosorb G-HP glass column. Solutions were dried over $MgSO_4$ and concentrated on a Büchi "Rotovap (R)" rotary evaporator. Photolyses were carried out at 28 ± 2° in quartz. The light source was a Hanovia 450-W medium-pressure mercury arc lamp of type 679436 surrounded by a quartz water jacket. All photolyses were carried out in methanol that had been boiled under reflux over magnesium and then distilled; the photolysis solutions were flushed with a stream of dry N_2 immediately prior to irradiation.

(E)-2-*Oximinocyclododecanone* (**12**). Cyclododecanone (10.0 g, 0.050 mol) and conc. HCl (2 ml) in ether (60 ml) were stirred at 0° while MeONO was passed through the system. MeONO was generated by the dropwise addition of H_2SO_4 aq (6.5 ml of H_2SO_4 in 12 ml of H_2O) into a soln of $NaNO_2$ (17.2 g, 0.25 mol) in MeOH (8 ml) and water (15 ml). After the addition of MeONO was complete, the mixture was stirred for 24 hr, and then was exhaustively extracted with 10% NaOH aq. The combined aqueous alkaline fractions were acidified with 6N HCl and extracted with $CHCl_3$ (3 × 5 ml). The organic fractions were combined, dried and concentrated to give a viscous yellow oil (9.4 g, 81%) which was crystallized from hexane to give **12** as white crystals, m.p. 72–73° (lit. [12]m.p. 74–75°); λ_{max} 2.85–3.10, 5.98 μ; λ_{max} 236 (ε 6650), 320 nm (ε 35); λ_{max} (MeOH/NaOH) 284 nm; $^{H}\delta$ 2.62–2.93 (m, 4H), 1.33–1.83 (br s, 16H); $^{C}\delta$ 201.7, 160.2, 38.4, 26.3, 26.2, 25.0, 24.5, 23.8, 23.4, 23.2, 21.9.

Irradiation of **12**. *Formation of* **13**, **14**, **17**, *and* **18**. In general, a 0.4–0.6% soln of **12** in anhyd. MeOH was irradiated. The irradiation was monitored by tlc and/or vpc. The photolysates were concentrated and separated by column chromatography on silica gel (50 : 1 w : w silica gel:crude photolysate with hexane-EtOac (8 : 2) as the eluent). The following products were isolated:

(a) (Z)-2-*Oximinocyclododecanone* (**13**) (tlc R_f 0.32). This was isolated in 18% yield as an amorphous white product after irradiation of **12** for 4.0 hr; λ_{max} 2.85–3.10, 5.93 μ; λ_{max} 237 nm (ε 6200); λ_{max} (MeOH/NaOH) 284 nm; $^{H}\delta$ 8.50 (br s, 1H), 2.80–3.00 (m, 2H), 2.60 (br s, 2H), 1.37–1.93 (m, 16H); $^{C}\delta$ 203.1, 157.9, 43.4, 30.6, 26.6, 26.1, 25.8, 25.6, 25.3, 23.5, 22.7, 22.4.

(b) 12-*Hydroxybicyclo*[8.2.0]*dodecan*-11-*one oxime* (**14**) (tlc R_f 0). This was isolated in 23–42% yield after irradiation of **12** for 6.0 hr as an amorphous, pale yellow solid. Repeated crystallizations from hexane gave white crystals, m.p. 121–123° (lit.[12] m.p. 120–122°); λ_{max} 2.90–3.15, 6.20 μ; $^{H}\delta$ 2.20–3.23 (br m, 4H), 1.50–1.80 (br s, 17H); $^{C}\delta$ 164.2, 83.4, 30.5, 29.2, 27.5, 27.4, 26.9, 23.6, 23.5, 22.7, 20.0, *m/e* 211 (M^+, 1), 194 (13).

(c) (2-*Oxocyclodecane*)*acetonitrile* (**17**) (tlc R_f 0.22). This was isolated in 5% yield as a viscous oil after irradiation of **12** for 12.0 hr and had spectra identical with those of an authentic sample (*vide infra*); λ_{max} 4.45, 5.86 μ; $^{H}\delta$ 2.77–3.23 (m, 2H), 2.33–2.57 (m, 3H), 1.73–2.20 (br m, 14H); *m/e* 193 (M^+ 13).

(d) *Methyl* 10-*undecenoate* (**18**) (tlc R_f 0.55). This was isolated in 13% yield as a viscous, pale yellow oil after irradiation of **12** for 12.0 hr and has spectra identical with those of an authentic sample (*vide infra*); λ_{max} 5.74, 6.04, 10.05, 10.95 μ; $^{H}\delta$ 5.50–6.00 (m, 1H), 4.83–5.07 (m, 2H), 3.67 (s, 3H), 1.33–2.50 (br s, 16H); *m/e* 166 (13), 124 (26), 96 (26), 87 (43), 82 (39), 74 (100).

Formation of **14**. *Formation of* **17**. A soln of **14** (150 mg, 0.71 mmol) in dry pyridine (0.5 ml) was stirred at 0° under N_2 for 0.5 hr. Freshly distilled Ac_2O (0.5 ml) was added dropwise to the soln over a period of 0.25 hr. The mixture was stirred for 4.0 hr at room temp., poured into water (10 ml), and extracted with $CHCl_3$ (3 × 5 ml). The organic fractions were combined and extracted with 2N HCl (2 × 5 ml), 10% $NaHCO_3$ aq (2 × 5 ml), and water (5 ml). The organic fraction was dried and concentrated to give a light brown oil. Column chromatography gave **17** (78 mg, 57%). The spectroscopic characteristics of the fragmentation product were identical with those of an authentic sample (*vide infra*).

2-*Carbomethoxycyclodecanone* (**22**). Cyclodecanone (570 mg, 3.4 mmol) was added dropwise with stirring to a suspension of NaH (50% in mineral oil, washed in hexane; 145 mg, 3.4 mmol) in Me_2CO_3 (374 mg, 3.6 mmol) and dry benzene (10 ml). The mixture was heated at 60° for 1.0 hr. After cooling, the mixture was treated dropwise with water (10 ml) at 0° and extracted with benzene (3 × 5 ml). The organic fractions were combined, dried, and concentrated to give **22** as a pale yellow oil (600 mg, 83%). Purification by column chromatography gave the β-keto ester as a colourless, viscous oil (486 mg, 68%): λ_{max} 5.75, 5.88, 6.08, 6.24 μ; $^{H}\delta$ 12.93 (m), 3.90 (m), 3.80 (s), 3.67 (s), 2.33–2.80 (m), 1.40–1.97 (br s).

(2 - *Oxo* - 1 - *carbomethoxycyclodecane*)*acetonitrile* (**23**). Compound **22** (450 mg, 2.10 mmol) and NaH (50% in mineral oil, washed with hexane; 110 mg, 2.20 mmol) were added to dry benzene (10 ml), and the mixture was boiled under reflux for 1.0 hr. After cooling, chloroacetonitrile (0.2 ml) in benzene was added dropwise over a period of 0.5 hr at room temp. The mixture was boiled under reflux for 3.0 hr, allowed to cool, and acidified by the careful addition of 10% AcOH aq (5.0 ml). The mixture was diluted with water (10 ml) and extracted with benzene (3 × 5 ml). The organic fractions were combined, dried, and concentrated to give a dark brown oil. Purification by column chromatography gave **23** as a colourless, viscous oil (350 mg, 66%); λ_{max} 4.50, 5.75, 5.83 μ; $^{H}\delta$ 3.83 (s, 3H), 2.16–3.20 (m, 7H), 1.33–1.70 (br s, 11H).

(2 - *Oxocyclodecane*)*acetonitrile* (**17**). β-Keto ester **23** (320 mg, 1.3 mmol) was stirred in freshly prepared methanolic KOH aq (2 g KOH/6 ml H_2O/4 ml MeOH; 3ml) for 4.0 hr. The mixture was acidified with 6N HCl at 0°, diluted with water (10 ml), and extracted with $CHCl_3$ (3 × 5 ml). The organic fractions were combined, dried, and concentrated to give a pale yellow oil. Purification by preparative tlc on silica gel and molecular distillation (1 mm, 75°) gave **17** as a colourless, viscous oil (180 mg, 67%): λ_{max} 4.45, 5.86 μ; $^{H}\delta$ 2.77–3.23 (m, 2H), 2.33–2.57 (m, 3H), 1.73–2.00 (br m, 14H); $^{C}\delta$ 212.1, 118.6, 48.2, 39.9, 28.8, 25.3, 24.6, 24.1, 23.8, 22.9, 22.4, 18.7; Found: C, 74.48; H, 9.94; N, 7.23. Calc. for $C_{12}H_{19}NO$: C, 74.61; H, 9.84; N, 7.25%.

Methyl (2-*oxo*-1-*carbomethoxycyclodecane*) *acetate* (**26**). Compound **22** (mg, 2.2 mmol), NaH (50% in mineral oil, washed with hexane; 110 mg, 2.3 mmol) were added to dry benzene ((10 ml), and the mixture was boiled under reflux for 1.0 hr. After the mixture had been allowed to cool, methyl bromoacetate (380 mg, 2.5 mmol) was added dropwise over a period of 0.5 hr at room temp. After the addition was complete, the mixture was boiled under reflux for 3.0 hr. The mixture was cooled, treated dropwise with water (20 ml), and extracted with $CHCl_3$ (3 × 5 ml). The organic fractions were combined, dried, and concentrated to give **26** as a viscous, pale yellow oil (447 mg, 71%); λ_{max} 5.75, 5.85 μ; $^{H}\delta$ 3.83 (s, 3H), 3.67 (s, 3H), 2.00–3.27 (m, 7H), 1.33–1.80 (m, 11H). This was used without further purification.

(2 - *Oxocyclodecane*)*acetic acid* (**25**). (a) A soln of **26** (400 mg, 1.4 mmol) in methanolic KOH aq (2 g KOH/6 ml H_2O/4 ml MeOH; 25 ml) was stirred at room temp. for 24 hr. The mixture was acidified with 6N HCl and extracted with $CHCl_3$ (3 × 5 ml). The organic fractions were combined, dried, and concentrated to give **25** as a viscous, pale yellow oil, which crystallized on standing (221 mg, 74%). Recrystallization from hexane gave **25** as white crystals, m.p. 73–74°; λ_{max} 3.0–3.45, 5.81 μ; $^{H}\delta$ 9.4 (br s, 1H), 2.16–3.00 (m, 5H), 1.33–1.83 (br s, 14H); $^{C}\delta$ 215.1, 178.6, 47.8, 40.3, 36.2, 30.0, 25.5, 24.4, 24.3, 23.8, 23.0, 22.8; (Found: C, 67.69; H, 9.53; *m/e* 212.1413. Calc. for $C_{12}H_{20}O_3$: C, 67.92; H, 9.43% M.W. 212.1413).

(b) A soln of **17** (82 mg, 0.43 mmol) in 10% ethanolic KOH (10 ml) was boiled under reflux overnight under N_2. The mixture was diluted with water (10 ml) and extracted with $CHCl_3$ (3 × 5 ml). The organic fractions were combined, dried, and concentrated to give a pale yellow oil, which was crystallized from hexane to afford **25** as yellow crystals (26 mg, 29%). Repeated recrystallization gave **25** as white crystals, m.p. 73–74°; on admixture with a sample of **25** prepared by method (*a*) it had m.p. 73–74°.

Methyl 10-*undecenoate* (**18**). A mixture of 10-undecenoic acid (2.00 g, 1.10 mmol) and $SOCl_2$ (2.50 g, 2.10 mmol) was boiled under reflux under N_2 for 3.0 hr. The excess $SOCl_2$ was removed by distillation. After the residue had been allowed to cool, excess

MeOH was added dropwise at 0°, and the mixture was stirred at room temp. overnight. The mixture was diluted with CH_2Cl_2 (10 ml) and extracted with 10% $NaHCO_3$ aq (3 × 5 ml). The organic fraction was washed with water dried and concentrated to give **18** as a colourless viscous oil (2.0 g, 91%); λ_{max} 5.74, 6.04, 10.15, 10.95 μ; $^{H}\delta$ 5.50–6.12 (m, 1H), 4.80–5.09 (m, 2H), 3.69 (s, 3H), 1.77–2.43 (m, 4H), 1.10–1.75 (br s, 12H); *m/e* 166 (17), 124 (28), 96 (28), 87 (39), 82 (35), 74 (100); vpc (5% Carbowax) retention time; 3.78 min.

Methyl 9 - decenoate (**27**). *A soln of 9 - decen - 1 - ol* (400 mg, 0.26 mmol) in acetone (20 ml) was stirred under N_2 at 0° and an aqueous CrO_3 soln (26 g CrO_3/23 ml conc H_2SO_4/77 ml H_2O; 1.5 ml) was added dropwise. The mixture was stirred for a further 20 hr at room temp. 2-Propanol (10 ml) was added dropwise at 0°, and the mixture was stirred for 1.0 hr, diluted with water (10 ml), and extracted with $CHCl_3$ (3 × 5 ml). The organic fractions were combined and extracted with 10% $NaHCO_3$ aq (2 × 5 ml). The combined aqueous alkaline fractions were acidified to pH 2 with 6N HCl and extracted with $CHCl_3$ (2 × 5 ml). The extracts were combined, dried, and concentrated to give 9-decenoic acid as a colourless, viscous oil (385 mg, 87%); λ_{max} 2.90–3.90, 5.83, 6.10 μ; $^{H}\delta$ 10.00 (br s, 1H), 5.40–6.07 (m, 1H), 4.80–5.20 (m, 2H), 1.60–2.50 (m, 6H), 1.50 (br s, 8H).

Without further purification, 9 - decenoic acid (300 mg, 1.80 mmol) was dissolved in $CHCl_3$ (4 ml), $SOCl_2$ (1 ml) was added, and the soln was boiled under reflux for 4.0 hr under N_2. The excess $SOCl_2$ was removed by distillation. After the residue had been allowed to cool excess dry MeOH was added dropwise at 0°, and the mixture was stirred at room temp. for 2.0 hr. The mixture was diluted with water (5 ml) and extracted with $CHCl_3$ (2 × 5 ml). The organic fractions were combined, dried, and concentrated to give a pale yellow oil. Purification by preparative tlc on silica gel followed by Kugelrohr distillation (120°/1.0 mm) (lit.[29] b.p. 123°/21 mm) gave **21** as a colourless, viscous oil (210 mg, 64%); λ_{max} 5.76, 6.08, 10.00, 10.90 μ; $^{H}\delta$ 6.20–5.50 (m, 1H), 5.20–4.80 (m, 2H), 3.67 (s, 3H), 2.47–1.80 (m, 4H), 1.80–1.20 (br s, 10H) *m/e* 152 (38), 135 (19), 110 (25), 96 (10), 87 (31), 74 (100); vpc (5% Carbowax) retention time: 2.35 min.

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