Photochemical Ring Enlargements of Two α-Cyanocycloalkanones[1]

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Received November 19, 1973

G. K. CHIP and T. R. LYNCH. Can. J. Chem. **52**, 2249 (1974).

The photochemical transformations undergone by 2-cyano-2-methylcycloheptanone (**1**) and 2-cyano-2-methylcyclohexanone (**2**) have been studied in methanol and aqueous dioxane. In the former solvent, **1** is isomerized to three products in the ratio 78:8:13, corresponding to the enals **3***a* and **3***b*, and a new ring expansion product **4**, respectively. In aqueous dioxane, the cyclic imide **6** was obtained in 18% yield. Cycloalkanone **2** in methanol produces four products in the ratio 61:30:7:1, these being the isomeric enals **8***a* and **8***b*, the ester **9**, and the ring expansion product **10**. No imide related to **6** could be obtained from irradiation of **2** in aqueous dioxane.

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On a étudié, dans le méthanol et le dioxanne aqueux, les transformations photochimiques subies par la cyano-2 méthyl-2 cycloheptanone (**1**) et la cyano-2 méthyl-2 cyclohexanone (**2**). Dans le premier solvant, **1** s'isomérise en trois produits présents dans le rapport 78:8:13 et ces produits sont respectivement les énals **3***a* et **3***b* et le nouveau produit d'extention **4**. Dans le dioxanne aqueux, on obtient l'imide cyclique **6** avec un rendement de 18%. Dans le méthanol, la cycloalkanone **2** conduit à quatre produits dans le rapport 61:30:7:1; ces produits sont respectivement les énals isomères **8***a* et **8***b*, l'ester **9** et le produit d'extention **10**. Aucune imide de structure similaire à **6** n'a pu être obtenue lors de l'irradiation de **2** dans le dioxanne aqueux.

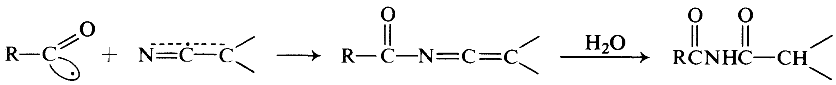
[Traduit par le journal]

The photochemical reactions undergone by cyclic ketones have for some time been of widespread interest (2), the principal products being carboxylic acid derivatives (3), enals (2), and cyclic ethers (4, 5). Acyl alkyl diradical intermediates (6, 7) are commonly invoked and may arise from either the singlet or triplet excited states of the ketone (4, 8, 9).

Photochemical ring enlargements of synthetic interest have recently been discovered, employing cycloalkanones with appropriate substituents in the 2-position as substrates. Thus, 2-vinyl- and 2-ethynylcycloalkanones on irradiation lead to a two-carbon expansion (10, 11), whereas the analogous 2-cyclopropyl and 2-oxiranyl cases enlarge the carbocyclic ring by three atoms (12, 13). Other one-atom reactions involving introduction of an additional carbon (14, 15), nitrogen (16–18), and oxygen (4, 5) into a ring are also known.

Recently, we have shown that simultaneously generated acyl and α-cyanoalkyl radicals combine predominantly on the nitrogen of the alkyl intermediate to give, in the presence of water, *N*-acylamides (19); it is assumed that an *N*-acylketenimine is first formed which subsequently undergoes rapid addition of water (Scheme 1). We were curious as to whether this same mode of recombination would occur when the radical pair were joined by a carbon chain. We have consequently studied the photochemistry of 2-cyano-2-methylcycloheptanone (**1**) and 2-cyano-2-methylcyclohexanone (**2**), both of which would be expected to undergo the Norrish Type I cleavage indicated to give examples of the desired diradicals. The irradiation of these cycloalkanones was also of interest since few cycloalkanones with two different substituents in the 2-position have been so examined and, relative to cyclopentanones and -hexanones, cycloheptanones have received little attention.

The ketone **1** was synthesized by the known



SCHEME 1

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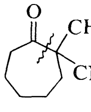
[1] A preliminary account of part of this work has appeared previously (1).



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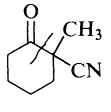

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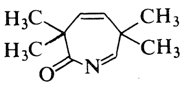
Thorpe cyclization of suberonitrile to 2-cyanocycloheptanone (20) followed by *C*-methylation with methyl iodide. 2-Cyano-2-methylcyclohexanone was obtained by a literature method (21).

Photolysis of a 5% solution of **1** in methanol under nitrogen caused the formation of three products in the ratio 78:8:13,[2] which were isolated by preparative g.l.c. The first and second components were identified as the *Z* and *E* aldehydes **3***a* and **3***b* (Scheme 2), respectively. In their i.r. spectra, each exhibited carbonyl and conjugated nitrile absorptions at 1720 and 2210 cm^{-1}, respectively, while the carbon–carbon double bond stretch appeared at 1640 cm^{-1} for the *Z* aldehyde and at 1660 cm^{-1} for the *E* isomer. The n.m.r. spectra are also consistent with the structural assignments and the isomers were distinguished by the relative positions of the single vinyl proton in each case, δ 6.17 p.p.m. for the *Z* isomer and δ 6.35 p.p.m. for the *E* isomer. This means of discrimination is in accord with two previous reports on the n.m.r. spectra of a number of acrylonitrile derivatives where the authors have observed that the β-vinyl hydrogen *cis* to the nitrile group absorbs *ca.* 0.1–0.15 p.p.m. further downfield than the β-vinyl hydrogen *trans* to the cyano function (22, 23).

Attempts to obtain analytical data on the 2,4-DNP derivatives of the aldehydes were unsuccessful, thus, accurate mass measurement of the molecular ion peaks was resorted to. For the *Z* and *E* aldehydes, the measured masses were 151.099439 and 151.099589, respectively, in good agreement with the calculated value of 151.099714 for $C_9H_{13}NO$.

The third product obtained from the irradiation of **1** was a colorless oil of molecular formula $C_{10}H_{17}NO_2$ (from accurate mass measurement: observed 183.12575, calculated 183.12592). The incorporation of a solvent molecule in this product was suggested by a three-proton singlet at δ 3.7 p.p.m. in the n.m.r. spectrum. Other features of the spectrum were a methyl doublet (J = 7 Hz) at 1.18 p.p.m., together with two multiplets totalling 11 hydrogens in the region 1.3–2.7 p.p.m. A structure consistent with these data, and the product hoped for at the genesis of this work, is the hexahydro-9-methoxyazonin-2-one, **4**. Added support is provided by the i.r. spectrum of this oil, which exhibits two strong overlapping bands at 1690 and 1660 cm^{-1}, assigned to the carbonyl and imino functions, respectively. These values compare reasonably well with those of 1710 and 1665 cm^{-1} reported for the dihydroazepin-2-one system **5** (24).



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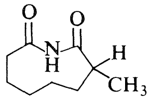

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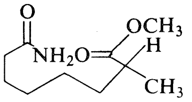

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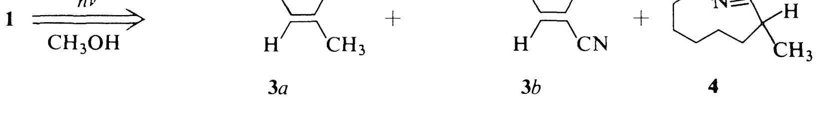
The results from the irradiation of the ketone **1** in a 1:1 water–dioxane medium were most gratifying, particularly since they provided a further elegant demonstration of the ring enlargement previously observed in methanol solution. Gas–liquid chromatographic examination of the photolysis product indicated the presence of the enals **3***a* and **3***b* together with a third product in 18% absolute yield and of long retention time. This was subsequently isolated by crystallization of the crude product from methanol and found to be a $C_9H_{15}NO_2$ compound, m.p. 138.5–139.5°, whose i.r. spectrum exhibited a sharp weak band at 3340 cm^{-1} indicative of the presence of an >N—H group, together with strong carbonyl



SCHEME 2

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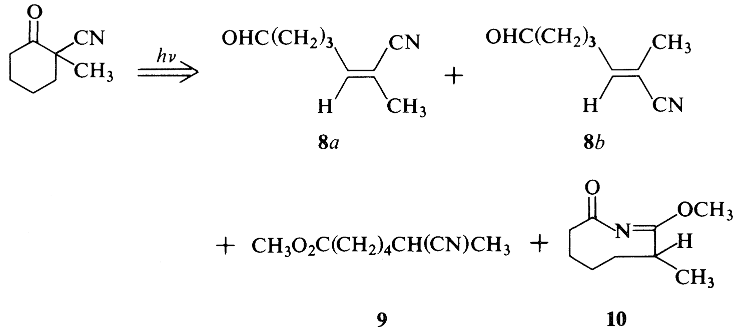
[2] From g.l.c. peak areas.



SCHEME 3

absorption at 1690 cm^{-1}. The n.m.r. spectrum had one exchangeable proton at δ 8.27 p.p.m., three- and eight-hydrogen multiplets at δ 2.83 and 1.7 p.p.m., respectively, together with a methyl doublet (J = 6 Hz) at 1.23 p.p.m. These spectra are quite consistent with the structure of this product being that of the cyclic imide **6**. Of course, this observation greatly enhances one's confidence in the correctness of the assignment of the structure **4** to the photoproduct in methanol.

Since **4** is one of the two possible O-methyl iminoethers related to **6**, we attempted the acid (2 N HCl) hydrolysis of **4** to **6** using the conditions previously reported for a related acyclic example (25). In the event, no **6** could be detected, the i.r. spectrum of the product suggesting the formation of an amide ester, possibly **7**, and thus the occurrence of preferential ring opening. Because of the small amount of **4** available, no further work on the hydrolysis product was possible. However, we were interested to observe that **6** itself did not survive these hydrolytic conditions.

Irradiation of a 10% methanol solution of 2-cyano-2-methycyclohexanone (**2**) led to the formation of four products in the ratio 61:30:7:1. The first two were the Z and E isomeric aldehydes **8***a* and **8***b* (Scheme 3), respectively, characterized by satisfactory elemental analyses on their 2,4-DNP derivatives and by their spectra. The isomers were distinguished by the chemical shifts of the vinyl protons, δ 6.17 p.p.m. for that of the Z compound, 6.33 p.p.m. for the E isomer. The third product was identified as the ester **9** by comparison with an authentic sample (26).

The fourth product was isolated only in small quantities but the assignment to it of structure **10** appears secure on the basis of the following. Both the i.r. (ν_{max} (CHCl$_3$) 1690 (m), 1660 cm^{-1} (s)) and n.m.r. (δ (CDCl$_3$) 1.22 (3H, d, J = 7 Hz), 1.5–2.6 (9H, two multiplets), and 3.7 p.p.m. (3H, s)) spectra are remarkably similar to those of the O-methyl iminoether **4** isolated from irradiation of **1**. In addition, alkaline hydrolysis of this photoproduct gave an oil whose i.r. and n.m.r. spectra corresponded very closely to those of an authentic sample of 2-methylheptanedioic acid (26). Methylation of the hydrolysis product gave material identical with the dimethyl ester of 2-methylheptanedioic acid. Irradiation of the cyclohexanone **2** in water–dioxane was found to give none of the anticipated cyclic imide.

Thus, our investigations have shown that the photochemical ring enlargement reaction of 2-cyanocycloalkanones is realizable in at least two cases and that it can provide either iminoethers or imides depending upon the solvent. However, the yields of these expansion products are significantly less than in the related cases reported by Carlson (10–13). The poorer yield of the eight-membered iminoether **10** relative to its nine-membered homolog **4** can be interpreted in terms of the relative ring strains in the precursor ketenimines (27).

The Z/E enal ratio from both **1** and **2** is in accord with the stereochemistry of enals observed in previous cases (28, 29). Enal/ester ratios of 1.7:2.9 have been reported for the photolysis in methanol for a number of 2-alkyl substituted cyclohexanones (30). For 2-cyano-2-methylcyclohexanone, this ratio is much larger, approximately 13. While conformational factors in the diradical almost certainly will play a role in controlling the relative amounts of enal and ester, it would appear very reasonable that the conjugation available in the product α,β-unsaturated nitrile would provide a driving force favoring this product over the alternative ketene (which leads to ester). Studies on 2-phenylcycloalkanones appear to support this argument (29).

Finally, it may be mentioned that in some related cases ring enlargement does not occur, *e.g.* 2-acetyl-2-methyl- and 2-benzoylcyclohexanone have been found to provide no ring expanded products on irradiation (31, 32). In contrast, a number of cyclic nonenolizable β-diketones are known to transform to enol lactones but without increase in ring size (33, 34).

Experimental

Spectroscopic and chromatographic instruments employed in this work have been described elsewhere (19).

Syntheses

(a) Suberonitrile

Finely powdered potassium cyanide (19.5 g, 0.3 mol) was added to a solution of 1,6-dibromohexane (Eastman, 24.4 g, 0.1 mol) in 95% ethanol (50 ml) and the mixture was refluxed overnight. When cool, the precipitated solids were dissolved by the addition of a small amount of water and the aqueous mixture was then extracted three times with ether (total, 300 ml); the combined ether extracts were washed successively with water, 5% aqueous sodium hydroxide, and water, and then dried. The manipulations above were all performed in a well-ventilated fume hood, using rubber gloves. The ether was distilled off, and the residue fractionated to give the desired suberonitrile (12 g, 90% yield) b.p. 140–145°/1 mm (lit. (35) b.p. 185°/15 mm). Gas–liquid chromatography indicated this material to be *ca.* 95% pure and it was employed in the next step.

(b) 2-Cyanocycloheptanone

The method of Iwanoff (20) was employed. The ethylmagnesium anilide (36) from *N*-methylaniline was prepared by dropwise addition of ethyl bromide (27.3 g, 0.25 mol) in anhydrous ether (100 ml) over 0.5 h to agitated magnesium turnings (7.2 g, 0.3 mol) in anhydrous ether (20 ml) in a carefully dried three-necked flask cooled in an ice bath, employing a dry nitrogen stream to exclude air. The reaction was moderately vigorous and the solution was stirred for a further 0.5 h after the ethyl bromide addition was complete. Then *N*-methylaniline (26.8 g, 0.25 mol) in anhydrous benzene (100 ml) was added over 0.5 h to the Grignard solution prepared as above and maintained at room temperature, the solution subsequently being stirred for a further 0.5–0.75 h, and then was heated to reflux.

Suberonitrile (23.12 g, 0.17 mol) in 250 ml of a 1:1 benzene–ether mixture was then added at the rate of 1 drop/0.5 min to this refluxing anilide solution; the addition required about 8 h. After refluxing overnight the cooled solution was treated with ice-cold 15% aqueous hydrochloric acid; the benzene–ether layer was separated and washed with a further 100 ml aliquot of 15% aqueous hydrochloric acid. The combined aqueous layers were extracted three times with ether (total, 300 ml), and then the combined organic layers were washed with water and dried. The solvents were distilled off, and the residue distilled to give 2-cyanocycloheptanone (8.1 g, 35%), b.p. 69–72°/0.05 mm (lit. (20) b.p. 135–136°/10 mm); ν_{max} ($CHCl_3$) 2250 (m), 1710 cm^{-1} (s); δ ($CDCl_3$) 3.8 (1H, m), 2.6 (2H, m), 1.4–2.2 p.p.m. (8H, br).

(c) 2-Cyano-2-methylcycloheptanone

Sodium metal (0.69 g, 0.03 g-atom) was dissolved in anhydrous ethanol (12 ml) followed by the addition of 2-cyanocycloheptanone (4.07 g, 0.027 mol) with stirring. After a few minutes, the sodium salt of the ketone separated, and stirring was continued for a further 20 min. Methyl iodide (7.66 ml, 0.054 mol) was then added dropwise; the reaction was not noticeably exothermic and after a further 15 min stirring, the mixture was warmed in an oil bath for 12 h. The ethanol was then removed, water added, and the solution extracted three times with ether; the combined ether extracts were washed twice with 2% aqueous sodium hydroxide, then with water, and dried. Distillation provided 2-cyano-2-methylcycloheptanone (3.3 g, 72%), b.p. 61–63°/0.15 mm, of *ca.* 99% purity by g.l.c.; ν_{max} ($CHCl_3$) 2240 (m), 1718 cm^{-1} (s); δ ($CDCl_3$) 3.7 (2H, m), 1.8 (8H, br), 1.5 p.p.m. (3H, s). A 2,4-dinitrophenylhydrazone derivative, m.p. 145–145.5°, was prepared (37).

Anal. Calcd. for $C_{15}H_{17}N_5O_4$: C, 54.38; H, 5.14; N, 21.14. Found: C, 54.22; H, 5.11; N, 20.94.

(d) 2-Cyanocyclohexanone

Finely powdered potassium cyanide (38 g, 0.58 mol) was added to a solution of 2-chlorocyclohexanone (26.5 g, 0.2 mol; obtained by the method of Newman *et al.* (38)) in 95% ethanol (100 ml) and after stirring for 20 min, the solution was refluxed for 40 min, cooled, poured into ice water, and the aqueous mixture was acidified with 15% aqueous hydrochloric acid to Congo Red p*H*, then extracted with ether. After drying, the ether was distilled off, and the residue fractionated to give the product (13.5 g, 55%), b.p. 87°/0.5 mm (lit. (39) b.p. 129–131°/7 mm); semicarbazide, m.p. 155–156° (lit. (40) m.p. 162°); ν_{max} ($CHCl_3$) 2250 (w), 1720 cm^{-1} (s); δ ($CDCl_3$) 3.8 (1H, m), 2.8–1.4 (8H, br).

(e) 2-Cyano-2-methylcyclohexanone

Sodium metal (1.2 g, 0.05 g-atom) was dissolved in anhydrous ethanol (10 ml) and 2-cyanocyclohexanone (6.15 g, 0.05 mol) added with stirring. A mildly exothermic reaction took place with the appearance of a white precipitate. Methyl iodide (11.36 g, 0.08 mol) was then dropped in and the mixture warmed on the water bath for 0.5 h. At the end of this time, all solid material had disappeared. The solvent was then removed, water added, and the mixture extracted with ether. The aqueous layer was saturated with sodium chloride and again extracted. The combined ether layers were washed twice with water, dried, and the solvent distilled. The residue was fractionated twice to give the desired product, b.p. 88–92°/15 mm (lit. (21) b.p. 94°/13 mm) which was contaminated with a small amount of 2-chlorocyclohexanone. Highly pure 2-cyano-2-methylcyclohexanone was produced by preparative g.l.c. on a 20 ft × 1/4 in. 5% SE-30 column. The purified material was a colorless liquid; ν_{max} ($CHCl_3$) 2240 (m), 1723 cm^{-1} (s); δ ($CDCl_3$) 3.9–1.7 (8H, complex), 1.4 p.p.m. (3H, s); semicarbazone, m.p. 200–202° (lit. (41) m.p. 201–202°).

(f) Methyl 6-Cyanoheptanoate

2-Methylcyclohexanone peroxide was obtained by reaction of 2-methylcyclohexanone with 30% hydrogen peroxide (42) and converted by the method of Minisci and Portolani (26) to the desired product which was isolated in poor yield as an oil; ν_{max} ($CHCl_3$) 3000 (v br), 1710 cm^{-1} (s); δ ($CDCl_3$) 10.9 (s), 2.4 (m), 1.6 (m), 1.3 (d, $J = 7$ Hz). Methylation of this acid with diazomethane gave the methyl ester, a pure sample of which was prepared by preparative g.l.c.; ν_{max} ($CHCl_3$) 2250 (w), 1735 cm^{-1} (s); δ ($CDCl_3$) 3.67 (3H, s), 2.35 (3H, m), 1.9–1.4 (6H, br), 1.31 (3H, $J = 7$ Hz).

(g) 2-Methylheptanedioic Acid and its Dimethyl Ester

6-Cyanoheptanoic acid was hydrolyzed with aqueous ethanolic potassium hydroxide solution, and the crude acid was obtained as an oil by acidification and ether extraction, followed by solvent removal. A portion crystallized from ether, m.p. 49–50° (lit. (26) m.p. 56–57°). The oil had ν_{max} ($CHCl_3$) 3000 (br), 1705 cm^{-1} (s); δ ($CDCl_3$) 11.2 (2H, s), 2.3 (3H, m), 1.5 (6H, br), 1.1 p.p.m. (3H, d, $J = 7$ Hz).

Treatment of this diacid with diazomethane in ether gave the dimethyl ester, obtained as a colorless oil, ν_{max} ($CHCl_3$) 1725 cm^{-1} (s), δ ($CDCl_3$) 3.65 (6H, s), 2.3 (3H, m), 1.4 (6H, br), 1.13 p.p.m. (3H, d, $J = 7$ Hz).

Irradiations

Photochemical studies were performed employing a Hanovia 450 W high pressure lamp in a quartz water-cooled jacket. All samples were irradiated in Pyrex; small scale solutions were degassed by several freeze–thaw cycles on a high-vacuum line, then sealed, while preparative scale ones had oxygen-free nitrogen continuously bubbled through for the irradiation period. Products were isolated using either a 10 ft × 1/4 in. 5% SE-30 column in a Varian Aerograph Model 700 gas chromatograph.

*(a) 2-Cyano-2-methylcycloheptanone (**1**) in Methanol*

A solution of **1** (1.03 g) in methanol (20 ml) was irradiated for 64 h, after which time most of the starting material had been consumed. The solvent was removed and the yellow oil remaining subjected to preparative g.l.c. to give:

Compound 3a: colorless oil; ν_{max} ($CHCl_3$) 2850, 2710, 2210, 1720, 1640 cm^{-1}; δ ($CDCl_3$) 9.92 (1H, t, $J \approx 1$ Hz), 6.17 (1H, m), 2.4 (4H, m), 1.93 (3H, s, fine splitting), 1.5 (4H, m); mass spectrum, *m/e* 151 (10%, M^+, accurate mass measurement, 151.099439; calcd. for $C_9H_{13}NO$, 151.099714), 123 (27%), 122 (24%), 108 (28%), 106 (29%), 94 (100%), 81 (45%), 64 (46%), 55 (53%), 53 (56%), 41 (100%), 39 (69%); 2,4-DNP, m.p. 88–92°;

Compound 3b: colorless oil, ν_{max} ($CHCl_3$) 2850, 2710, 2210, 1720, 1660 cm^{-1}; δ ($CDCl_3$) 9.95 (1H, t, $J \approx 1$ Hz), 6.35 (1H, m), 2.6–1.2 (8H, br), 1.87 (3H, s); mass spectrum, very similar to that of **3***a* (accurate mass measurement on *m/e* 151 peak, 151.099589; calcd. for $C_9H_{13}NO$, 151.099714).

Compound ***4***: colorless oil; ν_{max} ($CHCl_3$) 1690, 1660 cm^{-1}; δ ($CDCl_3$) 3.70 (3H, s), 2.5 (3H, m), 1.5 (8H, m), 1.18 (3H, d, $J = 7$ Hz); mass spectrum, *m/e* 183 (37%, $M^{+\cdot}$, accurate mass measurement, 183.12575; calcd. for $C_{10}H_{17}NO_2$, 183.12592), 154 (11%), 140 (52%), 126 (100%), 112 (75%), 97 (12%), 87 (58%), 70 (20%), 69 (20%), 55 (60%), 41 (85%), 39 (35%).

Aqueous hydrolysis (3 *N* hydrochloric acid – dioxane) of a sample of **4** at room temperature overnight gave material with ν_{max} ($CHCl_3$) 3500 (w), 3410 (w), 1735 (s), 1690 (s), 1600 cm^{-1} (m); δ ($CDCl_3$) 3.66 (3H, s), 2.2 (3H, br), 1.3 (8H, br), 1.1 (3H, d, $J = 7$ Hz).

(b) 2-Cyano-2-methylcycloheptanone in Aqueous Medium

A solution of **1** (0.21 g) in 1:1 dioxane–water (20 ml) was irradiated for 27 h. The cloudy solution was evaporated to dryness and the residue was crystallized from methanol to give **6** as white crystals, m.p. 139–139.5° (33 mg, 14%); ν_{max} ($CHCl_3$) 3340, 1690 cm^{-1}; δ ($CDCl_3$) 8.27 (1H, br, exchangeable), 2.8 (3H, br), 1.7 (8H, br), 1.23 (3H, d, $J = 7$ Hz), mass spectrum, *m/e* 169 (11%, $M^{+\cdot}$), 152 (52%), 142 (16%), 126 (22%), 113 (96%), 98 (74%), 82 (46%), 73 (63%), 69 (51%), 59 (74%), 55 (100%), 41 (100%), 39 (35%);

Anal. Calcd. for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.23. Found: C, 64.07; H, 9.08; N, 8.15.

Solution of a sample of this photoproduct in 3 *N* hydrochloric acid – dioxane at 20° overnight yielded, after work-up, an oily product with ν_{max} ($CHCl_3$) 3500 (w), 3410 (w), 1710 (s), 1660 (s), 1600 cm^{-1} (w).

*(c) 2-Cyano-2-methylcyclohexanone (**2**) in Methanol*

A solution of this ketone (1 g) in methanol (10 ml) was irradiated for 36 h, by which time about 75% of the starting material had been consumed. Preparative g.l.c. gave:

Compound 8a: ν_{max} ($CHCl_3$) 2820, 2720, 2210, 1720, 1640 cm^{-1}; δ ($CDCl_3$) 10.00 (1H, t, $J \approx 1$ Hz), 6.17 (1H, m), 2.5 (4H, m), 1.93 (3H, s, fine splitting), 1.9 (2H, m); mass spectrum, *m/e* 137 (7%, $M^{+\cdot}$), 108 (15%), 94 (80%), 93 (29%), 81 (21%), 67 (17%), 58 (90%), 53 (21%), 43 (100%); a 2,4-DNP derivative, m.p. 113.5–5.114.0°, was obtained (37).

Anal. Calcd. for $C_{14}H_{15}N_5O_4$: C, 52.99; H, 4.73; N, 22.08. Found: C, 52.89; H, 4.77; N, 22.01.

Compound 8b: ν_{max} ($CHCl_3$) 2820, 2720, 2210, 1720, 1640 cm^{-1}; δ ($CDCl_3$) 9.95 (1H, t, $J \approx 1$ Hz), 6.33 (1H, m), 2.7–1.5 (6H, m), 1.87 (3H, s, fine splitting); mass spectrum, apart from variations in peak intensities, identical to that of **8***a*; a 2,4-DNP derivative, m.p. 83–85° was obtained (37).

Anal. Calcd. for $C_{14}H_{15}N_5O_4$: C, 52.99; H, 4.73; N, 22.08. Found: C, 53.02; H, 4.72; N, 21.93.

Compound ***9***: i.r. and n.m.r. spectra identical with those of an authentic sample previously described.

Compound ***10***: ν_{max} ($CHCl_3$) 1690, 1660 cm^{-1}; δ ($CDCl_3$) 3.70 (3H, s), 2.5 (3H, br), 1.67 (6H, br), 1.22 p.p.m. (3H, d, $J = 7$ Hz); a sample (12 mg) was hydrolyzed by refluxing for 3 h in 10% aqueous potassium hydroxide solution to which a little methanol had been added. Work-up gave a semisolid whose i.r. and n.m.r. spectra were practically superimposable on those of an authentic sample of 2-methylheptanedioic acid. Treatment of this semisolid with diazomethane in ether gave a product whose i.r. and n.m.r. spectra and g.l.c. retention times (on 5 ft × 1/8 in. 3% SE-30 and Carbowax columns) were identical to those of a sample of the dimethyl ester of 2-methylheptanedioic acid.

The authors are grateful to the National Research Council of Canada for partial support of this work.

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