Photochemical Reactions of 2-(Alkoxycarbonyl)-, 2-Cyano-, and 2-(Phenylthio)-cycloalkanones in Alcoholic Solution. Formation of ω-Substituted Esters

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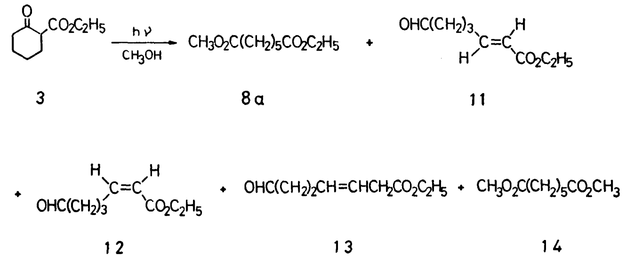
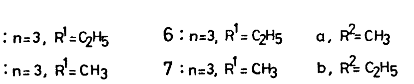
Photochemical reaction of ethyl 2-oxo-1-cyclohexanecarboxylate (**3**) in methanol gave ethyl methyl heptanedioate, *trans*- and *cis*-ethyl 7-oxo-2-heptenoate, and ethyl 7-oxo-3-heptenoate in 25, 7, 8, and 21% yields, respectively. Photochemical reactions of **3** in ethanol, isopropyl alcohol, and *t*-butyl alcohol gave the corresponding ω-alkoxycarbonyl esters. Other 2-(alkoxycarbonyl)-cyclopentanones and -cycloheptanone underwent similar reactions to give the corresponding ω-alkoxycarbonyl esters. Photochemical reactions of 2-cyanocyclohexanones in methanol similarly gave ω-cyano esters and ω-formyl α,β-unsaturated nitriles. However, photochemical reactions of 2-(phenylthio)- and 2-(methylthio)cyclohexanones in methanol did not give the corresponding ω-phenylthio or ω-methylthio carboxylic acid esters, products resulting from a preferential cleavage of a carbon-sulfur bond being obtained.

Photochemical reactions of cycloalkanones have been extensively studied.[1] Cycloalkanones undergo the Norrish Type I cleavage to give acyl alkyl biradical, which is then transformed in alcoholic solution into carboxylic acid ester *via* a ketene intermediate,[2] unsaturated aldehyde[2,3] and cyclic ether[4] as the main paths. Of these the transformation into carboxylic acid esters is of interest as regards synthesis since the employment of cycloalkanones with appropriate substituents at α-position would produce ω-substituted esters. In contrast to the photochemical reactions of 2-alkyl-substituted cycloalkanones,[1] those of other cycloalkanones substituted with alkoxycarbonyl, cyano,[5] or alkylthio groups[6] have received little attention. We have studied the photochemical reactions of such substituted cyclopentanones, cyclohexanones and cycloheptanones in alcohol solvent with emphasis placed on the ester forming reactions. Photochemical reactions of aliphatic β-keto esters undergo intermolecular hydrogen abstraction or α-cleavage to give various photoproducts.[7]

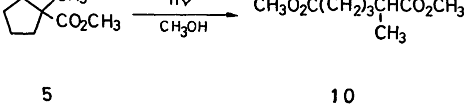
Results and Discussion

Photochemical Reaction of 2-(Alkoxycarbonyl)cycloalkanones. When a 0.16 M solution of ethyl 2-oxo-1-cyclohexanecarboxylate (**3**) in methanol was irradiated for 10 h with a 500 W high pressure mercury vapor lamp, cyclohexanone **3** was almost entirely consumed and ethyl methyl heptanedioate (**8a**), ethyl *trans*-7-oxo-2-heptenoate (**11**), ethyl *cis*-7-oxo-2-heptenoate (**12**), ethyl 7-oxo-3-heptenoate (**13**), and dimethyl heptanedioate (**14**) were produced in 25, 7, 8, 21, and 5% yields, respectively. It was confirmed that the dark reaction of **3** in methanol for 7 days gives no products. Irradiation of ethyl 2-oxo-1-cyclopentanecarboxylate (**1**), methyl 2-oxo-1-cyclopentanecarboxylate (**2**), ethyl 2-oxo-1-cycloheptanecarboxylate (**4**) and **3** in various alcohols gave the corresponding ω-alkoxycarbonyl esters (**6**—**9**) and ω-formyl unsaturated esters. We have been particularly interested in the ester forming reactions leading to products such as **6**—**9**. The yields of these products and the conversion of 2-(alkoxycarbonyl)-cycloalkanones are summarized in Table 1. We see that the ring size has no significant effect on the ester forming reaction, although the photochemical reaction of cyclohexanone **3** seems to be relatively slow. A large difference in conversion is seen in the photochemical reaction of **3** by employing different alcohols, but none in **1** probably due to its higher reactivity than **3**. Substitution of the alkyl group at 1-position has little effect on the yield of ω-alkoxycarbonyl ester. Irradiation of ethyl 1-methyl-2-oxo-1-cyclopentanecarboxylate (**5**) in methanol for 70 h gave dimethyl 2-methylhexanedioate (**10**) in a 29 % yield.





1 : $n=3$, $R^1=C_2H_5$	**6** : $n=3$, $R^1=C_2H_5$	a, $R^2=CH_3$
2 : $n=3$, $R^1=CH_3$	**7** : $n=3$, $R^1=CH_3$	b, $R^2=C_2H_5$
3 : $n=4$, $R^1=C_2H_5$	**8** : $n=4$, $R^1=C_2H_5$	c, $R^2=CH(CH_3)_2$
4 : $n=5$, $R^1=C_2H_5$	**9** : $n=5$, $R^1=C_2H_5$	d, $R^2=C(CH_3)_3$



$$CH_3O_2C(CH_2)_3\underset{CH_3}{\underset{|}{C}}HCO_2CH_3$$

5 **10**

All the products obtained were probably formed *via* an intermediate acyl(alkoxycarbonyl)alkyl biradical, which is then transformed into ω-alkoxycarbonyl ketene or ω-formyl α,β-unsaturated ester. The ketene was converted into ω-alkoxycarbonyl ester such as **6**—**9** in alcoholic media. Decreasing conversion of cycloalkanones in methanol, ethanol, isopropyl alcohol to *t*-butyl alcohol may be due to the increase in viscosity of the latter alcohols. In more viscous alcohols such as *t*-butyl alcohol, recombination of an intermediate birad-

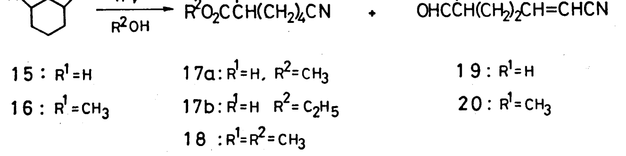
TABLE 1. PHOTOCHEMICAL REACTIONS OF 2-(ALKOXYCARBONYL)CYCLOALKANONES AND 2-CYANOCYCLOALKANONES IN ALCOHOLS[a)]

Substrate	Alcohol R^2	Product	Yield of products (%)[b)]	Conversion of cycloalkanones (%)
1	CH_3	**6a**	28	95
1[c)]	CH_3	**6a**	25	92
1	C_2H_5	**6b**	22	95
1	$(CH_3)_2CH$	**6c**[e)]	—	95
1	$(CH_3)_3C$	**6d**[e)]	—	95
2	CH_3	**7a**	32	95
2[c)]	CH_3	**7a**	29	93
3	CH_3	**8a**	25	71
3	C_2H_5	**8b**	16	43
3	$(CH_3)_2CH$	**8c**	14	33
3	$(CH_3)_3C$	**8d**	4	25
4	CH_3	**9a**	28	91
5	CH_3	**10**	29	95
15	CH_3	**17a**	28	60
15[d)]	C_2H_5	**17b**	14	77
16	CH_3	**18**	16	89

a) Externally irradiated with a 500 W high pressure mercury vapor lamp for 70 h. b) Based on 2-(alkoxycarbonyl)- or 2-cyanocycloalkanones consumed. c) Externally irradiated with a Pyrex filtered high pressure mercury vapor lamp for 70 h. d) Externally irradiated with a 500 W high pressure mercury vapor lamp for 90 h. e) Not isolated.

ical giving the starting cycloalkanone would occur to some extent. ω-Formyl β,γ-unsaturated ester **13** is produced by a photochemical deconjugation of ω-formyl α,β-unsaturated ester (**11**→**12**→**13**). This is seen from the results in which the decrease in the yields of **11** and **12** is accompanied by an increase in the yield of **13** with the prolongation of irradiation time. Facile photochemical isomerization of α,β-unsaturated ester to β,γ-unsaturated isomer has been studied.[8)]

The UV absorption spectra of 2-(alkoxycarbonyl)cycloalkanones show a high intensity absorption of the enol tautomer in the region 255—263 nm and a low intensity absorption of the keto tautomer in the region 280—300 nm.[9)] Although the latter is usually masked by the former, the non-enolizable cycloalkanones such as **5** have a low intensity absorption at 295 nm in ethanol solution, assigned to *n*,π* transition of the keto tautomer. Irradiation of cycloalkanones **1**—**4** with a Pyrex filtered light (>280 nm) gave almost the same yields of ω-alkoxycarbonyl esters **6**—**9** as those with an ordinary high pressure lamp, whereas no reaction occurred when the irradiation was carried out with a 253.7 nm light. These photochemical reactions are not greatly effected by the addition of oxygen, 1,3-pentadiene, or naphthalene. The present photochemical reactions of 2-(alkoxycarbonyl)cycloalkanones leading to ω-alkoxycarbonyl esters might proceed mainly *via* the excited *n*,π* singlet of the keto tautomers.



15 : R^1=H

16 : $R^1=CH_3$

17a: R^1=H, $R^2=CH_3$

17b: R^1=H $R^2=C_2H_5$

18 : $R^1=R^2=CH_3$

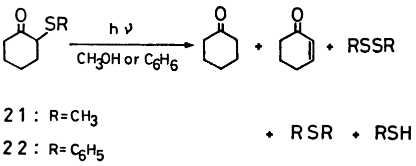
19 : R^1=H

20 : $R^1=CH_3$

Photochemical Reaction of 2-Cyanocycloalkanones. Photochemical reactions of 2-cyanocycloalkanones in alcohol solvent undergo similar reactions to those of 2-(alkoxycarbonyl)cycloalkanones. Irradiation of 2-oxo-1-cyclohexanecarbonitrile (**15**) and 3-methyl-2-oxo-1-cyclohexanecarbonitrile (**16**) in alcohols gave the corresponding ω-cyano esters **17** and **18** and ω-formyl α,β-unsaturated nitrile **19** and **20**. Yields and conversion in these photochemical reactions are given in Table 1.

The irradiation of 1-methyl-2-oxo-1-cyclohexanecarbonitrile in methanol has been reported to produce ω-cyano ester and ω-formyl α,β-unsaturated nitrile in a 1:13 ratio,[5)] but in the present photochemical reaction of **16** they were obtained in a 2:3 ratio. In the photochemical reaction of **16**, an abstraction of tertiary hydrogen at 3-position by α-cyanoalkyl radical moiety of the intermediate biradical would occur to a considerable extent as compared with that of secondary hydrogen at 6-position by acyl radical moiety. No products resulting from the alternative cleavage of the bond between C-2 and C-3 were detected.

Photochemical Reaction of 2-(Phenylthio)cyclohexanone. Irradiation of 2-methylthiocyclohexanone (**21**) in methanol, benzene, or ether gave polymeric products. Small amounts of cyclohexanone and dimethyl disulfide were detected by GLPC analysis. Irradiation of 2-phenylthiocyclohexanone (**22**) in methanol also gave polymeric products besides a small amount of cyclohexanone. However, irradiation of **22** in benzene for 70 h gave cyclohexanone, cyclohexenone, diphenyl disulfide, diphenyl sulfide and thiophenol in the yields 34, 2, 5, 3, and 3 %, respectively. All the products obtained resulted from a preferential cleavage of a carbon–sulfur bond. Diphenyl disulfide might be formed by a combination of phenylthio radical or further photolysis of thiophenol.[6)] As a result, no cleavage of Norrish Type I occurred in these photochemical reactions of 2-(phenylthio)- or 2-(methylthio)cyclohexanones.



21 : $R=CH_3$

22 : $R=C_6H_5$

Experimental

Gas-liquid chromatographic analyses were carried out with a Hitachi K-53 and a Hitachi 063, the preparative work being done with a Varian Autoprep 700. A SE-30 column supported on Diasolid L was mainly used in GLPC analyses. Other liquid phases were unsatisfactory because the starting 2-(alkoxycarbonyl)cycloalkanones were often decomposed in GLPC columns. Infrared spectra were obtained with a Hitachi EPI-G22, and nuclear magnetic resonance spectra were measured with a JEOL 3H-60 and a Hitachi R-22 using tetramethylsilane as an internal standard. Mass spectra were obtained with a Hitachi RM-50 GC. Quantitative GLPC analyses were carried out by an internal standard method.

General Procedure for Irradiation. The starting cycloalkanone in alcoholic solvent (0.16 M) in a quartz tube was cooled in water and externally irradiated with a 500 W high pressure mercury vapor lamp for 70 h. Nitrogen gas was allowed to pass through the mixture during the course of irradiation. An immersion apparatus was employed for preparation. Quantitative experiments in different alcohols were carried out with a merry-go-round procedure for irradiation.

Preparations of 2-Substituted Cycloalkanones. Ethyl 2-oxo-1-cyclopentanecarboxylate (**1**), bp 107 °C/18 mmHg, was prepared from diethyl adipate and metal sodium by the method of Pinkney.[10] Methyl 2-oxo-1-cyclopentanecarboxylate (**2**), bp 105 °C/17 mmHg, was also prepared by a similar method. Ethyl 2-oxo-1-cyclohexanecarboxylate (**3**), bp 103.5 °C/12 mmHg, was prepared by the method of Snyder *et al.*[11] from cyclohexanone and diethyl oxalate. Ethyl 2-oxo-1-cycloheptanecarboxylate (**4**), bp 136 °C/22 mmHg, was prepared by the method of Krapcho *et al.*[12] from cycloheptanone and diethyl carbonate. Methyl 1-methyl-2-oxo-1-cyclopentanecarboxylate (**5**) was prepared by methylation of **2**.[13] 2-Oxo-1-cyclohexanecarbonitrile (**15**), bp 138—140 °C/15 mmHg, was prepared by the method of Satoda *et al.*[15] or Meyer[16] from 2-chlorocyclohexanone[14] and sodium cyanate. 3-Methyl-2-oxo-1-cyclohexanecarbonitrile (**16**), bp 95—96 °C/3 mmHg, was prepared by the method of Kuehne[17] from 3-methyl-2-pyrrorydino-1-cyclohexene, bp 117 °C/20 mmHg, and cyanogen chloride. 2-Methylthiocyclohexanone (**21**), bp 98—100 °C/15 mmHg, was prepared by the method of Truce *et al.*[18] from 2-chlorocyclohexanone and sodium methanethiolate. 2-Phenylthiocyclohexanone (**22**), bp 115—117 °C/3 mmHg, was prepared by the method of Seebach *et al.*[19] from cyclohexanone and diphenyl disulfide or by the method of Wilputte *et al.*[20] from 2-chlorocyclohexanone and sodium benzenethiolate. All the 2-substituted cycloalkanones were purified by a distillation or a preparative GLPC.

Photochemical Reaction of Ethyl 2-Oxo-1-cyclohexanecarboxylate (3). A mixture of 6.8 g of **3** and 250 ml of dry methanol (0.16 M) was irradiated for 10 h with an immersion apparatus using a 500 W high pressure mercury vapor lamp. After removal of the solvent, distillation gave 4.7 g of crude product; bp 60.0—85.0 °C/1 mmHg. The distillate was separated into four principal components by preparative GLPC using a SE-30 column. The second component was identified as unreacted ester **3**. The fourth component was identified as ethyl methyl hexanedioate (**8a**): IR (CCl$_4$) 1735 cm^{-1}; NMR (CCl$_4$) δ 1.22 (t, 3H), 3.59 (s, 3H), 4.05 (q, 2H), 1.62 (m, 6H), 2.22 ppm (t, 4H); *m/e* (rel intensity) 171 (M$^+$−OCH$_3$, 40), 157 (M$^+$−OC$_2$H$_5$, 48), 88 (49), 55 (100). Found: C, 59.60; H, 9.06%. Calcd for C$_{10}$H$_{18}$O$_4$: C, 59.38; H, 8.97%. The first component was further separated into two products by preparative GLPC using a CW-20 M column. One was identified as ethyl *cis*-7-oxo-2-heptenoate (**12**): IR (CCl$_4$) 2820, 2720, 1720, 1645 cm^{-1}; NMR (CCl$_4$) δ 1.30 (t, 3H), 1.77 (qi, 2H), 2.48 (t, 2H), 2.73 (q, 2H), 4.17 (q, 2H), 5.78 (dm, 1H, J=10.5 Hz), 6.24 (dt, 1H, J=10.5 Hz, J=7.5 Hz), 9.85 ppm (s, 1H); *m/e* (rel intensity) 170 (M$^+$, 3), 142 (16), 127 (42), 125 (50), 114 (100), 99 (93), 86 (72), 81 (83), 68 (92). Found: C, 63.20; H, 8.30%. Calcd for C$_9$H$_{14}$O$_3$: C, 63.51; H, 8.29%. The other product was identified as ethyl 7-oxo-3-heptenoate (**13**): IR (CCl$_4$) 2820, 2720, 1735 cm^{-1}; NMR (CCl$_4$) δ 1.26 (t, 3H), 2.5 (m, 4H), 3.00 (m, 2H), 4.12 (q, 2H), 5.60 (m, 2H), 9.81 ppm (s, 1H); *m/e* (rel intensity) 170 (M$^+$, 8), 142 (51), 127 (12), 125 (33), 124 (47), 99 (37), 97 (82), 96 (70), 79 (76), 67 (100), 55 (83). Found: C, 63.73; H, 8.21%. Calcd for C$_9$H$_{14}$O$_3$: C, 63.51; H, 8.29%. The third component was further separated into two products by preparative GLPC using a CW-20M column. One was identified as dimethyl heptanedioate (**14**) by comparison with an authentic sample, the other as ethyl *trans*-7-oxo-2-heptenoate (**11**): IR (CCl$_4$) 2820, 2720, 1725, 1655 cm^{-1}; NMR (CCl$_4$) δ 1.27 (t, 3H), 1.80 (qi, 2H), 2.24 (q, 2H), 2.48 (t, 2H), 4.17 (q, 2H), 5.80 (d, 1H, J=16.0 Hz), 6.88 (dt, 1H, J=16.0 Hz, J=6.5 Hz), 9.83 ppm (s, 1H); *m/e* (rel intensity) 170 (M$^+$, 2), 142 (10), 127 (36), 125 (50), 114 (82), 99 (72), 81 (100), 68 (77), 55 (53). Found: C, 63.35; H, 8.20%. Calcd for C$_9$H$_{14}$O$_3$: C, 63.51; H, 8.29%. GLPC analysis showed that the conversion of **3** was 91% and yields of **8a**, **11**, **12**, **13**, and **14** were 25, 7, 8, 21, and 5%, respectively.

When a sample of 0.16 M **3** in methanol in a quartz tube was externally irradiated for 70 h, **8a** was obtained in 25% yield.

Irradiation of **3** in ethanol for 70 h gave diethyl heptanedioate (**8b**) in 16% yield as the major product. **8b** was identified by comparison with an authentic sample.

Irradiation of **3** in isopropyl alcohol for 70 h gave ethyl isopropyl heptanedioate (**8c**) in 14% yield: IR (CCl$_4$) 1735 cm^{-1}; NMR (CCl$_4$) δ 1.18 (d, 6H), 1.24 (t, 3H), 1.65 (m, 6H), 2.20 (t, 4H), 4.05 (q, 2H), 4.90 ppm (m, 1H); *m/e* (rel intensity) 230 (M$^+$, 6), 185 (26), 171 (72), 143 (80), 125 (81), 101 (78), 69 (78), 55 (89), 41 (100). Found: C, 62.70; H, 9.60%. Calcd for C$_{12}$H$_{22}$O$_4$: C, 62.58; H, 9.63%.

Irradiation of **3** in *t*-butyl alcohol for 70 h gave *t*-butyl ethyl heptanedioate (**8d**) in 4% yield: IR (CCl$_4$) 1735 cm^{-1}; NMR (CCl$_4$) δ 1.23 (t, 3H), 1.40 (s, 9H), 1.55 (m, 6H), 2.13 (t, 2H), 2.22 (t, 2H), 4.06 ppm (q, 2H); *m/e* (rel intensity) 171 (28), 143 (27), 125 (27), 57 (100). Found: C, 63.63; H, 9.70%. Calcd for C$_{13}$H$_{24}$O$_4$: C, 63.90; H, 9.90%.

When a 0.08 M solution of **3** in methanol was irradiated for 42 h with a 15 W low pressure mercury vapor lamp, products such as **8a**, **11**, **12**, **13**, and **14** were not obtained. Irradiation of a 0.16 M solution of **3** in methanol in the presence of oxygen, 0.1—0.5 M 1.3-pentadiene or 0.16 M naphthalene gave **8a** in almost the same yields with nearly the same conversion.

Photochemical Reaction of Ethyl 2-Oxo-1-cyclopentanecarboxylate (1). Irradiation of a 0.16 M solution of **1** in methanol for 70 h gave ethyl methyl hexanedioate (**6a**) in 28% yield: IR (CCl$_4$) 1735 cm^{-1}; NMR (CCl$_4$) δ 1.24 (t, 3H), 1.62 (m, 4H), 2.25 (m, 4H), 3.63 (s, 3H), 4.07 ppm (q, 2H); *m/e* (rel intensity) 188 (M$^+$, 2), 157 (36), 143 (32), 115 (52), 111 (60), 59 (57), 55 (100). Found: C, 57.35; H, 8.50%. Calcd for C$_9$H$_{16}$O$_4$: C, 57.43; H, 8.57%.

Irradiation of a 0.16 M solution of **1** in ethanol for 70 h gave diethyl hexanedioate (**6b**) in 22% yield. **6b** was identified by comparison with an authentic sample.

Photochemical Reaction of Methyl 2-Oxo-1-cyclopentanecarboxylate (2). Irradiation of a 0.16 M solution of **2** in methanol for 70 h gave dimethyl hexanedioate (**7a**) in 32% yield. **7a** was identified by comparison with an authentic sample.

Photochemical Reaction of Ethyl 2-Oxo-1-cycloheptanecarboxylate (4). Irradiation of a 0.16 M solution of **4** in methanol for 70 h gave ethyl methyl octanedioate (**9a**) in 28% yield: IR (CCl$_4$) 1735 cm^{-1}; NMR (CCl$_4$) δ 1.24 (t, 3H), 1.6 (m, 8H), 2.25 (t, 4H), 3.65 (s, 3H), 4.08 ppm (q, 2H); *m/e* (rel intensity) 185 (M$^+$−OCH$_3$, 43), 171 (90), 143 (62), 138 (100), 129 (76), 97 (72), 88 (59), 83 (60), 69 (93), 55 (83). Found: C, 61.09; H, 9.28%. Calcd for C$_{11}$H$_{20}$O$_4$: C, 61.09; H, 9.32%.

Photochemical Reaction of Methyl 1-Methyl-2-oxo-1-cyclopentanecarboxylate (5). Irradiation of a 0.16 M solution of **5** in methanol for 70 h gave dimethyl 2-methylhexanedioate

(**10**) in 29% yield: IR (CCl_4) 1735 cm^{-1}; NMR (CCl_4) δ 1.15 (d, 3H), 1.62 (m, 4H), 2.25 (t, 2H), 2.45 (m, 1H), 3.64 ppm (s, 6H); *m/e* (rel intensity) 157 (M^+-OCH_3, 17), 156 (30), 128 (48), 127 (40), 124 (47), 96 (60), 95 (59), 94 (70), 69 (100), 67 (98).

Photochemical Reaction of 3-Methyl-2-oxo-1-cyclohexanecarbonitrile (16). Irradiation of a 0.16 M solution of **16** in methanol gave three principal products. These were separated by preparative GLPC using a SE-30 column. From spectral data, the first was identified as *cis*-6-methyl-7-oxo-2-heptenenitrile (*cis*-**20**): IR (CCl_4) 2710, 2810, 2220, 1725 cm^{-1}; NMR (CCl_4) δ 1.18 (d, 3H), 1.3—2.1 (m, 2H), 2.50 (q, 2H), 2.5 (m, 1H), 5.36 (m, 1H, J=11.0 Hz), 6.47 (dt, 1H, J=11.0 Hz, J=7.5 Hz), 9.85 ppm (s, 1H), *m/e* (rel intensity) 137 (M^+), 122 (2), 108 (8), 94 (14), 81 (28), 80 (30), 67 (100), 58 (42). The second was identified as *trans*-6-methyl-7-oxo-2-heptenenitrile (*trans*-**20**): NMR (CCl_4) δ 1.14 (d, 3H), 1.3—2.0 (m, 2H), 2.27 (q, 2H), 2.54 (m, 1H), 5.37 (m, 1H, J=17.0 Hz), 6.68 (dt, 1H, J=17.0 Hz, J=7.0 Hz), 9.82 ppm (s, 1H). IR and mass spectra of *trans*-**20** were almost identical with those of *cis*-**20**. The third was identified as methyl 6-cyano-2-methylhexanoate (**18**): IR (CCl_4) 2250, 2230, 1735 cm^{-1}; NMR (CCl_4) δ 1.15 (d, 3H), 1.51 (m, 6H), 2.30 (t, 2H), 2.45 (m, 1H), 3.66 ppm (s, 3H); *m/e* (rel intensity) 138 (M^+-OCH_3, 13), 109 (47), 88 (100), 69 (44), 55 (29). Found: C, 63.75; H, 8.90; N, 8.12%. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.94; N, 8.28%. GLPC analysis showed that the yields of *cis*-**20**, *trans*-**20**, and **18** were 5, 19, and 16%, respectively.

Photochemical Reaction of 2-Oxo-1-cyclohexanecarbonitrile (15). Irradiation of a 0.16 M solution of **15** in methanol for 70 h gave methyl 6-cyanohexanoate (**17a**) in 28% yield: IR (CCl_4) 2230, 1735 cm^{-1}; NMR (CCl_4) δ1.58 (m, 6H,) 2.31 (t, 2H), 2.32 (t, 2H), 3.66 ppm (s, 3H); *m/e* (rel intensity) 124 (M^+-OCH_3, 42), 96 (40), 74 (100), 69 (27), 59 (26), 55 (25). Found: C, 62.22; H, 8.39; N, 9.18%. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03%. Although product **19** was not isolated, its presence in the irradiated mixture was shown by GC-mass spectroscopy.

Photochemical Reaction of 2-Methylthiocyclohexanone (21). When a 0.16 M solution of **21** in methanol was irradiated for 70 h, the solution turned red-brown with precipitation of a solid. Removal of solvent gave tar. A slight formation of cyclohexanone was detected by GLPC analysis. Irradiation in ether or benzene afforded similar results.

Photochemical Reaction of 2-Phenylthiocyclohexanone (22). When a 0.16 M solution of **22** in methanol was irradiated for 70 h, the solution turned red-brown with precipitation of a solid. GLPC analysis showed that 76% of **22** was consumed, a slight amount of cyclohexanone being produced. Similar irradiation in benzene produced cyclohexanone, cyclohexenone, diphenyl disulfide, diphenyl sulfide, and thiophenol in 34, 2, 5, 3, and 3% yields, respectively. The conversion of **22** was 94%.

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