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β, γ-불포화카르복시산, 카르복시아미드와 니트릴 유도체의 합성과 이들의 광화학적 반응에 관한 연구

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Synthesis and Exploratory Photochemistry of β, γ-unsaturated Carboxylic Acid, Carboxamide and Nitrile Derivatives

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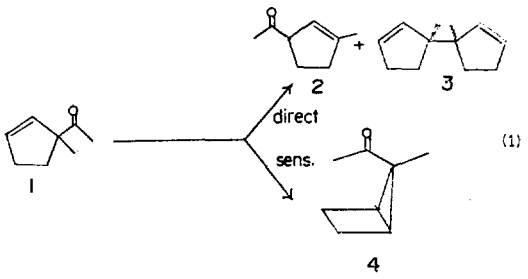
요 약. 1-아세틸-1-메틸-2-시클로펜텐 화합물의 케톤 Chromophore를 나트릴, 카르보시산, 아미드 등의 group으로 대치하여 이들의 광화학반응을 검토한 결과 케톤 Chromophore에서 볼 수 있는 1, 3-Acyl shift나 ODPM 반응은 일어나지 않았고 광화학적 중합및 환원반응등 Chromophore를 변화시키므로서 광화학반응에 큰 변화를 보여주었다. 1-Cyano-1-methy-2-cyclohexene의 경우도 Ketone chromophore와 비교하여 광화학 반응을 검토하였다.

ABSTRACT. The ketone chromophore of 1-Acetyl-1-methyl-2-cyclopentene (1) was replaced by nitrile, carboxylic acid and acetamide group, and their photochemical reactions were investigated. While the β, γ-unsaturated ketone **1** afforded 1, 2 ar 1, 3-Acyl shift product, these replaced chromophores did not afford any monomeric rearranged products. 1-cyano-1-methyl-2-cyclohexene also afforded no product anology of the 1, 2-acyl shift reaction. The replacement of the ketone chromophore by nitrile, carboxylic acid and carboxamide has greatly altered the photochemistry of β, γ-unsaturated ketones.

INTRODUCTION

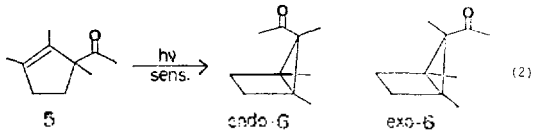
The photochemistry of β, γ-unsaturated ketones[1] has been exensively studied from the viewpoint of structural factors, stereochemistry and mechanism. Of the several β, γ-unsaturated ketones studied, one of the structurally least complicated is 1-acetyl-1-methyl-2-cyclopentene (**1**). Neywick[2] has studied the singlet and triplet photochemistry of **1** and observed that photolysis of **1** in dry benzene at 300nm resulted in the formation of two products, **2** and **3**, which mechanistically are equivalent to a 1, 3-acyl shift and to α-cleavage (Type I) followed by recombination of the methylcyclopentyl radicals (equation 1).

Acetone-sensitized irradiation of **1** afforded only *endo*-**4**, the *exo*-isomer was not detected by either column chromatography or vpc.[3] However, Schaffner[4] has reported that acetone-



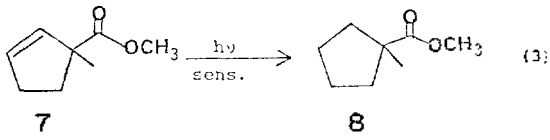
(1)

sensitized irradiation of **5**, the dimethyl analog of **1**, afforded both *exo*-and *endo*-**6** (equation 2).



(2)

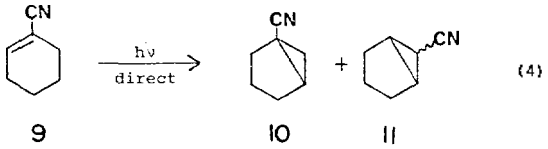
Liu and Givens[3] have also studied the photochemical reation of β,γ-unsaturated ester **7**. Acetone-sensitized irradiation of **7** afforded a low yield of the photoreduced ester **8** (equation 3) and no product analog of the 1,2-acyl shift



(3)

reaction (oxa-di-π-methane rearrangement). Thus replacement of the ketone chromophore by a carbomethoxy group has greatly altered the photochemistry of **1**.

In another study, McCullough and coworkers[5] have reported that the photorearrangement of 1-cyanocyclohexene (**9**) gave the two cyclopropane products **10** and **11**. This reaction formally resembles the "type A" rearrangement[6] of enones (equation 4). Since the ester chromophore altered the photochemistry of β,γ-unsaturated ketone while cyano chromophore did not alter the "type A" photorearrangement



(4)

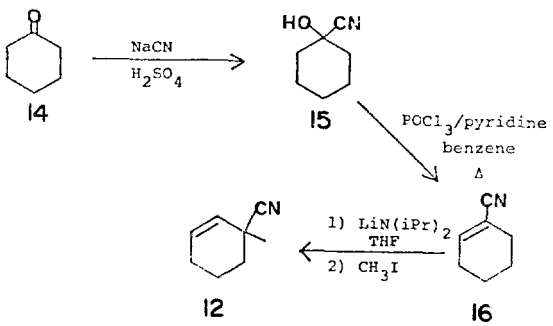
of enones, the effect of changing the chromophores on the photorearrangement is not clear. It was decided that the investigation of the photochemistry of several chromophores, other than the ketone, in β,γ-unsaturated framework might be profitable. For this purpose 1-cyano-1-methyl-2-cyclohexene (**12**), 1-methyl-2-cyclopentene-1-carboxylic acid (**13a**), 1-methyl-2-cyclopentene-1-carboxamide (**13b**) and 1-cyano-1-methyl-2-cyclopentene (**13c**) were synthesized (*Fig.* 1).

RESULTS AND DISCUSSION

Synthesis. The β,γ-unsaturated nitrile **12** was synthesized as shown in *Scheme* 1. Sodium cyanide treatment[7] of cyclohexanone (**14**) under acidic conditions gave the cyanohydrin (**15**) which was dehydrated with phosphorus oxychloride[7b] to give 1-cyano-cyclohexene (**16**). The nitrile **16** was then treated with lithium diisopropyl amide[8] followed by methyl iodide to afford nitrile **12** (*Scheme* 1). This methyla-

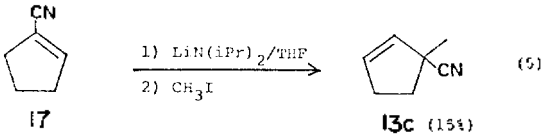
a, R = COOH **b**, R = $CONH_2$ **c**, R = CN

Fig. 1. Structure of **12** and **13**. **a**, R=COOH, **b**, R=$CONH_2$, **c**, R=CN

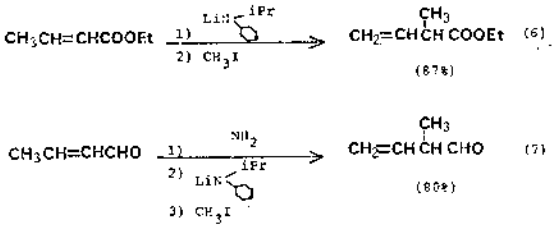


Scheme 1. Synthesis of Unsaturated Nitrile **12** and **13c**.

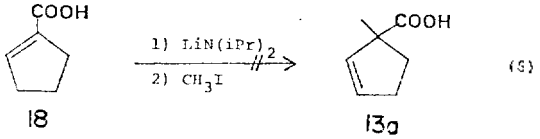
tion procedure was employed in an attempt to synthesize nitrile **13c**, but the yield was too low (~15%) to be useful as a synthetic method (equation 5).



Sullivan[9] and Schlessinger[10] have shown that alkylation at the α-carbon of α,β-unsaturated esters and aldehydes can be accomplished in high yield (equations 6 and 7) by reaction of

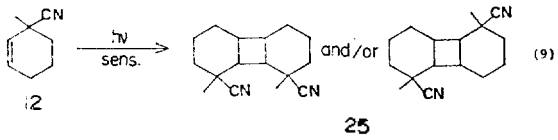


the anion generated with lithium isopropylcyclohexyl amide with methyl iodide. Using their procedure, cyclopentene carboxylic acid (**18**) was treated with lithium diisopropyl amide followed by methyl iodide. Little alkylation was observed (equation 8). Since the methylation of the nitrile **17** and carboxylic acid **18** were unsuccessful, the β,γ-unsaturated nitrile **12c** was prepared by a combination of the procedures developed by Neywick[2] and Sakai[11] (*Scheme* 2). The β-ketoester **20** was treated with sodium hydride[12] and methyl iodide to give **21**. The ketoester **21** was reduced with sodium borohydride to a mixture of hydroxy esters **22**. The mixture of methane-sulfonates **22** were prepared and these were heated in HMPA at 145°C for 4 hr to afford the unsaturated ester **7**. Hydrolysis of **7** with sodium hydroxide gave the unsaturated acid **13a** which

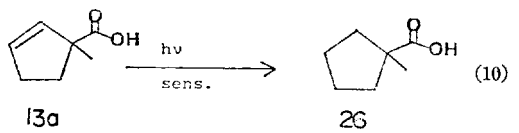


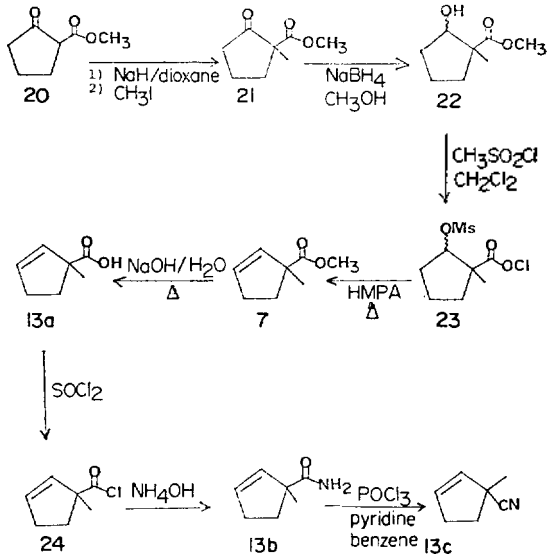
was treated with thionyl chloride to give acid chloride **24**. This acid chloride **24** was treated with ammonium hydroxide to give the amide **13b**, which was dehydrated to afforded the unsaturated nitrile **13c**.

Photochemistry. Acetone-sensitized irradiation of 1-cyano-1-methyl-2-cyclohexene(**12**) at 2537 Å resulted in photodimerization; the product was identified as **25** (equation 9). The stereochemistry and regiospecificity of the product **25** were not determined.



Acetone-sensitized irradiation of carboxylic acid **13a** at 2537Å gave the photoreduced product identified as **26** (equation 10) in analogy with the results of the metyl ester sensitized





Scheme 2. Synthesis of β,γ-Unsaturated Acid **13a**, Acidamide **13b** and Nitrile **13c**.

irradiation (equation 3). The photoreduction of double bonds shows that the carboxylic acid and ester chromophores follows divergent pathway form that of **1** and these two functional groups do not migrate as easily as ketone carbonyl.

Acetone-sensitized irradiation of the amide **13b** at 2537 Å showed a new peak on vpc analysihs. The column chromatography of this photoproduct did not afford any monomeric rearranged products. Acetone-sensitized irradiation of the nitrile **13c** at 3000 Å resulted in photodecomposition and did not show any volatile monomeric products.

Since compounds **12** and **13** have very weak absorptivities between 200~300 nm, direct irradiations were not carried out.

CONCLUSION

Photolysis of compounds **12** and **13a-c** did not afford any monomeric rearrangement products. Nitrile **12** gave photodimer **25** upon sensitized irradiation and acid **13a** gave reduced product **26** upon acetone-sensitized irradiation.

It is reasonable to postulate the photoreduction resulted from hydrogen abstractione of the triplet excited state of or by chemical sensitization with acetone. However, the absence of the rearranged product is a strong evidence that the replacement of ketone chromophore by several other groups has changed the photochemistry completely precluding an ODPM-Type of rearrangement.

Although some photoreactions of unsaturated ester have shown a skeletal rearrangement which are suggestive of the ODPM process, there appears to be no experimental evidence to support this mechanistic analogy with the ester chromophore or with other major modification in the carbonyl function.

EXPERIMENTAL

Synthesis

1-Cyanocyclohexene (9). In a 1 *l* three-necked flask fitted with an efficient stirrer, a dropping funnel, and a thermometer in a well was placed a solution of 120g (2.46 mole) of powdered 95% sodium cyanide in 480 m*l* of water and 100 g (1 mole) of cyclohexanone(14). The flask was surrounded by an ice bath and the solution was stirred vigorously. When the temperature reached 10 °C, 400 m*l* of 40% aqueous sulfuric acid was added over a period of 3 hr, the temperature being kept between 5 ~10 °C. After all the acid had been added, the stirring was continued for 30 min and then the flask was set aside for the salt to settle. A layer of cyanohydrin **15** was separated from the aqueous layer and the aqueous layer was extracted with ether several times. The combined ether solutions were dried over sodium sulfate. The distilled cyanohydrin, **15**, 120 g (0.96 mole, 96%, bp 82 °C at 0.4 mmHg) in 200 m*l* of pyridine and 200 m*l* of benzene was treated with amixture of 300 m*l* of phosphorus oxychloride and 100 m*l* of pyridine in an ice bath. The resulting mixture was refluxed for 30 min, then cooled and poured onto ice and extracted with ether. The extracts were washed with 10 % aqueou hydrochloric acid and dried over sodium sulfate. Vacuum distillation gave 70 g (0.65 mole, 68 %, bp 58 °C at 0.6 mmHg) of pure 1-cyanocyclohexene (16).

The spectral data were: nmr (CCl_4) δ 1.4~2.4 (multiplet, 8 H), 6.5 (multiplet, 1 H, olefinic); ir (CCl_4) 3040 (−C=C−H), 2930 (C−H), 2210 (−C≡N) and 1660 cm^{-1} (−C=C−).

1-Cyano-1-methyl-2-cyclohexene (12) (Methylation of 1-Cyanocyclohexene). To a solution of 14.241 g (141 mmole) of diisopropy-

lamine in 140 m*l* tetrahydrofuran was added 91.5 m*l* (140.91 mmole) of methyllithium at 4 °C. The resulting solution was stirred for 20 min and then 15 g (140.19 mmole) of nitrile **12** was added to the solution at −78 °C. The resulting solution was stirred for 1 hr then 9.5 m*l* of methyl iodide in 6 g of HMPA was added dropwise and stirred for 1hr at −78 °C. After the mixture had been warmed to room temperature, it was partitioned between ether and 10 % aqueous hydrochloric acid. The ether solution was washed with water and saturated sodium thiosulfate solution and then[7] dried over sodium sulfate. Vacuum distillation gave 13.5 g (111 mmole, 79 %, bp 40~43 °C at 0.1~0.4 mmHg) of pure product, 1-cyano-1-methyl-2-cyclohexene(**12**). The spectral data were: nmr (CCl_4) δ 1.25 (singlet, 3H, $-CH_3$), 1.3~2.3 (multiplet, 6H) and 5.3~6.0 (multiplet, 2H, olefinic); ir (CCl_4) 3030 (−C=C−H), 2940 (CH), 2240 (−C≡N) and 1650 cm^{-1} (−C=C−); uv λ_{max} (isooctane) 190 nm (ε 6000); mass spectrum (155) *m/e* 31(100), 41(32), 54 (88), 66(24), 77(23), 79(82), 93(23), 94(49), 106(27), 120(9), 121(12) and 122(2).

Anal Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15. Found: C, 79.35; H, 8.85.

2-Carbomethoxy-2-methylcyclopentanone (21). A solution of 71 g (0.5 mole) of β-ketoester **20** in 70 m*l* of dry dioxane (freshly distilled from lithium aluminum hydride) was added slowly under N_2 gas to a stirred suspension of 13.2 g (0.55 mole, 1.1 eqv) of sodium hydride in 500 m*l* of dry dioxane. To this mixture, after 15 min, was added 200 g of methyl iodide (3 eqv) and the reaction mixture was stirred for 2.5 hr at 40 °C. It was then cooled and acidified with 25 % acetic acid. After removal of solvent, the residue was diluted with water and extracted with ether. The ether extract was washed with aqueous sodium bicarbonate, saturated brine solution, then dried over sodium sulfate. Vacuum distillation afforded 59.3 g (0.38 mole, 76 %, bp 69~73 °C at 1.1 mmHg) of 2-carbomethoxy-2-methylcyclopentanone (**21**). The spectral data were: nmr (CCl_4) δ 1.1 (singlet, 3H, ($-OCH_3$), 1.5~2.5 (multiplet, 6H) and 3.5 (singlet, 3H, $-COOCH_3$); ir (CCl_4) 2900 (CH) and 1710~1750 cm^{-1} (ketone and ester).

2-Carbomethoxy-2-methylcyclopentanol (22) (Reduction of Ketoester 21). Ketoester **21**, 57 g (0.37 mole) in 300 m*l* of methanol was cooled to −78 °C and 13.2 g (0.35 mole) of sodium borohydride was added slowly. After stirring for 40 min the reaction was quenched by 10 % aqueous hydrochloric acid. The methanol solution was dissolved in ether, then washed with water, sodium bicarbonate solution, saturated brine solution and dried over magnesium sulfate. Vacuum distillation gave 41.3 g (0.26 mole, 70 %, bp 66~68 °C at 0.7 mmHg) of 2-carbomethoxy-2-methylcyclopentanol (**22**). The spectral data were: nmr (CCl_4) δ 1.15 (singlet, 3H, CH_3) 1.2~2.4 (multiplet, 6H), 3.0 and 3.25 (two doublets, 1H, OH), 3.6 (two singlets, 3H, OCH_3) and 3.9 and 4.2 (two multiplets, 1H, *CH*OH); ir (CCl_4) 3440 (OH), 2900 (CH), 1700 cm^{-1} (ester).

1-Carbomethoxy-1-methyl-2-cyclopentene (7). (Dehydration of Alcohol 22). A solution of 39 g (0.24 mole) of alcohol **22** in 250 m*l* of methylene chloride and 75 m*l* of pyridine was cooled to 0 °C in an ice bath and 32 g (0.28 mole) of freshly distilled methane sulfonyl chloride was added in one portion. The reaction mixture was allowed to warm to room temperature and was stirred under nitrogen for 5 hr at which time it was washed into a separatory funnel with methylene chloride. This was washed with cold 5 % aqueous hydrochloric acid and water, then dried over magnesium

sulfate. After evaporation of solvent *in vacuo*, the crude mesylate **23** was dissolved in 200 m*l* of HMPA and heated to 145 °C for 4hr. Then saturated brine solution was added to the reaction mixture and the mixture was extracted with ether and pentane. Vacuum distillation gave 17 g (55 %) of 1-carbomethoxy-1-1methyl-2-cyclopentene (**7**). The spectral data were: nmr (CCl_4) δ 1.15 (singlet, 3H, $-CH_3$), 1.2~2.5 (multiplet, 4H), 3.5 (singlet, 3H, $-OCH_3$) and 5.5 (multiplet, 2H, olefinic); ir (CCl_4) 3060 ($-C=C-H$), 2950 (C−H), 1720 ($-\overset{O}{\overset{\|}{C}}-O-$) and 1620 cm^{-1} ($-C=C-$).

1-Methyl-2-cyclopentene-1-carboxylic acid (13a). A solution of 14.5 g (0.1 mole) of ester **7** and 100 m*l* of 20 % aqueous sodium hydroxide was refluxed for 90 min. The resulting solution was neutralized with 10 % hydrochloric acid in an ice bath and extracted with ether to give 12.1 g (0.096 mole, 92 %) of 1-methyl-2-cyclopentene-1-carboxylic acid (**13a**). The spectral data were: nmr (CCl_4) δ 1.2 (singlet, 3H, $-CH_3$), 1.3~2.6 (multiplet, 4H), 5.6 (multiplet, 2H, olefinic) and 12.4 (singlet, 1H, −COOH); ir (CCl_4) 3000 (broad, −COOH) and 1680 cm^{-1} (−COOH); uv λ_{max} (isooctane) no absorption at 200~350 nm, 185 nm (ε 3×10^4); mass spectrum (73 °C) *m/e* 31(65), 32 (44), 53(9), 77(5), 79(26), 80(4), 81(100), 82(6), 126(5) and 127(1).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.86; H, 7.81.

1-Methyl-2-cyclopentene-1-carboxamide (13b). A 500m*l* three-necked flask was equipped with a dropping funnel, stirrer and condenser. In the flask was placed 15 g of thionyl chloride; to this was added, dropwise, 10 g (0.08 mole) of acid **12a**. After all of the acid had been added, the reaction mixture was refluxed for 40 min and then distilled *in vacuo* to give 10 g (0.069 mole, 86 %) of acid chloride **24**. This acid chloride was added dropwise to 100 m*l* af concentrated ammonium hydroxide in an ice bath and the solution was stirred for 1 hr, extracted with ether, chloroform and ethyl acetate to give 7 g (0.056 mole, 81 %) of white crystal (mp 85~86.5 °C) of 1-methyl-2-cyclopentene-1-carboxamide (**13b**). The spectral data were: nmr ($CDCl_3$) δ 1.3 (singlet, 3H, $-CH_3$), 1.6—2.6 (multiplet, 4H), 5.5~6.0 (multiplet, 2H, olefinic) and 6.7 (broad singlet, 2H, $-NH_2$); ir ($CHCl_3$) 3400~3500 (doublet, amide), 2950 (−C−H), 1660 ($-\overset{O}{\overset{\|}{C}}-$), and 1560$cm^{-1}$ (C−N); mass spectrum (13 °C) *m/e* 39(26), 41(34), 44(12), 53(34), 65(12), 67 (23), 77(13), 78(4), 79(57), 81(100), 82(21), 125(21) and 126(3); uv (isooctane) no absorption at 200~350nm.

Anal. Calcd for $C_7H_{11}NO$: N, 11.19; C, 67.17; H, 8.86. Found: N, 10.98; C, 67.22; H, 8.81.

1-Cyano-1-methyl-2-cyclopentene (13c). In a 100 m*l* three-necked round bottom flask, fitted with a powerful stirrer and a reflux condenser, were placed 5.5 g (0.044 mole) of amide **12b**, 3 g of NaCl, and 20 m*l* of ethylene dichloride. After the mixture had been stirred rapidly for 15 min, 3 m*l* of phosphorus oxychloride was added and the mixture was refluxed for 2 hr in an oil bath. Afer the mixture had been cooled to room temperature, it was filtered and the solid was washed with 500 m*l* of ethylene dichloride. The solvent was removed by fractional distillation and the residue was distilled *in vacuo* to give 1.21g (0.011 mole, 65 %, bp 36 °C (at 0.5 mmHg) of 1-cyano-1-methyl-2-cyclopentene (**13c**). The spectral data were: nmr (CCl_4) δ 1.3 (singlet, 3H, $-CH_3$), 1.5−2.7(multiplet, 4H) and 5.3~5.9 (multiplet, 2H, olefinic); ir (CCl_4) 3060 (−C=C−H), 2950 (−C−H) and 2240 (−C≡N); mass spectrum (m/e) 39(21), 41(71), 65(31), 79

(18); 92(100), 106(11), 107(19) and 108(2); uv no absorption at 200~350 nm.

Anal. Calcd for C_7H_9N: N, 13.07; C, 78.46; H, 8.47. Found: N, 9.95; C, 60.55; H, 6.87.

Exploratory Photochemistry

Acetone-sensitized Irradiation of 1-Cyano-1-methyl-2-cyclohexene (12). A solution of 1.3 g of nitrile **12** in 10 m*l* of acetone in a quartz tube was degassed with purified nitrogen. The sample was irradiated with 15 RPR-2537 Å lamps for 8 hr affording a crude yellow liquid after removal of solvent *in vacuo*. Vpc analysis of the photomixture showed a broad peak. This was separated by silica gel column chromatography to give 600 mg (45 %) of photodimer **25**, which was identified by ir and nmr spectra. The spectral data were: amr (CCl_4) δ 0.5~2.6 (multiplet, 22H); ir (CCl_4) 2900 (CH), 2240cm^{-1} (C≡N).

Anal. Calcd for $C_{16}H_{22}N_2$: C, 80.67; H, 9.24; N, 11.76. Found: C, 78.20; H, 8.89; N, 10.56.

Acetone-sensitized Irradiation of 1-Methyl-2-cyclopentene-1-carboxylic Acid 13a. A solution of 660 mg of acid **13** in 70 m*l* of acetone was divided into five quartz tubes and degassed with purified nitrogen. The samples were irradiated with 15 RPR-2537 Å lamps for 18hr. Vpc analysis using a 10 % FFAP column showed a new peak (retention time, 10 minutes) and starting material (retenion time, 12 minutes). Silical gel chromatography (5 % ether-hexane eluate) gave 119 mg of a mixture of photoreduced product **26** and starting material **13a**.

This mixture was rechromatographed to give 25 mg of 1-methylcyclopentane carboxylic acid **26**. Spectral data were: nmr (CCl_4) δ 1.2 (singlet, 3H, $-CH_3$) 1.3~2.3 (multiplet, 8H) and 12.5 (singlet, 1H, −COOH); ir (CCl_4) 3000 (broad, CH and COOH) and 1680cm^{-1} (−COOH); mass spectrum (156°) *m/e* 41(23), 42(4), 43(3), 44(4), 53(3), 55(59), 67(10), 84(6), 83(100), 82(4), 87(31), 113(16), 128(6) and 129(1).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 66.30; H, 9.40.

Acetone-Sensitized Irradiation of Amide 13b. A solution of 660 mg of acid amide **13b** in 70 m*l* of acetone was divided into 6 quartz tubes and degassed with purified nitrogen. The samples were irradiated with 15 RPR-2537 Å lamps for 18 hr. Vpc analysis using 10 % FFAP showed a new peak (retention time, 13 minutes) and starting material (retention time, 11 mintues). Column Chromatographic separation of photoproduct on silica gel was unsuccessful.

Direct Irradiation of 1-Cyano-1-methyl-2-cyclopentene(13c). The β,γ-unsaturated nitrile **13c**, 100 mg in 100 m*l* of ether was degassed with purified nitrogen. The sample was irradiated in a quirtz tube using 15 RPR 2537 Å lamps for 6 hr. The solvent was then evaporated *in vacuo* to give approximately 90 mg of a clear liquid Vpe analysis using SE-30, OV-17 and ββ′-oxydipropionitrile columns showed mainly starting material and no appreciable amounts of volatile photolyzed products. The nmr spectrum of the photolyzed mixture showed almost the same ratio of vinyl hydrogen integration as before photolysis. The photolyzed mixture was reirradiated for an additional 10 hr at 254 nm. The nmr spectrum of this mixture showed a new peak at δ 0.5~1.3 (multiplet) and the ratio of vinyl hydrogen integration decreased (olefinic: alkyl=9 : 1). However, vpc and column chromatographic analysis showed no detectable amounts of photolysis products. This was not investigated further.

Acetone-sensitized Irradiadiation of Nitrile 13c. A solution of 65 mg of nitrile **13c** in

15 m*l* reagent acetone in a pyrex tube was degassed with purified nitrogen. The sample was irradiated with 15 RPR-3000 Å lamps for 6 hr affording a crude yellow liquid after removal of the solvent *in vacuo*. Vpc analysis using FFAP, APL and CBW columns showed mainly starting material. This mixture was reirradiated for an additional 12 hr at 300 nm. The nmr spectrum of this photolyzed mixture showed a complex multiplet at δ 1.0~2.8 and a very weak vinyl hydrogen at δ 5.7. Vpc analysis showed mainly starting material and small amounts of a photoproduct (retention time, 3 minutes using 10 % FFAP). The photomixture was chromatographed on a silica gel column eluting with 20, 50 and 75 % ether-hexane eluate. These photoproducts obtained showed only a very weak methyl singlet (nmr) indicating that the photoproducts were significantly altered in the reaction; no clean rearrangement products were observed.

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