with stypodiol (4) by TLC and ^1H NMR (220 MHz). The synthetic product showed $[\alpha]_D$ -3.65° (c 0.52, $CHCl_3$).

Synthesis of Ether 12 from Epistypodiol (5). To a stirred solution of pyridine (5 mL, 0 °C) containing 56 mg (0.135 mm) of 4 was added 10 mL of a 1:1 solution of benzene and methanesulfonyl chloride (excess) dropwise over 0.5 h. After being warmed to 25 °C (12 h), the reaction mixture was quenched with ice and water and extracted with Et_2O (3 × 50 mL). The combined Et_2O phases were washed with water (3 × 50 mL), 5% HCl (3 × 50 mL), and saturated $NaHCO_3$ solution (3 × 50 mL) and dried over anhydrous $MgSO_4$. The Et_2O was removed in vacuo to yield 51.9 mg (0.103 mmol, 77% yield) of an oil which was homogeneous by TLC. The dimesylate was the sole product retrieved and its formation confirmed by the following spectral features: IR (CCl_4) 1370, 1340, 1230, 1180 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.13 (3 H, s), 3.03 (3 H, s). Without further purification, the dimesylate was reduced to the ether 12. A solution containing 20 mL of NH_3, 5 mL of Et_2O (-78 °C, under argon), and 55.5 mg (0.206 mmol, 2 equiv) of pounded, cut, and washed (pentane) Li was produced by dissolving the Li over a 30-min period. To the resultant blue solution was carefully added 51.9 mg (0.103 mmol) of epistypodiol dimesylate in Et_2O (7 mL) and the reaction was allowed to proceed for 90 min at -78 °C. The reaction was quenched by careful addition of excess NH_4Cl and diluted with Et_2O, and the NH_3 solution allowed to evaporate overnight. The Et_2O solution was washed with water (2 × 75 mL), dried over anhydrous $MgSO_4$ and reduced in vacuo to yield a mixture of products as analyzed by TLC. The least polar component was recovered by preparative TLC (6 mg, 0.016 mmol, 15.5% yield) and determined to be the desired aryl ether (12): ^1H NMR (220 MHz, $CDCl_3$) δ 6.95 (1 H, dd, J = 7, 1.0 Hz), 6.86 (1 H, dd, J = 7, 1.0 Hz), 6.66 (1 H, dd, J = 7, 7), 3.17 (1 H, d, J = 17), 2.97 (1 H, d, J = 17), 2.17 (3 H, d, J = 1), 1.2-1.8 (17 H, m), 1.17 (3 H, s), 0.86 (3 H, s), 0.79 (6 H, s), 0.72 (3 H, d, J = 7); low-resolution mass spectrum, m/e 380 (M^+, 9), 256 (6), 191 (5), 159 (7), 149 (3), 145 (7), 121 (16), 91 (20), 55 (65), 43 (85), 41 (100).

Base Treatment of Epitaondiol (6). Epitaondiol (6, 102.9 mg) was refluxed in 5% KOH in MeOH for 4 h. The MeOH was removed in vacuo and the residue was taken up in Et_2O. The Et_2O phase was washed with 5% HCl (3 × 50 mL) and finally with saturated $NaHCO_3$. The Et_2O mix was dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo to yield only starting material as determined by TLC and ^1H NMR analysis.

Air Oxidation of Hydroquinone 8. Filtered air was continuously bubbled through a room-temperature CH_2Cl_2 solution of the hydroquinone 8 for 24 h. CH_2Cl_2 was periodically replenished. Removal of the solvent in vacuo gave a two-component mixture which by high-performance LC (μ-Porasil, 50 cm, CH_2Cl_2) separated into starting material and a less polar component, identified as 7 by comparison with the natural product.

Acknowledgment. We thank Drs. Klaus Rützler and Jim Norris, Smithsonian Institution, for the kind invitation to participate in the IMSWE tropical reef research program, supported in part by a grant from Exxon Corporation, in Belize and for advice and guidance with the biological aspects of our research. We thank Dr. J. D. Martin for providing authentic samples of taondiol and atomaric acid and Dr. P. Crews for providing several ^{13}C NMR spectra. This research is a result of financial support from NOAA, Department of Commerce, Office of Sea Grant, under Grant No. 04-7-158-44121.

Registry No. 1, 71103-05-4; 2, 71106-25-7; 2 trimesylate, 75558-33-7; 3, 71103-04-3; 4, 75657-53-3; 4 diacetate, 75578-63-1; 5, 75578-65-3; 5 diacetate, 75657-52-2; 5 dimesylate, 75578-64-2; 6, 75598-52-6; 7, 57576-82-6; 8, 57576-81-5; 8 diacetate, 75558-34-8; 9, 34274-99-2; 10, 55907-34-1; 11, 75558-35-9; 12, 75598-51-5; 13, 75558-36-0.

Photochemistry of Aliphatic Imides. Synthesis of Azetidine-2,4-diones via Photochemical Isomerization of Succinimides and *N*-Formyl-*N*-methyl α,β-Unsaturated Amides[1]

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Photochemical reactions of alkyl-substituted succinimides and *N*-formyl-*N*-methyl α,β-unsaturated amides were studied. Photolysis of succinimide 1 gave azetidine-2,4-dione 2 together with a small amount of 3. The photoinduced ring-contraction reaction is explained in terms of a two-photon mechanism. Similarly, several other succinimide derivatives photochemically gave the corresponding azetidine-2,4-diones. In addition, the photochemical cyclization of 3 to 2 was extended to the synthesis of azetidine-2,4-diones from *N*-formyl-*N*-methyl α,β-unsaturated amides.

In recent years considerable interest has been shown in the photochemistry of alicyclic imides. A number of studies have revealed that alicyclic imides photochemically behave similarly to simple carbonyl compounds, i.e., ketones and aldehydes. For example, the Paterno–Büchi reaction,[2] hydrogen abstraction,[3] and α cleavage[4] have been investigated. In regard to the α-cleavage reaction of imides, however, only a few reports have been published, and the scope and generality of the reaction have not been thoroughly investigated. Recently we have reported in preliminary form evidence that succinimides undergo the α-cleavage reaction to give azetidine-2,4-diones.[5] In this paper we describe the details of the reaction as well as the photochemical cyclization of *N*-formyl-*N*-methyl α,β-unsaturated amides.[6] The reaction provides a new and general synthetic method for the synthesis of alkyl-substituted azetidine-2,4-diones. The previously reported

(1) This work is supported in a part by a grant from the Ministry of Education, Science, and Culture (No. 347017).

(2) (a) Maruyama, K.; Kubo, Y. *J. Org. Chem.* **1977**, *42*, 3215. (b) Maruyama, K.; Ogawa, T.; Kubo, Y. *Chem. Lett.* **1978**, 1107. (c) Kanaoka, Y.; Yoshida, K.; Hatanaka, Y. *J. Org. Chem.* **1979**, *44*, 664.

(3) (a) Kanaoka, Y.; Hatanaka, Y. *J. Org. Chem.* **1976**, *41*, 400. (b) Kanaoka, Y.; Okajima, H.; Hatanaka, Y. *Heterocycles* **1977**, *8*, 339. (c) Nakai, H.; Sato, Y.; Mizoguchi, T.; Yamazaki, M.; Kanaoka, Y. *Ibid.* **1977**, *8*, 345.

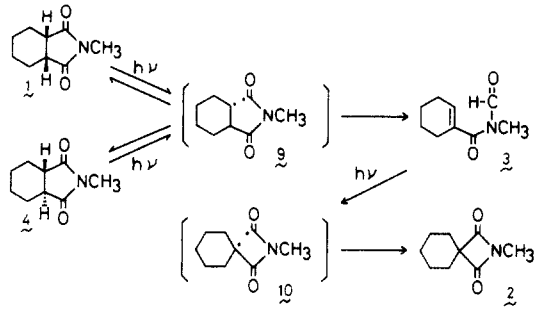
(4) (a) Gandhi, R. P.; Singh, M.; Sharma, T. D.; Mukherji, S. M. *Tetrahedron Lett.* **1973**, 675. (b) Scharf, G.; Fuchs, B. *J. Chem. Soc., Chem. Commun.* **1975**, 244. (c) Schtyser, J. A.; DeSchryver, F. C. *Tetrahedron* **1976**, *32*, 251.

(5) (a) Maruyama, K.; Ishitoku, T.; Kubo, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3671. (b) Kanaoka et al. independently published an analogous report on α cleavage of cyclic imides: Kanaoka, Y.; Okajima, H.; Hatanaka, Y. *J. Org. Chem.* **1979**, *44*, 1749.

(6) A preliminary report of this work has appeared previously: Maruyama, K.; Ishitoku, T.; Kubo, Y. *Chem. Lett.* **1980**, 265.

0022-3263/81/1946-0027$01.00/0

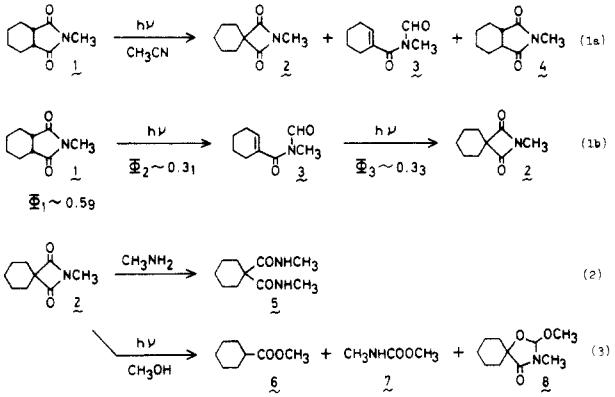
Scheme I



syntheses were tedious and sluggish, giving poor yields of the 2,4-dione system.[7]

Results and Discussion

Photochemical Reaction of *N*-Methylcyclohexane-*cis*-1,2-dicarboximide (1). Irradiation of 1 at 254 nm gave *N*-methylcyclohexane-1,1-dicarboximide (2) (43%) and *N*-formyl-*N*-methyl-1-cyclohexene-1-carboximide (3, 7.8%). The starting material recovered (60%) has been partly isomerized to its trans isomer 4 (1/4 ratio of 2/1 estimated by LC). The structure of 2 was deduced from its spectroscopic properties and was confirmed by the chemical reaction shown below. Compound 3 was identified by comparison with an authentic sample which was prepared from 1-cyclohexene-1-carbonyl chloride and *N*-methylformamide (see eq 1a, 2, 3).



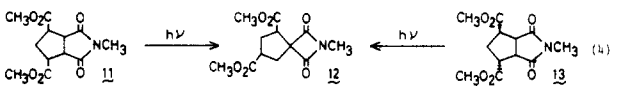
The photoinduced ring contraction can be most reasonably explained in terms of a two-photon mechanism as shown in Scheme I. This mechanism is supported by the following experimental facts. First, irradiation of 3 gave 2 in a yield of 85%. Second, the extinction coefficient of 3 was 10 times larger than that of 1 at 254 nm. Third, an induction period was observed in the time-dependent variation in the yield of 2 (see ref 5a). From these results, the pathway described in Scheme I must represent the main route from 1 to 2, though other competing possibilities cannot be completely excluded.[9]

Quantum efficiencies of the reaction at an early stage (conversion <10%) were measured, and the results are shown in eq 1b. Φ_1 is the quantum yield of disappearance of 1, Φ_2 that of formation of 3 from 1, and Φ_3 that of formation of 2 from 3. Taking account that biradical 9 would produce 1 (Scheme I), the quantum yield of the α-cleavage reaction must be larger than 0.5.[9] This indicates the high efficiency of the α-cleavage reaction of succinimides as well as the facility of the hydrogen abstraction step.[3a]

Table I. ^{13}C NMR Data (δ) of 11, 12, and 13 (in $CDCl_3$)

11	25.222 (NMe), 29.421 (methylene), 45.869, 46.972 (methine), 52.222 (OMe), 170.876, 175.665 (C=O)
12	24.765 (NMe), 31.898, 32.140 (methylene), 42.019, 46.326 (methine), 52.114, 52.409 (OMe), 69.045 (quaternary C), 170.635, 171.737, 172.624, 173.107 (C=O)
13	25.249 (NMe), 32.813 (methylene), 42.730, 47.969 (methine), 57.571 (OMe), 172.676, 177.767 (C=O)

Photochemical Reaction of Various Alkyl-Substituted Succinimides. Irradiation of *cis*-*N*-methyl-3,5-bis(methoxycarbonyl)cyclopentane-1,2-dicarboximide (11) gave the ring contracted product *N*-methyl-2,4-bis(methoxycarbonyl)cyclopentane-1,1-dicarboximide (12) in a yield of 50% (eq 4). Similarly, 13, which is a stereoisomer of



11, photochemically afforded the same product 12. ^1H NMR and IR spectra are completely in accord with the structure of 12. Although the mass spectrum of 12 did not show a parent peak (*m/e* 269), it did show a peak derived from $M^+ - OMe$ (*m/e* 238). Molecular weight measurement by means of the vapor pressure method showed the molecular weight of 12 to be 275 ± 10. Chemical shifts of the ^{13}C NMR signals of 11–13 are listed in Table I. From the results it is obvious that a methylene carbon and a quaternary carbon have been created, thereby supporting the structure of 12.

Several other succinimide derivatives were photochemically converted to the corresponding azetidine-2,4-diones. The results are summarized in Table II. The structures of the products were confirmed by their ^1H NMR, IR, and mass spectra and elemental analyses.

In addition to 33, the photolysis of 32 afforded *trans*-*N*-formyl-*N*,1,2-trimethylacrylamide (34) and the cis isomer 35 in a yield of 14% (34/35 ratio of 1/1 estimated by ^1H NMR). Presumably, compound 32 undergoes the α-cleavage reaction to give 34 and 35. Cis–trans isomerization can compete with the intramolecular hydrogen abstraction reaction (Scheme II). The rate of cyclization of 32 to 33 will be diminished, resulting in a lower yield. Independent experiments showed that the photolysis of 34 gave not only 33 but also 35. In contrast, owing to the rigidity of the cyclohexene ring, the rate of cis–trans isomerization of 3 is far slower than that of compound 34.

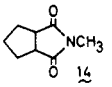
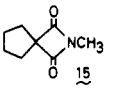
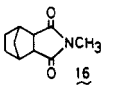
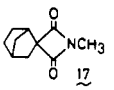
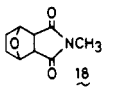
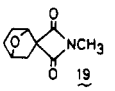
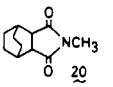
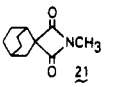
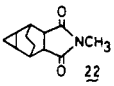
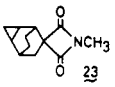
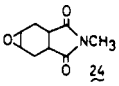
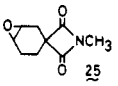
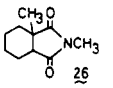
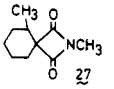
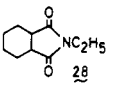
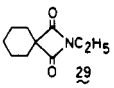
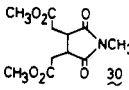
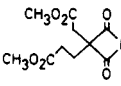
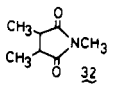
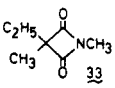
The photochemical reaction of *N*,1-dimethylcyclohexane-1,2-dicarboximide (26) afforded nearly equivalent amounts of *N*,2-dimethylcyclohexane-1,1-dicarboximide (27, 26%) and *N*,2-dimethyl-*N*-formyl-1-cyclohexene-1-carboxamide (36, 27%). This result clearly indicates (i) that the C(O)–C bond fission occurs preferentially at the alkyl substituted carbon and (ii) that in the photochemical cyclization of the ring-opened enimide, an appreciable steric hindrance is operative. The photoinduced ring closure of the enimide may be initiated via an intramolecular hydrogen abstraction by the olefinic β-carbon from the adjacent formyl group. This process is facilitated by the fact that the reaction occurs via a six-membered transition state, where the formyl hydrogen atom is transferred to the β-carbon. The large steric hindrance

(7) Poshkus, A. C.; Herweh, J. E. *J. Org. Chem.* **1965**, *30*, 2466 and references cited therein.

(8) All yields of products are calculated on the basis of consumed amounts of starting materials.

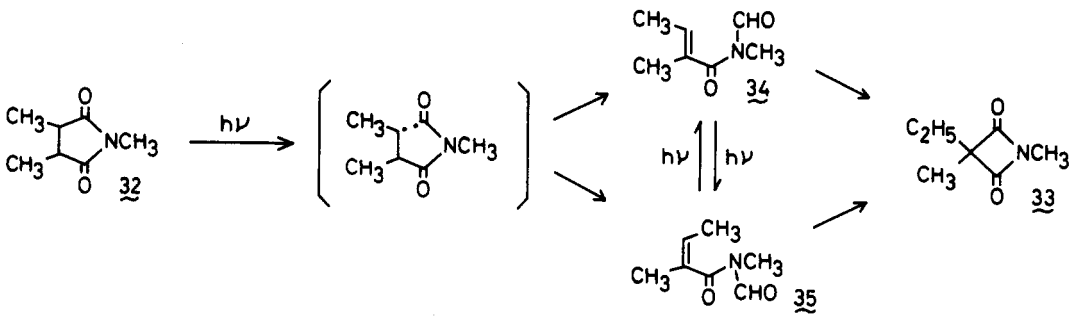
(9) For example, a mechanism involving direct 1,2 hydrogen shift to give more stable biradical 10 from biradical 9 is also possible, but it is known that 1,2 hydrogen shifts hardly occur in a liquid medium. See: Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; p 237.

Table II. Azetidine-2,4-diones from Succinimides

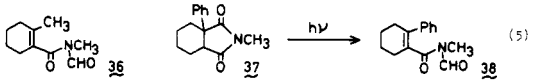
substrate	product	mp, °C	IR, cm^{-1}	yield, %[a]
 14	 15	38-42	1840, 1710, 955	51
 16	 17	oil	1733, 945	36
 18	 19	63-64	1820, 1730, 947	28
 20	 21	81-82	1720, 950	43
 22	 23	46-47	1817, 1721, 945	39
 24	 25	106-108	1712, 963	35
 26	 27	58-59	1720, 950	26
 28	 29	62-65	1712, 964	22
 30	 31	oil	1734, 960	25
 32	 33	oil	1805, 1720, 945	9

[a] Isolated yield calculated on the basis of the consumed amount of substrate.

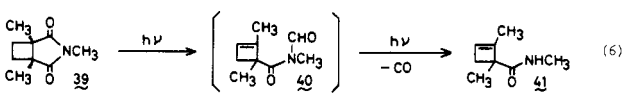
Scheme II



of a phenyl group completely suppressed the ring closure, giving only compound **38** (eq 5).



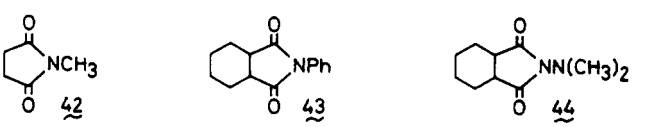
(5)



(6)

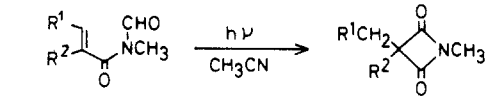
N,1,2-Trimethylcyclobutane-*cis*-1,2-dicarboximide (**39**), whose α-positions are occupied by four alkyl substituents, also undergoes the α-cleavage reaction. However, compound **39** can not isomerize to azetidine-2,4-dione on irradiation and instead gives *N*,1,2-trimethyl-2-cyclobutene-1-carboxamide (**41**, 59%), which corresponds to a decarbonylation product of **40** (eq 6).

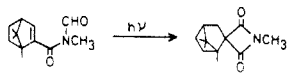
On the other hand, irradiation of succinimides **42**–**44**,



in acetonitrile gave no product under the same conditions

Table III. Azetidine-2,4-diones from *N*-Formyl-*N*-methyl α,β-Unsaturated Amides



material[a]	R^1	R^2	product	irradn time, h	yield, %[b]
3		$(CH_2)_4$	2	6	85 (72)
45		$(CH_2)_3$	15	5	81 (85)
34	CH_3	CH_3	33	24	29 (79)
46	H	CH_3	47	6	25 (82)
48	H	n-C_3H_7	49	9	55 (71)
50	H	i-C_3H_7	51	14	50 (81)
52	H	n-C_4H_9	53	16	72 (68)[c]
54	H	i-C_4H_9	55	13	33 (77)
56	H	n-C_6H_{13}	57	12	51 (80)
58	H	c-Hx	59	15	54 (81)
60			61	2	75 (94)

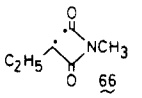
[a] Concentrations are 0.09–0.14 M. [b] Isolated yield calculated on the basis of the consumed amount of material. Conversions (in percent) are listed in parentheses. [c] NMR yield.

as those used for the reaction of **1**. Comparison of **42** with **32** reveals that the presence of an alkyl substituent at the α-position is essential for the C–C(O) α cleavage of the succinimides. This is to be expected on the basis of the stability of the biradical produced via the α-cleavage reaction. In the cases of imides **43** and **44**, which have phenyl or dimethylamino groups attached to the imide nitrogen, one would expect that the excited state of these succinimides would be influenced by conjugation of the imide nitrogen with the substituents. At the present time we have no information which bears on this problem, and further work will be necessary to clarify the situation.

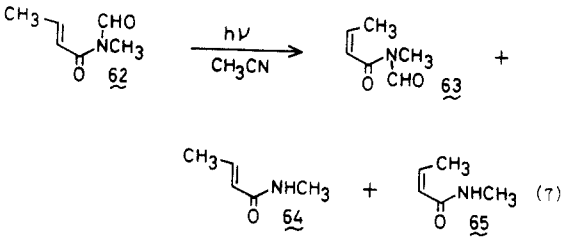
Taking into account the fact that alkyl-substituted succinimides photochemically gave both azetidine-2,4-diones and ring-opened enimides, it would appear that the α-cleavage reaction occurs at the C(O)–C bond, since these products are produced via the cleavage reaction. This result agrees with the previously reported α-cleavage reaction of alicyclic imides.[4,10] Thus, this work further establishes the generality and importance of the α-cleavage reaction of alicyclic imides, especially that involving C(O)–C fission. The C(O)–N bond fission, however, cannot be eliminated as a competing process since the material balances of the present reactions are not quantitative (~50%). Mazzocchi and co-workers recently reported that some open-chain imides and *N*-alkylpyrrolidinones photochemically undergo an α-cleavage reaction of the C(O)–N bond.[11,26] Detailed studies will be necessary in order to clarify the controlling factor of the mode of the two fissions.

Photochemical Cyclization of *N*-Formyl-*N*-methyl α,β-Unsaturated Amides. Irradiation of compound **3** gave the cyclized product **2** in a yield of 85%, as described in the previous section. This type of photocyclization was extended to several other related amides in order to explore a synthetic route of alkyl-substituted azetidine-2,4-diones. The results are summarized in Table III. As can be seen from Table III, compounds **3**, **45**, and **60**, whose substituents (R^1 and R^2) are part of a cyclic ring, give rise to better yields than the other compounds. This is compatible with the assumption described previously. The high yields of azetidine-2,4-diones **2**, **15**, and **33** are remarkable as compared with those obtained from the succinimides (see Table II), indicating the synthetic utility of this reaction.

In contrast, irradiation of *trans*-*N*-formyl-*N*-methylcrotonamide (**62**) gave rise to no azetidine-2,4-dione. This result suggests that the presence of an alkyl substituent at the α-position is essential for the photochemical cyclization of *N*-formyl-*N*-methyl α,β-unsaturated amides. This can be explained in terms of the less stable nature of 1,4-biradical **66** which is produced via intramolecular



hydrogen abstraction. Photolysis of **62** gave the cis isomer **63** and a mixture of decarbonylated products **64** and **65** (eq 7).



(7)

Although the photochemical isomerizations of succinimides and *N*-formyl-*N*-methyl α,β-unsaturated amides to azetidine-2,4-diones have some limitations as described above, the reaction does provide a convenient synthetic method for the synthesis of a wide variety of azetidine-2,4-diones. It should be noted that *N*-formyl-*N*-methyl α,β-unsaturated amides are easily obtained from *N*-methylformamide and α,β-unsaturated carboxylic acid chlorides and thus represent convenient starting materials for azetidine-2,4-diones.

Experimental Section

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory of Kyoto University, Kyoto, Japan. IR spectra were recorded with a JASCO IRA-1 spectrophotometer. ^1H NMR spectra were taken with a JEOL PS-100 spectrometer and ^{13}C NMR spectra with a JEOL FX-100, and chemical shifts are reported in parts per million on the δ scale from internal tetramethylsilane. Mass spectra were recorded with a Hitachi M-52 mass spectrometer. Column chromatography was carried out on Wakogel C-200 (silica gel). UV irradiation was carried out in a quartz tube at room temperature by using an Eikosha 120-W low-pressure Hg lamp.

Preparation of Succinimides. *N*-Methylcyclohexane-*cis*-1,2-dicarboximide (**1**; mp 51–52 °C, lit.[12] mp 47–48 °C) was prepared by the reaction of methylamine and cyclohexane-1,2-dicarboxylic anhydride. *N*-Ethylcyclohexane-1,2-dicarboximide [**28**; bp 154–157 °C (27 mmHg), lit.[13] bp 88–92 °C (0.05 mmHg)] was prepared from ethylamine and cyclohexane-1,2-dicarboxylic anhydride. *N*-Methylcyclopentane-1,2-dicarboximide [**14**; bp 135–142 °C (20 mmHg), lit.[14] bp 144–148 °C (29 mmHg)] was prepared from methylamine and cyclopentane-1,2-dicarboxylic anhydride. *N*,2,3-Trimethylsuccinimide [**32**; bp 158–160 °C (35

(10) Gandhi et al. suggested that the decarbonylated product from the glutarimide derivative would be produced via C(O)–N bond cleavage.[4a] However, even in this case a mechanism including the C(O)–C bond fission may be possible. Kanaoka et al. obtained photoproducts derived from C(O)–C bond cleavage in the photochemical reaction of glutarimide derivatives.[5b]

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mmHg), lit.[15] 98–100 °C (12 mmHg)] was prepared from methylamine and 2,3-dimethylsuccinic anhydride and consisted of meso and *dl* isomers.

N-Methylnorbornane-2,3-dicarboximide (**16**) was prepared as follows. 5-Norbornene-2,3-dicarboxylic anhydride, which is a Diels–Alder adduct derived from cyclopentadiene and maleic anhydride, was heated with methylamine in water at 95 °C for 2 h to give *N*-methyl-5-norbornene-2,3-dicarboximide (**67**). Compound **67** was hydrogenated in the presence of Pd/C (5%) under a pressure of 5 kg/cm^2 of hydrogen. Compound **16** was recrystallized from ethanol; mp 78–79 °C (lit.[16] mp 78 °C). The following five succinimides were prepared by similar procedures. *N*-Methyl-7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide (**18**; mp 133–134 °C, lit.[17] mp 135 °C) was prepared from furan and maleic anhydride. *N*-Methylbicyclo[2.2.2]octane-2,3-dicarboximide (**20**; mp 111–114 °C) was prepared from 1,3-cyclohexadiene and maleic anhydride. *N*,1-Dimethylcyclohexane-1,2-dicarboximide (**26**; mp 56–58 °C, lit.[12] mp 52–53 °C) was prepared from butadiene and citraconic anhydride. *N*-Methyl-1-phenylcyclohexane-1,2-dicarboximide (**37**; mp 98–100 °C, lit.[18] mp 95 °C) was prepared from butadiene and phenylmaleic anhydride. *N*-Methyltricyclo[3.2.2.0^{2,4}]nonane-6,7-dicarboximide (**22**) was prepared from cycloheptatriene and maleic anhydride. For compound **22**: mp 112–113 °C; IR (KBr) 1765 (sh), 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.46–0.88 (m, 2 H), 0.9–1.4 (m, 6 H), 2.47 (br s, 2 H), 2.74–2.90 (m, 2 H), 2.94 (s, 3 H); mass spectrum, *m/e* (relative intensity) 205 (M$^+$, 3), 113 (100). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.15; H, 7.43; N, 6.65.

all-cis-*N*-Methyl-3,5-bis(methoxycarbonyl)cyclopentane-1,2-dicarboximide (**11**) was prepared as follows. Compound **67** was oxidized with potassium permanganate by the method of Krapcho et al.[19] After the manganese oxide was reduced by addition of sodium hydrosulfite, the reaction mixture was condensed to dryness, and the dicarboxylic acid was extracted with acetone by using a Soxhlet extractor. The dicarboxylic acid was esterified in methanol in the presence of a catalytic amount of sulfuric acid. Recrystallization from methanol gave colorless crystals: yield 67%; mp 187–188 °C; IR (KBr) 1770 (sh), 1735, 1693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.16 (m, 2 H), 2.98 (s, 3 H), 2.90–3.28 (m, 2 H), 3.52 (dd, 2 H, J = 2, 7 Hz), 3.78 (s, 6 H); mass spectrum, *m/e* (relative intensity) 269 (M$^+$, 54), 238 (100). Anal. Calcd for $C_{12}H_{15}NO_6$: C, 53.53; H, 5.62; N, 5.20. Found: C, 53.54; H, 5.77; N, 5.13. The following two succinimides were prepared by similar procedures. *cis,trans,cis*-*N*-Methyl-3,5-bis(methoxycarbonyl)cyclopentane-1,2-dicarboximide (**13**) was prepared from the exo isomer of 5-norbornene-2,3-dicarboxylic anhydride. For compound **13**: mp 79–80 °C; IR (CCl_4) 1790 (sh), 1740, 1708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.02 (dt, 1 H, J = 8, 14 Hz), 2.61 (dt, 1 H, J = 4, 14 Hz), 3.00 (s, 3 H), 3.18 (dd, 2 H, J = 4, 8 Hz), 3.73 (s, 6 H), 3.80 (m, 2 H); mass spectrum, *m/e* (relative intensity) 269 (M$^+$, 24), 141 (100). Anal. Calcd for $C_{12}H_{15}NO_6$: C, 53.53; H, 5.62; N, 5.20. Found: C, 53.53; H, 5.65; N, 4.96. *cis*-*N*-Methyl-2,3-bis[methoxycarbonyl)methyl]succinimide (**30**) was prepared from *N*-methyl-1,2,3,6-tetrahydrophthalimide (**68**) which could readily be obtained from methylamine and 1,2,3,6-tetrahydrophthalic anhydride. For compound **30**: mp 89–91 °C; IR (KBr) 1778 (sh), 1726, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.76 (m, 4 H), 3.02 (s, 3 H), 3.38 (m, 2 H), 3.76 (s, 6 H); mass spectrum, *m/e* (relative intensity) 257 (M$^+$, 24), 197 (100). Anal. Calcd for $C_{11}H_{15}NO_6$: C, 51.36; H, 5.88; N, 5.45. Found: C, 51.44; H, 5.82; N, 5.30.

N-Methyl-7-oxabicyclo[4.1.0]heptane-3,4-dicarboximide (**24**) was prepared by oxidation of **68** with hydrogen peroxide and benzonitrile according to the method of Carlson and Behn.[20] For compound **24**: mp 109–111 °C; IR (KBr) 1770 (sh), 1687 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.04–2.28 (m, 2 H), 2.64–2.80 (m, 4 H), 2.97 (s, 3 H), 3.14 (m, 2 H); mass spectrum, *m/e* (relative intensity) 181 (M$^+$, 46), 152 (100). Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.63; H, 6.14; N, 7.64.

N,1,2-Trimethylcyclobutane-*cis*-1,2-dicarboximide (**39**; mp 95–96 °C) was obtained by the photochemical cyclization of *N*-methylmethacrylimide.[21]

Preparation of *N*-Formyl-*N*-methyl α,β-Unsaturated Amides. All these compounds were prepared from *N*-methylformamide and α,β-unsaturated carboxylic acid chlorides. A typical run is exemplified for the preparation of **3**. To a solution of *N*-methylformamide (0.5 g, 6.9 mmol) in 25 mL of dry ether was added 1-cyclohexene-1-carbonyl chloride (1 g, 6.9 mmol). The mixture was cooled at 0 °C with magnetic stirring. Triethylamine (1 mL) was added drop by drop, and then triethylamine hydrochloride was precipitated. The reaction mixture was stirred further for 1 h. Water was added, and the solution was extracted with ether. After the mixture was washed with water and dried with sodium sulfate, the ether was removed by evaporation. *N*-Formyl-*N*-methyl-1-cyclohexene-1-carboxamide (**3**) was isolated by column chromatography on silica gel and purified by distillation; yield 0.72 g (60%). α,β-Unsaturated carboxylic acid chlorides were obtained by the reaction of acids and thionyl chloride. 1-Cyclohexene-1-carboxylic acid and 1-cyclopentene-1-carboxylic acid were prepared from cyclohexanone and cyclopentanone, respectively, by the method of Ruzicka and Brugger.[22] α-Alkyl-substituted acrylic acids corresponding to **48**, **50**, **52**, **54**, **56**, and **58** were prepared from alkyl halides and diethyl malonate by the method of Mannich and Ganz.[23] Compound **60** was prepared from 1,7,7-trimethylbicyclo[2.2.1]hept-2-ene-2-carboxylic acid which can be derived from camphor by the method of Bredt.[24] Physical data of these *N*-formyl-*N*-methyl α,β-unsaturated amides are listed in Table IV.

Irradiation of *N*-Methylcyclohexane-*cis*-1,2-dicarboximide (1). A solution of **1** (500 mg) in 25 mL of acetonitrile was deaerated with nitrogen and irradiated for 7 h. Isolation by column chromatography on silica gel gave a mixture of **1** and **4** (298 mg), *N*-methylcyclohexane-1,1-dicarboximide (**2**; 88 mg, 43%), and *N*-formyl-*N*-methyl-1-cyclohexene-1-carboxamide (**3**; 14 mg, 7%). For compound **2**: colorless crystals; mp 96–97 °C; IR (KBr) 1822, 1710, 945 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2–2.0 (m, 10 H), 2.89 (s, 3 H); mass spectrum, *m/e* (relative intensity) 167 (M$^+$, 0.7), 110 (100), 67 (56). Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.36; H, 7.82; N, 8.35. Compound **3** was identical with an authentic sample (see Table IV).

Reaction of 2 with Methylamine. To a solution of **2** (100 mg) in 20 mL of methanol was added an excess amount of gaseous methylamine. The reaction mixture was allowed to stand overnight at room temperature. After removal of solvent, *N,N'*-dimethylcyclohexane-1,1-dicarboxamide (**5**) was obtained quantitatively: white crystals; mp 168–169 °C; IR (KBr) 3330, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2–1.8 (m, 6 H), 1.8–2.2 (m, 4 H), 2.81 (d, 6 H, J = 5 Hz), 6.86 (br q, 2 H, J = 5 Hz); mass spectrum, *m/e* (relative intensity) 198 (M$^+$, 34), 143 (83), 141 (100), 140 (53). Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.33; H, 9.04; N, 14.18.

Irradiation of 2 in Methanol. A solution of **2** (200 mg) in 25 mL of acetonitrile was irradiated for 10 h. Isolation of the products by column chromatography gave methyl cyclohexanecarboxylate (**6**; 35%), methyl *N*-methylcarbamate (**7**; 35%), and 2-methoxy-3-methyl-1-oxa-3-azaspiro[4.5]decan-4-one (**8**; 60%). Compound **6** was identical with an authentic sample which was commercially available. Compound **7** was identified by comparison with an authentic sample prepared by the reaction of an excess of methanol with methyl isocyanate. The structure of **8** was determined by spectral data: colorless crystals; mp 66–68 °C; IR (KBr) 1760, 1155, 1095 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2–2.0 (m, 10 H), 2.83 (s, 3 H), 5.71 (s, 1 H); mass spectrum, *m/e* (relative intensity) 199 (M$^+$, 28), 168 (25), 109 (31), 74 (100). Anal. Calcd for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.28; H, 8.81; N, 6.89.

Irradiation of 3. A solution of **3** (423 mg) in 25 mL of acetonitrile was irradiated for 6 h. Isolation by column chroma-

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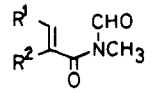
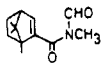
Table IV. Physical Data of *N*-Formyl-*N*-methyl α,β-Unsaturated Amides[a]



material	R^1	R^2	bp, °C (mmHg)[b]	IR, cm^{-1}	^1H NMR (in CCl_4), δ
3		$(CH_2)_4$	74-76 (0.04)	1718, 1660	1.6-1.9 (m, 4 H), 2.1-2.5 (m, 4 H), 3.15 (s, 3 H), 6.24 (m, 1 H), 9.21 (s, 1 H)[c]
45		$(CH_2)_3$	140-147 (21)	1710, 1655, 1617	1.81-2.15 (m, 2 H), 2.4-2.8 (m, 4 H), 3.07 (s, 3 H), 6.18 (m, 1 H), 9.04 (s, 1 H)
34	CH_3	CH_3	120-125 (16)	1720, 1657	1.82 (br s, 3 H), 1.90 (s, 3 H), 3.04 (s, 3 H), 5.94 (m, 1 H), 8.94 (s, 1 H)
46	H	CH_3	90-95 (20)	1728, 1660, 1632	2.04 (br s, 3 H), 3.10 (s, 3 H), 5.26 (br s, 1 H), 5.55 (br s, 1 H), 9.08 (s, 1 H)
48	H	*n*-C_3H_7	76-80 (3)	1727, 1665, 1630	0.98 (t, 3 H, J = 7 Hz), 1.24-1.70 (m, 2 H), 2.38 (t, 2 H, J = 7 Hz), 3.13 (s, 3 H), 5.35 (br s, 1 H), 5.59 (br s, 1 H), 9.18 (s, 1 H)
50	H	*i*-C_3H_7	65-66 (2)	1730, 1668, 1630	1.11 (d, 6 H, J = 7 Hz), 2.76 (sep, 1 H, J = 7 Hz), 3.04 (s, 3 H), 5.19 (br s, 1 H), 5.44 (br s, 1 H), 9.00 (s, 1 H)
52	H	*n*-C_4H_9	75-78 (2)	1727, 1665, 1630	0.95 (t, 3 H, J = 6 Hz), 1.2-1.8 (m, 6 H), 2.41 (t, 2 H, J = 7 Hz), 3.13 (s, 3 H), 5.36 (br s, 1 H), 5.62 (br s, 1 H), 9.19 (s, 1 H)
54	H	*i*-C_4H_9	74-76 (2)	1730, 1660, 1632	0.95 (d, 6 H, J = 7 Hz), 1.76 (m, 1 H), 2.25 (d, 2 H, J = 7 Hz), 3.09 (s, 3 H), 5.35 (br s, 1 H), 5.53 (br s, 1 H), 9.09 (s, 1 H)
56	H	*n*-C_6H_{13}	105-107 (2)	1730, 1665, 1632	0.90 (t, 3 H, J = 6 Hz), 1.1-1.6 (m, 8 H), 2.38 (t, 2 H, J = 7 Hz), 3.09 (s, 3 H), 5.27 (br s, 1 H), 5.50 (br s, 1 H), 9.05 (s, 1 H)
58	H	c-Hx	108-109 (3)	1730, 1670, 1630	1.0-1.4 (m, 4 H), 1.4-2.0 (m, 6 H), 2.24-2.52 (br s, 1 H), 9.00 (s, 1 H)
60			110-113 (2)	1717, 1658	0.85 (s, 3 H), 0.89 (s, 3 H), 1.13 (s, 3 H), 1.1-1.4 (m, 2 H), 1.6-2.1 (m, 2 H), 2.73 (d, 1 H, J = 3 Hz), 3.06 (s, 3 H), 6.11 (br s, 1 H), 9.07 (s, 1 H)

[a] These materials gave satisfactory elemental analyses. [b] Kugelrohr. [c] In $CDCl_3$.

tography afforded 120 mg of **3** and 258 mg of **2** (85%).

LC Analysis of the Time-Dependent Variation in the Yields of the Products in the Photochemical Reaction of 1. A solution of **1** (200 mg) in 20 mL of acetonitrile was irradiated at 4 °C in the usual manner. A 1-mL sample of the reacting solution was taken out at a determined interval, and an appropriate amount of internal standard (*N*-methylnorbornane-2,3-dicarboximide) was added. The conversion of **1** and the yields of **2**–**4**, were determined by high-performance liquid chromatography.

Quantum Yield Measurement. Quantum yields were determined as follows. A quartz cell containing 4 mL of acetonitrile solution was irradiated with an apparatus with fixed geometry in which the light from a 120-W, low-pressure Hg lamp was used. The photon numbers emitted in a definite time from the light source were determined by the method of Hachard and Parker,[25] using potassium ferrioxalate as an actinometer. The amount of **1** consumed and those of the products were determined by LC. The results were shown in eq 1.

Irradiation of *all-cis*-*N*-Methyl-3,5-bis(methoxycarbonyl)cyclopentane-1,2-dicarboximide (11). A solution of **11** (100 mg) in 25 mL of acetonitrile was irradiated for 1 h. Isolation by column chromatography afforded 50 mg of **11** and 25 mg (50%) of *N*-methyl-2,4-bis(methoxycarbonyl)cyclopentane-1,1-dicarboximide (**12**): colorless crystals; mp 99–100 °C; IR (KBr) 1840, 1730, 963 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2–2.5 (m, 4 H), 2.95 (m, 1 H), 2.95 (s, 3 H), 3.25 (dd, 1 H, J = 8, 13 Hz), 3.72 (s, 6 H); mass spectrum, m/e (relative intensity) 238 (16), 222 (22), 152 (100), 125 (31). Anal. Calcd for $C_{12}H_{15}NO_6$: C, 53.53; H, 5.62; N, 5.20. Found: C, 53.74; H, 5.75; N, 5.08. The molecular weight of **12** was measured with a Hitachi molecular weight apparatus, Model 115. Benzene was used as a solvent, and solutions of **11** in known concentrations were used to make a calibration curve.

Irradiation of **13** (319 mg) in 25 mL of acetonitrile for 4 h gave **12** in a yield of 58%. The product was identical with that from **11**.

Irradiation of *N*-Methylcyclopentane-1,2-dicarboximide (14). A solution of **14** (304 mg) in 20 mL of acetonitrile was irradiated for 8 h. Isolation by column chromatography afforded 150 mg of **14** and 80 mg (51%) of *N*-methylcyclopentane-1,1-dicarboximide (**15**): colorless crystals; mp 38–42 °C; IR (KBr) 1840, 1710, 955 cm^{-1}; ^1H NMR (CCl_4) δ 1.8–2.2 (m, 8 H), 2.87 (s, 3 H); mass spectrum, m/e (relative intensity) 153 (M^+, 0.5), 96 (100), 68 (70). Anal. Calcd for $C_8H_{11}NO_2$: C, 62.72; H, 7.24; N, 9.14. Found: C, 62.86; H, 7.40; N, 9.10.

Irradiation of *N*-Methylnorbornane-2,3-dicarboximide (16). A solution of **16** (332 mg) in 150 mL of acetonitrile was irradiated for 3 h. Isolation by column chromatography afforded 185 mg of **16** and 53 mg of (36%) of *N*-methylnorbornane-2,2-dicarboximide (**17**): colorless oil; IR (CCl_4) 1733, 945 cm^{-1}; ^1H NMR (CCl_4) δ 1.1–2.1 (m, 8 H), 2.38 (m, 1 H), 2.59 (m, 1 H), 2.85 (s, 3 H); mass spectrum, m/e (relative intensity) 122 (100), 93 (72). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.31; H, 7.51; N, 7.73.

Irradiation of *N*-Methyl-7-oxabicyclo[2.2.1]heptane-2,3-dicarboximide (18). A solution of **18** (200 mg) in 100 mL of acetonitrile was irradiated with an immerged 60-W, low-pressure Hg lamp for 1 h. Isolation by column chromatography afforded 56 mg of **18** and 40 mg (28%) of *N*-methyl-7-oxabicyclo[2.2.1]-heptane-2,2-dicarboximide (**19**): white crystals; mp 63–64 °C; IR ($CHCl_3$) 1820, 1730, 947 cm^{-1}; ^1H NMR (CCl_4) δ 1.56–1.94 (m, 4 H), 2.05–2.32 (m, 2 H), 2.98 (s, 3 H), 4.63–4.79 (m, 2 H); mass spectrum, m/e (relative intensity) 181 (M^+, 18), 124 (100), 96 (61), 95 (41). Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.88; H, 6.20; N, 7.68.

Irradiation of *N*-Methylbicyclo[2.2.2]octane-2,3-dicarboximide (20). A solution of **20** (439 mg) in 25 mL of acetonitrile was irradiated for 9 h. Isolation by column chromatography afforded 166 mg of **20** and 118 mg (43%) of *N*-methylbicyclo[2.2.2]octane-2,2-dicarboximide (**21**): white crystals; mp 81–82 °C; IR (KBr) 1720, 950 cm^{-1}; ^1H NMR (CCl_4) δ 1.2–2.2 (m, 12 H), 2.86 (s, 3 H); mass spectrum, m/e (relative intensity)

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193 (M^+, 0.2), 136 (100). Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.14; H, 7.91; N, 7.11.

Irradiation of *N*-Methyltricyclo[3.2.2.0^{2,4}]nonane-6,7-dicarboximide (22). A solution of **22** (500 mg) in 25 mL of acetonitrile was irradiated for 10 h. Isolation by column chromatography afforded 240 mg of **22** and 102 mg (39%) of *N*-methyltricyclo[3.2.2.0^{2,4}]nonane-6,6-dicarboximide (**23**): white crystals; mp 46–47 °C; IR (CCl_4) 1817, 1721, 945 cm^{-1}; ^1H NMR (CCl_4) δ 0.28–0.64 (m, 2 H), 0.8–2.3 (m, 10 H), 2.80 (s, 3 H); mass spectrum, *m/e* (relative intensity) 205 (M^+, 0.5), 148 (100), 120 (42), 105 (23), 92 (27). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.27; H, 7.38; N, 6.79.

Irradiation of *N*-Methyl-7-oxabicyclo[4.1.0]heptane-3,4-dicarboximide (24). A solution of **24** (450 mg) in 25 mL of acetonitrile was irradiated for 7 h. Isolation by column chromatography afforded 252 mg of **24** and 69 mg (35%) of *N*-methyl-7-oxabicyclo[4.1.0]heptane-3,3-dicarboximide (**25**): white crystals; mp 106–108 °C; IR (KBr) 1712, 963 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54–2.26 (m, 6 H), 2.90 (s, 3 H), 3.26 (m, 2 H); mass spectrum, *m/e* (relative intensity) 181 (M^+, 17), 141 (42), 138 (54), 124 (100), 96 (49), 95 (81), 80 (52). Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.56; H, 6.19; N, 7.69.

Irradiation of *N*,1-Dimethylcyclohexane-1,2-dicarboximide (26). A solution of **26** (462 mg) in 25 mL of acetonitrile was irradiated for 12 h. Isolation by column chromatography afforded 205 mg of **26**, 67 mg (26%) of *N*,2-dimethylcyclohexane-1,1-dicarboximide (**27**), and 70 mg (27%) of *N*,2-dimethyl-*N*-formyl-1-cyclohexene-1-carboxamide (**36**). For compound **27**: white crystals; mp 58–59 °C; IR (KBr) 1720, 950 cm^{-1}; ^1H NMR (CCl_4) δ 0.98 (d, 3 H, J = 6 Hz), 1.1–2.1 (m, 9 H), 2.88 (s, 3 H); mass spectrum, *m/e* (relative intensity) 125 (11), 124 (100), 109 (39). Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.22; H, 8.39; N, 7.62. For compound **36**: colorless oil; IR (CCl_4) 1727, 1665 cm^{-1}; ^1H NMR (CCl_4) δ 1.62 (br s, 3 H), 1.6–1.9 (m, 4 H), 1.9–2.3 (m, 4 H), 3.08 (s, 3 H), 8.98 (s, 1 H); mass spectrum, *m/e* (relative intensity) 181 (M^+, 32), 123 (28), 122 (100), 96 (35), 95 (25), 94 (21), 79 (27). Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.10; H, 8.22; N, 7.50.

Irradiation of *N*-Ethylcyclohexane-1,2-dicarboximide (28). A solution of **28** (500 mg) in 25 mL of acetonitrile was irradiated for 10 h. Isolation by column chromatography afforded 108 mg of **28** and 80 mg (22%) of *N*-ethylcyclohexane-1,1-dicarboximide (**29**): colorless crystals; mp 62–65 °C; IR (KBr) 1712, 964 cm^{-1}; ^1H NMR (CCl_4) δ 1.26 (t, 3 H, J = 7 Hz), 1.3–1.9 (m, 10 H), 3.24 (q, 2 H, J = 7 Hz); mass spectrum, *m/e* (relative intensity) 181 (M^+, 0.5), 110 (100), 82 (20). Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.43; H, 8.42; N, 7.65.

Irradiation of *cis*-*N*-Methyl-2,3-bis(methoxycarbonylmethyl)succinimide (30). A solution of **30** (352 mg) in 25 mL of acetonitrile was irradiated for 6 h. Isolation by column chromatography afforded 250 mg of **30** and 26 mg (25%) of 3-[(methoxycarbonyl)ethyl]-3-[(methoxycarbonyl)methyl]-1-methylazetidine-2,4-dione (**31**): colorless oil; IR ($CHCl_3$) 1734, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12 (t, 2 H, J = 8 Hz), 2.42 (t, 2 H, J = 8 Hz), 2.74 (s, 2 H), 2.94 (s, 3 H), 3.67 (s, 6 H); mass spectrum, *m/e* (relative intensity) 226 (15), 200 (31), 168 (100), 140 (31), 126 (61), 113 (38), 112 (31). Anal. Calcd for $C_{11}H_{15}NO_6$: C, 51.36; H, 5.88; N, 5.45. Found: C, 51.34; H, 5.93; N, 5.22.

Irradiation of *N*,2,3-Trimethylsuccinimide (32). A solution of **32** (615 mg) in 50 mL of acetonitrile was irradiated for 10 h. Isolation by column chromatography afforded 302 mg of **32**, 27 mg (9%) of 1,3-dimethyl-3-ethylazetidine-2,4-dione (**33**), and 44 mg (14%) of a mixture of *trans*-*N*-formyl-*N*,2,3-trimethylacrylamide (**34**) and cis isomer **35**: colorless oil; IR (neat) 1805, 1720, 945 cm^{-1}; ^1H NMR (CCl_4) δ 0.98 (t, 3 H, J = 8 Hz), 1.30 (s, 3 H), 1.68 (q, 2 H, J = 8 Hz), 2.86 (s, 3 H); mass spectrum, *m/e* (relative intensity) 84 (100), 69 (96). Anal. Calcd for $C_7H_{11}NO_2$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.38; H, 7.94; N, 9.96.

Irradiation of *N*-Methyl-1-phenylcyclohexane-1,2-dicarboximide (37). A solution of **37** (200 mg) in 50 mL of acetonitrile was irradiated for 49 h. After column chromatography and recrystallization from petroleum ether, 55 mg (28%) of *N*-formyl-*N*-methyl-2-phenyl-1-cyclohexene-1-carboxamide (**38**) was obtained: colorless crystals; mp 90–91 °C; IR (KBr) 1711, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–2.0 (m, 4 H), 2.2–2.7 (m, 4 H), 2.77 (s, 3 H), 7.0–7.4 (m, 5 H), 8.89 (s, 1 H); mass spectrum, *m/e* (relative intensity) 243 (M^+, 17), 185 (22), 184 (100), 156 (23). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.05; H, 7.20; N, 5.80. When a solution of **37** was irradiated for 10 h, **38** was produced in a yield of 70% [determined by ^1H NMR spectroscopy from the relative intensities of the NMe proton signal of **38** and OMe proton signal of 1,4-dimethoxybenzene (internal standard)].

Irradiation of *N*,1,2-Trimethylcyclobutane-1,2-dicarboximide (39). A solution of **39** (211 mg) in 100 mL of acetonitrile was irradiated with an immerged 60-W, low-pressure Hg lamp for 6 h. Isolation by column chromatography afforded 103 mg (59%) of *N*,1,2-trimethyl-2-cyclobutene-1-carboxamide (**41**): colorless oil; IR ($CHCl_3$) 3445, 1648 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (s, 3 H), 1.78 (br s, 3 H), 2.30 (d, 1 H, J = 13 Hz), 2.66 (d, 1 H, J = 13 Hz), 2.81 (d, 3 H, J = 5 Hz), 5.88 (m, 1 H), 6.13 (br s, 1 H); mass spectrum, *m/e* (relative intensity) 139 (M^+, 60), 124 (39), 96 (100), 81 (71); high-resolution mass spectrum, calcd for $C_8H_{13}NO$ *m/e* 139.099 708, found *m/e* 139.099 ± 0.005.

General Procedures for Photochemical Reaction of *N*-Formyl-*N*-methyl α,β-Unsaturated Amides. Solutions of *N*-formyl-*N*-methylα,β-unsaturated amides were deaerated with nitrogen and irradiated in a quartz tube with a 120-W, low-pressure Hg lamp for suitable times. After removal of solvent the products were separated by column chromatography on silica gel. The results were summarized in Table III.

Physical Data of Azetidine-2,4-diones Derived from Photochemical Reaction of *N*-Formyl-*N*-methyl α,β-Unsaturated Amides. 1,3,3-Trimethylazetidine-2,4-dione (47): colorless crystals; mp 65–66 °C; IR (KBr) 1715, 960 cm^{-1}; ^1H NMR (CCl_4) δ 1.35 (s, 6 H), 2.88 (s, 3 H); mass spectrum, *m/e* (relative intensity) 127 (M^+, 0.8), 70 (100). Anal. Calcd for $C_6H_9NO_2$: C, 56.65; H, 7.14; N, 11.02. Found: C, 56.55; H, 7.08; N, 11.00.

1,3-Dimethyl-3-propylazetidine-2,4-dione (49): colorless oil; IR (CCl_4) 1738, 956 cm^{-1}; ^1H NMR (CCl_4) δ 0.96 (t, 3 H, J = 7 Hz), 1.32 (s, 3 H), 1.36–1.72 (m, 4 H), 2.90 (s, 3 H); mass spectrum, *m/e* (relative intensity) 155 (M^+, 2), 98 (64), 69 (100). Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.66; H, 8.52; N, 8.97.

1,3-Dimethyl-3-(2-propyl)azetidine-2,4-dione (51): colorless oil; IR (CCl_4) 1737, 957 cm^{-1}; ^1H NMR (CCl_4) δ 1.04 (d, 6 H, J = 7 Hz), 1.32 (s, 3 H), 1.96 (sep, 1 H, J = 7 Hz), 2.90 (s, 3 H); mass spectrum, *m/e* (relative intensity) 155 (M^+, 4), 98 (86), 83 (100). Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.72; H, 8.56; N, 8.96.

3-Butyl-1,3-dimethylazetidine-2,4-dione (53): colorless oil; IR (CCl_4) 1738, 957 cm^{-1}; ^1H NMR (CCl_4) δ 0.93 (t, 3 H, J = 7 Hz), 1.32 (s, 3 H), 1.34–1.70 (m, 6 H), 2.90 (s, 3 H); mass spectrum, *m/e* (relative intensity) 169 (M^+, 3), 112 (100), 84 (24). Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.85; H, 9.03; N, 8.33. The yield of **53** was determined by ^1H NMR spectroscopy from the relative intensities of the NMe proton signal of **53** and the OMe proton signal of 1,4-dimethoxybenzene (internal standard).

1,3-Dimethyl-3-(2-methylpropyl)azetidine-2,4-dione (55): colorless oil; IR (CCl_4) 1735, 953 cm^{-1}; ^1H NMR (CCl_4) δ 0.93 (d, 6 H, J = 7 Hz), 1.29 (s, 3 H), 1.53 (d, 2 H, J = 6 Hz), 1.64 (m, 1 H), 2.85 (s, 3 H); mass spectrum, *m/e* (relative intensity) 169 (M^+, 2), 112 (66), 69 (100). Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.68; H, 8.95; N, 8.40.

1,3-Dimethyl-3-hexylazetidine-2,4-dione (57): white crystals; mp 37–38 °C; IR (CCl_4) 1737, 953 cm^{-1}; ^1H NMR (CCl_4) δ 0.87 (t, 3 H, J = 7 Hz), 1.30 (s, 3 H), 1.1–1.7 (m, 10 H), 2.85 (s, 3 H); mass spectrum, *m/e* (relative intensity) 140 (49), 112 (100), 98 (38), 69 (71). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.70; H, 9.68; N, 6.87.

3-Cyclohexyl-1,3-dimethylazetidine-2,4-dione (59): white crystals; mp 51–52 °C; IR (CCl_4) 1735, 958 cm^{-1}; ^1H NMR (CCl_4) δ 1.0–2.0 (m, 11 H), 1.31 (s, 3 H), 2.85 (s, 3 H); mass spectrum, *m/e* (relative intensity) 138 (100), 95 (75), 81 (24), 80 (53). Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.85; H, 8.86; N, 7.09.

***N*,1,7,7-Tetramethylbicyclo[2.2.1]heptane-2,2-dicarboximide (61):** white crystals; mp 65–66 °C; IR (CCl_4) 1830, 1735, 957 cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (s, 6 H), 1.80 (s, 3 H), 1.2–2.2 (m, 7 H), 2.88 (s, 3 H); mass spectrum, *m/e* (relative intensity)

221 (M^+, 1), 164 (100), 149 (16), 141 (18), 121 (36). Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.27; H, 8.44; N, 6.09.

Irradiation of *N*-Formyl-*N*-methylcrotonamide (62). A solution of **62** (406 mg) in 25 mL of acetonitrile was irradiated for 6 h. After the usual workup it was found that the products consisted of mixtures both of **62** and cis isomer **63** (195 mg, **62/63** ratio of 65/35) and of *N*-methylcrotonamide **64** and cis isomer **65** (63 mg, **64/65** ratio of 60/40 estimated by GLC). Compound **64** was identical with an authentic sample prepared from crotonyl chloride and methylamine.

Registry No. **1**, 64090-28-4; **2**, 70264-96-9; **3**, 71099-10-0; **4**, 70265-06-4; **5**, 71098-99-2; **6**, 4630-82-4; **7**, 6642-30-4; **8**, 71099-00-8; **11**, 75598-53-7; **12**, 71099-06-4; **13**, 75598-54-8; **14**, 71099-01-9; **15**, 71099-04-2; **16**, 75598-55-9; **17**, 70265-03-1; **18**, 7741-81-3; **19**, 75558-44-0; **20**, 75558-45-1; **21**, 74651-58-4; **22**, 75558-46-2; **23**, 74651-59-5; **24**, 75558-47-3; **25**, 75558-48-4; **26**, 71131-99-2; **27**, 71099-05-3; **28**, 71099-09-7; **29**, 70264-97-0; **30**, 18853-50-4; **31**, 71099-07-5; **32**, 71099-03-1; **33**, 71099-08-6; **34**, 75558-49-5; **35**, 75558-50-8; **36**, 75558-51-9; **37**, 75558-52-0; **38**, 75558-53-1; **39**, 75558-54-2; **40**, 75558-55-3; **41**, 75558-56-4; **42**, 1121-07-9; **43**, 26491-47-4; **44**, 75578-66-4; **45**, 74255-23-5; **46**, 74255-24-6; **47**, 74255-30-4; **48**, 74255-26-8; **49**, 74255-31-5; **50**, 74255-27-9; **51**, 74255-32-6; **52**, 74255-28-0; **53**, 74255-33-7; **54**, 75558-57-5; **55**, 75558-58-6; **56**, 75558-59-7; **57**, 75558-60-0; **58**, 74255-29-1; **59**, 74255-34-8; **60**, 75578-67-5; **61**, 75558-61-1; **62**, 75558-62-2; **63**, 75558-63-3; **64**, 1189-03-3; **65**, 70265-04-2.

Photoinitiated Radical-Forming Reactions of 2-Quinolinecarbonitrile At 77 and 331 K

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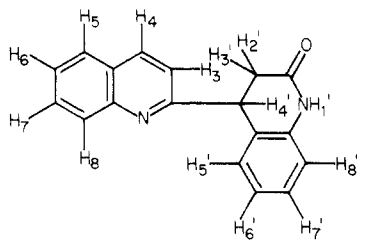
The photoinitiated dimerization of 2-quinolinecarbonitrile (1) in HCl-acidified 2-propanol/water (4:1) has been studied at 77 and 331 K at 250, 300 and 350 nm in unsensitized and benzophenone- and biphenyl-sensitized reactions. One principal product, a dimer lactam (5), is formed at all wavelengths through a triplet state of 1. ESR spectra taken in ethanol at 77 K show a signal for ethyl radical which is formed by a biphotonic process with 1 in acid solution. A mechanism is proposed for the reaction at 331 K which involves an electron transfer from 2-propanol to an upper triplet state of 1.

The photochemistry of 2-quinolinecarbonitrile (1) in HCl-acidified and unacidified alcohols has been the subject of a number of investigations.[3] These reactions generally lead to hydroxyalkylation of the 2-position with the replacement of the cyano group.[4] A second product, a triazapentaphene, is also isolated from reactions run in neutral alcohol. The benzophenone-photosensitized reaction of 1 in ethanol has been reported to yield only the pentaphene in a $T_1(\pi\pi^*)$ reaction.[5]

A few years ago we reported that when a solution of 4-pyridinecarbonitrile (2) and benzophenone in 1 M sulfuric acid in aqueous 2-propanol was irradiated at 350 nm, an electron-transfer–substitution reaction occurred, resulting in the formation of diphenyl(4-pyridyl)carbinol (3) and 4-benzhydrylpyridine (4) as major products.[6] We were surprised to find that when 2-quinolinecarbonitrile was used in this reaction, strikingly different results were obtained from those previously reported with 2-propanol alone.[4]

The reaction mixtures were prepared as described above for 2 by using hydrochloric acid instead of sulfuric acid and a ratio of alcohol to water of 4:1. The mixtures were deaerated by three successive freeze–vacuum–thaw cycles and the irradiations carried out under nitrogen in a Model RPR-100 Rayonet photochemical reactor at 350 nm. One major product (mp 248–249 dec) was isolated along with starting material.[7] The product was assigned structure 5 on the basis of the following data: IR (Nujol) 3030 (NH),



5

1680 (C=O, lactam), 1591, 831, 773, 747 cm^{-1}, no cyanide band is present; NMR (100 MHz, Me_2SO) δ 10.12 (s, 1 NH_1'), 8.34 (d, 1, H_8, J = 8.4 Hz), 7.97 (d, 1, H_4, J = 8.4 Hz), 7.72 (m, 3, H_5, H_6, H_7), 7.46 (d, 1, H_3, J = 8.4 Hz), 7.17 (d, 2, H_6', H_7', J = 7.0 Hz), 6.96 (d, 2, H_5', H_8', J = 7.0 Hz).

Decoupling experiments ($CDCl_3$) confirmed that H_2', H_3', and H_4' comprise an ABX system of which the AB part appears as a pair of doublets centered at δ 2.92 and 3.11 ($J_{H_2',H_3'}$ = 16 Hz) further split into four doublets by coupling with H_4' [$J_{H_2'H_4'}$(cis) = 6 Hz, $J_{H_3'H_4'}$(trans) = 7 Hz].

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(7) In reactions in which a small amount of 2-quinolinecarbonitrile was used (150 mg) with a relatively long irradiation time, a low yield of a second product was formed which eluted from a silica gel column with chloroform and melted at 193.5–195.5 °C. An infrared spectrum showed an OH peak but no CN peak, while the NMR spectrum showed only C–CH_3 and aromatic C–H.

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