

Photochemical Reactions of *N*-Methyl-1,2-naphthalenedicarboximide with Alkenes. Preferential Naphthazepinedione Formation

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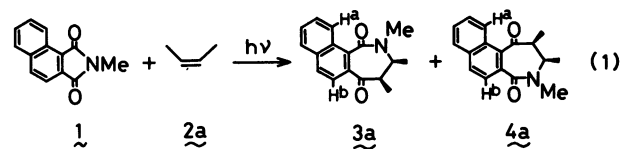
Irradiation of benzene solutions of *N*-methyl-1,2-naphthalenedicarboximide (**1**) in the presence of alkenes (**2a,b,d—i**) gave two regio-isomers of naphthazepinediones (**3a,b,d—i** and **4a,b,d—i**). Stereospecificity of the naphthazepinedione formation was observed in the reaction with *cis*- and *trans*-2-butene (**2a** and **2b**). Naphthazepinediones (**3j** and **4j**) produced by the irradiation of **1** with ethyl vinyl ether (**2j**) underwent secondary photoreactions to give **7** and **8**, respectively. On the other hand, irradiation of **1** with 2,3-dimethyl-2-butene (**2k**) resulted in the formation of oxetanes (**13a,b**) and 1:1-adducts of **1** and **2k** at the carbonyl groups of **1** (**14** and **15a,b**). Irradiation of **1** with *cis*-stilbene (**2l**) afforded oxetanes (**22a,b**) and fragmentation products of oxetanes (**23a,b**, and **24**). Stern-Volmer slopes ($k_q\tau$) obtained from quenching of fluorescence of **1** by alkenes (**2a—e,k**) correlated to some extent with relative rates for disappearance of **1** in the reaction. Preferential formation of the naphthazepinedione was rationalized by the nature of the excited singlet state of **1** compared with those of other *N*-methylarenedicarboximides.

In recent years, photochemistry of imides has been the subject of intensive investigations.¹⁾ Concerning the reactions with alkenes, there are remarkable differences between the photoreactions of alicyclic imides and arenedicarboximides (especially phthalimides). Aliphatic imides undergo effective intra-²⁾ or inter-molecular oxetane formation,³⁾ illustrating its normal $n\pi^*$ carbonyl photoreactivity. In contrast, phthalimides undergo alcohol-incorporated C—C coupling at the carbonyl carbon of phthalimides (electron transfer reaction),⁴⁾ insertion of alkene into C(=O)—N bond of the imide moiety,⁵⁾ and only in a few cases oxetane formation.⁶⁾ As there has been only a little information on the effects of arene structures in the photochemistry of arenedicarboximides,⁷⁾ our studies have been focused on the effects of extended π -conjugation systems. Recently we reported the photoreactions of three types of *N*-methyl-1,2-naphthalenedicarboximides with alkenes in benzene, in which the arene structure played a crucial role in determining the reaction pathways.⁸⁾ The predominant reactions of *N*-methyl-1,8- and 2,3-naphthalenedicarboximides with alkenes were cycloaddition to the aromatic C=C bond (cyclobutane formation) and oxetane formation, respectively. This paper describes the details of the photoreactions of *N*-methyl-1,2-naphthalenedicarboximide (**1**) with a variety of alkenes in benzene. In contrast to other naphthalenedicarboximides, the predominant reaction of **1** is found to be insertion of the alkene into C(=O)—N bond of the imide moiety (naphthazepinedione formation) accompanied, in some cases, by other types of reactions depending on the structure of the alkene.

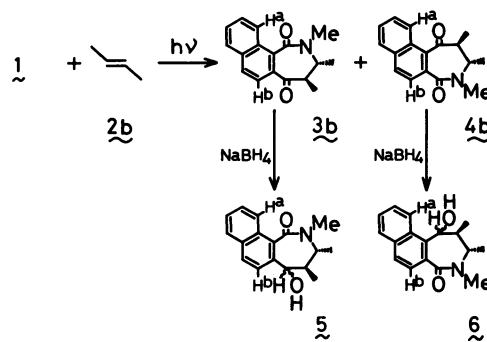
Results and Discussion

Naphthazepinedione Formation. The inser-

tion of alkene into the C(=O)—N bond of **1**, naphthazepinedione formation, was a most typical reaction observed in the photochemistry of **1** and alkenes in benzene. For example, irradiation of a benzene solution of **1** (10 mM, 1 M=1 mol dm⁻³) and *cis*-2-butene (**2a**) (100 mM) by a light of >320 nm (aq CuSO₄ filter) gave two regio-isomers of naphthazepinedione (**3a** and **4a**) (Eq. 1). The two isomers



were readily separated by column chromatography on silica gel to give 45% of **3a** and 29% of **4a**. Irradiation of **1** with *trans*-2-butene (**2b**) also gave **3b** (46%) and **4b** (33%) (Scheme 1). Other examples of



Scheme 1.

photoreactions of **1** and alkenes (**2c—i**) are shown in Table 1. The results indicate that the naphthazepinedione formation is characteristic of the reaction with ethylenes substituted by two or three alkyl groups and with some ethylenes substituted by

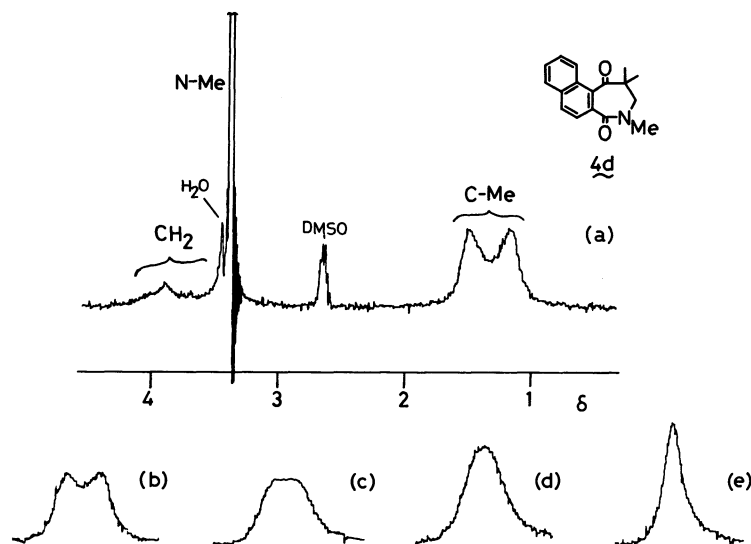


Fig. 1. ^1H NMR (100MHz) spectra of **4d** in CD_3SOCD_3 . Temperature (calibrated by the spectra of 1,3-propanediol). a): Ambient temperature, b): 32.5 $^\circ\text{C}$, c): 34.0 $^\circ\text{C}$, d): 37.5 $^\circ\text{C}$, e): 43.5 $^\circ\text{C}$.

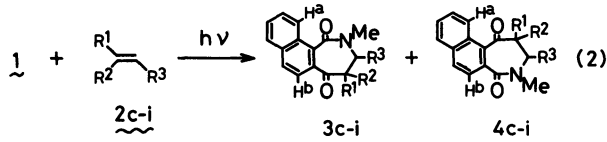


Table 1. Yields of Naphthazepinediones (**3c-i** and **4c-i**) from Photoreactions of **1** and Alkenes (**2c-i**) in Benzene^{a)}

R ¹	R ²	R ³	2	3	Yield ^{b)} /%	4	Yield ^{b)} /%
<i>n</i> -C ₄ H ₉ -	H-	H-	2c	3c	0	4c	0
Me-	Me-	H-	2d	3d	53	4d	46
Me-	Me-	Me-	2e	3e	46	4e	31
H-	-(CH ₂) ₃ -		2f	3f	40	4f	28
H-			2g	3g	40	4g	46
Ph-	H-	H-	2h	3h	54	4h	21
Ph-	Ph-	H-	2i	3i	41	4i	38

a) Reaction conditions: [**1**]=10 mM, [**2c-j**]=100 mM. b) Yields were based on consumed **1** (conversion: >70%).

phenyl groups. No reaction was observed in the photolysis of **1** with 1-hexene (**2c**), an ethylene substituted by one alkyl group.

The structures of the naphthazepinediones, including the position of the alkyl substituent of the azepine ring, were supported by the spectral resemblance to the benzo analogues obtained by the photoreactions of *N*-methylphthalimide with the alkenes.⁵⁾ ^1H NMR spectra of some naphthaze-

pinediones show coalesced signals. As the most typical example the ^1H NMR spectra of **4d** are shown in Fig. 1. Although signals of *N*-methyl and aromatic protons are sharp, signals of two *C*-methyl and methylene protons are broad at ambient temperature. The broad doublet signals of the two *C*-methyl protons were coalesced at 34.0 $^\circ\text{C}$ [(c) in Fig. 1] and changed to a more sharp singlet at higher temperatures [(d,e)]. The spectral changes probably arise from flipping of the azepine ring.

The regiochemistry of the naphthazepinediones shown in the structural formula are deduced from the following three observations: ^1H NMR behavior of H^a and H^b in addition to the spectral features of the reduction products. First, the H^a signals (double doublets) of **4a,b,d-i** showed low field shift ($\delta=8.38\text{--}8.55$) relative to those of **3a,b,d-i** ($\delta\approx 8$). This fact suggests that the H^a is close to the ketone carbonyl groups, in accord with the observations that the ketone carbonyl group exerts a stronger deshielding effect on the peri-hydrogens than the lactam carbonyl group.^{5b)} Second, the H^b signals (doublet) of **4a,b,d-i** were observed at slightly higher fields compared with those of **3a,b,d-i**. Third, reduction of **3b** and **4b** with sodium borohydride gave **5** and **6**, respectively (Scheme 1). The H^a signal of **5** was considerably shifted to a lower field ($\delta=9.10$) compared with that of **6** ($\delta=8.25$), probably due to the deshielding effect by the lactam carbonyl group remained.

The yields of the regio-isomers (**3a,b,d-i**) are generally higher than those of the other isomers (**4a,b,d-i**) except for the reaction of **1** with **2g**. Attack of alkene to the less hindered C(=O)-N bond of **1** seems to predominate over that to the other

C(=O)-N bond. In the irradiation of **1** and **2e** the ratio of the yields of the products (**3e:4e**) remained almost constant over the concentration region of 50 mM to 1 M of **2e**. The result may indicate that the two regio-isomers arise from the same excited state of **1**, since in the photoreactions of phthalimides and alkenes a marked concentration dependency on the ratio of the yields of products is reported when the products are generated from the distinct excited states.^{6c,d}

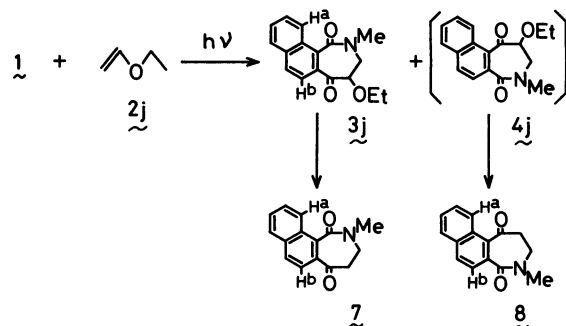
An important characteristic of the naphthazepinedione formation is stereochemical course of the reactions. Irradiation of **1** in the presence of **2a** and **2b** gave mixtures of **3a+4a** and **3b+4b**, respectively (Eq. 1 and Scheme 1). The facts that no detectable amounts of cis-trans isomerized products are observed in the irradiation of **1** with **2a** and **2b** obviously indicate the stereospecific formation of the naphthazepinedione, and suggest that the reaction occurs directly from the singlet excited state of **1**.

The stereochemistry of the products could be assigned by comparison of the coupling constants of the two methine hydrogens of the azepine ring with those of corresponding benzazepinediones, which were reported to be $J=2.3$ Hz for the cis-isomer and $J=10.1$ Hz for the trans-isomer.^{5b} The products (**3a**, **3b**, and **4b**) had the coupling constants of $J=3.2$, 11.0, and 11.6 Hz, respectively, although the coupling constant of **4a** could not be determined. These coupling constants suggested the cis-stereochemistry for **3a** and trans-stereochemistry for **3b** and **4b** as shown in Scheme 1. The stereochemistry of the products corresponds to that of the alkenes (**2a**, **b**) used.

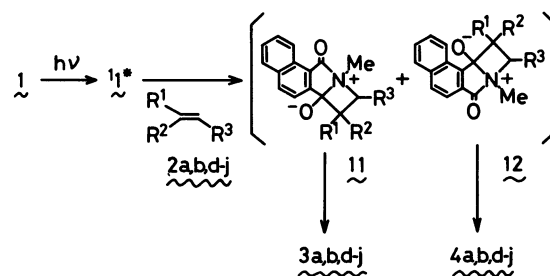
In the inter-^{5c,h} and intramolecular^{5b} photoreactions of phthalimides and alkenes, the stereospecificity of the benzazepinedione formation at the early stage of the photoreaction was already reported, but concomitant cis-trans isomerization of alkenes always occurred to give non-stereospecific mixtures of the products at a prolonged irradiation. No such cis-trans isomerization was observed in the photo reactions of **1** with **2a** and **2b**.

The mechanism of the cis-trans isomerization process in the reactions of phthalimides is not fully clarified.^{5b} However, the isomerization may arise via a triplet biradical, an intermediate of the oxetane formation from the triplet excited state of **1**,⁹ because the trans/cis ratio of 2-butene at the photosteady state is 4/1^{5b} and oxetane formation has been known to occur from the triplet excited state of phthalimides.^{6c,d} The fact that no isomerization is observed in the reaction of **1** seems to show a small contribution of the triplet excited state of **1** to the reaction of **1** with the alkenes.

Ethyl vinyl ether (**2j**) also reacted with excited **1** to give naphthazepinediones, but secondary photore-

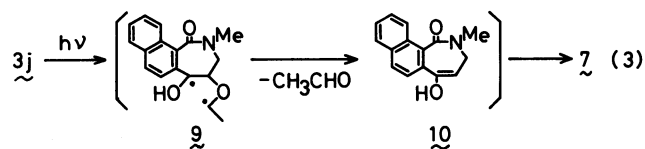


Scheme 2.



Scheme 3.

actions were observed at the same time. Prolonged irradiation of **1** and **2j** in benzene gave **7** (43%) and **8** (26%) which however were not the primary photo-products (Scheme 2). One of the primary products (**3j**) was isolated by the photoreaction of shorter irradiation-time. Further irradiation of **3j** in benzene quantitatively gave **7** probably through intramolecular γ -hydrogen abstraction (**3j**→**9**), followed by elimination of acetaldehyde (**9**→**10**), and tautomerization of **10** (**10**→**7**) (Eq. 3). This type of reaction series



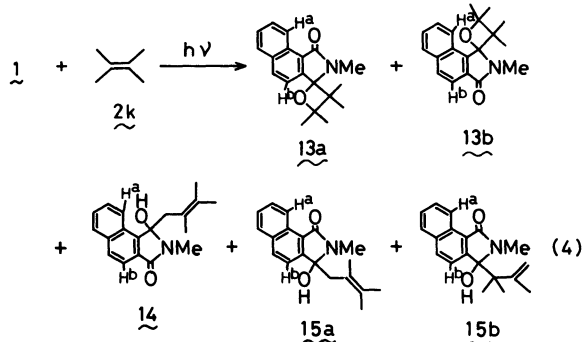
is familiar in photoreactions of benzazepinediones.^{1,6a}

The naphthazepinedione formation may be rationalized by a mechanism (Scheme 3) similar to that of the benzazepinedione formation⁵ on the basis of the structures of the naphthazepinediones and the stereospecificity of the reaction. Thus, reaction of singlet excited state of **1** and alkene (**2a,b,d-j**) gave two regioisomers of intermediate (**11** and **12**) with retention of the stereochemistry of the alkene, and then C(=O)-N bond cleavage of **11** and **12** results in the formation of **3a,b,d-j** and **4a,b,d-j**, respectively.

Other Reactions. Besides the naphthazepinedione formation, two types of reactions were observed in the irradiation of **1** with 2,3-dimethyl-2-butene

(**2k**) and *cis*-stilbene (**2l**).

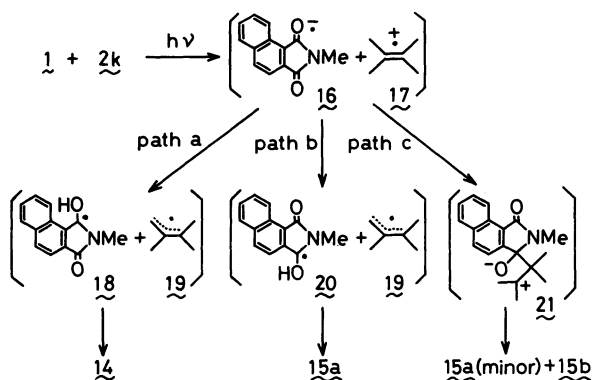
Irradiation of **1** and **2k** in benzene gave two regioisomers of oxetane [**13a** (30%) and **13b** (8%)] and additional products [**14** (16%), **15a** (11%), and **15b** (9%)] (Eq. 4). The reaction is analogous to that of



N-methylphthalimide and **2k**, and structures of the products were assigned from their spectral resemblance to the benzo analogues.^{6d}

The regiochemistries of **13**–**15** were assigned on the ¹H NMR spectra. ¹H NMR spectra of the products showed characteristic double-doublets signals due to H^a in a lower field region of $\delta=8.47$ to 9.19. The H^a signal of **13a** was shifted to a lower field ($\delta=9.19$) compared with that of **13b** ($\delta=8.94$) probably due to the deshielding effect from the lactam carbonyl group. The H^a signal of **15a** was likewise shifted to a lower field ($\delta=8.58$) compared with that of **14** ($\delta=8.47$). Attack of **2k** to the less hindered carbonyl group of **1** to give **13a** seems to predominate.

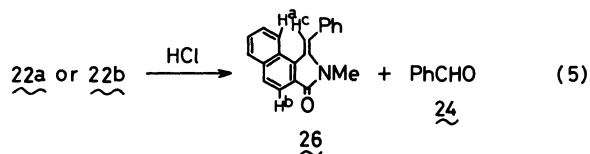
Formation of **14** and **15a, b** may be rationalized by a mechanism shown in Scheme 4, by referring the mechanism proposed by Mazzocchi and Klingler.^{6d} First of all, an ion pair (**16**+**17**) is generated by electron transfer. Subsequent proton transfer gives two types of radical pairs (**18**+**19** and **20**+**19**) via path a and path b, respectively. The former pair couples to give **14** and the latter to **15a**. Another possibility is the collapsing of the ion pair (**16**+**17**) to a zwitter



Scheme 4.

ionic intermediate (**21**) via path c, which converts to mainly **15b** by proton transfer.

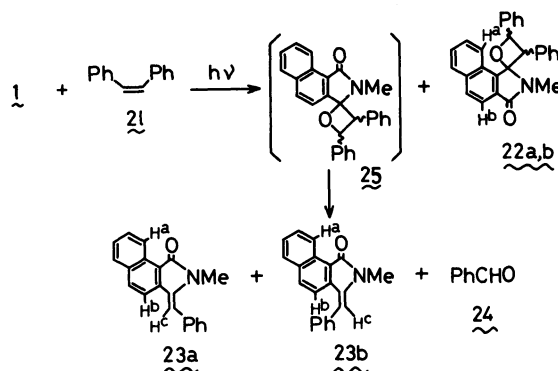
Irradiation of **1** and **2l** in benzene gave two stereoisomers of oxetane [**22a** (19%) and **22b** (19%)], a pair of unsaturated amides [**23a** (37%) and **23b** (15%)], and benzaldehyde [**24** (45%)] (Scheme 5). As reported in many cases,¹⁰ the productions of **23a, b**, and **24** were rationalized by fragmentation of the oxetane precursor (**25**), i.e., carbonyl-alkene metathesis. Acid-catalyzed decomposition of **22a** or **22b** in methanol afforded **26** and **24** (Eq. 5).



The configurations at the olefinic carbons in **23a, b** were assigned on the basis of the ¹H NMR spectra. First, the *N*-Me protons in **23a** were observed at a considerably higher field ($\delta=3.05$) compared with those of **23b** ($\delta=3.37$), probably due to the anisotropic shielding effect of the phenyl group. Second, the H^c signal of **23a** was shifted to a lower field ($\delta=6.83$) compared with that of **23b** ($\delta=6.60$), probably due to an anisotropic deshielding effect from the naphthyl ring current.

The positions of lactam carbonyl groups were assigned as follows: The H^a signals of **23a** ($\delta=9.11$) and **23b** ($\delta=9.20$) were significantly shifted to lower fields probably due to the deshielding effect of the lactam carbonyl groups, when compared with that of **26** ($\delta=8.55$).

The regiochemistry of the oxetane precursor (**25**) of **23a, b** can be readily deduced from the structures of **23a, b**. The compound **26** was a regio-isomer of **23a, b** and its *Z*-configuration was suggested as follows: It has deshielded *N*-Me protons ($\delta=2.97$) and shielded H^c proton ($\delta=7.2$ – 7.7 mixed with arom H's). The structure of **26** allows to deduce the regiochemistry of **22a, b**.



Scheme 5.

On the basis of these structures of the products, it is possible to suppose that **2l** attacks predominantly at the less hindered carbonyl group of **1**. The stereochemical course of the reaction, however, seems to be complicated by the concomitant cis-trans isomerization of the alkene (**2l**).

A common feature between **2k** and **2l** is that **2k** has the lowest ionization (oxidation) potential among the series of ethylenes substituted by alkyl groups (**2a—e, k**) and **2l** has the lowest among the series of ethylenes substituted by phenyl groups (**2h, i, l**). The requirement of dominant electron donor-acceptor interaction has been recognized in the oxetane formation from the $\pi\pi^*$ excited state.^{10,11} In this connection the formation of **14** and **15a, b** in the reaction of **1** with **2k** is rationalized by the electron transfer mechanism (Scheme 4).

Nature of the Singlet Excited State of 1 and Fluorescence Quenching. The absorption spectrum of **1** in benzene showed a broad band around 344 nm ($\log \epsilon \approx 4$), which were slightly shifted to longer wavelengths (≈ 2 nm) in ethanol. The fluorescence spectrum of **1** was obtained by using a diluted benzene solution (1×10^{-5} M) to avoid concentration quenching. The spectrum showed a strong and broad band (λ_{\max} , 430 nm, lifetime 42.0 ns at 25 °C in air-saturated benzene). The fluorescence excitation spectrum was almost identical with the absorption spectrum. These data suggest that the lowest singlet excited state of **1** is $\pi\pi^*$ in character. The energy of the excited singlet state (E_s) estimated from the absorption and fluorescence spectra was 308 kJ mol⁻¹.

Addition of aliphatic alkenes (**2a, b, d, e, k**) to the

Table 2. Ionization Potentials (I_p) of Alkenes (**2a—e, k**), Stern-Volmer Slopes ($k_q\tau$) for the Fluorescence Quenching by Alkenes (**2a—e, k**),^a Fluorescence Quenching Rate Constants (k_q),^b and Relative Rates for Disappearance of **1** in the Photo-reactions of **1** and Alkenes (**2a—e, k**) in Benzene^c

Alkenes	I_p eV	$k_q\tau$ dm ³ mol ⁻¹	k_q dm ³ mol ⁻¹ s ⁻¹	Relative rates for disappearance of 1
2c	9.46 ^d	0	0	0
2d	9.23 ^d	0.23	5.5×10^6	1 ^f
2a	9.12 ^e	0.034	8.1×10^5	0.10
2b	9.11 ^e	0.003	7.1×10^4	0.07
2e	8.68 ^d	2.57	6.1×10^7	1.1
2k	8.53 ^d	118	2.8×10^9	3.0

a) Conditions: [**1**]= 1×10^{-5} M, at room temperature, in air-saturated benzene. b) Calculated from $k_q\tau$ using the lifetime ($\tau=42.0$ ns) of the fluorescence of **1**. c) Reaction conditions: [**1**]=10 mM, [**2a—e, k**]=100 mM, conversion <20%. d) Ref. 5b. e) Ref. 12. f) Standard.

air-saturated benzene solutions of **1** (ca. 1×10^{-5} M) resulted in reduction of the fluorescence of **1** without varying the shape and the position of the maximum emission. Stern-Volmer plots of the fluorescence quenching by the alkenes (**2a—e, k**) gave straight lines against concentration of the alkenes (**2a—e, k**). Fluorescence quenching rate constants (k_q) calculated from the Stern-Volmer slopes ($k_q\tau$) using the lifetime (τ) of the fluorescence of **1** are shown in Table 2 together with ionization potentials (I_p) of the alkenes (**2a—e, k**) and relative rates for disappearance of **1** in the photoreaction with the alkenes. A good correlation was obtained between the k_q values and the relative rates for disappearance of **1**, which may indicate that the efficiency of the reaction mainly depends on the rate of reaction with excited singlet state of **1**. A correlation between the k_q values and the I_p values of alkenes is poor. This is probably due to the steric effect of the alkyl substituents, especially 1,2-dialkyl substituents, on the stage of interaction with the singlet excited state of **1**.

In summary, the most characteristic type of the reaction of **1** and alkenes was found to be naphthazepinedione formation. Other types of reactions, i.e., oxetane formation and electron

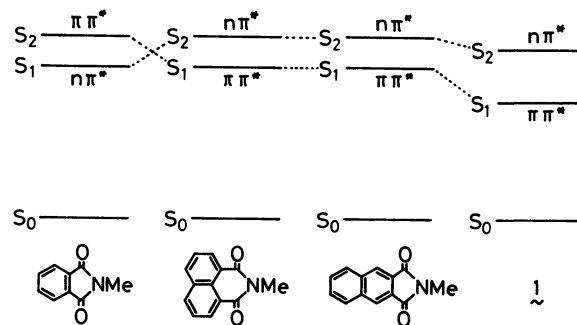


Fig. 2. Energy levels and nature of the singlet excited states of *N*-methylenedicarboximides.

Table 3. Lifetimes of Fluorescence (τ)^a and Energies of the Lowest Singlet Excited States (S_1) of *N*-Methylenedicarboximides^b

Imide	τ /ns	Energies of S_1 /kJ mol ⁻¹
<i>N</i> -Methylphthalimide	—	335 ^c
<i>N</i> -Methyl-1,8-naphthalene-dicarboximide	1.0	332
<i>N</i> -Methyl-2,3-naphthalene-dicarboximide	5.9	332
1	42.0	308

a) Conditions: at 25 °C, in air-saturated benzene. b) Estimated from the absorption and fluorescence spectra. c) Ref. 13.

transfer reaction (hydrogen abstraction), were observed only in the reactions with special alkenes (**2k**, **l**). The predominant types of reaction are found to depend largely upon the arene structure of naphthalenedicarboximides. For instance, **1**, is advantageous for the naphthazepinedione formation, but this reaction was minor for *N*-methyl-1,8- and 2,3-naphthalenedicarboximides.⁹⁾

The results of the structure-dependent photoreactions can be explained by considering the natures of the singlet energy levels as shown in Fig. 2. The energies of the lowest singlet excited states and the lifetimes of the fluorescence of *N*-methylarene-dicarboximides are shown in Table 3. The lowest and the second singlet excited states of *N*-methylphthalimide, $\pi\pi^*$ -S₁ and the $\pi\pi^*$ -S₂, respectively, are shown by referring a literature.¹³⁾ Change in the arene moiety from benzene to naphthalene alters the nature of the S₁ states from $\pi\pi^*$ to $\pi\pi^*$. For three *N*-methylnaphthalenedicarboximides the $\pi\pi^*$ -S₁ levels were supported by the strong fluorescence and the solvent effects. The energies of $\pi\pi^*$ -S₁ for 1,8- and 2,3-derivatives are virtually the same as that of $\pi\pi^*$ -S₁ for the phthalimide. Hence, $\pi\pi^*$ -S₁ of the 1,8- and 2,3-derivatives can interact with $\pi\pi^*$ -S₂ as in the case of the phthalimide. Shorter lifetimes of the fluorescence of 1,8- and 2,3-derivatives than that for **1** as shown in Table 3 may support the stronger interaction. The predominant reaction of the 2,3-derivative is found as oxetane formation caused from the $\pi\pi^*$ -S₁ strongly interacted with $\pi\pi^*$ -S₂. The $\pi\pi^*$ -S₁ level of **1** is however lowered to a "pure and simple" $\pi\pi^*$ state due to the decrease of the interaction. This nature of S₁ may be responsible for the formation of naphthazepinediones as the main products from **1**.

Experimental

The mps were measured by a Yanagimoto micromelting point apparatus, and are uncorrected. ¹H NMR spectra were determined on a JEOL JNM-MH-100 (100 MHz) and a JEOL JNM-GX-400 spectrometer (400 MHz) in CDCl₃ solution. IR spectra were obtained with a Hitachi 260-53 spectrophotometer. Mass spectra were measured on a JEOL JMS-DX-300 apparatus. Fluorescence spectra and the lifetimes were recorded by a Hitachi 650-40 spectrophotometer and a HORIBA NAES-1100 time-resolved spectrofluorometer, respectively. Microanalyses were performed on a Yanagimoto CHN corder MT-2.

Materials. *N*-Methyl-1,2-naphthalenedicarboximide (**1**)¹⁴⁾ were prepared by the reaction of the 1,2-naphthalene-dicarboxylic anhydride¹⁵⁾ with methylamine and purified by chromatography (eluant dichloromethane), then by recrystallization from ethanol. Alkenes (**2a**—**l**) were commercially available and purified by distillation for liquid materials and by recrystallization for solid materials.

General Procedure for Irradiation and Product Isolation.

UV irradiation of 25 cm³ of N₂ purged benzene solutions containing 10 mM of **1** and 100 mM of alkenes (**2a**—**l**) was carried out with an Eikosha PIH 300-W high-pressure Hg-lamp through aq CuSO₄ filter about 1 cm in thickness (>320 nm) at ambient temperature. The reaction was monitored by TLC (Merck, Kieselgel 60 F₂₅₄) analyses and ¹H NMR measurements. After evaporation of the solvent, the residue was subjected to column chromatography [Wakogel C-200 (silica gel, 74—149 μ)]. Dichloromethane-ether was used as the eluant for the separation of the products.

Irradiation of 1 and *cis*-2-Butene (2a**).** *cis*-2,3,4-Trimethyl-3,4-dihydro-1*H*-naphth[1,2-*c*]azepine-1,5(2*H*)-dione (**3a**): Mp 145—147 °C; ¹H NMR (400 MHz) δ =1.38 (d, *J*=7.3 Hz, 3H, NCHMe), 1.41 (d, *J*=7.0 Hz, 3H, COCHMe), 2.85 (q of d, *J*_{CH-CH}=3.2 Hz, *J*_{CH-Me}=7.0 Hz, 1H, COCHMe), 3.14 (s, 3H, NMe), 4.68 (q of d, *J*_{CH-CH}=3.2 Hz, *J*_{CH-Me}=7.3 Hz, 1H, NCHMe), 7.5—7.6 (m, 2H, Arom H), 7.83 (d, *J*=8.6 Hz, 1H, CHCH^b), 7.8—7.9 (m, 2H, Arom H), 7.99 (d, *J*=8.6 Hz, 1H, H^b); IR (KBr) 1683 (ketone), 1635 (lactam), 1423, 1358, 762 cm⁻¹. Found: C, 76.61; H, 6.52; N, 5.26%; M⁺, 267. Calcd for C₁₇H₁₇NO₂: C, 76.38; H, 6.41; N, 5.24%; M, 267.

cis-2,3,4-Trimethyl-3,4-dihydro-1*H*-naphth[2,1-*c*]azepine-1,5(2*H*)-dione (**4a**): Mp 130—133 °C; ¹H NMR (400 MHz) δ =1.39 (d, *J*=7.3 Hz, 6H, NCHMeCHMeCO), 2.61 (m, 1H, COCHMe), 3.23 (s, 3H, NMe), 4.72 (m, 1H, NCHMe), 7.4—7.6 (m, 3H, Arom H), 7.8—7.9 (m, 1H, Arom H), 7.95 (d, *J*=8.6 Hz, 1H, H^b), 8.41 (dd, 1H, H^a); IR (KBr) 1682 (ketone), 1640 (lactam), 1403, 1328, 824 cm⁻¹. Found: C, 76.53; H, 6.57; N, 5.29%; M⁺, 267. Calcd for C₁₇H₁₇NO₂: C, 76.38; H, 6.41; N, 5.24%; M, 267.

Irradiation of 1 and *trans*-2-Butene (2b**).** *trans*-2,3,4-Trimethyl-3,4-dihydro-1*H*-naphth[1,2-*c*]azepine-1,5(2*H*)-dione (**3b**): Mp 177—180 °C; ¹H NMR (400 MHz) δ =1.18 (d, *J*=7.3 Hz, 3H, COCHMe), 1.35 (d, *J*=6.7 Hz, 3H, NCHMe), 3.09 (q of d, *J*_{CH-CH}=11.0 Hz, *J*_{CH-Me}=7.3 Hz, 1H, COCHMe), 3.10 (s, 3H, NMe), 4.03 (q of d, *J*_{CH-CH}=11.0 Hz, *J*_{CH-Me}=6.7 Hz, 1H, NCHMe), 7.5—7.6 (m, 2H, Arom H), 7.84 (d, *J*=8.6 Hz, 1H, CHCH^b), 7.8—7.9 (m, 2H, Arom H), 8.01 (d, *J*=8.6 Hz, 1H, H^b); IR (KBr) 1698 (ketone), 1640 (lactam), 1424, 1396, 846 cm⁻¹. Found: C, 76.58; H, 6.55; N, 5.29%; M⁺, 267. Calcd for C₁₇H₁₇NO₂: C, 76.38; H, 6.41; N, 5.24%; M, 267.

trans-2,3,4-Trimethyl-3,4-dihydro-1*H*-naphth[2,1-*c*]azepine-1,5(2*H*)-dione (**4b**): Mp 151—154 °C; ¹H NMR (400 MHz) δ =1.11 (d, *J*=7.3 Hz, 3H, COCHMe), 1.33 (d, *J*=6.9 Hz, 3H, NCHMe), 2.97 (q of d, *J*_{CH-CH}=11.6 Hz, *J*_{CH-Me}=7.3 Hz, 1H, COCHMe), 3.14 (s, 3H, NMe), 4.11 (q of d, *J*_{CH-CH}=11.6 Hz, *J*_{CH-Me}=6.9 Hz, 1H, NCHMe), 7.39 (d, *J*=8.6 Hz, 1H, CHCH^b), 7.6—7.7 (m, 2H, Arom H), 7.87 (dd, 1H, Arom H), 7.97 (d, *J*=8.6 Hz, 1H, H^b), 8.45 (dd, 1H, H^a); IR (KBr) 1686 (ketone), 1642 (lactam), 1322, 1252, 768 cm⁻¹. Found: C, 76.49; H, 6.53; N, 5.28%; M⁺, 267. Calcd for C₁₇H₁₇CO₂: C, 76.38; H, 6.41; N, 5.24%; M, 267.

Reduction of **3b and **4b**.** To a solution of 50 mg of **3b** in 20 cm³ of ethanol was added 5 mg of sodium borohydride with stirring and the solution was kept overnight at room temperature. Then, the solution was poured into 10 cm³ of 0.1 M-hydrochloric acid and extracted with 20 cm³ of chloroform. The extract was washed several times with water and dried over magnesium sulfate. After

evaporation of the solvent, the residue was chromatographed (eluant dichloromethane-ether) to give **5** (60%).

Reduction of **4b** (50 mg) by sodium borohydride as described above gave **6** (60%).

5-Hydroxy-2,3,4-trimethyl-2,3,4,5-tetrahydro-1*H*-naphth[1,2-*c*]azepine-1-one (5): Mp 187–190 °C; ¹H NMR δ=1.02 (d, 3H, COCHMe), 1.10 (d, 3H, NCHMe), 2.1–2.5 (m, 1H, CH), 2.85 (s, 3H, NMe), 2.9–3.0 (m, 2H, HCOH), 4.9–5.1 (m, 1H, NCHMe), 7.3–7.8 (m, 5H, Arom H), 9.10 (m, 1H, H^a); IR (KBr) 3220 (OH), 1612 (lactam), 1401, 842, 770 cm⁻¹. Found: C, 76.07; H, 7.25; N, 5.23%; M⁺, 269. Calcd for C₁₇H₁₉NO₂: C, 75.81; H, 7.11; N, 5.20%; M, 269.

1-Hydroxy-2,3,4-trimethyl-2,3,4,5-tetrahydro-1*H*-naphth[2,1-*c*]azepine-5-one (6): Mp 260–262 °C; ¹H NMR δ=0.61 (d, 3H, NCHMe), 1.19 (d, 3H, COCHMe), 2.1–2.5 (m, 1H, CH), 2.8–3.0 (m, 2H, HCOH), 3.05 (s, 3H, NMe), 4.5–4.7 (m, 1H, NCHMe), 7.2–7.9 (m, 5H, Arom H), 8.25 (m, 1H, H^a); IR (KBr) 3290 (OH), 1611 (lactam), 1401, 1088, 763 cm⁻¹. Found: C, 76.10; H, 7.28; N, 5.23%; M⁺, 269. Calcd for C₁₇H₁₉NO₂: C, 75.81; H, 7.11; N, 5.20%; M, 269.

Irradiation of 1 and Isobutene (2d). 2,4,4-Trimethyl-3,4-dihydro-1*H*-naphth[1,2-*c*]azepine-1,5(2*H*)-dione (3d): Mp 149–151 °C; ¹H NMR δ=1.28 (d, 6H, CMe₂), 3.23 (s, 3H, NMe), 3.42 (s, 2H, CH₂), 7.4–8.0 (m, 5H, Arom H), 7.96 (d, 1H, H^b); IR (KBr) 1708 (ketone), 1652 (lactam), 1392, 1088, 778 cm⁻¹. Found: C, 76.57; H, 6.54; N, 5.29%; M⁺, 267. Calcd for C₁₇H₁₇NO₂: C, 76.38; H, 6.41; N, 5.24%; M, 267.

2,2,4-Trimethyl-3,4-dihydro-1*H*-naphth[2,1-*c*]azepine-1,5(2*H*)-dione (4d): Mp 151–153 °C; ¹H NMR δ=0.8–1.7 (coalesced br s, 6H, CMe₂), 2.9–3.2 (coalesced br s, 1H, 1H of CH₂), 3.30 (s, 3H, NMe), 3.7–4.2 (coalesced br s, 1H, 1H of CH₂), 7.36 (d, 1H, CHCH^b), 7.4–7.7 (m, 2H, Arom H), 7.7–7.9 (m, 1H, Arom H), 7.89 (d, 1H, H^b), 8.48 (dd, *J*=3.9, 8.0 Hz, 1H, H^a); IR (KBr) 1705 (ketone), 1648 (lactam), 1475, 1403, 842, 774 cm⁻¹. Found: C, 76.48; H, 6.50; N, 5.27%; M⁺, 267. Calcd for C₁₇H₁₇NO₂: C, 76.38; H, 6.41; N, 5.24%; M, 267.

Irradiation of 1 and 2-Methyl-2-butene (2e). 2,3,4,4-Tetramethyl-3,4-dihydro-1*H*-naphth[1,2-*c*]azepine-1,5(2*H*)-dione (3e): Mp 141–143 °C; ¹H NMR δ=0.98 (s, 3H, CMe), 1.22 (d, 3H, CHMe), 1.27 (s, 3H, CMe), 3.00 (s, 3H, NMe), 4.17 (q, 2H, CHMe), 7.3–7.8 (m, 5H, Arom H), 7.87 (d, 1H, H^b); IR (KBr) 1695 (ketone), 1646 (lactam), 1468, 1401, 841, 759 cm⁻¹. Found: C, 77.00; H, 6.95; N, 5.03%. Calcd for C₁₈H₁₉NO₂: C, 76.84; H, 6.81; N, 4.98%.

2,2,3,4-Tetramethyl-3,4-dihydro-1*H*-naphth[2,1-*c*]azepine-1,5(2*H*)-dione (4e): Mp 136–138 °C; ¹H NMR δ=0.88 (s, 3H, CMe), 1.21 (d, 3H, CHMe), 1.22 (s, 3H, CMe), 3.04 (s, 3H, NMe), 4.18 (q, 2H, CHMe), 7.22 (d, 1H, CHCH^b), 7.4–7.6 (m, 2H, Arom H), 7.6–7.8 (m, 2H, Arom H), 7.81 (d, 1H, H^b), 8.40 (dd, 1H, H^a); IR (KBr) 1680 (ketone), 1642 (lactam), 1402, 1324, 833, 763 cm⁻¹. Found: C, 76.96; H, 6.90; N, 5.00%. Calcd for C₁₈H₁₉NO₂: C, 76.84; H, 6.81; N, 4.98%.

Irradiation of 1 and Cyclopentene (2f). 7,7a,8,9,10,10a,11,12-Octahydrocyclopenta[*b*]naphth[2,1-*c*]azepine-7,12-dione (3f): Mp 156–159 °C; ¹H NMR δ=1.2–2.2 (m, 6H), 3.13 (s, 3H, NMe), 3.3–3.6 (m, 1H, COCH), 4.0–4.3 (m, 1H, NCH), 7.4–7.6 (m, 2H, Arom H), 7.7–7.9 (m, 3H, Arom H), 8.03 (d, 1H, H^b); IR (KBr) 1698 (ketone), 1636 (lactam), 1462, 1418, 1392, 763 cm⁻¹. Found: 77.57; H, 6.31; N, 5.04%. Calcd for C₁₈H₁₇NO₂: C, 77.39; H, 6.13; N, 5.01%.

7,8,8a,9,10,11,11a,12-Octahydrocyclopenta[*b*]naphth[1,2-*c*]azepine-7,12-dione (4f): Mp 143–146 °C; ¹H NMR δ=1.3–2.4 (m, 6H), 2.8–3.2 (m, 1H, COCH), 3.24 (s, 3H, NMe), 4.1–4.5 (m, 1H, NCH), 7.36 (d, 1H, CHCH^b), 7.5–8.0 (m, 3H, Arom H), 8.00 (d, 1H, H^b), 8.38 (dd, 1H, H^a); IR (KBr) 1682 (ketone), 1638 (lactam), 1459, 1402, 1328, 763 cm⁻¹. Found: C, 77.20; H, 6.25; N, 4.87%. Calcd for C₁₈H₁₇NO₂: C, 77.39; H, 6.13; N, 5.01%.

Irradiation of 1 and 2-Norbornene (2g). 9,10,11,11a-Tetrahydro-8,11-methano-8*H*-benzo[*b*]naphth[2,1-*c*]azepine-7,13(7*aH*,12*H*)-dione (3g): Mp 176–179 °C; ¹H NMR δ=1.0–2.0 (m, 6H), 2.8–3.0 (m, 1H), 3.0–3.3 (m, 2H), 3.14 (s, 3H, NMe), 3.9–4.1 (m, 1H, NCH), 7.5–7.8 (m, 2H, Arom H), 7.9–8.1 (m, 4H, Arom H); IR (KBr) 1711 (ketone), 1634 (lactam), 1372, 838, 762 cm⁻¹. Found: C, 78.72; H, 6.39; N, 4.63%. Calcd for C₂₀H₁₉NO₂: C, 78.66; H, 6.27; N, 4.59%.

9,10,11,12-Tetrahydro-9,12-methano-8*aH*-benzo[*b*]naphth[1,2-*c*]azepine-7,13(8*H*,12*aH*)-dione (4g): Mp 153–156 °C; ¹H NMR δ=0.9–2.0 (m, 6H), 2.7–3.1 (m, 3H), 3.21 (s, 3H, NMe), 3.9–4.1 (m, 1H, NCH), 7.35 (d, 1H, CHCH^b), 7.5–7.8 (m, 2H, Arom H), 7.8–8.0 (m, 1H, Arom H), 8.01 (d, 1H, H^b), 8.55 (dd, 1H, H^a); IR (KBr) 1712 (ketone), 1624 (lactam), 1383, 1362, 1096, 763 cm⁻¹. Found: C, 78.83; H, 6.36; N, 4.61%. Calcd for C₂₀H₁₉NO₂: C, 78.66; H, 6.27; N, 4.59%.

Irradiation of 1 and Styrene (2h). 2-Methyl-4-phenyl-3,4-dihydro-1*H*-naphth[1,2-*c*]azepine-1,5(2*H*)-dione (3h): Mp 157–159 °C; ¹H NMR δ=3.15 (s, 3H, NMe), 3.49 (dd, *J*=2, 12 Hz, 1H, PhCH), 4.17 (t, *J*=12 Hz, 1H, 1H of CH₂), 4.35 (dd, *J*=2, 12 Hz, 1H, 1H of CH₂), 6.9–7.6 (m, 7H, Arom H), 7.7–7.9 (m, 3H, Arom H), 7.96 (d, 1H, H^b); IR (KBr) 1702 (ketone), 1652 (lactam), 1483, 1398, 774 cm⁻¹. Found: C, 80.14; H, 5.59; N, 4.50%; M⁺, 315. Calcd for C₂₁H₁₇NO₂: C, 79.98; H, 5.43; N, 4.44%; M, 315.

4-Methyl-2-phenyl-3,4-dihydro-1*H*-naphth[2,1-*c*]azepine-1,5(2*H*)-dione (4h): Mp 144–147 °C; ¹H NMR δ=3.27 (coalesced br s, 3H, NMe), 3.3–3.8 (coalesced br s, 1H), 4.0–4.4 (coalesced br s, 2H), 7.0–8.0 (m, 9H, Arom H), 7.94 (d, 1H, H^b), 8.45 (dd, 1H, H^a); IR (KBr) 1682 (ketone), 1652 (lactam), 1398, 1258, 834, 754 cm⁻¹. Found: C, 80.20; H, 5.61; N, 4.42%; M⁺, 315. Calcd for C₂₁H₁₇NO₂: C, 79.98; H, 5.43; N, 4.44%; M, 315.

Irradiation of 1 and 1,1-Diphenylethylene (2i). 4,4-Diphenyl-2-methyl-3,4-dihydro-1*H*-naphth[1,2-*c*]azepine-1,5(2*H*)-dione (3i): Mp 195–198 °C; ¹H NMR δ=2.48 (s, 3H, NMe), 4.28 (br s, 2H, CH₂), 6.8–7.9 (m, 15H, Arom H), 7.96 (d, 1H, H^b); IR (KBr) 1712 (ketone), 1656 (lactam), 1483, 1401, 772, 713 cm⁻¹. Found: C, 83.01; H, 5.55; N, 3.46%. Calcd for C₂₇H₂₁NO₂: C, 82.84; H, 5.41; N, 3.58%.

2,2-Diphenyl-4-methyl-3,4-dihydro-1*H*-naphth[2,1-*c*]azepine-1,5(2*H*)-dione (4i): Mp 191–193 °C; ¹H NMR δ=2.53 (s, 3H, NMe), 3.62 and 5.04 (coalesced br ABq, 2H, CH₂), 7.12 (d, 1H, CHCH^b), 7.1–7.4 (m, 13H, Arom H), 7.5–7.7 (m, 1H, Arom H), 7.79 (d, 1H, H^b), 8.51 (dd, 1H, H^a); IR (KBr) 1690 (ketone), 1658 (lactam), 1456, 1402, 758, 716 cm⁻¹. Found: C, 82.92; H, 5.38; N, 3.40%. Calcd for C₂₇H₂₁NO₂: C, 82.84; H, 5.41; N, 3.58%.

Irradiation of 1 and Ethyl Vinyl Ether (2j). 4-Ethoxy-2-methyl-3,4-dihydro-1*H*-naphth[1,2-*c*]azepine-1,5(2*H*)-dione (3j): Mp 141–143 °C; ¹H NMR δ=1.29 (t, 3H, OCH₂Me), 3.20 (s, 3H, NMe), 3.4–4.4 (m, 5H), 7.4–7.7 (m,

2H, Arom H), 7.7–8.0 (m, 3H, Arom H), 8.00 (d, $J=9$ Hz, 1H, H^b); IR (in CHCl_3) 1710 (ketone), 1646 (lactam), 1482, 1400, 1081 cm^{-1} . Found: C, 72.32; H, 6.21; N, 5.09%; M^+ , 283. Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$: C, 72.06; H, 6.05; N, 4.94%; M, 283.

2-Methyl-3,4-dihydro-1H-naphth[1,2-c]azepine-1,5(2H)-dione (7): Mp 186–188 °C; ^1H NMR $\delta=3.23$ (s, 3H, NMe), 3.0–3.4 (m, 2H, COCH_2), 3.6–3.8 (m, 2H, NCH_2), 7.5–7.7 (m, 2H, Arom H), 7.8–8.0 (m, 3H, Arom H), 8.03 (d, $J=9$ Hz, 1H, H^b); IR (KBr) 1690 (ketone), 1638 (lactam), 1493, 1392, 1256, 764 cm^{-1} . Found: C, 75.20; H, 5.69; N, 5.94%; M^+ , 239. Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 75.30; H, 5.48; N, 5.85%; M, 239.

4-Methyl-3,4-dihydro-1H-naphth[2,1-c]azepine-1,5(2H)-dione (8): Mp 151–145 °C; ^1H NMR $\delta=2.9$ –3.1 (m, 2H, COCH_2), 3.28 (s, 3H, NMe), 3.6–3.8 (m, 2H, NCH_2), 7.5–7.7 (m, 3H, Arom H), 7.8–7.9 (m, 1H, Arom H), 7.98 (d, $J=9$ Hz, 1H, H^b), 8.41 (dd, 1H, H^a); IR (in CHCl_3) 1696 (ketone), 1646 (lactam), 1400, 1263, 828 cm^{-1} . Found: C, 75.57; H, 5.73; N, 5.90%; M^+ , 239. Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 75.30; H, 5.48; N, 5.85%; M, 239.

Irradiation of 1 and 2,3-Dimethyl-2-butene (2k). 2,3',3',4',4'-Pentamethylspiro[3H-benz[e]isoindole-3,2'-oxetan]-1(2H)-one (13a): Oil; ^1H NMR $\delta=1.05$ (s, 3H, CMe), 1.25 (s, 3H, CMe), 1.53 (s, 3H, CMe), 1.63 (s, 3H, CMe), 3.24 (s, 3H, NMe), 7.4–7.9 (m, 4H, Arom H), 7.94 (d, $J=9$ Hz, 1H, H^b), 9.19 (dd, 1H, H^a); IR (oil) 1692 (lactam), 1372, 1356, 1068, 942, 783 cm^{-1} . Found: C, 77.53; H, 7.32; N, 4.47%; M^+ , 295. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2$: C, 77.26; H, 7.17; N, 4.74%; M, 295.

2,3',3',4',4'-Pentamethylspiro[1H-benz[e]isoindole-1,2'-oxetan]-3(2H)-one (13b): Mp 168–170 °C; ^1H NMR $\delta=0.89$ (s, 3H, CMe), 1.12 (s, 3H, CMe), 1.67 (s, 3H, CMe), 1.77 (s, 3H, CMe), 3.32 (s, 3H, NMe), 7.3–7.9 (m, 5H, Arom H), 8.94 (dd, 1H, H^a); IR (KBr) 1698 (lactam), 1418, 1384, 1038, 776 cm^{-1} . Found: C, 77.30; H, 7.21; N, 4.81%; M^+ , 295. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2$: C, 77.26; H, 7.17; N, 4.74%; M, 295.

1-(2,3-Dimethyl-2-butenyl)-1-hydroxy-2-methyl-1,2-dihydro-3H-benz[e]isoindol-3-one (14): Mp 191–193 °C; ^1H NMR $\delta=1.12$ (s, 3H, CMe), 1.21 (s, 3H, CMe), 1.33 (s, 3H, CMe), 2.84 (s, 3H, NMe), 2.88 and 3.08 (ABq, $J=14$ Hz, 2H, CH_2), 3.97 (s, 1H, OH), 7.3–8.0 (m, 5H, Arom H), 8.47 (dd, 1H, H^a); IR (KBr) 3300 (OH), 1694 (lactam), 1440, 1411, 768 cm^{-1} . Found: C, 77.46; H, 7.30; N, 4.79%; M^+ , 295. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2$: C, 77.26; H, 7.17; N, 4.74%; M, 295.

3-(2,3-Dimethyl-2-butenyl)-3-hydroxy-2-methyl-2,3-dihydro-1H-benz[e]isoindol-1-one (15a): Mp 124–127 °C; ^1H NMR $\delta=1.17$ (s, 3H, CMe), 1.52 (s, 3H, CMe), 1.59 (s, 3H, CMe), 2.38 and 2.73 (ABq, $J=14$ Hz, 2H, CH_2), 2.62 (s, 3H, NMe), 4.64 (s, 1H, OH), 7.2–7.7 (m, 5H, Arom H), 8.58 (dd, 1H, H^a); IR (KBr) 3280 (OH), 1684 (lactam), 1381, 1360, 1018, 811 cm^{-1} . Found: C, 77.50; H, 7.28; N, 4.78%; M^+ , 295. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2$: C, 77.26; H, 7.17; N, 4.74%; M, 295.

3-Hydroxy-2-methyl-3-(1,1,2-trimethyl-2-propenyl)-2,3-dihydro-1H-benz[e]isoindol-1-one (15b): Mp 122–125 °C; ^1H NMR $\delta=0.94$ (s, 3H, CMe), 1.03 (s, 3H, CMe), 1.96 (s, 3H, =CMe), 2.41 (s, 3H, NMe), 4.31 (s, 1H, OH), 4.52 and 4.76 (two br s, 2H, = CH_2), 7.2–7.7 (m, 5H, Arom H), 8.72 (dd, 1H, H^a); IR (KBr) 3350 (OH), 1682 (lactam), 1386, 1362, 1080, 824 cm^{-1} . Found: C, 77.47; H, 7.24; N, 4.78%; M^+ , 295. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2$: C, 77.26; H, 7.17; N, 4.74%; M, 295.

Irradiation of 1 and cis-Stilbene (2l). One Stereoisomer of 2-Methyl-3',4'-diphenylspiro[1H-benz[e]isoindole-1,2'-oxetan]-3(2H)-one (22a): Mp 187–190 °C; ^1H NMR $\delta=2.87$ (s, 3H, NMe), 5.61 (d, $J=9$ Hz, 1H, OCHCHPh), 6.4–6.6 (m, 2H, Arom H), 6.85 (d, $J=9$ Hz, 1H, OCHPh), 6.9–7.1 (m, 2H, Arom H), 7.3–8.2 (m, 10H, Arom H), 8.76 (dd, 1H, H^a); IR (KBr) 1718 (lactam), 1395, 968, 768, 714 cm^{-1} . Found: C, 83.02; H, 5.65; N, 3.61%; M^+ , 391. Calcd for $\text{C}_{27}\text{H}_{21}\text{NO}_2$: C, 82.84; H, 5.41; N, 3.58%; M, 391.

Another Stereoisomer (22b): Mp 255–258 °C; ^1H NMR $\delta=2.89$ (s, 3H, NMe), 5.43 (d, $J=9$ Hz, 1H, OCHCHPh), 6.67 (d, $J=9$ Hz, 1H, OCHPh), 6.9–7.1 (m, 2H, Arom H), 7.2–8.1 (m, 13H, Arom H), 8.26 (dd, 1H, H^a); IR (KBr) 1711 (lactam), 1382, 954, 764, 702 cm^{-1} . Found: C, 82.97; H, 5.42; N, 3.63%; M^+ , 391. Calcd for $\text{C}_{27}\text{H}_{21}\text{NO}_2$: C, 82.84; H, 5.41; N, 3.58%; M, 391.

(Z)-3-Benzylidene-2-methyl-2,3-dihydro-1H-benz[e]-isoidol-1-one (23a): Mp 143–146 °C; ^1H NMR $\delta=3.05$ (s, 3H, NMe), 6.83 (s, 1H, H^c), 7.1–7.9 (m, 9H, Arom H), 7.96 (d, 1H, H^b), 9.11 (dd, 1H, H^a); IR (KBr) 1682 (lactam), 1283, 824, 751, 708 cm^{-1} . Found: C, 84.36; H, 5.49; N, 4.98%; M^+ , 285. Calcd for $\text{C}_{20}\text{H}_{15}\text{NO}$: C, 84.18; H, 5.30; N, 4.91%; M, 285.

(E)-3-Benzylidene-2-methyl-2,3-dihydro-1H-benz[e]-isoidol-1-one (23b): Mp 136–139 °C; ^1H NMR $\delta=3.37$ (s, 3H, NMe), 6.60 (s, 1H, H^c), 7.0–8.0 (m, 10H, Arom H), 9.20 (dd, 1H, H^a); IR (KBr) 1697 (lactam), 1434, 828, 756, 702 cm^{-1} . Found: C, 84.41; H, 5.52; N, 4.87%. Calcd for $\text{C}_{20}\text{H}_{15}\text{NO}$: C, 84.18; H, 5.30; N, 4.91%.

Acid Decomposition of 22a and 22b. To a solution of 50 mg of 22a in 20 cm^3 of methanol was added a few drops of hydrochloric acid. After 1 d, to the solution was added 30 cm^3 of chloroform and the solution was washed successively with water, and then dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed (eluant dichloromethane) to give **26** (53%).

Acid decomposition of 22b (50 mg) by hydrochloric acid as described above gave **26** (58%).

(Z)-1-Benzylidene-2-methyl-1,2-dihydro-3H-benz[e]-isoidol-3-one (26): Mp 166–168 °C; ^1H NMR $\delta=2.97$ (s, 3H, NMe), 7.2–7.7 (m, 7H, Arom H+ H^c), 7.8–8.0 (m, 3H, Arom H), 8.55 (dd, 1H, H^a); IR (KBr) 1710 (lactam), 1378, 1086, 784, 759, 703 cm^{-1} . Found: C, 84.05; H, 5.52; N, 4.91%; M^+ , 285. Calcd for $\text{C}_{20}\text{H}_{15}\text{NO}$: C, 84.18; H, 5.30; N, 4.91%; M, 285.

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