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Methanol-Incorporated Photoaddition of *N*-Methyl-9,10-phenanthrenedicarboximide to Alkenes. Addition at Carbonyl and Phenanthrene-Ring Carbon Atoms

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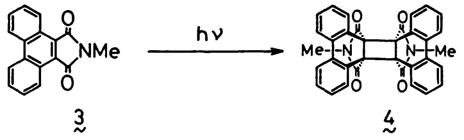
Irradiation of acetonitrile–methanol (2 : 1 v/v) solutions of *N*-methyl-9,10-phenanthrenedicarboximide (**3**) with alkenes **5a—g** gave methanol-incorporated adducts (**9c—f**) at a carbonyl carbon atom in **3**, those (**10c,f**) at a phenanthrene-ring carbon atom, and a methanol-adduct **11g** to alkene **5g**, together with products **4**, **6b,e—g**, **7b,e—g**, and **8e,f** obtained by the photoreactions in benzene. The concentration effect of alkenes **5e,f** on yields of products **6e,f**, **7e,f**, **8e,f**, **9e,f**, and **10f** showed that both **9e,f** and **10f** arose from a relatively short-lived singlet excited state of **3**. The values of the free-energy change associated with an electron transfer (ΔG_{et}) from alkenes **5a—d,g** to the singlet excited state of **3** and fluorescence quenching rate constants support a photochemical electron transfer mechanism for the methanol-incorporated addition. Both $LiClO_4$ and Bu_4NClO_4 caused only slight decreases in the relative ratios **10c**/**9c** indicating that both the methanol-incorporated addition at the phenanthrene-ring carbon atom and that at the carbonyl carbon atom might arise from a contact ion pair state. The fact that the methanol-incorporated addition at the arene-ring carbon atom was observed only in the reaction of **3** in a series of *N*-methylarenedicarboximides, possessing a five-membered imide ring, is interpreted on the basis of the spin density of the radical anions of the imides derived from the photochemical electron transfer.

The area of electron transfer photochemistry has received much attention with regard to both synthetic and mechanistic aspects in organic photochemisry.[1] A unique feature of transformations occurring by electron transfer mechanisms is that the key reactive intermediates are radical ion and neutral radical species rather than the initially populated excited states. Consequently, the chemical properties and reactivity profiles of these reactive intermediates have been clarified by investigations on the nature of the reactions.

During the course of investigations of the photochemistry of imides, a wide variety of alcohol (solvent)-incorporated intramolecular cyclization[2] and intermolecular addition reactions[3] in the photoreactions of arenedicarboximide–alkene systems, via an electron transfer process, have been found. The position, at which the alcohol-incorporated addition occurs, largely depends on the arene structures of the arenedicarboximides. Thus, the methanol-incorporated addition has been reported to occur only at the carbonyl carbon atoms of the imide for the reactions of the five-membered imides such as *N*-methylphthalimide (**1**),[3a—e] *N*-methyl-1,2-naphthalenedicarboximide (**2**),[3i] and its 2,3-isomer,[3g] while the addition solely at a naphthalene-ring carbon atom has been observed in the reaction of *N*-methyl-1,8-naphthalenedicarboximide, a six-membered imide.[3f,h] Furthermore, a preferential addition at the sterically more hindered carbonyl carbon atom in the reaction of **2** has been found.[3i] The effect of the arene structures has been explained on the basis of the spin density of the radical anion of the arenedicarboximides derived by the photochemical electron transfer.[3h,i]

Here, we report on the methanol-incorporated photoaddition of *N*-methyl-9,10-phenanthrenedicarboximide (**3**) to alkenes in acetonitrile–methanol (2/1 v/v), in which the first example of the methanol-incorporated addition at an arene-ring carbon atom in the reactions of arenedicarboximides with a five-membered imide ring is observed.

We have already reported the photoreactions of **3** with alkenes in benzene.[4] Thus, photoreaction (>400 nm) of **3** gives the syn-dimer (**4**) (Eq. 1). Photoreactions of **3** with alkenes (**5**) give **4**, insertion products (**6**) of the double bond of the alkenes into the C–N bond of **3**, and cyclobutanes (**7** and **8**) (Eq. 2).



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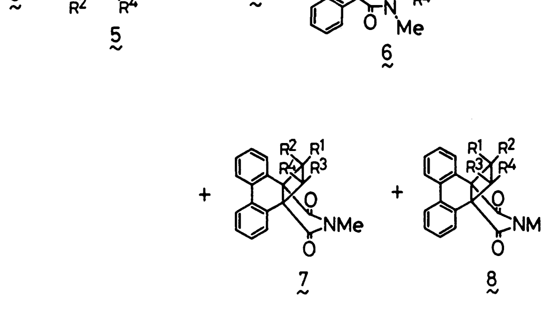

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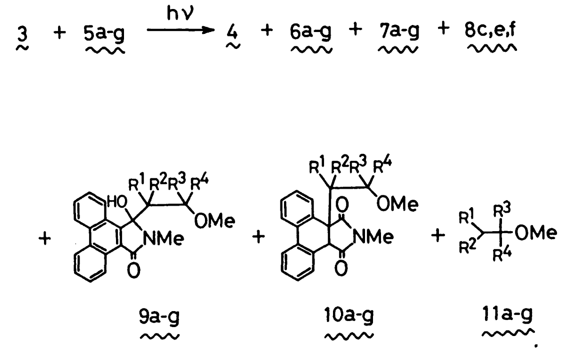
The syn dimerization and the insertion occur from the singlet excited state of **3**, and **7** and **8** arises mainly from the triplet excited state of **3** and remarkable heavy atom effect by halides is observed in this system.

Results and Discussion

Results of the photoreactions (>400 nm) of **3** and alkenes **5a**—**g** in N_2-purged acetonitrile-methanol (2/1 v/v) are summarized in Eq. 3 and Table 1. The methanol-incorporated addition was observed in the reactions with ethylenes substituted by more than three alkyl groups, 2-methyl-2-butene (**5c**), 2,3-dimethyl-2-butene (**5d**), as for the reaction with aliphatic alkenes. The fact that the dimerization of **3** to give **4** was only observed in the reaction with 1-hexene (**5a**), an ethylene substituted by one alkyl group, indicates that no interaction occurs between the excited states of **3** and **5a**. Photoreaction with isobutene (**5b**), an ethylene substituted by two alkyl groups, in acetonitrile-methanol and in benzene gave the same products, an insertion product **6b** and a cyclobutane **7b**, as those obtained by the reaction in benzene. The results show that **3** is less reactive on the methanol-incorporated addition than **1** since irradiation of **1** with **5b** gave a methanol-incorporated adduct together with an insertion product.[3d] and **3** has a similar reactivity to **2** because the methanol-incorporated addition was observed in the reactions with the same alkenes **5c,d**.[3i]



(3)

Irradiation of **3** with **5c** in acetonitrile-methanol gave a pair of diastereomers of a methanol-incorporated adduct (**9c**, diastereomer ratio=2.8 : 1) at the carbonyl carbon atom of **3** and a pair of diastereomers of a methanol-incorporated adduct (**10c**, diastereomer ratio=1.2 : 1) at a phenanthrene-ring carbon atom with complete quenching of the formation of products **4**, **6c**, **7c**, and **8c** obtained in benzene.[4] The diastereomers of **9c** were isolated as a mixture and those of **10c** were separated by silica-gel column chromatography. The structure of **9c**, including the position of the methyl substituents in the side chain, was supported by the spectral resemblances to the methanol-incorporated adducts obtained by the photoreactions of **1**[3d] and **2**[3i] with **5c**. The structure of **10c** was assigned on the basis of the spectral data: ^{1}H NMR δ=5.07 (s, 1H, CH, for the major diastereomer), 4.35 (s, 1H, CH, for the minor diastereomer); IR 1766 and 1700 (imide moiety for the major diastereomer), 1776 snd 1706 (imide moiety for the minor diastereomer).

Irradiation of **3** with **5d** in acetonitrile-methanol (2/1 v/v) gave no detectable amounts of products. However, irradiation in benzene-methanol (9/1 v/v), a less polar solvent system, gave a methanol-incorporated adduct (**9d**) at the carbonyl carbon atom of **3**. A similar solvent effect was observed in the reactions of **2** with alkenes.[3i]

Irradiation of **3** with styrene (**5e**) in acetonitrile-methanol gave a pair of diastereomers of a methanol-

Table 1. Yields of Photoproducts from *N*-Methyl-9,10-phenanthrenedicarboximide (**3**) and Alkenes **5a**—**g** in Acetonitrile-Methanol (2/1 v/v)[a]

R^1	R^2	R^3	R^4	5	[5] mM[c]	Yield[b]/% 4	6	7	8	9	10	11
Bu	H	H	H	**5a**	320	90	**6a** 0	**7a** 0	—	**9a** 0	**10a** 0	—[d]
Me	Me	H	H	**5b**	360	16	**6b** 35	**7b** 35	—	**9b** 0	**10b** 0	—[d]
Me	Me	Me	H	**5c**	380	0	**6c** 0	**7c** 0	**8c** 0	**9c** 29[e]	**10c** 41[f]	—[d]
Me	Me	Me	Me	**5d**	320	0	**6d** 0	**7d** 0	—	**9d** 25[g]	**10d** 0	—[d]
Ph	H	H	H	**5e**	190	0	**6e** 17	**7e** 8	**8e** 10	**9e** 25[h]	**10e** 0	**11e** 0
					380		22	6	7	33[h]		
					760		27	5	6	38[h]		
Ph	Me	H	H	**5f**	60	0	**6f** 16	**7f** 7	**8f** 6	**9f** 50[i]	**10f** 3[j]	**11f** 0
					160		19	4	3	55[i]	4[j]	
					310		22	4	2	55[i]	5[j]	
					620		25	3	2	56[i]	5[j]	
Ph	Ph	H	H	**5g**	400	0	**6g** 36	**7g** 8	—	**9g** 0	**10g** 0	**11g** 142

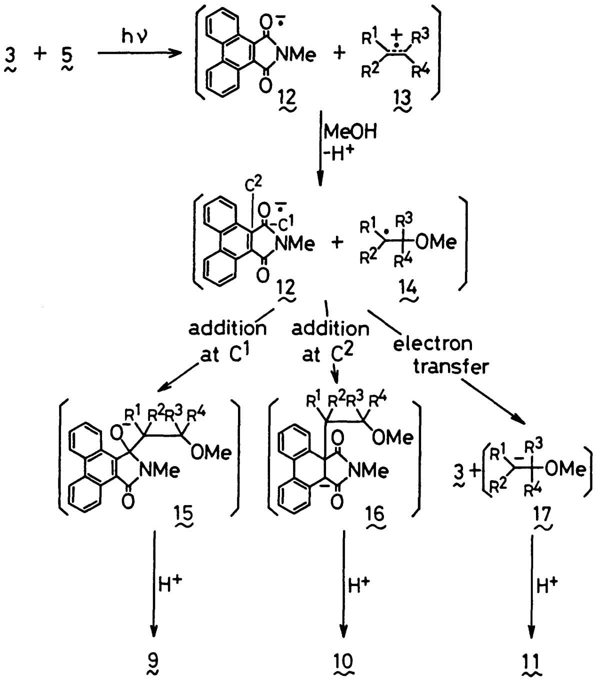
a) Reaction conditions: [**3**]=15 mM, under N_2, *hν* (λ>400 nm). b) Yields were based on consumed **3**. c) 1 M=1 mol dm^{-3}. d) Not checked. e) A mixture (2.8 : 1) of two diastereomers. f) A mixture (1.2 : 1) of two diastereomers. g) In benzene-methanol (9/1 v/v). h) A mixture (1.4 : 1) of two diastereomers. i) A mixture (1.2 :1) of two diastereomers. j) A mixture (1.3 : 1) of two diastereomers.

incorporated adduct (**9e**) at the carbonyl carbon atom together with products **6e**, **7e**, and **8e** obtained in benzene.[4] Photoreaction with α-methylstyrene (**5f**) afforded a pair of diastereomers of a methanol-incorporated adduct (**9f**) at the carbonyl carbon atom and a pair of diastereomers of a methanol-incorporated adduct (**10f**) at the phenanthrene-ring carbon atom together with products **6f**, **7f**, and **8f** obtained in benzene.[4]

The concentration effect of the alkenes **5e**,**f** on the yields of the photoproducts was examined in the reactions with **5e**,**f** to clarify the multiplicity of the excited states of **3** which led to **9e**,**f** and **10f**. A marked concentration dependency of the yields of products was observed in the reaction of **3** with **5f** in benzene; the yield of **6f** increased and those of **7f** and **8f** decreased with increase of the concentration of **5f**.[4] These results are rationalized by a mechanistic scheme, in which **6f** arises from the relatively short-lived singlet excited state of **3**, and **7f** and **8f** mainly from the relatively long-lived triplet excited state. A similar concentration dependency of the yields of **6e**,**f**, **7e**,**f**, and **8e**,**f** was observed in acetonitrile–methanol (Table 1). At the same time, the yields of **9e**,**f** and **10f** increased with increase of the concentration of **5e**,**f**, indicating that **9e**,**f** and **10f** arose from the relatively short-lived singlet excited state of **3**.

Irradiation of **3** with 1,1-diphenylethylene (**5g**) in acetonitrile–methanol gave 2,2-diphenylethyl methyl ether (**11g**), an anti-Markovnikoff adduct of methanol to **5g**, and products **6g** and **7g** obtained in benzene. No methanol-incorporated adducts of **3** to **5g** were obtained.

A possible mechanism which can interpret the general feature of the methanol-incorporated addition observed in the photoreaction of **3** with alkenes (**5**) is shown in Scheme 1. The initial step of the reaction is the single electron transfer from the alkenes to the singlet excited state of **3**. The singlet multiplicity of the excited state of **3**, which lead to the methanol-incorporated adducts **9** and **10**, is substantiated by the concentration effect of **5e**,**f**. The electron transfer mechanism is supported by the estimation of the free-energy changes (ΔG_{et}) associated with the electron transfer from alkenes to the singlet excited state of **3** and the fluorescence quenching rate constants (k_q) (vide infra). Concerning the electron transfer mechanism, **11g** by the reaction with **5g** could be one of the typical electron transfer photosensitized products, as reported by Arnold and his co-workers.[5] The electron transfer photo-sensitized addition of methanol to alkenes giving **11** and the methanol-incorporated addition of alkenes to **3** giving **9** and **10** appear to be closely related processes via common intermediates **12**+**14**. Coupling of the two components at the carbonyl carbon atom (C^1) and that at the phenanthrene-ring carbon atom (C^2) of **12** results in the formation of **9** and **10**, respectively, and the back electron transfer from **12** to **14** gives **3** and **11** (Scheme 1).



Scheme 1.

The values of ΔG_{et} can be estimated by using[6]

$$\Delta G_{et} = 96.49[E(D/D^+) - E(A^-/A)] - \Delta E_{0,0}. \quad (4)$$

In this equation $E(D/D^+)$ is the oxidation potential of the alkenes, $E(A^-/A)$ is the reduction potential of **3**, and $\Delta E_{0,0}$ is the singlet excitation energy of **3**. With these parameters, we can calculate the ΔG_{et} values for reactions with alkenes **5a**—**d**,**g** as shown in Table 2, which shows that the methanol-incorporated addition occurs only in the cases having negative ΔG_{et} values, as expected from the electron transfer mechanism.

An addition of alkenes **5b**—**g** to air-saturated acetonitrile solutions of **3** (1×10^{-5} M) resulted in a reduction of the fluorescence of **3** without varying the shape and the position of the emission. Stern–Volmer plots of the fluorescence quenching by alkenes **5c**—**g** gave straight lines against concentration of **5c**—**g**. The values of k_q in acetonitrile calculated from the Stern–Volmer slopes ($k_q\tau$) using the lifetime of the fluores-

Table 2. Calculated Free Energy Changes (ΔG_{et}) Associated with Electron Transfer from Alkenes **5a**—**d**, **g** to the Singlet Excited State of *N*-Methyl-9,10-phenanthrenedicarboximide (**3**)

Alkenes	$E(D/D^+)$/V	$\Delta G_{et}{}^{a)}$/kJ mol^{-1}
5a	2.64$^{b)}$	+64.2
5b	2.39$^{b)}$	+40.0
5c	1.79$^{b)}$	−17.9
5d	1.63$^{b)}$	−33.3
5g	1.48$^{c)}$	−47.8

a) Calculated by Eq. 4: $E(A^-/A) = -1.02$ V (in 0.5 M Et_4NClO_4/acetonitrile vs. Ag/0.01 M $AgClO_4$), $\Delta E_{0,0} =$ 289 kJ mol^{-1} from Ref. 4. b) Ref. 3b. c) Ref. 7.

Table 3. Fluorescence Quenching Rate Constants (k_q) for *N*-Methyl-9,10-phenanthrenedicarboximide (**3**) and Alkene **5a—g** Systems[a)]

Alkenes	$k_q\tau$[b)]	k_q[c)]	k_q[d)]
	M^{-1}	$M^{-1}\,s^{-1}$	$M^{-1}\,s^{-1}$
5a	0	0	0
5b	—[e)]	—[e)]	—[e)]
5c	5.7	3.90×10^8	4.0×10^7
5d	153	1.05×10^{10}	9.3×10^7
5e	11.7	8.01×10^8	8.0×10^7
5f	16.2	1.11×10^9	4.5×10^8
5g	22.0	1.51×10^9	4.9×10^8

a) Conditions: [3]=1×10^{-5} M, at 25 °C. b) Stern-Volmer slopes for the fluorescence quenching in air-saturated acetonitrile. c) Calculated from $k_q\tau$ using the lifetime (τ=14.6 ns) of the fluorescence of **3** in air-saturated acetonitrile. d) In air-saturated benzene from Ref. 4. e) A very low value.

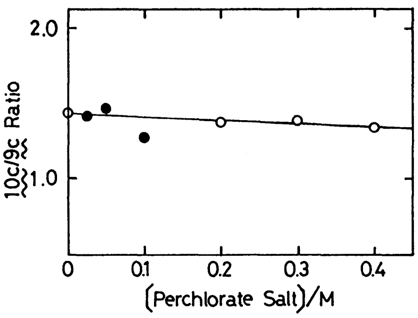
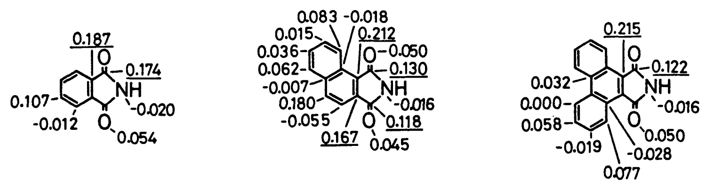


Fig. 1. Methanol-incorporated adducts at a phenanthrene-ring carbon atom to those at the carbonyl carbon atom ratios (**10c**/**9c**) obtained by irradiation of acetonitrile-methanol (2/1 v/v) solutions of *N*-methyl-9,10-phenanthrenedicarboximide (**3**, 1.9 mM) and 2-methyl-2-butene (**5c**, 240 mM) in the presence of varying concentrations of $LiClO_4$ (○) and Bu_4NClO_4 (●).

cence of **3**, together with k_q values in benzene, are shown in Table 3. The k_q values in acetonitrile are larger than those in benzene. The large k_q values in acetonitrile may also support the electron transfer mechanism.

In the area of electron transfer photochemistry, chemistry of ion pairs, involving solvent-separated ion pairs and contact ion pairs, have received much attention in recent years.[1,8)] The salt effect was examined in the present system to obtain the information on the ion-pair states involved in the reaction, since the salt effect had been known to play a role in determining preferred ion-pair states of photogenerated radical ions.[9)] Thus the relative ratios **10c**/**9c** were determined for the photoreactions of **3** with **5c** in acetonitrile-methanol (2/1 v/v) containing increasing concentrations of $LiClO_4$ and Bu_4NClO_4 in the range of 0—0.4 M. The results are shown in Fig. 1, which indicates that $LiClO_4$ causes only slight decreases in **10c**/**9c** and the effect of Bu_4NClO_4 is similar to that of $LiClO_4$. The lithium cation is known to be a much stronger acceptor than Bu_4N^+ in interactions with oxide anion donors.[9)] Thus, $LiClO_4$ should be more capable of intercepting the solvent-separated ion pairs and transforming them to free radical ions, compared with Bu_4NClO_4. The results from the salt effect may indicate that both the methanol-incorporated addition at the phenanthrene-ring carbon atom and that at the carbonyl carbon atom arise from the contact ion pair state.

The variation of the arene structures of arenedicarboximides caused a change in the reaction site at which the methanol-incorporated addition occurred. Thus, the methanol-incorporated addition of **1** and **2** occurs exclusively at the carbonyl carbon atoms,[3a—e,g,i)] while that of **3**, possessing a more extended arene structures, occurs both at the arene-ring carbon atom and at the carbonyl carbon stom. Whether the carbonyl carbon atom or the arene-ring carbon atom is attacked may depend on the reactivity of the respective carbons in the imide radical anions toward alkyl radicals such as **14** based on the mechanistic scheme shown in Scheme 1. The relative spin density of the respective carbons in the imide radical anions calculated by the McLachlan method[10)] can be used as an index for the reactivity. Of course, other factors such as a steric effect can disturb the reactivity estimated from the spin density.[3i)] The spin density of the respective carbons in the radical anions of phthalimide (**18**), 1,2-naphthalenedicarboximide (**19**), and 9,10-phenanthrenedicarboximide (**20**), as model compounds for the radical anions of **1**, **2**, and **3**, respectively, is shown in Fig. 2. In a series of the imide radical anions **18**—**20** the values of the spin density of



18 **19** **20**

Fig. 2. Spin density of radical anions of phthalimide (**18**), 1,2-naphthalenedicarboximide (**19**), and 9,10-phenanthrenedicarboximide (**20**) calculated by McLachlan method.

the arene-ring carbon atoms shown with underlines in Fig. 2 increased and those of the carbonyl carbon atoms shown with underlines in Fig. 2 decreased from **18** to **20**, although the difference in the relative spin density is not large. Therefore, the methanol-incorporated addition at the arene-ring carbon atom should be favorable in the photoreaction of **3** with alkenes compared with those of **1** and **2** with alkenes, in accord with the fact that the methanol-incorporated addition at the arene-ring carbon atom was observed only in the reaction of **3**.

Experimental

^{1}H NMR spectra were obtained on a JEOL JNM-GX-270 (270 MHz) instrument. Chemical shifts are reported in ppm (δ) relative to internal $SiMe_4$. IR spectra were determined by use of a Hitachi 260-50 spectrometer. Fluorescence spectra and lifetimes were recorded by a Hitachi 850 spectrophotometer and by a Horiba NAES-1100 time-resolved spectrofluorometer, respectively. Melting points were recorded by using a Yanagimoto micro melting point apparatus and are uncorrected. Microanalyses were performed on a Yanagimoto CHN corder MT-2.

Materials. *N*-Methyl-9,10-phenanthrenedicarboximide (**3**) was prepared and purified as described previously.[4] Alkenes **5a—g** were commercially available and purified by distillation of liquid.

General Procedure for Irradiation and Product Isolation. UV irradiation of **3** (15 mM) with alkenes **5a—g** in 25 ml of N_2 purged acetonitrile–methanol (2/1 v/v) was carried out at ambient temperature with an Eikosha EHB-W-300 high-pressure Hg-lamp through a 1-cm path-length aqueous filter, prepared from 27 g of $CuSO_4\cdot 5H_2O$, 30 g of $NaNO_2$, and 50 ml of concd aqueous ammonia diluted with water to 1000 ml (>400 nm).[11] The reaction was monitored by TLC (Merck, Kieselgel 60 F$_{254}$) analyses and ^{1}H NMR measurements. After evaporation of the solvent, the residue was subjected to column chromatography (Wakogel C-200). Dichloromethane–ether was used as the eluant for the separation of the products.

Irradiation of 3 with 2-Methyl-2-butene (5c). A mixture (2 : 1) of diastereomers of 3-(1,1-dimethyl-2-methoxypropyl)-3-hydroxy-2-methyl-2,3-dihydro-1*H*-dibenz[*e*,*g*]isoindol-1-one (**9c**): mp 172—180 °C: ^{1}H NMR of the major diastereomer δ=0.42 (s, 3H, CMe), 0.99 (d, *J*=6.4 Hz, 3H, CH**Me**), 1.25 (s, 3H, CMe), 3.23 (s, 3H, NMe), 3.45 (s, 3H, OMe), 4.07 (q, *J*=6.4 Hz, 1H, **CH**Me), 6.46 (s, 1H, OH), 7.5—7.8 (m, 4H, Arom H), 8.6—8.8 (m, 3H, Arom H), 9.3—9.4 (m, 1H, Arom H); ^{1}H NMR of the minor diastereomer δ=0.43 (s, 3H, CMe), 1.19 (d, *J*=6.4 Hz, 3H, CH**Me**), 1.25 (s, 3H, CMe), 3.27 (s, 3H, NMe), 3.54 (s, 3H, OMe), 3.97 (q, *J*=6.4 Hz, 1H, **CH**Me), 6.46 (s, 1H, OH), 7.5—7.8 (m, 4H, Arom H), 8.6—9.0 (m, 3H, Arom H), 9.3—9.5 (m, 1H, Arom H); IR (KBr) 3220 (OH), 1666 (lactam), 1438, 1108, 762, 728 cm^{-1}. Found: C, 75.93; H, 7.04; N, 3.67%. Calcd for $C_{23}H_{25}NO_3$: C, 76.00; H, 6.93; N, 3.85%.

A major diastereomer of 3a-(1,1-dimethyl-2-methoxypropyl)-2-methyl-3a,11b-dihydro-1*H*-dibenz[*e*,*g*]isoindol-1,3(2*H*)-dione (**10c**): mp 229—232 °C; ^{1}H NMR δ=0.60 (s, 3H, CMe), 0.95 (s, 3H, CMe), 1.07 (d, *J*=6.3 Hz, 3H, CH**Me**), 2.96 (s, 3H, NMe), 3.12 (s, 3H, OMe), 3.79 (q, *J*=6.3 Hz, 1H, **CH**Me), 5.07 (s, 1H, CHC=O), 7.2—7.5 (m, 5H, Arom H), 7.7—7.9 (m, 3H, Arom H); IR (KBr) 1766 and 1700 (imide), 1448, 1432, 1380, 1118, 750 cm^{-1}. Found: C, 75.75; H, 6.88; N, 3.77%. Calcd for $C_{23}H_{25}NO_3$: C, 76.00; H, 6.93; N, 3.85%.

A minor diastereomer of **10c**: mp 157—160 °C: ^{1}H NMR δ=0.58 (s, 3H, CMe), 1.04 (d, *J*=6.1 Hz, 3H, CH**Me**), 1.31 (s, 3H, CMe), 2.94 (s, 3H, NMe), 3.01 (s, 3H, OMe), 3.26 (q, *J*=6.1 Hz, 1H, **CH**Me), 4.35 (s, 1H, CHC=O), 7.2—7.5 (m, 5H, Arom H), 7.8—8.0 (m, 3H, Arom H); IR (KBr) 1776 and 1706 (imide), 1440, 1386, 1132, 1118, 760 cm^{-1}. Found: C, 75.84; H, 6.70; N, 3.75%. Calcd for $C_{23}H_{25}NO_3$: C, 76.00; H, 6.93; N, 3.85%.

Irradiation of 3 with 2,3-Dimethyl-2-butene (5d). 3-Hydroxy-3-(2-methoxy-1,1,2-trimethylpropyl)-2-methyl-2,3-dihydro-1*H*-dibenz[*e*,*g*]isoindol-1-one (**9d**): mp 178—180 °C; ^{1}H NMR δ=0.55 (s, 3H, CMe), 1.15 (s, 3H, CMe), 1.27 (s, 3H, CMe), 1.37 (s, 3H, CMe), 3.17 (s, 3H, NMe), 3.40 (s, 3H, OMe), 6.42 (s, 1H, OH), 7.6—7.8 (m, 4H, Arom H), 8.68 (d, 1H, Arom H), 8.71 (d, 1H, Arom H), 8.91 (d, 1H, Arom H), 9.40 (d, 1H, Arom H); IR (KBr) 3300 (OH), 1674 (lactam), 1446, 1078, 724 cm^{-1}. Found: C, 76.51; H, 7.06; N, 3.88%. Calcd for $C_{24}H_{27}NO_3$: C, 76.36; H, 7.21; N, 3.71%.

Irradiation of 3 with Styrene (5e). A mixture (1.2 : 1) of diastereomers of 3-hydroxy-3-(2-methoxy-1-phenylethyl)-2-methyl-2,3-dihydro-1*H*-dibenz[*e*,*g*]isoindol-1-one (**9e**): mp 192—197 °C: ^{1}H NMR δ=3.02 (s, 3H, NMe for the minor diastereomer), 3.31 (s, 3H, NMe for the major diastereomer), 3.43 (s, 3H, OMe), 3.60 (s, 3H, OMe), 3.5—3.7 (m, 2H), 3.8—3.9 (m, 2H), 3.9—4.1 (m, 1H), 4.3—4.5 (m, 1H), 4.92 (s, 1H, OH), 6.18 (s, 1H, OH), 6.4—6.6 (m, 2H, Arom H), 6.7—6.9 (m, 4H, Arom H), 6.9—7.2 (m, 3H, Arom H), 7.4—7.9 (m, 8H, Arom H), 8.5—8.8 (m, 7H, Arom H), 9.0—9.1 (m, 2H, Arom H); IR (KBr) 3300 (OH), 1678 (lactam), 1446, 1086, 766, 706 cm^{-1}. Found: C, 78.29; H, 6.01; N, 3.46%. Calcd for $C_{26}H_{23}NO_3$: C, 78.57; H, 5.83; N, 3.52%.

Irradiation of 3 and α-Methylstyrene (5f). A mixture (1.2 : 1) of diastereomers of 3-hydroxy-3-(2-methoxy-1-methyl-1-phenylethyl)-2-methyl-2,3-dihydro-1*H*-dibenz[*e*,*g*]isoindol-1-one (**9f**): mp 184—188 °C; ^{1}H NMR δ=1.53 (s, 6H, 2CMe), 3.12 (s, 3H, NMe for the minor diastereomer), 3.27 (s, 3H, NMe for the major diastereomer), 3.56 (s, 3H, OMe), 3.58 (s, 3H, OMe), 3.63 and 4.35 (ABq, *J*=9.3 Hz, 2H, CH_2), 3.85 and 4.00 (ABq, *J*=9.8 Hz, 2H, CH_2), 5.84 (s, 1H, OH), 6.07 (s, 1H, OH), 6.7—7.8 (m, 18H, Arom H), 8.5—8.7 (m, 5H, Arom H), 8.77 (d, *J*=7.1 Hz, 1H, Arom H), 8.99 (d, *J*=9.0 Hz, 1H, Arom H); IR (KBr) 3300 (OH), 1676 (lactam), 1448, 1374, 762, 696 cm^{-1}. Found: C, 78.99; H, 6.35; N, 3.45%. Calcd for $C_{27}H_{25}NO_3$: C, 78.81; H, 6.12; N, 3.40%.

A mixture (1.2 : 1) of diastereomers of 3a-(2-methoxy-1-methyl-1-phenylethyl)-2-methyl-3a,11b-dihydro-1*H*-dibenz[*e*,*g*]isoindol-1,3(2*H*)-dione (**10f**): mp 242—245 °C; ^{1}H NMR of the major diastereomer δ=1.31 (s, 3H, CMe), 2.90 (s, 3H, NMe), 3.30 (s, 3H, OMe), 3.89 and 4.37 (ABq, *J*=9.5 Hz, 2H, CH_2), 4.74 (s, 1H, CHC=O), 6.8—7.5 (m, 10H, Arom H), 7.62 (d, *J*=7.1 Hz, 1H), 7.84 (d, *J*=6.4 Hz, 1H), 7.92 (d, *J*=8.7 Hz, 1 H); ^{1}H NMR of the minor diastereomer δ=1.73 (s, 3H, CMe), 2.86 (s, 3H, NMe), 3.06 (s, 3H, OMe), 3.33 and 3.72 (ABq, *J*=16.8 Hz, 2H, CH_2), 4.25 (s, 1H, OH), 7.0—7.5 (m, 10H, Arom H), 7.74 (d, *J*=9.0 Hz, 1H, Arom H), 7.80 (d, *J*=7.8 Hz, 1H, Arom H), 7.85 (d, *J*=8.1 Hz, 1H, Arom H); IR (KBr) 1773 and 1698 (imide), 1448, 1382, 1296, 1108 cm^{-1}. Found: C, 78.73; H, 6.03; N, 3.37%. Calcd for $C_{27}H_{25}NO_3$: C, 78.81; H, 6.12; N, 3.40%.

Irradiation of 3 and 1,1-Diphenylethylene (5g). 2,2-Diphenylethyl methyl ether (**11g**) was identical with a sample prepared by irradiation of **5g**, *p*-dicyanobenzene, and phenanthrene (sensitizer) in methanol.[12]

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