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Methanol-Incorporated Photoaddition of *N*-Methyl-1,2-naphthalenedicarboximide with Alkenes and Dienes

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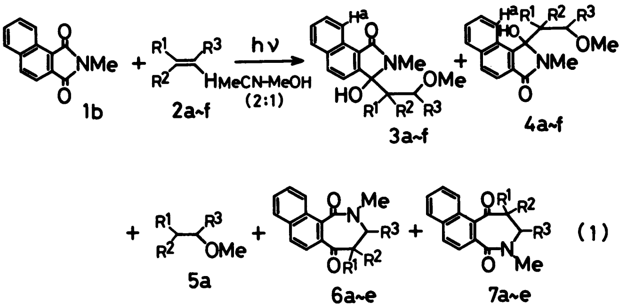
Irradiation of acetonitrile-methanol solutions of *N*-methyl-1,2-naphthalenedicarboximide (**1b**) with 1,1-diphenylethylene gave a methanol-incorporated adduct at a carbonyl carbon atom in **1b** together with 2,2-diphenylethyl methyl ether as a typical electron-transfer photosensitized product. The photoreaction of **1b** with α-methylstyrene, styrene (**2c**), or 2-methyl-2-butene in the same solvent system gave a regio-isomeric pair of a mixture of two diastereomers of methanol-incorporated adducts at carbonyl carbon atoms. The irradiation of **1b** with 2,3-dimethyl-2-butene and ethyl vinyl ether (**2h**) in benzene–methanol afforded methanol-incorporated adducts, although no reaction was observed for irradiation in acetonitrile–methanol. The irradiation of **1b** with 2,5-dimethyl-2,4-hexadiene in acetonitrile–methanol also resulted in the formation of methanol-incorporated adducts. The values of the free-energy change associated with an electron-transfer (ΔG_{et}) from the alkenes to the singlet excited state of **1b** and fluorescence quenching rate constants support the photochemical single-electron-transfer mechanism for the addition. A preferential addition at the carbonyl carbon atom in **1b** as well as that at the more sterically hindered carbonyl carbon atom in the reaction of **1b** with **2c** and **2h** is explainable on the basis of the spin densities of the radical anion of **1b** derived by a photochemical single-electron-transfer.

Recently, photoreactions involving electron-transfer processes have received much attention with regard to both synthetic and mechanistic aspects in organic photochemistry.[1)] During the course of studies on the photochemistry of imides, our and other groups have found a variety of alcohol (solvent)-incorporated intramolecular cyclization[2)] and intermolecular addition products[3)] in the photoreactions of phthalimide-alkene systems, possibly via a single-electron-transfer processes. However, imide compounds employed in the previous investigations have been confined to phthalimides, and only little information has been reported on the effect of the arene structures of arenedicarboximides. Mazzocchi and his co-workers reported that in the photoreaction of *N*-methyl-1,8-naphthalenedicarboximide (**1a**) and α-methylstyrene (**2b**) a methanol-incorporated addition occurred solely at a naphthalene ring carbon atoms.[4)] We have recently reported that in the photolyses of *N*-(3-phenylallyl)arenedicarboximides methanol-incorporated intramolecular cyclization occurs at the carbonyl carbon atom.[5)] Here, we report on the results of the intermolecular photoreaction of *N*-methyl-1,2-naphthalenedicarboximide (**1b**) with alkenes and dienes in solvents containing methanol. The results show that the methanol-incorporated addition generally occurs at the carbonyl carbon atoms, in contrast to the reaction of **1a**. The effect of the arene structure of the imides is discussed on the basis of spin densities in the imide radical anions derived by the photochemical single-electron-transfer.

We have already reported the photoreactions of **1b** and alkenes in benzene.[6)] The predominant reaction in benzene was an insertion of the alkene into C(=O)–N bonds of **1b**, in contrast to the fact that the predominant photoreactions of **1a** and its 2,3-isomer were cyclobutane[6a,7)] and oxetane formation,[6a)] respectively.

Results and Discussion

Irradiation (>320 nm) of a mixture of **1b** and 1,1-diphenylethylene (**2a**) in N_2-purged acetonitrile–methanol (2/1 v/v) gave a methanol-incorporated adduct at the carbonyl carbon atom (**3a**), 2,2-diphenylethyl methyl ether (**5a**), and two naphthoazepinediones (**6a** and **7a**) (Eq. 1 and Table 1). The last two products (**6a** and **7a**) are the main products obtained in the photolysis of **1b** and **2a** in benzene and are formed by the insertion of **2a** into C(=O)–N bonds of **1b**.[6b)] Other examples of the photoreactions of **1b** with alkenes (**2b**—**f**) are summarized in Table 1, which indicates that the methanol-incorporated addition to the carbonyl carbon atoms is characteristic of the reactions of **1b** with some ethylenes substituted by a phenyl group, **2b** and styrene (**2c**), and with an ethylene substituted by three alkyl groups, 2-methyl-2-butene (**2f**). No reaction was observed in the photolysis of **1b** with 1-hexene (**2d**), an ethylene substituted by one alkyl group. Only an insertion to give **6e** and **7e** was observed in the reaction with 2-

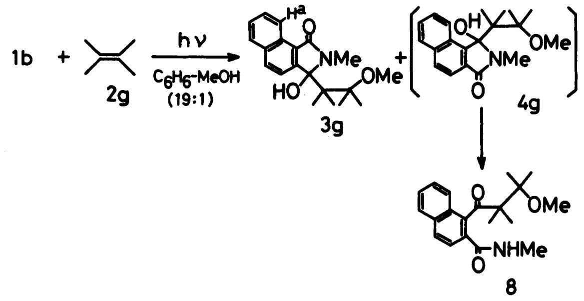


(1)

methylpropene (**2e**).[6e)] The result shows that **1b** is less reactive toward a methanol-incorporated addition than *N*-methylphthalimide (**1c**) since irradiation of **1c** with **2e** gave the methanol-incorporated adduct together with the insertion product.[3d)]

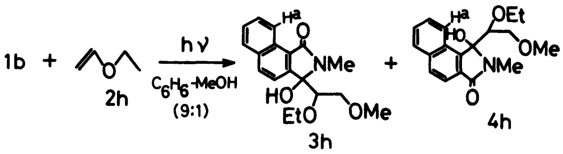
In the reaction with **2b**, **2c**, or **2f** a regioisomeric pair of a mixture of two diastereomers of the methanol-incorporated adduct (**3b,c,f** and **4b,c,f**) was obtained, although in the reaction with **2a** one of the regioisomers (**4a**) could not be isolated in a pure form because of the trace amount. The structures of the adducts are supported by a spectral resemblance to the benzo analogues obtained by the photoreactions of **1c**.[3d)] The regiochemistry of the adducts shown in the structural formulas are deduced from the chemical shift of an aromatic proton H^a which was observed as ortho- and meta-coupled double doublets. The H^a protons in **3f** was observed in a lower field region (δ=9.18, 9.35) than those in **4f** (δ=8.62, 8.79) and the difference in chemical shift was 0.39—0.73 ppm. The molecular model examination indicates that the H^a proton in **3f** should be deshielded by the proximate lactam carbonyl group. This analysis is applicable to determination of the regiochemistry of the isomeric pairs of adducts having phenyl substituents (**3a—c** and **4b,c**), in which slight higher field shift of H^a protons compared with those in **3f** and **4f** is observed possibly due to the shielding effect of the phenyl substituent: H^a protons in **3a—c** and **4b,c** appear at δ=8.78—9.08 and at δ=8.36—8.52, respectively, and the difference in chemical shift is 0.26—0.72 ppm.

In the irradiation of **1b** (19 mM†) and 2,3-dimethyl-2-butene (**2g**, 480 mM), an ethylene substituted by four alkyl groups, in acetonitrile-methanol (2/1 v/v) no reaction was observed (at least with respect to conversion of **1b**). However, irradiation in benzene-methanol (19/1 v/v), a less-polar solvent, gave a methanol-incorporated adduct (**3g**, 32%) and **8** (14%) (Scheme 1). The keto amide structure of **8** was assigned on the basis of the spectral data: ^{1}H NMR δ=2.90 (d, NH*Me*, coalesced to a singlet after D_2O exchange), 6.10 (br s, NH, disappeared after the D_2O exchange); IR 1678 (ketone), 1646 (amide) cm^{-1}. The regiochemistry shown in the structural formula was tentatively assigned on the basis of the assumption that **8** was derived by a ring-opening reaction which accompanied the hydrogen-migration of the initially formed **4g** (Scheme 1); it was not isolated in this system although both of the regioisomers were obtained in the other reaction systems (such as in the reaction with **2f**). Such a ring-opening reaction was reported to occur in the photoreaction of **1c** with **2g**.[3b)]



Scheme 1.

A similar solvent effect to reactions with **2g** was observed in reactions with ethyl vinyl ether (**2h**). No reaction was observed during irradiation in acetonitrile-methanol (2:1 v/v), but irradiation of **1b** (19 mM) and **2h** (560 mM) in benzene-methanol (9/1 v/v) gave methanol-incorporated adducts (**3h**, 26% and **4h**, 34%) (Eq. 2). An addition at the more sterically hindered carbonyl carbon atom in **1b** predominated, as in the reaction with **2c**.



(2)

Table 1. Yields of Photoproducts from *N*-Methyl-1,2-naphthalenedicarboximide (**1b**) and Alkenes **2a**—**f** in Acetonitrile-Methanol (2/1 v/v)[a)]

R^1	R^2	R^3	**2**	[2]/mM	Yield[b)]/% **3**	**4**	**5**	**6**	**7**
Ph	Ph	H	**2a**	152	**3a** 70	**4a** 13	**5a** 105	**6a** 10	**7a** 5
Ph	Me	H	**2b**	340	**3b** 38	**4b** 26	—	—	—
Ph	H	H	**2c**	385	**3c** 27	**4c** 36	—	—	—
Bu	H	H	**2d**	476	**3d** 0	**4d** 0	—	**6d** 0	**7d** 0
Me	Me	H	**2e**	714	**3e** 0	**4e** 0	—	**6e** 56	**7e** 42
Me	Me	Me	**2f**	571	**3f** 31	**4f** 25	—	—	—

a) Reaction conditions: [**1b**]=19 mM. b) Yields were based on consumed **1b**.

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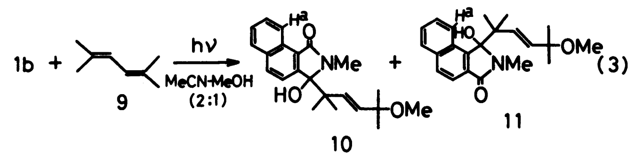
† 1 M=1 mol dm^{-3}.

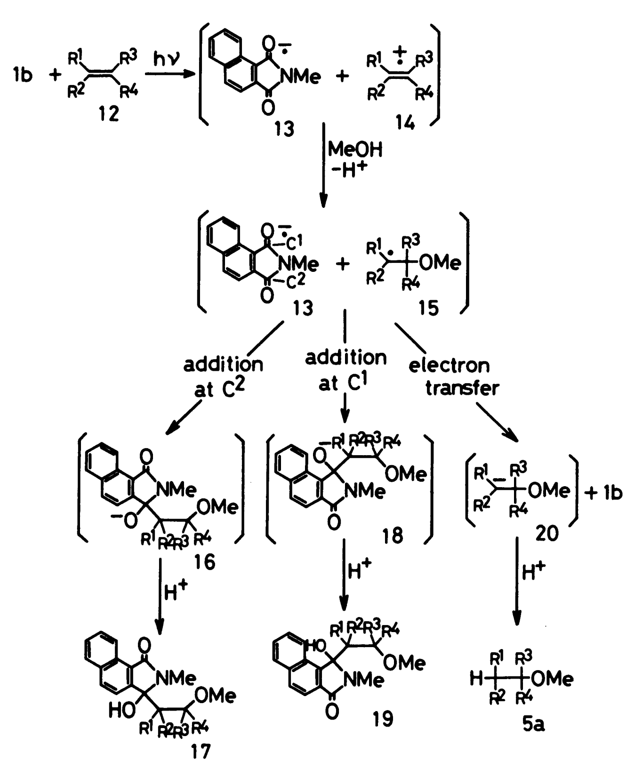
As for the reaction with dienes, photoreaction with 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, poorly alkyl substituted dienes, in acetonitrile–methanol (2/1 v/v) gave no methanol-incorporated adducts, but the irradiation of **1b** (19 mM) with 2,5-dimethyl-2,4-hexadiene (**9**, 360 mM) gave methanol-incorporated adducts (**10**, 43% and **11**, 27%) (Eq. 3). The trans-configurations of the aliphatic double bonds in **10** and **11** were assigned on the basis of the large coupling constants between the vinyl hydrogens (16.7 and 16.8 Hz, respectively). This reaction is the first example of an alcohol-incorporated addition of diene to arenedicarboximide.



A possible mechanism which can be used to interpret the general feature of the methanol-incorporated addition is shown in Scheme 2, in which alkenes are denoted as **12**. The initial step of the reaction is a single-electron-transfer from **12** to the singlet excited state of **1b**. The approximate values of the free-energy change associated with the electron-transfer (ΔG_{et}) can be estimated[8] by using

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

In this equation $E(D/D^{+})$ is the oxidation potential of the alkenes, $E(A^{-}/A)$ is the reduction potential of **1b**, and $\Delta E_{0,0}$ is the singlet excitation energy of **1b**. With these values, we can calculate the ΔG_{et} values for reactions with **2a,d—g** (Table 2). This table shows that the methanol-incorporated addition occurs only in the cases having negative ΔG_{et} values as expected from the electron-transfer mechanism.



Scheme 2.

An addition of alkenes (**2e—g**) to air-saturated acetonitrile solutions of **1b** (1×10^{-5} M) resulted in a reduction of the fluorescence of **1b** without varying the shape and the position of the emission. Stern-Volmer plots of the fluorescence quenching by **2e—g** gave straight lines against concentration of **2e—g**. Fluorescence quenching rate constants (k_q) in acetonitrile calculated from the Stern-Volmer slopes ($k_q\tau$) using the lifetime of the fluorescence of **1b**, 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 obtained in quenching by **2f** and **2g** in acetonitrile and by **2g** in benzene may also support the electron-transfer mechanism.

Concerning the electron-transfer mechanism, the by-product **5a** in the reaction with **2a** could be one of the typical electron-transfer photosensitized products,

Table 2. Calculated Free Energy Changes (ΔG_{et}) Associated with Electron Transfer from Alkenes **2a, d—g** to the Singlet Excited State of *N*-Methyl-1,2-naphthalenedicarboximide (**1b**)

Alkenes	$E(D/D^{+})$/V	ΔG_{et}[a)]/kJ mol^{-1}
2a	1.48[b)]	−56.4
2d	2.64[c)]	+55.4
2e	2.39[c)]	+31.3
2f	1.79[c)]	−26.5
2g	1.63[c)]	−42.0

a) Calculated by Eq. 4: $E(A^{-}/A) = -1.13$ V (in 0.5 M Et_4NClO_4/acetonitrile vs. Ag/0.01 M $AgClO_4$) from Ref. 7, $\Delta E_{0,0} = 308$ kJ mol^{-1} from Ref. 6b. b) Ref. 9. c) Ref. 3b.

Table 3. Fluorescence Quenching Rate Constants (k_q) for *N*-Methyl-1,2-naphthalenedicarboximide (**1b**) and Alkenes **2d, e—g** Systems[a)]

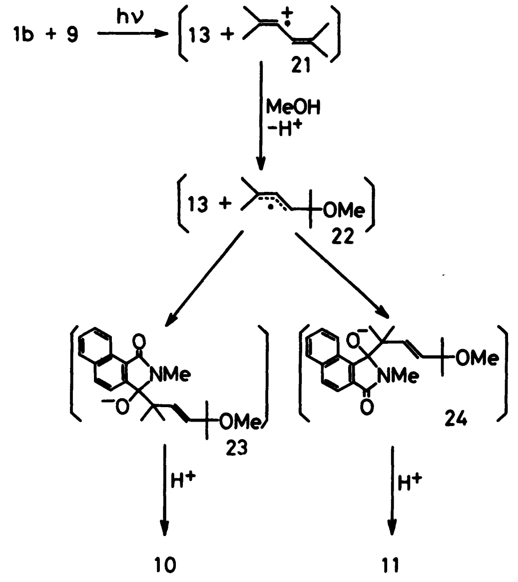
Alkenes	$k_q\tau$[b)] dm^3 mol^{-1}	k_q[c)] dm^3 mol^{-1} s^{-1}	k_q[d)] dm^3 mol^{-1} s^{-1}
2d	0	0	0
2e	0.39	7.13×10^{6}	5.5×10^{6}
2f	48.7	8.90×10^{8}	6.1×10^{7}
2g	600	1.10×10^{10}	2.8×10^{9}

a) Conditions: $[\mathbf{1b}] = 1\times10^{-5}$ mol dm^{-3}, at 25 °C, in air-saturated acetonitrile. b) Stern-Volmer slopes for the flnorescence quenching. c) Calculated from $k_q\tau$ using the lifetime ($\tau = 54.7$ ns) of the fluorescence of **1b**. d) In air-saturated benzene from Ref. 6b.

as reported by Arnold and his co-workers.[10] The electron-transfer photosensitized addition of methanol to **2a** giving **5a** and the methanol-incorporated addition of **2a** to **1b** giving **17** and **19** appear to be closely related processes via common intermediates (**13**+**15**). A combination reaction of the two components at the carbonyl carbon atoms (C^2 and C^1) of **1b** results in the formation of **17** and **19**, and the back electron-transfer from **13** to **15** results in the formation of **1b** and **5a** (Scheme 2).

A similar electron-transfer mechanism (Scheme 3) can be used to interpret the methanol-incorporated addition of **9** to **1b**. The addition of methanol to the radical cation **21** to give a radical **22** and a radical coupling at the tertiary carbon atom of **22** has already been reported.[11]

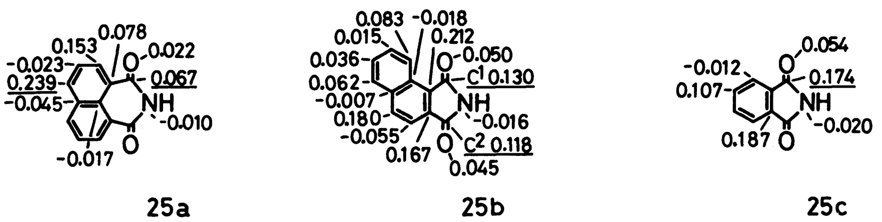
In the reaction with **2g** and **2h** peculiar solvent effects were observed. Thus, in a polar solvent system, acetonitrile–methanol (2/1 v/v), **1b** did not change upon irradiation, but in nonpolar solvent systems, benzene–methanol, an methanol-incorporated addition was observed. These results may be interpreted on the basis of an inclusion of different reaction intermediates. There is significant interest in the mechanism of reactions proceeded by a single-electron-transfer, particularly with respect to whether contact ion pairs and solvent separated ion pairs are involved.[1b,12] Solvent-separated ion pairs should be formed in a polar solvent if a sufficient electron-transfer could occur. Thus, in reactions with electron-donating alkenes such as **2g** and **2h** the solvent separated ion pair of **13** and **14** (Scheme 2) may be formed in a polar solvent and may reproduce **1b** by reaction pathways other than the methanol-incorporated addition, and the methanol-incorporated addition may arise only from the contact ion pair formed in nonpolar solvent.



Scheme 3.

It should be emphasized here that the variation of the imide ring size caused a remarkable change in the reaction. Thus, a methanol-incorporated addition of **1b** as well as **1c**, possessing a five-membered imide ring, occurs exclusively at the carbonyl carbon atoms, while that of **1a**, possessing six-membered imide ring, occurs at the naphthalene ring carbon atom.[4] Whether the carbonyl carbon atom is attacked or the naphthalene ring carbon atom is attacked may depend on the reactivity of the respective carbon in the imide radical anion toward alkyl radicals such as **15** (Scheme 2). The relative spin density in the imide radical anion can be used as an index for the reactivity. The spin density of radical anions of 1,8-naphthalenedicarboximide (**25a**),[13] 1,2-naphthalenedicarboximide (**25b**),[5] and phthalimide (**25c**)[13] calculated by McLachlan method[14] as model compounds for radical anions of **1a**, **1b**, and **1c**, respectively, is shown in Fig. 1. That the spin density at the carbonyl carbon atom in **25a** is remarkably low compared with that at the naphthalene ring C^4 carbon atom in **25a** as well as that at the carbonyl carbon atom in **25b** and **25c** may support the preferential methanol-incorporated addition at the naphthalene ring carbon atom observed in the photoreaction of **1a**. The result that the spin density distribution in **25b** is similar to that in **25c** might account for the similar photoreaction pattern of **1b** and **1c**.

Another problem related to the spin density is which of the two types of carbonyl carbon atoms in **1b** is attacked during the methanol-incorporated addition. The spin density at the C^1 carbonyl carbon atom in a radical anion of **25b** is relatively high compared



25a 25b 25c

Fig. 1. Spin density of radical anions of 1,8-naphthalenedicarboximide (**25a**), 1,2-naphthalenedicarboximide (**25b**), and phthalimide (**25c**) calculated by McLachlan method.

with that at the C^2 carbon atom, although the difference in the spin density is not so large. Therefore, an addition at the C^1 carbon atom should be favorable to some extent. Since the C^1 carbonyl carbon atom is essentially more sterically hindered than the C^2 atom, the result that in the photolysis of **1b** with **2c** the yield of the products **4c** from the addition at the C^1 carbonyl carbon atom is larger than that of the products **3c** from the addition at C^2 atom may reflect the inherent preference of the addition at the C^1 atom because of the high spin density. A similar preference regarding an addition at the C^1 carbonyl carbon atom was observed in a reaction with **2h**, which was also an ethylene having only one substituent. In a series of reactions with **2c**, **2b**, and **2a**, the ratio of the products from the addition at the C^1 carbonyl carbon atom to those from the addition at the C^2 atom decreased in that order, probably due to a steric effect of the substituent of the alkenes on the addition.

Experimental

The mps were measured by a Yanagimoto micromelting-point apparatus and are uncorrected. ^{1}H NMR spectra were determined on a JEOL JNM-MH-100 (100 MHz) in $CDCl_3$ solution. IR spectra were obtained with a Hitachi 260-50 spectrophotometer. Mass spectra were measured on a JEOL JMS-DX-300 apparatus. Fluorescence spectra and the lifetimes were recorded by a Hitachi 850 spectrophotometer and a HORIBA NAES-1100 time-resolved spectrofluorometer, respectively. Microanalyses were performed on a Yanagimoto CHN corder MT-2.

Materials. *N*-Methylnaphthalene-1,2-dicarboximide (**1b**) was prepared and purified as described previously.[6b] Alkenes (**2a**—**h**) and dienes (**9**, 1,3-butadiene, and 2,3-dimethyl-1,3-butadiene) were commercially available and purified by distillation for liquid materials.

General Procedure for Irradiation and Product Isolation. Unless otherwise noted, UV irradiation of **1b** (19 mM) with alkenes (**2a**—**h**) and dienes (**9**, 1,3-butadiene, and 2,3-dimethyl-1,3-butadiene) in 25 ml of N_2 purged acetonitrile-methanol (2/1 v/v) was carried out with an Eikosha EHB-W-300 high-pressure Hg-lamp through aq $CuSO_4$ filter about 1 cm in thickness (>320 nm) at ambient temperature. The reaction was monitored by TLC (Merk, Kieselgel 60 F_{254}) analyses and ^{1}H NMR measurements. After an 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. Yields were determined by measurement of the weight of the isolated products.

Irradiation of 1b and 1,1-Diphenylethylene (2a). 2,2-Diphenylethyl methyl ether (**5a**) was identical with a sample prepared by irradiation of **2a**, *p*-dicyanobenzene, and phenanthrene (sensitizer) in methanol.[15]

3-(1,1-Diphenyl-2-methoxyethyl)-3-hydroxy-2-methyl-2,3-dihydro-1*H*-benz[*e*]isoindol-1-one (**3a**): Mp 182—185 °C; ^{1}H NMR δ=2.93 (s, 3H, NMe), 3.23 (s, 3H, OMe), 4.31 and 4.62 (ABq, J=11 Hz, 2H, CH_2), 5.78 (s, 1H, OH), 6.8—7.9 (m, 15H, Arom H), 8.79 (dd, 1H, H^a); IR (KBr) 3250 (OH), 1665 (lactam), 1428, 1108, 712 cm^{-1}. Found: C, 79.65; H, 6.03; N, 3.41%; M^+-H_2O, 405. Calcd for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31%; $M-H_2O$, 405.

Irradiation of 1b and α-Methylstyrene (2b). A mixture of diastereomers of 3-hydroxy-3-(2-methoxy-1-methyl-1-phenylethyl)-2-methyl-2,3-dihydro-1*H*-benz[*e*]isoindol-1-one (**3b**): Mp 166—172 °C; ^{1}H NMR of one diastereomer δ=1.20 (s, 3H, CMe), 2.88 (s, 3H, NMe), 3.33 (s, 3H, OMe), 3.74 and 3.93 (ABq, 2H, CH_2), 6.43 (s, 1H, OH), 7.1—8.0 (m, 10H, Arom H), 9.08 (dd, 1H, H^a); ^{1}H NMR of another diastereomer δ=1.37 (s, 3H, CMe), 2.60 (s, 3H, NMe), 3.37 (s, 3H, OMe), 3.80 (s, 2H, CH_2), 6.35 (s, 1H, OH), 7.1—8.0 (m, 10H, Arom H), 9.04 (dd, 1H, H^a); IR (KBr) 3300 (OH), 1662 (lactam), 1448, 1382, 1108, 702 cm^{-1}. Found: C, 76.63; H, 6.56; N, 3.96%; M^+-H_2O, 343. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88%; $M-H_2O$, 343.

A mixture of diastereomers of 1-hydroxy-1-(2-methoxy-1-methyl-1-phenylethyl)-2-methyl-1,2-dihydro-3*H*-benz[*e*]isoindol-3-one (**4b**): Mp 158—160 °C; ^{1}H NMR of one diastereomer δ=1.18 (s, 3H, CMe), 2.85 (s, 3H, NMe), 3.37 (s, 3H, OMe), 3.65 and 4.05 (ABq, 2H, CH_2), 5.85 (s, 1H, OH), 7.8—8.0 (m, 10H, Arom H), 8.39 (dd, 1H, H^a); ^{1}H NMR of another diastereomer δ=1.48 (s, 3H, CMe), 2.77 (s, 3H, NMe), 3.37 (s, 3H, OMe), 3.72 (s, 2H, CH_2), 5.82 (s, 1H, OH), 7.8—8.0 (m, 10H, Arom H), 8.36 (dd, 1H, H^a); IR (KBr) 3310 (OH), 1692 (lactam), 1461, 1386, 1106, 702 cm^{-1}. Found: C, 76.64; H, 6.52; N, 3.93%; M^+-H_2O, 343. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88%; $M-H_2O$, 343.

Irradiation of 1b and Styrene (2c). A mixture of diastereomers of 3-hydroxy-3-(2-methoxy-1-phenylethyl)-2-methyl-2,3-dihydro-1*H*-benz[*e*]isoindol-1-one (**3c**): Mp 153—161 °C; ^{1}H NMR of one diastereomer δ=2.85 (s, 3H, NMe), 3.42 (s, 3H, OMe), 3.4—4.0 (m, 2H), 4.1—4.3 (m, 1H), 5.21 (s, 1H, OH), 6.4—8.1 (m, 10H, Arom H), 8.83 (dd, 1H, H^a); ^{1}H NMR of another diastereomer δ=3.06 (s, 3H, NMe), 3.21 (s, 3H, OMe), 3.4—4.0 (m, 3H), 5.21 (s, 1H, OH), 6.4—8.1 (m, 10H, Arom H), 8.78 (dd, 1H, H^a); IR (KBr) 3320 (OH), 1680 (lactam), 1424, 1384, 1120, 760, 702 cm^{-1}. Found: C, 76.25; H, 6.18; N, 4.11%; M^+-H_2O, 329. Calcd for $C_{22}H_{21}NO_3$: C, 76.06; H, 6.09; N, 4.03%; $M-H_2O$, 329.

A mixture of diastereomers of 1-hydroxy-1-(2-methoxy-1-phenylethyl)-2-methyl-1,2-dihydro-3*H*-benz[*e*]isoindol-3-one (**4c**): Mp 146—152 °C; ^{1}H NMR of one diastereomer δ=3.26 (s, 3H, NMe), 3.50 (s, 3H, OMe), 3.5—4.4 (m, 3H), 6.15 (s, 1H, OH), 6.4—8.1 (m, 10H, Arom H), 8.52 (dd, 1H, H^a); ^{1}H NMR of another diastereomer δ=2.89 (s, 3H, NMe), 3.32 (s, 3H, OMe), 3.5—4.4 (m, 3H), 6.18 (s, 1H, OH), 6.4—8.1 (m, 10H, Arom H), 8.52 (dd, 1H, H^a); IR (KBr) 3300 (OH), 1680 (lactam), 1424, 1384, 1118, 760, 702 cm^{-1}. Found: C, 76.30; H, 6.27; N, 4.14%; M^+-H_2O, 329. Calcd for $C_{22}H_{21}NO_3$: C, 76.06; H, 6.09; N, 4.03%; $M-H_2O$, 329.

Irradiation of 1b and 2-Methyl-2-butene (2f). A mixture of diastereomers of 3-(1,1-dimethyl-2-methoxypropyl)-3-hydroxy-2-methyl-2,3-dihydro-1*H*-benz[*e*]isoindol-1-one (**3f**): Mp 148—151 °C; ^{1}H NMR of one diastereomer δ=0.52 (s, 3H, CMe), 1.18 (d, 3H, CH*Me*), 1.36 (s, 3H, CMe), 3.14 (s, 3H, NMe), 3.47 (s, 3H, OMe), 3.89 (q, 1H, C*H*Me), 6.28 (s, 1H, OH), 7.2—8.2 (m, 5H, Arom H), 9.35 (dd, 1H, H^a); ^{1}H NMR of another diastereomer δ=0.57 (s, 3H, CMe), 1.08 (d, 3H, CH*Me*), 1.25 (s, 3H, CMe), 3.09 (s, 3H, NMe), 3.30 (s, 3H, OMe), 3.75 (q, 1H, C*H*Me), 5.67 (s, 1H, OH), 7.4—8.18

(m, 5H, Arom H), 9.18 (dd, 1H, H^a); IR (KBr) 3280 (OH), 1694 (lactam), 1462, 1428, 1392, 1104 cm^{-1}. Found: C, 72.95; H, 7.54; N, 4.51%; M$^+$−H$_2$O, 295. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47%; M−H$_2$O, 295.

A mixture of diastereomers of 1-(1,1-dimethyl-2-methoxypropyl)-1-hydroxy-2-methyl-1,2-dihydro-3*H*-benz[*e*]-isoindol-3-one (**4f**): Mp 145—148 °C; ^{1}H NMR of one diastereomer δ=0.40 (s, 3H, CMe), 1.18 (d, 3H, CH*Me*), 1.27 (s, 3H, CMe), 3.22 (s, 3H, NMe), 3.52 (s, 3H, OMe), 3.95 (q, 1H, C*H*Me), 7.17 (s, 1H, OH), 7.5—8.1 (m, 5H, Arom H), 8.79 (dd, 1H, H^a); ^{1}H NMR of another diastereomer δ=0.49 (s, 3H, CMe), 0.99 (d, 3H, CH*Me*), 1.22 (s, 3H, CMe), 3.17 (s, 3H, NMe), 3.32 (s, 3H, OMe), 3.89 (q, 1H, C*H*Me), 6.71 (s, 1H, OH), 7.5—8.2 (m, 5H, Arom H), 8.62 (dd, 1H, H^a); IR (KBr) 3280 (OH), 1694 (lactam), 1376, 1122, 1102, 758 cm^{-1}. Found: C, 72.97; H, 7.54; N, 4.51%; M$^+$−H$_2$O, 295. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47%; M−H$_2$O, 295.

Irradiation of 1b and 2,3-Dimethyl-2-butene (2g). 3-Hydroxy-3-(2-methoxy-1,1,2-trimethylpropyl)-2-methyl-2,3-dihydro-1*H*-benz[*e*]isoindol-1-one (**3g**): Mp 158—161 °C; ^{1}H NMR δ=0.97 (s, 3H, CMe), 1.07 (s, 6H, CMe), 1.22 (s, 3H, CMe), 3.05 (s, 3H, NMe), 3.10 (s, 3H, OMe), 4.85 (s, 1H, OH), 7.6—8.0 (m, 5H, Arom H), 9.25 (dd, 1H, H^a); IR (KBr) 3280 (OH), 1666 (lactam), 1394, 1060, 800 cm^{-1}. Found: C, 73.54; H, 7.83; N, 4.33%; M$^+$−H$_2$O, 309. Calcd for $C_{20}H_{25}NO_3$: C, 73.36; H, 7.70; N, 4.28%; M−H$_2$O, 309.

N-Methyl-1-(3-methoxy-1-oxo-2,2,3-trimethylbutyl)-2-naphthalenecarboxamide (**8**): Mp 200—202 °C; ^{1}H NMR δ=1.12 (s, 3H, CMe), 1.19 (s, 3H, CMe), 1.26 (s, 3H, CMe), 1.38 (s, 3H, CMe), 2.90 (d, 3H, NH*Me*), 3.15 (s, 3H, OMe), 6.10 (br s, 1H, NH), 7.4—8.0 (m, 6H, Arom H); IR (KBr) 3380 (NH), 1678 (ketone), 1646 (amide), 1538, 1298, 1058, 762 cm^{-1}. Found:C, 73.51; H, 7.82; N, 4.31%; M$^+$, 327. Calcd for $C_{20}H_{25}NO_3$:C, 73.36; H, 7.70; N, 4.28%; M, 327.

Irradiation of 1b and Ethyl Vinyl Ether (2h). A mixture of diastereomers of 3-(1-ethoxy-2-methoxyethyl)-3-hydroxy-2-methyl-2,3-dihydro-1*H*-benz[*e*]isoindol-1-one (**3h**): Mp 155—158 °C; ^{1}H NMR of one diastereomer δ=1.29 (t, 3H, OCH$_2$*Me*), 2.99 (s, 3H, NMe), 3.11 (s, 3H, OMe), 2.9—3.5 (m, 2H), 3.6—4.2 (m, 3H), 5.53 (s, 1H, OH), 7.4—8.1 (m, 5H, Arom H), 9.07 (dd, 1H, H^a); ^{1}H NMR of another diastereomer δ=1.23 (t, 3H, OCH$_2$*Me*), 3.02 (s, 3H, NMe), 3.09 (s, 3H, OMe), 2.9—3.5 (m, 2H), 3.6—4.2 (m, 3H), 5.50 (s, 1H, OH), 7.4—8.1 (m, 5H, Arom H), 9.00 (dd, 1H, H^a); IR (KBr) 3320 (OH), 1665 (lactam), 1130, 1114, 702 cm^{-1}. Found: C, 68.62; H, 6.63; N, 4.54%; M$^+$−H$_2$O, 297. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44%; M−H$_2$O, 297.

One of the diastereomers of 1-(1-ethoxy-2-methoxyethyl)-1-hydroxy-2-methyl-1,2-dihydro-3*H*-benz[*e*]isoindol-3-one (**4h**): Mp 176—177 °C; ^{1}H NMR δ=1.41 (t, 3H, OCH$_2$*Me*), 2.96 (s, 3H, NMe), 3.11 (s, 3H, OMe), 2.7—3.4 (m, 2H), 3.6—4.2 (m, 2H), 4.45 (dd, 1H, CH), 4.82 (s, 1H, OH), 7.6—8.1 (m, 5H, Arom H), 8.35 (dd, 1H, H^a); IR (KBr) 3280 (OH), 1681 (lactam), 1428, 1392, 1115, 768 cm^{-1}. Found: C, 68.62; H, 6.88; N, 4.43%; M$^+$−H$_2$O, 297. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44%; M−H$_2$O, 297.

Another of the diastereomers of 1-(1-ethoxy-2-methoxyethyl)-1-hydroxy-2-methyl-1,2-dihydro-3*H*-benz[*e*]-isoindol-3-one (**4h**): Mp 136—139 °C; ^{1}H NMR δ=0.95 (t, 3H, OCH$_2$*Me*), 2.90 (s, 3H, NMe), 3.11 (s, 3H, OMe), 2.8—3.7 (m, 4H), 4.08 (dd, 1H, CH), 5.14 (s, 1H, OH), 7.3—8.0 (m, 5H, Arom H), 8.66 (dd, 1H, H^a); IR (KBr) 3280 (OH), 1682 (lactam), 1422, 1103, 1062, 702 cm^{-1}. Found: C, 68.72; H, 6.98; N, 4.51%; M$^+$−H$_2$O, 297. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44%; M−H$_2$O, 297.

Irradiation of 1b and 2,5-Dimethyl-2,4-hexadiene (9). 3-Hydroxy-3-(4-methoxy-1,1,4-trimethyl-2-pentenyl)-2-methyl-2,3-dihydro-1*H*-benz[*e*]isoindol-1-one (**10**): Mp 176—178 °C; ^{1}H NMR δ=0.98 (s, 3H, CMe), 1.15 (s, 3H, CMe), 1.21 (s, 3H, CMe), 1.24 (s, 3H, CMe), 2.77 (s, 3H, NMe), 3.06 (s, 3H, OMe), 3.52 (s, 1H, OH), 5.35 and 6.09 (ABq, *J*=16.8 Hz, 2H, CH=CH), 7.4—8.0 (m, 5H, Arom H), 9.11 (dd, 1H, H^a); IR (KBr) 3320 (OH), 1662 (lactam), 1424, 1380, 1068, 768 cm^{-1}. Found: C, 74.81; H, 7.83; N, 4.03%; M$^+$−H$_2$O, 335. Calcd for $C_{22}H_{27}NO_3$: C, 74.75; H, 7.70; N, 3.96%; M−H$_2$O, 335.

1-Hydroxy-1-(4-methoxy-1,1,4-trimethyl-2-pentenyl)-2-methyl-1,2-dihydro-3*H*-benz[*e*]isoindol-1-one (**11**): Mp 139—142 °C; ^{1}H NMR δ=0.88 (s, 3H, CMe), 1.09 (s, 6H, CMe), 1.14 (s, 3H, CMe), 2.79 (s, 3H, NMe), 2.97 (s, 3H, OMe), 4.46 (s, 1H, OH), 5.20 and 5.87 (ABq, *J*=16.7 Hz, 2H, CH=CH), 7.3—8.0 (m, 5H, Arom H), 8.58 (dd, 1H, H^a); IR (KBr) 3270 (OH), 1668 (lactam), 1422, 1384, 1070, 763 cm^{-1}. Found: C, 74.97; H, 7.84; N, 4.04%; M$^+$−H$_2$O, 335. Calcd for $C_{22}H_{27}NO_3$: C, 74.75; H, 7.70; N, 3.96%; M−H$_2$O, 335.

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