units, 6 μmol) was adjusted to 4.0 with 10% HOAc. The solution was incubated at 37 °C for 5 h, neutralized with 5% NH_4OH, and then applied to a column (1 × 20 cm) of DEAE-Sephadex A-25 which was eluted with a linear gradient of 0.1–0.4 M triethylammonium bicarbonate buffer (pH 7.6, 250 and 250 mL). From a total of 82 fractions, numbers 47–58 were pooled and evaporated to dryness in vacuo. After several additions and evaporations of water, the residue was dissolved in CH_3OH (200 μL) and poured into a solution of sodium iodide in acetone (0.1 M, 4 mL). The resulting white precipitating was centrifuged down and washed several times with acetone. After in vacuo drying, pA2′p5′A2′p5′A (**1a**, 203 A_{258} units, 5.88 μmol) was obtained as the sodium salt in a yield of 98%. By HPLC (program 1), the purity of **1a** was 99.9%.

Other trinucleotide 5′-monophosphates were generated in an analogous fashion; thus, hydrolysis of MopA2′p5′A2′p5′(2′dA) (**26**) gave p5′A2′p5′A2′p5′(2′dA) (**28**, 136 A_{258} units, 3.94 μmol, 97% yield), MopI2′p5′A2′p5′A gave p5′I2′p5′A2′p5′A (**3a**, 194 A_{258} units, 98% yield). MopA2′p5′I2′p5′A (**30**) gave p5′A2′p5′I2′p5′A (**4a**, 152 A_{258} units, 98% yield) and MopA2′p5′A2′p5′I (**32**) gave p5′A2′p5′A2′p5′I (**5a**, 128 A_{258} units, 98% yield). HPLC retention times and UV ε values are given in Table II whereas proton and ^{31}P NMR spectra of these products are listed in Tables IV and V.

Preparation of Trinucleotide 5′-Triphosphates. Preparation of ppp5′A2′p5′A2′p5′A (2-5A, 1b). Compound **24** (MopA2′p5′A2′p5′A, triethylammonium salt, 207 A_{258} units, 6 μmol) was dissolved in a solution (200 μL) of tri-*n*-butylammonium pyrophosphate in DMF (0.5 M), and the reaction mixture was kept at room temperature for 3 days. After dilution with H_2O (1 mL), the solution was applied to a DEAE Sephadex A25 column (HCO_3^- form, 1 × 20 cm) which then was eluted with a linear gradient of 0.2–0.56 M triethylammonium bicarbonate (pH 7.6, 250 and 250 mL). From the 82 fractions collected, fractions 53–63 were pooled and reduced to dryness in vacuo. After several additions and evaporations of water, the residue was dissolved in CH_3OH (200 μL) and treated with a solution of sodium iodide in methanol (0.1 M, 4 mL). The resultant white precipitate was centrifuged down, washed with acetone, and dried in vacuo over P_2O_5 for 1 h. In this way, 2-5A (pppA2′p5′A2′p5′A, **1b**, 152 A_{258} units, 4.48 μmol) was obtained in 75% yield. The product had identical TLC and HPLC properties with authentic material and its UV, ^1H, and ^{31}P spectra were also identical with authentic 2-5A.

The other trinucleotide 5′-triphosphates (**2b**, **3b**, **4b**, and **5b**) were synthesized in the same manner from their respective morpholidates. Tables II–IV give pertinent chromatographic and spectral characteristics.

Registry No. **1a** (Na salt), 95314-17-3; **1b**, 65954-93-0; **2a**, 95314-26-4; **2b**, 82137-97-1; **3a**, 95314-27-5; **3b**, 95313-96-5; **4a**, 95314-28-6; **4b**, 95313-97-6; **5a**, 95314-29-7; **5b**, 95313-98-7; **6**, 58-61-7; **7** (Na salt), 60031-83-6; **8**, 2273-76-9; **10** (free acid), 61-19-8; **11a** (triethylammonium salt), 95314-02-6; **11b** (triethylammonium salt), 95314-03-7; **11c** (Na salt), 95313-99-8; **12**, 70062-83-8; **13**, 75074-06-5; **14** (Na salt), 95314-00-4; **15**, 27908-35-6; **16**, 26568-05-8; **17**, 66536-80-9; **18a**, 95314-04-8; **18b**, 95314-10-6; **18c**, 95314-11-7; **19a**, 95314-06-0; **19b**, 95314-09-3; **19c**, 95314-12-8; **20a**, 95314-07-1; **20b**, 95314-08-2; **20c**, 95314-13-9; **21a**, 95314-05-9; **23**, 95314-30-0; **24** (trimethylammonium salt), 95314-15-1; **25**, 95314-16-2; **26**, 95314-18-4; **27**, 95314-22-0; **28**, 95314-19-5; **29**, 95314-23-1; **30**, 95314-20-8; **31**, 95314-24-2; **32**, 95314-21-9; **33**, 95314-25-3; A3′p5′A, 2391-46-0; p5′A3′p5′A2′p5′A, 78983-51-4.

Photochemistry of Phthalimides with Olefins. Solvent-Incorporated Addition vs. Cycloaddition to Imide C(=O)—N Bond Accompanying Ring Enlargement

Kazuhiro Maruyama

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

Yasuo Kubo*

Department of Chemistry, Faculty of Science, Shimane University, Matsue, Shimane 690, Japan

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The photoreactions of phthalimides **1a–c** and a variety of olefins (**2a–g**) have been investigated. Irradiation of methanol solutions of **1a** in the presence of electron-rich olefins **2a–f** leads to formation of methanol-incorporated adducts **3a** + **4a**, **9a,b**, **19**, **29a,b**, **30a,b**, and **31**. Irradiation of acetonitrile solutions of **1a** in the presence of relatively electron-poor aliphatic olefins **2f,g** gives ring-enlarged cycloaddition products **23**, **32**, and **34**, probably by a mechanism which involves collapse of an exciplex. Photolyses of **1a** and **2a** in less polar alcohols afford the two types of products, simultaneously. With decrease of the solvent polarity, the yields of the solvent-incorporated adducts decrease and that of the ring-enlarged cycloaddition products increase. Irradiation of **1a** and **2c** leads to formation of the other types of products: in methanol **20** is obtained together with **19**, and in acetonitrile **22** and **24** are formed together with **23**. The formation of **24** is rationalized by a mechanism in which degradation of an oxetane (**27**) is involved. The products **20** and **22** appear to be derived through electron transfer from **2c** to the excited state of **1a**. Phenanthrene (electron-transfer) sensitization of the reaction **1a** + **2c** gives **20** and **23** in methanol and **22** in acetonitrile, selectively. These results and ΔG values associated with the electron transfer support an electron-transfer mechanism for the solvent-incorporated adduct formation.

The photochemistry of imides has been the subject of intensive investigations over several years.[1] Concerning the photochemistry of imides with olefins, we found that oxetane formation was the most typical process in the photolyses of alicyclic imides with olefins (eq 1), illustrating its normal $n\pi^*$ carbonyl photoreactivity.[2] On the other hand, photoreactions of phthalimides with olefins are quite different from those of alicyclic imides. On the intramolecular photoreactions of *N*-alkenylphthalimides, the re-

(1) For reviews, see: (a) Mazzocchi, P. H. "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 421. (b) Kanaoka, Y. *Acc. Chem. Res.* **1978**, *11*, 407. (c) Kanaoka, Y. *Yuki Gosei Kagaku Kyokaishi* **1975**, *33*, 989.

(2) (a) Maruyama, K.; Kubo, Y. *J. Org. Chem.* **1977**, *42*, 3215. (b) Maruyama, K.; Ogawa, T.; Kubo, Y. *Chem. Lett.* **1978**, 1107.

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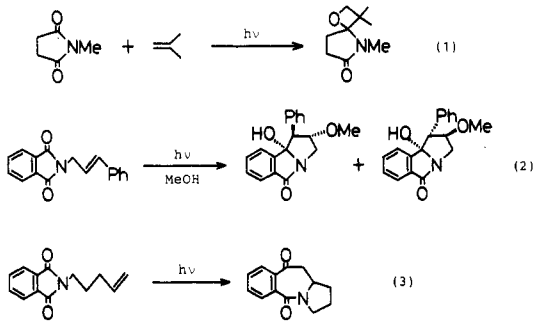


actions are classified mainly into two types. One is solvent (alcohol)-incorporated cyclization and elimination reactions, by pathways which involve intramolecular electron transfer from the olefinic moiety to the excited phthalimide moiety. This sort of the reactions has been found in the photolyses of a wide variety of *N*-alkenylphthalimides involving *N*-2-alkenyl systems (eq 2)[3] and *N*-3- to *N*-12-alkenyl systems.[4] The other is cyclization reactions accompanying C(=O)—N bond cleavage of phthalimide and hence results in ring enlargement to form benzazepinedione derivatives. This type of reaction has been found in the photolysis of *N*-4- and *N*-5-alkenylphthalimides (eq 3).[5]

We previously reported a short paper on the intermolecular photoreactions of phthalimides with olefins.[6] It is the purpose of this paper to describe the full details of the investigations. The results demonstrate that as in the cases of intramolecular reactions olefins undergo mainly two types of reactions; i.e., (i) alcohol-incorporated addition (C–C coupling) reactions by pathways involving electron transfer and (ii) cycloaddition to the C(=O)—N bond of phthalimides accompanying ring enlargement. Other minor reactions involving photo-redox-sensitization and oxetane formation reaction are also observed. We will discuss effects of solvents and structures of olefins in phthalimide–olefin photochemistry.

Results and Discussion

Irradiation of 1a with 2a. A methanol solution of *N*-methylphthalimide (**1a**) (14 mM) and styrene (**2a**) (0.1 M) was irradiated under N_2 for 3 h. Chromatography gave two isomeric products **3a** (40%) and **4a** (34%), together with a complex mixture of hydrocarbons derived probably from **2a**. The yields were based on the consumed imide **1a** during the irradiation. The structures of the products, which were analyzed for $C_{18}H_{19}NO_3$ (**1a** + **2a** + MeOH) by mass spectra and elemental analyses, was assigned on the basis of the spectral data and chemical manipulation (Scheme I).

Each of **3a** and **4a** was easily dehydrated by refluxing with sodium acetate in acetic anhydride to give a respective mixture of **5a** and **6a**. The structures of **5a** and **6a** were assigned by the ^1H NMR, IR, and mass spectra and elemental analyses. Especially, ^1H NMR spectrum of **5a** showed considerably shielded doublet signals (1 H) at δ 6.15 due to one of the ortho-phenyl protons which lay over the fixed benzene ring. Similar effects were observed in alkylidenephthalide systems.[7] Thus, the configuration of

Scheme I

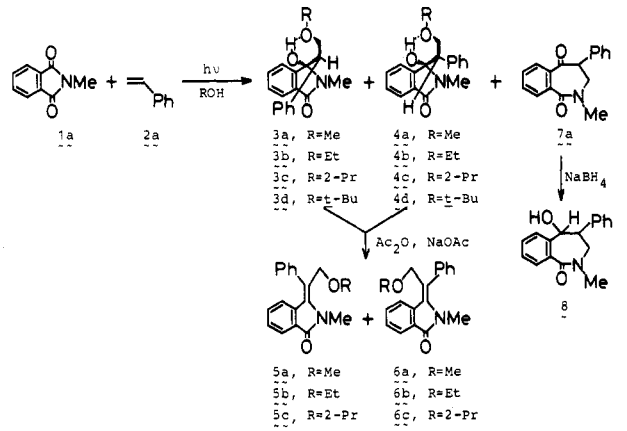


Table I. Photoreaction of *N*-Methylphthalimide (1a) with Styrene (2a) in Alcohols[a]

	R	alcohol	isolated yields,[b] % 3	4	7a
a,	Me	methanol	40	34	
b,	Et	ethanol	38	31	trace
c,	2-Pr	2-propyl alcohol	32	25	18
d,	*t*-Bu	*tert*-butyl alcohol	28	26	30

[a] The alcohol solution of **1a** (14 mM) and **2a** (0.1 M) was irradiated. [b] The yields were based on the amount of imide **1a** consumed. The conversion was 10–15%.

5a was deduced as *Z* as shown in Scheme I. This dehydration clearly demonstrates the presence of the tertiary OH group in the structure of **3a** and **4a**.

Assignment of the stereochemistry of **3a** and **4a** was tentatively made on the basis of the IR spectra and ^1H NMR spectra. The IR spectra of **3a** in carbon tetrachloride solutions show a single amide carbonyl band at 1712 cm^{-1} and a single hydroxy band at 3450 cm^{-1}, presumably due to the intramolecular hydrogen bonding with the ether group [–OH···O(Me)–]. No band shift was observed by concentrating the solution. We already reported that in similar systems free, intramolecular, and intermolecular hydrogen-bonded hydroxy bands appeared at 3580, 3490, and 3300 cm^{-1} and in addition free and intermolecular hydrogen-bonded amide carbonyl bands appeared at 1715 and 1695 cm^{-1}.[3a] These results support the assumption that the intramolecular hydrogen bonding between the hydroxy group and the methoxy group[–OH···O(Me)–] fixes the molecules of **3a** and **4a** in a particular conformation in the solution.

The ^1H NMR spectra of **3a** and **4a** in carbon tetrachloride solutions show OH signals at δ 4.92 and 4.80, similarly due to the intramolecular hydrogen bonding. No shift of these signals was observed by concentrating the solution, and in chloroform-d_1 chemical shifts of the signals were not appreciably altered at δ 5.1–5.3. The most characteristic feature of the ^1H NMR spectra was considerable shielding of the benzene protons observed in that of **3a** at δ 6.3–6.5 (m, 2 H), probably due to the anisotropic shielding effect from the eclipsing benzene rings. No such high-field shift of benzene protons was observed in the spectrum of **4a**. The result combined with the assumption of intramolecular hydrogen bonding supports the stereochemistry of **3a** as shown in Scheme I. Similar structural analysis for diastereomers obtained in the photo-hydrogen abstraction of phthalimide was performed by Kanaoka and

(3) (a) Maruyama, K.; Kubo, Y. *J. Org. Chem.* **1981**, *46*, 3612. (b) Maruyama, K.; Kubo, Y.; Machida, M.; Oda, K.; Kanaoka, Y.; Fukuyama, K. *Ibid.* **1978**, *43*, 2303.
(4) (a) Maruyama, K.; Kubo, Y. *J. Am. Chem. Soc.* **1978**, *100*, 7772. (b) Machida, M.; Oda, K.; Maruyama, K.; Kubo, Y.; Kanaoka, Y. *Heterocycles* **1980**, *14*, 779.
(5) Maruyama, K.; Kubo, Y. *Chem. Lett.* **1978**, 769.
(6) Maruyama, K.; Kubo, Y. *Chem. Lett.* **1978**, 851.
(7) (a) Arakawa, S. *J. Org. Chem.* **1977**, *42*, 3800. (b) Rigaudy, J.; Derible, P. *Bull. Soc. Chim. Fr.* **1965**, 3047.

Table II. Photoreaction of *N*-Methylphthalimide (1a), Phthalimide (1b), or *N*-(Acetoxymethyl)phthalimide (1c) with Styrene (2a) or α-Methylstyrene (2b) in Alcohol[a]

imide, R^1	olefin, R^2	alcohol, R^3	yield,[b] %			
				a	b	7, yield,[b] %
1a, Me	2b, Me	Me	9,	40	30	7b
1a, Me	2b, Me	Et	10,	29	16	7b, 11
1b, H	2a, H	Me	11,	39	30	7c
1b, H	2a, H	Et	12,	32	22	7c, 13
1b, H	2b, Me	Me	13,	40	35	7d
1b, H	2b, Me	Et	14,	37	34	7d, 8
1b, H	2b, Me	2-Pr	15,	16	16	7d, 30
1c, CH_2OAc	2a, H	Me	16,	32	32	

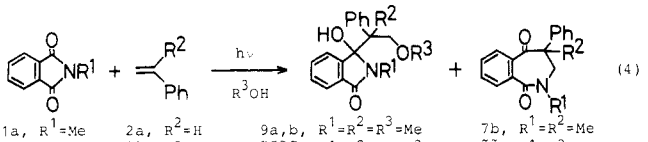
[a] The alcohol solution of imide (14 mM) and olefin (0.1 M) was irradiated. [b] The yields were based on the amount of imide consumed. The conversion was 10–15%.

Hatanaka.[8] The other features of the ^1H NMR spectra were consistent with the assigned diastereomeric structures.

Irradiation of **1a** and **2a** in various alcohols (ethanol, 2-propyl alcohol, *tert*-butyl alcohol) gave the corresponding solvent-incorporated diastereomeric adducts **3b–d** and **4b–d**, together with another type of product, **7a**, cycloaddition products to C(=O)—N bond of **1a** accompanying ring enlargement, as shown in Scheme I and Table I. The table shows that the yields of **3a–d** and **4a–d** decrease and at the same time the yield of **7a** increases, with a decrease of the solvent polarity.

The structure of **7a** was assigned by ^1H NMR, IR, and mass spectra. In addition, **7a** was reduced by sodium borohydride to give alcohols (Scheme I). The ^1H NMR spectrum of the major product **8** shows methine signals (*H*COH) at δ 4.84 (d, J = 8 Hz, 1 H) coupled with the adjacent methine proton (*H*CPh).

Irradiation of 1a–c with 2a,b. Irradiation of each pair of **1a**–α-methylstyrene (**2b**), phthalimide (**1b**)–**2a**, **1b**–**2b**, and *N*-(acetoxymethyl)phthalimide (**1c**)–**2a** in alcohol gave the corresponding alcohol-incorporated diastereomeric adducts **9a,b–16a,b**, together with ring-enlarged cycloaddition products **7b–d** in some cases (eq 4 and Table II).



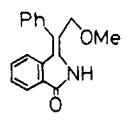
(4)

1a, R^1=Me 2a, R^2=H
1b, R^1=H 2b, R^2=Me
1c, R^1=CH_2OAc

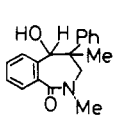
9a,b, R^1=R^2=R^3=Me
10a,b, R^1=R^2=Me,R^3=Et
11a,b, R^1=R^2=H,R^3=Me
12a,b, R^1=R^2=H,R^3=Et
13a,b, R^1=H,R^2=R^3=Me
14a,b, R^1=H,R^2=Me,R^3=Et
15a,b, R^1=H,R^2=Me,R^3=2-Pr
16a,b, R^1=CH_2OAc,R^2=H,R^3=Me

7b, R^1=R^2=Me
7c, R^1=R^2=H
7d, R^1=H,R^2=Me

The Table II also shows that with decrease of the solvent polarity the yields of the solvent-incorporated products decrease, and that of **7b–d** increases. The structures of the products were assigned from the spectral data. In addition, on treatment with acid **11a,b** were dehydrated with ease of **17** and **7b** was reduced by sodium borohydride



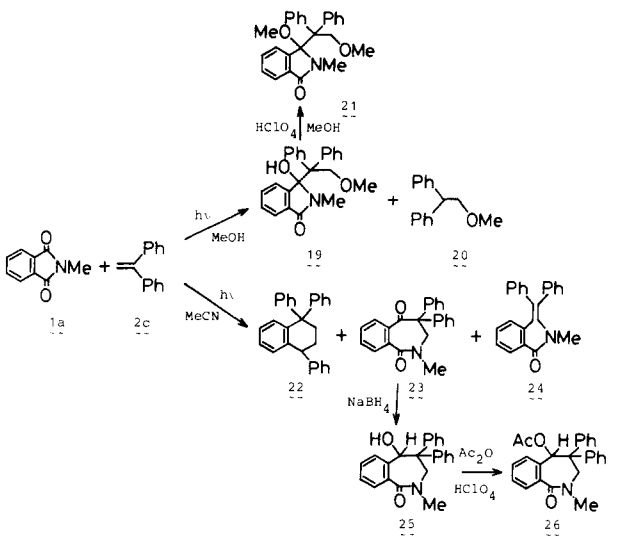
17



18a,b

to a mixture of diastereomers, **18a** and **18b**. The ^1H NMR spectra of **7c** and **7d** showed the presence of vicinal coupling between the NH proton and the methylene protons (–NHCH_2C–) and supported the assigned structures.

Scheme II



1a 2c 19 20 21 22 23 24 25 26

Irradiation of 1a with 2c. Extensive studies were conducted with the use of 1,1-diphenylethylene (**2c**) as a model olefin. In favor of this choice are the symmetrical structure, its inefficient polymerization, and the definite information concerning the behavior of the radical cation of **2c** derived from the electron-transfer photochemistry.[9]

Irradiation of **1a** (30 mM) and **2c** (80 mM) in methanol gave a methanol-incorporated addition product **19** (83%) and 2,2-diphenylethyl methyl ether (**20**) (20%) (Scheme II). The structure of **19** was confirmed by methyl esterification by the action of a few drops of perchloric acid in methanol to **21**. The ether **20** was identified with a sample prepared by irradiation of *p*-dicyanobenzene, **2c**, and phenanthrene (sensitizer) in methanol.[9c,d]

Irradiation of **1a** (30 mM) and **2c** (80 mM) in acetonitrile gave 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (**22**) as the major product. The yield of **22** was 93% on the basis of the consumed imide. The minor products were cycloaddition product **23** (11%) and **24** (10%). The major product **22**, the dimer of **2c**, was identified with a sample prepared by irradiation of *p*-dicyanobenzene, **2c**, and phenanthrene (sensitizer) in acetonitrile.[9c,d] The structure of the ketone **23** was confirmed by reduction by sodium borohydride to **25** and then acetylation to **26**. Assignment of the structure of **24**, which was analyzed for $C_{22}H_{17}NO$ by mass spectrum and elemental analysis, was made on the basis of the spectral data. The IR spectrum showed

(8) Kanaoka, Y.; Hatanaka, Y. *Chem. Pharm. Bull.* **1974**, *22*, 2205.

(9) (a) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. (b) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *Ibid.* **1978**, *100*, 535. (c) Pac, C.; Nakasone, A.; Sakurai, H. *Ibid.* **1977**, *99*, 5806. (d) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *Ibid.* **1981**, *103*, 4499.

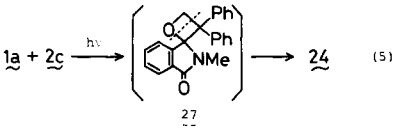
Table III. Photoreaction of *N*-Methylphthalimide (1a) with 1,1-Diphenylethylene (2c) in the Presence or Absence of Phenanthrene[a]

solvent	phenanthrene mM	yields, % 19[b]	20[b]	22[b]	23[b]	24[b]	1a[c]	2c[c]
methanol	0	83	20				34	*d*
methanol	5	76	23				36	*d*
acetonitrile	0			93 (30)[e]	11	10	72	67
acetonitrile	5			(60)[e]	*f*	*f*	>90	16

[a] The solution of 1a (30 mM) and 2c (80 mM) was irradiated. [b] The yields were based on the amount of consumed imide 1a. [c] The recovery (%) of the starting materials. [d] Not measured. [e] The yields were based on the amount of consumed olefin 2c. [f] Not detected.

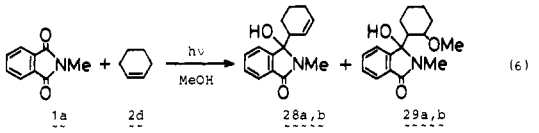
an amide carbonyl band at 1688 cm^{-1}, as well as a characteristic band due to the enamine structure at 1610 cm^{-1}. The ^1H NMR spectrum showed considerably shielded doublet signals (1 H) at δ 6.48 due to the one of the ortho-phenyl protons as observed in that of **5a**. The other features of the spectral data were consistent with the assigned structure.

The formation of **24** in acetonitrile may be most reasonably rationalized by a mechanism in which an oxetane intermediate (**27**) is involved (eq 5).[10]



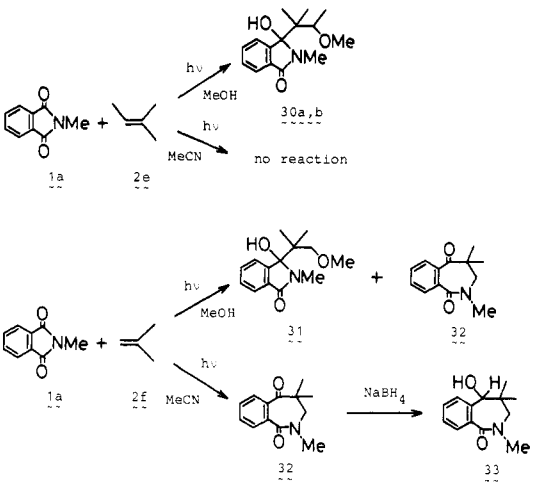
Effects on addition of phenanthrene (5 mM) to the irradiating solutions were examined and the results are shown in Table III. Under these conditions, irradiated light (>300 nm) can be efficiently absorbed by phenanthrene, which is known to act as a typical redox-photosensitizer in a system containing **2c** as the electron donor.[9c,d] Table III shows that none of the adducts **23** and **24** were formed in acetonitrile by the phenanthrene-sensitized reaction.

Irradiation of 1a with Aliphatic Olefins. Concerning the photolysis of **1a** with cyclohexene (**2d**) in acetonitrile, α-hydrogen abstraction to give **28a,b** was already reported by Kanaoka and Hatanaka.[8] In our experiment, no other products were obtained. On the other hand, irradiation of **1a** and **2d** in methanol gave methanol-incorporated adducts **29a** (15%) and **29b** (12%), together with a diastereomeric mixture of α-hydrogen abstraction products **28a,b** (25%) (eq 6).



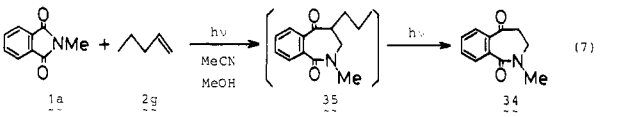
Irradiation of **1a** and 2-methyl-2-butene (**2e**), which is an example of trialkyl-substituted ethylenes, in methanol gave methanol-incorporated adducts **30a** (26%) and **30b** (26%) (Scheme III). However, the photolysis in acetonitrile was slow and resulted only in recovery of the starting material **1a**. Irradiation of **1a** and isobutene (**2f**), which was an example of dialkyl-substituted ethylenes, in methanol gave methanol-incorporated adduct **31** (18%),

Scheme III



together with cycloadduct **32** (50%). The product **32** was also obtained in the photolysis of **1a** and **2f** in acetonitrile in a yield of 67%. The structure of **31** was confirmed by reduction to **33**.

Irradiation of **1a** and 1-pentene (**2g**), which is an example of monoalkyl-substituted ethylenes, in methanol gave **34** (60%) (eq 7). The product **34** was also obtained in the



photolysis in acetonitrile in a yield of 25%. The spectral data of **34** were identical with those previously reported.[11] Formation of **34** is rationalized on the basis of a mechanism (eq 7) which involves initial photocycloaddition to **35** followed by type II photoelimination to **34**.

As described above, the course of the photoreactions of **1a** with aliphatic olefins is significantly influenced by a number of alkyl substituents of olefins. The methanol-incorporated adducts were obtained by the reaction of **1a** and olefins possessing more than two alkyl substituents. In contrast, ring-enlarged cycloaddition products were obtained by the reaction of **1a** with olefins possessing less than two alkyl substituents, although **1d** was an exception.

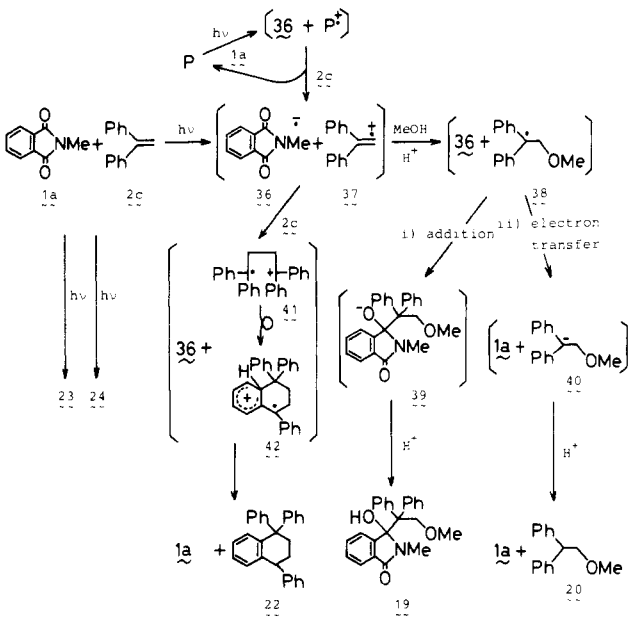
Alcohol-Incorporated Addition. The observations outlined above demonstrate that phthalimides undergo efficient alcohol-incorporated photoaddition to olefins including aromatic and aliphatic olefins when irradiated in alcohols. A number of results have prompted us to study the mechanistic details of these novel reactions. These include the investigations on the regiochemistry for the adduct formation, on the reaction course depending on the nature of the olefin, and on the byproduct formation in the addition reaction.

These characteristics are best rationalized by a mechanism involving electron transfer as outlined in Scheme IV, in which the reaction of **1a** and **2c** is representive. The first step is photoinduced intermolecular electron transfer from the electron-donating olefin **2c** to the excited imide **1a** to a pair of **36**, a radical anion of **1a**, and **37**, a radical cation of **2c**. Later, we will describe in a more detailed discussion the energetics of the process. Then, the radical cation **37** is captured by methanol followed by deprotonation to give radical **38**. Finally, C–C coupling between **36** and **38** followed by protonation results in the formation

(10) (a) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P.; Bowen, M.; Narian, N. *J. Org. Chem.* **1981**, *46*, 4846. (b) Mazzocchi, P. H.; Minamikawa, S.; Bowen, M. *Heterocycles* **1978**, *9*, 1713. (c) Machida, M.; Takeuchi, H.; Kanaoka, Y. *Tetrahedron Lett.* **1982**, *23*, 4981. (d) Mazzocchi, P. H.; Klingler, L.; Edwards, M.; Wilson, P.; Shook, D. *Ibid.* **1983**, *24*, 143.

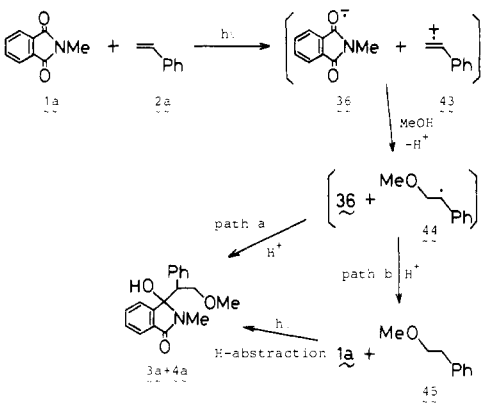
(11) Mazzocchi, P. H.; Bowen, M.; Narain, N. *J. Am. Chem. Soc.* **1977**, *99*, 7063.

Scheme IV



P:Phenanthrene

Scheme V



of the methanol-incorporated adduct **19**.

It is important to note the regiochemistry of the process. Addition of **1a** and methanol to **2c** proceeded in the anti-Markovnikov fasion, the same reaction mode as that observed for the related electron-trnasfer-photosensitized reactions.[9]

In this connection, byproduct **20** could be one of the typical electron-transfer-photosensitized products as reported by Arnold and his co-workers.[9a] Thus, the electron-transfer-photosensitized addition of methanol to **2c** giving **20** and the methanol-incorporated addition of **1a** to **2c** giving **19** appear to be closely related process via common intermediates (**36** + **38**). Combination of the two components results in the formation of **19**, and the back-electron transfer from **36** to **38** results in the formation of **20** and **1a**. Furthermore, the formation of **22** in acetonitrile supports the electron-transfer mechanism. As reported by Arnold and his co-workers,[9a] dimer radical cation **31**, derived from the reaction of the photoinduced radical cation **37** and **2c**, cyclizes to **42** and then back-electron transfer from **36** to generate **22**. The electron-transfer mechanism is also supported by the phenanthrene-sensitized reactions. The reaction may lead to formation of a common key radical ion pair (**36** + **37**), giving **19** and **20** in methanol but **22** in acetonitrile. Formation of **23** and **24**, which were not sensitized by phenanthrene, appears

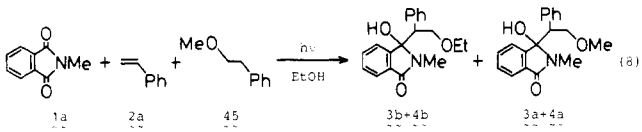
Table IV. Calculated Free Energy Change (ΔG) Associated with Electron Transfer from Olefins to the Singlet Excited State of *N*-Methylphthalimide (1a)

olefin	$E(D/D^+)$, V	ΔG,[a] kcal/mol
1,1-diphenylethylene (**2c**)	+1.48[b]	−15.8
2-methyl-2-butene (**2e**)	+1.79[c]	−8.7
cyclohexene (**2d**)	+2.05[d]	−2.7
isobutene (**2f**)	+2.39[c]	+5.2
1-pentene (**2g**)	+2.74[d]	+13.2

[a] Calculated by eq 10, see the text. [b] Reference 13. [c] Reference 14. [d] Reference 15.

to be derived by different mechanisms, which do not involve the electron-transfer process.

Another possible mechanism shown in Scheme V (path b) via photochemical hydrogen abstraction might be considered. However, the hydrogen abstraction mechanism is inconsistent with the following experimental results. Photolysis of an ethanol solution containing **1a** (40 mM), **2a** (60 mM), and **45** (60 mM) resulted in the formation of adducts **3a** + **4a** / **3b** + **4b** < 1/100 at a low conversion of **1a** (<20%) (eq 8). Thus, we conclude that the alcohol-incorporated adducts could not be formed via the intermediate **45** or at least not in the major parts.



A qualitative test has been undertaken to ascertain the electron-transfer mechanism. The efficiency of the electron transfer from olefins to the excited imide **1a** should be dependent upon the free energy changes associated with the electron-transfer processes, which could be roughly estimated by using eq 9.[12] In this equation $E(D/D^+)$ is

$$\Delta G = 23.06[E(D/D^+) - E(A^-/A)] - C - \Delta E_{0,0} \quad (9)$$

the one-electron oxidation potential of the donor (in volts), $E(A^-/A)$ is the one-electron reduction potential of the acceptor (in volts), $\Delta E_{0,0}$ is the energy of the excited species (kcal/mol), and C is the "Coulombic attraction term". The oxidation potentials of olefins are listed in Table IV. The reduction potential for **1a** was determined to be −1.36 V (in 0.5 M Et_4NClO_4/acetonitrile; cyclic voltammetry with a platinum electrode vs. Ag/0.01 M $AgClO_4$). The energy of the excited singlet of **1a**, E_s = 80 kcal/mol,[16] is used for the $\Delta E_{0,0}$ value, because the photochemical alcohol-incorporated adducts have been considered to be formed by reaction directly from the excited singlet state of phthalimides.[3a] The C value is 1.3 kcal/mol (in acetonitrile).[12] With these data, calculated free energy changes (ΔG) with electron transfer from olefins to the singlet excited state of **1a** are shown in Table IV. Though the absolute magnitudes of these values are certainly ill-defined, it seems reasonable to conclude that the intermolecular electron transfer in methanol may be possible from **2c**, **2e**, and **2d** to **1a** by judging from the free energy change.[17] However, this process is impossible in the

(12) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(13) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931.
(14) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *Tetrahedron Lett.* **1978**, 4361.
(15) Fleischmann, M.; Pletcher, D. *Tetrahedron Lett.* **1968**, 6255.
(16) Coyle, J. D.; Newport, G. L.; Harriman, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 133.
(17) Independently Mazzocchi and his co-workers reported similar results.[14]

photolysis of **1a** and **2g**. In fact, in the reaction of **1a** and **2g** in methanol, **34** was the sole product.

Although there have been a number of examples of solvent-incorporated adduct formation in the photoreaction of electron-donor–acceptor pairs,[10,20] the present photoreactions of phthalimides with olefins is to be considered as an example of the solvent-incorporated olefin addition to the carbonyl system.

Cycloaddition Accompanying Ring Enlargement. As outlined above cycloaddition accompanying ring enlargement was observed in the photoreaction of phthalimides with mono- or 1,1-disubstituted ethylenes in acetonitrile, and in some cases in alcohols together with solvent-incorporated addition. The cycloaddition accompanying ring enlargement has been found by other groups in the photoreaction of **1a** with dienes,[11] alkenes,[10a,20] vinyl ethers,[10] and allens.[10] Furthermore, Mazzocchi and his co-workers reported that the cycloaddition with *cis*- and *trans*-2-butene was stereospecific, and the reaction of 4-methoxy-*N*-methylphthalimide with olefins was regioselective.[21] We reported that the corresponding intramolecular photoreactions in the photolysis of *N*-4- and *N*-5-alkenylphthalimides took place.[5] The reaction probably proceeded through an exciplex between the singlet excited phthalimide moiety and the olefinic moiety in the ground state.[5]

In polar solvents, exciplexes are known to dissociate into pairs of radical ions.[9,19] Therefore, in the reactions of **1a** with a series of aliphatic olefins possessing the relatively lower oxidation potentials (Table IV), exciplexes derived from **1a** and **2d** (or **2e**) may easily dissociate into pairs of radical ions, giving efficiently methanol-incorporated products in methanol. On the other hand, back-electron transfer to starting materials may become the competing process in acetonitrile. Similarly, in the reactions of **1a** with **2a** in alcohols, the degree of dissociation of an exciplex derived from **1a** and **2a** into a pair of radical ions (**36** + **43**) may increase with an increase of the solvent (alcohol) polarity, consistent with the results.

Experimental Section

Microanalyses were performed by the Microanalytical Laboratory of Kyoto University, Kyoto, Japan. UV irradiation was carried out with an Eikosha PIH 300-W high-pressure mercury lamp through quartz under N_2 at ambient temperature. Column chromatography was carried out on Wakogel C-200 (SiO_2).

Materials. *N*-Methylphthalimide (**1a**), mp 132–133 °C (lit. mp 130-131 °C), was prepared by the method of Sachs.[22] *N*-(Acetoxymethyl)phthalimide (**1c**), mp 119–120 °C (lit. mp 118 °C), was also prepared by the method of Sachs.[23] Phthalimide (**1b**) and olefins **2a–g** were commercially available and purified by recrystallization or distillation.

Irradiation of 1a with 2a. A solution of 0.9 g (5.6 mmol) of *N*-methylphthalimide (**1a**) and 4.2 g (40 mmol) of styrene (**2a**) in 400 mL of methanol was irradiated for 3 h. Products were isolated by column chromatography, eluting with hexane–chloroform–ether.

Irradiation of **1a** and **2a** in other alcohols (ethanol, 2-propyl alcohol, and *tert*-butyl alcohol) were carried out in similar ways. The results are summarized in Table I.

(18) (a) Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130. (b) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499. (c) Mizuno, K.; Kaji, R.; Okada, H.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* **1978**, 594.

(19) (a) Hino, T.; Masuhara, H.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 394. (b) Ottolenghi, M. *Acc. Chem. Res.* **1973**, *6*, 153.

(20) Kanaoka, Y.; Yoshida, Y.; Hatanaka, Y. *J. Org. Chem.* **1979**, *44*, 664.

(21) Mazzocchi, P. H.; Wilson, P.; Khachik, L.; Minamikawa, S. *J. Org. Chem.* **1983**, *48*, 2981.

(22) Sachs, F. *Chem. Ber.* **1898**, *31*, 1228.

(23) Sachs, F. *Chem. Ber.* **1898**, *31*, 3233.

(***R***,***S*** and ***S***,***R***)-3-Hydroxy-3-(2-methoxy-1-phenylethyl)-2-methylisoindolin-1-one (**3a**): mp 131–132 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 2.89 (s, 3 H, NMe), 3.50 (s, 3 H, OMe), 3.6–3.9 (m, 2 H), 4.0–4.3 (m, 1 H), 5.29 (s, 1 H, OH), 6.4–6.6 (m, 2 H), 6.9–7.2 (m, 3 H), 7.3–7.7 (m, 4 H, Ar H); IR (KBr) 3280 (OH), 1673 (amide), 1428, 1015, 720 cm^{-1}; MS, *m/e* (relative intensity) 279 ($M^+ - H_2O$, 3), 249 (12), 248 (35), 176 (12), 163 (9), 162 (71), 161 (20), 105 (14), 104 (100). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 27.70; H, 6.44; N, 4.71. Found: C, 72.83; H, 6.38; N, 4.68.

(***R***,***R*** and ***S***,***S***)-3-Hydroxy-3-(2-methoxy-1-phenylethyl)-2-methylisoindolin-1-one (**4a**): mp 159–162 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 3 H, NMe), 3.31 (s, 3 H, OMe), 3.4–3.8 (m, 3 H), 5.10 (s, 1 H, OH), 6.9–7.3 (m, 9 H); IR (KBr) 3210 (OH), 1684 (amide), 1434, 1050, 722 cm^{-1}; MS, *m/e* (relative intensity) 279 ($M^+ - H_2O$, 9), 249 (9), 248 (27), 176 (9), 163 (9), 162 (64), 161 (18), 105 (15), 104 (100). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71. Found: C, 72.44; H, 6.41; N, 4.63.

(***R***,***S*** and ***S***,***R***)-3-(2-Ethoxy-1-phenylethyl)-3-hydroxy-2-methylisoindolin-1-one (**3b**): mp 179–181 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7 Hz, 3 H, OCH_2CH_3), 2.98 (s, 3 H, NMe), 3.6–3.9 (m, 4 H), 4.0–4.4 (m, 1 H), 5.50 (s, 1 H, OH), 6.3–6.6 (m, 2 H), 6.9–7.1 (m, 3 H), 7.3–7.7 (m, 4 H, Ar H); IR (KBr) 3270 (OH), 1676 (amide), 1428, 1400, 1115, 1082, 715 cm^{-1}; MS, *m/e* (relative intensity) 293 (100), 249 (8), 248 (20), 162 (50), 161 (15), 105 (100), 104 (100). Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.10; H, 6.64; N, 4.40.

(***R***,***R*** and ***S***,***S***)-3-(2-Ethoxy-1-phenylethyl)-3-hydroxy-2-methylisoindolin-1-one (**4b**): mp 141–144 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7 Hz, 3 H, OCH_2CH_3), 3.12 (s, 3 H, NMe), 3.3–4.0 (m, 5 H, OCH_2CH_3 + methylene + methine), 5.45 (s, 1 H, OH), 6.9–7.6 (m, 9 H, Ar H); IR (KBr) 3260 (OH), 1674 (amide), 1423, 1390, 1105, 1070, 712 cm^{-1}; MS, *m/e* (relative intensity) 293 (11), 249 (11), 248 (26), 162 (47), 161 (16), 105 (12), 104 (100). Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.52; H, 6.86; N, 4.34.

(***R***,***S*** and ***S***,***R***)-3-Hydroxy-3-(2-isopropoxy-1-phenylethyl)-2-methylisoindolin-1-one (**3c**): mp 139.5–141.0 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.30 and 1.38 (two d, J = 6 Hz, 6 H, $OCHMe_2$), 3.01 (s, 3 H, NMe), 3.6–4.0 (m, 3 H), 4.1–4.4 (m, 1 H), 5.83 (s, 1 H, OH), 6.4–6.6 (m, 2 H), 6.9–7.2 (m, 3 H), 7.3–7.8 (m, 4 H, Ar H); IR (KBr) 3270 (OH), 1670 (amide), 1430, 1080, 714, 698 cm^{-1}; MS, *m/e* (relative intensity) 307 (9), 264 (10), 249 (9), 248 (16), 236 (14), 162 (50), 161 (23), 105 (15), 104 (100). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.94; H, 7.16; N, 4.36.

(***R***,***R*** and ***S***,***S***)-3-Hydroxy-3-(2-isopropoxy-1-phenylethyl)-2-methylisoindolin-1-one (**4c**): mp 113–114 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.22 and 1.24 (two d, J = 6 Hz, 6 H, $OCHMe_2$), 3.25 (s, 3 H, NMe), 3.6–4.1 (m, 4 H, $OCHMe_2$ + methylene + methine), 5.88 (s, 1 H, OH), 6.8–7.7 (m, 9 H, Ar H); IR (KBr) 3255 (OH), 1676 (amide), 1434, 1122, 774, 706 cm^{-1}; MS, *m/e* (relative intensity) 307 (11), 264 (13), 249 (13), 248 (21), 236 (17), 162 (56), 161 (19), 105 (14), 104 (100). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 74.10; H, 7.11; N, 4.22.

(***R***,***S*** and ***S***,***R***)-3-(2-*tert*-Butoxy-1-phenylethyl)-3-hydroxy-2-methylisoindolin-1-one (**3d**): mp 136–138 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9 H, *t*-**Bu**), 3.01 (s, 3 H, NMe), 3.5–3.9 (m, 2 H), 4.0–4.3 (m, 1 H), 6.05 (s, 1 H, OH), 6.4–6.6 (m, 2 H), 6.9–7.2 (m, 3 H), 7.3–7.8 (m, 4 H, Ar H); IR (KBr) 3260 (OH), 1680 (amide), 1428, 1200, 1084, 708, 696 cm^{-1}; MS, *m/e* (relative intensity) 321 (12), 265 (10), 264 (15), 248 (19), 236 (24), 161 (50), 161 (20), 105 (15), 104 (100). Anal. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.10; H, 7.33; N, 4.12.

(***R***,***R*** and ***S***,***S***)-3-(2-*tert*-Butoxy-1-phenylethyl)-3-hydroxy-2-methylisoindolin-1-one (**4d**): mp 123–125 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 9 H, *t*-**Bu**), 3.31 (s, 3 H, NMe), 3.6–4.2 (m, 3 H, methylene + methine), 6.31 (s, 1 H, OH), 6.8–7.6 (m, 9 H, Ar H); IR (KBr) 3255 (OH), 1674 (amide), 1480, 1433, 1091, 1082, 1054, 778, 700 cm^{-1}; MS, *m/e* (relative intensity) 321 (9), 265 (9), 264 (18), 248 (17), 236 (24), 162 (52), 161 (15), 105 (13), 104 (100). Anal. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.19; H, 7.47; N, 4.09.

6,7-Dihydro-1-methyl-6-phenyl-3,4-benzazepine-2,5-dione (7a): oil; ^{1}H NMR ($CDCl_3$) δ 3.06 (s, 3 H, NMe), 3.6–4.3 (m, 3 H), 7.0–8.1 (m, 9 H, Ar H); IR (neat) 1688 (keto), 1643 (amide), 1593, 1397, 1074 cm^{-1}; MS, m/e (relative intensity) 265 (M^+, 6), 223 (30), 222 (100), 105 (18), 104 (75).

To a solution of 85 mg of **7a** in 20 mL of methanol was added 4 mg of sodium borohydride with stirring. The solution was kept overnight at room temperature. The solution was poured into 10 mL of 0.1 N hydrochloric acid and extracted with 20 mL of chloroform. The extract was washed several times with water and dried over magnesium sulfate, and the solvent was evaporated. TLC analysis of the residue showed the presence of **8**, together with a minor product which was probably the stereoisomer of **8**. Recrystallization of the residue from ethanol gave 46 mg of **8**.

6,7-Dihydro-5-hydroxy-1-methyl-6-phenyl-3,4-benzazepin-2(5*H*)-one (8): mp 176–178 °C; ^{1}H NMR ($CDCl_3$) δ 3.24 (s, 3 H, NMe), 3.1–3.5 (m, 2 H, OH + 1 H of NCH_2), 3.60 (dd, J = 13, 15 Hz, 1 H, 1 H of NCH_2), 3.94 (m, 1 H, *H*CPh), 4.84 (d, J = 8 Hz, *H*COH), 7.0–8.1 (m, 9 H, Ar H); IR (KBr) 3280 (OH), 1621 (amide), 1400, 1252, 732, 700 cm^{-1}; MS, m/e (relative intensity) 267 (M^+, 20), 104 (20), 86 (52), 84 (72), 51 (32), 49 (100). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.47; H, 6.44; N, 5.20.

Dehydration of 3a–c and 4a–c. A solution of 215 mg of **3a** and 20 mg of sodium acetate in 10 mL of acetic anhydride was refluxed for 0.5 h. The cooled solution was poured into 50 mL of water. The solution was neutralized by sodium hydrogen carbonate solution and extracted with chloroform. The extract was washed with sodium hydrogen carbonate and water and dried over magnesium sulfate. After evaporation of the solvent, chromatography of the residue gave dehydrated products **5a** and **6a** in yields of 56 mg (28%) and 72 mg (36%), respectively. In a similar way, **4a** was dehydrated to give **5a** and **6a** in yields of 42% and 37%, respectively.

(*Z*)-3-(2-Methoxy-1-phenylethylidene)-2-methylisoindolin-1-one (5a): mp 148.5–151.0 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 3.40 (s, 3 H, OMe), 3.69 (s, 3 H, NMe), 4.50 (s, 2 H, $-CH_2OMe$), 6.15 (d, J = 8 Hz, 1 H), 7.0–7.6 (m, 7 H), 7.8–7.9 (m, 1 H, Ar H); IR (KBr) 2925, 1698 (amide), 1627, 1380, 1078, 1046, 946, 713 cm^{-1}; MS, m/e (relative intensity) 280 (13), 279 (M^+, 47), 249 (24), 248 (100), 247 (9), 246 (10), 233 (14), 176 (21), 105 (10). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.62; H, 6.08; N, 4.98.

(*E*)-3-(2-Methoxy-1-phenylethylidene)-2-methylisoindolin-1-one (6a): mp 146–147 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 2.70 (s, 3 H, NMe), 3.46 (s, 3 H, OMe), 4.65 (s, 2 H, $-CH_2OMe$), 7.3–8.0 (m, 9 H); IR (KBr) 1688 (amide), 1628, 1368, 1094, 1056, 710 cm^{-1}; MS, m/e (relative intensity) 280 (12), 279 (M^+, 46), 249 (28), 248 (100), 247 (11), 246 (12), 233 (13), 176 (32), 105 (12). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.65; H, 6.09; N, 5.03.

In a similar manner as desribed above, a mixture of **3b** and **4b** was dehydrated to give **5b** (36%) and **6b** (32%). A mixture of **3c** and **4c** was also dehydrated to give **5c** (29%) and 6c (31%).

(*Z*)-3-(2-Ethoxy-1-phenylethylidene)-2-methylisoindolin-1-one (5b): mp 109.5–111.5 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 7 Hz, 3 H, OCH_2CH_3), 3.52 (q, J = 7 Hz, 2 H, OCH_2CH_3), 3.68 (s, 3 H, NMe), 4.49 (s, 2 H, CH_2OEt), 6.07 (d, J = 8 Hz, 1 H), 6.9–7.6 (m, 7 H), 7.7–7.9 (m, Ar H); IR (KBr) 2980, 1700 (amide), 1368, 1105, 1052, 774, 706 cm^{-1}; MS, m/e (relative intensity) 294 (11), 293 (M^+, 42), 249 (30), 248 (100). Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.84; H, 6.44; N, 4.58.

(*E*)-3-(2-Ethoxy-1-phenylethylidene)-2-methylisoindolin-1-one (6b): mp 98.5–99.5 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 7 Hz, 3 H), 2.69 (s, 3 H, NMe), 3.61 (q, J = 7 Hz, 2 H), 4.66 (s, 2 H, $-CH_2OEt$), 7.1–8.1 (m, 9 H); IR (KBr) 2870, 1688 (amide), 1363, 1089, 1079, 1056, 764, 708 cm^{-1}; MS, m/e (relative intensity) 294 (10), 293 (M^+, 38), 249 (30), 248 (100). Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.84; H, 6.44; N, 4.58.

(*Z*)-3-(2-Isopropoxy-1-phenylethylidene)-2-methylisoindolin-1-one (5c): mp 111–112 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 1.17 (d, J = 6 Hz, 6 H, $OCHMe_2$), 3.71 (s, 3 H, NMe), 3.5–3.8 (m, 1 H, $OCHMe_2$), 4.52 (s, 2 H, $-CH_2OCHMe_2$), 6.10 (d, J = 6 Hz, 1 H), 7.0–7.6 (m, 7 H), 7.7–7.9 (m, 1 H, Ar H); IR (KBr) 1694 (amide), 1372, 1134, 1124, 700 cm^{-1}; MS, m/e (relative intensity) 307 (M^+, 60), 265 (19), 264 (62), 249 (45), 248 (100), 236 (71). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.14; H, 6.89; N, 4.56. Found: C, 78.02; H, 6.97; N, 4.50.

(*E*)-3-(2-Isopropoxy-1-phenylethylidene)-2-methylisoindolin-1-one (6c): mp 122–124 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 1.20 (d, J = 6 Hz, 6 H, $OCHMe_2$), 2.69 (s, 3 H, NMe), 3.5–3.9 (m, 1 H, $OCHMe_2$), 4.65 (s, 2 H, $-CH_2OCHMe_2$), 7.2–8.1 (m, 9 H, Ar H); IR (KBr) 2980, 1692 (amide), 1628, 1368, 1036, 768, 703 cm^{-1}; MS, m/e (relative intensity) 307 (M^+, 51), 265 (17), 264 (57), 249 (43), 248 (100), 236 (66). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.14; H, 6.89; N, 4.56. Found: C, 78.24; H, 6.85; N, 4.83.

Irradiation of 1a with 2b. Photolyses of *N*-methylphthalimide (**1a**) with α-methylstyrene (**2b**) were carried out in methanol and ethanol. The results are shown in Table II.

3-Hydroxy-3-(2-methoxy-1-methyl-1-phenylethyl)-2-methylisoindolin-1-one, diastereomer a (9a): mp 170–171.5 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3 H, CMe), 2.97 (s, 3 H, NMe), 3.44 (s, 3 H, OMe), 3.85 (s, 2 H, $-CH_2OMe$), 5.33 (s, 1 H, OH), 6.3–6.5 (m, 1 H), 7.1–7.7 (m, 8 H, Ar H); IR (KBr) 3275 (OH), 1667 (amide), 1667, 1424, 1392, 1105, 1068, 704 cm^{-1}; MS, m/e (relative intensity) 249 (9), 163 (15), 162 (100), 161 (23), 118 (77), 117 (19). Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.10; H, 7.04; N, 4.41.

3-Hydroxy-3-(2-methoxy-1-methyl-1-phenylethyl)-2-methylisoindolin-1-one, diastereomer b (9b): mp 158.5–160.0 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 3 H, CMe), 2.82 (s, 3 H, OMe), 3.76 and 4.08 (ABq, J = 10 Hz, 2 H, $-CH_2OMe$), 5.36 (s, 1 H, OH), 7.2–7.8 (m, 9 H); IR (KBr) 3240 (OH), 1678 (amide), 1425, 1390, 1104, 1068, 698 cm^{-1}; MS, m/e (relative intensity) 249 (8), 163 (14), 162 (100), 161 (22), 118 (75), 117 (18). Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.29; H, 6.88; N, 4.31.

When a $CDCl_3$ solution of **9a** or **9b** with a drop of D_2O was followed by measurement of the ^{1}H NMR spectrum at different times, an interconversion between **9a** and **9b** was observed and an equilibrium, **9a**:**9b** = 1:1 (from integration of the ^{1}H NMR spectrum), was achieved after 1 day at room temperature.

3-(2-Ethoxy-1-methyl-1-phenylethyl)-3-hydroxy-2-methylisoindolin-1-one, diastereomer a (10a): mp 147–150 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 3 H, CMe), 1.34 (t, J = 7 Hz, 3 H, OCH_2CH_3), 3.06 (s, 3 H, NMe), 3.5–3.7 (m, 2 H, OCH_2CH_3), 3.80 and 3.95 (ABq, J = 9 Hz, 2 H, $-CH_2OMe$), 5.75 (s, 1 H, OH), 6.3–6.5 (m, 1 H), 7.0–7.7 (m, 9 H, Ar H); IR (KBr) 3275 (OH), 1664 (amide), 1478, 1422, 1392, 1102, 1067, 764, 698 cm^{-1}; MS, m/e (relative intensity) 163 (6), 162 (49), 161 (8), 119 (10), 118 (100), 117 (9). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.71; H, 7.19; N, 4.38.

The other diastereomer b was not isolated in a pure form.

6,7-Dihydro-1,6-dimethyl-6-phenyl-3,4-benzazepine-2,5-dione (7b): oil; ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3 H, CMe), 2.97 (s, 3 H, NMe), 3.67 and 3.94 (ABq, J = 15 Hz, 2 H, NCH_2-), 7.1–8.1 (m, 9 H, Ar H); IR (neat) 1687 (keto), 1644 (amide), 1593, 1397 cm^{-1}; MS, m/e (relative intensity) 279 (M^+, 3), 23 7 (12), 236 (100), 119 (21), 118 (56).

The ketone **7b** was reduced by sodium borohydride in a similar way as the that of **7a**. The products were separated by chromatography to give **18a** (47%) and **18b** (14%).

6,7-Dihydro-1,6-dimethyl-5-hydroxy-6-phenyl-3,4-benzazepin-2(5*H*)-one, stereoisomer a (18a): mp 197–198 °C (from ethanol–benzene); ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 3 H, CMe), 2.85 and 3.79 (ABq, J = 15 Hz, 2 H, NCH_2-), 3.17 (s, 3 H, NMe), 3.40 (s, 1 H, OH), 4.22 (s, 1 *H*, *H*COH), 6.9–7.9 (m, 9 H, Ar H); IR (KBr) 3240 (OH), 1613 (amide), 1594, 1396, 1248, 1058 cm^{-1}; MS, m/e (relative intensity) 282 (21), 281 (84), 238 (15), 236 (21), 165 (20), 163 (15), 119 (100), 118 (22). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.78; H, 6.86; N, 4.88.

6,7-Dihydro-1,6-dimethyl-5-hydroxy-6-phenyl-3,4-benzazepin-2(5*H*)-one, stereoisomer b (18b): mp 237–239 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 3 H, CMe), 2.59 (s, 3 H, NMe), 2.97 and 3.16 (ABq, J = 15 Hz, 2 H, NCH_2-), 4.24 (d, J = 3 Hz, 1 H, OH), 4.78 (d, J = 3 Hz, 1 H, *H*COH), 7.1–7.8 (m, 9 H, Ar H); IR (KBr) 3260 (OH), 1618 (amide), 1598, 1432, 1398 cm^{-1}; MS, m/e (relative intensity) 281 (M^+, 41), 263 (12), 238 (21), 236 (31), 147 (30), 119 (100). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; H, 4.98. Found: C, 76.55; H, 6.72; N, 4.99.

Irradiation of 1b with 2a. Photolyses of phthalimide (**1b**) with **2a** were carried out in methanol and ethanol. The results are shown in Table II.

3-Hydroxy-3-(2-methoxy-1-phenylethyl)isoindolin-1-one, diastereomer a (11a): mp 152–154 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 3.15 (dd, J = 5, 9 Hz, 1 H), 3.35 (s, 3 H, OMe), 3.55 (dd, J = 5, 9 Hz, 1 H), 4.20 (t, J = 9 Hz, 1 H), 4.20 (s, 1 H, OH), 6.2–6.4 (m, 1 H), 6.9–7.5 (m, 9 H, Ar H + NH); IR (KBr) 3380 and 3250 (OH and NH), 1682 (amide), 1109, 1079, 769, 698 cm^{-1}; MS, m/e (relative intensity) 266 (6), 265 (30), 235 (22), 234 (65), 233 (57), 232 (58), 148 (32), 147 (16), 105 (30), 104 (100), 103 (16). Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.06; H, 6.05; N, 4.94. Found: C, 72.20; H, 6.00; N, 4.86.

3-Hydroxy-3-(2-methoxy-1-phenylethyl)isoindolin-1-one, diastereomer b (11b): mp 154–156.5 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 3.49 (s, 3 H, OMe), 3.64 (t, J = 6 Hz, 1 H), 4.07 (d, J = 6 Hz, 2 H), 5.06 (s, 1 H, OH), 6.8–7.1 (m, 5 H), 7.1–7.6 (m, 4 H, Ar H), 7.88 (s, 1 H, NH); IR (KBr) 3340 and 3180 (OH and NH), 1692 (amide), 1109, 702 cm^{-1}; MS, m/e (relative intensity) 266 (8), 265 (26), 235 (24), 234 (64), 233 (60), 232 (56), 148 (32), 147 (16), 105 (24), 104 (100), 103 (14). Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.06; H, 6.05; N, 4.94. Found: C, 71.78; H, 5.97; N, 4.82.

The products **11a,b** were easily dehydrated by a trace of hydrochloric acid in chloroform as follows. To a solution of 230 mg of a mixture of **11a** and **11b** (about 1:1) in 30 mL of chloroform was added a drop of hydrochloric acid. After evaporation of the solvent, chromatography gave 132 mg (61%) of **17**.

(*Z*)-3-(2-Methoxy-1-phenylethylidene)isoindolin-1-one (17): mp 157–160 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 3.53 (s, 3 H, OMe), 4.48 (s, 2 H, methylene), 6.4–6.6 (m, 1 H), 7.1–7.7 (m, 7 H), 7.8–8.0 (m, 2 H, Ar H), 9.40 (br s, 1 H, NH); IR (KBr) 3170 (NH), 1686 (amide), 1084, 769, 712 cm^{-1}; MS, m/e (relative intensity) 266 (15), 265 (M$^+$, 59), 235 (22), 234 (100), 233 (87), 232 (91), 204 (17), 105 (33). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.14; H, 5.59; N, 5.37.

3-(2-Ethoxy-1-phenylethyl)-3-hydroxyisoindolin-1-one, diastereomer a (12a): mp 115–117 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.26 (t, J = 7 Hz, 3 H, OCH_2CH_3), 3.18 (dd, J = 5, 10 Hz, 1 H), 3.4–3.8 (m, 3 H), 4.26 (t, J = 10 Hz, 1 H), 4.70 (s, 1 H, OH), 6.2–6.4 (m, 1 H), 7.0–7.7 (m, 9 H, Ar H + NH); IR (KBr) 3370, 3270 (NH + OH), 1685 (amide), 1470, 1430, 1122, 1102, 764, 709, 692 cm^{-1}; MS, m/e (relative intensity) 280 (6), 279 (25), 235 (28), 234 (57), 233 (54), 232 (56), 148 (21), 147 (18), 105 (34), 104 (100), 103 (14). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71. Found: C, 72.92; H, 6.69; N, 4.73.

3-(2-Ethoxy-1-phenylethyl)-3-hydroxyisoindolin-1-one, diastereomer b (12b): mp 124–127 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.33 (t, J = 7 Hz, 3 H, OCH_2CH_3), 3.5–3.9 (m, 3 H), 4.12 (d, J = 5 Hz, 5 H), 4.50 (s, 1 H, OH), 7.0–7.7 (m, 10 H, Ar H + NM); IR (KBr) 3320 and 3190 (NH + OH), 1692 (amide), 1110, 1090, 1058, 756, 698 cm^{-1}; MS, m/e (relative intensity) 280 (4), 279 (24), 235 (26), 234 (56), 233 (62), 232 (60), 148 (24), 147 (22), 105 (36), 104 (100), 103 (24). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71. Found: C, 72,70; H, 6.53; N, 4.63.

6,7-Dihydro-6-phenyl-3,4-benzazepine-2,5-dione (7c): mp 127–130 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 3.59 (ddd, J = 4, 6, 15 Hz, 1 H, these signals collapsed to dd, J = 4, 15 Hz, with D_2O exchange), 3.82 (ddd, J = 6, 9, 15 Hz, 1 H, these signals collapsed to dd, J = 9, 15 Hz, with D_2O exchange, methylene), 4.19 (dd, J = 4, 9 Hz, 1 H, PhC*H*), 7.0–8.1 (m, 10 H, Ar H + NH); IR (KBr) 3180 (NH), 1668 (ketone), 1596 (amide), 1403, 1348, 705 cm^{-1}; MS, m/e (relative intensity) 251 (M$^+$, 1), 250 (7), 249 (25), 248 (14), 202 (35), 201 (53), 106 (17), 105 (100). Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57. Found: C, 76.49; H, 5.39; N, 5.36.

Irradiation of 1b with 2b. Photolyses of **1b** with **2b** were carried out in methanol, ethanol, and 2-propyl alcohol. The results are shown in Table II.

3-Hydroxy-3-(2-methoxy-1-methyl-1-phenylethyl)isoindolin-1-one, diastereomer a (13a): mp 167–169 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 3 H, CMe), 3.25 and 4.59 (ABq, J = 8 Hz, 2 H, methylene), 3.46 (s, 3 H, OMe), 3.82 (s, 1 H, OH), 5.8–6.1 (m, 1 H), 7.0–7.8 (m, 9 H, Ar H + NH); IR (KBr) 3380 and 3260 (NH + OH), 1688 (amide), 1464, 1390, 1092, 698 cm^{-1}; MS, m/e (relative intensity) 279 (16), 264 (20), 248 (32), 247 (52), 246 (40), 148 (36), 147 (32), 118 (100), 117 (28). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71. Found: C, 72.46; H, 6.40; N, 4.77.

3-Hydroxy-3-(2-methoxy-1-methyl-1-phenylethyl)isoindolin-1-one, diastereomer b (13b): mp 143.5–146.5 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 3 H, CMe), 3.52 (s, 3 H, OMe), 3.98 (s, 2 H, methylene), 4.40 (s, 1 H, OH), 7.00 (br s, 1 H, NH), 7.0–7.7 (m, 9 H, Ar H); IR (KBr) 3400 and 3270 (NH + OH), 1690 (amide), 1096, 701 cm^{-1}; MS, m/e (relative intensity) 279 (14), 264 (21), 248 (35), 247 (56), 246 (42), 234 (64), 148 (35), 147 (35), 118 (100), 117 (28). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44; N, 4.71. Found: C, 72.56; H, 6.50; N, 4.76.

3-(2-Ethoxy-1-methyl-1-phenylethyl)-3-hydroxyisoindolin-1-one, diastereomer a (14a): mp 162–163.5 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 3 H, CMe), 1.30 (t, J = 7 Hz, 3 H, OCH_2CH_3), 3.28 and 4.66 (ABq, J = 9 Hz, 2 H, methylene), 3.4–3.9 (m, 3 H, methylene + OH), 5.9–6.1 (m, 1 H), 7.0–7.8 (m, 9 H, Ar H + NH); IR (KBr) 3395 and 3280 (NH + OH), 1692 (amide), 1382, 1096, 1067, 760, 728, 695 cm^{-1}; MS, m/e (relative intensity) 247 (3), 234 (3), 148 (13), 147 (5), 119 (10), 118 (100), 117 (7), 104 (4), 103 (5), 78 (3). Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.01; H, 6.66; N, 4.48.

3-(2-Ethoxy-1-methyl-1-phenylethyl)-3-hydroxyisoindolin-1-one, diastereomer b (14b): mp 153–154 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.40 (t, J = 7 Hz, 3 H, OCH_2CH_3), 1.52 (s, 3 H, CMe), 3.85 (q, 2 H, OCH_2CH_3), 4.07 and 4.27 (ABq, J = 10 Hz, 2 H, methylene), 4,74 (s, 1 H, OH), 7.2–8.0 (m, 10 H, Ar H + NH); IR (KBr) 3385 and 3210 (NH + OH), 1698 (amide), 1470, 1386, 1108, 1064, 762, 695 cm^{-1}; MS, m/e (relative intensity) 247 (4), 234 (4), 148 (14), 147 (5), 119 (9), 118 (100), 117 (6), 104 (3), 78 (3). Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.10; H, 6.60; N, 4.54.

3-Hydroxy-3-(2-isopropoxy-1-methyl-1-phenylethyl)isoindolin-1-one, diastereomer a (15a): mp 163–165 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 3 H, CMe), 1.22 and 1.32 (two d, J = 6 Hz, 6 H, $OCHMe_2$), 3.27 and 4.62 (ABq, J = 9 Hz, 2 H, methylene), 3.5–3.9 (m, 2 H, OH + $OCHMe_2$), 5.8–6.0 (m, 1 H), 7.0–7.7 (m, 9 H, Ar H + NH); IR (KBr) 3395 and 3285 (NH + OH), 1692 (amide), 1466, 1382, 1059, 760, 693 cm^{-1}; MS, m/e (relative intensity) 247 (3), 234 (3), 148 (14), 119 (10), 118 (100). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.70; H, 7.11, N, 4.50.

3-Hydroxy-3-(2-isopropoxy-1-methyl-1-phenylethyl)isoindolin-1-one, diastereomer b (15b): mp 158–161 °C (from benzene–hexene); ^{1}H NMR ($CDCl_3$) δ 1.32 (d, J = 6 Hz, 6 H, $OCHMe_2$), 1.45 (s, 3 H, CMe), 3.87 and 4.13 (ABq, J = 9 Hz, 2 H, methylene), 3.6–4.0 (m, 1 H, $OCHMe_2$), 4.74 (s, 1 H, OH), 7.0–7.8 (m, 10 H, Ar H + NH); IR (KBr) 3380 and 3190 (NH + OH), 1700 (amide), 1111, 1058, 760, 695 cm^{-1}; MS, m/e (relative intensity) 247 (3), 234 (4), 148 (14), 119 (11), 118 (100). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.58; H, 7.02; N, 4.18.

6,7-Dihydro-6-methyl-6-phenyl-3,4-benzazepine-2,5-dione (7d): mp 137.5–138 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 3 H, CMe), 3.51 (dd, J = 7, 14 Hz, 1 H, these signals collapsed to d, J = 14 Hz, with D_2O exchange), 3.94 (dd, J = 7, 14 Hz, 1 H, these signals collapsed to d, J = 14 Hz, with D_2O exchange), 7.1–8.1 (m, 10 H, Ar H + NH); IR (KBr) 3230 (NH), 1683 (ketone), 1662 (amide), 708 cm^{-1}; MS, m/e (relative intensity) 265 (M$^+$, 2), 264 (7), 263 (29), 245 (7), 236 (20), 120 (11), 119 (100), 118 (11). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.83; H, 5.54; N, 5.39.

Irradiation of 1c with 2a in Methanol. Photolysis of *N*-(acetoxymethyl)phthalimide (**1c**) with **2a** in methanol was carried out. The results are shown in Table II.

(*R*,*S* and *S*,*R*)-2-(Acetoxymethyl)-3-hydroxy-3-(2-methoxy-1-phenylethyl)isoindolin-1-one (16a): mp 101.0–104.0 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 2.60 (s, 3 H, OAc), 3.52 (s, 3 H, OMe), 3.7–4.0 (m, 2 H), 4.0–4.2 (m, 1 H), 5.49 and 5.70 (ABq, J = 11 Hz, 2 H, NCH_2OAc), 5.50 (s, 1 H, OH), 6.4–7.2 (m, 5 H), 7.3–7.8 (m, 4 H, Ar H); IR (KBr) 3290 (OH), 1720 (br, amide and ester), 1400, 1233, 1106, 958, 718 cm^{-1}; MS, m/e (relative intensity) 277 (15), 263 (40), 234 (30), 161 (25), 160 (60), 135 (30), 116 (20), 105 (30), 104 (100). Anal. Calcd for $C_{20}H_{21}NO_5$:

C, 67.59; H, 5.96; N, 3.94. Found: C, 67.80; H, 5.84; N, 3.98.

(*R*,*R* and *S*,*S*)-2-(Acetoxymethyl)-3-hydroxy-3-(2-methoxy-1-phenylethyl)isoindolin-1-one (16b): mp 130–131.5 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 3 H, OAc), 3.34 (s, 3 H, OMe), 3.5–4.0 (m, 3 H, methylene + methine), 5.42 (s, 1 H, OH), 5.58 and 5.76 (ABq, J = 11 Hz, 2 H, NCH_2OAc), 7.0–7.7 (m, 9 H, Ar H); IR (KBr) 3365 (OH), 1752 (ester), 1700 (amide), 1410, 1218, 1018, 715 cm^{-1}; MS, m/e (relative intensity) 277 (16), 263 (45), 234 (32), 161 (30), 160 (68), 135 (32), 116 (27), 105 (32), 104 (100). Anal. Calcd for $C_{20}H_{21}NO_5$: C, 67.59; H, 5.96; N, 3.94. Found: C, 67.37; H, 5.92; N, 4.14.

Irradiation of 1a with 2c. Photolyses of **1a** with 1,1-diphenylethylene (**2c**) were carried out in methanol and acetonitrile. The results are shown in Table III.

3-(1,1-Diphenyl-2-methoxyethyl)-3-hydroxy-2-methylisoindolin-1-one (19): mp 145–146 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 2.88 (s, 3 H, NMe), 3.26 (s, 3 H, OMe), 4.31 and 4.67 (ABq, J = 10 Hz, 2 H, –CH_2OMe), 5.93 (s, 1 H, OH), 6.8–7.7 (m, 14 H, Ar H); IR (KBr) 3230 (OH), 1668 (amide), 1424, 1388, 1114, 738, 700 cm^{-1}; MS, m/e (relative intensity) 311 (7), 181 (18), 180 (100), 179 (40), 178 (15), 167 (35), 165 (40), 162 (21), 161 (63), 117 (18), 104 (15). Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.22; H, 6.07; N, 3.91.

To a solution of 200 mg of **19** in 200 mL of methanol was added a few drops of perchloric acid, and the solution was left overnight at room temperature. Then the solution was poured into 50 mL of saturated sodium hydrogen carbonate solution and extracted with chloroform. The extract was washed with water and dried over magnesium salfate. After evaporation of the solvent, chromatography of the residue gave 198 mg (95%) of **21**.

3-(1,1-Diphenyl-2-methoxyethyl)-3-methoxy-2-methylisoindolin-1-one (21): mp 158–159 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 2.74 (s, 3 H), 2.87 (s, 3 H), 3.09 (s, 3 H), 4.50 (s, 2 H, –CH_2OMe), 6.8–7.6 (m, 14 H, Ar H); IR (KBr) 1706 (amide), 1378, 1118, 1081, 1024, 738, 702 cm^{-1}; MS, m/e (relative intensity) 311 (33), 211 (20), 210 (100), 180 (57), 179 (36), 176 (33), 167 (47), 165 (29), 161 (74). Anal. Calcd for $C_{22}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.62. Found: C, 77.34; H, 6.44; N, 3.44.

1,1,4-Triphenyl-1,2,3,4-tetrahydronaphthalene (22): mp 80–84 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 1.5–2.2 (m, 2 H), 2.6–2.8 (m, 2 H), 4.25 (dd, J = 6, 7 Hz, 1 H, methine), 6.7–7.5 (m, 19 H, Ar H); IR (KBr) 3020, 2920, 1595, 1483, 1442, 1028 cm^{-1}; MS, m/e (relative intesity) 360 (M$^+$, 13), 358 (8), 283 (29), 280 (100), 191 (29). Anal. Calcd for $C_{28}H_{24}$: C, 93.29; H, 6.71. Found: C, 93.19; H, 6.78.

6,7-Dihydro-6,6-diphenyl-1-methyl-3,4-benzazepine-2,5-dione (23): oil; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H, NMe), 4.30 (br s, 2 H, NCH_2), 7.0–8.0 (m, 14 H, Ar H); IR (neat) 1687 (ketone), 1647 (amide), 1595, 1492, 1397, 1300, 1264 cm^{-1}; MS, m/e (relative intensity) 311 (15), 298 (100), 183 (92), 180 (62).

Reduction of **23** was performed in a similar way as that of **7a**. Starting from 100 mg of **23**, 87 mg of **25** was obtained. The alcohol **25** was insoluble in chloroform, acetone, and Me_2SO. Thus, the ^{1}H NMR data were not obtained.

6,7-Dihydro-6,6-diphenyl-5-hydroxyl-1-methyl-3,4-benzazepin-2(5*H*)-one (25): mp >300 °C; IR (KBr) 3250 (OH), 1627 (amide), 1490, 1444, 1433, 1398, 1250 cm^{-1}; MS, m/e (relative intensity) 343 (M$^+$, 27), 300 (24), 255 (11), 181 (15), 180 (100). Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.17; H, 6.20; N, 3.86.

To a solution of 50 mg of **25** in 10 mL of acetic anhydride was added a few drops of perchloric acid, and the solution was left overnight at room temperature. The solution was poured into 50 mL of water and neutralized by sodium hydrogen carbonate solution. Then, the solution was extracted with chloroform. The extract was washed with water and dried over magnesium sulfate. After evaporation of the solvent, chromatography of the residue gave 41 mg of **26**.

5-Acetoxy-6,7-dihydro-6,6-diphenyl-1-methyl-3,4-benzazepin-2(5*H*)-one (26): mp 192–193 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 2.01 (s, 3 H, OAc), 2.63 (s, 3 H, NMe), 3.56 and 4.41 (ABq, J = 15 Hz, 2 H, NCH_2), 6.7–7.0 (m, 3 H), 6.98 (s, 1 H, *H*COAc), 7.1–7.6 (m, 10 H), 7.7–7.9 (m, 1 H); IR (KBr) 1737 (ester), 1638 (amide), 1430, 1393, 1222, 1038 cm^{-1}; MS, m/e (relative intensity) 386 (17), 385 (M$^+$, 61), 342 (13), 300 (100), 255 (13), 180 (31), 161 (14). Anal. Calcd for $C_{25}H_{23}NO_3$: C, 77.90; H, 6.01; N, 3.63. Found: C, 77.90; H, 6.25; N, 3.58.

3-(Diphenylmethylidene)-2-methylisoindolin-1-one (24): mp 184–185 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 2.92 (s, 3 H, NMe), 6.48 (d, J = 7 Hz, 1 H), 7.1–7.7 (m, 12 H), 7.7–7.9 (m, 1 H); IR (KBr) 1688 (amide), 1610, 1362, 1020 cm^{-1}; MS, m/e (relative intensity) 312 (25), 311 (M$^+$, 100), 310 (9). Anal. Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.63; H, 5.50; N, 4.49.

Irradiation of 1a with 2d. Irraidation of 1.9 g (12 mmol) of **1a** and 10 g (77 mmol) of cyclohexene (**2d**) in 400 mL of methanol gave a mixture of diastereomers **28a + 28b** and **29a + 29b**. The results were described in the text.

3-(2-Cyclohexenyl)-3-hydroxy-2-methylisoindolin-1-one (28a and 28b) as a mixture of the diastereomers: mp 156–161 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 0.7–2.1 (m, 6 H), 2.70 (br s, 3 H, NMe), 2.7–3.1 (m, 1 H), 4.32 (br s, 1 H, OH), 5.72 (br s, 2 H, vinyl H), 7.3–7.7 (m, 4 H, Ar H); IR (KBr) 3210 (OH), 1677 (amide), 1431, 1388, 1094, 1048 cm^{-1}; MS, m/e (relative intensity) 225 (8), 163 (11), 162 (100). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.70. Found: C, 74.15; H, 7.12; N, 5.62.

3-Hydroxy-3-(2-methoxycyclohexyl)-2-methylisoindolin-1-one, diastereomer a (29a): mp 169–171 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 0.6–2.0 (m, 7 H), 2.1–2.5 (m, 2 H), 3.14 (s, 3 H, NMe), 3.51 (s, 3 H, OMe), 3.5–3.8 (m, 1 H, *H*COMe), 6.98 (s, 1 H, OH), 7.3–7.6 (m, 3 H), 7.6–7.9 (m, 1 H); IR (KBr) 3260 (OH), 1668 (amide), 1434, 1082 cm^{-1}; MS, m/e (relative intensity) 163 (13), 162 (100), 82 (9), 67 (6). Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.05. Found: C, 69.60; H, 7.76; N, 4.85.

3-Hydroxy-3-(2-methoxycyclohexyl)-2-methylisoindolin-1-one, diastereomer b (29b): mp 137–138 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 0.0–0.5 (m, 1 H), 0.9–2.5 (m, 8 H), 3.00 (s, 3 H, NMe), 3.61 (s, 3 H, OMe), 3.5–3.8 (m, 1 H, *H*COMe), 6.32 (s, 1 H, OH), 7.2–7.9 (m, 4 H); IR (KBr) 3250 (OH), 1680 (amide), 1428, 1395, 1075 cm^{-1}; MS, m/e (relative intensity) 163 (12), 162 (100), 82 (7), 67 (6). Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.05. Found: C, 70.04; H, 7.94; N, 4.95.

Irradiation of 1a with 2e. Irradiation of 1.9 g (12 mmol) of **1a** and 5 g (71 mmol) of 2-methyl-2-butene (**2e**) in 400 mL of methanol or acetonitrile was performed. The results were described in the text.

3-(1,1-Dimethyl-2-methoxypropyl)-3-hydroxy-2-methylisoindolin-1-one, diastereomer a (30a): mp 132–134 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 0.49 (s, 3 H, MeC*Me*), 1.13 (d, J = 6 Hz, 3 H, HC*Me*), 1.24 (s, 3 H, *Me*CMe), 3.09 (s, 3 H, NMe), 3.43 (s, 3 H, OMe), 3.78 (Q, J = 6 Hz, 1 H, *H*CMe), 5.73 (s, 1 H, OH), 7.3–7.8 (m, 4 H, Ar H); IR (KBr) 3280 (OH), 1668 (amide), 1475, 1426, 1389, 1098 cm^{-1}; MS, m/e (relative intensity) 187 (96), 186 (23), 172 (73), 162 (100), 161 (87), 117 (38), 104 (21). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32. Found: C, 68.26; H, 8.11; N, 5.30.

3-(1,1-Dimethyl-2-methoxypropyl)-3-hydroxy-2-methylisoindolin-1-one, diastereomer b (30b): mp 129–131 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 0.46 (s, 3 H, MeC*Me*), 1.19 (d, J = 6 Hz, 3 H, HC*Me*), 1.35 (s, 3 H, *Me*CMe), 3.15 (s, 3 H, NMe), 3.44 (s, 3 H, OMe), 3.86 (q, J = 6 Hz, 1 H, *H*CMe), 6.62 (s, 1 H, OH), 7.3–7.8 (m, 4 H, Ar H); IR (KBr) 3270 (OH), 1660 (amide), 1432, 1395, 1106, 762 cm^{-1}; MS, m/e (relative intensity) 187 (100), 186 (25), 172 (71), 162 (89), 161 (71), 117 (39), 104 (21), 70 (39). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N. 5.32. Found: C, 68.37; H, 8.10; N, 5.23.

Irradiation of 1a with 2f. Irradiation of 1.9 g (12 mmol) of **1a** and 5 g (91 mmol) of isobutene (**2f**) in 400 mL of methanol or acetonitrile was performed. The results were described in the text.

3-(1,1-Dimethyl-2-methoxyethyl)-3-hydroxy-2-methylisoindolin-1-one (31): oil; ^{1}H NMR ($CDCl_3$) δ 0.81 (s, 3 H, MeC*Me*), 1.07 (s, 3 H, *Me*CMe), 3.05 (s, 3 H, NMe), 3.43 (s, 3 H, OMe), 3.2–3.5 (m, 2 H), 5.50 (s, 1 H, OH), 7.3–7.8 (m, 4 H, Ar H); IR (neat) 3350 (OH), 1690 (amide), 1427, 1394, 1097, 1038, 697 cm^{-1}; MS, m/e (relative intensity) 163 (15), 162 (89), 58 (56), 43 (100). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.71; H, 7.71; N, 5.47.

6,7-Dihydro-1,6,6-trimethyl-3,4-benzazepine-2,5-dione (32): mp 74–75 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 6 H, MeC*Me*), 3.23 (s, 3 H, NMe), 3.47 (s, 2 H, NCH_2), 7.4–8.0 (m, 4 H, Ar H); IR (KBr) 1692 (ketone), 1643 (amide), 1593, 1461, 1390,

1316 cm^{-1}; MS, *m/e* (relative intensity) 217 (M^+, 4), 175 (13), 174 (100), 162 (16), 159 (28), 56 (15), 43 (36). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.86; N, 6.45. Found: C, 72.10; H, 6.98; N, 6.49.

The ketone **32** was reduced in a similar way as that of **7a** to give **33** (85%).

6,7-Dihydro-5-hydroxy-1,6,6-trimethyl-3,4-benzazepin-2-(5*H*)-one (33): mp 188–189 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 3 H, MeC*Me*), 2.10 (s, 3 H, *Me*CMe), 2.62 and 2.90 (ABq, J = 14 Hz, 2 H, NCH_2), 3.08 (s, 3 H, NMe), 3.57 (s, 1 H, *H*COH), 4.20 (s, 1 H, OH), 7.2–7.8 (m, 4 H, Ar H); IR (KBr) 3305 (OH), 1625 (amide), 1595, 1428, 1256, 1058 cm^{-1}; MS, *m/e* relative intensity) 219 (M^+, 100), 190 (61), 161 (56), 44 (100). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82; N, 6.39. Found: C, 71.20; H, 7.82; N, 6.40.

Irradiation of 1a with 2g. Irradiation of 1.9 g (12 mmol) of **1a** and 5 g (71 mmol) of 1-pentene (**2g**) in 400 mL of methanol or acetonitrile was performed. The results were described in the text.

Registry No. **1a**, 550-44-7; **1b**, 85-41-6; **1c**, 5493-24-3; **2a**, 100-42-5; **2b**, 98-83-9; **2c**, 530-48-3; **2d**, 110-83-8; **2e**, 513-35-9; **2f**, 115-11-7; **2g**, 109-67-1; (±)-**3a**, 95362-93-9; (±)-**3b**, 95362-75-7; (±)-**3c**, 95362-76-8; (±)-**3d**, 95362-77-9; (±)-**4a**, 95362-78-0; (±)-**4b**, 95362-79-1; (±)-**4c**, 95362-80-4; (±)-**4d**, 95362-81-5; **5a**, 68085-76-7; **5b**, 95362-82-6; **5c**, 95362-83-7; **6a**, 68085-75-6; **6b**, 95362-84-8; **6c**, 95362-85-9; (±)-**7a**, 95362-86-0; (±)-**7b**, 95362-90-6; (±)-**7c**, 95362-91-7; (±)-**7d**, 95362-92-8; **8**, 67643-55-4; (±)-(*R**,*R**)-**9**, 95362-88-2; (±)-(*R**,*S**)-**9**, 95362-87-1; (±)-(*R**,*R**)-**10**, 95363-20-5; (±)-(*R**,*S**)-**10**, 95362-89-3; (±)-(*R**,*R**)-**11**, 95362-94-0; (±)-(*R**,*S**)-**11**, 95362-95-1; (±)-(*R**,*R**)-**12**, 95362-96-2; (±)-(*R**,*S**)-**12**, 95406-38-5; (±)-(*R**,*R**)-**13**, 95362-98-4; (±)-(*R**,*S**)-**13**, 95362-97-3; (±)-(*R**,*R**)-**14**, 95363-00-1; (±)-(*R**,*S**)-**14**, 95362-99-5; (±)-(*R**,*R**)-**15**, 95363-02-3; (±)-(*R**,*S**)-**15**, 95363-01-2; (±)-(*R**,*R**)-**16**, 95363-03-4; (±)-(*R**,*S**)-**16**, 95363-04-5; **17**, 95363-05-6; (±)-*cis*-**18**, 95363-06-7; (±)-*trans*-**18**, 95363-07-8; (±)-**19**, 95363-08-9; **20**, 41976-80-1; (±)-**21**, 95363-09-0; (±)-**22**, 95363-10-3; **23**, 95363-11-4; **24**, 92172-54-8; (±)-**25**, 95363-12-5; (±)-**26**, 95363-13-6; (±)-(*R**,*R**)-**28**, 95363-14-7; (±)-(*R**,*S**)-**28**, 95363-15-8; **29**, 70113-69-8; (±)-(*R**,*R**)-**30**, 95363-16-9; (±)-(*R**,*S**)-**30**, 95363-17-0; (±)-**31**, 95363-18-1; **32**, 67177-35-9; (±)-**33**, 95363-19-2; **34**, 64837-64-5; phenanthrene, 85-01-8.

Sterols in Marine Invertebrates. 49.[1] Isolation and Structure Elucidation of Eight New Polyhydroxylated Sterols from the Soft Coral *Sinularia dissecta*

Barbara M. Jagodzinska,[†] James S. Trimmer,[‡] William Fenical,[‡] and Carl Djerassi*[†]

Department of Chemistry, Stanford University, Stanford, California 94305, and Institute of Marine Resources, Scripps Institution of Oceanography, La Jolla, California 92093

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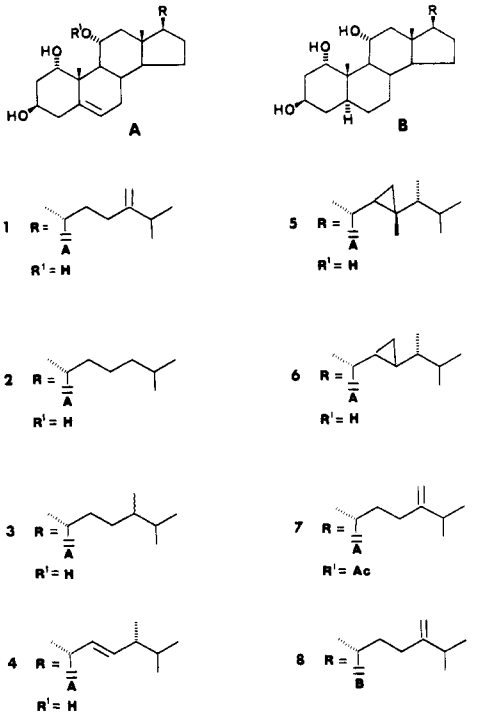
A new group of polyhydroxylated sterols—all of them possessing an 11α-hydroxy substituent of potential utility as corticosteroid intermediates—has been isolated from the soft coral *Sinularia dissecta*. Their general structure was deduced from spectral data (500-MHz and 360-MHz ^{1}H and ^{13}C NMR and MS) and their stereochemistry was determined by correlating the respective spectral data (^{1}H and ^{13}C NMR) with those of synthetic sterols with similar structure and known configuration.

Sterols with three or four hydroxyl functionalities have been previously reported in marine organisms such as soft corals,[2] sponges,[3] and starfish.[4] Our investigation of the sterol mixture from the Pacific soft coral *Sinularia dissecta* Tixier–Durivault collected near Palau led to the isolation and characterization of eight polyhydroxylated sterols (**1**–**8**), all with hydroxyl functions located in the nucleus including the important C-11 position. The crude sterol mixture contained, as major constituents, relatively polar metabolites. These polar fractions were separated into individual compounds by a combination of rapid-elution column chromatography (silica gel) and repeated reverse-phase high-performance liquid chromatography (HPLC) using several different solvent systems. The separation process was monitored at initial stages by TLC and in the latter stages by differential refractometry.

Extensive research has been performed in our laboratories to establish GC and HPLC standards to facilitate the structure determination of marine sterols. Unfortunately, in the present instance the typical standardized gas chromatography conditions were useless because of the excessively long retention times (up to 5 h) required at temperatures which do not decompose these sterols. The same remarks relate also to typical solvent systems for HPLC separations. In general, the best separations of



polyhydroxylated sterols were achieved by using acetonitrile–water systems and repeated separation with dif-

[†] Department of Chemistry.
[‡] Institute of Marine Resources.

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