1200), λ_{max} 274 nm (ϵ 7600); HR-MS for M^+, calcd m/z 145.9883, found 145.9864. Anal. Calcd for $C_4H_3ClN_2O_2$: C, 32.79; H, 2.06; N, 19.19; Cl, 24.19. Found: C, 32.69; H, 2.04; N, 18.86; Cl, 24.14.

Halogenation of Unprotected Nucleosides 5 or 6. A mixture of **5** or **6** (0.5 mmol), halogen sources as above, CAN, and solvent (see Table II) was stirred at 70 or 80 °C. Reaction progress was monitored by TLC (solvent C). After halogenation was complete, the mixture was evarpoated and coevaporated with EtOH/toluene (1:2, 10 mL × 3) and then H_2O/EtOH (1:2, 10 mL × 3). The residual **4d** was twice recrystallized from H_2O/MeOH to give 136 mg (77%, in two crops) of **4d** as colorless crystals. The residual **4a**, **4b**, **4c**, or **4e** was coevaporated with solvent C (10 mL × 2) and dissolved in a minimum volume of that solvent. This sample was applied to a dry-packed columm (Merck silica gel 60, 70–230 mesh, 55 g, 2.2 × 27 cm) and eluted with solvent C. Appropriately pooled fractions were evaporated and coevaporated with toluene/EtOH (2:1, 10 mL × 2) to give a colorless crystalline solid. This was recrystallized from MeOH/Et_2O (diffusion[26b]) to an analytically pure product: **4a**, 147 mg, 80%; **4b**, 132 mg, 82%; **4c**, 115 mg, 83%; **4e**, 124 mg, 81%.

Acknowledgment. We thank members of the Analytical Center of Dainippon Pharmaceutical Co., Ltd., for elemental analyses; Dr. M. Morita of the Mass Spectroscopy Laboratory, Faculty of Science and Engineering, Kinki University, for measurement of mass spectra; and Y. Mine of the NMR Spectroscopy Laboratory, Institute of Life Sience, Kinki University School of Medicine, for help with obtaining NMR spectra.

Photoinduced Molecular Transformations. 110.[1] Formation of Furoquinolinones via β-Scission of Cyclobutanoxyl Radicals Generated from [2 + 2] Photoadducts of 4-Hydroxy-2-quinolone and Acyclic and Cyclic Alkenes. X-ray Crystal Structure of (6aα,6bβ,10aβ,10bα)-(±)-10b-Acetoxy-6a,6b,7,8,9,10,10a,10b-octahydro-5-methylbenzo[3,4]cyclobuta[1,2-*c*]quinolin-6(5*H*)-one[2,3]

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Several [2 + 2] photocycloadducts were prepared by the photoaddition of 4-acetoxy-2-quinolone or 4-hydroxy-*N*-methyl-2-quinolone with cyclic and acyclic olefins. The photoaddition of 4-acetoxy-2-quinolone with cyclopentene gave, exclusively, cis-cisoid-cis adduct while that with 1-methoxycyclopentene gave, exclusively, a head-to-head cis-transoid-cis adduct. Photoaddition with cyclohexene, on the other hand, afforded cis-cisoid-cis together with cis-transoid-cis adducts. The molecular structure of the latter was determined by an X-ray crystallographic analysis of its *N*-methyl derivative. Photoadditions of 4-acetoxy-2-quinolone and 4-hydroxy-*N*-methyl-2-quinolone with ethyl vinyl ether, 2-methoxypropene, isopropenyl acetate, and vinyl benzoate were all regioselective, each giving the corresponding single or double stereoisomers of head-to-head adduct(s). The photolysis of the hypoiodites generated from cyclobutanols derived from the photocycloadducts between 4-acetoxy-2-quinolone and cyclopentene or 2,3-dimethylbut-2-ene induced regioselective rearrangements of the corresponding alkoxyl radicals to give 2,3-furo-4-quinolinones. In contrast, 3,4-furo-2-quinolinones are regioselectively formed when the hypoiodites generated from cyclobutanols derived from the photoadducts of 4-acetoxy-2-quinolone with vinyl ethyl ether, isopropenyl acetate, or 1-methoxycyclopentene in benzene are irradiated. Both 3,4-furo-2-quinolinone and 2,3-furo-4-quinolinone are formed when the hypoiodites of cyclobutanols derived from the photoadducts between 4-hydroxy-2-quinolone and vinyl esters in benzene are irradiated. The pathways leading to the 2,3-furo-4-quinolinones and 3,4-furo-2-quinolinones as well as the selectivity in the formation of the two isomeric furoquinolinones from the cyclobutanoxyl radicals are discussed.

The [2 + 2]π cycloaddition is one of the most synthetically useful photoreactions. Numerous applications of both inter- and intramolecular [2 + 2] photoaddition to the synthetic problems have been reported using a variety of conjugated and nonconjugated cyclic and acyclic alkenes.[4] One of the remarkable applications is photoaddition of an alkene to an enolyzed 1,3-diketone or its acetate to form a β-ketocyclobutanol or its acetate, which can ionically fragment to give a 1,5-diketone by retro-aldolization.[5]

As part of our investigation to explore the potential of the β-scission of alkoxyl radicals for organic synthesis,[6] we

(1) For part 109, see: Suginome, H.; Ohtsuka, T.; Yamamoto, Y.; Orito, K.; Jaime, C.; Osawa, E. *J. Chem. Soc., Perkin Trans. I* **1990**, 1247.
(2) Presented at the 11th International Congress of Heterocyclic Chemistry, Heidelberg, August, 1987; Abstr. p 348.
(3) Preliminary communication: Suginome, H.; Kobayashi, K.; Itoh, M.; Furusaki, A. *Chem. Lett.* **1985**, 727.
(4) For reviews of enone photochemical cycloaddition, see; (a) Baldwin, S. W. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 123. (b) Weedon, A. C. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1980; p 91.
(5) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41.

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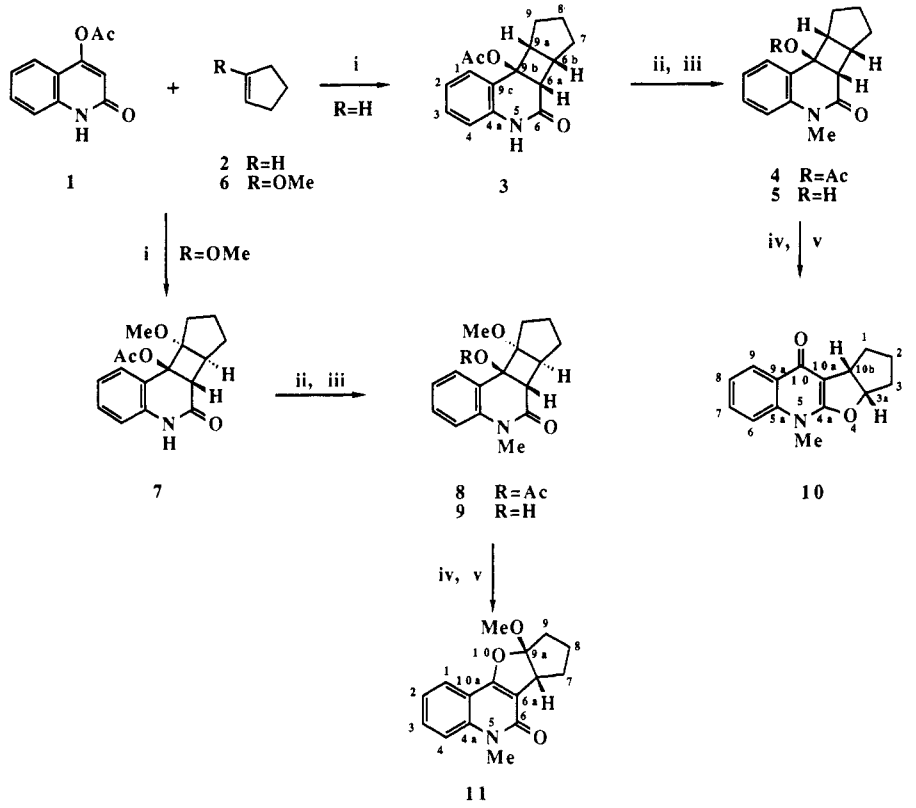
Scheme I



recently investigated an application of the regioselective radical opening of cyclobutane rings, induced by alkoxyl radicals generated from cyclobutanols, to organic synthesis.[7,8] We considered that if the scission is regioselective the radical cleavage of the strained cyclobutane rings would become a valuable process in synthesis since, in contrast to ionic cleavage, the process does not require a base and the presence of an extra functional group such as a carbonyl in the cyclobutanols. We in fact found that when the alkoxyl radicals are generated from cyclobutanols obtained by the [2 + 2] photoaddition of 4-hydroxycoumarin as an enolized 1,3-diketone to various acyclic and cyclic alkenes, a regioselective β-scission took place to afford a fused furan ring arising from an intramolecular combination of a carbonyl oxygen and a carbon-centered radical generated from β-scission. Several new furocoumarins and furochromones were thus synthesized via this new process.

From a synthetic point of view, it was considered to be worth while to explore an extension of this oxygen insertion to the cyclobutane ring to the cyclobutanols obtained by a [2 + 2] photocycloaddition of 4-hydroxy-2-quinolone with olefins, since a number of natural products having a furoquinolinone skeleton have been isolated.[9,10] An extention of the reaction of the coumarin adducts to the quinolone series in order to examine the effects of replacing the ring oxygen of the coumarin adducts by a nitrogen atom is also of considerable mechanistic interest.

In this paper we report on the results of an investigation which has shown that the reaction is useful for the synthesis of 2,3-furo-4-quinolinones and 3,4-furo-2-quinolinones and that there are appreciable differences in the selectivity in forming the two types of products in this reaction involving a β-scission of alkoxyl radicals when the ring oxygen of the coumarin adducts is replaced by a nitrogen atom.

Results

[2 + 2] Photoadditions of 4-Acetoxy- or 4-Hydroxy-2-quinolone with Alkenes, Vinyl Ethers, or Vinyl Esters and Preparation of Cyclobutanols 5, 9, 17, 18, 19, 23, 30, and 34 from the [2 + 2] Photoadducts (Schemes I–IV). Four cyclobutanols, **5**, **17**, **18** and **23**, obtainable by a [2 + 2] photocycloaddition of quinolones

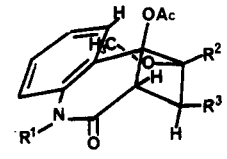
(6) For our recent papers on synthetic applications of β-scission of alkoxyl radicals, see: (a) Suginome, H.; Yamada, S. *Chem. Lett.* **1984**, 2079. (b) Suginome, H.; Liu, C. F.; Tokuda, M. *J. Chem. Soc., Perkin Trans. I* **1985**, 3227. (c) Suginome, H.; Yamada, S. *J. Org. Chem.* **1985**, *50*, 2489. (d) Suginome, H.; Kobayashi, K.; Itoh, M.; Furusaki, A. *Chem. Lett.* **1985**, 727. (e) Suginome, H.; Yamada, S.; *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3055. (f) Suginome, H.; Yamada, S.; *Synthesis* **1986**, 7421. (g) Suginome, H.; Yamada, S. *Tetrahedron Lett.* **1987**, *28*, 3963. (h) Suginome, H.; Washiyama, H.; Yamada, S. *Bull. Chem. Soc. Jpn.* **1987**, 1071. (i) Suginome, H.; Yamada, S.; *Tetrahedron* **1987**, *43*, 3371. (j) Suginome, H.; Yamada, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2453. (k) Kobayashi, K.; Itoh, M.; Suginome, H. *Tetrahedron Lett.* **1987**, *28*, 3369. (l) Suginome, H.; Itoh, M.; Kobayashi, K. *Chem. Lett.* **1987**, 1527. (m) Suginome, H.; Itoh, M.; Kobayashi, K. *J. Chem. Soc., Perkin Trans. I* **1988**, 491. (n) Suginome, H.; Wang, J. B. *Bull. Chem. Soc. Jpn.* **1989**, *52*, 193. (o) Suginome, H.; Yamada, S. *Chem. Lett.* **1988**, 245. (p) Suginome, H.; Satoh, G.; Wang, J. B.; Yamada, S.; Kobayashi, K. *J. Chem. Soc., Perkin Trans. I* **1990**, 1239. (q) Suginome, H.; Yamada, S.; Wang, J. B. *J. Org. Chem.* **1990**, *55*, 2170.

(7) Suginome, H.; Liu, C. F.; Furusaki, A. *Chem. Lett.* **1984**, 911. Suginome, H.; Liu, C. F.; Furusaki, A. Ibid. **1985**, 27.

(8) Suginome, H.; Liu, C. F.; Seko, S.; Kobayashi, K.; Furusaki, A. *J. Org. Chem.* **1988**, *53*, 5952 and references cited therein.

(9) E.g.; (a) Rapoport, H.; Holden, K. G. *J. Am. Chem. Soc.* **1959**, *81*, 3738. (b) Goodwin, S.; Shoolery, J. N.; Johnson, S. F. *Ibid.* **1959**, *81*, 3065. (c) Goodwin, S.; Smith, A. F.; Velasquez, A. A.; Horning, E. C. *Ibid.* **1959**, *81*, 6209. (d) Goodwin, S.; Horning, E. C. *J. Am. Chem. Soc.* **1959**, *81*, 1908. (e) Rapoport, H.; Holden, K. G. *J. Am. Chem. Soc.* **1960**, *82*, 4395. (f) Clarke, E. A.; Grundon, M. F. *J. Chem. Soc.* **1964**, 438. (g) Toube, T. P.; Murphy, J. W.; Cross, A. D. *Tetrahedron* **1967**, *23*, 2061. (h) Chamberlain, T. R.; Grundon, M. F. *J. Chem. Soc. C* **1971**, 910. (i) Collins, J. F.; Gray, G. A.; Grundon, M. F.; Harrison, D. M.; Spyropoulos, C. G. *J. Chem. Soc., Perkin Trans. I* **1973**, 94. (j) Gaston, J. L.; Greer, R. J.; Grundon, M. F. *J. Chem. Res., Synop.* **1985**, 135; *J. Chem. Res., Miniprint* **1985**, 1877.

(10) For a review on quinoline alkaloids, see: Grundon, M. F. *The Alkaloids*; Brossi, A., Ed.; Academic Press: San Diego, 1988; Vol. 32, p 341.



$R^1=R^2=Me$, $R^3=H$
$R^1=H$, R^2, $R^3=-(CH_2)_3-$

Figure 1.

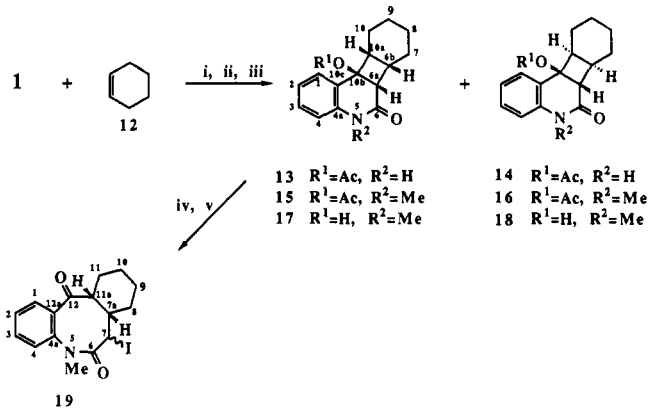
with cyclopentene, cyclohexene, and dimethylbut-2-ene, as well as seven cyclobutanols, **9**, **29**, **30**, **34**, **41**, **43**, and **44**, obtainable by the photoaddition of quinolones with cyclic and acyclic vinyl ethers and vinyl esters were used in the present investigation. The formation of a cyclobutanol by the photocycloaddition of 4-hydroxy-*N*-methyl-2-quinolone with cyclohexene was first reported by Reid and his colleagues[11] in England. Kaneko and his colleagues[12] in Japan subsequently reported on their extensive studies regarding the photoaddition of 4-alkoxy-2-quinolone with alkenes and the application of the adducts to the synthetic problems. We have found that the [2 + 2] photoaddition of 4-acetoxy-2-quinolone (**1**), rather than 4-hydroxy-*N*-methyl-2-quinolone,[11] with the above olefins gave better yields of the photocycloadducts. Thus, all cyclobutanols in the present study, with the exception of the cyclobutanols obtained by a [2 + 2] photocycloaddition of 4-hydroxy-*N*-methyl-2-quinolone (**39**) with vinyl esters **40** and **42**, were synthesized by a [2 + 2] photoaddition of 4-acetoxy-2-quinolone (**1**) with appropriate olefins or vinyl ethers, followed by *N*-methylation of the resulting photoadducts and hydrolysis of the acetoxyl group of the resulting *N*-methyl derivatives.

Irradiation of 4-acetoxy-2-quinolone and cyclopentene in methanol for 12 h under a nitrogen atmosphere with a 400-W high-pressure mercury are through a Pyrex-filter gave, exclusively, crystalline adduct **3** in 64% yield (Scheme I). A cis-cisoid-cis stereochemistry has been assigned to adduct **3** on the basis of a comparison of the ^1H NMR spectrum with that of the oxygen analogue for which a cis-cisoid-cis stereochemistry was established by means of an X-ray crystallographic analysis.[8]

It should be noted that the exclusive formation of the sterically disfavored cis-cisoid-cis adduct in the photocycloaddition of 4-acetoxy-2-quinolone (**1**) with cyclopentene is entirely parallel to the behavior of the excited 4-hydroxycoumarin, although sterically favored cis-transoid-cis isomers have always been preferential addition products in the photoaddition of cyclic enones and cycloalkenes.[4b]

The photoaddition of 4-acetoxy-2-quinolone (**1**) with 1-methoxycyclopentene (**6**) in methanol was also regioselective to give a single crystalline photoadduct (**7**) in 70% yield (Scheme I). The ^1H NMR spectrum exhibited a doublet at δ 2.66 with J = 7.69 Hz. This result indicated that adduct **7** was 9a-methoxy-9b-acetoxy-5,6a,6b,7,-8,9,9a,9b-octahydro-6*H*-cyclopenta[3,4]cyclobuta[1,2-*c*]-quinolin-6-one. The results of the ^1H NMR spectrum with the aide of NOE studies indicated that in contrast to adduct **3**, it had a cis-transoid-cis configuration; when the methoxyl signal (δ 1.99) was irradiated, an enhancement of the signal areas of a multiplet centered at δ 2.6 (6b-H) as well as a doublet of δ 7.30 (1-H) was observed. An inspection of the molecular model of adduct **3** (Figure 1) indicated that when adduct **3** has a cis-transoid-cis stereochemistry, the aromatic peri hydrogen (1-H) is in close vicinity of the methoxyl group and the NOE should be observed. The assigned cis-transoid-cis configuration of adduct **7** was also supported by the results of NOE studies of the *N*-methyl derivative **8**; irradiation of the doublet due to 6a-H (δ 2.75) resulted in no enhancement of the multiplet signal due to 6b-H (δ 2.4–2.5) while irradiation of the methoxyl signal (δ 2.97) resulted in an enhancement of the integrals of the multiplet (6b-H) and a doublet of doublets at δ 7.34 (aromatic 1-H).

Scheme II[a]



13 R^1=Ac, R^2=H
15 R^1=Ac, R^2=Me
17 R^1=H, R^2=Me

14 R^1=Ac, R^2=H
16 R^1=Ac, R^2=Me
18 R^1=H, R^2=Me

19

[a] (i) *hν*–MeOH; (ii) NaH–MeI–DMF; (iii) K_2CO_3–aq MeOH; (iv) HgO–I_2–benzene; (v) *hν*.

The photocycloaddition of **1** with cyclohexene under conditions similar to those stated above, on the other hand, afforded two stereoisomeric photocycloadducts, **13** and **14**, which are separable by means of preparative TLC in 41 and 52% yields (Scheme II). The ^1H NMR spectra of **13** and **14** exhibited a doublet at δ 3.79 (J = 8.97) and 3.37 (J = 10.33) assignable to protons attached to their carbon atoms adjacent to their carbonyls. The IR spectrum of **13** exhibited a band due to the carbonyl group at a wavelength very similar to that of adduct **3**. These spectral results suggested that adducts **13** and **14** had a cis-cisoid-cis and a cis-transoid-cis stereochemistry, respectively. The molecular structure of adduct **14** was then independently determined by an X-ray crystallographic analysis of its *N*-methyl derivative **16** (vide infra) to have the cis-transoid-cis stereochemistry (see Experimental Section).

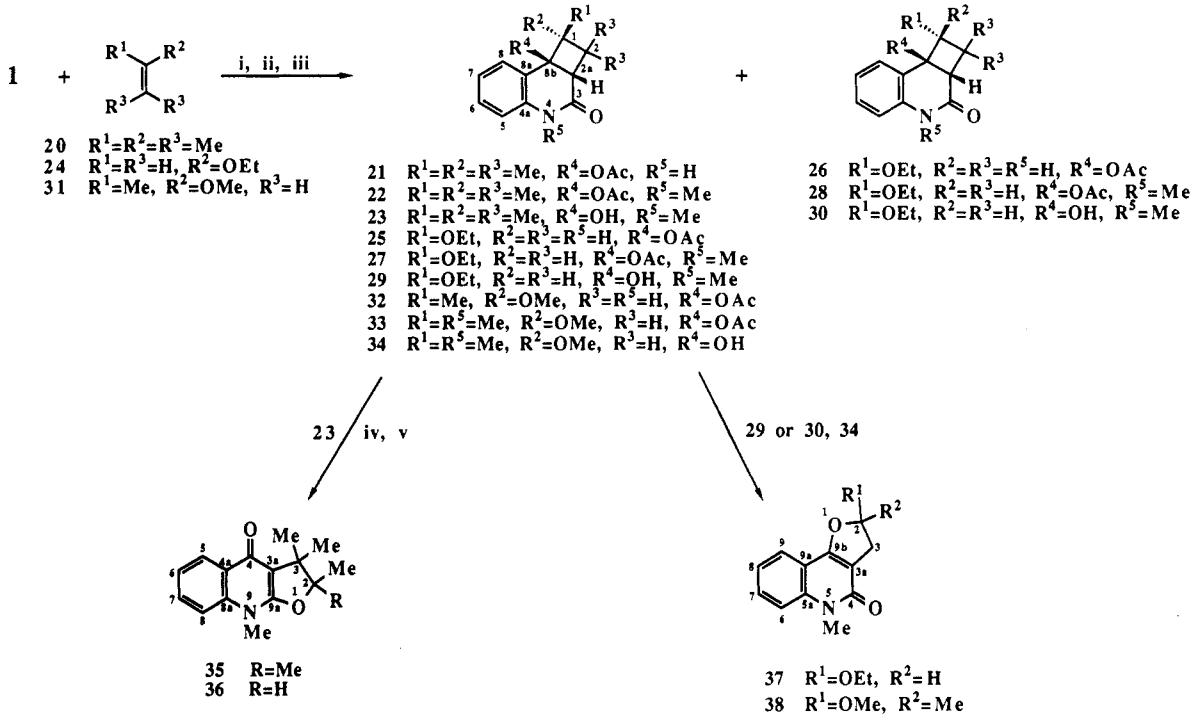
The photocycloaddition of **1** with 2,3-dimethylbut-2-ene (**20**) as a representative alkene gave cycloadduct **21** in poor yield (11%) (Scheme III).

We then prepared several cycloadducts of 4-hydroxy-2-quinolone with vinyl ethers or vinyl esters. The photocycloaddition of 4-acetoxy-2-quinolone (**1**) with ethyl vinyl ether (**24**) in methanol was regioselective and gave two isomeric photoadducts, **25** and **26**, in a combined yield of 90% (Scheme III). The ^1H NMR spectra of adducts **25** and **26** exhibited 2a-H protons adjacent to their carbonyl at δ 3.69 (dd, J = 10.99 and 9.89 Hz) and at δ 2.93 (dd, J = 9.52 and 9.16 Hz), each as a doublet of doublets. These results indicated that both isomers are head-to-head-type adducts. The high regioselectivity of the photoaddition, which is parallel to the photoaddition of 4-hydroxycoumarin and vinyl ethyl ether,[8] is remarkable.

The stereochemistry of adducts **25** and **26** was established by ^1H NMR spectroscopy; the cyclobutane and quinolone rings of **25** and **26** should be cis-fused. NOE studies indicated that when signals ascribable to the 1-H of **26** are irradiated, the enhancement of the signal area of a proton attached to the C(2a) could be observed. This result indicated that the 1-H and 2a-H of **25** and **26** are

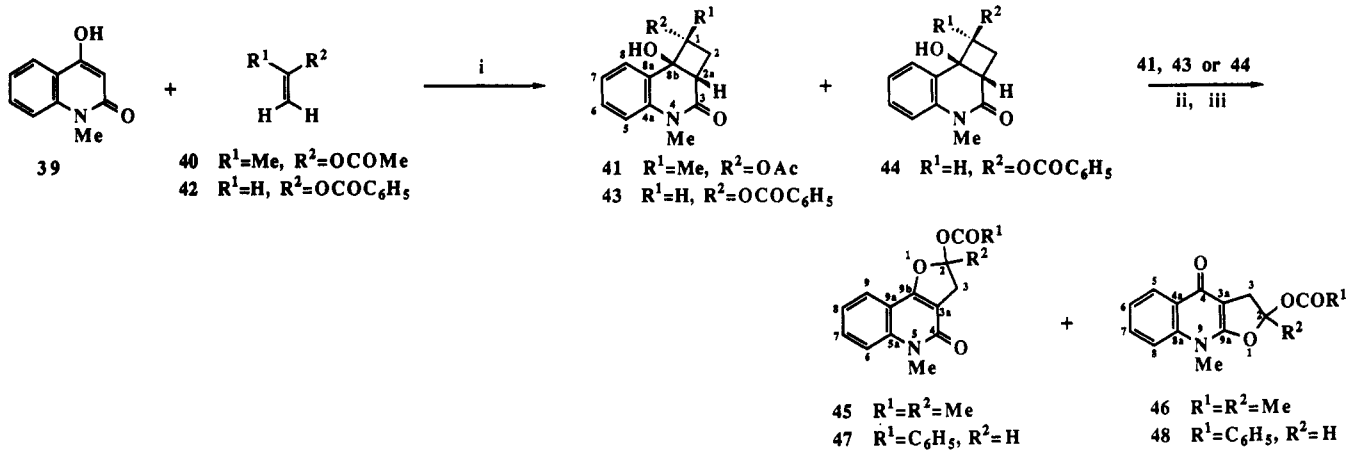
(11) Hunt, R. G.; Potter, C. J.; Reid, S. T.; Roantree, M. L. *Tetrahedron Lett.* **1975**, 2327.
(12) Kaneko, C.; Naito, T.; Ito, M. *Chem. Pharm. Bull.* **1980**, *28*, 3150 and subsequent papers by Kaneko and his colleagues.

Scheme III[a]



[a] (i) $h\nu$–MeOH; (ii) NaH–MeI–DMF; (iii) K_2CO_3–aq MeOH; (iv) HgO–I_2–benzene; (v) $h\nu$.

Scheme IV[a]



[a] (i) $h\nu$–MeOH; (ii) HgO–I_2–benzene; (iii) $h\nu$.

oriented trans and cis, respectively.

The photoaddition of 4-acetoxy-2-quinolone (**1**) and 2-methoxypropene (**31**) in methanol was again regio- and stereoselective and gave a single crystalline adduct (**32**) in 84% yield (Scheme III). The ^{1}H NMR spectra of adduct **32**, the *N*-methyl derivative, and the cyclobutanol derived from hydrolysis (vide infra) have indicated that it was again a head-to-head-type adduct.

The stereochemistry of adduct **32** was again established by means of NOE measurements of the *N*-methyl derivative **33** (vide infra). Thus, irradiation of the methyl group signal in the ^{1}H NMR spectrum of **33** resulted in an enhancement of the 2a-H signal integral. This result has indicated that the 1-Me and 2a-H are oriented cis to each other.

Finally, the photocycloaddition of 4-hydroxy-2-quinolone **39** and vinyl esters **40** and **42** were undertaken. The photocycloaddition of 4-hydroxy-*N*-methyl-2-quinolone (**39**) with isopropenyl acetate (**40**) in methanol under the conditions above led to a regioselective addition to give rise to a single crystalline photoadduct (**41**) in 65% yield (Scheme IV). The ^{1}H NMR spectrum exhibited a doublet of doublets with J = 10.62 and 9.98 Hz, assignable to the 2a-H, indicating it to be a head-to-head cycloadduct. It remained uncertain whether the hydroxyl and acetoxyl are cis or trans. The high regio- and stereoselectivity of the cycloaddition is again remarkable.

The photocycloaddition of 4-hydroxy-*N*-methyl-2-quinolone (**39**) with vinyl benzoate (**42**), on the other hand, gave two isomeric cycloadducts, **43** and **44**, in moderate yields (23% and 28%) (Scheme IV). The ^{1}H NMR spectra of cycloadducts **43** and **44** indicated that both isomers are head-to-head-type adducts. The ^{1}H NMR spectrum of **43** exhibited a proton attached to the 2a-carbon as a doublet of doublets at δ 3.24 (J = 10.26 and 9.16 Hz) and that of **44** exhibited a corresponding proton at δ 3.75 (ddd, J = 10.99, 9.90, and 1.10 Hz), indicating that they are head-to-head-type adducts. The stereochemistry of the hydroxyl

and benzoyloxy groups of adducts **43** and **44** were again determined by means of NOE measurements. Irradiation of the signal at δ 5.49 (1 H, dd), ascribable to 1-H in the ^{1}H NMR spectrum of **43**, resulted in an enhancement of a signal of the 2a-H at δ 3.24 (1 H, dd), while irradiation of the signal of 1-H at δ 5.37 (1 H, ddd) of **44** resulted in no enhancement of the signal at δ 3.75 (1 H, ddd) due to the 2a-H but did result in an enhancement of the signal at δ 2.59 (1 H, ddd), ascribable to the exo-2H. These results clearly indicated that the hydroxyl and benzoyloxy groups of **43** and **44** are oriented trans and cis, respectively.

The cycloadducts of 4-acetoxy-2-quinolone with cycloalkenes, alkenes, or vinyl ethers, obtained as mentioned above, were then subjected to N-methylation with methyl iodide–sodium hydride in DMF at −20 °C to give the corresponding *N*-methyl derivatives **4**, **8**, **15**, **16**, **22**, **27**, **28**, and **33**. Hydrolysis of the acetoxyl group of the *N*-methyl derivatives with potassium carbonate in aqueous methanol at room temperature afforded the corresponding cyclobutanols **5**, **9**, **17**, **18**, **23**, **29**, **30**, and **34** in good yields. The preparation of an adduct (mp 237–238 °C) of undefined stereochemistry corresponding to cyclobutanol **17** or **18** or their mixture by a [2 + 2] photoaddition of 4-hydroxy-*N*-methyl-2-quinolone with cyclohexene has been reported by previous investigators.[11]

Formation of Furoquinolinones vis β-Scission of Cyclobutanoxyl Radicals Generated from the Fused Cyclobutanols (Schemes I–IV). The irradiation of cyclobutanol **5** in benzene containing mercury(II) oxide and iodine (each 3 equiv) in a Pyrex vessel with a 100-W high-pressure mercury arc under a nitrogen atmosphere for 6 h gave crystalline product **10** in 21% isolated yield. The molecular formula of **10** was established to be $C_{15}H_{15}NO_2$ by high-resolution mass spectrometry. The IR spectrum exhibited two bands at 1589 and 1615 cm^{-1}, assignable to a quinolinone structure. The ^{1}H NMR spectrum exhibited a multiplet at δ 5.4–5.5, ascribable to a proton attached to a carbon carrying an oxygen. These spectral results have indicated that the structure of the product was *cis*-1,2,3,3a,5,10b-hexahydro-5-methyl-10*H*-cyclopenta[4,5]furo[2,3-*b*]quinolin-10-one (**10**) (Scheme I).

In contrast to the results of the photolysis of photocycloadduct **5**, an analogous reaction of cyclohexene photocycloadduct **17** resulted in a ring expansion to give a 3:2 mixture of two stereoisomeric eight-membered lactams **19** in 14% yield, that of the isomeric cyclohexene adduct **18** resulted only in a complex mixture of products (Scheme II).

The photolysis of cyclobutanol **23** under similar conditions gave, exclusively, a single product (**35**) in 63% yield (Scheme III). High-resolution mass spectrometry indicated that it had the molecular formula $C_{16}H_{19}NO_2$. The presence of two bands at 1585 and 1617 cm^{-1}, assignable to the enaminone group in the IR spectrum, indicated that it is a 2,3-furoquinol-4-one, 3,9-dihydro-2,2,3,3,9-pentamethylfuro[2,3-*b*]quinolin-4(2*H*)-one (**35**). Furoquinolone **36**, devoid of the 2-Me in furoquinolone **35**, is an alkaloid, ifflaiamin.[9h]

The photolysis of the hypoiodite of cyclobutanol **9** prepared from the photoadduct between 4-acetoxy-2-quinolone and cyclopentanone enol ether **6** afforded a single crystalline product (**11**) in 62% yield (Scheme I). The IR spectrum of **11** indicated that the 2-quinolone nucleus was intact, and all of the spectroscopic data indicated the structure to be *cis*-(±)-6b,8,9,9a-tetrahydro-9a-methoxy-6*H*,7*H*-cyclopenta[4,5]furo[3,2-*c*][1]benzopyridin-6-one. The spectroscopic data of 3,4-furo-2-quinolinone **11** are recorded in the Experimental Section. None of the isomeric 2,3-furo-4-quinolone derivatives were detected in the product. The irradiation of the hypoiodites of cyclobutanols **29**, **30**, and **34** derived from the photocycloadducts between 4-acetoxy-2-quinolone and vinyl ethers **24** and **31** similarly gave, exclusively, the 3,4-furo-2-quinolones **37** and **38** (50–55%), which arose from an intramolecular regioselective combination of the carbonyl oxygen and the carbon radical generated from β-scission of the alkoxyl radicals (Scheme III). Their structures were readily established on the basis of their spectroscopic data (recorded in the Experimental Section).

Finally, the photolysis of the hypoiodite of cyclobutanols **41** and **44**, obtained by the photocycloaddition between *N*-methyl-4-hydroxy-2-quinolone and vinyl esters, was undertaken. The irradiation of the hypoiodite of cyclobutanol **41**, obtained by photoaddition of quinolone **39** with isopropenyl acetate (**40**), in benzene gave two crystalline products, **45** and **46**, in 40 and 21% yields (Scheme IV). Elemental analysis and mass spectrometry indicated that both products had the molecular formula $C_{15}H_{15}NO_4$. The IR spectrum of product **44** exhibited two bands at 1671 and 1639 cm^{-1}, assignable to the lactam carbonyl. This result, together with the result of the ^{1}H NMR and mass spectrum, indicated that the structure of product **45** was 3,4-furo-2-quinolone **45**. The IR spectrum of isomeric product **46**, on other hand, exhibited two bands at 1639 and 1588 cm^{-1}, assignable to the enone-type carbonyl group. The ^{1}H NMR spectrum exhibited a one-proton doublet at δ 8.45 with J = 7.91 Hz. These spectral data indicated that the product is enaminone **46** and that the deshielded proton at δ 8.45 is ascribable to the peri hydrogen (5-H).

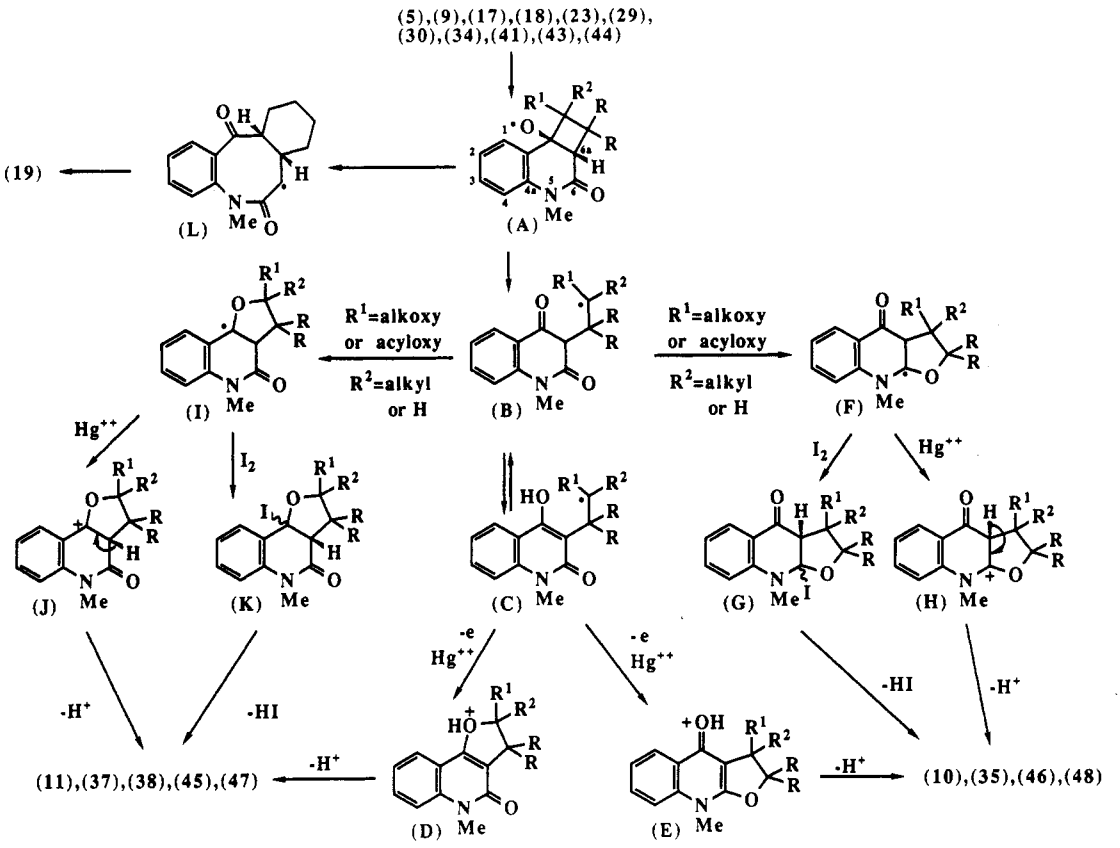
Irradiation of the hypoiodite of cyclobutanol **44**, obtained by photoaddition of quinolone **39** with vinyl benzoate (**42**), also gave two crystalline products, **47** and **48**, and 17 and 31% yields (Scheme IV). High-resolution mass spectrometry indicated that both products had the molecular formula $C_{19}H_{19}NO_4$. The IR and ^{1}H NMR spectra proved that the products were 3,4-furo-2-quinolone **47** and 2,3-furo-4-quinolone **48**. (Details of their spectroscopic data are recorded in the Experimental Section.)

Discussion

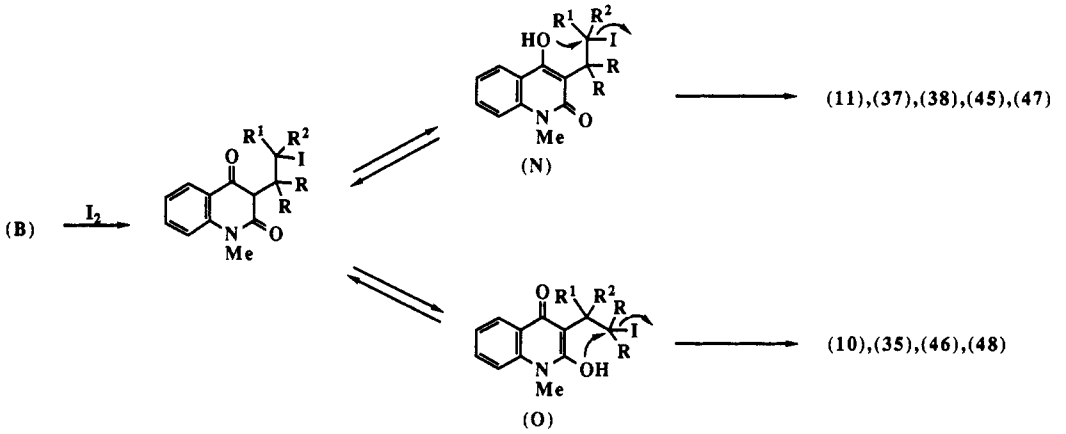
The above-mentioned experiments have revealed that the cyclobutanols derived from a [2 + 2] photocycloaddition between 4-hydroxy-2-quinolone and various types of olefins gives 2,3-furo-4-quinolone (the linear type) and/or 3,4-furo-2-quinolones (the angular type) when their benzene solutions containing 3 equiv each of mercury(II) oxide and iodine are irradiated with Pyrex-filtered light.

The probable paths that led to the formation of 2,3-furo-4-quinolones **10**, **35**, **46**, and **48**, 3,4-furo-2-quinolones **11**, **37**, **38**, **45**, and **47**, and an eight-membered lactam (**19**) from the photolysis of the hypoiodites of cyclobutanols **4**, **8**, **17**, **18**, **23**, **29**, **30**, **34**, **41**, **43**, and **44** are outlined in Scheme V. These paths are parallel to those leading to the reported formation of furochromones (the linear type) and/or furocoumarins (the angular type) when benzene solutions of cyclobutanols derived from the [2 + 2] photocycloaddition between 4-hydroxycoumarin and various olefins are treated with mercury(II) oxide and iodine and then irradiated under conditions comparable to the present experiments.[8] As in the case of the photolysis of the hypoiodites of the cyclobutanols derived from the cycloaddition of coumarin and olefins,[8] most of the alkoxyl radicals A, generated from quinolone–olefin adducts, gave a carbon-centered radical (B) by a regioselective β-scission of the outer bond of their fused cyclobutane ring. Only the alkoxyl radical A generated from quinolone–cyclo-

Scheme V



Scheme VI

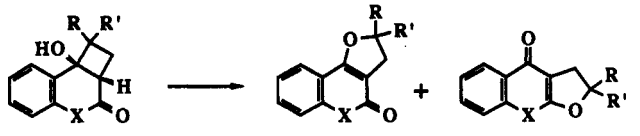


hexene adducts **17** and **18** behaved differently and gave a carbon-centered radical (L) by a β-scission of the inner bond of the fused cyclobutane ring.

As outlined, there are two principal paths (each) for the formation of the linear-type products [**10**, **35**, **46**, **48**] and the angular-type products [**11**, **37**, **38**, **45**, and **47**] from the radical B. The radical B may well be in equilibrium with the enol form C. One-electron oxidation of species C followed by an intramolecular combination with oxygen[15] may give rise to linear- and angular-type products, D and E. Alternatively, the keto form of the radical B combines with the carbonyl oxygen intramolecularly to form a dihydrofuranyl radical, I or F. Linear and angular products may be formed either through an elimination of HI from species K or G or through oxidation to carbocation J or H, followed by the removal of a proton. Yet, there is a third hypothetical path (Scheme VI) for the formation of the products. The radical B may abstract an iodine atom from ROI or I_2 in a free radical chain process to give iodides M. An intramolecular nucleophilic displacement of the iodine atom by the enol oxygen of the iodide N or O may give the products. This third path is, however, very unlikely since it involves the formation of such an improbable species as tertary iodide N or O and the intramolecular nucleophilic displacement of the iodine atom by the enol oxygen of species N and O, as in the case of the corresponding reactions of coumarin adducts previously reported by us.[8]

The selectivity for the formation of angular- and linear-type products in the present furoquinolone formation should be determined by many factors. At the present stage we can only state some distinct features in the selectivity of the formation of the two types of products in the above-mentioned experiments. The selectivity in the formation of the angular- and linear-type products in the furoquinolone formation is summarized in Table I. For a comparison, the results[8] concerning the coumarin adduct series are also included in the table.

Table I



A B

substitutents			product	
X	R	R′	A	B
NMe	Me	Me	–	+
O	Me	Me	+	+
NMe	OEt	H	+	–
O	OEt	H	+	–
NMe	OMe	Me	+	–
NMe	OCOMe	Me	+	+
O	OCOMe	Me	+	–
NMe	OCOPh	H	+	+
NMe	OMe	cyclopentane	+	–
NMe	cyclopentane	H	–	+
O	cyclopentane	H	+	–

The most distinct feature is the effect of alkoxyl groups on the selectivity: the exclusive formation of angular-type products was found, without exception, in the photolysis of cyclobutanol adducts carrying an alkoxyl group on the cyclobutane ring. This same feature has also been found in reactions of the coumarin series.[8] Although the reason for this directing effect is not yet clear, one of the reasons would be that a repulsive force between the alkoxyl group and the amide moiety in intermediate B may prohibit an intramolecular combination of the radical with the amide oxygen.

The directing effects of the acetoxyl and benzoyloxy group are not as strong as that of the alkoxyl groups; both angular and linear furoquinolones are produced when the hypoiodites of cyclobutanols carrying these groups on the cyclobutane ring are irradiated.

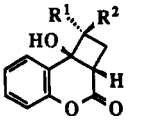
Another clear outcome is the effect of alkyl groups: an exclusive formation of the angular-type products was found when the hypoiodites of cyclobutanols carrying methyl groups or a fused cyclopentane ring were irradiated. This effect is reverse to that of the alkoxyl groups mentioned above. The effect of the fused cyclopentane ring is also reverse to that of the fused cyclopentane ring in the coumarin adduct series.[8]

Thus, there are several differences regarding selectivity in the formation of angular- and linear-type products between the alkoxyl radicals generated from quinoline cyclobutanols and those generated from coumarin cyclobutanols. This difference may be an indication of the importance of electronic effects on selectivity.

The present synthesis of furoquinolones may find application to the synthesis of natural products[10] having a furoquinolone skeleton as well as related compounds.

Corrections of the Assigned Stereochemistry of the Photoadducts[8] of 4-Hydroxycoumarin with Isopropenyl Acetate and Ethyl Vinyl Ether. In a previous paper[8] we reported on photoadditions of 4-hydroxycoumarin with isopropenyl acetate and ethyl vinyl ether. The stereochemistry of these coumarin–olefin adducts (A, B, and C) were tentatively assigned, as depicted in **49**, **51**, and **52**.

These assignments of spacial arrangements of OH and OAc of adducts A, B, and C were based on analyses of their ^{1}H NMR signals and comparisons of their coupling patterns with those of their nitrogen analogues **41**, **29**, and **30**; the large difference in the chemical shifts between their exo and endo protons attached to the C-2 of both coumarin



49 R^1=Me, R^2=OAc
50 R^1=OAc, R^2=Me
51 R^1=OEt, R^2=H
52 R^1=H, R^2=OEt

adduct A and its nitrogen analogue **41** indicated similar spacial arrangements of the OH and OAc of the two compounds. In an analogous manner, the spacial arrangements of OEt and OH of adducts B and C, obtained from coumarin and ethyl vinyl ether, were assigned to be trans and cis, as depicted in **51** and **52**, respectively. However, since the above-mentioned NOE studies established that the OH and OAc (or OEt) of quinoline adducts **41**, **29**, and **30** are oriented trans, cis, and trans, respectively, the previous assignments for the coumarin adducts A, B, and C should be reversed. The stereochemistries of coumarin adducts A, B, and C reported in a previous paper[8] are, thus, correctly represented as depicted in **50**, **52**, and **51**, respectively.

Experimental Section

General Method. For the instruments used and a description of the general procedure of photolysis, see ref 8.

Preparation of (6aα,6bα,9aα,9bα)-9b-Acetoxy-5,6a,6b,7,8,9,9a,9b-octahydro-6*H*-cyclopenta[3,4]cyclobuta[1,2-*c*]quinolin-6-one (3). A solution of 4-acetoxy-2-quinolone (1) (547 mg, 2.57 mmol) and cyclopentene (20 mL) in methanol (50 mL) was irradiated for 12 h under a nitrogen atmosphere through Pyrex with a 400-W high-pressure mercury arc. The removal of the solvent and an excess of cyclopentene gave an yellow oil, which was subjected to preparative TLC with a 1:1 ethyl acetate–hexane to afford crystalline adduct **3** (445 mg, 64%): R_f 0.64; mp 238–240 °C (diethyl ether–hexane–methanol); IR 1740 cm^{-1} (OAc), 1684 (lactam C=O), 1234, and 1247; ^{1}H NMR (200 MHz) δ 1.98 (3 H, s, OAc), 2.92 (1 H, d, J = 6.83 Hz, 6a-H), 8.37 (1 H, br s, NH); MS, m/z 271 (M^+, 2.0), 203 [(M – cyclopentane)$^+$, 21.1], and 161 [(M – cyclopentane – CH_3CO)$^+$, 100]; high-resolution mass spectrum for $C_{16}H_{17}NO_3$ calcd 271.1208, found 271.1227.

N-Methylation of Photoadduct 3. Photoadduct **3** (320 mg, 1.18 mmol) dissolved in DMF (3 ml) was added to a stirred suspension of NaH (58 mg, 50% oil suspension, 1.2 mmol) in DMF (2 mL) at 0 °C, and the solution was stirred for 15 min. Methyl iodide (170 mg, 1.2 mmol) was then added and the solution was stirred for another 30 min at room temperature. The reaction was quenched with aqueous NH_4Cl, and the product was extracted with diethyl ether three times. The combined extracts were washed with water and then brine and dried over anhydrous $MgSO_4$. Usual workup gave an oily residue, which was purified by preparative TLC (silica gel) with 1:1 ethyl acetate and hexane to give the *N*-methyl derivative **4** as a crystalline solid (278 mg, 82%): mp 180–182 °C (diethyl ether–hexane–methanol); IR (Nujol) 1665 cm^{-1} (lactam C=O) and 1729 (OAc); ^{1}H NMR δ 1.96 (3 H, s, OAc), 3.00 (1 H, d, J = 6.83 Hz, 6a-H) and 3.44 (3 H, s, NMe); MS, m/z 285 (M^+, 2.4), 217 [(M – cyclopentane ring)$^+$, 31.9] and 175 [(M – cyclopentane – CH_3CO)$^+$, 100]. Anal. Calcd for $C_{17}H_{19}NO_3$; C, 71.56; H, 6.71; N, 4.91. Found; C, 71.67; H, 6.58; N, 4.80.

Cyclobutanol 5 by Hydrolysis of *N*-Methyl Photoproduct 4. A solution of **4** (140 mg, 0.48 mmol) in 80% aqueous methanol (5 mL) containing K_2CO_3 (40 mg) was stirred for 24 h at room temperature. The solvent was then removed under reduced pressure, and the residue extracted with diethyl ether. The combined extracts were washed with brine and dried over anhydrous $MgSO_4$. Usual workup gave an oily residue, which was purified by preparative TLC (silica gel) with 1:1 ethyl acetate–hexane to give (6aα,6bα,9aα,9bα)-5,6a,6b,7,8,9,9a,9b-octahydro-9b-hydroxy-5-methyl-6*H*-cyclopenta[3,4]cyclobuta[1,2-*c*]-quinolin-6-one (**5**) (88 mg, 75%): mp 132 °C (ethyl acetate–

hexane); IR (Nujol) 1594 and 1627 cm^{-1} (lactam C=O) and 3360 (OH); ^1H NMR δ 2.86 (1 H, t, J = 9.27 Hz, 9a-H), 2.88 (1 H, d, J = 6.84 Hz, 6a-H) and 3.34 (3 H, s, NMe); MS, m/z 243 (M^+, 0.46) and 175 [(M - cyclopentane)$^+$, 100]. Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.93; H, 7.06; N, 5.63.

Photoaddition of 4-Acetoxy-2-quinolone (1) to 1-Methoxycyclopentene (6). A solution of quinolone 1 (812 mg, 4 mmol) in 1-methoxycyclopentene (20 mL) and methanol (130 mL) was irradiated for 80 h under a nitrogen atmosphere, as described above. The removal of the solvent and excess 1-methoxycyclopentene gave an oil. It was subjected to preparative TLC with a 1:1 ethyl acetate–hexane solution to give cis-cisoid-cis photoadduct (7) (843 mg, 70%): mp 260 °C (diethyl ether–hexane–dichloromethane); IR (thin film) 1674 cm^{-1} (lactam C=O), 1738 (OAc), and 3210 (NH); ^1H NMR δ 1.99 (3 H, s, OAc), 1.85–2.05 (5 H, m, methylene protons), 2.4–2.5 (1 H, m, one of methylene protons), 2.55–2.65 (1 H, m, 6b-H), 2.66 (1 H, d, J = 7.69 Hz, 6a-H), 3.00 (3 H, s, OMe), 6.75 (1 H, dd, J = 8.06 and 1.10 Hz, 4-H), 7.02 (1 H, ddd, J = 7.69, 7.33, and 1.10 Hz, 2-H), 7.23 (1 H, ddd, J = 8.06, 7.33, and 1.47 Hz, 3-H), 7.30 (1 H, dd, J = 7.69 and 1.47 Hz, 1-H), and 8.14 (1 H, br s, NH); MS, m/z 214 [(M - CH_3COOH)$^+$, 3.4], 204 [(M - methoxycyclopentane ring + H)$^+$, 55.8], 162 [(M - methoxycyclopentane ring - CH_3CO + H)$^+$, 100], and 98 (62.8, MeO^+=$CCH_2CH_2CH_2$). Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.99; H, 6.28; N, 4.59.

N-Methylation of Photoadduct 7. The N-methyl derivative 8 (448 mg, 87%) was obtained by treatment of photoadduct 7 (495 mg, 1.64 mmol) in DMF (5 plus 15 mL) with NaH (82 mg, 50% suspension in mineral oil, 1.7 mmol) and methyl iodide (241 mg, 1.7 mmol). The product was purified by means of preparative TLC with 1:1 ethyl acetate–hexane: mp 176–178 °C (diethyl ether–hexane–dichloromethane); IR (thin film) 1664 cm^{-1} (lactam C=O) and 1740 (OAc); ^1H NMR δ 1.97 (3 H, s, OAc), 2.4–2.5 (2 H, m, 6b-H and one of methylene protons), 2.75 (1 H, d, J = 7.32 Hz, 6a-H), 2.97 (3 H, s, OMe), 3.44 (3 H, s, NMe), and 7.0–7.4 (4 H, m, aromatic H): MS, m/z 255 [(M - CH_3CO_2H)$^+$, 2.4], 218 [(M - methoxycyclopentane ring)$^+$, 66.6], and 176 [(M - methoxycyclopentane ring - CH_2=C=O)$^+$, 100]. Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.29; H, 6.62; N, 4.50.

Cyclobutanol 9 by Hydrolysis of N-Methyl Photoadduct 8. The hydrolysis of N-methyl photoadduct 8 (424 mg, 1.35 mmol) was carried out with potassium carbonate (32 mg, 2.34 mmol) in 8:9 water–methanol (34 mL) for 2 h at room temperature, as described regarding the hydrolysis of photoadduct 4, to give cyclobutanol 9 (331 mg, 90%) in 90% yield: R_f 0.30 (preparative TLC with a 1:1 ethyl acetate–hexane); mp 139–141 °C (diethyl ether–hexane–methanol); IR (thin film) 1639 cm^{-1} (lactam C=O), and 3380 (OH); ^1H NMR δ 2.35 (1 H, t, J = 6.4 Hz, 6b-H), 2.45–2.55 (1 H, m, one of methylene protons), 2.63 (1 H, d, J = 6.96 Hz, 6a-H), 2.98 (3 H, s, OMe), 3.33 (3 H, s, NMe), and 7.01–7.52 (4 H, m, aromatic H); MS, m/z 255 [(M - H_2O)$^+$, 1.8], 176 [(M - methoxycyclopentane ring)$^+$, 100], and 98 [(methoxycyclopentene)$^+$, 36.3]. Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.23; H, 7.11; N, 4.95.

Photoadditions of 4-Acetoxy-2-quinolone (1) to Cyclohexene (12). A solution of quinolone 1 (1.50 g, 7.38 mmol) in cyclohexene (75 mL) and methanol (250 mL) was irradiated for 15 h under the conditions described above. Removal of the solvent and excess cyclohexane gave a yellow oil. It was subjected to preparative TLC with ethyl acetate to give adducts 13 (0.87 g, 41%) and 14 (1.09, 52%) in order of mobility. Photoadduct 13: mp 225–227 °C (diethyl ether–hexane–methanol); IR (Nujol) 1666 (lactam C=O) and 1750 cm^{-1} (OAc); ^1H NMR δ 2.19 (3 H, s, OAc), 2.4–2.55 (1 H, m, 10a-H), 3.69 (1 H, d, J = 8.79 Hz, 6a-H), and 8.78 (1 H, br s, NH); MS, m/z 285 (M^+, 0.2), 203 [(M - cyclohexane ring)$^+$, 25.1], and 161 [(M - cyclohexane ring - CH_3CO^+), 100]. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.52; H, 6.88; N, 4.81.

Photoadduct 14: mp 255–258 °C (diethyl ether–hexane–methanol); IR (Nujol) 1683 (lactam C=O), 1717 (OAc), and 3255 cm^{-1} (NH); ^1H NMR δ 1.96 (3 H, s, OAc), 2.6–2.7 (1 H, m, 10a-H), 3.37 (1 H, d, J = 10.36 Hz, 6a-H), and 8.63 (1 H, br s, NH); MS, m/z 285 (M^+, 2.4), 203 [(M - cyclohexane)$^+$, 27.0], and 161 [(M - cyclohexane - CH_3CO)$^+$, 100]. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.50; H, 6.75; N, 4.80.

N-Methylation of Photoadduct 13. N-Methylation of photoadduct 13 was carried out as described for the N-methylation of photoadduct 3 to give (6aα,6bα,10aα,10bα)-10b-acetoxy-6a,6b,7,8,9,10,10a,10b-octahydro-5-methylbenzo[3,4]cyclobuta[1,2-c]quinolin-6(5H)-one (15) in 98% yield: R_f 0.46 in preparative TLC with 1:3 ethyl acetate–hexane; mp 169–171 °C (hexane–chloroform); IR (Nujol) 1661 cm^{-1} (lactam C=O) and 1743 (OAc); ^1H NMR δ 2.18 (3 H, s, OAc), 2.45–2.55 (1 H, m, 10a-H) 3.43 (3 H, s, NMe), and 3.70 (1 H, d, J = 8.79 Hz, 6a-H); MS, m/z 299 (M^+, 0.4), 217 [(M - cyclohexane)$^+$, 27.3)], and 175 [(M - cyclohexane - CH_3CO)$^+$, 100]. Anal. Calcd for $C_{18}H_{21}NO_3$; C, 72.22; H, 7.07; N, 4.68. Found: C, 72.12; H, 7.06; N, 4.71.

N-Methylation of Photoadduct 14. Similar N-methylation as above gave N-methyl derivative 16 ((6aα,6bβ,10aβ,10bα)-10b-acetoxy-6a,6b,7,8,9,10,10a,10b-octahydro-5-methylbenzo-[3,4]cyclobuta[1,2-c]quinolin-6(5H)-one) in 81% yield: R_f 0.81 in preparative TLC with ethyl acetate; mp 189–191 °C (diethyl ether–hexane–methanol); IR (Nujol) 1665 cm^{-1} (lactam C=O) and 1735 (OAc); ^1H NMR δ 1.94 (3 H, s, OAc), 3.43 (3 H, s, NMe), and 3.46 (1 H, d, J = 11.2 Hz, 6a-H); MS, m/z 299 (M^+, 4.5), 217 [(M - cyclohexane)$^+$, 36.9], and 175 [(M - cyclohexane - CH_3CO)$^+$, 100].

X-ray Structure Determination of N-Methyl Derivative 16 of Photoadduct 14. The crystal data for 16 were as follows: $C_{18}H_{21}NO_3$, mol wt 299.37, triclinic, space group $P\bar{1}$, a = 9.664 (2), b = 9.711 (2), and c = 9.305 (2) Å, α = 110.12 (2)°, β = 95.88 (2)°, and γ = 71.36 (2)°, z = 2, D_c = 1.280 g cm^{-3}. Diffraction intensities were measured on a Rigaku four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using the ω–2θ scanning mode.[13] The intensities obtained were corrected for both Lorentz and polarization factors, but not for absorption or the extinction effect. In the range of 2θ values up to 58°, 3421 unique structure factors above the 2σ(F) level were selected for the structural study. The structure was elucidated by a Monte Carlo direct method[14] and refined by the block-diagonal least-squares method with anisotropic thermal parameters. A difference Fourier map revealed all of the hydrogen atoms. The R value reached 0.048 by further refinements, including the hydrogen atoms. There were no significant peaks in the final difference Fourier map. The molecular skeleton, thus obtained, is shown in ref 3.

Cyclobutanol 17 by Hydrolysis of N-Methyl Photoadduct 15. The hydrolysis of N-methyl photoadduct 15 was carried out as described for the hydrolysis of N-methyl photoadduct 4, with the exception that the hydrolysis was undertaken at 0 °C to give cyclobutanol 17 ((6aα,6bα,10aα,10bα)-6a,6b,7,8,9,10,10a,10b-octahydro-10b-hydroxy-5-methylbenzo[3,4]cyclobuta[1,2-c]-quinolin-6(5H)-one) in 52% yield: R_f 0.33 in preparative TLC (1:3 ethyl acetate–hexane): mp 173–175 °C (diethyl ether–hexane–methanol); IR (Nujol) 1597 and 1637 cm^{-1} (lactam C=O) and 3400 (OH); ^1H NMR δ 2.45–2.55 (1 H, m, 10a-H), 3.16 (1 H, d, J = 8.30 Hz, 6a-H), and 3.42 (3 H, s, NMe); MS, m/z 257 (M^+, 15.6) and 175 [M - cyclohexane ring)$^+$, 100].

Cyclobutanol 18 by Hydrolysis of N-Methyl Photoadduct 16. The hydrolysis of N-methyl photoadduct 16 was carried out as described above to give cyclobutanol 18 ((6aα,6bα,-10aβ,10bα)-6a,6b,7,8,9,10,10a,10b-octahydro-10b-hydroxy-5-methylbenzo[3,4]cyclobuta[1,2-c]quinolin-6(5H)-one) in 81% yield: R_f 0.45 in preparative TLC (1:3 ethyl acetate–hexane); mp 168.5–171.5 °C; IR (Nujol) 1592 and 1631 cm^{-1} (lactam C=O) and 3300 (OH); ^1H NMR δ 3.35 (3 H, s, NMe) and 3.37 (1 H, d, J = 7.81 Hz, 6a-H); MS, m/z 257 (M^+, 0.17) and 175 [(M - cyclohexane ring)$^+$, 100].

Photoaddition of 4-Acetoxy-2-quinolone (1) to 2,3-Dimethyl-2-butene (20). A solution of quinolone 1 (620 mg, 2.91 mmol) in 2,3-dimethyl-2-butene (20) (15 mL) and methanol (30 mL) was irradiated for 24 h under the conditions described above. Removal of the solvent and excess olefin gave a yellow oil. It was subjected to preparative TLC with 1:1 ethyl acetate–hexane to

(13) The intensity measurements were performed at the High Brilliance X-Ray Laboratory of Hokkaido University.

(14) Furusaki, A. *Acta. Crystallogr., Sect. A* **1979**, *35*, 220.

(15) Cf. Ward, H. R.; Sherman, P. D., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 3812.

give adduct **21** (100 mg, 11%): mp 192–194 °C (diethyl ether–hexane–methanol); IR (Nujol) 1673 cm^{-1} (lactam C=O) and 1733 cm^{-1} (OAc); ^1H NMR δ 0.84, 0.88, 1.18, and 1.36 (each 3 H, each s, 1-Me_2 and 2Me_2), 1.93 (3 H, s, OAc), 3.26 (1 H, s, 2a-H), and 7.97 (1 H, br s, NH); MS, *m/z* 287 (M^+, 3.4), 204 [(M – (C_3H_3)$_2$CC(CH_3)$_2$ + H), 49.4], and 162 [(M – (CH_3)$_2$CC(CH_3)$_2$ + H – CH_2CO), 100].

N-Methylation of Photoadduct 21. N-Methylation of **21** was carried out as described for the N-methylation of photoadduct **3** to give *cis*-2,2a,4,8b-tetrahydro-8b-acetoxy-1,1,2,2,4-pentamethylcyclobuta[*c*]quinolin-3(1*H*)-one (**22**) in 90% yield: R_f 0.50 in preparative TLC with 1:1 ethyl acetate–hexane; mp 145–146 °C (diethyl ether–hexane–methanol); IR (Nujol) 1652 cm^{-1} (lactam C=O) and 1730 (OAc); ^1H NMR δ 0.71, 0.85, 1.16, and 1.35 (each 3 H, each s, 1-Me_2 and 2-Me_2), 1.91 (3 H, s, OAc), 3.34 (1 H, s, 2a-H), and 3.44 (3 H, s, NMe); MS, *m/z* 301 (M^+, 5.0), 218 [(M – (CH_3)$_2$CC(CH_3)$_2$)$^+$, 51.9], and 175 [(M – (CH_3)$_2$CC(CH_3)$_2$) – CH_3CO)$^+$, 100]. Anal. Calcd for $C_{18}H_{23}NO_4$: C, 71.74; H, 7.69; N, 4.65. Found: C, 71.77; H, 7.81; N, 4.55.

Cyclobutanol 23 by Means of Hydrolysis of *N*-Methyl Photoadduct 22. The hydrolysis of *N*-methyl photoadduct **22** was carried out as described for photoadduct **4** to give *cis*-2,2a,4,8b-tetrahydro-8b-hydroxy-1,1,2,2,4-pentamethylcyclobuta[*c*]quinolin-3(1*H*)-one (**23**) in 81% yield: R_f 0.30 in preparative TLC (1:3 ethyl acetate–hexane); mp 187–188 °C; IR (Nujol) 1589 and 1635 cm^{-1} (lactam C=O) and 3484 (OH); ^1H NMR δ 0.71, 0.84, 1.20, and 1.33 (each 3 H, each s, 1-Me_2 and 2-Me_2), 3.20 (1 H, s, 2a-H), and 3.38 (3 H, s, NMe); MS, *m/z* 260 (M^+ + 1, 2), 226 (25.8), 176 [(M – (CH_3)$_2$C(CH_3)$_2$ + H)$^+$, 100], and 175 [(M – (CH_3)$_2$C(CH_3)$_2$)$^+$, 58.2]; high-resolution mass spectrum for $C_{16}H_{23}NO_2$ calcd 260.1651, found 260.1615.

Photoadditions of 4-Acetoxy-2-quinolone (1) with Ethyl Vinyl Ether (24). A solution of quinolone **1** (872 mg, 4.30 mmol) and ethyl vinyl ether (45 ml) in methanol (130 ml) was irradiated with a 500-W high-pressure mercury arc through a Pyrex filter for 16 h under a nitrogen atmosphere. After removing the solvent under reduced pressure, the residue was subjected to preparative TLC with 1:1 ethyl acetate–hexane to give a mixture of products **25** and **26** (1.07 g, 90%). A portion of the photoadduct was subjected to preparative TLC with 1:1 ethyl acetate–hexane to obtain samples for the analysis. The more mobile isomer **25** was recrystallized from diethyl ether–hexane–methanol: mp 195–197 °C; IR (Nujol) 1681 cm^{-1} (lactam C=O), 1731 (OAc), and 3180 (NH); ^1H NMR δ 1.22 (3 H, t, *J* = 6.96 Hz, Me of ethyl group), 2.03 (3 H, s, OAc), 2.16 (1 H, ddd, *J* = 12.82, 9.89, and 5.86 Hz, 2-H), 2.38 (1 H, ddd, *J* = 12.82, 10.99, and 1.47 Hz, 2-H), 3.69 (1 H, dd, *J* = 10.99 and 9.89 Hz, 2a-H), 3.66 and 3.93 (each 1 H, each dq, *J* = 9.16 and 6.96 Hz, CH_2 of ethyl group), 4.10 (1 H, dd, *J* = 5.86 and 1.47 Hz, 1-H), 6.85–7.35 (4 H, m, aromatic protons), and 9.02 (1 H, br s, NH); MS, *m/z* 275 (M^+, 0.6), 203 [(M – CH_2=CHOEt)$^+$, 26.8], and 161 [(M – CH_2=CHOEt – CH_3CO)$^+$, 100]. Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.26; H, 6.20; N, 5.14.

The less mobile isomer **26** was recrystallized from diethyl ether–hexane–dichloromethane: mp 225–226 °C; IR (Nujol) 1683 cm^{-1} (lactam C=O), 1742 (OAc), and 3200 (NH); ^1H NMR δ 1.21 (3 H, t, *J* = 6.96 Hz, Me of ethyl group), 1.72 (1 H, dt *J* = 10.99 and 9.52 Hz, 2-H), 2.93 (1 H, dd, *J* = 9.52 and 9.16 Hz, 2a-H), 3.36 and 3.69 (each 1 H, each dq, *J* = 7.33 and 6.96 Hz, CH_2 of ethyl group), 4.25 (1 H, dd, *J* = 9.52 and 8.06 Hz, 1-H), 6.80 (1 H, dd, *J* = 8.06 and 1.10 Hz, 5-H), 7.06 (1 H, ddd, *J* = 7.69, 6.96, and 1.10 Hz, 7-H), 7.27 (1 H, ddd, *J* = 8.06, 7.69, and 1.47 Hz, 6-H), 7.31 (1 H, dd, *J* = 6.96 and 1.47 Hz, 8-H), and 8.40 (1 H, s, NH); MS, *m/z* 275 (M^+, 1.3), 203 [(M – CH_2=CHOEt)$^+$, 28.0) and 161 [(M – CH_2 – CHOEt – $COCH_3$)$^+$, 100]; high-resolution mass spectrum for $C_{15}H_{17}NO_4$ calcd 275.1158, found 275.1166.

N-Methylation of a Mixture of Photoadducts 25 and 26. N-Methylation of the above-mentioned mixture was carried out essentially as described for the foregoing photoadducts. To a stirred suspension of NaH (161 mg, 50% suspension in mineral oil, 3.35 mmol) in DMF (10 mL) under a nitrogen atmosphere was added a solution of a mixture of adducts **25** and **26** (865 mg, 3.15 mmol) in DMF (20 ml) at –20 °C. After the solution was stirred for 10 min, methyl iodide (209 mg, 3.35 mmol) was added, and the solution was stirred for another 30 min at –20 °C. The reaction was quenched by addition of aqueous NH_4Cl and extracted with diethyl ether. The combined extracts were washed with water and then brine and dried over anhydrous $MgSO_4$. Usual workup gave a residue, which was purified by preparative TLC with 1:1 ethyl acetate–hexane to give more mobile *N*-methyl derivative **27** (365 mg, 40%) and less mobile *N*-methylate **28** (210 mg, 23%). ***N*-Methyl derivative 27**: mp 104–106 °C (diethyl ether–hexane–dichloromethane); IR (Nujol) 1666 cm^{-1} (lactam C=O) and 1731 (OAc); ^1H NMR δ 1.32 (3 H, t, *J* = 6.96 Hz, Me of ethyl group), 2.01 (3 H, s, OAc), 2.03 (1 H, ddd, *J* = 12.82, 9.89, and 5.86 Hz, 2-H), 2.33 (1 H, ddd, *J* = 12.82, 10.62, and 1.10 Hz, 2-H), 3.44 (3 H, s, NMe), 3.52 and 3.92 (each 1 H, each qd, *J* = 9.16 and 6.96 Hz, CH_2 of ethyl group), 3.78 (1 H, ddd, *J* = 10.62, 9.89, and 0.73 Hz, 2a-H), 4.08 (ddd, *J* = 5.86, 1.10, and 0.73 Hz, 1-H), and 7.0–7.4 (4 H, m, aromatic protons); MS, *m/z* 289 (M^+, 0.6), 217 [(M – CH_2=OEt)$^+$, 33.0), and 175 [(M – CH_2=CHOEt – CH_3CO)$^+$, 100]. Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.41; H, 6.52; N, 4.94.

***N*-Methyl derivative 28**: mp 173–175 °C (diethyl ether–hexane–dichloromethane); IR (Nujol) 1677 cm^{-1} (lactam C=O) and 1748 (OAc); ^1H NMR δ 1.20 (3 H, t, *J* = 6.96 Hz, Me of ethyl group), 1.59 (1 H, dt, *J* = 10.62 and 9.89 Hz, 2-H), 1.96 (3 H, s, OAc), 2.59 (1 H, ddd, *J* = 9.89, 9.16, and 8.06 Hz, 2-H), 3.02 (1 H, dd, *J* = 10.62 and 9.16 Hz, 2a-H), 3.44 (3 H, s, NMe), 3.62 and 3.68 (each 1 H, each dq, *J* = 9.52 and 6.96 Hz, CH_2 of the ethyl group), 4.21 (1 H, dd, *J* = 9.89 and 8.06 Hz, 1-H), and 7.0–7.4 (4 H, m, aromatic protons); MS, *m/z* 289 (M^+, 1.4), 217 [(M – CH_2=CHOEt)$^+$, 38.0), and 175 [(M – CH_2=CHOEt – CH_3CO)$^+$, 100]. Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.35; H, 6.56; N, 5.27.

Cyclobutanol 29 by Hydrolysis of *N*-Methyl Photoadduct 27. The *N*-methyl photoadduct **27** (301 mg, 1.04 mmol) and potassium carbonate (120 mg, 0.87 mmol) in a 1:3 mixture of water and methanol (20 mL) was stirred for 17 h at room temperature. The starting material disappeared by this period (TLC). The solution was extracted with diethyl ether and the combined extract was washed first with aqueous NH_4Cl and then brine and dried over $MgSO_4$. Usual workup gave a residue, which was subjected to preparative TLC with 1:1 ethyl acetate–hexane to give cyclobutanol **29** (210 mg, 81%): mp 66–68 °C (diethyl ether–hexane–dichloromethane); IR (neat) 1658 cm^{-1} (lactam C=O) and 3420 (OH); ^1H NMR δ 1.28 (3 H, t, *J* = 6.96 Hz, Me of the ethyl group), 2.14 (1 H, ddd, *J* = 12.82, 6.23, and 1.47 Hz, 2-H), 2.41 (1 H, ddd, *J* = 12.82, 10.99, and 3.67 Hz, 2-H), 3.39 (3 H, s, NMe), 3.35–3.5 (1 H, m, 2a-H), 3.62 (2 H, q, *J* = 6.96 Hz, CH_2 of the ethyl group), and 7.03–7.49 (4 H, m, aromatic protons); MS, *m/z* 247 (M, 0.2), 175 [(M – CH_2=CHOEt)$^+$, 100], and 146 (27.0). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 68.08; H, 7.02; N, 5.60.

Cyclobutanol 30 by Hydrolysis of *N*-Methyl Photoadduct 28. The hydrolysis of the adduct **28** (135 mg, 0.47 mmol) was carried out as mentioned above with potassium carbonate (70 mg, 0.51 mmol) in a mixed solvent of 1:3 water–methanol (8 mL) at room temperature for 17 h to give cyclobutanol **23** (94 mg, 82%): R_f 0.21 (1:1 ethyl acetate–hexane); mp 125–126 °C (diethyl ether); IR (neat) 1600 and 1638 cm^{-1} (lactam C=O) and 3360 (OH); ^1H NMR δ 1.19 (3 H, t, *J* = 6.96 Hz, Me of the ethyl group); 1.39 (1 H, td, *J* = 10.62 and 9.89 Hz, 2-H), 2.45 (1 H, ddd, *J* = 10.62, 9.16, and 7.69 Hz, 2-H), 2.93 (1 H, dd, *J* = 10.62 and 9.16 Hz, 2a-H), 3.35 (3 H, s, NMe), 3.62 and 3.68 (each 1 H, each dq, *J* = 7.33 and 6.96 Hz, CH_2 of the ethyl group), 4.12 (1 H, dd, *J* = 9.89 and 7.69 Hz, 1-H), 7.04–7.6 (4 H, m, aromatic protons); MS, *m/z* 247 (M^+, 0.2), 175 [(M – CH_2=CHOEt)$^+$, 100], and 146 (27.3); high-resolution mass spectrum for $C_{14}H_{17}NO_3$ calcd 247.1209, found 247.1215.

Photoaddition of 4-Acetoxy-2-quinolone with 2-Methoxypropene (31). A solution of quinolone **1** (1.02 g, 5 mmol) and 2-methoxypropene (4.8 mL) in methanol (150 mL) was irradiated for 24 h under the conditions described above. Removal of the solvent and excess 2-methoxypropene gave a product, which was subjected to preparative TLC with 1:3 ethyl acetate–hexane to yield photoadduct **32** (1.15 g, 84%): mp 229–230 °C (diethyl ether–hexane–dichloromethane); IR (Nujol) 1673 cm^{-1} (lactam C=O), 1720 (OAc), and 3180 (NH); ^1H NMR δ 1.56 (3 H, s, Me), 1.90 (1 H, dd, *J* = 11.00 and 10.63 Hz, 2-H), 1.97 (3 H, s, OAc), 2.33 (1 H, dd, *J* = 11.00 and 9.90 Hz, 2-H), 3.07 (3 H, s, OMe), 6.77–7.3 (4 H, m, aromatic protons) and 8.27 (1 H, br s, NH); MS,

m/z 215 [(M - AcOH)$^+$, 1.8)], 204 [(M - CH_2=C(Me)OMe)$^+$, 27.7], and 161 [(M - CH_2=C(Me)OMe - CH_3CO)$^+$, 100]. Anal. Calcd for $C_{15}H_{17}O_4N$; C, 65.44; H, 6.22; N, 5.09. Found: C, 65.36; H, 6.36; N, 5.18.

N-Methylation of Photoproduct 32. Photoadduct **32** (1.15 g, 4.2 mmol) dissolved in DMF (10 mL) was added to a stirred suspension of NaH (202 mg, 50% oil suspension, 4.2 mmol) in DMF (20 mL) at 20 °C. The solution was stirred for 10 min. Methyl iodide (596 mg, 4.2 mmol) was then added, and the solution was stirred for another 30 min at −20 °C. The reaction mixture was then worked up as described for the above N-methylation. The product was purified by preparative TLC with 1:1 ethyl acetate–hexane to give *N*-methyl derivative **33** (920 mg, 76%): mp 211–212 °C (diethyl ether–hexane–dichloromethane); IR (thin film) 1668 cm^{-1} (lactam C=O) and 1735 (OAc): ^{1}H NMR δ 1.55 (3 H, s, Me), 1.80 (1 H, dd, J = 10.99 and 10.26 Hz, 2-H), 1.95 (3 H, s, OAc), 2.29 (1 H, dd, J = 10.99 and 9.53 Hz, 2-H), 3.04 (3 H, s, OMe), 3.15 (1 H, dd, J = 10.26 and 9.53 Hz, 2a-H), 3.44 (3 H, s, NMe), and 7.0–7.4 (4 H, m, aromatic protons); MS, m/z 289 (M$^+$, 0.4), 217 [(M - CH_2=C(Me)OMe)$^+$, 34.2], and 175 [(M - CH_2=C(Me)OMe - CH_3CO)$^+$, 100]. Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.39; H, 6.59; N, 4.89:

Cyclobutanol 34 by Hydrolysis of *N*-Methyl Photoadduct 33. The hydrolysis of *N*-methyl derivative **33** (390 mg, 1.35 mmol) was carried out with potassium carbonate (250 mg, 1.82 mmol) in a 1:4 mixture of water and methanol (20 mL) at room temperature for 14 h. The product was purified by preparative TLC with 1:1 ethyl acetate–hexane to give cyclobutanol **34** (256 mg, 77%): mp 178–179 °C (diethyl ether–hexane–methanol); IR (thin film) 1639 cm^{-1} (lactam C=O) and 3470 (OH); ^{1}H NMR δ 1.52 (3 H, s, Me), 1.65 (1 H, t, J = 10.25 Hz, 2-H), 2.21 (1 H, dd, J = 10.99 and 9.89 Hz, 2-H), 3.01 (1 H, t, J = 9.89 Hz, 2a-H), 3.04 (3 H, s, OMe), 3.34 (3 H, s, NMe), and 7.03–7.52 (4 H, m, aromatic hydrogens); MS, m/z 247 (M$^+$, 0.7), 175 [(M - CH_2=CMe(OMe))$^+$, 100], and 146 (23.2). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.78; H, 6.79; N, 5.65.

Photoaddition of 4-Hydroxy-*N*-methyl-2-quinolone (39) with Isopropenyl Acetate (40). A solution of quinolone **39** (115 mg, 1.23 mmol) and isopropenyl acetate (**40**) (2.72 g, 27.2 mmol) in methanol (50 mL) was irradiated for 5.5 h under a nitrogen atmosphere through Pyrex with a 500-W high-pressure Hg arc (EIKOSHA). Removal of the solvent gave a residue, which was purified by preparative TLC with 1:1 ethyl acetate–hexane to give adduct **41** (221 mg, 65%): mp 182 °C (diethyl ether–hexane–methanol); IR (Nujol) 1634 cm^{-1} (lactam C=O), 1732 (OAc), and 3280 (OH); ^{1}H NMR (270 MHz) δ 1.74 (3 H, s, 1-Me), 1.83 (3 H, s, 1-OAc), 1.8–1.9 (1 H, m, 2-H), 2.65 (1 H, dd, J = 12.11 and 9.89 Hz, 2-H), 3.13 (1 H, dd, J = 10.62 and 9.89 Hz, 2a-H), 3.37 (3 H, s, NMe), and 7.06–7.58 (4 H, m, aromatic H); MS, m/z 257 [(M - H_2O)$^+$, 0.2)], 232 [(M - CH_3CO)$^+$, 5.1], and 175 [(M - CH_2=C(Me)OAc)$^+$, 100]. Anal. Calcd for $C_{15}H_{17}NO_3$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.24; H, 6.23; N, 5.07.

Photoaddition of 4-Hydroxy-*N*-methyl-2-quinolone (39) to Vinyl Benzoate (42). A solution of vinyl benzoate (**42**) (850 mg, 5.72 mmol) and quinolone **39** (500 mg, 2.86 mmol) in methanol(120 ml) was irradiated for 23 h under conditions similar to those mentioned above. Workup of the reaction mixture and a separation of the product by preparative TLC with 1:1 ethyl acetate–hexane (as described above) gave adducts **43** (216 mg, 23%) and **44** (261 mg, 28%). **Photoadduct 43**: R_f 0.25; mp 188.5–190 °C (diethyl ether–hexane–methanol); IR (Nujol) 3320 (OH), 1721 (COC_6H_5), and 1636 cm^{-1} (lactam C=O); ^{1}H NMR (270 MHz) δ 1.75 (1 H, td, J = 10.26 and 9.53 Hz, 2-H), 2.75 (1 H, ddd, J = 10.26, 9.16, and 8.43 Hz, 2-H), 3.24 (1 H, dd, J = 10.26 and 9.16 Hz, 2a-H), 3.42 (3 H, s, N-Me), 5.49 (1 H, dd, J = 9.53 and 8.43 Hz, 1-H), 7.1–7.55 (5 H, m, aromatic H) and 7.93 (2 H, dd, J = 8.42 and 1.46 Hz, aromatic H); MS, m/z 218 [(M - benzoyl)$^+$, 10], 175 [(M - CH_2=CHObenzoyl)$^+$, 100]; high resolution mass spectrum for $C_{12}H_{12}NO_3$ (M - benzoyl)$^+$ 218.0817, found 218.0808. **Photoadduct 44**: R_f 0.36; mp 163–165 °C (diethyl ether–hexane–methanol); IR (Nujol) 3350 (OH), 1719 (COC_6H_5), and 1640 cm^{-1} (lactam C=O); ^{1}H NMR (270 MHz) δ 2.24 (1 H, ddd, J = 13.18, 9.90, and 6.23 Hz, 2-H), 2.59 (1 H, ddd, J = 13.18, 10.99, and 1.47 Hz, 2 H), 3.42 (3 H, s, N-Me), 3.75 (1 H, ddd, J = 10.99, 9.90, and 1.10 Hz, 2a-H), 5.37 (1 H, ddd, J = 6.23, 1.47, and 1.10 Hz, 1-H), 7.09–7.84 (7 H, m, aromatic H), and 8.1–8.15 (2 H, m, aromatic H); MS, m/z 323 (M$^+$, 0.1), 218 [(M - benzoyl)$^+$, 10], 175 [(M - CH_2=CHObenzoyl)$^+$, 100]; high-resolution mass spectrum for $C_{19}H_{17}NO_4$ calcd 323.1157, found 323.1137.

Irradiation of Hypoiodites of the Cyclobutanols in the Presence of Mercury(II) Oxide and Iodine in Benzene. (a) Cyclobutanol 5. Photoadduct **5** (84 mg, 0.35 mmol) in dry benzene (10 mL) containing mercury(II) oxide (216 mg, 1 mmol) and iodine (254 mg, 1 mmol) in a Pyrex vessel was irradiated with a 100-W high-pressure Hg arc while being stirred for 6 h under a nitrogen atmosphere. The solution was filtered, and the filtrate was washed with a 5% sodium thiosulfate solution and water and dried over anhydrous sodium sulfate. Usual workup gave an oily product, which was purified by preparative TLC (1:1 ethyl acetate–hexane) to afford *cis*-1,2,3,3a,5,10b-hexahydro-5-methyl-10*H*-cyclopenta[4,5]furo[2-3*b*]quinoliln-10-one (**10**) (18 mg, 21%): mp 175–177.5 °C (ethyl acetate–hexane); IR (Nujol) 1589 and 1615 cm^{-1} (C=CC=O); ^{1}H NMR δ 3.67 (3 H, s, NMe) 4.05–4.15 (1 H, m, 9a-H), 5.4–5.5 (1 H, m, 6a-H), and 8.46 (1 H, dd, J = 6.83), and 1.47 Hz, 1-H); MS, m/z 241 (M$^+$, 100) and 200 (33); high-resolution mass spectrum for $C_{15}H_{15}NO_2$ calcd 241.1103, found 241.1105.

(b) Cyclobutanol 9. Irradiation of cyclobutanol **9** (283 mg, 1.04 mmol) in benzene (30 mL) containing mercury(II) oxide (674 mg, 3.11 mmol) and iodine (789 mg, 3.11 mol) for 2 h gave furoquinolone **11** (175 mg, 62%): R_f 0.26 (1:1 ethyl acetate–hexane); mp 111–114 °C (hexane); IR (thin film) 1656 and 1637 cm^{-1} (lactam C=O); ^{1}H NMR (270 MHz) δ 1.55–1.65 (1 H, m), 1.75–1.85 (1 H, m), 1.95–2.2 (3 H, m), 2.25–2.35 (m, 1 H), 3.39 (3 H, s, OMe), 3.70 (3 H, s, NMe), 3.74 (1 H, dd, J = 8.79 and 2.56 Hz, 6b-H), and 7.2–7.83 (4 H, m, aromatic H); MS, m/z 271 (M$^+$, 26), and 256 [(M - Me)$^+$, 100]. Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.94; H, 6.32; N, 5.20.

(c) Cyclobutanol 17. Photoadduct **17** (88 mg, 0.34 mmol) in dry benzene (10 ml) containing mercury(II) oxide (217 mg, 1 mmol) and iodine (254 mg, 1 mmol) in a Pyrex vessel was irradiated as described above for 7 h. Workup, as described above, gave a crude product, which was purified by preparative TLC (1:3 ethyl acetate–hexane) to afford a 2:3 stereoisomeric mixture of 7a,8,9,10,11,11a-hexahydro-7-iodo-5-methyldibenz[*b*,*e*]azocin-6,12(5*H*,7*H*)-dione (**19**) in 14% yield: mp 162–165 °C; IR (Nujol) 1591 and 1650 cm^{-1} (lactam C=O) and 1700 (C=O); ^{1}H NMR (90 MHz) δ 3.17 (3 H, s, NMe of major isomer), 3.27 (s, MMe of minor isomer), 4.28 (1 H, d, J = 9.25 Hz, 7-H of major isomer), 4.80 (d, J = 10.75 Hz, 7-H of minor isomer); MS, m/z 383 (M$^+$, 89.3), 256 [(M - I)$^+$, 93.2)], and 134 (100); high-resolution mass spectrum for $C_{16}H_{18}NO_2$ calcd 383.0383, found 383.0357.

(d) Cyclobutanol 23. Cyclobutanol **23** (60 mg, 0.24 mmol) in dry benzene (15 mL) containing mercury(II) oxide (156 mg, 0.72 mmol) and iodine (186 mg, 0.72 mmol) in a Pyrex vessel was irradiated with a 100-W high-pressure Hg arc for 3 h under the conditions described above. The product was purified by means of preparative TLC (1:1 ethyl acetate–hexane) to give quinolone **35** in 63% yield: mp 217–218 °C (diethyl ether–hexane–methanol); IR (Nujol) 1585 and 1617 cm^{-1} (COC=C); ^{1}H NMR δ 1.43 and 1.44 (each 6 H, each s, 2-Me_2 and 3-Me_2), 3.67 (3 H, s, NMe), and 8.45 (1 H, d, J = 7.81 Hz, 5-H); MS, m/z 257 (M$^+$, 13.7), 242 [(M - Me)$^+$, 100], and 214 (18.0); high-resolution mass spectrum for $C_{16}H_{19}NO_2$ calcd 257.1414, found 257.1409.

(e) Cyclobutanol 29. Cyclobutanol **29** or **30** (187 mg, 0.76 mmol) in benzene (30 mL) containing mercury(II) oxide and iodine (576 mg, 2.27 mmol) was irradiated with a 100-W high-pressure mercury arc through a Pyrex-filter under a nitrogen atmosphere. After the disappearance of the starting material (3 h), the solution was filtered through Celite. The filtrate was washed with 5% aqueous sodium thiosulfate and brine and dried over anhydrous $MgSO_4$. Removal of the solvent gave a residue, which was purified by preparative TLC (solvent 1:1 ethyl acetate–hexane) to give 3,4-furo-2-quinolone **37** (97 mg, 52%): mp 85–86 °C (hexane–dichloromethane); IR (thin film) 1659 and 1635 cm^{-1} (lactam C=O); ^{1}H NMR (270 MHz) δ 1.28 (3 H, t, J = 7.32 Hz, CH_2H_3), 3.10 (1 H, dd, J = 16.48 and 2.93 Hz, 3-H), 3.37 (1 H, dd, J = 16.48 and 6.97 Hz, 3-H), 3.71 (3 H, s, NMe), 3.75 and 4.02 (each 1 H, each qd, J = 7.32 and 6.73 Hz, CH_2CH_3), 6.01 (1 H, dd, J = 6.97 and 2.93 Hz, 2-H), and 7.2–7.79 (4 H, m, aromatic H); MS,

m/z 245 (M^+, 66), 200 [$(M - OEt)^+$, 100], and 188 (52.6). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.49; H, 6.20; N, 5.59.

3,4-Furo-2-quinolone **37** (47 mg, 55%) was also obtained when isomeric adduct **30** (86 mg, 0.35 mmol) in benzene (10 mL) containing mercury(II) oxide (226 mg, 1.04 mmol) and iodine (265 mg, 1.04 mmol) was irradiated for 3 h.

(f) Cyclobutanol 34. Irradiation of cyclobutanol **34** (100 mg, 0.41 mol) in benzene (20 mL) containing mercury(II) oxide (263 mg, 1.22 mmol) and iodine (307 mg, 1.22 mmol) for 2 h as above gave furoquinolone **38** (50 mg, 50%): R_f 0.27 (1:1 ethyl acetate–hexane); mp 69–72 °C (diethyl ether–hexane); IR (thin film) 1650 and 1638 cm^{-1} (lactam C=O); ^1H NMR (90 MHz) δ 1.76 (3 H, s, Me), 3.07 and 3.20 (each 1 H, each d, J = 16.7 Hz, 3-H), 3.35 (3 H, s, OMe), 3.71 (3 H, s, NMe), and 7.1–8.1 (4 H, m, aromatic H); MS, m/z 245 (M^+, 66) and 200 [$(M - OEt)^+$, 100); high-resolution mass spectrum for $C_{14}H_{15}NO_3$ calcd 245.1051, found 245.1045.

(g) Cyclobutanol 41. Irradiation of cyclobutanol **41** (210 mg, 0.76 mmol) in benzene (35 mL) containing mercury(II) oxide (494 mg, 2.28 mmol) and iodine (579 mg, 2.28 mmol) for 2.5 h and workup as above gave a mixture of products, which was subjected to preparative TLC to give furoquinolines **45** (84 mg, 40%) and **46** (43 mg, 21%) in order of their mobility. **Photoproduct 45**: R_f 0.17 (1:1 ethyl acetate–hexane); mp 179–181 °C (hexane–dichloromethane–methanol); IR (Nujol) 1745 (OAc), 1671 and 1639 cm^{-1} (lactam C=O); ^1H NMR (90 MHz) δ 1.97 and 2.06 (each 3 H, each s, OAc and Me), 3.24 and 3.60 (each 1 H, each d, J = 17.15, 3-H), 3.70 (3 H, s, NMe), 7.2–7.7 (4 H, m, aromatic H); MS, m/z 273 (M^+, 5.2), 213 [$(M - CH_3COOH)^+$, 100], 189 (92.6), and 188 (84.3). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53; N, 5.13. Found: C, 65.66: H, 5.41; N, 5.24.

Photoproduct 46: R_f 0.08 (1:1 ethyl acetate–hexane); mp 180 °C (diethyl ether–hexane–dichloromethane); IR (Nujol) 1739 (OAc), 1639 and 1588 cm^{-1} (enone C=O); ^1H NMR (90 MHz) δ 2.07 and 1.97 (each 3 H, each s, OAc and Me), 3.28 and 3.61 (each 1 H, each d, J = 15.8, 3-H), 3.70 (3 H, s, NMe), 7.3–7.7 (3 H, m, aromatic H), and 8.45 (1 H, d, J = 7.91, aromatic H); MS, m/z 273 (M^+, 10.5), 213 [$(M - AcOH)^+$, 42], and 188 (100). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53; N, 5.13. Found: C, 65.66; H, 5.42; N, 5.21.

(h) Cyclobutanol 44. Irradiation of cyclobutanol **44** (255 mg, 0.79 mmol) in benzene (30 mL) containing mercury(II) oxide (513 mg, 2.37 mmol) and iodine (602 mg, 2.37 mmol) for 4.5 h and workup as above gave furoquinolones **47** (42 mg, 17%) and **48** (78 mg, 31%) in order of their mobility. **47**: R_f 0.26 (1:1 ethyl acetate–hexane); mp 182–183 °C (diethyl ether–hexane–methanol): IR (thin film) 1730 ($OCOC_6H_5$), 1664 and 1639 cm^{-1} (lactam C=O); ^1H NMR (270 MHz) δ 3.40 (1 H, dd, J = 17.22 and 2.20 Hz, 3-H), 3.63 (1 H, dd, J = 17.22 and 7.33 Hz, 3-H), 3.75 (3 H, s, NMe), 7.2–7.3 (2 H, m, aromatic H), 7.4–7.5 (3 H, m, aromatic H), 7.55–7.65 (2 H, m, aromatic H), 7.82 (1 H, dd, J = 1.47 and 7.70 Hz, 9-H), and 8.06 [2 H, dd, J = 1.10 and 7.32 Hz, benzoyl H(ortho)]; MS, m/z 321 (M^+, 0.6), 293 (3.7), 199 [$(M - C_6H_5COOH)^+$, 51], and 105 (100); high-resolution mass spectrum for $C_{19}H_{19}NO_4$ calcd 321.1000, found 321.0984. **48**: R_f 0.06 (1:1 ethyl acetate–hexane); mp 211 °C (diethyl ether–hexane–dichloromethane); IR (thin film) 1732 ($OCOC_6H_5$), 1630 and 1592 cm^{-1} (enone C=O); ^1H NMR (270 MHz) δ 3.47 (1 H, dd, J = 16.12 and 2.19 Hz, 3-H), 3.66 (1 H, dd, J = 16.12 and 6.96 Hz, 3-H), 3.73 (3 H, s, NMe), 7.89 (1 H, dd, J = 6.96 and 2.19 Hz, 1-H), 7.35–7.5 (3 H, m, aromatic H), 7.55–7.7 (2 H, m, aromatic H), 8.07 [2 H, dd, J = 8.43 and 1.19 Hz, benzoyl H_2 (ortho)], and 8.50 (1 H, dd, J = 7.69 and 1.46 Hz, 5-H); MS, m/z 321 (M^+, 1.7), 199 [$(M - C_6H_5COOH)^+$, 18], and 105 (100); high-resolution mass spectrum for $C_{19}H_{15}NO_4$ calcd 321.1000, found 321.0990. Similar irradiation of **43** (198 mg, 0.61 mmol) in benzene (31 mL) containing mercury(II) oxide (396 mg, 1.83 mmol) and iodine (464 mg, 1.83 mmol) for 5 h gave **47** (42 mg, 22%) and **48** (79 mg, 40%).

Supplementary Material Available: Anisotropic thermal parameters for the non-hydrogen atoms (Table II), fractional atomic coordinates, (Table III), bond distances and angles for compound **16** (Table IV), and perspective view of the molecule (Figure II) (4 pages). Ordering information is given on any current masthead page.

Static and Dynamic Stereochemistry of a Chiral, Doubly Bridged 9,10-Diphenylanthracene from a Stereospecific Polycyclic Aromatic Dicarbonyl Coupling

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The reductive coupling of dibenzo[*b*,*f*]suberone (**5**) with a low-valent titanium reagent generated from $TiCl_4$, Zn, and pyridine in THF gave two dimeric hydrocarbons, the tetrahydrobis(benzocyclohept)anthracene **6** and the tetrahydrobi(dibenzocycloheptenyl) **7**. The same reaction with reagents generated from $TiCl_3$ or $TiCl_4$ with $LiAlH_4$ in THF gave only **7**. Analogous couplings of dibenzo[*b*,*f*]tropone (**4**) gave bi(dibenzo[*a*,*d*]cycloheptenyl) (**9**) and *syn*-bis(dibenzo[*a*,*d*]cycloheptenylidene) (**3**). X-ray cryystallography showed **6** to be a chiral, syn-bridged 9,10-diphenylanthracene. Molecular mechanics calculations (MM2-85) predicted a very similar syn-bridged structure to be the lowest energy conformation and a centrosymmetric anti form to be 1.39 kcal/mol higher in energy. **6** could be resolved into enantiomers by chromatography at 5 °C on swollen, microcrystalline triacetylcellulose with ethanol as eluent. Analysis of the CD spectrum in terms of the coupled oscillator model led to the assignment of (−)-**6** to the *S*,*S* configuration. Thermal racemization, monitored by the CD spectrum, in the temperature range 20–50 °C gave $\Delta G^{\ddagger}$ = 22.6 kcal/mol for the ring inversion. Analysis of the ^1H NMR spectrum showed the conformations of the CH_2–CH_2 bridges in solution to be similar to those in the crystal, and simulation of the exchange-broadened spectra in the temperature range 144–169 °C gave $\Delta G^{\ddagger}_{inv}$ = 22.9 kcal/mol. No resonances due to an anti form could be observed in the NMR spectra.

The bistricyclic ethylene (**1**; Chart I) enigma has fascinated chemists since thermochromism and photochromism were revealed in bianthrones (**1**, X = C=O).[1,2] The bistricyclic ethylenes are attractive substrates for the study

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