Photoinduced Molecular Transformations. 100.[1] Formation of Furocoumarins and Furochromones via a β-Scission of Cyclobutanoxyl Radicals Generated from [2 + 2] Photoadducts from 4-Hydroxycoumarin and Acyclic and Cyclic Alkenes. X-ray Crystal Structures of (6aα,6bα,9aα,9bα)-(±)-6b,7,8,9,9a,9b-Hexahydro-9b-hydroxybenzo[*b*]cyclopenta[3,4]cyclobuta[1,2-*d*]pyran-6(6a*H*)-one, *cis*-(±)-6b,8,9,9a-Tetrahydro-6*H*,7*H*-cyclopenta[4,5]furo[3,2-*c*][1]benzopyran-6-one, and *cis*-1,2,2a,8b-Tetrahydro-8b-hydroxy-1,1,2,2-tetramethyl-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one[2]

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We describe the formation of several new furocoumarins and furochromones by means of the photolysis of hypoiodites generated by the treatment of cyclobutanols obtained by [2 + 2] photocycloaddition of 4-hydroxycoumarin and (a) three cycloalkenes, (b) two acyclic alkenes, (c) vinyl ethyl ether, and (d) isopropenyl acetate, with mercury(II) oxide and iodine. The irradiation of the hypoiodites of the photoadducts between 4-hydroxycoumarin and the cycloalkenes, ethyl vinyl ether, or isopropenyl acetate gave furocoumarin as the only product arising from the insertion of an hydroxyl oxygen into their cyclobutane ring. A product having a novel spirocyclopropane structure is formed together with furocoumarin in the photolysis of the hypoiodite of the photoadduct between 2-hydroxycoumarin and cyclooctene. The irradiation of the hypoiodites of the photoadducts between 4-hydroxycoumarin and acyclic alkenes, however, led to the formation of furochromone as accompanying products together with furocoumarin. The molecular structures of the [2 + 2] photoadducts from 4-hydroxycoumarin and cyclopentene or dimethylbut-2-ene as well as the molecular structure of the furocoumarin formed from the photoadduct between 4-hydroxycoumarin and cyclopentene were established by X-ray crystallographic analysis. The pathways leading to the formation of all these products are discussed.

The synthesis of heterocycles by the insertion of a heteroatom into alicyclics is of great importance in organic synthesis, and a variety of methods for achieving it have been reported. As a part of our program to explore the potential of the β-scission of alkoxyl radicals for organic synthesis,[1,3,4,14] we have investigated the β-scission of the alkoxyl radicals of the cyclobutanols obtainable by the [2 + 2] photoaddition[5] of 4-hydroxycoumarin (1) as an enolized carbonyl compound to various types of acyclic and cyclic alkenes. We found that furocoumarins formed by the insertion of an oxygen atom of the hydroxyl group to their cyclobutane ring are the products when the hypoiodites of the photoadducts of 4-hydroxycoumarin with cycloalkenes, ethyl vinyl ether, or isopropenyl acetate are irradiated. We also found that a mixture of furocoumarins and furochromones is obtained when the hypoiodites of the photoadducts betwen 4-hydroxycoumarin and cyclic alkenes are irradiated.

Fused cyclobutanols used in this study were (a) the three photochemical cycloadducts **3**, **7**, and **8** obtained by the photoadditions of **1** with cyclopentene, cyclohexene, or cyclooctene reported by Reid and his colleagues[5] (Scheme I), (b) five photochemical cycloadducts **14**,[5] **19**, **20**, **21**, and **22** obtained by the photoadditions of **1** with dimethylbut-2-ene or 2-methyl-2-butene (Scheme II), (c) a photochemical cycloadduct **29** obtained by the photoadditions of **1** with isopropenyl acetate (Scheme III), and (d) photoadducts **31** and **32** obtained by the photoadditions of **1** with ethyl vinyl ether (Scheme III).

The preparations of the photoadducts **3**, **7**, **8**, and **14** were carried out according to the procedure reported by Reid and his colleagues.[5] These photoadditions gave a single adduct in each case without any formation of their accompanying isomers. As the stereochemistry of all these

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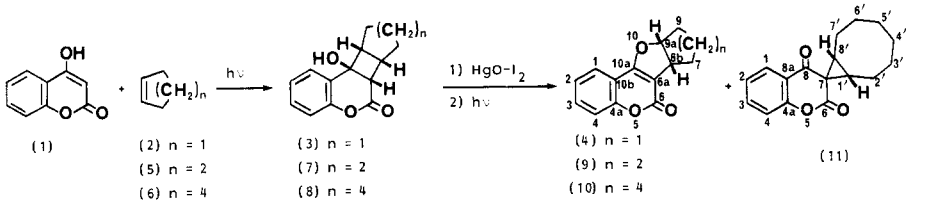
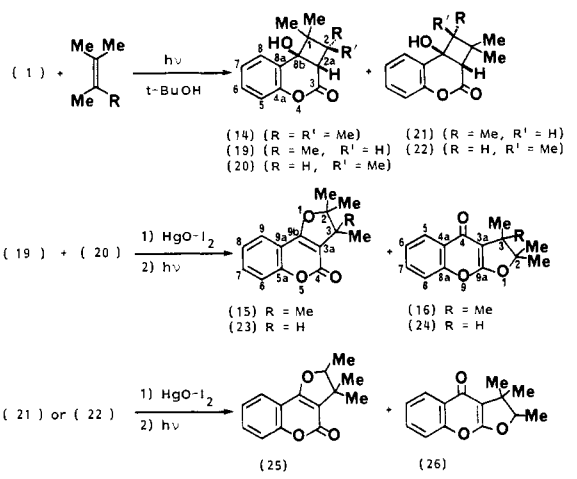
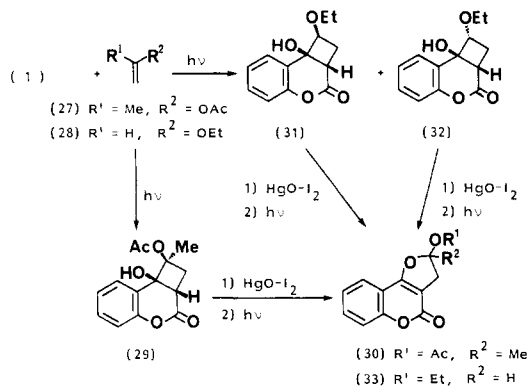
Scheme I



Scheme II



Scheme III



photoadducts has not been determined, we subjected the crystalline adduct **3** of 4-hydroxycoumarin and cyclopentene to X-ray crystallographic analysis. The X-ray diffraction data (see the Experimental Section) disclosed that it has a cis-cisoid-cis configuration.[2]

The photoaddition of a coumarin and an alkene with[6,7] or without a sensitizer[8,9] as well as the photoaddition of a coumarin and a cycloalkene with a sensitizer[7,10] have been reported previously. The present example, however, is the first case where the stereochemistry of the photoadduct of a coumarin and a cycloalkene has been firmly established. Although numerous photoadditions of a variety of cyclic enones and cycloalkenes have been reported,[11] the present photoaddition is the first case where the photoaddition of not only coumarins but also enones in general with cycloalkenes leads to an exclusive formation of a single stereoisomer with a sterically disfavored cis-cisoid-cis configuration. In the photoaddition of cyclic enones and cycloalkenes, which involves a triplet exciplex or a triplet biradical, sterically favored cis-transoid-cis isomer have always been preferential addition products. No investigation has been carried out on whether the formation of the cis-cisoid-cis isomer **3** involved a singlet or a triplet exciplex, although the exclusive formation of the sterically

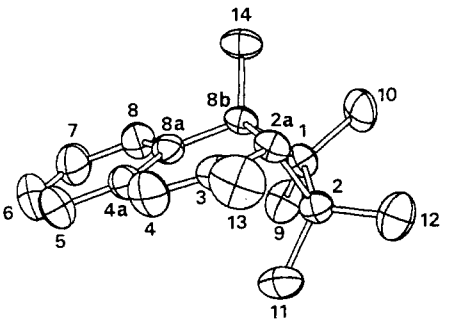


Figure 1. A perspective view of the *cis*-1,2,2a,8b-tetrahydro-8b-hydroxy-1,1,2,2-tetramethyl-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one molecule, and the numbering system of atoms. Non-hydrogen atoms are represented as thermal elipsoids enclosing 50% probabilities.

disfavored isomer may well involve a singlet exciplex.[8,12]

It is very likely that the formation of the other two photoadducts, **7** and **8**, may involve a same mechanism and that they may have a cis-cisoid-cis stereochemistry; the stereochemistry of these adducts have not yet been established, however. The formation of the photoadduct **14** of 4-hydroxycoumarin and alkenes required no sensitizer. This behavior of the excited 4-hydroxycoumarin is contrasted to the excited coumarin itself since photoaddition of coumarin itself with alkenes has been reported to require a sensitizer and the unsensitized addition was reported to take place with a low quantum efficiency and leads to only a very poor yield of the adduct.[8,9]

The molecular structure of the adduct **14** was again determined by X-ray crystallographic analysis and is shown in Figure 1 together with the numbering system of atoms. It has a cis ring junction as expected. The present example is again the first case in which the stereochemistry of the photocycloadduct of a coumarin and an alkene where cis and trans fusion are possible[11] has been rigorously established by X-ray technique. The details of the analysis are recorded in the Experimental Section.

A direct irradiation of 4-hydroxycoumarin (**1**) and 2-methylbut-2-ene under the same conditions as the previous cases gave a mixture of four isomeric photoadducts **19–22** in a combined yield of 81% (Scheme II). It is interesting that the head-to-head adducts **19** and **20** are predominantly formed in this photocycloaddition. The ratio of the head-to-head adducts **19** and **20** to the head-to-tail adducts **21** and **22** was 2 to 1. Among these four isomers of the cycloadducts, only adducts **19** and **22** were obtained in pure forms by preparative TLC and recrystallization (see the Experimental Section), and adducts **20** and **21** were obtained only as a mixture of three adducts **19–21**. The yields of the adducts **19**, **20**, and **21** estimated by ^{1}H NMR were 32%, 22%, and 11%, respectively, and the yield of **22** was 16%. The stereochemistry of these adducts were established by ^{1}H NMR spectroscopy. Thus, adducts **19** and **20** were readily distinguished with adducts **21** and **22** by signals of 2a-H adjacent to their carbonyl group since those of the former two appeared as a doublet while those of the latter two appeared as a singlet. Exo adduct **19** and

endo adduct **20** were also distinguished by means of ^1H NMR spectroscopy since a doublet arising from the 2-Me of exo adduct **19** appeared at a field lower than a doublet due to the 2-Me of endo adduct **20**, owing to the deshielding by the hydroxyl group attached to the 8b carbon. Similarly, **21** and **22** were discernible by the difference of the chemical shifts between the 1-Me of exo adduct **21** and endo adduct **22**.

The photocycloaddition of 4-hydroxycoumarin (**1**) with isopropenyl acetate (**27**) under the above conditions took place with remarkably high regio- and stereoselectivity and gave a single crystalline adduct **29** in a 75% yield. The proton attached to the 2a carbon appeared as a doublet of a doublet at δ 3.18, which proved the head-to-head constitution of the adduct. The relative stereochemistry of OH and OAc was only tentatively assigned as cis on the basis of the results of the ^1H NMR spectrum. Thus, the exo and endo protons attached to the C-2 appeared at δ 1.99 (dd, J = 12.09 and 10.63 Hz) and 2.65 (dd, J = 12.09 and 9.89 Hz). This large difference of the chemical shifts between the exo and endo protons is analogous to the large difference of those between the corresponding exo and endo protons of adduct **31** and its nitrogen analogue.[13] High regio- and stereoselectivity of the photoaddition suggests that the acetoxyl group of the olefin is playing an important role for controlling the stereo- and regioselectivity of the photoaddition.

Finally, the photoaddition of 4-hydroxycoumarin (**1**) with ethyl vinyl ether (**28**) in *tert*-butyl alcohol gave two stereoisomeric cycloadducts **31** and **32** in 16% and 10% yields. The high regioselectivity of the photoaddition is again remarkable. These adducts were unstable, and the poor yields are attributable to the partial decomposition during their isolation. The ethoxyl and hydroxyl groups of adducts **31** and **32** were tentatively assigned as cis and trans by the comparison with the ^1H NMR spectra of the nitrogen analogues.[13] The exo and endo protons attached to the C-2 of adduct **31** appeared at δ 1.55 (ddd, J = 10.99, 10.63, and 9.16 Hz) and 2.51 (ddd, J = 10.99, 9.16, and 8.06 Hz), while the corresponding protons of the isomeric adduct **32** appeared at δ 2.2 and 2.4. The large difference of the chemical shifts of the exo and endo protons was similar to the large difference of the chemical shifts between the exo and endo protons attached to the C-2 of its nitrogen analogue (HO-C_{8b}-C_1-OEt; cis) where the ring oxygen was replaced by the NMe group.[13]

The Preparation of Furocoumarins. The next step was to transform cyclobutanol **3** in benzene into the corresponding hypoiodite with each the usual 3 equiv of mercury(II) oxide and iodine in a Pyrex vessel;[4] the solution was then irradiated with a 100-W high-pressure mercury arc for 2 h under a nitrogen atmosphere to give a mixture of products. A major crystalline product, **4**, $C_{14}H_{12}O_2$, was then obtained by preparative TLC in a 45% yield. The other products were very minor. The IR as well as UV spectra of **4** indicated that the coumarin nucleus was intact; X-ray crystallographic analysis (see the Experimental Section) established the molecular structure to be *cis*-6b,8,9,9a-tetrahydro-6*H*,7*H*-cyclopenta[4,5]furo[3,2-*c*][1]benzopyran-6-one.[2] All the spectroscopic properties of product **4** are recorded in the Experimental Section. The mass spectrum of furocoumarin **4** exhibited a base peak at m/z 199 arising from the removal of the C-9 and C-10 from the molecular ion. The cyclobutanol **1** was then transformed into furanocoumarin **4** with $Hg^{18}O$ (48.9 atom % ^{18}O)[4] and iodine under the condition described above. A mass spectrometric analysis showed no incorporation of ^{18}O into **4**. This O-18 labeling study provided evidence that the oxygen atom inserted into the cyclobutane ring of **3** originated exclusively from the hydroxyl group and that no scrambling with the oxygen derived from the HgO was involved.

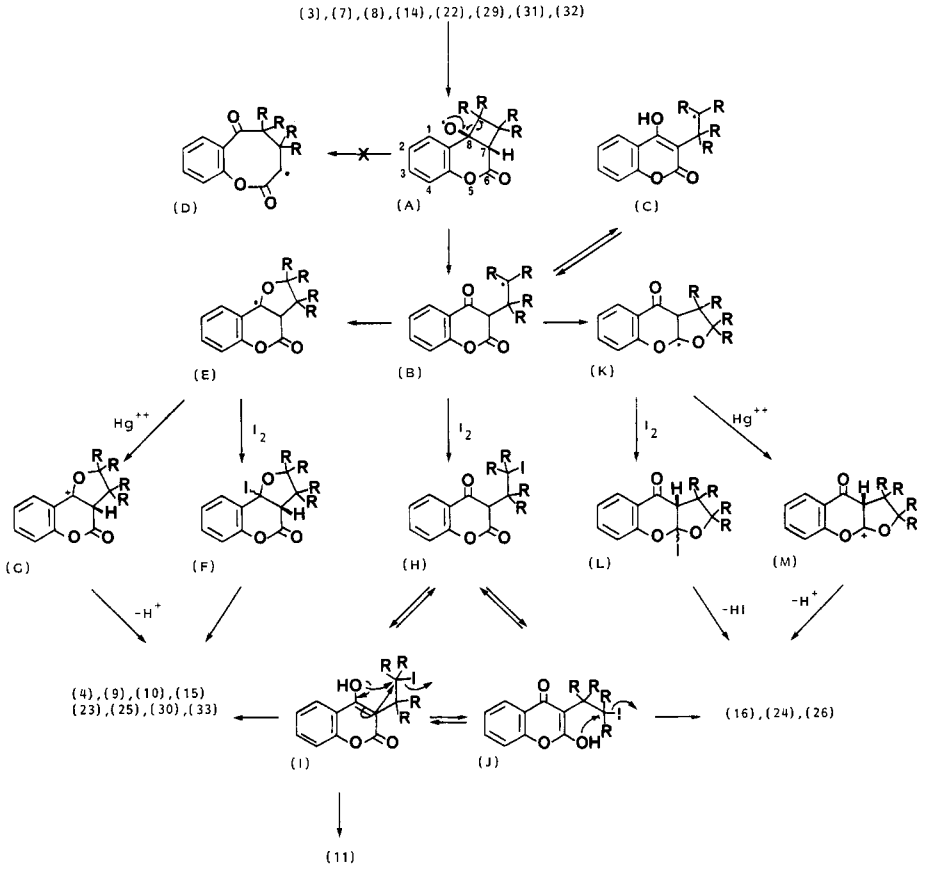
The product **4** was found to be very stable even under conditions of the acidic hydrolysis of vinyl ethers. For example, when the product **4** in a 5:1 mixture (volume) of diethyl ether–60% perchloric acid was heated under reflux for 1 h, it was recovered unchanged. It was also recovered unchanged when it was dissolved in a 4:1 mixture of acetic acid and concentrated sulfuric acid and heated under reflux for 2 h.

The photoadduct **7** was similarly subjected to hypoiodite photolysis (Scheme I). This, however, resulted in a much more complex product mixture than that derived from the cyclopentene adduct. We did, however, succeed in isolating homologous furocoumarin, 6b,7,8,9,10,10a-hexahydro-6*H*-benzofuro[3,2-*c*][1]benzopyran-6-one (**9**), in a 10% yield by preparative TLC. The assigned structure **9** was apparent on the basis of its IR, ^1H NMR, ^{13}C NMR, UV, and the mass spectral data, which are recorded in the Experimental Section. The mass spectrum exhibited a base peak at m/z 199, which is identical with that of the ion m/z 199 generated from product **4**. No other well-defined product was isolated from the reaction mixture.

The photolysis of the hypoiodite of the cyclooctene adduct **8** again gave a mixture of the products from which a major product **10** and minor ones **11** and **12** were isolated by preparative TLC. The major product **10** (20% yield) was again identified to be a homologous furocoumarin, 6b,7,8,9,10,11,12,12a-octahydro-6*H*-cycloocta[4,5]furo[3,2-*c*][1]benzopyran-6-one (**10**) by the mass spectrum, which showed the base peak at m/z 199; this ion is characteristic of the furocoumarins **4**, **9**, and **10**. The ^1H NMR, IR, and UV spectral data that are consistent with the assigned structure are recorded in the Experimental Section. Of the other two minor products, **11** and **12**, the former obtained in a 15% yield was found by high-resolution mass spectrometry to be isomeric with the furocoumarin **10**. The infrared spectrum showed three bands in the carbonyl region. A band at 1755 cm^{-1} can be assigned to a lactonic C=O, and the two bands at 1663 and 1610 cm^{-1} belong to a carbonyl group conjugated with an aromatic ring. The ^1H and ^{13}C NMR spectra indicated the absence of the tetrasubstituted carbon–carbon double bond and the methine proton attached to a carbon-bearing ethereal oxygen atom. Based on this spectroscopic evidence together with an analysis of the ^{13}C NMR spectra, the spirodihydrocoumarin structure in Scheme I was assigned to **11**. The assignments of the signals of the ^{13}C NMR spectrum of **11** are recorded in the Experimental Section. The structure of **12** has not yet been deduced.

Adduct **14** in benzene containing mercury(II) oxide and iodine was similarly irradiated for 3 h (Scheme II). Two products **15** and **16** were obtained in 37% and 21% yields by preparative TLC. High-resolution mass spectrometry established the molecular formulas of both **15** and **16** to be $C_{15}H_{16}O_3$. The structure of product **15** was deduced to be a furocoumarin, 2,3-dihydro-2,2,3,3-tetramethyl-4*H*-furo[3,2-*c*][1]benzopyran-4-one, after spectroscopic analysis. The coumarin nucleus was readily identified by its ^{13}C NMR spectrum, which gave a series of signals very similar to those of the furocoumarins formed from cyclobutanols derived from the [2 + 2] cycloadducts of 4-hydroxycoumarin and cycloalkenes. The UV spectrum revealed intense absorption due to the coumarin nucleus. The ^{13}C NMR, UV, and the mass spectral data are described in the Experimental Section together with details

Scheme IV



of the IR and ^{1}H NMR spectra.

The isomeric product **16**, on the other hand, was assigned to be a furobenzo-γ-pyrone, 2,3-dihydro-2,2,3,3-tetramethyl-4*H*-furo[2,3-*b*][1]benzopyran-4-one, on the basis of its ^{13}C and ^{1}H NMR, IR, mass, and UV spectra. The γ-pyrone nucleus was again identified by the ^{13}C NMR spectrum, and the assignment of the signals is described in the Experimental Section together with the ^{1}H NMR, IR, and UV spectral data. A 3:2:1 mixture of three isomeric photoadducts **19**, **20**, and **21** obtained as above was subjected to the hypoiodite photolysis under the conditions as in the case of the aforementioned photolysis to yield a mixture of the four products **23**–**26**. Separation of the products by means of preparative TLC gave a pair of isomers of crystalline furocoumarins **23** and **25** in 33% and 7% yields as well as a pair of isomers of crystalline furochromones **24** and **26** in 19% and 3% yields. The mass spectra of all the four products exhibited their base peaks at *m*/*z* 251, arising from the expulsion of the methyl group. Their structures as assigned were confirmed by the spectroscopic analysis, details of which are described in the Experimental Section. It is apparent that furocoumarin **23** and furochromone **24** are derived from adducts **19** and/or **20** and furocoumarin **25** and furochromone **26** are derived from adduct **21**. The yields of furocoumarin **23** (40%) and furochromone **24** (23%) are those calculated on the basis of the results of the photolysis of the mixtures and the yields of furocoumarin **25** and furochromone **26** were similarly calculated to be 42% and 18%.

Finally, the pure photoadduct **22** was subjected to the hypoiodite photolysis under the above conditions and found to yield furocoumarin **25** and furochromone **26** in 43% and 16% yields. The hypoiodite photolysis in this case was also carried out in carbon tetrachloride as the solvent to give a similar result (**25**, 42%, and **26**, 25%).

The photolysis of photocycloadduct **29**, derived from 4-hydroxycoumarin and vinyl acetate, in benzene containing mercury(II) oxide and iodine gave a mixture of products from which only a crystalline furocoumarin **30** was isolated in a 29% yield.

Finally, the hypoiodite photolysis of stereoisomeric photoadducts **31** and **32**, derived from 4-hydroxycoumarin and vinyl ether, was undertaken. The photolysis of endo adduct **31** under the above conditions gave a mixture of products, and a crystalline furocoumarin **33** was only obtained in a 35% yield.

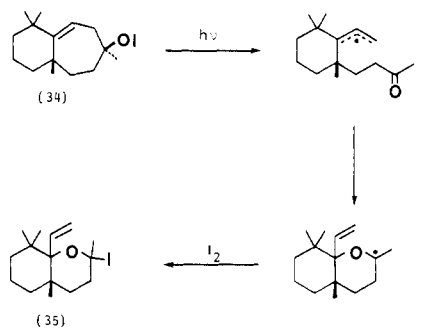
The furocoumarin **33** was similarly obtained in a 29% yield by the hypoiodite photolysis of exo adduct **32**.

The assigned structures of furocoumarins **30** and **33** were defined by means of spectroscopy, the details of which are recorded in the Experimental Section.

Discussion

The probable paths leading to the formation of the furocoumarins **4**, **9**, and **10** from the hypoiodites of cyclobutanols **3**, **7**, and **8** are outlined in Scheme IV. Thus, photolysis of the hypoiodites, the initial intermediates, generates an alkoxyl radical A, a β-scission of which gives rise to a carbon-centered radical B rather than a carbon-centered radical D. The radical B may well be in equilibrium with a resonance-stabilized coumarin radical C, and this explains why β-scission between the heterocyclic ring and the cycloalkane rather than that leading to a ring expansion is preferred. The radical B then combines with the carbonyl oxygen intramolecularly to form a dihydrofuranyl radical E.[4] The furocoumarins **4**, **9**, **10**, **15**, **23**, **25**, **30**, and **33** may be formed either through the elimination of HI from the species F under the conditions of the experiments or through oxidation to the corresponding carbocation G followed by the removal of a proton. We

Scheme V



have already reported that the irradiation of the hypoiodite **34** gave iodide **35** (Scheme V)[14] corresponding to the species F.

There is, although less likely, an alternative hypothetical pathway for the formation of the furocoumarins. The carbon-centered radical B may abstract an iodine atom from ROI or I_2 in a free radical chain process to give iodides H, which will be in equilibrium with the enol forms I, as outlined. An intramolecular nucleophilic displacement of the iodine atom by the enol oxygen of iodide I may give the furocoumarins.

The spirodihydrocoumarin **11** is formed by a cyclization of the iodide I as we have already confirmed in an other system.[15]

In contrast to the case of cyclobutanols derived from cycloalkenes and 4-hydroxycoumarin, the hypoiodite photolysis of cyclobutanols derived from alkenes and 4-hydroxycoumarin led to the formation of both furocoumarin **15**, **23**, and **25** and furochromones **16**, **24**, and **26**.

The probable paths, by which these products are formed, are outlined in Scheme IV. As shown, the furochromones are considered to be formed from an intermediate radical B. As outlined, there are again two principal paths each for the formation of the furocoumarin and furochromones. Of the two mechanistic possibilities for the formation for the two types of the products, the paths involving an intramolecular combination of the carbonyl oxygen with the carbon-centered radical (B → E → G or F → **4**, **9**, **10**, **15**, **23**, **25**, **30**, **33** and B → K → L or M → **16**, **24**, **26**) are evidently likely since the alternative paths (B → H → I → **4**, **9**, **10**, **15**, **23**, **25**, **30**, **33** and B → H → J → **16**, **24**, **26**) involve the formation of such an unlikely species as tertiary iodide I and the intramolecular nucleophilic displacement of the iodine atom by the enol oxygen of the species I and J. The formation of furochromones from H or J is very unlikely. It has already been found that the tertiary carbon radical formed by the β-scission of steroidal alkoxyl radicals combines with the carbonyl oxygen intramolecularly rather than with iodine present in the solution.[4]

Whatever the exact pathway of the formation of the furocoumarins is, the formation of the furocoumarins via [2 + 2] photocycloaddition of an enol and alkenes followed by β-scission of the alkoxyl radicals generated from the cyclobutanols formed by the cycloaddition is of value in the synthesis of a series of oxygen heterocycles that are not readily accessible by other methods. The results of further studies on a variety of cyclobutanol derivatives that originate from the [2 + 2] photoaddition of enols and cycloalkenes designed to explore the synthetic potential of the oxygen insertion described in this paper will be the subject of future publication.

Experimental Section

General Method. For the instruments used and the procedure of the photolysis see ref 3.

(6aα,6bα,9aα,9bα)-(±)-6b,7,8,9,9a,9b-Hexahydro-9b-hydroxybenzo[*b*]cyclopenta[3,4]cyclobuta[1,2-*d*]pyran-6-(6a*H*)-one (3). This adduct was prepared according to the procedure reported by Reid et al.:[5] mp 164–165 °C (lit.[5] mp 162 °C).

X-ray Structure Determination of (6aα,6bα,9aα,9bα)-6b,7,8,9,9a,9b-Hexahydro-9b-hydroxybenzo[*b*]cyclopenta-[3,4]cyclobuta[1,2-*d*]pyran-6(6a*H*)-one (3). Crystal data are as follows: $C_{14}H_{14}O_3$, M = 230.26; triclinic; space group $P\bar{1}$; a = 10.484 (4), b = 13.525 (5), and c = 8.384 (2) Å; α = 90.05 (3), β = 103.07 (2), and γ = 106.46 (3)°; U = 1107.9 Å^3; z = 4; D_c = 1.380 g cm^{-3}; $F(000)$ = 488; μ(Mo Kα) = 0.900 cm^{-1}.

The sample used for the X-ray experiment had dimensions of ca. 0.5 × 0.5 × 0.2 mm. The unit-cell dimensions and reflection intensities were obtained on a Rigaku automatic four-circle diffractometer at the High Brilliance X-Ray Laboratory of Hokkaido University, with use of graphite monochromated Mo Kα radiation (λ 0.710 73 Å). The $\omega - 2\theta$ scan technique was applied at an ω scan rate of 2 deg min^{-1}; the background was counted for 10 s at each end of the scan range. Three standard reflections (4, 1, 1; 2, $\bar{6}$, 1; $\bar{1}$, $\bar{2}$, 4), measured at intervals of every 100 reflections, showed no significant decrease in intensity during the course of data collection. The intensities were corrected for the Lorentz and polarization factors, but not for the absorption or the extinction effects. In the range of 2θ values up to 50°, 3199 independent structure factores above the $\sigma(F)$ level were selected for the structure determination.

The space group was assumed to be $P\bar{1}$ at the beginning of the structural analysis; this choice was later confirmed by a successful refinement. The structure was solved by the Monte Carlo direct method,[16] with the 10 reflections with the greatest $|E|$ values as the starting set. The 16th random phase set led to the correct solution; an E map based on 735 phases revealed the locations of all the 34 non-hydrogen atoms. The structure was refined by the block-diagonal least-squares method with anisotropic temperature factors. After all the 28 hydrogen atoms had been located in a difference Fourier map, further least-squares refinements were carried out including the hydrogen atoms with isotropic temperature factors. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma(F)^2 \exp(AX^2 + BY^2 + CXY + DX + EY)]$, where $X = |F_o|$ and $Y = \sin\theta/\lambda$. The A, B, C, D, and E coefficients were evaluated from the $(\Delta F)^2$ distribution; A = −0.000 106, B = 19.4, C = 0.201, D = 0.0247, and E = −23.9. The final R value was 0.063. The results are given in Tables I–IV of the supplementary material. The calculations were made on a HITAC M-280H computer at the Hokkaido University Computing Center, with our own programs. The atomic scattering factors were taken from the International Tables.[17]

Irradiation of Hypoiodite of the Photoadduct 3 in the Presence of Mercury(II) Oxide and Iodine. The adduct 3 (460 mg, 2 mmol) in dry benzene (80 mL) containing mercury(II) oxide (1.3 g, 7 mmol) and iodine (1.5 g, 6 mmol) in a Pyrex vessel was irradiated with a 100-W high-pressure mercury arc (EIKOSHA) while being stirred for 2 h under a nitrogen atmosphere. The solution was filtered, and the filtrate was washed with a 5% sodium thiosulfate solution (50 mL × 2) and water (50 mL × 2) successively. The organic layer was washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a residue, which was subjected to preparative TLC with 7:3 diethyl ether–benzene to give a major fraction (205 mg). It was then recrystallized from diethyl ether to yield pure crystals of **4** (150 mg): mp 103–104 °C; IR (Nujol) 1713 (C=O) and 1646 cm^{-1} (C=C); ^{1}H NMR δ 1.41–2.31 (6 H, m, 3 methylenes), 3.94 (1 H, br t, 6b-H), 5.57 (1 H, br q, 9a-H), and 7.19–7.37 (4 H, m, aromatic H); ^{13}C NMR 23.39, 31.59, and 35.21 (each t, C-7, C-8, and C-9), 44.76 (d, C-6b), 93.58 (d, C-9a), 105.15 (s, C-6a), 112.56 (s, C-10b), 116.86, 122.85, 123.75, and 132.13 (each d, C-1–C-4), 154.99 (s, C-4a), 160.68 (s, C-10a), and 166.98 (s, C-6); UV (EtOH) 327 nm (ε 4920), 313 (ε 6800), 289 (ε 6330), 277 (ε 4450), and 207 (ε 24 200); MS, m/z 228 (M$^+$, 76.7), 199 (100), 187 (14.9), and 121 (34.9). Anal.

(15) Suginome, H.; Itoh, M.; Kobayashi, K. *J. Chem. Soc. Perkin. Trans. 1* **1988**, 491.
(16) Furusaki, A. *Acta Crystallogr., Sect. A* **1979**, *A25*, 220.
(17) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, 1974; Vol. 4.

Calcd for $C_{14}H_{12}O_3$: C, 76.67; H, 5.30. Found: C, 73.70; H, 5.28.

X-ray Structure Determination of *cis*-(±)-6b,8,9,9a-Tetrahydro-6*H*,7*H*-cyclopenta[4,5]furo[3,2-*c*][1]benzopyran-6-one (4). Crystal data are as follows: $C_{14}H_{12}O_3$, M 228.25; monoclinic; a = 10.582 (2), b = 13.224 (2), and x = 8.070 (2) Å; β = 99.55 (2)°; U = 1113.6 Å^3; z = 4; D_c = 1.361 g cm^{-1}; $F(000)$ = 480; μ(Cu Kα) = 7.42 cm^{-1}. Systematic absences: $h0l$ for l odd $0k0$ for k odd, space group $P2_1/c$.

A single crystal with dimensions of ca. 0.4 × 0.2 × 0.1 nm was used for the diffraction experiment. The integrated intensities of independent reflections in the range of $2\theta < 135°$ were measured on the Rigaku diffractometer by the use of the $\omega - 2\theta$ scan mode and graphite-monochromated Cu Kα radiation (λ 1.541 78 Å). The ω scan speed was 2 deg min^{-1}; the background-counting time at each end of the scan range was 15 s. During the data collection, the intensities of three standard reflections (5, 4, 0; $\bar{3}$, 6, 2; 2, 0, 4) showed no significant variation. The Lorentz and polarization corrections were applied. A total of 1811 unique structure factors above the $\sigma(F)$ level were obtained.

The structure was elucidated by the Monte Carlo direct method[16] on the basis of 377 $|E|$ values above 1.30. The first-generated random phase set for the 10 strongest reflections led to the correct solution; an E map calculated with 374 phases afforded all the 17 non-hydrogen atoms. After the structure has been refined by the block-diagonal least-squares method with anisotropic temperature factors, a difference Fourier synthesis was carried out; the resulting map yielded all the 12 hydrogen atoms. Further full-matrix least-squares refinements were performed including the hydrogen atoms with isotropic temperature factors. The weighting scheme was similar to that used for 1; A = −0.000 073 4, B = 34.9, C = 0.413, D = 0.0187, and E = −39.6. The final R value was 0.062. The results are shown in Table V–VII of the supplementary material.

The calculations were made on a HITAC M-280H computer at the Hokkaido University Computing Center, with our own programs. The atomic scattering factors were taken from the International Tables.[17]

6a,6b,7,8,9,10,10a,10b-Octahydro-10b-hydroxy-6*H*-benzo[*b*]benzo[3,4]cyclobuta[1,2-*d*]pyran-6-one (7). This adduct was prepared according to the procedure reported by Reid et al.:[5] mp 118–119 °C (diethyl ether–petroleum) (lit.[5] mp 116–117 °C).

Preparation of Furocoumarin 9 from the Photoadduct 7. Photolysis of the hypoiodite of adduct 7 (488 mg) in benzene (80 mL) was carried out as described for the hypoiodite of adduct 3 (2 h). A product mixture was subjected to preparative TLC with 7:3 benzene–diethyl ether to give four fractions. The third mobile fraction (47 mg) was 6b,7,8,9,10,10a-hexahydro-6*H*-benzofuro[3,2-*c*][1]benzopyran-6-one (**9**), which was recrystallized from diethyl ether: mp 76–78 °C; IR (Nujol) 1710 (C=O) and 1735 cm^{-1} (C=C); ^{1}H NMR δ 1.29–2.31 (8 H, m, 4 methylenes), 3.37 (1 H, ddd, J = 6, 7.6, and 8.1 Hz, 6b-H), 5.03 (1 H, dd, J = 4.4, 4.2, and 8.1 Hz, 10a-H), and 7.20–7.73 (4 H, m, the four aromatic protons); MS, m/z 242 (M$^+$, 85), 199 (100), and 121 (52); high-resolution mass calcd for $C_{15}H_{14}O_3$ m/z 242.0943, found 242.0955; UV (EtOH) 327 nm (ϵ 2040), 312 (3570), 289 (3220), 277 (2240) and 206 (11 400). The fourth crystalline fraction, mp 150–152 °C, (16 mg) had the molecular ion at m/z 256 in the mass spectrum: IR 3500 (OH) and 1725 cm^{-1} (lactone C=O); mass, m/z 256 (M$^+$, 43), 228 (55), 200 (100), and 121 (26).

6a,6b,7,8,9,10,11,12,12a,12b-Decahydro-12b-hydroxy-6*H*-cycloocta[3,4]cyclobuta[1,2-*c*][1]benzopyran-6-one (8). This adduct was prepared according to the procedure reported by Reid et al.:[5] mp 132–133 °C (benzene–petroleum ether) (lit.[5] mp 178–180 °C).

Irradiation of Hypoiodite of the Photoadduct 8 in the Presence of Mercury(II) Oxide and Iodine. The photolysis (2 h) of the hypoiodite of the adduct (272 mg) under the conditions described for adduct 3 gave an oily product (273 mg). The product was subjected to preparative TLC with dichloromethane to yield three fractions. The most mobile fraction (41 mg, 14%) was a colorless product **11**, which was recrystallized from diethyl ether to yields crystals: mp 164–165 °C; IR 1755 (lactone C=O), 1663 and 1610 (C=O conjugated with phenyl), 1310 and 765 cm^{-1}; ^{1}H NMR δ 1.31–2.76 (14 H, m, 6 methylenes and 2 methines), and 7.19–8.00 (4 H, m, 4 aromatic protons); ^{13}C NMR 136.15, 124.41, 117.42, and 126.40 (each d, C-1–C-4 aromatic carbons), 130.81 (s, C-4a aromatic carbon), 155.95 (s, OC=O), 41.80 (s, C-7 spiro carbon), 189.52 (s, C-8, C=O), 128.75 (s, C-8a, aromatic carbon), 48.24 (d, C-1′ and C-8′), 28.42, 26.13, 20.90 (each t, 6 methylenes); MS, m/z 270 (M$^+$, 47), 199 (76), 176 (70), and 121 (100). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.56; H, 6.67. Found: C, 75.70; H, 6.84. The second mobile fraction (15 mg) was recrystallized from diethyl ether to give crystals (5 mg) of **12**: mp 127–129 °C; IR (Nujol) 1665, 1755 cm^{-1}; mass, m/z 270 (M$^+$) and 121 (100). The third mobile fraction (79 mg) was recrystallized from diethyl ether to give crystals of 6b,7,8,9,10,11,12,12a-octahydro-6*H*-cycloocta-[4,5]furo[3,2-*c*][1]benzopyran-6-one (**10**): mp 137–139 °C; IR (Nujol) 1713 and 1643 cm^{-1} (C=CC=O); ^{1}H NMR δ 1.21–2.31 (12 H, m, 6 methylenes), 3.41 (1 H, br t, C=CCH), 4.88–5.61 (1 H, m, OCH), and 7.16–7.60 (4 H, m, aromatic protons); ^{13}C NMR δ 25.36, 25.71, 26.24, 27.18, 29.71 (each t, C-7–C-12), 43.92 (d, C-6b), 91.82 (d, C-12a), 107.32 (s, C-6a), 112.66 (s, C-13b), 116.77, 122.76, 123.64 and 132.04 (each d, C-1–C-4 aromatic carbons), 154.82 (s, C-4a), 160.51 (s, C-13a), and 164.68 (s, C-6 carbonyl); UV (EtOH) λ_{max} (ϵ) 288 (3300), 291 (4550), 316 (5060), and 328 (3540); MS, m/z 270 (M$^+$, 38), 199 (100), and 121 (17). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.56; H, 6.67. Found: C, 75.41; H, 6.80.

***cis*-1,2,2a,8b-Tetrahydro-8b-hydroxy-1,1,2,2-tetramethyl-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-one (14).** This photocycloadduct was prepared according to the procedure reported by Reid et al.[5]

X-ray Structure Determination of Adduct 14. Crystal data are as follows: $C_{15}H_{18}O_3$; monoclinic; space group $P2_1/c$; a = 15.508 (7), b = 6.644 (6), and c = 14.099 (8) Å; β = 115.96 (4)°; z = 4; D_c = 1.252 g cm^{-3}. The intensities of 1810 independent reflections with $2\theta < 50°$ were obtained on a Rigaku four-circle diffractometer with graphite-monochromated Mo K radiation using the ω–2θ scanning technique. The structure was deduced by the Monte Carlo direct method,[15] using 15 reflections as the starting set; an E-map derived from the 73rd random phase set afforded all the non-hydrogen atoms. After the structure had been refined by the block-diagonal least-squares method with anisotropic thermal parameters, a difference Fourier synthesis was carried out; the resulting map revealed all the hydrogen atoms. Further full-matrix least-squares refinements were performed to include the hydrogen atoms with isotropic temperature factors. The final R value was 0.065. The final atomic positional parameters are listed in Table II of the supplementary material.

Irradiation of the Photoadduct 14 in the Presence of Mercury(II) Oxide and Iodine. The photolysis of the hypoiodite of adduct 14 (246 mg) in benzene as in the case of the photolysis of the hypoiodite of adduct 3 gave a product mixture. The product mixture was subjected to preparative TLC with dichloromethane to give three major fractions. The most mobile TLC fraction (66 mg) was furocoumarin **15**. Recrystallization from diethyl ether gave colorless crystals, mp 91–92 °C; IR (Nujol) 1643 and 1714 cm^{-1} (OCOC=C); ^{1}H NMR (100 MHz) δ 1.34 (6 H, s, 2-dimethyl), 1.47 (6 H, s, 3-dimethyl), 7.23–7.70 (4 H, m, aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.90 (2-dimethyl), 23.07 (3-dimethyl), 96.96 (C-2), 45.97 (C-3), 110.20 (C-3a), 113.25 (C-9a), 116.72, 122.70, 123.53, and 131.92 (the four aromatic carbons with hydrogen each), 154.87 (C-5a), 160.2 (C-9b), and 163.98 (C-4); UV (EtOH) 328 (ϵ 5700), 313 (8400), 289 (8000), 378 (5800), and 207 nm (24 500); MS (70 eV), m/z 244 (M$^+$, 14) and 229 (M$^+$ − CH_3, 100). Anal. Calcd for $C_{15}H_{16}O_3$ 244.1096, found (M$^+$), 244.1134.

The second mobile fraction (38 mg) was an oily furochromone **16**: IR (neat) 1622 and 1563 cm^{-1} (COC=C); ^{1}H NMR (100 MHz) δ 1.42 (6 H, s, 3-dimethyl), 1.48 (6 H, s, 2-dimethyl), 7.28–7.67 (4 H, m, aromatic H); ^{13}C NMR ($CDCl_3$) δ 22.27 (q, 3-dimethyl), 22.97 (q, 2-dimethyl), 45.53 (s, C-3), 96.15 (s, C-2), 102.77 (s, C-3a), 117.07, 124.98, 125.39, and 131.84 (each d, 4 aromatic carbons with a hydrogen each), 124.51 (s, C-4a), 153.05 (s, C-8a), 167.11 (s, C-4), and 174.67 (s, C-9a); UV (EtOH) 277 (ϵ 2500) and 206 nm (16 800); MS (70 eV), m/z (relative intensity) 244 (M$^+$, 55) and 299 (M$^+$ − CH_3, 100). Anal. Calcd for $C_{15}H_{16}O_3$ 244.1096, found (M$^+$) 244.1063.

The least mobile fraction (64 mg) was the starting material **14**.

Photocycloaddition between 4-Hydroxycoumarin (1) and 2-Methy-2-butene. A solution of 1 (486 mg, 3.0 mmol) and 2-methyl-2-butene (4.2 g, 60 mmol) in *tert*-butyl alcohol (40 mL) was irradiated with a 500-W high-pressure Hg arc through a Pyrex filter under a nitrogen atmosphere for 72 h. After the solvent

was removed in vacuo, the residue was subjected to preparative TLC with ethyl acetate–hexane (1:2) to yield two fractions. The more mobile fraction (450 mg) was a mixture of three isomeric cycloadducts, **19**, **20**, and **21** in a ratio of 3:2:1. Recrystallization of the mixture from diethyl ether–hexane gave a pure isomer **19**, mp 101–103 °C. Two other isomers, **20** and **21**, were unable to obtain in pure forms. The less mobile fraction (110 mg, 16%) was a cycloadduct **22**, which was recrystallized from diethyl ether–hexane, mp 115–116 °C. Cycloadduct **19**: IR (Nujol) 1720 (C=O) and 3470 cm^{-1} (OH); ^1H NMR δ 0.76 (3 H, s, exo 1-Me), 0.87 (3 H, d, J = 7.70 Hz, exo 2-Me), 1.35 (3 H, s, endo 1-Me), 2.55 (1 H, dq, J = 10.99 and 7.70 Hz, endo 2-H), and 3.60 (1 H, d, J = 10.99 Hz, endo 2a-H); MS, m/z 232 (M^+, 0.4), 214 ($M^+ - H_2O$, 1.3) and 163 (100). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.26; H, 6.89. Cycloadduct **20** (as a mixture of adducts **19**, **20**, and **21**): ^1H NMR δ 0.85 (3 H, s, exo 1-Me), 1.09 (3 H, d, J = 6.96 Hz, endo 2-Me), 1.25 (3 H, s, endo 1-Me), 1.80 (1 H, dq, J = 9.96 and 9.89 Hz, exo 2-H), and 3.07 (1 H, d, J = 9.89 Hz, endo 2a-H). Cycloadduct **21** (as a mixture of adducts **19**, **20** and **21**): ^1H NMR δ 0.98 (3 H, s, exo 2-Me), 1.22 (3 H, d, J = 7.7 Hz, exo 1-Me), 1.25 (3 H, s, endo 2-Me), 2.39 (1 H, qd, J = 7.70 and 1.10 Hz, endo 1-H), and 3.18 (1 H, d, J = 1.10 Hz, endo 2a-H). Cycloadduct **22**: IR (Nujol) 3420 (OH) and 1722 cm^{-1} (C=O); ^1H NMR δ 0.72 (3 H, s, exo 2-Me), 0.85 (3 H, d, J = 6.96 Hz, endo 2-Me), 1.34 (3 H, s, endo 2-Me), 2.66 (1 H, q, J = 6.96 Hz, exo 1-H), and 3.24 (1 H, s, endo 2a-H); MS, m/z 232 (M^+, 0.2) and 163 (100). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.51; H, 6.93.

Photocycloaddition between 4-Hydroxycoumarin and Isopropenyl Acetate. A solution of **1** (810 mg, 5.0 mmol) and isopropenyl acetate (10 g, 100 mmol) in *tert*-butyl alcohol (120 mL) was irradiated for 70 h as with 2-methyl-2-butene. After the removal of the solvent in vacuo, the resulting crystals were washed with diethyl ether–hexane (1:1), and the crystals of cycloadduct **29** (254 mg) were collected by filtration. The combined filtrates were evaporated, and the residue was purified by preparative TLC with ethyl acetate–hexane (1:2) to yield pure cycloadduct **29** (732 mg). The yield of **29** was thus 75%. Specimens for analysis were obtained by recrystallization from diethyl ether–hexane–methanol: mp 143–145 °C; IR (Nujol) 3450 (OH), 1760 ($OCOCH_3$), and 1736 cm^{-1} (C=O); ^1H NMR δ 1.73 (3 H, s, exo 1-Me), 1.83 (3 H, s, endo 1-OAc), 1.99 (1 H, dd, J = 12.09 and 10.63 Hz, exo 2-H), 2.65 (1 H, dd, J = 12.09 and 9.89 Hz, endo 2-H), and 3.18 (1 H, dd, J = 10.63 and 9.89 Hz, endo 2a-H), 7.1–7.55 (4 H, m, aromatic H); MS, m/z 219 (M^+ – Ac, 6.9) and 163 (100). Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 63.97; H, 5.48.

Photoaddition between 4-Hydroxycoumarin and Ethyl Vinyl Ether. A solution of **1** (486 mg, 3.0 mmol) and ethyl vinyl ether (1.51 g, 21.0 mmol) in *tert*-butyl alcohol (40 mL) was irradiated for 119 h as above. The solvent was removed under vacuum to yield an unstable oily residue, which was subjected to column chromatography (Merck Kieselgel 60, 70–230 mesh, ASTM). Elution with 1:2 ethyl acetate–hexane gave two fractions. The first fraction (67 mg, 10%) was gummy cycloadduct **32** and the second fraction (110 mg, 16%) was gummy cycloadduct **31**. Cycloadduct **31**: IR (neat) 3400 (OH), and 1761 cm^{-1} (C=O); ^1H NMR δ 1.18 (3 H, t, J = 6.69 Hz, OCH_2CH_3), 1.55 (1 H, ddd, J = 10.99, 10.63 and 9.16 Hz, exo 2-H), 2.51 (1 H, dd, J = 10.99, 9.16, and 8.06 Hz, endo 2-H), 3.00 (1 H, dd, J = 10.63 and 9.16 Hz, endo 2a-H), 3.66 (2 H, m, OCH_2CH_3), and 4.15 (1 H, dd, J = 9.16 and 8.06 Hz, exo 1-H); MS, m/z 234 (M^+, 0.7), 162 (64, $M^+ - CH_2{=}CHOEt$), and 120 (100, $^{\bullet}C_6H_4OC{\equiv}O^+$). Anal. Calcd for $C_{13}H_{14}O_4$: (M) 234.0892. Found: 234.0893. Cycloadduct **32**: IR (neat) 3430 (OH) and 1746 cm^{-1} (C=O). Analysis of ^1H NMR was difficult owing to a rapid partial decomposition of the adduct in solution; MS, m/z 234 (M^+, 0.8), 162 ($M^+ - CH_2{=}CHOEt$), and 120 ($^{\bullet}C_6H_4OC{\equiv}O^+$, 100). Anal. Calcd for $C_{13}H_{14}O_4$: (M) 234.0892. Found: 234.0882.

Each adduct was subjected to the next step without further purification.

Irradiation of Hypoiodites of Photoadducts 19, 20, and 21. A mixture of cycloadducts **19**, **20**, and **21** (3:2:1) (307 mg, 1.32 mmol) in benzene (40 mL) containing mercury(II) oxide (3.96 mmol) and iodine (3.96 mmol) was photolyzed as above for 2.5 h to give a mixture of furocoumarins **23** and **25** as well as furochromones **24** and **26**. The product mixture was subjected to preparative TLC with 1:2 ethyl acetate–hexane to yield **23** (100 mg, 33%), **24** (58 mg, 19%), **25** (21 mg, 7%), and **26** (9 mg, 3%). Product **23**: R_f 0.63; the specimen for analysis was obtained by recrystallization from hexane; mp 80–82 °C; IR (Nujol) 1702 and 1640 cm^{-1} (C=C—C=O); ^1H NMR δ 1.31 (3 H, d, J = 6.96 Hz, 3-Me), 1.49 (3 H, s, 2-Me), 1.53 (3 H, s, 2-Me), 3.21 (1 H, q, J = 6.96 Hz, 3-H) and 7.23–7.66 (4 H, m, aromatic H); MS, m/z 230 (M^+, 52) and 215 (M^+ – Me, 100). Anal. Calcd for $C_{14}H_{14}O_3$: (M) 230.0943. Found: 230.0943. Product **24**: R_f 0.34; the specimen for analysis was obtained by recrystallization from hexane; mp 121.5–122.5 °C; IR (Nujol) 1628 and 1558 cm^{-1} (C=C—C=O); ^1H NMR δ 1.35 (3 H, d, J = 6.96 Hz, 3-Me), 1.49 (3 H, s, 2-Me), 1.55 (3 H, s, 2-Me), 3.32 (1 H, q, J = 9.69 Hz, 3-H), 7.35–7.6 (3 H, m, aromatic H), and 8.22 (1 H, dd, J = 7.69 and 1.47 Hz, aromatic H); MS, m/z 230 (M^+, 70) and 215 (M^+ – Me, 100). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.84; H, 6.12. Product **25**: R_f 0.69; the specimen for analysis was obtained by recrystallization from hexane; mp 64.5–66.0 °C; IR (Nujol) 1718 and 1640 cm^{-1} (C=C—C=O); ^1H NMR δ 1.72 (3 H, s, 3-Me), 1.46 (3 H, s, 3-Me), 1.48 (3 H, d, J = 6.59 Hz, 2-Me), 4.69 (1 H, q, J = 6.59 Hz, 2-H), 7.2–7.55 (3 H, m, aromatic H), and 7.65 (1 H, dd, J = 7.69 and 1.46 Hz, aromatic H); MS, m/z 230 (M^+, 20, and M^+ – Me, 100). Anal. Calcd for $C_{14}H_{14}O_3$: (M) 230.0943. Found: 230.0955. Product **26**: R_f 0.56; the specimen for analysis was obtained by recrystallization from hexane: mp 106–108 °C; IR (Nujol) 1625 and 1558 cm^{-1} (C=C—C=O); ^1H NMR δ 1.34 (3 H, s, 2-Me), 1.46 (3 H, d, J = 6.59 Hz, 3-Me), 1.52 (3 H, s, 2-Me), 4.56 (1 H, q, J = 6.59 Hz, 3-H), 7.35–7.6 (3 H, m, aromatic H), and 8.20 (1 H, dd, J = 8.06 and 1.47 Hz, aromatic H); MS, m/z 230 (M^+, 37) and 215 (M^+ – Me, 100). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.31. Found: C, 72.96; H, 6.10.

Irradiation of Hypoiodite of Photoadduct 22. (a) Adduct **22** (105 mg, 0.47 mmol) in benzene (30 mL) containing mercury(II) oxide (1.45 mmol) and iodine (1.45 mmol) was irradiated for 2.5 h as above to yield **25** (47 mg, 43%) and **26** (18 mg, 16%). (b) Adduct **22** (105 mg, 0.45 mmol) in carbon tetrachloride (30 mL) containing mercury(II) oxide (1.35 mmol) and iodine (1.35 mmol) was irradiated for 1 h as above to yield **25** (44 mg, 42%) and **26** (26 mg, 25%).

Photolysis of Hypoiodite of Photoadduct 29. The photolysis of adduct **29** (320 mg, 1.22 mmol) in dry benzene (60 mL) containing mercury(II) oxide (3.66 mmol) and iodine (3.66 mmol) was carried out as above to give a mixture of products. It was purified by means of preparative TLC to give furocoumarin **30** (93 mg, 29%). The specimen for analysis was obtained by recrystallizing it from diethyl ether–hexane: mp 129–132 °C; IR (Nujol) 1745 (OAc), 1722, and 1653 cm^{-1} (—C=C—C=O); ^1H NMR (90 MHz) δ 1.96 (3 H, s, Me), 2.09 (3 H, s, OCOMe), 3.17 (1 H, d, J = 16.9 Hz, 2-H), 3.53 (1 H, d, J = 16.9 Hz, 2-H), and 7.15–7.70 (4 H, m, aromatic H); MS, m/z 260 (M^+, 0.8), 218 ($M^+ - CH_2{=}C{=}O$, 8.1), 200 (M^+ – AcOH, 37), 176 (67), and 43 (100). Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.51; H, 4.67.

Photolysis of Hypoiodite of Photoadduct 31 or 32. (a) Adduct **32** (67 mg, 0.29 mmol) in benzene (20 mL) in the presence of mercury(II) oxide and iodine (each 0.86 mmol) was photolyzed for 40 min to give a product mixture. The product was subjected to preparative TLC with a 1:2 ethyl acetate–hexane to yield furocoumarin **33** (23 mg, 35%). The specimen for analysis was obtained by recrystallization from diethyl ether–hexane–dichloromethane: mp 110–111 °C; IR (Nujol) 1700 and 1640 cm^{-1} (C=C—C=O); ^1H NMR δ 1.30 (3 H, t, J = 6.96 Hz, OCH_2CH_3), 3.03 (1 H, dd, J = 16.49 and 3.30 Hz, 3-H), 3.32 (1 H, dd, J = 16.49 and 7.33 Hz, 3-H), 3.77 (1 H, dq, J = 9.53 and 6.96 Hz, OCH_2CH_3), 4.04 (1 H, dq, J = 9.53 and 6.96 Hz, OCH_2CH_3), 6.07 (1 H, dd, J = 7.33 and 3.30 Hz, 2-H), and 7.25–7.4 (4 H, m, aromatic H); MS, m/z 232 (M^+, 88) and 121 (100). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.16; H, 5.17. (b) Similar photolysis of **31** (100 mg, 0.43 mmol) in benzene (30 ML) containing mercury(II) oxide and iodine (each, 1.28 mmol) for 40 min gave **33** (29 mg, 29%). (c) Photolysis of **31** (30 mg, 0.13 mmol) in carbon tetrachloride (25 mL) containing mercury(II) oxide and iodine (each 0.39 mmol) for 1 h afforded **33** (9 mg, 31%). (d) Photolysis of **31** (80 mg, 0.43 mmol) in THF (30 mL) containing mercury(II) oxide and iodine (each 1.30 mmol) for 1.5 h afforded **33** (6 mg, 7%).

Registry No. 1, 1076-38-6; 3, 91739-58-1; 4, 91663-61-5; 7, 116947-03-6; 8, 116947-04-7; 9, 116864-01-8; 10, 116864-02-9; 11, 116864-03-0; 14, 116864-04-1; 15, 95598-16-6; 16, 95598-17-7; 19, 116864-05-2; 20, 116947-05-8; 21, 116864-06-3; 22, 116947-06-9; 23, 116864-07-4; 24, 116864-08-5; 25, 92809-86-4; 26, 116864-09-6; 29, 116864-10-9; 30, 116864-11-0; 31, 116864-12-1; 32, 116947-07-0; 33, 116864-13-2; 2-methyl-2-butene, 513-35-9; isopropenyl acetate, 108-22-5; ethyl vinyl ether, 109-92-2.

Supplementary Material Available: The anisotropic thermal parameters for the non-hydrogen atoms and the coordinates and temperature factors for the hydrogen atoms for compounds 3, 4, and 14 can be found in Tables I–XIV (16 pages). Ordering information is given on any current masthead page.

Notes

Amination of 3,3′,5,5′-Tetramethyl-4,4′-diphenoquinone

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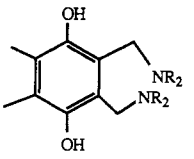
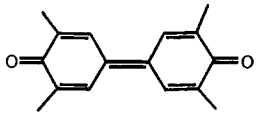
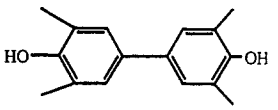
Cameron, Scott, and Todd have reported[1] that fully alkylated quinones, such as duroquinone, readily undergo a novel amination to give the bis(aminomethyl)quinol derivative 1, together with the corresponding tris and tetrakis derivatives. However, Brown and Todd[2] reported earlier that 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (2) reacts with cyclohexylamine, piperidine, or morpholine in air to yield only its reduction product 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (3). Here we report different results from the reaction between 2 and several amines and ϵ-caprolactam.



1

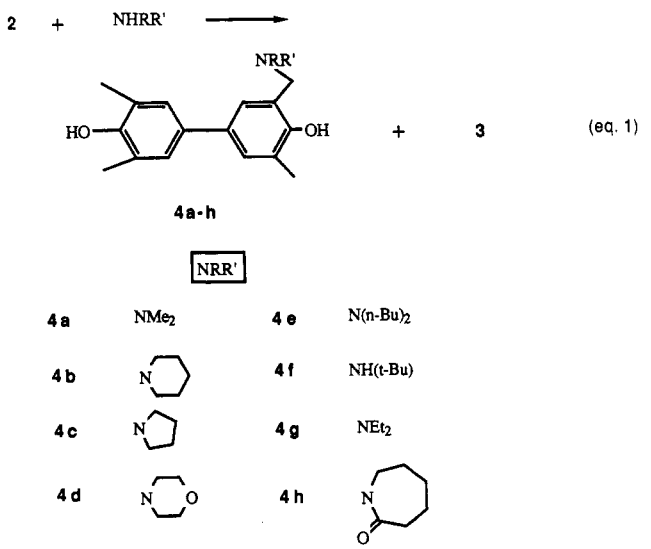


2



3

The reactions of 2 with various amines including dimethylamine, piperidine, pyrrolidine, morpholine, di-*n*-butylamine, *tert*-butylamine, and diethylamine at room temperature gave monoaminated products **4a–g** as the major products (eq 1). Various amounts of reduced diol 3 were the second major component. The bisaminated adducts were usually formed in trace amounts. The best yields of **4a–g** were obtained when the reactions were performed in 1-methyl-2-pyrrolidinone (NMP). No reaction occurred between the weaker nucleophile ϵ-caprolactam and 2 at room temperature in NMP. The adduct **4h** was obtained only after heating for several hours at elevated temperature. The molar ratios of monoadducts **4a–h** to 3 in the reaction mixture are listed in Table I. The yields of monoadduct are in general higher than those of the diol 2 except in the case of morpholine and ϵ-caprolactam, which may be due to the reduced nucleophilicity of the amines. Also, it may be reasoned that the monoadducts **4a–g** are less prone to oxidation to diphenoquinone, the suspected intermediate in the formation of the bisaminated derivative.



No reaction occurred between 2 and di-*n*-butylamine in nonpolar solvents such as toluene and benzene at room temperature. In summary, we found a unique method of preparing mono-*o*-(aminomethyl)biphenyldiol derivatives which were not readily available synthetically.

Experimental Section

Compounds were used as received without further purification, unless otherwise noted. The GC data was obtained from a Shimadzu GC-9A gas chromatograph using a Supelco SPB-5 (30 m, 0.32-mm i.d.) column with a Shimadzu C-R3A integrator. The ratios of each monoadduct **4a–h** to 3, respectively, were obtained from GC after silylation of the reaction aliquot with *N,O*-bis(trimethylsilyl)trifluoroacetamide to prevent the decomposition of **4a–h**. Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. Infrared (IR) spectra were obtained on a Perkin-Elmer 598 or a Nicolet 7199 infrared spectrophotometer. NMR spectra were obtained with a Varian EM-390 (^{1}H NMR, 90 MHz) or a Varian XL-300 (^{13}C NMR, 75 MHz) spectrometer relative to an internal tetramethylsilane standard. High-resolution and field-desorption mass spectra were recorded on a Varian MAT 731 mass spectrometer. A Shimadzu UV-240 UV–visible recording spectrophotometer was used for obtaining UV–visible spectral data.

General Procedure for the Synthesis of Compounds 4a–g. To a round-bottom flask with a magnetic stirring bar were added amine (0.1 mol), compound 2 (5.0 g, 0.021 mol), and 100 mL of NMP. In the case of dimethylamine, the amine was slowly bubbled into the solvent containing 2. The reaction mixture was

(1) Cameron, D. W.; Scott, P. M.; Todd, A. R. *J. Chem. Soc.* **1964**, 42.
(2) Brown, B. R.; Todd, A. R. *J. Chem. Soc.* **1954**, 1280.

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