isotherms on relaxing and recompression, the mixed films showed significant changes at $\Pi < 40$ mN/m (Figure 2, b and c).

We were unable to transfer monolayer Langmuir-Blodgett (L-B) films of C_{60} by vertical dipping onto a variety of substrates, e.g., freshly cleaved, highly oriented pyrolytic graphite, polycrystalline Pt or Au, indium tin oxide on glass, or glassy carbon. Attempts to transfer films with larger samples apparently led to aggregation of the C_{60} at the air-water interface, as discussed above. Thus, independent of the substrate, films transferred at ~30 mN/m were not uniform but appeared visibly patchy with yellow clumps interspersed with large domains of clean substrate surface. Contact angle (θ) measurements with water on C_{60} patches showed them to be very hydrophobic ($\theta \sim 100°$). Exposure of the immobilized C_{60} on any of the substrates to 3:1 H_2SO_4/H_2O_2, followed by copious water and EtOH washes and drying in Ar, did not remove the C_{60}. Contact angles on the C_{60} patches after such treatment were much lower ($\theta \sim 25°$), suggesting that the C_{60} surface had oxidized and become more hydrophilic. This preliminary experiment suggests that films containing small amounts of C_{60}, characterized by contact angle, spectroscopic, or electrochemical measurements, might be useful in studies of the chemical modification of C_{60}.

The high surface pressures sustained by C_{60} monolayers at the air-water interface suggest large attractive interactions between the C_{60} molecules with the formation of rigid films. Similarly, the electrochemical studies of C_{60} films suggest a high degree of structural organization.[5] Although C_{60} has been proposed as a potential lubricant, the strong intermolecular interactions and film stiffness suggest that this application of unmodified C_{60} is unlikely.

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Photochemistry of Codeinone Derivatives. Development of Potential Photoaffinity Labeling Techniques for Opiate Receptors

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Although the chemistry and pharmacology of morphine and related opium alkaloids has been studied in great detail,[1] very little is known about the photochemistry of this important class of naturally occurring materials.[2,3] Herein, we report photochemistry of codeinone derivatives that involves unique photoreactivity of the benzodihydrofuran ring system.[4] The photorearrangements to be described are carried out by utilization of 366-nm ultraviolet irradiation and appear to offer a conceptually new approach to opiate receptor photoaffinity labeling.[5]

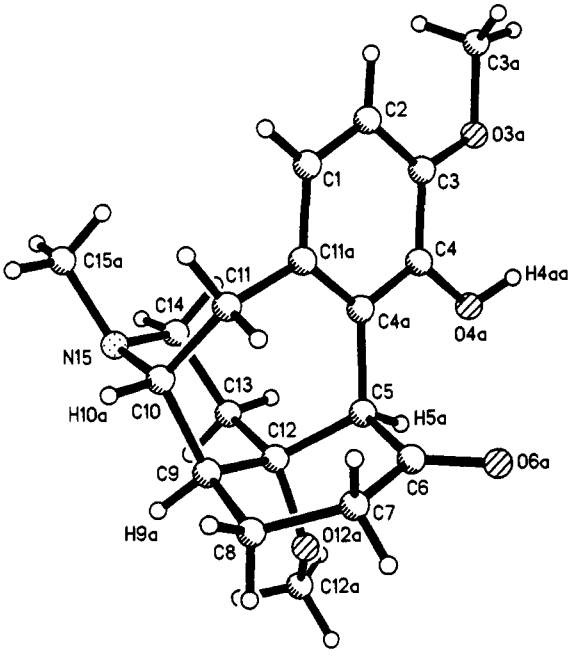
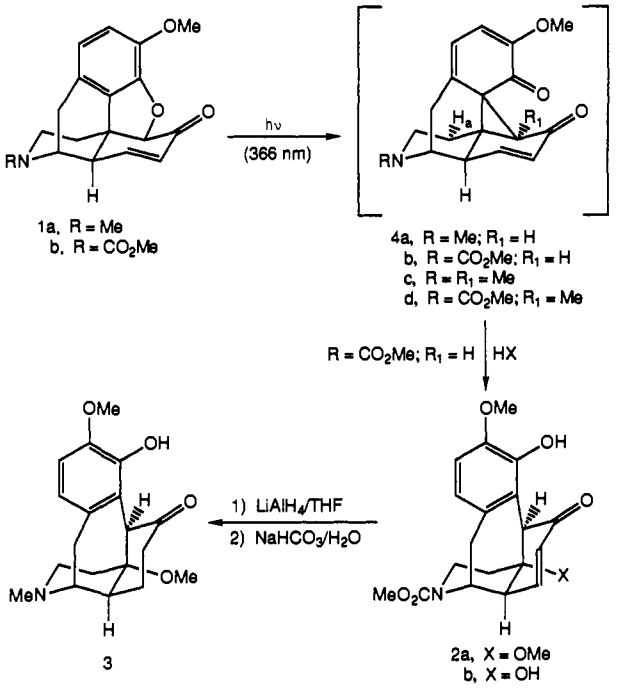


Figure 1. Molecular structure of **3**.

Scheme I



Codeinone (**1a**) has been reported to be photostable,[2b,6] and we have found that irradiations at 366 nm in benzene or methanol solutions result in recovery of **1a**. By contrast, irradiation of *N*-carbomethoxynorcodeinone (**1b**) in methanol (0.02 M, 20 h) gave the rearranged methyl ether **2a** in 90% isolated yield (Scheme I).[7] In THF-H_2O solution, **1b** gave the analogous alcohol **2b**

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(2) For reports of photochemistry of 7,14-cyclodihydrocodeinone, 14-methyl-*C*-nordihydrocodeinone, and related derivatives, see: (a) Bos, M.; Fleischhacker, W. *Liebigs Ann. Chem.* **1981**, 1994. (b) Bos, M.; Fleischhacker, W. *Liebigs Ann. Chem.* **1981**, 2002. (c) Bos, M.; Fleischhacker, W. *Liebigs Ann. Chem.* **1982**, 112.
(3) For photorearrangements of thebaine, see: Theuns, H. G.; La Vos, G. F.; ten Noever de Brauw, M. C.; Salemink, C. A. *Tetrahedron Lett.* **1984**, *25*, 4161.
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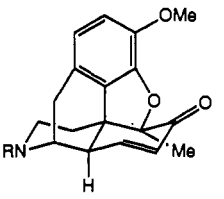
(80%); **1b** was stable to extended irradiation in benzene solution at 366 nm.

Reduction of **2a** with lithium aluminum hydride gave the highly crystalline saturated keto amine **3** in 90% isolated yield. An X-ray diffraction study of **3** provided the molecular structure shown in Figure 1. It is noteworthy that the solvolytic photorearrangement of **1b** results in cleavage of the dihydrofuran ring with overall 1,2-migration of the aryl nucleus.

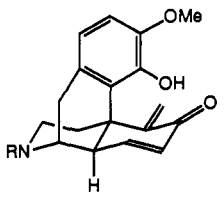
A plausible mechanism for photorearrangement of **1b** to **2a** and **2b** involves benzodihydrofuran rearrangement[4,8] of **1b** to an intermediate cyclopropanespiro-2,4-cyclohexadien-1-one, **4b**. Abnormal Claisen rearrangement[9] of **4b** (C–O migration of H_a) does not occur presumably because the resulting bridgehead olefin (not shown) would have excessive ring strain. Instead, **4b** reverts to **1b**. In methanol, solvolytic opening of the cyclopropane ring in **4b** gives the methyl ether **2a**; in the presence of water, **4b** gives the alcohol **2b**.

It was suspected that the failure to observe photorearrangement of codeinone (**1a**) was a result of competing electron transfer processes involving the tertiary amine group in **1a**.[10] To test this supposition, the C(5)-methyl-substituted codeinone analogues **5a** and **5b** were prepared from thebaine.[11]

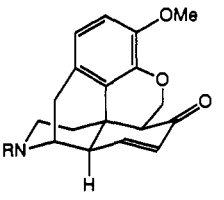
Irradiation of **5a** in methanol solution at 366 nm gave benzopyran **7a** in quantitative yield. This product presumably is formed by photorearrangement of **5a** to cyclopropanespiro-2,4-cyclohexadien-1-one **4c**, from which abnormal Claisen rearrangement involving the C(5) methyl substituent gives the intermediate phenolic dienone **6a** (not observed). An intramolecular Michael addition would convert **6a** to benzopyran **7a**.



5a, R = Me
b, R = CO_2Me



6a, R = Me
b, R = CO_2Me



7a, R = Me
b, R = CO_2Me

Irradiation of **5b** in benzene solution gave the dienone **6b** as the exclusive reaction product. In methanol, **5b** gave a mixture of **6b** (44%) and pyran **7b** (54%), which was separated by flash chromatography on silica gel. Thus, solvolytic rearrangement of **4d** in methanol is not competitive with the thermal abnormal Claisen rearrangement to give **6b**. Dienone **6b** was converted to pyran **7b** in quantitative yield by treatment with diethylamine in CH_2Cl_2.

These data suggest that the apparent absence of photoreactivity of **1a** in benzene or methanol and **1b** in benzene is a result of reversible photorearrangements of **1** to **4**. The reaction **4a** → **1a** might be initiated by photoexcitation of **4a** followed by electron transfer from the amine group to the cyclopropane-coupled enone and dienone chromophores.[12] Such electron transfer is less probable in carbamate **4b**, although **4b** might revert to **1b** by another, less efficient photochemical or thermal pathway.[4b,8] In both **4c** and **4d**, back reactions to **5a** and **5b** are not competitive with the apparently efficient abnormal Claisen rearrangements.

Alternatively, there may be reversible photoinitiated electron transfer in **1a**, but with **5a** photorearrangement to **4c** may be faster than the electron-transfer process. We reserve further discussion of mechanistic questions until more detailed studies of **1a**, **1b**, **5a**, and **5b** have been completed. The receptor binding and photoaffinity properties of these and related opiate derivatives will be reported in due course.

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Supplementary Material Available: Tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic parameters, and hydrogen atom coordinates for **3** (6 pages). Ordering information is given on any current masthead page.

(8) Flash photolysis studies of spiro[benzofuran-2(3*H*),1′-cyclohexane]-2-carboxylic acid methyl ester[4] and a tetradeuterio derivative provided spectroscopic evidence for the 2,4-cyclohexadien-1-one chromophore in the photogenerated intermediate as well as activation parameters and a deuterium isotope effect for the thermal abnormal Claisen rearrangement to α-(1-cyclohexenyl)-2-hydroxybenzeneacetic acid methyl ester; see: Wisniewski, K. Ph.D. Thesis, Rensselaer Polytechnic Institute, 1985.

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The Endocyclic Restriction Test: An Experimental Evaluation of the Geometry at Oxygen in the Transition Structure for Epoxidation of an Alkene by a Peroxy Acid

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The epoxidation of olefins by peroxy acids is a widely used reaction of synthetic value and mechanistic interest.[1] The bimolecularity and stereospecificity of the process have been generally rationalized by the Bartlett "butterfly" transition structure, shown as A, which was suggested over 40 years ago.[2] According to this mechanism, an S_N2-like reaction takes place at the terminal oxygen of the hydroperoxide group with the π HOMO of the olefin approaching the σ* LUMO of the O–O bond at 180°. An alternative transition structure, which resembles a 1,3-dipolar cycloaddition, has been suggested and is shown as B.[3] In this communication we provide evidence based on the endocyclic restriction test that shows that the geometry at oxygen in this reaction is consistent with the transition-structure geometry expected for A and inconsistent with that shown for B.[4]

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