Intramolecular Photochemical Cycloaddition Reactions of *N*-[(ω-Alkenyloxy)carbonyl]indoles and *N*-(ω-Alkenoyl)indoles[1]

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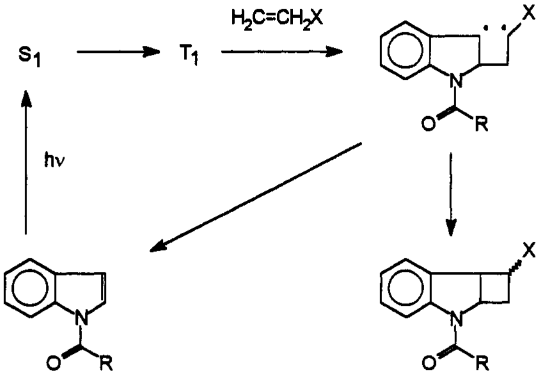
Ultraviolet light irradiation of N-(but-3′-enoyl)indole (**3i**), *N*-(pent-4′-enoyl)indole (**3j**), and *N*-(hex-5′-enoyl)indole (**3k**) affords intramolecular photocycloadducts **17a–19a** in which the termini of the side-chain alkene have become bonded to the 2- and 3-positions of the indole ring. The regiochemistry of the addition of the alkene is the opposite to that obtained in the corresponding intermolecular reaction of an *N*-acylindole with a monosubstituted alkene. The length of the methylene linkage between the tethered alkene and the *N*-acyl activating group in these *N*-alkenoylindoles affects the quantum efficiency of intramolecular cycloaddition as well as the ability of the reaction to compete with intermolecular cycloaddition in the presence of added cyclopentene. In contrast, the *N*-(ω-alkenyloxycarbonyl)indoles **3a–e** are relatively photostable, apparently because they are frozen in an unreactive conformation for the duration of the excited state lifetime. Compounds **3a–e** are, however, capable of undergoing intermolecular photocycloaddition in the presence of added alkenes and they also photodimerize. These reaction pathways dominate when lower energy wavelengths (λ>300 nm) of ultraviolet light are used; irradiations performed at higher energy wavelength (254 nm) give predominantly photo-Fries rearrangement products.

Introduction

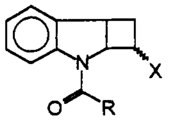
Ultraviolet light irradiation of *N*-acylindoles in the presence of monosubstituted alkenes leads to regioselective cyclobutane ring formation by addition of the alkene termini to the 2- and 3-positions of the five-membered ring of the heterocycle (Scheme 1).[2,3] We have examined the mechanism of this reaction[4–12] and have concluded that it proceeds by way of a triplet 1,4-biradical intermediate produced by bonding between the *N*-aroylindole triplet excited state and the less-substituted end of the alkene, as illustrated in Scheme 1.

Scheme 1



1

The structure of the biradical intermediate controls the regiochemistry of the reaction and leads to preferential formation of the "head-to-tail" regioisomer 1 rather than the "head-to-head" regioisomer **2**.[13] The regioselectivity limits the potential synthetic utility of the reaction should the head-to-head regioisomers **2** be required. In principle, this problem could be overcome by tethering the alkene to the acyl substituent of the N-substituted indole as shown in Scheme 2; this could direct the regiochemistry of the cycloaddition reaction if the length of the tether were to restrict bonding of the indole 2-position to the closest (i.e. more substituted) terminus of the alkene. Cleavage of the *N*-acyl bond then yields the otherwise inaccessible head-to-head isomers.



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We are aware of only two published examples of intramolecular photocycloaddition reactions of *N*-acylindoles; one of these involves Paterno–Büchi reaction of an *N*-acylindole with a carbonyl group,[14] while in the other the alkene is tethered to the 3-position of an *N*-acylindole.[15] Both of these reactions are regioselective. We have not encountered an example where the alkene is tethered to the acyl substituent of the N-substituted indole. To test

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[1] Contribution no. 497 from the Photochemistry Unit, University of Western Ontario.

[●] Abstract published in *Advance ACS Abstracts*, February 15, 1994.

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[11] Weedon, A. C.; Zhang, B. *Synthesis* 1992, 95.

[12] Andrew, D.; Hastings, D. J.; Oldroyd, D. L.; Rudolph, A.; Weedon, A. C.; Wong, D. F.; Zhang, B. *Pure Appl. Chem.* 1992, *64*, 1327.

[13] In this nomenclature, derived from that commonly used in enone 2 + 2 cycloaddition photochemistry, the "head" of the indole molecule is the nitrogen atom, while the "head" of the alkene is the substituent X.

[14] Machida, M.; Takechi, H.; Kanaoka, Y. *Tetrahedron Lett.* 1982, *23*, 4981.

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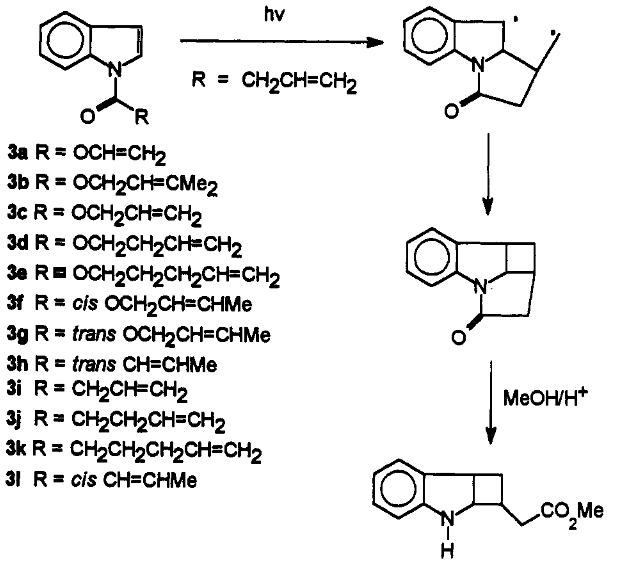
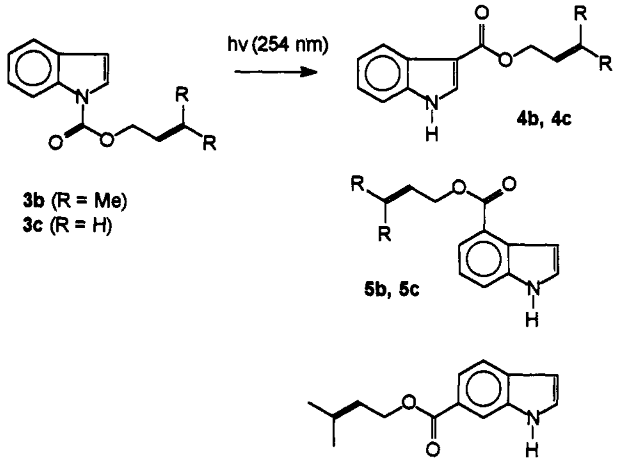
Scheme 2



3a R = $OCH=CH_2$
3b R = $OCH_2CH=CMe_2$
3c R = $OCH_2CH=CH_2$
3d R = $OCH_2CH_2CH=CH_2$
3e R = $OCH_2CH_2CH_2CH=CH_2$
3f R = *cis* $OCH_2CH=CHMe$
3g R = *trans* $OCH_2CH=CHMe$
3h R = *trans* $CH=CHMe$
3i R = $CH_2CH=CH_2$
3j R = $CH_2CH_2CH=CH_2$
3k R = $CH_2CH_2CH_2CH=CH_2$
3l R = *cis* $CH=CHMe$

Scheme 3



3b (R = Me)
3c (R = H)

4b, 4c

5b, 5c

6b, 6c

whether such compounds allow control of reaction regiochemistry the *N*-[(ω-alkenyloxy)carbonyl]indoles **3a–g** and the *N*-(ω-alkenoyl)indoles **3h–k** were prepared and their photochemistry examined; the results of this study are reported here in detail.[16]

Results and Discussion

Preparation and Photochemistry of *N*-[(ω-Alkenyloxy)carbonyl]indoles 3a–g. Boger and Patel[17] have described a preparation of *N*-(alkoxycarbonyl)indoles in which the anhydride of indole-*N*-carboxylic acid is treated with the appropriate alkoxide. Application of this procedure proved successful for the preparation of the *N*-[(ω-alkenyloxy)carbonyl]indoles **3b–g**. *N*-[(vinyloxy)carbonyl]indole (**3a**) was prepared by treatment of indole with vinyl chloroformate in the presence sodium hydride. This procedure is a modification of that reported by Illi[18] for the preparation of *N*-acylindoles.

Ultraviolet light irradiation of **3b** using light of wavelength 254 nm resulted in photo-Fries rearrangement to give mainly **4b** along with smaller amounts of **5b** and **6b** as shown in Scheme 3. Similarly, photolysis of **3c** yielded mainly **4c** along with **5c** and **6c**. No evidence for the formation of intramolecular photocycloaddition products was obtained. Analogous rearrangements have previously been observed for *N*-(ethoxycarbonyl)indole and *N*-benzoylindole;[6,19,20] for these compounds the photo-Fries reaction apparently occurs from an upper excited state or from a vibrationally hot first singlet excited state[6] and consequently is a wavelength-dependent reaction requiring shorter wavelength light to excite the higher energy transitions. In order to suppress photo-Fries reaction in favor of the desired cycloaddition photochemistry the irradiation of the *N*-[(ω-alkenyloxy)carbonyl]indoles **3b–e** was examined using Pyrex-filtered light of wavelengths greater than *circa* 300 nm. Under these conditions no detectable quantities of the corresponding photo-Fries rearrangement products **4–6** were observed. However, even under extended irradiation times no intramolecular cycloaddition products could be detected either; the *N*-(alkenyloxy)indoles **3b–e** were remarkably photostable and only a small amount of conversion was observed to yield what was assumed to be polymeric material because of its low solubility and resistance to analysis by gas and thin-layer chromatography.

The *N*-[(ω-alkenyloxy)carbonyl]indoles **3b–e** were also excited indirectly using acetophenone as a triplet sensitizer in an attempt to determine if the lack of cycloaddition photochemistry observed was a consequence of an inability to access the triplet excited state. The triplet excited state energies of *N*-acylindoles have been determined[21] from their phosphorescence spectra to be *circa* 69 kcal/mol, which is lower than that of acetophenone (74 kcal/mol). The sensitized reactions achieved slightly higher conversions over shorter irradiation periods as compared with the direct irradiation; however, the products were once again apparently polymeric materials.

It was be expected that of the compounds **3a–e**, **3a** would be the most likely to undergo intramolecular cycloaddition since the intermediate 1,4-biradical could result from formation of a five-membered ring as shown in Scheme 2. This is predicted to be favorable by the "rule of five", a general concept which holds true for intramolecular photocycloaddition of many enone systems.[22] Very extended irradiation of **3a** using Pyrex-filtered light did in fact result in slow conversion to at least one product, as suggested by TLC analysis. Careful GC/MS analysis revealed a product which possessed a parent ion with a molecular weight twice that of **3a**. This dimer was eventually assigned the *anti* head-to-head structure **7**. We have subsequently found that photodimerization is a general reaction of the triplet excited state of *N*-acylindoles if the *N*-acylindole concentration is high enough; a description of this dimerization reaction has been published elsewhere.[21] As far as we are aware the photodimerization of 1,3-diacetylindole to give the *syn* head-

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(16) A preliminary report of this work has appeared: Oldroyd, D. L.; Weedon, A. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1491.

(17) Boger. D.; Patel, M. *J. Org. Chem.* **1987**, *52*, 3934.

(18) Illi, V. O. *Synthesis* **1979**, 387.

(19) Somei, M.; Natsume, M. *Tetrahedron Lett.* **1973**, 2451.

(20) Carruthers, W.; Evans, N. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1523.

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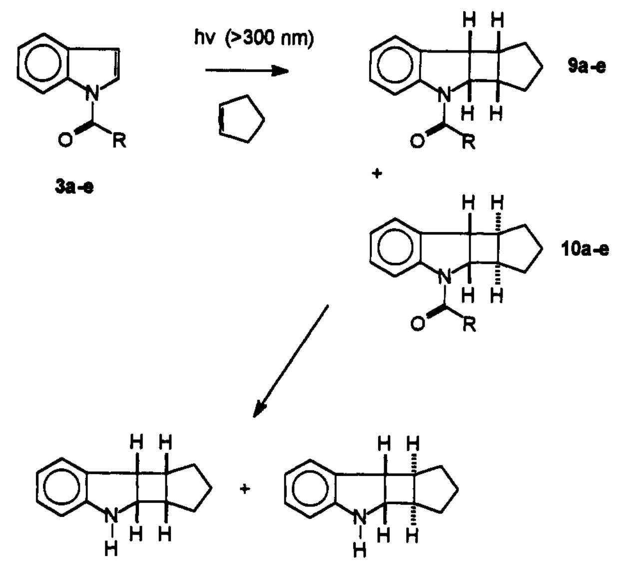
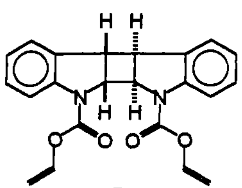
Scheme 4



11 12

to-tail structure **8** is the only previously published example of a formal 2 + 2 photochemical dimerization reaction of the indole nucleus.[23]



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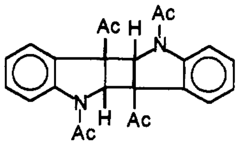
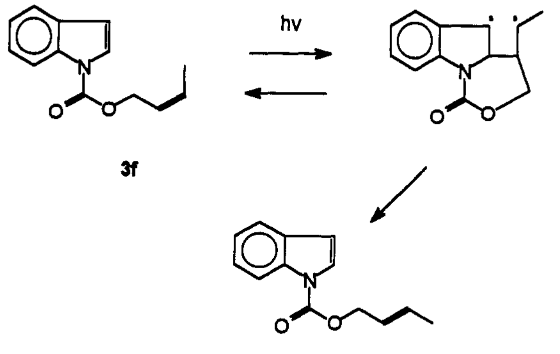


8

It has previously been shown that the presence of a carbonyl substituent on the indole nitrogen is essential to facilitate the intermolecular photocycloaddition reaction with alkenes to give cyclobutane adducts.[2,3] The failure of **3a–e** to undergo intramolecular photocycloaddition led us to perform experiments designed to determine if the acyl substituents of **3a–e** were sufficient to activate indole cycloaddition photochemistry. To this end, each of compounds **3a–e** was irradiated in the presence of cyclopentene using Pyrex-filtered light. In all cases the formation of two products was observed. GC/MS analysis indicated these to be 1:1 adducts of the *N*-[(ω-alkenyloxy)carbonyl]indole and cyclopentene, and structures **9** and **10** were tentatively assigned (Scheme 4). This assignment was confirmed by sequential hydrolysis and decarboxylation of the products to give the previously described indolines **11** and **12**.[8]

The quantum efficiency of formation of the intermolecular cycloadducts **9c** and **10c** in the presence of 1.5 M cyclopentene was determined to be 0.024 ± 0.001 which is similar to values obtained for the quantum efficiency of cycloaddition of *N*-(ethoxycarbonyl)indole or *N*-benzoylindole with cyclopentene.[6] One explanation for the failure of compounds **3a–e** to yield intramolecular photocycloadducts is that the biradical intermediates formed by reaction with the side-chain alkene revert exclusively to ground-state starting materials. However, if intramolecular biradical formation were efficient for **3c** then this would be expected to quench the intermolecular reaction and yield a value of the quantum yield for intermolecular addition much lower than the value of 0.024 measured. This result establishes that the *N*-[(ω-alkenyloxy)carbonyl]indoles are sufficiently activated to undergo photocycloaddition reaction with alkenes and indicates that intramolecular interaction of the acylindole triplet excited state with the tethered alkene is for some reason inefficient and does not lead to biradical formation or other modes of quenching of the triplet excited state.

Scheme 5



3g

Additional evidence for the inability of the *N*-[(alkenyloxy)carbonyl]indole triplet excited state to interact with the tethered alkene was obtained by examining the efficiency of Schenck isomerization of the alkene present in compound **3f**. It was anticipated that if biradical formation were efficient but not productive (as shown in Scheme 5) then collapse to starting materials would give **3g** in which the tethered alkene has undergone geometrical isomerization via a Schenck-type mechanism. Similar Schenck isomerization studies have been reported previously for the intermolecular photocycloaddition reaction of *N*-benzoylindole or *N*-(ethoxycarbonyl)indole with *cis*-alkenes; the formation of *trans*-alkenes was used as proof of biradical intermediacy.[8]

The sample of **3f** used contained 2% of the *trans*-isomer **3g** as determined by GC and ^{1}H-NMR spectroscopy. Irradiations using Pyrex-filtered ultraviolet light were carried out and monitored by GC and ^{1}H-NMR spectroscopy. Under these conditions **3f** was found to be relatively photostable and only small quantities were converted to yield undetected products and the *trans*-isomer **3g**. Using an inert internal standard it was shown that the absolute quantity of the *trans*-isomer **3g** increased during the irradiation and therefore that **3f** was being converted to **3g** rather than simply being depleted preferentially. The quantum yield of the isomerization of **3f** to **3g** was 0.0018 ± 0.0002 when light of wavelength 305 nm was used. This value is considerably smaller than that reported[8] for the reaction of *N*-benzoylindole with *cis*-4-octene where the isomerization of *cis*-octene to *trans*-octene due to intermolecular biradical formation proceeded with a quantum yield of 0.074 ± 0.004 at an alkene concentration of 5.31 M. The low value of the quantum yield of Schenck isomerization of the alkene component of **3f** provides an additional indication that the failure of this compound to undergo intramolecular photocycloaddition arises from inefficient formation of the biradical intermediate rather than from preferential reversion of the biradical to starting material. It should be noted that the small amount of geometrical isomerization which did occur for **3f** is unlikely to have its origins in energy transfer from the acylindole

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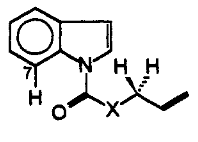
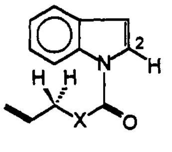
(23) Hino, T.; Taniguchi, M.; Date, T.; Iidaka, Y. *Heterocycles* **1977**, 7, 105.

triplet to the side-chain alkene since this process would be highly endothermic.

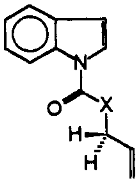
A possible explanation for the failure of the triplet excited state of the indole chromophore in compounds **3a–f** to undergo intramolecular photocycloaddition with the tethered alkene is that the urethane linkage present in these compounds causes the alkenyloxy side chain to adopt conformations which are unsuitable for intramolecular cycloaddition. If interconversion in the excited state between reactive conformations and unreactive but more stable conformations were slow relative to the excited state lifetime, then intramolecular cycloaddition would not proceed. Our intuition suggested to us that the more stable conformations of the urethane linkage of **3b** should be close to those represented by structures **13a–d**. Of these, **13a** would appear to be nearest to the conformation **13e** required for closest approach of the side-chain alkene to the 2,3-positions of the indole ring. To probe the possibility that the conformational arrangement illustrated in **13a** might be of too high an energy to be accessible during the excited state lifetime, the photochemistry of **3e** was examined at elevated temperature in the hope that this would increase the probability of population of the reactive conformation during the excited state lifetime. The *N*-[(ω-alkenyloxy)carbonyl]indole **3e** was irradiated in toluene solution at 70 °C with Pyrex-filtered ultraviolet light; analysis of the reaction mixture by gas chromatography suggested 56% conversion. However, the products appeared to be polymeric and no intramolecular cycloadduct was found.



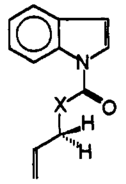
13a X = O
14a X = CH$_2$



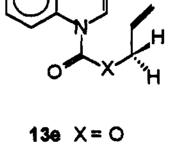
13b X = O
14b X = CH$_2$



13c X = O
14c X = CH$_2$



13d X = O
14d X = CH$_2$



13e X = O
14e X = CH$_2$

The possibility that **3a–f** adopt stable, unreactive conformations for the duration of the excited state lifetime was explored further using ^{1}H-NMR spectroscopy and force field calculations. The results are presented below.

Conformational Analysis of *N*-[(Alkenyloxy)carbonyl]indoles. Variable temperature ^{1}H-NMR spectroscopy has been used to demonstrate that the acyl group of *N*-acylindoles undergoes relatively slow rotation around the bond between the nitrogen and the carbonyl carbon *in the ground state*.[5,24] At sufficiently low temperatures two conformations can be frozen out in the ^{1}H-NMR spectrum corresponding to a *syn* and an *anti* orientation of the acyl carbonyl group relative to the indole 2-position. These conformations are distinguished by the chemical shift of the 7-position hydrogen which is deshielded by the *N*-acyl carbonyl group in the *anti* conformers (e.g., structures **13a** and **13c**) and so appears downfield from the corresponding signal in the spectrum of the *syn* conformers (e.g., structures **13b** and **13d**). Similar results were obtained by Morales-Rios and Joseph-Nathan with *N*-(ethoxycarbonyl)indole which possesses a urethane function similar to those in compounds **3a–g**.[25] Variable temperature ^{1}H-NMR spectroscopic studies were carried out in this work using **3c–e** in order to probe the preferred conformations and their rates of interconversion in an attempt to determine whether the molecule was indeed effectively frozen in an unreactive conformation during the excited state lifetime.

The 200-MHz ^{1}H-NMR spectra of compounds **3c–e** were obtained at 10° intervals at temperatures from −50 °C to 20 °C. In all cases, at −50 °C the 7-position hydrogen appeared as two broadened doublets in a 2:1 ratio; the larger of the two appeared slightly downfield from 8 ppm, while the smaller of the two appeared slightly upfield from 8 ppm. This would suggest that at −50 °C these compounds exist as *syn*- and *anti*-conformers which do not interconvert on the NMR time scale. The conformer ratio indicates that the *anti*-rotamer[26] is favored over the *syn*-rotamer by approximately 0.4 kcal mol^{-1}. At room temperature the 7-position hydrogen appeared as a broad doublet for each *N*-[(ω-alkenyloxy)carbonyl]indole suggesting that coalescence of the 7-position signals had occurred, although the broadening indicates that interconversion of conformers is still relatively slow. Compounds **3c–e** all had coalescence temperatures (T_c) of −10 °C ± 5°, at which point the 7-position signal of each conformer had just coalesced to one broad signal.[27] These spectra allowed the calculation[27] of the average lifetime of the two conformers to be *circa* 7×10^{-3} s at −10 °C. This corresponds to a rate of rotation around the nitrogen to carbonyl bond of approximately 150 s^{-1}. The activation energy for the rotation was calculated to be 12.3 ± 0.3 kcal mol^{-1}.

These results show that interconversion between conformers by rotation around the nitrogen to carbonyl bond of the *N*-[(alkenyloxy)carbonyl]indoles occurs very slowly near room temperature *in the ground state* relative to the rates of decay of the *N*-acylindole triplet excited state which have been estimated[8] to be *ca.* $10^7 - 10^8$ s^{-1}. If the rate of rotation is not greatly different in the excited state then the *syn*- and *anti*-conformers of the [(alkenyloxy)carbonyl]indole triplet excited states are effectively frozen and would decay to the ground state much faster than they can interconvert. The ratio of *syn*- to *anti*-conformers present also indicates that two-thirds of the molecules

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[24] Weedon, A. C.; Wong, D. F.; Zhang, B., unpublished results.

[25] Morales-Rios, M. S.; Joseph-Nathan, P. *Mag. Res. Chem.* **1987**, *25*, 911.

[26] In this context, the *syn*-rotamer is designated as the conformer in which the *N*-acyl carbonyl group is oriented toward the 2-position of the indole ring.

[27] Abrahams, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy*; New York, 1983; pp 194–200.

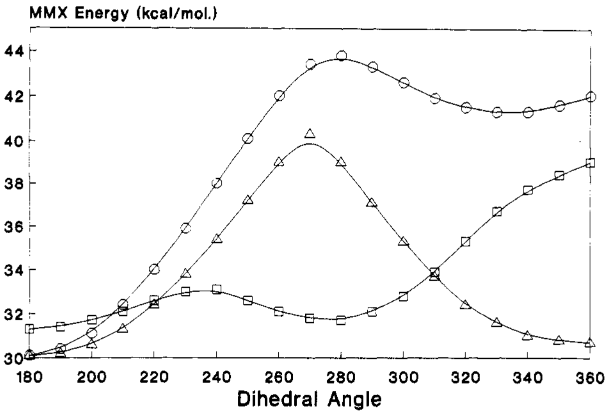


Figure 1. Force field calculated energy as a function of dihedral angle: (△) rotation around N–CO bond for conversion of **13c** (dihedral angle 180°) to **13d** (dihedral angle 360°); (○) rotation around O–CO bond for conversion of **13c** (dihedral angle 180°) to **13a** (dihedral angle 360°); (□) rotation around CO–CH_2 bond for conversion of **14c** (dihedral angle 180°) to **14a** (dihedral angle 360°).

Table 1. Force Field Calculated Relative Energies of Conformers 13a–d

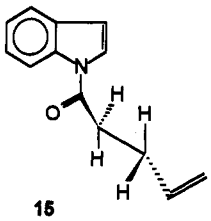
MMX energy (kcal/mol)	conformer
40.9	**13a**
43.6	**13b**
30.2	**13c**
30.8	**13d**

exist in an *anti*-conformation where the alkene side chain can, in principle, approach the indole 2,3-positions. The results do not, however, give any indication about which of the conformations **13a** or **13c** is preferred and whether conformations close to **13e** can be accessed during the excited state lifetime. An answer to this question can be inferred from the numerous literature reports suggesting that both esters and urethanes[28–33] adopt conformations which favor the orientation shown in **13c** rather than that shown in **13a**. The possibility that the *N*-[(ω-alkenyloxy)-carbonyl]indoles adopt this conformation preferentially, which would disfavor intramolecular photocycloaddition, was examined using force field calculations[34] at the MMX level.

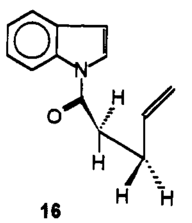
The conformations **13a–d** were minimized and their relative energies were calculated;[34] this was also done for the intermediate conformers present during rotation about the carbonyl to nitrogen and carbonyl to oxygen bonds of the urethane function (i.e., the energies of the conformers intermediate between **13c** and **13d**, and between **13c** and **13a**, respectively). The minimized relative energies of **13a–d** are listed in Table 1 and the minimized relative energies of the intermediate conformations between **13c** and **13d**, and between **13c** and **13a**, are shown in Figure 1.

The data in Table 1 suggest that conformers **13c** and **13d** are the most stable with **13c** being more stable than **13d** by 0.6 kcal/mol; the activation barrier for conversion of **13c** to **13d** was calculated (cf. Figure 1) to be 10 kcal/mol. Both values are in good agreement with the values of 0.4 and 12 kcal/mol obtained experimentally using variable temperature ^{1}H-NMR spectroscopy. The data in Table 1 also indicate that conformation **13a** is less stable than **13c** by 10 kcal/mol; consequently, at room temperature access to the even higher energy conformations close to **13e** which are required for reaction becomes improbable. If these energies and barriers are unchanged in the excited state then this would mean that the *N*-[(ω-alkenyloxy)-carbonyl]indoles **3a–g** would have great difficulty in orienting the alkenyl function appropriately in order to enable interaction with the 2-position of the indole ring during the excited state lifetime. This is completely in accord with the observed photochemistry of **3a–g**.

Substitution of a methylene group for the oxygen atom of the urethane linkage of **3a–g** removes the double bond character which exists between the carbonyl group and the oxygen atom of the urethane linkage and hence lowers the activation energy for the bond's rotation. In addition, it removes the preference for adoption of a conformation in which the N–CO–X–C (X = O or C) σ-framework is planar. In order to examine the consequences of this the energies of the conformations **14a–d** of the *N*-(ω-alkenoyl)-indole **3j** were calculated as well as the energies of the conformations intermediate in the interconversion of **14c** to **14a**. The results are shown in Figure 1. As the N–CO–CH_2–CH_2 dihedral angle of 180° in **14c** is increased, the energy of the molecule changes by less than 1.5 kcal/mol until a dihedral angle greater than 280° is reached. At this point the conformation can be represented by the projection **15**; in the corresponding gauche conformer **16** the side chain alkene comes into close proximity with the indole 2-position. Minimization of **16** predicts it to be only 0.3 kcal/mol in energy above **15**. The data imply that in contrast to the urethane linked systems **3a–g**, the amide-linked analogues such as **3h–k** should be able to access readily conformers in which the alkene approaches the indole 2-position closely enough to react. Accordingly the photochemistry of compounds **3h–k** was examined.



15



16

Preparation and Photochemistry of *N*-Alkenoylindoles 3h–k. The *N*-alkenoylindoles **3h,j,k** were prepared by treatment of indole with the appropriate acid chloride in the presence of a base under phase-transfer conditions. This procedure has been described by Illi[18] for the preparation of *N*-acylindoles from indole and acid chlorides. This procedure could not be used for the preparation of **3i** because the basic conditions were sufficient to isomerize the product to **3h**; instead the *N*-alkenoylindole **3i** was prepared by treatment of the anion of indole with the anhydride of 3-butenoic acid.

Compound **3h** was irradiated in benzene solution using Pyrex-filtered ultraviolet light. Analysis by gas chroma-

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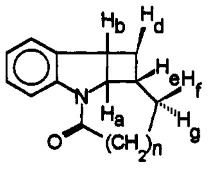
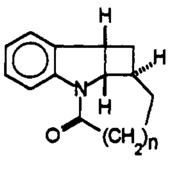
[34] PCMODEL Software, version 1.1, Serena Software (1987), Box 3076, Bloomington, IN.

tography suggested 55% conversion to two products in a 1:5 ratio. The minor product was identified as indole by comparison with an authentic sample; presumably it is produced by homolytic photodissociation of the *N*-acyl bond of **3h** followed by failure of the radical pair to couple to give Fries-type products. The major product was readily identified as the *cis*-*N*-(ω-alkenoyl)indole **31** formed by light-induced geometrical isomerization of the side-chain alkene. Intermolecular cycloaddition with added cyclopentene was unable to compete with isomerization of **3h** to **31**. Apparently, geometrical isomerization of the double bond of the conjugated amide function in **3h** provides a mode for rapid decay of the triplet excited state of the *N*-acylindole. This is analogous to the situation with α,β-unsaturated ketones where *E*–*Z* isomerization from the enone excited state occurs faster than [2 + 2] cycloaddition with alkenes unless the enone is structurally constrained so as to prevent relaxation of the excited state by rotation of the conjugated double bond.[22] The quantum yield of formation of **31** from **3h** was measured and a value of 0.068 ± 0.006 was obtained; the quantum yield of indole formation in the same reaction was determined to be 0.008 ± 0.001.

Direct irradiation of compounds **3i–k** with light of wavelength 254 nm resulted in the formation of products identified as resulting from photo-Fries rearrangement, based upon inspection of the GC-MS and ^{1}H-NMR spectra of the mixture. As with the urethanes **3a–e**, the photo-Fries reaction was suppressed when the reaction was sensitized or when light of wavelength greater than 300 nm was used. Both acetophenone-sensitized and direct irradiation of compounds **3i–k** with Pyrex-filtered ultraviolet light afforded products identified as intramolecular cycloadducts **17a–19a**, respectively, in moderate yields.



17a n = 0
18a n = 1
19a n = 2



17b n = 0
18b n = 1
19b n = 2

The structural assignments are based primarily upon the appearance of the NMR spectra of the compounds, although the regiochemistry of the alkene addition can also be inferred from the fact that "crossed" adducts derived from bonding of the indole 2-position to the less substituted end of the alkene would be impossibly strained. The ^{13}C-NMR spectrum of each adduct showed the disappearance of the side-chain alkene sp^2 carbons, as well as two aromatic methine signals. These had been replaced by three sp^3 methine signals and one sp^3 methylene signal. The protons on these four carbons, designated H_a, H_b, H_c, H_d, and H_e, as shown in structure **17**, were observable in the ^{1}H-NMR spectrum of each adduct and allowed unambiguous confirmation of the regiochemistry and assignment of the stereochemistry. In all the cycloadducts formed by photochemical reaction of *N*-acylindoles with alkenes which have been reported to date[17-20] the signal of H_a is to lower field of H_b which in turn is to lower field of the remaining cyclobutane protons if no polar substituents are present on the alkene-derived carbons of the cyclobutane ring. The signals assigned to H_a and H_b for the cycloadducts **17–19** were identified using this correlation. Decoupling experiments then allowed their relationships to the remaining cyclobutane protons to be determined. In this manner it was possible to assign the regiochemistry since H_a possesses only two vicinal couplings (one to H_b and one to H_e) while H_b possesses three vicinal couplings (one to each of H_a, H_c, and H_d).

Table 2. Calculated Dihedral Angles,[a] and Calculated and Observed Coupling Constants (in hertz) for 17–19

structure	J_{ab}	J_{bd}	J_{bc}	J_{ae}	strain energy (kcal/mol)
17a (calcd)	8.3 (23)	9.7 (14)	8.2 (141)	7.9 (26)	54.0
17a (obsd)	5	9	5	5	
17b (calcd)	8.3 (26)	7.9 (29)	1.4 (97)	11.5 (172)	94.0
18a (calcd)	8.3 (23)	9.0 (21)	9.3 (148)	7.7 (27)	45.8
18a (obsd)	7	7	7	7	
18b (calcd)	9.4 (16)	8.7 (23)	2.0 (104)	10.5 (158)	63.1
19a (calcd)	9.4 (14)	9.8 (12)	8.1 (140)	9.1 (15)	44.6
19a (obsd)	8	8	8	6	
19b (calcd)	9.9 (10)	9.5 (17)	2.8 (110)	9.5 (151)	55.0

[a] Dihedral angles in parentheses.

The stereochemistry of the cycloadducts was assigned using the magnitudes of the coupling constants between the hydrogen atoms on the cyclobutane ring. In relatively rigid cyclobutanes such as those in the cyclopentene adducts **9–12** the dihedral angles between the cyclobutane ring hydrogens are fixed; for **9–12** this has the consequence that the vicinal coupling constants are larger (7–9 Hz) for hydrogens with a *cis* relationship and smaller (2–4 Hz) for hydrogens which are *trans* to one another. In more flexible cyclobutane rings, such as those formed between *N*-acylindoles and acyclic alkenes, rapid equilibration between the cyclobutane-puckered conformations frequently results in *trans* coupling constants being increased so that their values approach the lower end of the range of values observed for *cis* coupling constants. Assignment of stereochemistry on the basis of coupling constant data is unsatisfactory in such systems.[8]

In the intramolecular cycloadducts **17–19** it was anticipated that the cyclobutane rings would be held rigidly in a single conformation so that the values of the coupling constants could be informative. Accordingly, the dihedral angles between the cyclobutane hydrogens in **17a–19a** were estimated from the force field calculated minimum energy structures[34] and the expected coupling constants calculated making allowance for polar substituent effects.[35] This was also done for the alternative stereoisomers **17b–19b** and the values of the coupling constants were compared with those observed in the isolated cycloadducts. The results are shown in Table 2 and indicate that the value of the coupling constant J_{bc} is predicted to be small for the adducts **17b–19b** and large for **17a–19a**. The observed values indicate that the intramolecular cycloadducts produced from **3i–k** possess the stereochemistry shown in **17a–19a** since the values of J_{bc} were large in all three cases.

The *trans* ring fusion in **17b–19b** would be expected to induce ring strain. The MMX force field calculation gives a measure of the strain energy and the results are also listed in Table 2. Thus **17b** is calculated to be 40 kcal/mol higher in energy than **17a**, **18a** is calculated to be 16 kcal/mol higher than **18b**, and **19b** is calculated to be 10 kcal/mol higher than **19a**. The greater ring strain in the *trans*-fused stereoisomers would inhibit ring closure of their

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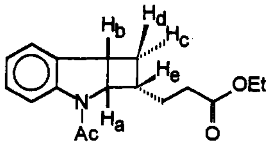
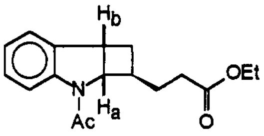
biradical precursors and promote reversion of the biradical to the ground-state starting materials. This could account for the preferential formation of the *cis* fused products **17a–19a** from **3i–k**, respectively.

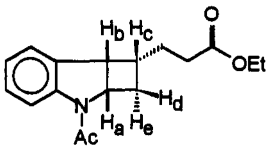
The regiochemistry of the intramolecular photocycloaddition reaction was compared with that of the corresponding intermolecular photocycloaddition reaction between *N*-acetylindole and ethyl 4-pentenoate. To achieve this the cycloadduct **18a** was treated with acidic ethanol followed by acetyl chloride. It was anticipated that this would yield **20a**, which possesses the opposite regiochemistry to that of the expected products of the intermolecular photocycloaddition reaction. The product formed from **18a** possessed the signals expected for **20a** in the ^{13}C-NMR spectrum; the cyclobutane ring appeared intact and new signals corresponding to the acetyl group (169.7, 26.9 ppm) and the ethoxy group (61.3, 15.1 ppm) were observed. The ^{1}H-NMR spectrum confirmed the regiochemistry of **20a**. In this spectrum the signals of H_a (4.89 ppm) and H_b (4.03 ppm) were identified from their chemical shifts; H_a was a triplet coupled to H_b and H_e only ($J_{ab} = J_{ae} = 7$ Hz) while H_b was coupled to H_c and H_d as well as to H_a ($J_{ab} = J_{bd} = 7$ Hz, $J_{bc} = 4$ Hz). As noted above, the conformational flexibility of a nonrigid cyclobutane ring makes stereochemical assignment using coupling constant data difficult. The stereochemical assignment of **20a** is therefore made on the basis of the stereochemistry present in **18a**.



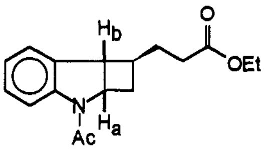
20a



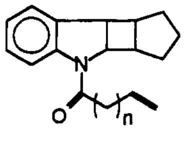
20b



21a



21b



22i-k

The acetophenone sensitized intermolecular photocycloaddition reaction between *N*-acetylindole and ethyl 4-pentenoate yielded two major products in a 2:1 ratio. Analysis by GC-MS indicated that these were 1:1 adducts; GC comparison indicated that neither of these compounds were identical with the sample of **20a** produced by ethanolysis and acetylation of **18a**. The major product was isolated in pure form by chromatography while the minor product was obtained in enriched form contaminated by the major product. In the ^{1}H-NMR spectrum of the major product the cyclobutane hydrogens H_a and H_b were clearly visible at 4.74 and 3.65 ppm, respectively. The remaining cyclobutane hydrogens H_c, H_d, and H_e appeared as a multiplet at 2.33 ppm, along with hydrogens α to the carbonyl of the ethyl ester. Decoupling the multiplet at 2.33 ppm caused H_a and H_b to collapse from multiplets to doublets ($J_{ab} = 7.6$ Hz). Decoupling H_b caused H_a to collapse from a multiplet to a triplet ($J_{ae} = J_{ad} = 4.7$ Hz) and decoupling H_a caused H_b to collapse from a multiplet to a doublet ($J_{bc} = 4.0$ Hz). These results are indicative of a head-to-tail cycloadduct of *N*-acetylindole and ethyl 4-pentenoate and are inconsistent with a head-to-head cycloadduct. The addition of monosubstituted alkenes to *N*-acylindoles normally gives the head-to-tail *exo* isomer as the major product, along with smaller quantities of the head-to-tail *endo* isomer; consequently, the major product of the intermolecular reaction was assigned the stereochemistry shown in structure **21a** and the minor product was tentatively assigned structure **21b**.

Table 3. Quantum Yields of Formation of Intramolecular Photocycloadducts 17–19 from 3i–k under Direct and Sensitized Conditions

compound	Φ (direct)	Φ (sensitized)
17	0.0078 ± 0.0008	0.087 ± 0.008
18	0.017 ± 0.002	0.177 ± 0.004
19	0.0032 ± 0.0004	0.021 ± 0.002

Table 4. UV Irradiation of 3i–k in the Presence of Cyclopentene: Relative Yields of Intermolecular Adducts 17–19 and Intramolecular Adducts 17–19 and 22i–k

compound	3i with 1.98 M cyclopentene	3j with 1.33 M cyclopentene	3k with 1.47 M cyclopentene
intramolecular adduct relative yield (%)	39.0	90.5	18.6
intermolecular adduct relative yield (%)	61.0	9.5	81.4

These results show clearly that the intramolecular reaction of **3e** yields a product with regiochemistry opposite to that favored in the corresponding intermolecular reaction.

The quantum yields $\Phi^{\circ}_{\mathrm{intra}}$ for formation of the intramolecular photocycloadducts **17a–19a** from **3i–k**, respectively, were measured under direct and sensitized conditions. These quantum yields were determined at low conversion in order to avoid secondary photochemistry of the products; in addition, light of wavelength 313 nm was used so as to avoid competing photo-Fries rearrangement. The sensitized reaction quantum yields were measured under conditions designed to ensure complete light absorption by the sensitizer and quantitative quenching of the sensitiser triplet excited states by the *N*-acylindoles. The results are shown in Table 3 and indicate that the intramolecular photocycloaddition is most efficient for **3j** and least efficient for **3k**.

Competition experiments were also performed in which the *N*-acylindoles **3i–k** were irradiated in the presence of cyclopentene. This resulted in the formation of intermolecular cycloadducts **22i–k** as well as the intramolecular adducts **17–19**. The intermolecular adducts were identified by GC-MS and by conversion to the known[8] indoline adducts **11** and **12**. The relative chemical yields of the inter- and intramolecular cycloadducts are shown in Table 4. The relative yields of the inter- and intramolecular adducts confirm that the intramolecular photocycloaddition reaction is most efficient for **3j**.

Conclusions

The results described reveal that intramolecular photocycloaddition between indole and an alkene tethered to the indole nitrogen by a urethane linkage fails, apparently because the alkene is held in an unreactive conformation for the duration of the excited state lifetime. This problem can be overcome if the urethane linkage is replaced by an amide function. The length of the tether between the indole and the alkene affects the efficiency of the intramolecular photocycloaddition and its ability to compete with intermolecular photocycloaddition. The regiochemistry of the photocycloaddition reaction between monosubstituted alkenes and *N*-acylindoles can be controlled by tethering the alkene to the indole nitrogen through an amide linkage; this yields the head-to-head regioisomer, which is the opposite to that obtained in the intermolecular reaction.

Experimental Section

Preparation of *N*-[(Vinyloxy)carbonyl]indole (3a). A solution of vinyl chloroformate (Aldrich, 227 mg, 2.13 mmol) in dry THF (20 mL) was stirred under an atmosphere of dry nitrogen and maintained at 0 °C. A solution prepared from indole (180 mg, 1.59 mmol) and NaH (107 mg, 4.47 mmol) in dry THF was added dropwise over a period of 5 min. After stirring the mixture for 15 min, analysis by gas chromatography suggested a 1:1 mixture of indole (confirmed by coinjection with authentic samples) and one product had been formed. The reaction was quenched by careful addition of trifluoroacetic acid (1 mL) in dry THF (3 mL). Distilled water (30 mL) was added and the mixture was extracted with ether (3 × 40 mL). The organic layers were combined and dried ($MgSO_4$), and solvent was removed *in vacuo* to afford a yellow oil (262 mg). Purification of this oil by column chromatography (50 g of silica gel eluted using 96% hexanes/4% ether) gave **3a** (134 mg, 47%) as a clear, colorless oil: *m/z* 187, 144, 116 (100), 89; HRMS calcd for $C_{11}H_9NO_2$ 187.0633, found 187.0635; ^{1}H-NMR ($CDCl_3$) δ 8.24 (d, 1H, J = 7.9 Hz), 7.62 (m, 2H), 7.35 (m, 3H), 6.66 (dd, 1H, J = 3.8, 0.8 Hz), 5.15 (dd, 1H, J = 13.9, 2.1 Hz), 4.79 (dd, 1H, J = 6.2, 2.1 Hz); ^{13}C-NMR ($CDCl_3$) δ 150.0, 142.3, 136.0, 131.5, 126.1, 125.7, 124.4, 122.1, 116.1, 109.9, 99.6

General Procedure for the Preparation of the N-(ω-Alkenyloxycarbonyl)indoles 3b–g. The procedure of Boger and Patel was adapted.[17] *N*-Carboxyindole anhydride[17] (1.0 g; 3.3 mmol) in dry THF (5 mL) was stirred in an ice–water bath and under an atmosphere of dry nitrogen. A solution of the sodium salt of the appropriate alcohol (prepared, for example, by adding 0.8 equiv of 3-methyl-2-buten-1-ol in 5 mL of dry THF to hexanes-washed NaH in 5 mL of dry THF) was then added rapidly to the reaction flask. After stirring for 30 min, the mixture was poured into distilled water and the products were extracted into ether. The ether layers were combined, dried ($MgSO_4$), and filtered, and excess solvent was removed *in vacuo*. The crude product was then purified by column chromatography to give the *N*-[(ω-alkenyloxy)carbonyl]indole as an oil.

3b: yield 30%; *m/z* 229, 185, 117 (100), 90, 65; HRMS calcd for $C_{14}H_{15}NO_2$ 229.1103, found 229.1104; λ_{max} (hexanes) 226, 254, 284, 292 nm; ν (neat) 1734 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.20 (d, 1H, J = 8.1 Hz), 7.59 (m, 2H), 7.33 (m, 2H), 6.58 (dd, 1H, J = 3.8, 0.8 Hz), 5.53 (m, 1H), 4.92 (d, 2H, J = 7.2 Hz), 1.81 (d, 6H, J = 1.0 Hz).

3c: yield 60%; *m/z* 201, 156, 116, 78 (100); HRMS calcd for $C_{12}H_{11}NO_2$ 201.0793, found 201.0790; λ_{max} (hexanes) 227, 254, 284, 292 nm; ν_{max} (neat) 1740 cm^{-1}; E_T (hexane) 69 kcal mol^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.21 (d, 1H, J = 8.1 Hz), 7.59 (m, 2H), 7.30 (m, 2H), 6.60 (d, 1H, J = 3.8 Hz), 6.07 (m, 1H), 5.42 (m, 2H), 4.92 (dt, 2H, J = 5.8, 1.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 151.0, 133.5, 130.5, 131.5, 125.5, 124.5, 123.0, 121.0, 115.2, 108.2, 119.3 , 67.5 .

3d: yield 20%; λ_{max} (pentane) 226, 254, 284, 292 nm; ^{1}H-NMR ($CDCl_3$) δ 8.16 (d, 1H, J = 8.0 Hz), 7.56 (m, 2H), 7.25 (m, 2H), 6.56 (d, 1H, J = 3.8 Hz), 5.80 (m, 2H), 4.81 (d, 2H, J = 6.5 Hz), 1.75 (m, 3H); *m/z* 215, 131, 117 (100); HRMS calcd for $C_{13}H_{13}NO_2$ 215.0946, found 215.0945.

3e: yield 45%; *m/z* 215, 117, 89, 55 (100); HRMS calcd for $C_{13}H_{13}NO_2$ 215.0946, found 215.0949; ^{1}H-NMR ($CDCl_3$) δ 8.18 (d, 1H, J = 7.9 Hz), 7.60 (m, 2H), 7.26 (m, 2H), 6.59 (dd, 1H, J = 7.7, 0.7 Hz), 5.75 (m, 2H), 4.98 (dd, 2H, J = 6.0, 2.3 Hz), 1.82 (dd, 3H, J = 5.3, 1.4 Hz); ^{13}C-NMR ($CDCl_3$) δ 151.1, 135.2, 130.5, 130.9, 128.3, 125.6, 124.5, 123.0, 121.0, 115.2, 108.0, 62.5, 13.3.

3f: yield 25%; *m/z* 215, 130, 117, 89, 55 (100); HRMS calcd for $C_{13}H_{13}NO_2$ 215.0946, found 215.0950; ^{1}H-NMR ($CDCl_3$) δ 8.06 (d, 1H, J = 8.1 Hz), 7.46 (m, 2H), 7.19 (m, 2H), 6.47 (dd, 1H, J = 3.8, 0.7 Hz), 5.75 (m, 1H), 5.04 (m, 2H), 4.36 (t, 2H, J = 6.6 Hz), 2.46 (m, 2H).

3g: yield 30%; *m/z* 229, 161, 117 (100), 89; HRMS calcd for $C_{14}H_{15}NO_2$ 229.1103, found 229.1106; ^{1}H-NMR ($CDCl_3$) δ 8.18 (d, 1H, J = 8.1 Hz), 7.57 (m, 2H), 7.29 (m, 2H), 6.58 (dd, 1H, J = 3.8, 0.8 Hz), 5.82 (m, 1H), 5.07 (m, 2H), 4.42 (t, 2H, J = 6.6 Hz), 2.23 (m, 2H), 1.91 (m, 2H).

General Procedure for the Photolysis of *N*-[(ω-Alkenyloxy)carbonyl]indoles 3b,c (254 nm). A stirred solution of *N*-[(ω-alkenyloxy)carbonyl]indole **3b** or **3c** (250 mg) in benzene (250 mL) was irradiated using quartz and water-filtered light from a 400-W Hanovia medium-pressure mercury vapor lamp which was immersed in the solution undergoing irradiation. After 10 h of irradiation, analysis by gas chromatography indicated 95% conversion to 3 products. The solvent was then removed by distillation under reduced pressure.

The products were purified using column chromatography (silica gel column eluted using 50% hexanes/50% diethyl ether), followed by preparative thin-layer chromatography (one elution using 25% hexanes/75% ether) which gave the following fractions:

From **3b**, one fraction gave **4b** (oil): yield 23%; ^{1}H-NMR ($CDCl_3$) δ 8.68 (br s, NH), 8.17 (m, 1H), 7.91 (d, 1H, J = 2.9 Hz), 7.32 (m, 3H), 5.50 (t, 1H, J = 7 Hz), 4.83 (d, 2H, J = 7.1 Hz), 1.77 (s, 6H); HRMS calcd for $C_{14}H_{15}NO_2$ 229.1103, found 229.1102. A second fraction gave a mixture of **5b** and **6b**: yield 15%; *m/z* 229 (1%) 185 (5) 170 (5) 118 (20) 116 (20) 90 (100) 89 (60).

From **3c**, one fraction gave **4c**: yield 26%; *m/z* 201, 144 (100), 116, 89. HRMS calcd for $C_{12}H_{11}NO_2$ 201.0790; found 201.0795. ^{1}H-NMR ($CDCl_3$) δ 9.60 (br s, 1H), 8.18 (m, 1H), 7.90 (d, 1H, J = 3.0 Hz), 7.38 (m, 1H), 7.24 (m, 2H), 6.05 (m, 1H), 5.32 (m, 2H), 4.84 (dt, 2H, J = 5.5, 1.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 165.8, 136.8, 126.4, 108.8, 133.4, 132.1, 123.6, 122.5, 121.9, 118.2, 112.2, 66.2. A second fraction gave a mixture of **5c** and **6c**: yield 3%; *m/z* 201, 144 (100), 116, 89.

Photolysis of *N*-[(ω-Alkenyloxy)carbonyl]indole 3f (>300 nm). A solution was prepared consisting of *N*-[(ω-alkenyloxy)carbonyl]indole **3f** (47.7 mg) and heptadecane (14.6 mg) in benzene (2.00 mL). This mixture was divided equally between two Pyrex NMR tubes. One was wrapped with aluminum foil and kept as a dark reaction control. Both tubes were purged with N_2 and sealed. The unwrapped tube was irradiated using water and Pyrex-filtered light from a medium-pressure Hg vapor lamp. The irradiation was continued for 235 h with periodic analysis by gas chromatography. Following the irradiation, solvent was removed from both samples *in vacuo* and the residues were analyzed by ^{1}H-NMR spectroscopy. The spectrum of the irradiated sample indicated that a mixture of **3g** and **3f** had been isolated containing the two components in a 1:3 ratio; the relative amounts of these species in the mixture was determined by comparing integration ratios of the sp^2-methylene proton of **3g** (4.81 ppm) to the analogous sp^2-methylene proton of **3f** (4.98 ppm). An accurate determination of the absolute amounts of **3g** and **3f** in the photolysis mixture at various irradiation times was obtained by GC using heptadecane as an internal standard, whence: t = 0, **3g** (1.7%), **3f** (98.3%); t = 93 h, **3g** (7.7%), **3f** (80.7%); t = 235 h, **3g** (11.7%), **3f** (70.3%).

General Procedure for the Direct and Sensitized Photolysis of *N*-[(ω-Alkenyloxy)carbonyl]indoles 3a,c,f,g and Cyclopentene (>300 nm). Two solutions were prepared for irradiation; the first contained *N*-[(ω-alkenyloxy)carbonyl]indole (20 mg), heptadecane (10 mg), and cyclopentene (175 mg) in benzene (1 mL), and the second contained the above with the addition of acetophenone (20 mg). Both samples were placed into Pyrex NMR tubes, purged with N_2, sealed, and irradiated using a medium-pressure Hg vapor lamp. Analysis by gas chromatography suggested moderate conversion (*ca.* 40%) after 90 h to two products for the direct photolysis and high conversion (*ca.* 85%) after 20 h to the same two products for the sensitized photolysis.

Analysis using coupled gas chromatography/mass spectrometry was carried out on both the irradiated samples. For each compound, similar fragmentation patterns were observed in both the sensitized and direct irradiations. Products were tentatively assigned as the cyclopentene adducts; this was later confirmed by hydrolysis and comparison with authentic samples of **11** and **12** using the method of Hastings and Weedon,[8] and Weedon and Zhang.[11] From **3a**, products **9a** and **10a**: *m/z* 255, 187 (100), 158, 144, 116. From **3c**, products **9c** and **10c**: *m/z* 269, 201 (100), 156, 130, 116. From **3f**, products **9f** and **10f**: *m/z* 283, 215 (100), 130, 117, 55. From **3g**, products **9g** and **10g**: *m/z* 297, 229 (100), 161, 117, 69.

Quantum Yield of Formation of Cyclopentene Adducts 9c and 10c. A stock solution was prepared consisting of *N*-[(ω-alkenyloxy)carbonyl]indole **3c** (58.3 mg), nonadecane (8.5 mg), and cyclopentene (1.0225 g; 1.501 M) in spectroscopic grade benzene (10.00 mL). A 3.00-mL aliquot was pipetted into a quartz irradiation cuvette, degassed via the freeze-pump-thaw method three times to a residual pressure of 10^{-4} Torr, and irradiated to 3% conversion (**9c** and **10c**, analysis by gas chromatography) at 295 nm. Intramolecular adducts could not be detected.

The irradiated sample was analyzed by gas chromatography to determine the absolute quantity of cycloadducts formed. A minimum of five injections were performed in order to establish limits of error. Nonadecane was used as an internal standard in the irradiation mixture and a calibration curve constructed using purified products (silica gel column eluted using 80% hexanes/20% ether) so that absolute amounts of products formed in the irradiated sample could be estimated. A value for Φ_{adducts} of 0.024 ± 0.001 was determined (moles of product formed = 2.31×10^{-6} and photons absorbed = 9.62×10^{-5} Einsteins).

Quantum Yield of *cis–trans* Isomerization of 3e. A stock solution consisting of *N*-[(ω-alkenyloxy)carbonyl]indole **3e** (94.0 mg) and heptadecane (29.5 mg) in benzene (10.00 mL) was prepared. A 3.00-mL aliquot was pipetted into a quartz irradiation cuvette; this sample was degassed via the freeze-pump-thaw method three times (10^{-4} Torr) and then irradiated at 305 nm to less than 5% conversion. Three irradiations were performed to selected % conversions to establish limits of error. Errors were determined by obtaining a statistical average of the quantum yield of isomerization calculated for the three irradiations and using the resulting standard deviation as the measured error. From this procedure, $\Phi_{\text{isomerisation}} = 0.0018 \pm 0.0002$ (moles of product = 4.25×10^{-7} and photons absorbed = 2.36×10^{-4} Einsteins).

Photolysis of *N*-[(ω-Alkenyloxy)carbonyl]indole 3g at an Elevated Temperature. *N*-[(ω-Alkenyloxy)carbonyl]indole **3g** (25.6 mg) and heptadecane (9.7 mg) in toluene (2 mL) was prepared in a Pyrex NMR tube, purged with N_2, sealed, and irradiated using a medium-pressure Hg vapor lamp immersed in a 70 °C water bath. After irradiating for 19 h, analysis by gas chromatography suggested 56% conversion to unintegrated products. Analysis by coupled gas chromatography/mass spectrometry and ^{1}H-NMR spectroscopy failed to identify the products formed. At this point, conversion was assumed to be to polymeric products and the irradiation not pursued further.

General Procedure for the Preparation of N-(ω-Alkenoyl)indoles 3h–k. The method of Illi was adapted.[18] To a stirred suspension of indole (0.05 mol), powdered NaOH (0.20 mol), and $(Bu)_4NBr$ (0.001 mol) in methylene chloride (75 mL) was added a solution of the appropriate acid chloride (e.g. crotonyl chloride in the case of **3h**) (0.06 mol) in methylene chloride (20 mL) over 30 min at 0 °C. The solution was stirred for an additional 3 h, followed by quenching with distilled water (100 mL). The organic layer was washed with distilled water (2 × 50 mL), dried (Na_2SO_4), and filtered, and excess solvent was removed *in vacuo*. Purification by column chromatography (150 g silica gel eluted using 95% hexanes/5% ether) afforded the *N*-(ω-alkenoyl)indoles desired.

3h: white crystalline solid after crystallization from MeOH, melting point 86–88 °C; yield 7%; *m/z* 185, 117 (100), 89, 69; HRMS calcd for $C_{12}H_{11}NO_2$ 185.0840, found 185.0837; $\lambda_{\max}$ (CH_3-CN) 212, 252, 305; ^{1}H-NMR ($CDCl_3$) δ 8.49 (d, 1H, *J* = 8.0 Hz), 7.55 (m, 2H), 7.30 (m, 3H), 6.66 (m, 2H), 2.02 (dd, 3H, *J* = 6.9, 1.6 Hz). ^{13}C-NMR ($CDCl_3$) δ 164.1, 146.7, 124.9, 124.7, 123.7, 122.3, 120.8, 116.8, 108.9, 135.8, 130.6, 18.6.

3j: clear, colorless oil; yield 60%; *m/z* 199, 117 (100), 89; exact mass calcd 199.0997, observed 199.0992; $\lambda_{\max}$ (MeOH) 203, 239, 290, 299 nm; ^{1}H-NMR ($CDCl_3$) δ 8.48 (d, 1H, *J* = 8.1 Hz), 7.57 (dt, 1H, *J* = 7.3, 1.0 Hz), 7.47 (d, 1H, *J* = 3.8 Hz), 7.30 (m, 2H), 6.65 (dd, 1H, *J* = 3.8, 0.8 Hz), 5.92 (m, 1H), 5.11 (m, 2H), 3.03 (t, 2H, *J* = 6.5 Hz), 2.60 (dt, 2H, *J* = 6.5, 1.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 171.2, 140.2, 130.8, 137.0, 125.6, 125.0, 124.1, 121.3, 117.1, 109.7, 116.6, 35.6, 28.9.

3k: clear, colorless oil; yield 40%; *m/z* 213, 159, 117 (100), 89; HRMS calcd for $C_{14}H_{15}NO_2$ 213.153, found 213.1153; $\lambda_{\max}$ (hexane) 207, 235, 254, 281, 290, 299 nm; ^{1}H-NMR ($CDCl_3$) δ 8.49 (d, 1H, *J* = 7.5 Hz), 7.35 (m, 4H), 6.64 (dd, 1H, *J* = 3.8, 0.8 Hz), 5.85 (m, 1H), 5.10 (m, 2H), 2.92 (t, 2H, *J* = 7.4 Hz), 2.24 (m, 2H,), 1.98 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 172.3, 138.5, 136.5, 131.2, 126.0, 125.5, 124.5, 121.7, 117.5, 109.9, 116.6 , 35.8, 33.9, 24.5.

Preparation of Vinylacetic Acid. The method of Duhaime et al was used.[36] A stirred solution of crotonic acid (15.0 g) in spectroscopic grade MeOH (275 mL) was irradiated in quartz glassware using water-filtered light from a 400-W Hanovia medium-pressure mercury vapor lamp. After 48 h of irradiation, analysis by gas chromatography indicated 98% conversion to one product. Removal of excess solvent *in vacuo* gave a brown oil (13.2 g) which was purified by distillation (1 mmHg, dry ice/acetone trap), affording a clear colorless liquid (8.20 g, 55%; boiling point 78 °C at 20 mmHg, lit.[37] 69–70 °C at 12 mmHg): ^{1}H-NMR ($CDCl_3$) δ 11.36 (br s, 1H), 5.91 (m, 1H), 5.16 (m, 2H), 3.12 (dt, 2H, *J* = 6.9, 1.4 Hz); ^{13}C-NMR ($CDCl_3$) δ 178.4, 129.5, 119.1, 38.8.

Preparation of Vinylacetic Acid Anhydride. Vinylacetic acid (8.36 g, 0.097 mol) in dichloromethane (100 mL, washed with saturated aqueous $NaHCO_3$) was stirred at room temperature. A solution of dicyclohexylcarbodiimide (9.60 g, 0.046 mol) in dichloromethane (200 mL, washed with saturated aqueous $NaHCO_3$) was added dropwise over a period of 6 h. Analysis by gas chromatography suggested complete conversion to one major product. The reaction mixture was filtered to remove the large quantities of urea produced, and excess solvent was removed *in vacuo*. As the urea was slightly soluble in the product and dichloromethane, ether was added to precipitate the remaining quantities. The resulting suspension was refiltered, and excess solvent was removed *in vacuo*, affording the product as a yellow oil (4.94 g, 70%): $\nu_{\max}$ (neat) 1821, 1752 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 5.90 (m, 1H), 5.27 (m, 1H), 5.21 (dq, 1H, *J* = 7.4, 1.4 Hz), 3.23 (dt, 2H, *J* = 6.8, 1.4 Hz).

Preparation of *N*-(ω-Alkenoyl)indole 3i. Vinylacetic acid anhydride (2.67 g, 0.017 mol) in dry THF (30 mL) was stirred in an ice bath. A solution of indole (2.10 g, 0.017 mol) and NaH (1.20 g, 0.050 mol) in dry THF (20 mL) was added dropwise over a period of 15 min. Analysis by gas chromatography suggested that incomplete conversion to one product had occurred with large quantities of indole remaining in solution. A further quantity of indole (3.90 g) and NaH (2.0 g) in dry THF (35 mL) was added dropwise to fully consume all of the vinylacetic acid anhydride present. The reaction mixture was quenched carefully using distilled water (50 mL) and extracted with ether (3 × 50 mL). The organic layers were combined, dried ($MgSO_4$), and filtered, and solvent was removed *in vacuo*, affording a brown oil (7.82 g). Since separation of **3i** from indole was difficult, small quantities were purified as needed using preparative thin-layer chromatography (typically 100 mg applied to five preparative silica gel plates and eluted three times using 95% hexanes/5% diethyl ether). This afforded **3i** as a clear, colorless oil (1.15 g total, 73%): m/e 185, 117 (100), 89, 63; HRMS calcd for $C_{12}H_{11}NO_2$ 185.0840, found 185.0835; ^{1}H-NMR (benzene-d_6) δ 8.82 (d, 1H, *J* = 8.2 Hz), 7.42 (m, 1H), 7.19 (m, 2H), 6.67 (d, 1H, *J* = 3.8 Hz), 6.25 (d, 1H, *J* = 3.8 Hz), 5.87 (m, 1H), 4.90 (m, 2H), 2.87 (dt, 2H, *J* = 6.5, 1.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 169.8, 134.7, 130.8, 130.3, 125.7, 125.1, 124.3, 121.3, 117.1, 109.9, 120.0, 41.3.

Photolysis of *N*-(ω-Alkenoyl)indole 3h (>300 nm). A solution of *N*-(ω-alkenoyl)indole **3h** (24 mg) in benzene (2 mL) was placed in a Pyrex NMR tube, purged with N_2, sealed, and irradiated using a medium-pressure Hg vapor lamp for 7 h.

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(36) Duhaime, R.; Lombardo, D. A.; Skinner, I. A.; Weedon, A. C. *J. Org. Chem.* **1985**, *50*, 873.

(37) Linstead, R. P. *J. Chem. Soc.* **1933**, 560.

Analysis by gas chromatography suggested 55% conversion to two products in a 1:5 ratio.

Analysis using gas chromatography/mass spectrometry suggested the minor product formed was indole (confirmed by GC coinjections with authentic samples): *m/e* 117 (100), 90, 63. The major product formed was identified as the *cis-N*-(ω-alkenoyl)indole **3l**: *m/z* 185, 117 (100), 89, 69. Analysis of the irradiation mixture by ^{1}H-NMR spectroscopy showed a "doubling" of many of the signals of **3h**. For example, the Me group of **3h** at 2.02 (dd, 3H, $J = 6.9, 1.7$ Hz) was adjacent to a new Me group of **3l** at 2.15 (dd, 3H, $J = 7.0, 1.6$ Hz).

Quantum Yield of Isomerization of 3h. A stock solution was prepared consisting of *N*-(ω-alkenoyl)indole **3h** (35.7 mg), pentadecane (14.3 mg), and cyclopentene (377 mg; 1.11 M) in benzene (5.00 mL). A 3.00-mL aliquot was added to a quartz irradiation cuvette, degassed *via* the freeze-pump-thaw technique three times (10^{-4} Torr), and irradiated at 295 nm (bandwidth 10 nm) using a PTI quantacount apparatus. The irradiated sample was analyzed by gas chromatography; a minimum of five injections were carried out in order to establish limits of error. Peak areas were compared with that of an internal standard (pentadecane) and calibration curves constructed to obtain values for absolute amount of product produced. The quantum yields obtained were as follows: $\Phi_{\text{isomerization}} = 0.068 \pm 0.006$; $\Phi_{\text{cycloaddition}} = 0$; $\Phi_{\text{indole}} = 0.008 \pm 0.001$.

Photolysis of *N*-(ω-Alkenoyl)indole 3i (>300 nm). A solution of *N*-(ω-alkenoyl)indole **3i** (20 mg) in benzene (2 mL) was purged with N_2 in a Pyrex NMR tube, sealed, and irradiated using a medium-pressure Hg vapor lamp for 41 h. Analysis by gas chromatography suggested 47% conversion to two products.

Purification using preparative thin-layer chromatography (silica gel; 90% hexanes/10% ether) yielded three fractions: the first (0.2 mg) was identified as indole (confirmed by GC coinjections with authentic samples); the second (6.0 mg) was identified as *N*-(ω-alkenoyl)indole **3i** (confirmed by GC coinjections with authentic samples); the third fraction was identified as intramolecular cycloadduct **17a** (4.0 mg), isolated as a clear, colorless oil. For **17a**: *m/e* 185, 156, 130, 117 (100), 89; HRMS calcd for $C_{12}H_{11}NO_2$ 185.0840, found 185.0836; ^{1}H-NMR ($CDCl_3$) δ 7.50 (d, 1H, $J = 7.7$ Hz), 7.18 (m, 3H), 4.84 (dt, H$_a$, $J_{ab} = J_{ae} = 5$ Hz, $J_{ad} = 2$ Hz), 3.48 (dt, H$_b$, $J_{ab} = J_{bc} = 5$ Hz, $J_{bd} = 9$ Hz), 3.17 (m, 1H), 2.95 (m, 2H), 2.34 (d, 1H, $J = 17.0$ Hz), 1.87 (dt, 1H, $J = 6, 6, 12$ Hz); ^{13}C-NMR ($CDCl_3$) δ 162.0, 147.5, 139.7, 128.3, 126.3, 124.6, 119.2, 71.0, 39.1, 32.2, 41.3, 35.3.

Photolysis of *N*-(ω-Alkenoyl)indole 3j. A solution of *N*-(ω-alkenoyl)indole **3j** (19 mg) in benzene (1 mL) was purged with N_2 in a Pyrex NMR tube, sealed, and irradiated using a medium-pressure Hg vapor lamp for 25 h. Analysis by gas chromatography suggested 70% conversion to one product. The mixture was purified using preparative thin-layer chromatography (silica gel; 70% hexanes/30% ether) which afforded two fractions: the upper band was identified as *N*-(ω-alkenoyl)indole **3j** (3 mg, confirmed by GC coinjections with authentic samples), while the lower band was identified as intramolecular cycloadduct **18a** (9.1 mg, 48% yield), isolated as a clear, colorless oil. For **18a**: *m/z* 199, 130, 117 (100); exact mass calculated 199.0997, observed, 199.0996; ^{1}H-NMR ($CDCl_3$) δ 7.81 (d, 1H, $J = 7.8$ Hz), 6.95 (m, 3H), 4.55 (dt, H$_a$, $J_{ab} = J_{ae} = 7$ Hz, $J_{ad} = 3$ Hz), 3.55 (q, H$_b$, $J_{ab} = J_{bd} = J_{bc} = 7$ Hz), 2.99 (m, H$_e$, $J_{ae} = J_{de} = 7$ Hz, $J_{ce} = 8$ Hz), 2.80 (ddt, H$_d$, $J_{de} = J_{bd} = 7$ Hz, $J_{cd} = 12$ Hz, $J_{ad} = 3$ Hz), 2.34 (m, 1H), 2.15 (m, 2H), 1.84 (ddd, H$_e$, $J_{bc} = 7$ Hz, $J_{cd} = 11$ Hz, $J_{ce} = 8$ Hz), 1.47 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 172.2, 146.3, 137.0, 128.1, 124.8, 124.2, 118.1, 64.2, 38.9, 30.7, 38.1, 35.7, 27.7. Repetition of the reaction in the presence of acetophenone (100 mg), using 275 mg of **3j** gave adduct **18a** (225 mg, 82%) after irradiation (medium-pressure mercury lamp filtered through Pyrex) for 80 h.

Ethanolysis/Acylation of Intramolecular Adduct 18a. Adduct **18a** was dissolved in absolute EtOH (30 mL) containing 1 M H_2SO_4. The solution was refluxed for 14 h, cooled to room temperature, neutralized with 3 M aqueous NaOH (pH 8), and diluted with distilled water (25 mL). The products were extracted into dichloromethane (2 × 50 mL); the combined organic layers were dried (Na_2SO_4) and filtered, and the solvent was removed *in vacuo*. The residue was immediately dissolved in dichloromethane (20 mL). Pyridine (100 mg) and acetyl chloride (2.0 g) were added rapidly and the solution was stirred for 2.5 h. The reaction mixture was diluted with distilled water (30 mL) and the products were extracted into dichloromethane (2 × 50 mL). The organic layers were combined, dried (Na_2SO_4), and filtered, and the solvent was removed *in vacuo*, affording a brown oil (42 mg). This was purified by preparative thin-layer chromatography (silica gel; 40% hexanes/60% ether) to give two fractions. The less-polar fraction (5 mg) was identified as **18a** (confirmed by GC coinjection with authentic samples). The more-polar fraction (10.3 mg) was identified as **20a**: *m/z* 287, 200, 159, 117 (100); exact mass calcd 287.1521; obsd 287.1517; ^{1}H-NMR ($CDCl_3$) δ 8.25 (d, 1H, $J = 8.1$ Hz), 7.10 (m, 3H), 4.89 (t, H$_a$, $J_{ab} = J_{ae} = 7$ Hz), 4.07 (q, 2H, $J = 7$ Hz), 4.03 (br m, H$_b$, $J_{ab} = 7$ Hz, $J_{bc} = 7$ Hz, $J_{bd} = 4$ Hz), 2.77 (m, H$_e$, $J_{ae} = 7$ Hz, $J_{ce} = 7$ Hz, $J_{de} = 4$ Hz), 2.72 (dt, H$_c$, $J_{bc} = 7$ Hz, $J_{cd} = 11$ Hz, $J_{ce} = 7$ Hz), 2.18 (s, 3H), 2.12 (m, 2H), 1.80 (m, 1H), 1.65 (dt, H$_d$, $J_{bd} = 4$ Hz, $J_{cd} = 11$ Hz, $J_{de} = 4$ Hz), 1.47 (m, 1H), 1.21 (t, 3H, $J = 7$ Hz); ^{13}C-NMR ($CDCl_3$) δ 173.9, 169.7, 145.5, 137.5, 128.8, 125.1, 125.0, 118.2, 61.3, 61.2, 39.7, 39.3, 32.9, 31.8, 26.9 , 26.9, 15.1.

Sensitized Photolysis of *N*-(ω-Alkenoyl)indole 3k (>300 nm). A solution containing *N*-(ω-alkenoyl)indole **3k** (65 mg) and acetophenone (110 mg) in benzene (1 mL) was purged with N_2 and placed in a Pyrex NMR tube which was sealed and irradiated using a medium-pressure Hg vapor lamp for 110 h. Analysis by gas chromatography suggested 60% conversion to several products. Purification using preparative thin-layer chromatography (silica gel; 80% hexanes/20% ether) afforded a less-polar fraction which was identified as *N*-(ω-alkenoyl)indole **3k** (10 mg, confirmed by GC coinjection with authentic samples), and a more-polar fraction identified as the intramolecular adduct **19a** (14 mg). For **19a**: *m/z* 213, 130, 117 (100); exact mass calcd 213.11536; obsd 213.11538; ^{1}H-NMR ($CDCl_3$) δ 8.14 (dd, 1H, $J = 8.0, 0.5$ Hz), 7.15 (m, 3H), 4.78 (ddd, H$_a$, $J_{ab} = 8$ Hz, $J_{ae} = 6$ Hz, $J_{ad} = 3$ Hz), 3.85 (q, H$_b$, $J_{ab} = J_{bc} = J_{bd} = 8$ Hz), 2.80 (m, 2H), 2.48 (m, 2H), 2.20 (m, 1H), 1.75 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 171.1, 144.3, 136.8, 127.7, 123.8, 123.7, 116.9, 62.1, 37.3, 34.7, 35.3, 35.2, 28.1, 21.8.

General Procedure for the Photolysis of N-(ω-Alkenoyl)-indoles 3i–k with Cyclopentene (>300 nm). Solutions of each of the *N*-(ω-alkenoyl)indoles **3i–k** (20 mg) and cyclopentene (2 M, 1.3 M, and 1.5 M for **3i–k**, respectively) in benzene (2 mL) were placed in Pyrex NMR tubes, purged briefly with N_2, sealed, and irradiated using a medium-pressure Hg vapor lamp for 41, 17, and 18 h, respectively (the photolysis of **3j** was sensitized using 20 mg of acetophenone to avoid photo-Fries rearrangement products). Analysis by gas chromatography suggested conversions of **3i–k** of 48, 57, and 50%, respectively. Analysis by gas chromatography and coinjections with authentic samples, revealed that the irradiated mixtures contained small quantities of indole and the *N*-(ω-alkenoyl)indoles **3i–k**, as well as intramolecular cycloadducts **17a** (39% of adduct total), **18a** (91% of adduct total), and **19a** (19% of adduct total) and intermolecular cyclopentene adducts **21b** and **22b** (61% of adduct total), **21c** and **22c** (9% of adduct total), and **21d** and **22d** (81% of adduct total). The identity of each diastereomeric pair of cyclopentene adducts was tentatively assigned using gas chromatography/mass spectrometry; this was confirmed by hydrolysis and comparison with authentic samples of **11** and **12** using the method of Hastings and Weedon.[8] For **21b and 22b**: *m/z* 253, 185, 117 (100). For **21c** and **22c**: *m/z* (CI/MS) 268, 199, 117 (100). For **21d** and **22d**: *m/z* 281, 213, 117 (100), 91.

Sensitized Photolysis of *N*-Acetylindole and Ethyl 4-Pentenoate . A solution was prepared consisting of *N*-acetylindole (218 mg), acetophenone (360 mg), octadecane (55 mg), and ethyl 4-pentenoate (303 mg) in benzene (3 mL). The solution was placed in a Pyrex tube, purged with N_2, sealed, and irradiated using a medium pressure Hg vapor lamp for 120 h. Analysis by gas chromatography suggested 40% conversion to at least three products in the ratio 0.3:3.9:95.8 (listed in order of elution). The solvent was removed under reduced pressure and the residue was purified by column chromatography (75 g silica gel eluted using 80% hexanes/20% ether) to yield two fractions: the first was a mixture of acetophenone and *N*-acetylindole (200 mg total, identification confirmed by GC coinjections with authentic samples), while the second was identified as a 1:2 mixture of the diastereomeric mixture (95.8% of product mixture) of the head-to-tail cycloadducts **20a** and **20b** (98 mg). These had *m/z* 287, 200, 159, 117 (100). Exact mass: calculated, 287.1521; observed, 287.1520. Because the diastereomers were in an approximately 2:1 ratio, it was possible to assign the signals of each in the NMR spectra separately. **20a** (minor): ^{1}H-NMR (CDCl$_3$) δ 8.23 (d, 1H, J = 7.8 Hz), 7.12 (m, 3H), 4.74 (m, 1H), 4.12 (q, 2H, J = 7.2 Hz), 3.65 (m, 1H), 2.33 (m, 5H), 2.11 (s, 3H), 1.98 (m, 2H), 1.24 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (CDCl$_3$) δ 173.1, 168.1, 144.4, 136.6, 128.1, 126.3, 122.1, 117.7, 60.3, 35.2, 34.7, 31.6, 27.2, 55.5, 44.7, 34.7, 23.7, 14.1. **20b** (major): ^{1}H-NMR (CDCl$_3$) δ 8.23 (d, 1H, J = 7.8 Hz), 7.12 (m, 3H), 4.74 (m, 1H), 4.12 (q, 2H, J = 7.2 Hz), 3.65 (m, 1H), 2.33 (m, 5H), 2.11 (s, 3H), 1.98 (m, 2H), 1.24 (t, 3H, J = 7.2 Hz); ^{13}C-NMR (CDCl$_3$) δ 173.0, 168.5, 143.8, 134.5, 127.8, 124.1, 124.0, 117.3, 60.4, 35.2, 34.5, 32.1, 31.5, 56.7, 46.2, 40.7, 23.7, 14.1. Further purification of this mixture using preparative thin-layer chromatography (six plates eluted 3× using 25% hexanes/75% ether) yielded a pure sample of **20b** as a glass and a mixture of **20a** and **20b** enriched in the former.

General Procedure for Quantum Yield of Formation of Intramolecular Cycloadducts 17–19. Solutions of the *N*-(ω-alkenoyl)indoles **3i–k** were prepared in benzene, and pentadecane or heptadecane was added as an internal standard. Some solutions also contained cyclopentene and some contained acetophenone as a triplet sensitizer. Aliquots (3.00 mL) of these solutions were pipetted into quartz irradiation cuvettes and degassed three times *via* the freeze-pump-thaw method to a residual pressure of 10^{-4} Torr. Samples were irradiated for a known period of time with ultraviolet light of known intensity and of wavelength 315–325 nm (direct) or 330–340 nm (sensitized) in a PTI Quantacount apparatus. Reactions were taken to 2–5% conversion. Subsequent analysis by gas chromatography allowed determination of absolute amounts of products formed.

Supplementary Material Available: Copies of ^{1}H-NMR spectra of **3a–f, 3f** and **3g, 3h–k, 4b, 4c, 17a, 18a, 19a, 20a,** and **21b** (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.