CASE studentships, and Drs. J. W. Daly and T. Spande (NIH) for a preprint of ref 2c. A.L.S. is the recipient of a Sidney Sussex College research studentship.

Registry No. (±)-**3**·HCl, 130884-95-6; (±)-**4**, 118015-96-6; (±)-**4**·HCl, 130979-70-3; (±)-**5**, 117982-91-9; (±)-**5**·HCl, 130979-71-4; (−)-**6**, 117959-79-2; (−)-**6**·HCl, 131319-70-5; (±)-**6**·HCl, 130979-72-5; **7b**, 117959-91-8; (*E*)-**8a**, 87830-32-8; (*Z*)-**8a**, 87830-48-6; (*E*)-**8b**, 130884-96-7; (*Z*)-**8b**, 130885-07-3; (±)-**10b**, 117959-94-1; **10d**, 117960-10-8; (±)-**11a**, 117959-84-9; (±)-**11a**·$C_2H_2O_4$, 130884-97-8; (±)-**11b**, 117959-95-2; (±)-**11b**·$C_2H_2O_4$, 130884-99-0; (+)-**11d**, 117960-11-9; (±)-**12a**, 117959-85-0; (±)-**12b**, 130885-01-7; (+)-**12d**, 117960-12-0; (±)-**13a**, 117959-86-1; (±)-**13b**, 117959-97-4; **13d**, 117960-13-1; **14**, 107-87-9; (*E*)-**15**, 65457-34-3; (*Z*)-**15**, 65457-31-0; (*E*)-**16**, 130885-00-6; (*Z*)-**16**, 130885-06-2; (±)-**17**, 117959-87-2; (±)-**19**, 117959-89-4; (±)-8-epi-**19**, 130979-79-2; **21**, 5323-87-5; **22**, 22627-45-8; (±)-**23**, 117959-90-7; (±)-**24b**, 117959-98-5; **24d**, 117960-14-2; (±)-**25b**, 118015-97-7; **25d**, 118016-00-5; (±)-**26b**, 118015-98-8; **26d**, 118016-01-6; (±)-**27b**, 117959-99-6; **27d**, 117960-15-3; (±)-**28**, 130885-02-8; (±)-**29**, 130885-03-9; **30**, 17342-08-4; **31**, 51693-17-5; **32**, 118015-99-9; **33**, 117960-00-6; **34**, 117960-01-7; **35**, 117960-02-8; **36**, 117960-03-9; *cis*-**37**, 130885-04-0; *trans*-**37**, 130979-76-9; **38**, 117960-05-1; **39**, 130885-05-1; **40**, 117960-06-2; **41**, 130979-73-6; **42** (isomer 1), 130979-74-7; **42** (isomer 2), 130979-75-8; **42** (isomer 3), 130979-77-0; **42** (isomer 4), 130979-78-1; $AcO(CH_2)_4OH$, 35435-68-8; $AcO(CH_2)_3CHO$, 6564-95-0; $Br(CH_2)_2CH{=}CH_2$, 5162-44-7.

Supplementary Material Available: NMR spectra for compounds **15**, **16**, **13a**, **19**, **3**·HCl salt, **29**, **12b**, **13b**, **25b**, **26b**, **4**, **5**·HCl salt, **6**·HCl salt, **33**, **34**, **37**, **38**, **39**, **40**, **41**, **42**, **10d**, **11d**, **12d**, **13d**, **24d**, and **6** (51 pages). Ordering information is given on any current masthead page.

Photochemically Induced Radical Cation Diels–Alder Reaction of Indole and Electron-Rich Dienes[1]

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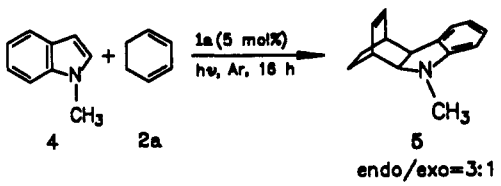
Diels–Alder reactions between indole (**3**) and substituted cyclohexa-1,3-dienes (**2**) can be effected by a photoinduced catalyzed electron transfer reaction using catalytic amounts of triarylpyrylium tetrafluoroborates (**1**) as sensitizers and an acid chloride as a trapping agent. Irradiation generates *N*-acyl-1,4,4a,9a-tetrahydro-1,4-ethanocarbazoles in one step. The products are formed with nearly total regioselectivity, such that a substituent in the 1-position of the cyclohexa-1,3-diene is always found in the 1-position of the tetrahydrocarbazole, and a substituent in the 2-position of the diene always appears in the 3-position of the product.

Introduction

Complex indole compounds often show broad and rich physiological activity. The indole nucleus of such compounds usually must be *constructed* in the course of a synthesis. Because it would be economically attractive to develop a synthesis of indole compounds starting from an *existing* indole nucleus, attempts[2] have been made to use the 2,3-double bond of indole (**3**) in stereoselective cycloaddition reactions of the Diels–Alder type. However, electron-rich indole shows only a low tendency to act as a dienophile. Its use mainly has been limited to reactions with electron-poor heterodienes such as tetrazine derivatives or tetrachlorothiophene 1,1-dioxide, in so-called Diels–Alder reactions with inverse electron demand.[3] The indole 2,3-double bond can act as a dienophile in "normal" Diels–Alder reactions, if electron-withdrawing groups are present in the 2- and 3-positions.[4] However, high temperatures (195–200 °C) and long reaction times are necessary. On the other hand, indole acrylates have been employed in Diels–Alder reactions as *electron-poor dienes*.[5,6] The indole nucleus has also been used as a link joining diene and a dienophile in intramolecular Diels–Alder reactions.[7]

We report here a Diels–Alder reaction in which indole, as the electron-rich dienophile, undergoes cycloaddition with electron-rich dienes by a photochemically induced catalyzed electron transfer reaction. As we reported earlier,[8] photoexcited triphenylpyrylium tetrafluoroborate (**1a**) can be used as the catalyst.

Scheme I



Results and Discussion

Irradiation of salt **1a**, cyclohexa-1,3-diene (**2a**), and either indole (**3**) or *N*-methylindole (**4**) in dichloromethane

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(1) Presented in part at the 32nd Congress of the International Union of Pure and Applied Chemistry, Stockholm, Sweden, 2–7 Aug 1989.

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(6) Magnus, P.; Gallagher, T.; Brown, P.; Pappalardo, P. *Acc. Chem. Res.* **1984**, *17*, 35. Exon, C.; Gallagher, T.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 4739.

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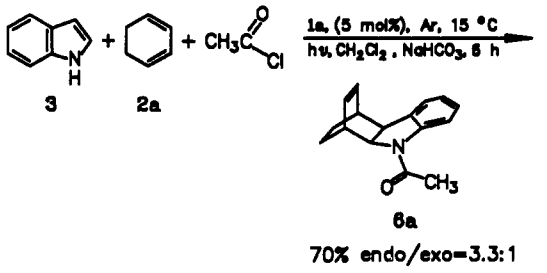
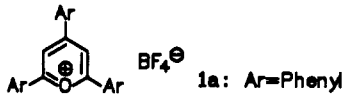
Scheme II



at $\lambda \geq 345$ nm for up to 16 h gave low (<9.5%) yields of Diels–Alder products (Scheme I). Gas chromatography/mass spectrometry (GC/MS) showed that the reaction started with a fast rate and then progressively slowed with increasing product formation. Presumably, the



photoexcited pyrylium salt **1a** (calculated oxidation potential, E° = 2.53 V vs NHE)[9] was quenched by the relatively easily oxidized Diels–Alder products, if the latter were present in higher concentrations. The tetrahydroethanocarbazole **5**, the expected Diels–Alder product of *N*-methylindole (**4**) and cyclohexa-1,3-diene (**2a**), in fact had an $E_{p_{ox}}$ (determined by cyclic voltammetry) of 0.7 V, much lower than that of the photoexcited salt **1a** (E° = 2.53 V), indole (**3**) ($E_{p_{ox}}$ = 1.31 V), or *N*-methylindole (**4**) ($E_{p_{ox}}$ = 1.28 V). Separate photolysis experiments with Diels–Alder product **5** showed that it was stable under the reaction conditions and that no retro-Diels–Alder reaction took place.

It seemed obvious that the reaction could go to completion if it were possible to trap the products by transforming them to compounds that were more difficult to oxidize than the starting indoles. This proved possible, in a very effective way, by in situ N-acetylation (acetyl chloride/$NaHCO_3$). Thus, in the presence of acetyl chloride, irradiation of salt **1a**, cyclohexa-1,3-diene (**2a**), and indole (**3**) gave the N-acetylated Diels–Alder product **6a** in 70% yield after 6 h (Scheme II). Cyclic voltammetry showed that **6a** ($E_{p_{ox}}$ = 1.54 V vs NHE) was indeed more difficult to oxidize.

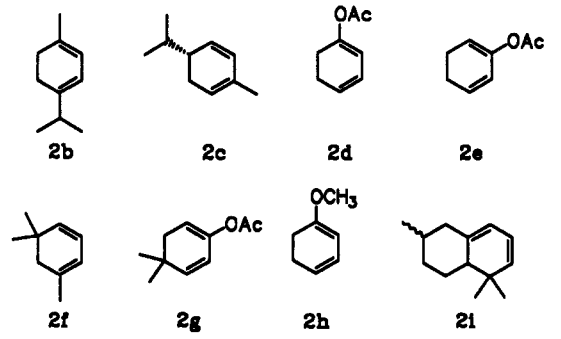
Control experiments showed that reaction did not occur without irradiation or in the absence of salt **1a**. Under such conditions the starting materials only decomposed slowly. Also, *N*-acetylindole was not formed under the reaction conditions. Irradiation of *N*-acetylindole and cyclohexa-1,3-diene (**2a**) in the presence of salt **1a** gave only traces of Diels–Alder product. Irradiation of a mixture of **1a**, **2a**, and **3** in the absence of acetyl chloride gave only small amounts of the N-unsubstituted Diels–Alder product. Addition of acetyl chloride to the reaction mixture in the *dark* transformed the N-unsubstituted Diels–Alder product spontaneously into **6a**. Therefore, the Diels–Alder reaction takes place between the two electron-rich components, indole (**3**) and the 1,3-diene, in the sense of a redox pole reversal or "umpolung", and acetylation occurred in a second step, with formation of an electron-poor, oxidation-resistant product.

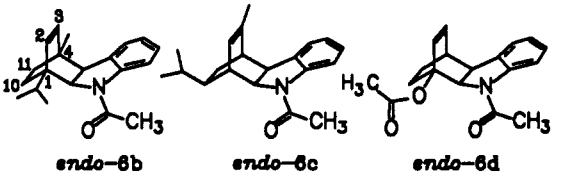
The results of a number of photochemically induced Diels–Alder reactions between indole (**3**) and substituted cyclohexa-1,3-dienes (**2a–f**) in the presence of acetyl chloride to yield adducts **6a–f** are summarized in Table I. Compound **2g** and indole (**3**) and compound **2i** and indole (**3**) after 8 and 10 h irradiation, respectively, yielded the expected products in only low yield. Reaction of **2h** was not successful because it was unstable under the reaction conditions. In contrast to the cyclohexa-1,3-dienes **2a–f**, open-chain 1,3-dienes without a rigid s-cis conformation of the double bonds gave only low yields of the Diels–Alder products.

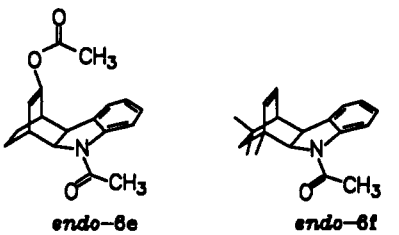
Table I. Results of the Photochemically Induced Diels–Alder Reaction of Indole (3) and Dienes 2a–f with Triarylpyrylium Tetrafluoroborates 1a,b as Sensitizers under Standard Conditions[a]

diene 2	sensitizer 1 (mol %)	t,[b] h	product 6 (yield, %)	endo:exo
2a	**1a** (5)	6	**6a** (70)	3.3:1
2b	**1a** (5)	8	**6b** (43)	1.7:1
2c	**1a** (5)	8	**6c** (57)	2.4:1
2c[c]	**1b** (5)	8	**6c** (67)	4.6:1
2d	**1a** (5)	8	**6d** (31)	2.3:1
2e	**1a** (5)	8	**6e** (59)	3:1
2f	**1a** (2.5)	18	**6f** (23)	endo

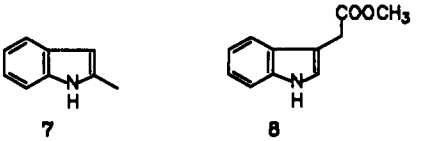
[a] Standard conditions: mixture of 2.5–5 mol % of **1**, 4 mmol of **2**, 2 mmol of **3**, 2 mmol of acetyl chloride, and 350 mg of $NaHCO_3$ in oxygen-free CH_2Cl_2 irradiated at 15 °C with a 450-W xenon lamp ($\lambda \geq 345$ nm). [b] Irradiation time. [c] Irradiation with a 250-W halogen lamp.





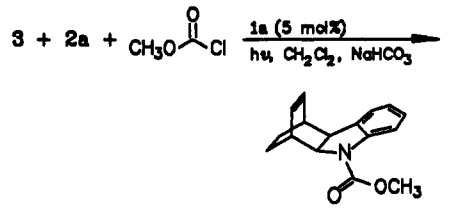


Substituted indoles were relatively unreactive, perhaps because of steric factors. Thus, 2-methylindole (**7**) and cyclohexa-1,3-diene (**2a**) did not react at all under standard conditions. The 3-substituted indoleacetate **8** and **2a** did give a Diels–Alder product, but in low yield.



(9) The oxidation potential of excited **1a** was calculated on the basis of the reduction potential of ground-state **1a** and the excitation energy of the 0 → 0 transition (from the fluorescence spectrum): Martiny, M. Ph.D. Thesis, University of Bonn, 1990.

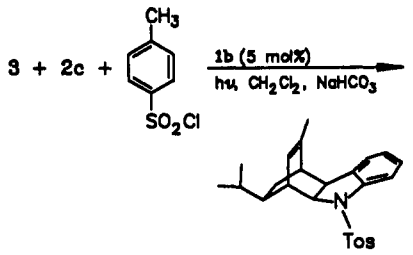
Scheme III



9a

(33 %; endo/exo=4:1)

Scheme IV



10c

(46 %; endo/exo=2.2:1)

In the successful reactions, usually only one regioisomer was formed, as a mixture of the endo and exo diastereomers in ratios of between 2:1 and 4.6:1. In very few cases, small amounts of other isomers could be detected.

Furthermore, it appeared to be possible to improve yields. For example, halogen lamp irradiation of indole (**3**) and diene **2c** in the presence of tris(4-methoxyphenyl)pyrylium tetrafluoroborate (**1b**) gave adduct **6c** in 67% yield, as compared to 57% yield under standard conditions.

1b: Ar=4–Methoxyphenyl

Reaction occurred with total regioselectivity. Thus, a substituent in the 1-position of the cyclohexa-1,3-diene was always found in the 1-position of the tetrahydroethanocarbazole product, while a substituent in the 2-position of the diene was always found in the 3-position of the product.

The possibility existed that [2 + 2] cycloaddition occurred along with the expected [2 + 4] cycloaddition. For example, the electron transfer catalyzed Diels–Alder reaction of enamides and cyclohexa-1,3-dienes was reported[10] to give vinylcyclobutanes as [2 + 2] cycloaddition products. However, in the present case, continuous GC/MS monitoring of the reaction gave no indication of the presence of [2 + 2] adducts.

The Diels–Alder products could be trapped not only with acetyl chloride but also by methyl chloroformate, thus introducing a protecting group that was easier to remove. In the case of the reaction between indole (**3**) and **2a**, the *N*-Moc derivative **9a** was formed in 33% yield (86% based on turnover) (Scheme III). *p*-Toluenesulfonyl chloride was also very effective. In the reaction between indole (**3**) and **2c**, with **1b** as catalyst, the tosyl amide **10c** was produced in 46% yield (endo:exo = 2.2:1) (Scheme IV). Benzoyl chloride appeared to be ineffective. The expected *N*-benzoyl derivatives were produced in such low yields that they were not isolated and were characterized only by GC/MS.

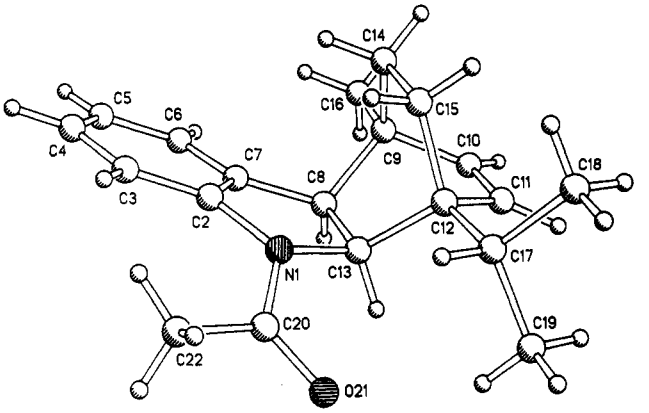


Figure 1. Molecular structure of *exo*-**6b**.

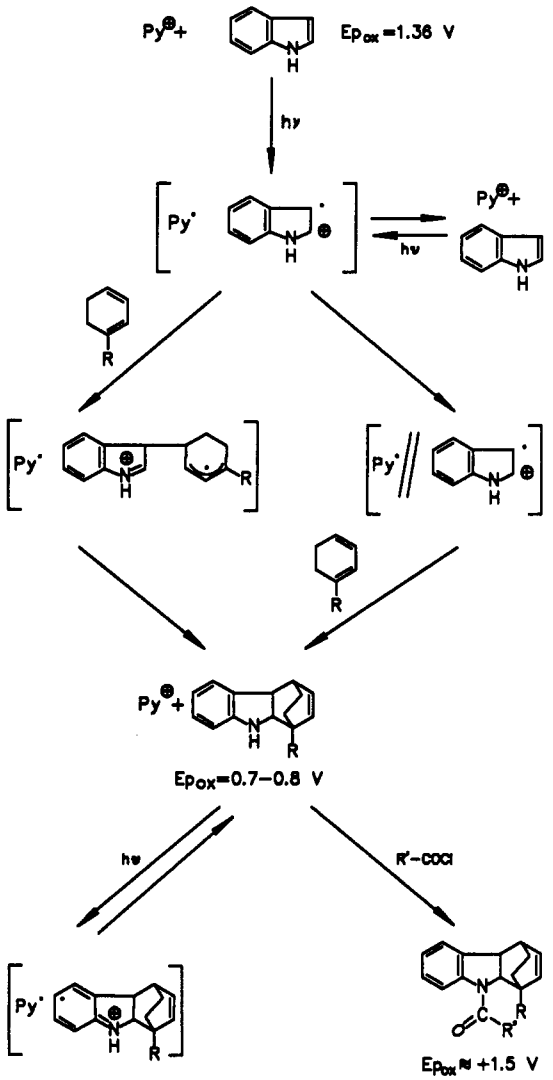
It appears that compounds **6a–f**, **9a**, and **10f** can be useful synthetic building blocks because the olefinic double bond can be readily cleaved. For example, in the case of **6e**, the enol acetate can be hydrolyzed (methanolic potassium hydroxide) to the corresponding ketone. Baeyer–Villiger oxidation of the ketone would lead to a lactone and, eventually, a hydroxy acid.

Mass spectrometry, ^1H and ^{13}C NMR spectroscopy, and X-ray crystallography were employed for structure elucidation. The determination of configuration and regiochemistry, as well as the differentiation between [2 + 4] and possible [2 + 2] products, could be accomplished by NMR methods, especially 2D techniques. The NMR spectra were especially complex because the *N*-acetyltetrahydroethanocarbazoles were usually present as two rotamers arising from hindered rotation around the amide bond. Consequently, double signals appeared in both the ^1H and ^{13}C spectra. In the ^1H NMR spectra, signals due to protons H-8, H-1, H-9a, and H-4a were influenced by rotamer formation. In the case of *endo*-**6c**, the existence of two rotamers was inferred from the temperature dependence of the ^1H NMR spectrum. Signal coalescence occurred at 61 °C. Due to the effect of substituents in the 1-position of the carbazole ring, compounds **6d** and **6f** showed signal coalescence at room temperature. That the amide carbonyl group of **6b** was fixed in a trans position was inferred from the observation that proton H-9a, not proton H-8, showed a low-field shift. The X-ray data for *exo*-**6b** confirmed the regio- and stereochemistry predicted by the NMR spectra and also established the conformation of the amide group. The molecular structure of *exo*-**6b** is shown in Figure 1. The configuration of C-10 of compound **10c**, with the isopropyl group in the exo position, was established by a nuclear Overhauser effect (NOE) experiment. 2D-NMR permitted the correlation of signals with the responsible hydrogen or carbon atom. The ^1H NMR spectra were useful for differentiating between endo and exo products. The olefinic proton signals of the endo compounds showed a smaller downfield shift than those of the exo compounds, while the signals due to the ethano-bridge protons of the endo compounds showed a larger downfield shift than those of the exo compounds. The mass spectra of the compounds all showed a significant molecular ion and were characterized by retro-Diels–Alder fragmentation.

That an indole cation radical is involved in the reaction is supported by several facts. Cyclohexadiene dimers were formed in low (always <10%) yields. The oxidation potential of indole (**3**) is much lower than that of cyclohexa-1,3-diene (**2a**) and salt **1a**; hence the former can more

(10) Bauld, N. L.; Harirchian, B.; Reynolds, D. W.; White, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 8111.

Scheme V



readily be oxidized. The reaction could also be catalyzed by tris(4-bromophenyl)aminium hexachloroantimonate, a well-known initiator of cation radical Diels–Alder reactions.[11] The reaction was quenched if aromatic compounds with oxidation potentials lower than that of indole (**3**) were added to the reaction mixture. Indole (**3**) quenches the fluorescence of salt **1a** with an efficiency that is in agreement with its oxidation potential and with the data given for the fluorescence quenching efficiencies of substituted aromatic compounds, via cation radical formation.[12]

The regioselectivity of the reaction can be explained by a pathway involving radical attack of the 3-position of the indole cation radical on the 4-position of cyclohexa-1,3-diene. As an initial product, a new cation radical is formed, combining the features of an allylic radical favorably stabilized by substituents and an immonium ion (Scheme V).

All the experimental results support a mechanism in which the initial formation of a ternary complex between **1**, **2**, and **3** is rapidly followed by bond formation between the indole cation radical and **2**. Bond formation is immediately followed by back-electron-transfer from the pyranyl radical to form the product. The Diels–Alder adduct is then trapped by the acyl chloride to yield the oxidation-resistant product **6**. Such a "triplex" mechanism (left side of Scheme V) has been proposed[13,14] for similar reactions. In earlier studies,[15] we observed a very high Lewis acidity among excited pyrylium ions. Thus, the complex between **1** and **2** could be described as a Lewis acid complex, a concept also invoked[13] in the case of the 1,4-dicyanonaphthalene- and 9,10-dicyanoanthracene-sensitized Diels–Alder reaction of indene and cyclohexa-1,3-diene. Alternatively, the reaction could involve solvent-separated ion pairs (right side of Scheme V). In this case, however, rapid polymerization of neutral indole molecules induced by indole cation radicals would be expected.

Experimental Section

General Methods. Proton magnetic spectra (^1H and ^{13}C NMR) were recorded in $CDCl_3$. For liquid chromatography at atmospheric pressure (LC), Baker silica gel (30–60 μm) and Woelm SiliTech (63–200 μm) were used. Two Knauer Vertex HPLC columns, one a 2.5 cm × 25 cm preparative column and the other a 0.45 cm × 25 cm analytical column, both packed with 7-μm Lichrosorb Si60, were employed for HPLC. Melting points are uncorrected. Elemental microanalyses were obtained with Perkin-Elmer CH-Analyser 240 or Heraeus CHNO-Rapid instruments or were performed by Microanalytical Laboratory Beller, Göttingen. For photolyses, analytical reagent grade solvents were employed. All other solvents were distilled before use.

Photolyses were performed with a light-source system consisting of an Osram XBO 450 OFR 450-W xenon lamp, a Müller-Elektronik LAX 1450 lamp housing, and an Oriel 5146 long-pass filter. The system was designed for use with wavelengths (λ) greater than 345 nm. For the reaction of **3** and **2c** under sensitization by **1b**, a 250-W halogen lamp (an ordinary slide projector) was employed.

Cyclic voltammetric measurements on acetonitrile solutions containing 0.1 M $LiClO_4$ as electrolyte were made with a system consisting of an Amel 553 potentiostat, a Kontron Messtechnik 8299 programmable function generator, a Hewlett-Packard 7045 XY recorder, a Metrohm EA 875-5 electrolysis cell, a glassy carbon anode (ϕ = 3 mm), a platinum wire cathode, and an $Ag/AgNO_3$ (0.1 M, in CH_3CN) reference electrode.

Sensitizers **1a** and **1b** were prepared according to a literature procedure.[16] Cyclohexadienes **2a–c,h** were obtained commercially. Compound **2f** was prepared by a literature method.[17]

General Procedure for the Synthesis of Acetoxy-Substituted Cyclohexa-1,3-dienes. Compounds **2d**, **2e**, and **2g** were prepared by a modified literature procedure.[18] To 40 mmol of the ketone and 20 mL of isopropenyl acetate were added 3 drops of concentrated H_2SO_4. The mixture was slowly heated under a slow flow of argon in such a way that the acetone formed was distilled off through a short Vigreux column. At the end of the reaction period, sodium carbonate was added and the product was purified by fractional distillation.

1-Acetoxycyclohexa-1,3-diene (2d) and 2-acetoxycyclohexa-1,3-diene (2e): reaction time, 24 h; yield, 4.5 g (82%), bp 79–85 °C (15 Torr). The two isomers were separated by LC (petroleum ether/ethyl acetate, 20:1). Physical constants were in agreement with literature values.[19]

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2-Acetoxy-5,5-dimethylcyclohexa-1,3-diene (2g): reaction time, 8 h; yield, 5.6 g (84%), bp 52 °C (0.15 Torr); ^{1}H NMR (200 MHz) δ 5.63 (1 H, dd, J = 10, 1 Hz, CH=), 5.55 (1 H, dd, J = 10, 1.8 Hz, CH=), 5.27 (1 H, ddd, J = 5.8, 1.8, 1 Hz, CH=), 2.22 (2 H, d, J = 5.8 Hz, CH_2), 2.13 (3 H, s, OCH_3), 1.04 (6 H, s, 2 CH_3); ^{13}C NMR (50 MHz) δ 169.47 (C=O), 145.06 (C=), 140.20 (CH), 120.51 (CH), 110.0 (CH), 36.53 (CH_2), 31.27 (C), 27.74 (2 CH_3), 20.96 (CH_3); EIMS m/z (rel intensity) 166 (12, M^+), 124 (29), 109 (100), 91 (8), 77 (7), 43 (25).

General Procedure for the Photolysis. Indole (3) and diene (**2a–f**) were dissolved in CH_2Cl_2. The solution was transferred to a 50-mL Schlenk tube. Powdered $NaHCO_3$ (350 mg) and the acyl chloride were added. The mixture was purged of oxygen with argon for 15 min. The solid pyrylium salt (1) was added under argon atmosphere. The closed Schlenk tube was placed in a water bath (15 °C) and irradiated. After irradiation, the organic phase was washed with water and dried ($MgSO_4$). The solvent was carefully evaporated. Unreacted starting materials and the very small amount of produced cyclohexa-1,3-diene dimers were separated by bulb-to-bulb (Kugelrohr) distillation (100 °C/0.3–0.1 Torr). Increasing the temperature to ca. 180 °C allowed the cross Diels–Alder products to be separated from the pyrylium salt. Separation of the endo and exo isomers was effected by LC or HPLC.

***N*-Acetyl-1,4,4a,9a-tetrahydro-1,4-ethanocarbazole (6a).** A mixture of 234 mg (2 mmol) of **3**, 320 mg (4 mmol) of **2a**, 40 mg (5 mol %) of **1a**, 157 mg (2 mmol) of acetyl chloride, and 350 mg of $NaHCO_3$ was irradiated for 6 h. Separation by LC (cyclohexane/ethyl acetate, 3:1) gave 335 mg (70%) of **6a** (exo:endo = 1:3.3).

***endo*-6a**: mp 92–94 °C; ^{1}H NMR (200 MHz) δ 7.2–6.9 (4 H, m, H-5, H-6, H-7, H-8), 8.1 (1 H, d, J = 7.8 Hz, H-8 of amide rotamer with carbonyl group cis to aromatic ring), 6.3 (1 H, dd, J = 12, 7 Hz, H-2 or H-3), 5.9 (1 H, dd, J = 12, 6.5 Hz, H-2 or H-3), 4.63 and 4.38 (1 H, 2 dd, J = 9.1, 2.6 Hz, H-9a, two rotamers), 3.66 and 3.52 (1 H, 2 dd, J = 9.1, 2.6 Hz, H-4a, two rotamers), 3.05–2.86 and 3.38 (2 H, m and br, H-1, H-4, two rotamers), 2.3 and 2.36 (3 H, 2 s, amide CH_3, two rotamers), 1.5–1.2 (2 H, m, CH_2-10 or CH_2-11), 1.8–1.5 (2 H, m, CH_2-10 or CH_2-11); ^{13}C NMR (50 MHz) δ 169.07 and 168.77 (amide CO), 144.49 and 143.25 (C-8a or C-4b), 134.42 and 136.63 (C-8a or C-4b), 134.32 and 133.29 (C-2 or C-3), 129.72 and 131.12 (C-2 or C-3), 127.43 and 127.25 (C-7), 124.89 and 123.66 (C-6 or C-5), 123.39 and 123.01 (C-6 or C-5), 116.89 and 113.47 (C-8), 64.41 and 63.75 (C-9a), 46.49 and 44.67 (C-4a), 34.81 and 35.12 (C-1 or C-4), 34.23 and 31.66 (C-1 or C-4), 23.45 and 25.46 (amide CH_3), 22.48 and 22.14 (C-10 or C-11), 23.45 and 23.64 (C-10 or C-11), all signals doubled due to two amide rotamers; EIMS m/z (rel intensity) 239 (8, M^+), 159 (63), 117 (100), 90 (8), 43 (15). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 79.99; H, 7.38; N, 5.83.

***exo*-6a**: mp 92–94 °C; ^{1}H NMR (200 MHz) δ 7.25–6.96 (4 H, m, H-5, H-6, H-7, H-8), 8.22 (1 H, d, J = 7.8 Hz, H-8 of amide rotamer with carbonyl group cis to aromatic ring), 4.23 and 4.48 (1 H, 2 dm, J = 10.4 Hz, H-9a, two rotamers), 3.5 and 3.37 (1 H, 2 dd, J = 10.4, 4 Hz, H-4a, two rotamers), 2.29–2.82 and 3.28 (2 H, m and br, H-1, H-4, two rotamers), 6.55 (1 H, dd, J = 9, 6.5 Hz, H-2 or H-3), 6.28 (1 H, dd, J = 9, 6.5 Hz, H-2 or H-3), 2.26 and 2.44 (3 H, 2 s, amide CH_3, two rotamers), 1.7–0.9 (4 H, m, CH_2-10 and CH_2-11); ^{13}C NMR (50 MHz) δ 169.50 and 168.97 (amide CO), 144.37 and 143.15 (C-8a or C-4b), 132.54 and 134.55 (C-8a or C-4b), 137.02 and 134.69 (C-2 or C-3), 131.77 and 133.41 (C-2 or C-3), 127.82 and 127.25 (C-7), 124.11 and 125.61 (C-6 or C-5), 123.75 and 123.16 (C-6 or C-5), 117.49 and 114.10 (C-8), 63.90 and 63.37 (C-9a), 43.38 and 42.03 (C-4a), 34.09 and 33.51 (C-1 or C-4), 33.29 and 31.73 (C-1 or C-4), 23.61 and 25.47 (amide CH_3), 21.13, 17.72, and 17.10 (C-10 and C-11), all signals doubled due to two amide rotamers; EIMS m/z (rel intensity) 239 (8, M^+), 159 (63), 117 (100), 90 (8), 43 (15). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.08; H, 7.37; N, 5.74.

***N*-Acetyl-1-isopropyl-4-methyl-1,4,4a,9a-tetrahydro-1,4-ethanocarbazole (6b).** A mixture of 234 mg (2 mmol) of **3**, 544 mg (4 mmol) of **2b**, 40 mg (5 mol %) of **1a**, 157 mg (2 mmol) of acetyl chloride, and 350 mg of $NaHCO_3$ was irradiated for 8 h. Separation of isomers by HPLC (petroleum ether/ethyl acetate/dichloromethane, 10:1:1) gave 252 mg (43%) of **6b** (exo:endo = 1:1.7). Only one amide rotamer was formed, with the carbonyl group trans to the aromatic ring.

***endo*-6b**: mp 104–105 °C; ^{1}H NMR (200 MHz) δ 7.03–7.18 (2 H, m, H-4, H-7), 6.95 (1 H, ddd, J = 7.5, 7.5, 1.6 Hz, H-6), 7.31 (1 H, d, J = 8 Hz, H-8), 4.92 (1 H, dd, J = 8.5, 0.8 Hz, H-9a), 3.43 (1 H, d, J = 8.5 Hz, H-4a), 5.98 (1 H, d, J = 8.5 Hz, H-2 or H-3), 5.47 (1 H, d, J = 8.5 Hz, H-2 or H-3), 2.27 (3 H, s, amide CH_3), 1.45–1.7 (2 H, m, CH_2-10 or CH_2-11), 1.1–1.3 (2 H, m, CH_2-10 or CH_2-11), 2.1 (1 H, sep, J = 6.5 Hz, isopropyl CH), 1.05 (3 H, d, J = 6.5 Hz, isopropyl CH_3), 0.98 (3 H, d, J = 6.5 Hz, isopropyl CH_3), 1.45 (3 H, s, CH_3-4); ^{13}C NMR (50 MHz) δ 171.46 (amide CO), 144.51 (C-8a or C-4b), 136.32 (C-8a or C-4b), 137.17 (C-2 or C-3), 132.63 (C-2 or C-3), 126.68 (C-7), 125.07 (C-6 or C-5), 123.06 (C-6 or C-5), 116.05 (C-8), 66.26 (C-9a), 53.26 (C-4a), 44.72 (C-1 or C-4), 37.69 (C-1 or C-4), 24.81 (amide CH_3 or CH_3-4), 24.38 (amide CH_3 or CH_3-4), 33.72 (C-10 or C-11), 25.81 (C-10 or C-11), 29.37 (isopropyl CH), 19.49 (isopropyl CH_3), 19.06 (isopropyl CH_3); EIMS m/z (rel intensity) 295 (2, M^+), 136 (100), 121 (55), 117 (24), 93 (34), 43 (21). Anal. Calcd for $C_{20}H_{25}NO$: C, 81.31; H, 8.53. Found: C, 81.20; H, 8.50.

***exo*-6b**: mp 83–85 °C; ^{1}H NMR (200 MHz) δ 7.18–7.28 and 6.98–7.10 (3 H, 2 m, H-4, H-6, H-7), 7.36 (1 H, d, J = 7 Hz, H-8) 4.73 (1 H, dd, J = 10, 2 Hz, H-9a), 3.24 (1 H, d, J = 10 Hz, H-4a), 6.22 (1 H, d, J = 8.8 Hz, H-2 or H-3), 6.03 (1 H, d, J = 8.8 Hz, H-2 or H-3), 2.35 (3 H, s, amide CH_3), 1.05–1.28 (2 H, m, CH_2-10 or CH_2-11), 0.7–1.05 (2 H, m, CH_2-10 or CH_2-11), 1.81 (1 H, sep, J = 6.6 Hz, isopropyl CH), 1.18 (3 H, d, J = 6.6 Hz, isopropyl CH_3), 0.86 (3 H, d, J = 6.6 Hz, isopropyl CH_3), 1.38 (3 H, s, CH_3-4); ^{13}C NMR (50 MHz) δ 171.94 (amide CO), 144.60 (C-8a or C-4b), 135.34 (C-8a or C-4b), 144.60 (C-2 or C-3), 132.75 (C-2 or C-3), 127.27 (C-7), 125.58 (C-6 or C-5), 123.24 (C-6 or C-5), 116.87 (C-8), 66.23 (C-9a), 49.16 (C-4a), 45.45 (C-1 or C-4), 36.79 (C-1 or C-4), 24.90 (amide CH_3 or CH_3-4), 24.36 (amide CH_3 or CH_3-4), 30.98 (C-10 or C-11), 22.77 (C-10 or C-11), 29.76 (C-14), 19.88 (isopropyl CH_3), 19.16 (isopropyl CH_3). Anal. Calcd for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.38; H, 8.44; N, 4.78.

X-ray Crystallographic Stereostructure Determination of *exo*-6b. Colorless single crystals suitable for the collection of X-ray diffraction data were obtained by recrystallization from a solution of diethyl ether. A crystal having the dimensions 0.30 × 0.20 × 0.10 mm was selected for data collection and mounted on a Nicolet R3m/V automated four-circle diffractometer. The radiation used was MO Kα monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, were as follows: space group, $P2_1/n$, monoclinic; cell constants, a = 752.1 (3) pm, b = 1301.8 (5) pm; c = 1680.5 (7) pm; β = 97.38 (3)°; V = 1.632 (1) nm^3; molecular formula, $C_{20}H_{25}NO$; formula weight, 295.426; formula units per cell, Z = 4; density, d_{calcd} = 1.20 g cm^{-3}; collection range, 3° < 2θ < 54°; ω-scan with scan speed range 3.0–15 deg min^{-1}; total of reflections collected, 5293; unique structure factors, 3560; "observed" reflections with $F > 6\sigma(F)$, 1354; refined parameters, 200; R = 0.084; R_w = 0.065. The structure was solved by the SHELXTL-PLUS direct-methods program. The non-hydrogen atoms were refined anisotropically. The positions of the phenyl hydrogens were calculated for ideal geometry and fixed during refinement. The hydrogens of the methyl and methylene groups were treated as ideal rigid bodies and allowed to rotate around the central C atom during refinement. Hydrogen atoms were entered with a common isotropic temperature factor.[20]

***N*-Acetyl-10-isopropyl-3-methyl-1,4,4a,9a-tetrahydro-1,4-ethanocarbazole (6c).** A mixture of 234 mg (2 mmol) of **3**, 544 mg (4 mmol) of **2c**, 40 mg (5 mol %) of **1a** or 49 mg (5 mol %) of **1b**, 157 mg (2 mmol) of acetyl chloride, and 350 mg of $NaHCO_3$ was irradiated for 7–8 h. Separation of the diastereoisomers by HPLC (*n*-heptane/ethyl acetate/dichloromethane, 10:1:1) gave 336 mg (57%) of **6c** (exo:endo = 1:2.4) with **1a** as sensitizer and 395 mg (67%) of **6c** (exo:endo = 1:4.6) with **1b** as sensitizer.

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(20) The details of the crystal structure of *exo*-**6b** can also be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, upon quoting the depository number CSD-320058, the names of the authors, and the literature citation.

***endo*-6c**: mp 81–83 °C; ^{1}H NMR (400 MHz) δ 7.1 and 7.17 (1 H, 2 d, J = 7.25 Hz, H-5, two rotamers), 6.92 (1 H, dd, J = 7.5, 7.25 Hz, H-6), 7.075 (1 H, dd, J = 7.5, 8.2 Hz, H-7), 8.075 and 6.97 (1 H, 2 d, J = 8.25 Hz, H-8, two rotamers), 4.285 and 4.54 (1 H, 2 dd, J = 9, 2.5 Hz, H-9a, two rotamers), 3.63 and 3.48 (1 H, 2 dd, J = 9, 3 Hz, H-4a, two rotamers), 2.95–3.0 (1 H, m, H-1), 2.66–2.71 (1 H, m, H-4), 5.42–5.5 (1 H, m, H-2), 2.28 and 2.63 (3 H, 2 s, amide CH_3, two rotamers), 1.25–1.4 (1 H, m, H-10), 1.77–1.89 (1 H, m, H-11), 0.96–1.1 (1 H, m, H-11), 1.335 and 1.305 (3 H, 2 s, CH_3-3, two rotamers), 1.1–1.25 (1 H, m, isopropyl CH), 0.89 and 0.79 (3 H, 2 d, J = 6.5 Hz, isopropyl CH_3, two rotamers), 0.83 and 0.77 (3 H, 2 d, J = 6.5 Hz, isopropyl CH_3, two rotamers); ^{13}C NMR (100 MHz) δ 169.08 and 168.72 (amide CO), 144.81 and 143.59 (C-8a or C-4b), 143.07 and 141.75 (C-8a or C-4b), 133.92 and 136.21 (C-3), 119.29 and 120.77 (C-2), 127.34 and 127.12 (C-7), 123.32 and 122.66 (C-6), 123.32 and 124.81 (C-5), 116.79 and 113.45 (C-8), 65.67 and 64.91 (C-9a), 45.63 and 43.91 (C-4a), 43.56 and 43.00 (C-10), 41.05 and 41.43 (C-4), 37.84 and 35.29 (C-1), 32.62 and 32.95 (isopropyl CH), 30.46 and 29.73 (C-11), 23.62 and 25.50 (amide CH_3), 21.32 and 21.25 (CH_3-3), 21.18 (isopropyl CH_3), 20.46 (isopropyl CH_3), most signals doubled due to two amide rotamers; EIMS m/z (rel intensity) 295 (15, M^+), 159 (17), 136 (54), 117 (63), 93 (100), 43 (27). Anal. Calcd for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.43; H, 8.56; N, 4.79.

***exo*-6c**: mp 88–89 °C; ^{1}H NMR (200 MHz) δ 7.3–6.9 (4 H, m, H-5, H-6, H-7, H-8), 8.22 (1 H, d, J = 7.8 Hz, H-8 of second rotamer with carbonyl group cis to aromatic ring), 5.73 (1 H, dm, J = 7 Hz, H-2), 4.23 and 4.7 (1 H, 2 dd, J = 11, 3.4 Hz, H-9a, two rotamers), 3.49 and 3.36 (1 H, 2 dd, J = 11, 4 Hz, H-4a, two rotamers), 2.9–3.0 and 3.27–3.35 (1 H, 2 m, H-1, two rotamers), 2.5–2.64 (1 H, m, H-4), 2.28 and 2.50 (3 H, 2 s, amide CH_3, two rotamers), 1.6–0.83 (4 H, m, CH_2-10, CH_2-11, isopropyl CH), 1.87 and 1.85 (3 H, 2 s, CH_3-3, two rotamers), 0.76 (3 H, d, J = 6.0 Hz, isopropyl CH_3), 0.63 (3 H, d, J = 6.0 Hz, isopropyl CH_3); ^{13}C NMR (50 MHz) δ 169.80 (amide CO), 144.58 (C-8a or C-4b), 145.71 (C-8a or C-4b), 132.68 (C-3), 122.21 (C-2), 127.92 and 130.07 (C-7), 124.06 (C-6 or C-5), 123.92 (C-6 or C-5), 117.68 and 114.24 (C-8), 65.05 and 64.52 (C-9a), 42.67 and 41.16 (C-4a), 39.82 and 38.29 (C-4), 37.51 and 36.96 (C-1 or C-10), 35.72 and 35.43 (C-1 or C-10), 32.86 and 32.64 (isopropyl CH), 28.04 and 27.72 (C-11), 23.67 and 25.42 (amide CH_3), 20.86 (CH_3-3 or isopropyl CH_3), 20.21 (CH_3-3 or isopropyl CH_3), 20.16 (CH_3-3 or isopropyl CH_3); EIMS m/z (rel intensity) 295 (11, M^+), 159 (19), 136 (75), 117 (81), 93 (100), 43 (34); high-resolution MS calcd for $C_{20}H_{25}NO$ (M^+) 295.1936, found 295.1939.

***N*-Acetyl-1-acetoxy-1,4,4a,9a-tetrahydro-1,4-ethanocarbazole (6d).** A mixture of 234 mg (2 mmol) of **3**, 552 mg (4 mmol) of **2d**, 40 mg (5 mol %) of **1a**, 157 mg (2 mmol) of acetyl chloride, and 350 mg of $NaHCO_3$ was irradiated for 8 h. Separation of isomers by LC (cyclohexane/ethyl acetate, 2:1) gave 184 mg (31%) of **6d** (exo:endo = 1:2.3).

***endo*-6d**: mp 126–128 °C; ^{1}H NMR (200 MHz) δ 8.0–7.7 (1 H, br, H-8 of rotamer with carbonyl group cis to aromatic ring), 7.18–6.93 (3 H, m, H-5, H-6, H-7), 4.8–4.55 (1 H, br, H-9a), 3.86 (1 H, dd, J = 9, 3 Hz, H-4a), 3.0 (1 H, m, H-4), 6.14 (1 H, d, J = 9 Hz, H-2), 5.72 (1 H, dd, J = 9, 6.3 Hz, H-3), 2.4 (3 H, s, amide CH_3), 2.12 (3 H, s, acetate CH_3), 2.0–1.5 (4 H, m, H-10, H-11); ^{13}C NMR (50 MHz) δ 171.4 (acetate CH_3), 169.7 (amide CO), 144.7 (C-4b or C-8a), 136.1 (C-4b or C-8a), 131.5 (C-2 or C-3), 130.8 (C-2 or C-3), 127.4 (C-7), 123.9 (C-5 or C-6), 123.1 (C-5 or C-6), 117.1 (br, C-8), 82.2 (C-1), 66.1 (br, C-9a), 46.7 (C-4a), 34.44 (C-4), 27.4 (C-10 or C-11), 24.1 (C-10 or C-11), 24.1 (amide CH_3 or acetate CH_3), 22.3 (amide CH_3 or acetate CH_3); EIMS m/z (rel intensity) 297 (7, M^+), 138 (29), 117 (36), 96 (100), 43 (34). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.30; H, 6.50; N, 4.67.

***exo*-6d**: mp 116–118 °C; ^{1}H NMR (400 MHz) δ 8.1 (1 H, br, H-8 of rotamer with carbonyl group cis to aromatic ring), 7.23 (1 H, m, H-7 or H-8), 7.05 (1 H, ddd, J = 7.5, 7.5, 0.9 Hz, H-7 or H-8), 4.50 (1 H, br, H-9a), 7.09 (1 H, br, H-5), 6.48 (1 H, m, H-2 or H-3), 6.40 (1 H, m, H-2 or H-3), 3.67 (1 H, dd, J = 7, 4 Hz, H-4a), 2.85 (1 H, m, H-4), 2.4 (3 H, br, amide CH_3 or acetate CH_3), 2.08 (3 H, br, amide CH_3 or acetate CH_3), 1.7–1.0 (4 H, m, H-10, H-11); ^{13}C NMR (22.5 MHz) δ 171.6 (amide CO or acetate CO), 171.0 (amide CO or acetate CO), 144.6 (br, C-4b or C-8a), 134.2 (C-4b or C-8a), 134.2 (C-2 or C-3), 132.8 (C-2 or C-3), 128.1 (C-7), 124.3 (C-6 or C-5), 124.1 (C-6 or C-5), 117.5 (C-8), 82.1 (C-1), 65.6 (br, C-9a), 44.0 (C-4a), 33.0 (C-4), 24.3 (amide CH_3 or acetate CH_3), 22.3 (amide CH_3 or acetate CH_3), 22.4 (C-10 or C-11), 21.5 (br, C-10 or C-11); EIMS m/z (rel intensity) 297 (7, M^+), 138 (29), 117 (36), 96 (100), 43 (34). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.74; H, 6.59; N, 4.82.

***N*-Acetyl-3-acetoxy-1,4,4a,9a-tetrahydro-1,4-ethanocarbazole (6e).** A mixture of 234 mg (2 mmol) of **3**, 552 mg (4 mmol) of **2e**, 40 mg (5 mol %) of **1a**, 157 mg (2 mmol) of acetyl chloride, and 350 mg of $NaHCO_3$ was irradiated for 8 h. Separation of isomers by LC (cyclohexane/ethyl acetate, 2:1) gave 355 mg (59%) of **6e** (exo:endo = 1:3).

***endo*-6e**: mp 145–147 °C; ^{1}H NMR (400 MHz) δ 8.1 (1 H, d, J = 7.8 Hz, H-8 of rotamer with carbonyl group cis to aromatic ring), 7.18–6.92 (3 H, m, H-5, H-6, H-7), 5.53 (1 H, m, H-2), 4.73 and 4.62 (1 H, dd, J = 8.8, 2.5 Hz, H-9a), 3.76 and 3.60 (1 H, dd, J = 8.8, 3 Hz, H-4a, two rotamers), 3.17–3.07 and 3.53–3.42 (1 H, m, H-1, two rotamers), 2.94–2.8 (1 H, m, H-4), 2.30 and 2.38 (3 H, s, amide CH_3), 1.95 and 1.94 (3 H, s, acetate CH_3, two rotamers), 1.9–1.1 (4 H, m, H-10, H-11); ^{13}C NMR (100 MHz) δ 168.79, 168.69, 168.55 (amide CO, two rotamers, acetate CO), 151.68 and 151.29 (C-3), 144.38 and 143.17 (C-4b or C-8a), 132.9 and 134.95 (C-4b or C-8a), 127.69 and 127.30 (C-7), 123.51 and 124.97 (C-5 or C-6), 123.27 and 122.86 (C-5 or C-6), 116.98 and 113.53 (C-8), 110.81 and 111.97 (C-2), 64.03 and 63.42 (C-9a), 46.98 and 45.12 (C-4a), 39.23 and 39.49 (C-1 or C-4), 35.04 and 32.53 (C-1 or C-4), 23.49 nd 25.25 (amide CH_3), 20.67 (acetate CH_3), 23.28, 23.23, 23.38, and 22.85 (C-10, C-11), nearly all signals doubled due to two amide rotamers; EIMS m/z (rel intensity) 297 (20, M^+), 159 (56), 138 (23), 117 (100), 96 (77), 43 (38). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44. Found: C, 72.65; H, 6.47.

***exo*-6e**: mp 121–123 °C; ^{1}H NMR (400 MHz) δ 8.22 (1 H, d, J = 8 Hz, H-8 of rotamer with carbonyl group cis to aromatic ring), 7.25–7.0 (3 H, H-5, H-6, H-7), 5.78 (1 H, m, H-2), 4.33 and 4.58 (1 H, dm, J = 11 Hz, H-9a, two rotamers), 3.92 and 3.79 (1 H, dm, J = 11 Hz, H-4a, two rotamers), 3.03 and 3.40 (1 H, br, H-1, two rotamers), 2.78 and 2.73 (1 H, m, H-4, two rotamers), 2.28 and 2.64 (3 H, s, amide CH_3, two rotamers), 2.18 (3 H, s, acetate CH_3), 1.75–0.9 (4 H, m, H-10, H-11); ^{13}C NMR (100 MHz) δ 169.47, 169.36, and 169.03 (amide CO, two rotamers, acetate CO), 155.88 and 154.94 (C-3), 144.43 and 143.11 (C-4b or C-8a), 133.52 and 124.49 (C-4b or C-8a), 128.17 and 128.00 (C-7), 124.27 and 125.80 (C-5 or C-6), 123.95 and 123.33 (C-5 or C-6), 117.64 and 114.81 (C-8), 113.27 and 114.19 (C-2), 64.45 and 63.91 (C-9a), 43.55 and 42.27 (C-4a), 37.63 and 37.80 (C-1 or C-4), 34.73 and 32.55 (C-1 or C-4), 23.62 and 25.49 (amide CH_3), 21.76 (acetate CH_3), 20.93 and 29.87 (C-10 or C-11), 17.96 and 17.56 (C-10 or C-11), most signals doubled due to two amide rotamers; EIMS m/z (rel intensity) 297 (20, M^+), 159 (56), 138 (23), 117 (100), 96 (77), 43 (38); high-resolution MS calcd for $C_{18}H_{19}NO_3$ (M^+) 297.1365, found 297.1367.

***N*-Acetyl-1,11,11-trimethyl-1,4,4a,9a-tetrahydro-1,4-ethanocarbazole (6f).** A mixture of 234 mg (2 mmol) of **3**, 488 mg (4 mmol) of **2f**, 20 mg (2.5 mol %) of **1a**, 157 mg (2 mmol) of acetyl chloride, and 350 mg of $NaHCO_3$ was irradiated for 18 h. Separation of isomers by LC (cyclohexane/ethyl acetate, 2:1) gave 130 mg (23%) of **6f** (one isomer, presumably endo): mp 176–178 °C; ^{1}H NMR (200 MHz) δ 7.15–6.9 (4 H, m, H-5, H-6, H-7, H-8), 5.73 (1 H, dd, J = 8.5, 6 Hz, H-3), 5.59 (1 H, d, J = 8.5 Hz, H-2), 4.85–4.4 (1 H, br, H-9a), 4.1–3.95 (1 H, br, H-4a), 2.54 (1 H, m, H-4), 2.33 (3 H, s, amide CH_3), 1.38 (1 H, d, J = 13 Hz, H-10), 1.0 (1 H, d, J = 13 Hz, H-10), 1.22 (3 H, s, CH_3-1 or CH_3-11), 1.18 (3 H, s, CH_3-1 or CH_3-11), 0.9 (3 H, s, CH_3-1 or CH_3-11), all signals broad due to coalescence; ^{13}C NMR (22.5 MHz) δ 170.73 (amide CO), 144.3 (C-4b or C-8a), 134.4 (br, C-2 or C-3), 133.6 (br, C-2 or C-3), 124 (C-4b or C-8a), 126.6 (br, C-5 or C-6 or C-7), 123.7 (2 C, br, C-5 or C-6 or C-7), 116 (br, C-8), 65.7 (br, C-9a), 48.7 (C-10), 46.67 (C-4), 42.8 (br, C-4a), 41.23 (C-1 or C-11), 34.45 (C-1 or C-11), 31.79 (amide CH_3 or C-14 or C-15 or C-16), 29.82 (amide CH_3 or CH_3-1 or CH_3-11), 24.41 (amide CH_3 or CH_3-1 or CH_3-11), 23.17 (amide CH_3 or CH_3-1 or CH_3-11); EIMS m/z (rel intensity) 281 (7, M^+), 159 (9), 122 (92), 117 (50), 107 (100), 91 (22), 43 (18). Anal. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 81.13; H, 8.15; N, 5.01.

***N*-Carbomethoxy-1,4,4a,9a-tetrahydro-1,4-ethanocarbazole (9a).** A mixture of 234 mg (2 mmol) of **3**, 360 mg (4 mmol) of

2a, 40 mg (5 mol %) of **1a**, 378 mg (4 mmol) of methyl chloroformate, and 350 mg of $NaHCO_3$ was irradiated for 8 h. Separation of isomers by LC (cyclohexane/ethyl acetate, 5:1) gave 170 mg (23%, or 86% based on turnover) of **9a** (exo:endo = 1:4).

***endo*-9a**: oil; ^1H NMR (200 MHz) δ 7.78 (1 H, br, H-8 of rotamer with carbonyl group cis to aromatic ring), 7.5–6.85 (3 H, m, H-5, H-6, H-7), 6.05 (1 H, dd, J = 6.5, 6.5 H, H-2 or H-3), 5.93 (1 H, dd, J = 6.5, 6.0 Hz, H-2 or H-3), 4.42 (1 H, br, H-9a), 3.84 (3 H, s, amide CH_3), 3.54 (1 H, dd, J = 10, 3 Hz, H-4a), 3.23 and 3.38 (1 H, br, H-1, two rotamers), 2.93 (1 H, br, H-4), 1.8–1.5 (2 H, m, CH_2-10 or CH_2-11), 1.45–1.2 (2 H, m, CH_2-10 or CH_2-11); ^{13}C NMR (50 MHz) δ 153.82 (amide CO), 143.68 (C-4b or C-8a), 136.42 (C-5a or C-8a), 133.70 (C-2 or C-3), 130.81 (C-2 or C-3), 127.43 and 127.91 (C-7), 123.59 (C-5 or C-6), 122.51 and 122.74 (C-5 or C-6), 63.42 and 63.82 (C-9a), 52.45 (amide CH_3), 45.93 and 45.38 (C-4a), 35.04 and 33.52 (C-1 or C-4), 32.75 and 29.27 (C-1 or C-4), 23.83, 21.89, and 20.94 (C-10 and C-11, one signal doubled because of two rotamers), most signals doubled due to two amide rotamers; EIMS m/z (rel intensity) 255 (8, M^+), 175 (100), 130 (22), 80 (7), 79 (8), 59 (5); high-resolution MS calcd for $C_{16}H_{17}NO_2$ (M^+) 255.1260, found 255.1230.

***exo*-9a**: oil; ^1H NMR (200 MHz) δ 7.9 (1 H, br, H-8 of rotamer with carbonyl group cis to aromatic ring), 7.5–6.9 (3 H, m, H-5, H-6, H-7), 6.51 (1 H, dd, J = 7, 7 Hz, H-2 or H-3), 6.31 (1 H, dd, J = 7, 7 Hz, H-2 or H-3), 4.25 (1 H, br, H-9a), 3.82 (3 H, s, amide CH_3), 3.43 (1 H, dd, J = 11, 4 Hz, H-4a), 3.09 and 3.25 (1 H, br, H-1, two rotamers), 2.79 (1 H, br, H-4), 1.65–1.5, 1.3–1.15, and 1.1–0.9 (4 H, 3 m, CH_2-10 and CH_2-11, one signal doubled because of two rotamers); ^{13}C NMR (50 MHz) δ 154.16 (amide CO), 144.13 (C-4b or C-8a), 132.06 (C-5a or C-8a), 136.57 and 136.23 (C-2 or C-3), 132.84 and 133.24 (C-2 or C-3), 127.98 (C-7), 122.81 (C-5 or C-6), 124.35 and 124.81 (C-5 or C-6), 62.82 and 63.17 (C-9a), 52.47 and 52.70 (amide CH_3), 43.62 and 43.03 (C-4a), 33.57 and 31.98 (C-1 or C-4), 32.80 and 29.75 (C-1 or C-4), 20.97 and 17.80 (C-10 and C-11), most signals doubled due to two amide rotamers; EIMS m/z (rel intensity) 255 (8, M^+), 175 (100), 130 (22), 80 (7), 79 (8), 59 (5); high-resolution MS calcd for $C_{16}H_{17}NO_2$ (M^+) 255.1260, found 255.1260.

***N*-(*p*-Tolylsulfonyl)-10-isopropyl-3-methyl-1,4,4a,9a-tetrahydro-1,4-ethanocarbazole (10c).** A mixture of 234 mg (2 mmol) of **3**, 544 mg (4 mmol) of **2c**, 49 mg (5 mol %) of **1b**, 380 mg (2 mmol) of *p*-toluenesulfonyl chloride, and 350 mg of $NaHCO_3$ was irradiated for 7 h. Salt **1b** was removed by filtration on silica gel. Purification by LC (cyclohexane/ethyl acetate, 5:1) gave 375 mg (46%) of **10c**. Separation of the isomers was effected by HPLC (*n*-heptane/ethyl acetate/dichloromethane, 10:0.15:0.15).

***endo*-10c**: mp 135–137 °C (from *n*-heptane/ethyl acetate); ^1H NMR (400 MHz) δ 7.96 (1 H, d, J = 8.2 Hz, H-8), 7.75 (2 H, dd, J = 8.4, 2.0 Hz, aromatic H), 6.93–6.98 (1 H, m, H-6), 6.75 (1 H, td, J = 8.2, 1.0 Hz, H-7), 6.73 (1 H, dd, J = 3.4, 1.0 Hz, H-5), 6.60 (2 H, dd, J = 8.4, 2.0 Hz, aromatic H), 5.59 (1 H, dd, J = 6.4, 1.0 Hz, H-2), 4.27 (1 H, dd, J = 9.6, 3.2 Hz, H-9a), 3.56 (1 H, ddd, J = 6.4, 3.2, 1.6 Hz, H-1), 2.94 (1 H, dd, J = 9.6, 3 Hz, H-4a), 2.18 (1 H, ddd, J = 3, 2.8, 1.8 Hz, H-4), 1.73 (3 H, s, aromatic CH_3), 1.26 (3 H, d, J = 1.6 Hz, CH_3-3), 1.14–1.2 (1 H, m, H-10), 1.11 (1 H, dsep, J = 9.4, 6.4 Hz, isopropyl CH), 0.92 (3 H, d, J = 6.4 Hz, isopropyl CH_3), 0.76–0.82 (1 H, m, H-11), 0.78 (3 H, d, J = 6.4 Hz, isopropyl CH_3); ^{13}C NMR (100 MHz) δ 144.5 (C-8a or C-4b), 143.3 (C-8a or C-4b), 141.5 (aromatic C), 136.2 (aromatic C), 134.8 (C-3), 129.6 (two aromatic CH), 128.1 (C-7), 127.5 (two aromatic CH), 124.4 (C-5 or C-6), 123.4 (C-5 or C-6), 121.9 (C-2), 115.5 (C-8), 67.9 (C-9a), 45.8 (C-4a), 43.6 (C-10), 41.1 (C-4), 39.3 (C-1), 33.1 (isopropyl CH), 31.2 (C-11), 21.4 (CH_3-3 or aromatic CH_3), 21.3 (isopropyl CH_3), 21.0 (CH_3-3 or aromatic CH_3), 20.5 (isopropyl CH_3); EIMS m/z (rel intensity) 407 (10, M^+), 271 (100), 155 (25), 136 (75), 117 (20), 93 (80); high-resolution MS calcd for $C_{25}H_{29}NO_2S$ (M^+) 407.1919, found 407.1915.

***N*-Methyl-1,4,4a,9a-tetrahydro-1,4-ethanocarbazole (5).** A mixture of 524 mg (4 mmol) of **4**, 480 mg (6 mmol) of **2a**, and 40 mg (5 mol %) of **1a** was irradiated for 16 h. Separation of isomers by LC (petroleum ether/trichloromethane, 10:1) gave 81 mg (9.5%) of **5** (exo:endo = 1:2.8).

***endo*-5**: oil; ^1H NMR (200 MHz) δ 7.2 (1 H, ddd, J = 7.5, 7.5, 1 Hz, H-7), 6.99 (1 H, ddd, J = 7.5, 7.5, 0.8 Hz, H-6), 6.98 (1 H, d, J = 7.5 Hz, H-5), 6.21 (1 H, d, J = 7.5 Hz, H-8), 6.14–6.08 (2 H, m, H-2, H-3), 3.80 (1 H, dd, J = 10, 3.2 Hz, H-4a), 3.50 (1 H, dd, J = 10, 2.8 Hz, H-9a), 2.98–2.87 (1 H, m, H-4), 2.93–2.83 (1 H, m, H-1), 2.77 (3 H, s, NCH_3), 1.7–1.23 (4 H, m, H-10, H-11); EIMS m/z (rel intensity) 211 (11, M^+), 167 (3), 131 (100), 103 (3), 77 (7).

***exo*-5**: oil; ^1H NMR (200 MHz) δ 7.6–6.9 (4 H, m, H-5, H-6, H-7, H-8), 6.5 (1 H, dd, J = 7, 7 Hz, H-2 or H-3), 6.3 (1 H, dd, J = 7, 7 Hz, H-2 or H-3), 3.65 (1 H, dd, J = 10, 2.5 Hz, H-4a), 3.4 (1 H, dd, J = 10, 2 Hz, H-9a), 2.95–2.65 (2 H, m, H-1, H-4), 2.8 (3 H, s, NCH_3), 1.45–0.9 (4 H, m, H-10, H-11); EIMS m/z (rel intensity) 211 (11, M^+), 167 (3), 131 (100), 103 (3), 77 (7).

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Supplementary Material Available: Tables of final atomic positional coordinates, bond distances, bond angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters for the X-ray structure of *exo*-**6b** (3 pages). Ordering information is given on any current masthead page.