Type B Semiconductor Photocatalysis: The Synthesis of Homoallyl Amines by Cadmium Sulfide-Catalyzed Linear Photoaddition of Olefins and Enol/Allyl Ethers to *N*-Phenylbenzophenone Imine**

Helmut Keck, Wolfram Schindler, Falk Knoch, and Horst Kisch*

Abstract: Homoallyl amines were synthesized by visible-light irradiation of CdS powder in the presence of *N*-phenylbenzophenone imine and cyclohexene, 2,3-dihydrofuran, 2,5-dihydrofuran, 3,4-dihydropyran, 2-pentene, cyclopentene, 1-methylcyclohexene, or α-pinene. The structures of the products from the last three olefins were determined by single-crystal X-ray analysis to prove that *C*-alkylation of the imine had occurred. Thus, the reaction is formally an insertion of the imine into an allylic C–H bond of the olefin. It is proposed that a photogenerated electron–hole pair reduces the imine to an α-aminodiphenylmethyl radical and oxidizes the olefin with concomitant deprotonation to the corresponding allyl radical. Heterocoupling of these intermediates affords the final addition product. The overall reaction is therefore classified as type B semiconductor photocatalysis. The presence of acetic acid accelerates the reaction by rendering the reduction potential of the imine more positive. In the series 2,5-dihydrofuran/cyclopentene/3,4-dihydropyran, the decrease in apparent quantum yield with increasing driving force of olefin oxidation points to a significant contribution of secondary back electron transfer.

Keywords
cadmium sulfide · catalysis · photochemistry · semiconductors · unsaturated amines

Introduction

In recent work on the use of metal sulfide powders as heterogeneous photocatalysts for the synthesis of new organic compounds, two general types of reaction pathways have become apparent. While all reactions are initiated by electron transfer between the excited semiconductor surface and adsorbed substrates, the further transformation to the final products falls into two categories. In the most frequently observed, type A reactions two or more redox products are obtained, analogously to photoelectrolysis and conventional electrolysis. A typical example is the formation of hydrogen and dehydrodimers upon irradiation of zinc sulfide in the presence of olefins or enol/allyl ethers.[1] In the very rare case of type B reactions, only one product is formed as observed in the cadmium sulfide catalyzed photoaddition of 1,2-diazenes[2] or aldimines[3] to selected olefins or enol/allyl ethers. This transformation has no counterpart in photoelectrochemistry, but corresponds to the case of paired electrolysis, recently observed on a femtoliter scale in an unconventional microelectrochemical cell.[4] In contrast, the above-mentioned photoaddition occurs on a gram scale and can be viewed as paired photoelectrolysis.

In the proposed mechanism the photogenerated electron–hole pair is trapped and separated into the reactive redox surface centers e_r^- and h_r^+. Proton-coupled reduction and oxidation afford hydrazyl or α-aminobenzyl and allyl ($R^\bullet$) radicals, respectively [Eqs. (1) and (2), X = CH, N]. Heterocoupling of the two radicals leads to the final product [Eq. (3)]. The corresponding

$$\mathrm{Ar{-}X{=}N{-}Ar} + \mathrm{H_3O^+} + e_r^- \longrightarrow \mathrm{Ar{-}\dot{X}{-}N(H){-}Ar} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{RH} + h_r^+ + \mathrm{H_2O} \longrightarrow \mathrm{R^\bullet} + \mathrm{H_3O^+} \qquad (2)$$

$$\mathrm{Ar{-}\dot{X}{-}N(H){-}Ar} + \mathrm{R^\bullet} \longrightarrow \mathrm{Ar{-}X(R){-}N(H){-}Ar} \qquad (3)$$

hydrazo compound or the aldimine hydrodimers are obtained as two-electron reduction by-products.[2, 3] Thus, the most significant reaction steps of this novel photoaddition reaction are a primary electron transfer followed by radical C–N or C–C coupling. In the case of aldimines, only cyclopentene has been investigated as the olefinic substrate.[3] In order to explore the general applicability of this unusual reaction and to learn about the factors which control the product selectivity, we investigated the addition of a series of cyclic olefins and enol/allyl ethers to *N*-phenylbenzophenone imine (**1**).

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[*] Prof. Dr. H. Kisch, Dipl.-Chem. H. Keck, Dr. W. Schindler, Dr. F. Knoch
Institut für Anorganische Chemie der Universität Erlangen-Nürnberg
Egerlandstrasse 1, 91058 Erlangen (Germany)
Fax: Int. code +(9131)857-363
e-mail: kisch@anorganik.chemie.uni-erlangen.de

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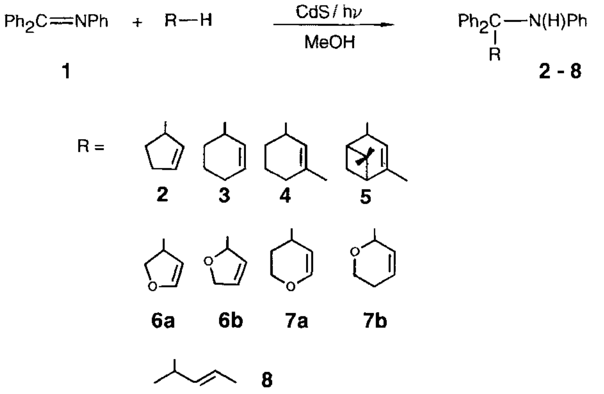
Results

1. Syntheses and Structures: Irradiation (tungsten halogen lamp, $\lambda > 350$ nm) of a methanolic suspension of freshly prepared cadmium sulfide powder (CdS-A) in the presence of **1** and an excess of olefin afforded the addition products **2**–**8** (Scheme 1). No similar reaction occurred when commercially available CdS was employed.



Scheme 1. Addition of olefins and enol/allyl ethers to *N*-phenylbenzophenone imine.

After complete consumption of **1**, as indicated by TLC or UV/Vis spectroscopy (Figure 1), the reaction was stopped, CdS was filtered off, and the products were isolated by direct crystallization or by column chromatography. Except for the oily adducts of 1-methylcyclohexene and 2-pentene, all products were obtained as white microcrystalline powders. For the adducts **2**–**5**, **6** and **7**, and **8**, isolated yields were about 75, 55, and 30%, respectively. The reaction of 2,5-dihydrofuran (2,5-DHF) was also performed by exposing the suspension to sunlight; over 4 h a linear decrease of the initial concentration of **1** from 0.012 to 0.002 M was observed.

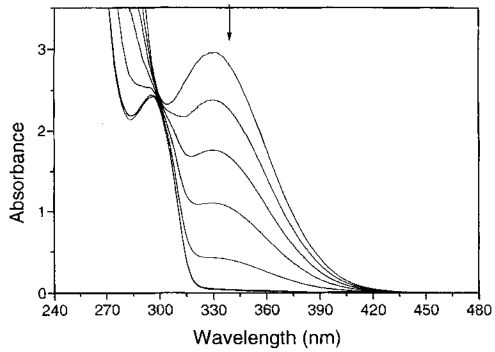


Figure 1. UV/Vis spectra for the CdS-catalyzed photoaddition of cyclopentene to **1**.

Abstract in German: *Neue Homoallylamine werden durch Belichtung von CdS-Pulver in Gegenwart von N-Phenylbenzophenonimin und Cyclohexen, 2,3-Dihydrofuran, 2,5-Dihydrofuran, 3,4-Dihydropyran, 2-Penten, Cyclopenten, 1-Methylcyclohexen oder α-Pinen synthetisiert. Die durch Röntgenbeugung bestimmten Strukturen der Additionsprodukte der drei letzteren Olefine beweisen, daß eine C-Alkylierung des Imins stattgefunden hat. Die Reaktion ist daher formal die Einschiebung der Imingruppe in eine allylische C–H Bindung des Olefins. Vermutlich reduziert das durch Lichtabsorption gebildete Elektron-Loch-Paar das Imin in einer protonengekoppelten Elektronentransfer-Reaktion zu einem α-Aminodiphenylmethylradikal, während das Olefin zum entsprechenden Allylradikal oxidiert wird. Heterokupplung dieser Intermediate führt zum Additionsprodukt, und die Gesamtreaktion kann daher als Typ-B-Halbleiterphotokatalyse klassifiziert werden. Die Beschleunigung nach Zugabe von Essigsäure läßt sich auf eine leichtere Reduktion des Imins zurückführen. In der Reihe 2,5-Dihydrofuran, Cyclopenten und 3,4-Dihydropyran deutet die Abnahme der Quantenausbeute mit steigender Triebkraft der Olefinoxidation auf einen signifikanten Beitrag der sekundären Elektronenrückübertragung hin.*

The structures of the new compounds were confirmed by single-crystal X-ray analyses of **2**, **4**, and **5**, and by comparative NMR data for the other products. According to the X-ray data (Table 1), in all three adducts the allylic carbon atom of the olefin is connected to the carbon atom of the imine group. At the newly formed sp^3 atoms C1 of these adducts the N-C1-C2 angles are slightly smaller (102–105°) than expected for a perfect tetrahedron, while the angles C20-C1-C30 have a somewhat larger mean value of 113.6°; the C1–C2 and the C1–C20/C1–C30 bonds are slightly longer (around 157.7 and 153.8/155.8 pm) than the expected value of 153 pm for sp^3–sp^3 and 151 pm for sp^2–sp^3 bonds;[5] the C1–N distances of about 147.4 pm are within the usual range. Bond lengths and angles in the pinenyl group of **5** (Figure 2) are similar to other pinene

Table 1. Selected bond lengths [pm] and bond angles [°] of **2**, **4**, and **5**.

	2	4	5
C1–N1	147.8(6)	146.5(5)	147.9(2)
C1–C20	154.4(7)	153.8(6)	153.2(2)
C1–C30	156.6(7)	155.7(5)	155.0(2)
C1–C2	157.9(7)	157.8(6)	157.5(2)
N1-C1-C2	102.5(4)	104.9(3)	103.94(12)
C20-C1-C30	113.9(4)	113.6(3)	113.56(13)

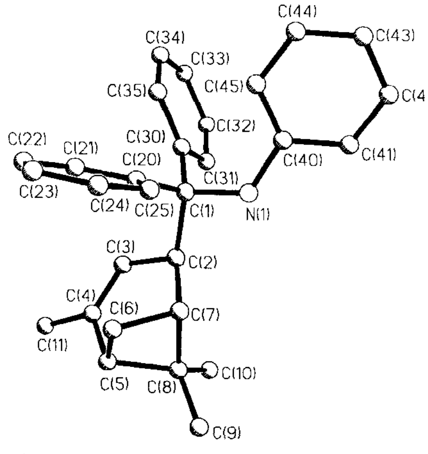


Figure 2. Crystal structure of adduct **5**.

derivatives,[6] and no remarkable features are present in the cycloalkenyl groups of **2** and **4**.

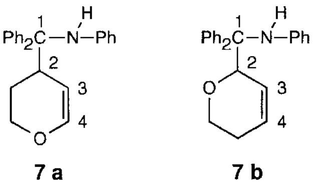
The mass spectra of all compounds contain the molecular ion peak. In the IR spectra the absorption of the characteristic NH stretching vibration occurs in the range of 3387 to 3431 cm^{-1} (Table 2). The presence of an alkenyl group in **3** and **6**–**8** follows from comparison of the NMR spectra with the spectrum of **2** (Table 2). In the latter, the signals of the olefinic protons at C3 and C4 appear as multiplets at δ = 5.57 and 5.75, respectively, while the aliphatic protons at C5/C6 and C2 give rise to multiplets at δ = 1.63–2.18 and 3.94, respectively. The singlet of the NH group at δ = 4.54 almost completely disappears upon addition of D_2O. In the ^{13}C NMR spectrum, the signals of C3 and C4 are found at δ = 131.26 and 134.49, while C5 and C6 appear at 32.09 and 25.89, and C2 and C1 at 58.24 and 68.01. These assignments are based on DEPT and $^1H-^{13}C$ COSY spectra.

Table 2. Selected IR, ^1H NMR, and ^{13}C NMR data.

	2	**3**	**4**	**5**	**6a**	**6b**	**7a**	**7b**	**8**
IR [cm^{-1}] [a]									
$\tilde{\nu}$(NH)	3427	3413	3431	3387	3415	3415	3392	3402	3411
^1H NMR ($CDCl_3$, TMS)									
NH	4.54	4.50	4.55	4.46	4.77	4.83	4.54	5.27	4.69
H2	3.94	3.19	3.15	3.34	4.21	5.74	3.31	4.87	3.11
^{13}C NMR ($CDCl_3$, TMS)									
C1	68.01	68.58	68.68	68.23	67.14	68.64	67.78	68.70	67.72
C2	58.24	49.08	49.44	52.15	55.07	93.44	43.00	81.86	50.20
C3	131.26	127.71	121.57	115.74	100.36	129.32	100.83	127.08	127.31
C4	134.49	130.57	137.88	147.44	148.72	127.02	146.48	126.45	132.60

[a] In KBr; **8**: in CCl_4.

According to HPLC and NMR data, the products **6** and **7** consist of two regioisomers, which in the case of **7** could be separated by preparative HPLC (Scheme 2). The assumption of the presence of an enol ether fragment in **7a** is based on the characteristic IR absorption at 1641 cm^{-1}, which is absent in the allyl ether isomer **7b**. By analogy with **2**, the ^{13}C NMR signals of C3 and C4 in **7a** occur at δ = 100.83 and 146.48, while for **7b** they are observed at δ = 127.08 and 126.45 (Table 1). Similar signals in the isomeric mixture **6** indicate the presence of the regioisomers **6a** and **6b**.



Scheme 2.

In the ^1H and ^{13}C NMR spectra of **5**, the signals of the pinenyl group correspond to those of α-pinene,[7, 8] except for a larger chemical shift difference between the two protons at C6. While the signal of H6a (Figure 2) shows only a small shift, that of H6b is displaced from δ = 1.17 to 0.05. This can be rationalized by anisotropic shielding by the proximate phenyl ring. According to the X-ray structural results, H6b is located 255 pm above the center of this aromatic ring. For this central location the Haigh model[9] predicts a high-field shift of $\Delta\delta$ = 0.9, which is in good agreement with the experimentally observed value of $\Delta\delta$ = 1.1. The corresponding shifts of $\Delta\delta$ = 0.65 and 0.40 observed for **4** and **2**, respectively, are much smaller, but also in accord with the model, which predicts a smaller effect when the atom is located above a ring carbon atom instead of above the center of the aromatic ring. In **4** the distance H7a–C20 is 248 pm. Due to the unfavorable location of H6a in **2** outside the ring, this effect is less pronounced. The correlation of solution NMR data with details of the solid-state molecular structure suggests that the rotation around the C1–C2 axis is also restricted in solution.

2. Variation of CdS concentration: To determine the experimental conditions necessary for maximum light absorption in the addition of cyclopentene to **1**, the disappearance rate of **1** was measured as a function of increasing CdS-A concentration. After a short linear increase, the rate reaches a constant value at about 2.5 g L^{-1}, a behavior well-known for powder suspensions.[10] In all of the following experiments, the amount of CdS was sufficient to ensure a maximum reaction rate.

3. Influences of air and pH value: In Figure 3 the influence of various additives on the disappearance rate of **1** is summarized for the addition of 2,5-DHF. In the presence of air, the relative decay is slower, but on prolonged irradiation it becomes faster and almost reaches the value obtained in argon-saturated solution. Addition of pyridine has no significant effect, while HOAc leads to a linear decrease in the concentration of **1** and a much faster reaction.

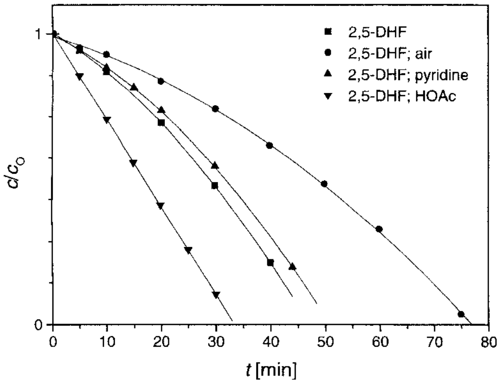


Figure 3. The influence of air, pyridine, and acetic acid on the addition of 2,5-dihydrofuran (2,5-DHF) to **1**.

The presence of acetic acid induces hydrolysis of **1** and leads to formation of small amounts of the two-electron reduction product $Ph_2CHN(H)Ph$. Figure 4 reveals that the concentration of the latter and of **6a**,**b** increases linearly with time, while only marginal changes are observed with benzophenone. When stronger acids like trifluoroacetic acid are added, adduct formation is completely inhibited in favor of hydrolysis of **1**. The accelerating effect of HOAc does not arise from a feasible benzophenone-sensitized adduct formation by triplet sensitization,[11] since a 4 h irradiation of the system Ph_2CO/**1**/2,5-DHF/HOAc/MeOH afforded only traces of **6**. To prevent hydrolysis of **1**, a dehydrated sample of CdS-B was employed when the effect of increasing HOAc concentration on the addition of cyclopentene to **1** was studied. Six- and threefold acceleration occurred in methanol and THF solution, respectively, when the concentration was increased from 0.014 to 0.15 M.

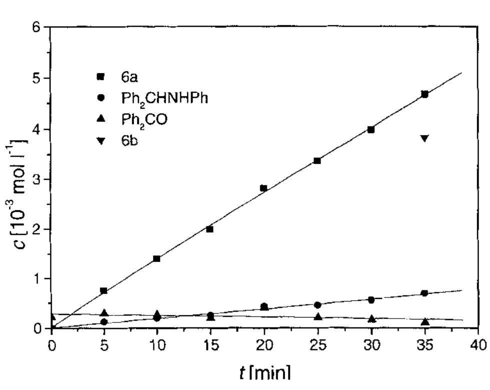


Figure 4. Formation of major (**6a, b**) and by-products ($Ph_2CHNHPh$, Ph_2CO) during the addition of 2,5-DHF to **1** in the presence of HOAc (0.188 M); due to the identical retention times of **1** and **6b** only the final concentration of **6b** could be measured.

4. Influence of various olefinic substrates: The influence of the different olefinic components on the reaction rate is depicted in Figure 5. Consumption of **1** was monitored by measuring the absorbance at 330 nm (Figure 1). In MeOH the reaction rate decreases in the order 2,5-DHF > 1-methylcyclohexene > 3,4-DHP ≈ 2,3-DHF > cyclopentene ≈ α-pinene > cyclohexene > 2-pentene.

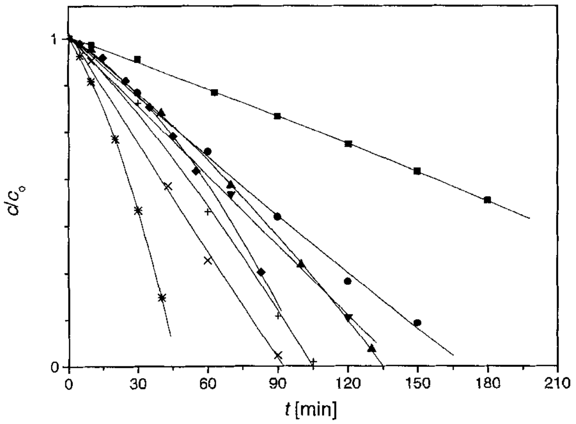


Figure 5. Disappearance of **1** in the presence of the various olefins and enol/allyl ethers. * 2,5-DHF, × 1-methylcyclohexene, + 3,4-DHP, ◆ 2,3-DHF, ▼ cyclopentene, ▲ α-pinene, ● cyclohexene, ■ 2-pentene.

For the measurement of apparent quantum yields (λ_{exc} = 437 nm) for imine disappearance, HOAc (0.16 M) and a thousandfold excess of the olefin/enol ether (relative to **1**) had to be present to facilitate detection of adduct formation by HPLC within the first hour of the reaction (in the preparative reactions only about a 40-fold excess was added). Values of 0.018, 0.011, 0.009, and 0.008 were measured for 2,5-DHF, cyclopentene, 3,4-DHP, and cyclohexene, respectively. These values are lower limits, and their reproducibility was not better than ±20% because varying amounts of light were reflected, owing to the slightly different natures of the particular CdS suspensions.

5. Reactivity of other imine derivatives: Cathodic photocorrosion of CdS-A was observed when **1** was replaced by 2,2′-bipyridyl or histidine, both of which contain aromatic C=N bonds. In the case of an α-diimine derivative like N,N′-dicyclohexyl-1,4-diaza-1,3-butadiene, a very slow reaction afforded a complicated product mixture that was not analyzed further. When the olefin/ether was omitted, irradiation of CdS-A in the presence of **1** produced small quantities of benzophenone and aniline by hydrolysis, the two-electron reduction product $Ph_2CHNHPh$, and a new product, probably an adduct of **1** with methanol, analogously to the photoaddition of alcohols to aldimines.[3] In this latter system disappearance of **1** was accelerated by a factor of 1.5 and 2.3 when methanol was replaced by ethanol and isopropanol, respectively. However, concomitantly the amount of alcohol adduct decreased in favor of the hydrolysis and two-electron reduction products. In isopropanol, only traces of the corresponding adducts were observed.

Discussion

The title reaction is a new type of imine *C*-alkylation and opens a simple route to homoallyl amines. Electrochemical alkylations with methyl iodide usually proceed with *N*-alkylation,[12] while conventional *C*-alkylation requires initial reduction by alkali metals[13] or the use of Grignard reagents.[14] In contrast, the CdS-catalyzed reaction can be performed simply by using a cheap tungsten halogen lamp or even diffuse sunlight. In the latter case, an exposure time of 4 h induced the addition of 0.5 mmol of 2,5-DHF to **1** (see Experimental Section).

The overall mechanism is the same as briefly summarized in the Introduction for the addition to aldimines [Eqs. (1)–(3); X = PhC, Ar = Ph].[3] In contrast to that case, no hydrodimer of the ketimine **1** was observed. This is most likely a consequence of the presence of the second phenyl substituent on the imine group, which imposes considerable steric hindrance on the C–C homocoupling of the α-aminodiphenylmethyl radicals. This parallels the electrochemical reduction, which affords hydrodimers from aldimines[15] but not from the ketimine **1**.[15, 16] However, formation of these intermediate radicals is strongly supported by the structure of the addition products.

The accelerating effect of HOAc (Figure 3) most likely stems from a positive influence on the primary reductive step according to Equation (1). Furthermore, polarographic measurements on **1** in 40% aqueous ethanol reveal that the reduction potential shifts from −1.0 V at pH 13 to −0.1 V at pH 5.1.[17] Although the flat-band potential of CdS in methanol is not known, it is expected to be in the range of −0.9 to −1.5 V,[18] so that the driving force and, therefore, rate of reduction should increase with decreasing pH value. Due to the low basicity of imines ($pK_B > 9$)[19] the protonation equilibrium [Eq. (4)] lies far to the

$$Ph_2C{=}NPh + HOAc \overset{K}{\rightleftharpoons} Ph_2C{=}NPh^+ + OAc^- \qquad (4)$$

left. Under the assumptions of $c(HOAc) > x$ and $c(\mathbf{1}) > x$, one obtains for the equilibrium concentration x of the protonated imine the expression given in Equation (5). Assuming that the

$$x = [Kc_0c(HOAc)]^{1/2} \qquad (5)$$

reduction of the protonated imine is rate-determining, as evidenced by the strong influence on the reduction potential of the aldimine,[20a] the rate should increase linearly with the square root of x. The corresponding plot in Figure 6 displays the expected linearity.

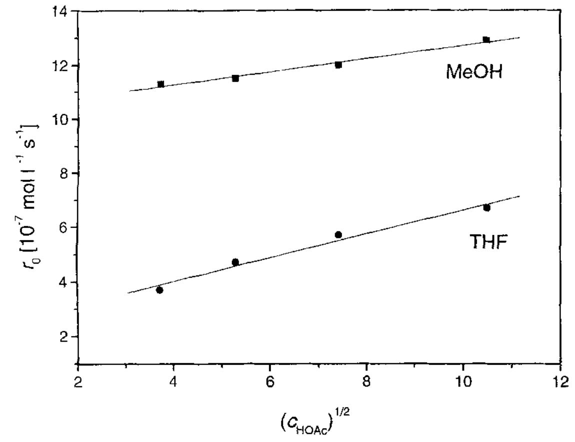


Figure 6. Plot of the initial rate of the addition of cyclopentene to **1** as function of the square root of the acetic acid concentration.

As expected for the imine reduction step [Eq. (1)], the presence of air leads to a slower reaction (Figure 3) due to competitive reduction of oxygen.

The isolation of the regioisomers **7a** and **7b** indicates the involvement of the corresponding allyl radicals. The same radical is obtained regardless of whether 2,5- or 2,3-DHF is employed as starting material, and therefore the ratio **6a**:**6b** = 1.1:0.9 is the same for both ethers. The deviation from the expected statistical 1:1 value reflects the hydrolytic sensitivity of **6b** and the different electron density at the terminal allyl carbon atoms.

These results and the structures of the other addition products strongly support the presence of intermediate allyl radicals, but it is unclear whether their formation [Eq. (2)] occurs through direct [Eqs. (6) and (7)] or indirect [Eqs. (8)–(10)] oxidation of

$$RH_{ad} + h_r^+ \longrightarrow RH_{ad}^{\cdot+} \qquad (6)$$

$$RH_{ad}^{\cdot+} + H_2O_{ad} \longrightarrow R_{ad}^{\cdot} + H_3O_{ad}^+ \qquad (7)$$

$$\text{-[S]}^- + h_r^+ \longrightarrow \text{-[S]}^{\cdot} \qquad (8)$$

$$\text{-[S]}^{\cdot} + RH_{ad} \longrightarrow \text{-[S]-H} + R_{ad}^{\cdot} \qquad (9)$$

$$\text{-[S]-H} + H_2O_{ad} \longrightarrow \text{-[S]}^- + H_3O_{ad}^+ \qquad (10)$$

RH (brackets denote surface species). From the position of the flat-band potential and the band-gap of 2.4 eV, an oxidation potential of the reactive hole (h_r^+) of 0.9 to 1.5 V can be estimated, while the calculated oxidation potentials of RH in solution (see Experimental Section) are in the range of 2.6 to 1.9 V. Thus, formation of the radical cation [Eq. (6)] appears to be endergonic.[20b] However, when the overall process [Eqs. (6) and (7)] is considered, the free enthalpy change of the reaction $RH \rightarrow R^{\cdot} + H^+$ is calculated to be 1.6 eV for 2,5-DHF.[20c] Thus, formation of the radical appears thermodynamically feasible, and since this value applies for the gas phase, it should become more favorable in solution, owing to the high solvation energy of the proton. However, since sulfur radicals have been detected on the CdS surface by ESR spectroscopy[21a–c] and it is known that, for example, MeS$^{\cdot}$ radicals readily abstract hydrogen from 2,3-dihydrofuran and 2,3-dihydropyran, the indirect pathway seems more likely.[21d] On the other hand, this is not supported by the fact that THF does not undergo hydrogen abstraction,[21d] although it is quite reactive.[20f]

The relationship between the quantum yield and E_{ox} (Figure 7) can be interpreted by assuming a direct-oxidation mechanism. In this case a competitive secondary back electron transfer according to Equation (11) could successfully compete with the

$$RH_{ad}^{\cdot+} + e_r^- \longrightarrow RH_{ad} \qquad (11)$$

deprotonation reaction [Eq. (7)]. A less positive E_{ox} should lead to better matching with the redox potential of e_r^- and therefore to a faster reaction.[21e] In addition, the longer lifetime of less acidic radical cations [21f] should also accelerate the reaction. In agreement with this rationalization, 2,3-DHF, which is more easily oxidized (by 0.6 V; E_{ox} = 1.98 V) and whose radical cation should be less acidic, reacts only half as fast as 2,5-DHF (Figure 5). However, no final decision in favor of a particular mechanism can be made on the basis of the present experimental data.

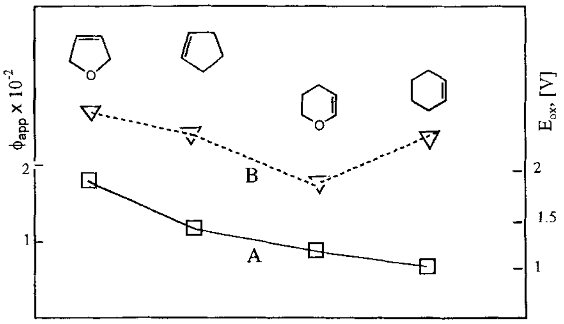


Figure 7. Variation of apparent quantum yield (A) and E_{ox} (B) as function of substrate structure.

Experimental Section

All experiments were performed under an argon atmosphere. Unless otherwise noted, all yields are for analytically pure isolated material and were not optimized. Compound **1** was prepared according to ref. [22]; all olefinic substrates were, until otherwise stated, commercially available.

Instruments: NMR: Joel FT-JNM-EX270 (TMS as internal standard); IR: Perkin Elmer 983 and FT IR 1600; MS: Varian MAT212 (70 eV); UV/Vis: Shimadzu UV/VIS/NIR-3100, quartz cuvette (Hellma, d = 0.1 cm); HPLC: Knauer HPLC pump 64, semipreparative pump head with 20 µL sample loop, column: Spherisorb ODS 2 (250 × 8 mm, 5 µm, Knauer) with precolumn (30 × 8 mm), CH_3CN/H_2O (5/1; v/v), 5 mL min^{-1}, detection by Knauer UV/Vis Filter-Photometer at λ = 254 nm (analytical und semipreparative samples); Knauer HPLC pump 64, semipreparative pump head with 1000 µL sample loop. Column: Spherisorb ODS2 (250 mm × 32 mm, 5 µm, Knauer) with precolumn (30 × 32 mm), CH_3CN/H_2O (5/1), 70 mL min^{-1}, detection with Knauer UV/Vis Filter-Photometer at λ = 254 nm (preparative samples). Preparative irradiations were performed with a tungsten halogen lamp (100 W, 12 V, Osram, λ > 350 nm) in a solidex immersion lamp apparatus (sample volume: semipreparative 100 mL; preparative 220 mL). Irradiations in the cylindrical 15 mL quartz cuvette were performed on an optical train equipped with an Osram XBO 150 W xenon arc lamp [I_0 (400–520 nm) = 2.0 × 10^{-6} Einstein s^{-1} cm^{-2}] installed in a light-condensing lamp housing (PTI, A 1010S), a cutoff filter of λ > 400 nm was placed in front of the cuvette. All redox potentials are referred to NHE and were calculated for acetonitrile solution from the following ionization potentials according to ref. [23]: 9.02, 8.95, 8.37, and 9.14 for cyclopentene,[24a] cyclohexene,[24a] 3,4-DHP,[24b] and 2,5-DHF,[25] respectively. CdS-A was used in all experiments, unless noted otherwise.

CdS-A: $\mathrm{Na_2S{\cdot}H_2O}$ (38.7 g, 0.17 mol, 35 wt% $\mathrm{Na_2S}$) dissolved in $\mathrm{H_2O}$ (150 mL) was added dropwise over 1 h to a solution of $\mathrm{CdSO_4{\cdot}8/3\,H_2O}$ (38.0 g, 0.14 mol) in aqueous $\mathrm{NH_3}$ (450 mL, 10%). Stirring was continued for 1.5 h, and the powder was then washed to neutrality by multiple decanting. The remaining paste was washed with 2 M HOAc and then four times with $\mathrm{H_2O}$ to neutrality. After separation by suction filtration, the residue was dried over $\mathrm{P_2O_5}$ in a desiccator. After grinding in an agate mortar the yellow powder was stored under $\mathrm{N_2}$; specific surface area: 73 $\mathrm{m^2\,g^{-1}}$ (BET, $\mathrm{N_2}$); microanalysis: CdS (144.47): found S 17.43; calcd S 22.19.

CdS-B: A solution of $\mathrm{Na_2S{\cdot}9\,H_2O}$ (24.0 g, 0.1 mol) in $\mathrm{H_2O}$ (200 mL) and a solution of $\mathrm{CdSO_4{\cdot}8/3\,H_2O}$ (25.7 g, 0.1 mol) in $\mathrm{H_2O}$ (200 mL) were added dropwise and simultaneously to $\mathrm{H_2O}$ (200 mL). Stirring was continued for 12 h, and the powder was then washed by multiple decanting with $\mathrm{H_2O}$. After separation by suction filtration, the residue was dried over $\mathrm{P_2O_5}$ in a desiccator. The ground powder was heated at 150 °C under reduced pressure for 5 h (gravimetric weight loss 4–8%), thoroughly ground in an agate mortar to an orange powder and stored under $\mathrm{N_2}$; microanalysis: found S 21.62, C 0.13, H 0.15, N 0.00; calcd S 22.19; particle size 1–50 µm; specific surface area 60–80 $\mathrm{m^2\,g^{-1}}$ (BET, $\mathrm{N_2}$).

Adduct 2: CdS (300 mg, 2.08 mmol), **1** (1500 mg, 5.84 mmol), cyclopentene (20.5 mL, 0.23 mol), and MeOH (200 mL) were suspended in a Pyrex immersion lamp apparatus by sonicating for 20 min while bubbling Ar through the suspension. Irradiation was performed with water cooling until TLC analysis indicated that all **1** had reacted (22 h). CdS was removed by suction filtration, and the remaining liquid was evaporated in vacuo. The white powder was recrystallized from heptane. Yield: 1402 mg (74%) of colorless crystals. M.p. 139–144 °C. IR (KBr): $\tilde{\nu}$ = 3427 (NH), 3055, 3015, 2926 (CH), 1601, 1501 (C=C); MS: m/z = 325 [M^+]. $\mathrm{C_{24}H_{23}N}$ (325.5): calcd C 88.57, H 7.12, N 4.30; found C 88.80, H 7.29, N 4.42; ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 270 MHz): δ = 1.63–2.18 (m, 4H, $\mathrm{=CHC}H_2\mathrm{C}H_2$), 3.89–3.99 (m, 1H, $\mathrm{C}H\mathrm{CN}$), 4.54 (br, 1H, NH), 5.55–5.60 (m, 1H, $\mathrm{C}H\mathrm{{=}CHCH_2}$), 5.72–5.79 (m, 1H, $\mathrm{CH{=}C}H\mathrm{CH_2}$), 6.25–6.32, 6.50–6.58, 6.85–6.95 (m, 5H, $\mathrm{NC_6}H_5$), 7.13–7.31, 7.42–7.53 (m, 10H, $\mathrm{CC_6}H_5$); ^{13}C NMR ($\mathrm{CDCl_3}$, 67.7 MHz): δ = 25.89 ($\mathrm{=CHCH_2}C\mathrm{H_2}$), 32.09 ($\mathrm{=CH}C\mathrm{H_2}$), 58.24 ($C\mathrm{HCN}$), 68.01 ($C\mathrm{NC_6H_5}$), 115.80, 117.01, 128.33 ($\mathrm{N}C_6\mathrm{H_5}$), 126.54, 126.60, 127.50, 127.57, 128.65, 129.22 ($\mathrm{C}C_6\mathrm{H_5}$), 131.26 ($C\mathrm{H{=}CHCH_2}$), 134.49 ($\mathrm{CH{=}}C\mathrm{HCH_2}$), 142.01, 143.31 ($C\mathrm{CN, C_6H_5}$), 146.11 ($C\mathrm{N, C_6H_5}$).

Adduct 3: Analogous to **2**. CdS (300 mg, 2.08 mmol), **1** (1589 mg, 6.18 mmol), and cyclohexene (23,6 mL, 0.23 mol) in MeOH (200 mL) for 27.5 h. Yield: 1637 mg (78%) of white powder. M.p. 129–133 °C. IR (KBr): $\tilde{\nu}$ = 3413 (NH), 3024, 2934 (CH), 1600, 1499 (C=C); MS: m/z = 339 [M^+]; $\mathrm{C_{25}H_{25}N}$ (339.5): calcd C 88.45, H 7.42, N 4.13; found C 88.39, H 7.58, N 4.13; ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 270 MHz): δ = 1.13–1.29 (m, 1H, $\mathrm{=CHCH_2}H\mathrm{CH}$), 1.37–1.62 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2CH{=}}$), 1.73–1.97 (m, 3H, $\mathrm{=CHC}H_2\mathrm{CH_2HC}H$), 3.14–3.24 (m, 1H, $\mathrm{C}H\mathrm{CN}$), 4.50 (br, 1H, NH), 5.42 (d, 1H, J = 10.3 Hz, $\mathrm{C}H\mathrm{{=}CHCH_2}$), 5.65–5.74 (m, 1H, $\mathrm{CH{=}C}H\mathrm{CH_2}$), 6.23–6.31, 6.48–6.55, 6.83–6.92 (m, 5H, $\mathrm{NC_6}H_5$), 7.13–7.34, 7.48–7.57 (m, 10H, $\mathrm{CC_6}H_5$); ^{13}C NMR ($\mathrm{CDCl_3}$, 67.7 MHz): δ = 21.11 ($C\mathrm{H_2CH_2CH{=}}$), 21.98 ($\mathrm{=CHCH_2}C\mathrm{H_2}$), 25.17 ($\mathrm{=CH}C\mathrm{H_2}$), 49.08 ($C\mathrm{HCN}$), 68.58 ($C\mathrm{NC_6H_5}$), 115.74, 116.85, 128.21 ($\mathrm{N}C_6\mathrm{H_5}$), 126.60, 126.64, 127.36, 127.65, 128.98, 129.50 ($\mathrm{C}C_6\mathrm{H_5}$), 127.71 ($C\mathrm{H{=}CHCH_2}$), 130.57 ($\mathrm{CH{=}}C\mathrm{HCH_2}$), 140.68, 141.75 ($C\mathrm{CN, C_6H_5}$), 146.19 ($C\mathrm{N, C_6H_5}$).

Adduct 4: Analogous to **2**. CdS (200 mg, 1.39 mmol), **1** (1500 mg, 5.84 mmol), and 1-methylcyclohexene (10 mL, 0.076 mol) in MeOH (180 mL) for 27 h. After separation by chromatography (quartz glass column 50 × 2 cm, 100 g of $\mathrm{Al_2O_3}$, activity 3, fluorescence label; eluent: petroleum ether/diethyl ether 5/1) 1625 mg (79%) of a yellow oil was obtained containing 80% of the regioisomer **4** (HPLC); after HPLC separation: 355 mg (17%) of crystalline **4**. M.p. 140–144 °C. IR (KBr): $\tilde{\nu}$ = 3431 (NH), 3052, 2933 (CH), 1601, 1505 (C=C); MS: m/z = 354 [M^+]; $\mathrm{C_{26}H_{27}N}$ (353.5): calcd C 88.34, H 7.70, N 3.96; found C 88.00, H 7.90, N 3.98; ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 270 MHz): δ = 1.15–1.55 (br m, 3H, $\mathrm{=C(CH_3)}H\mathrm{CHC}H_2$), 1.60 (s, 3H, $\mathrm{C{=}CC}H_3$), 1.70–1.80 (br m, 3H, $\mathrm{=C(CH_3)HC}H\mathrm{CH2C}H_2$), 3.15 (br s, 1H, $\mathrm{C}H\mathrm{CN}$), 4.55 (s, 1H, NH), 5.20 (d, 1H, $\mathrm{C}H\mathrm{{=}C(C)C}$), 6.25–6.95 (m, 5H, $\mathrm{NC_6}H_5$), 7.20–7.60 (m, 10H, $\mathrm{CC_6}H_5$); ^{13}C NMR ($\mathrm{CDCl_3}$, 67.7 MHz): δ = 22.17 ($\mathrm{=C(CH_3)CH_2}C\mathrm{H_2}$), 24.82 ($C\mathrm{H_2CH(C)CH{=}}$), 24.13 ($C\mathrm{H_3C(C){=}CH}$), 29.98 ($\mathrm{=C(CH_3)}C\mathrm{H_2CH_2}$), 49.44 ($C\mathrm{HCN}$), 68.68 ($C\mathrm{NC_6H_5}$), 115.70, 116.71, 128.14 ($\mathrm{N}C_6\mathrm{H_5}$), 121.57 ($C\mathrm{H{=}C(C)CH_2}$), 126.47, 126.52, 127.36, 127.63, 128.82, 129.70 ($\mathrm{C}C_6\mathrm{H_5}$), 137.88 ($\mathrm{CH{=}}C\mathrm{(C)C}$), 140.67, 141.84 ($C\mathrm{CN, C_6H_5}$), 146.25 ($C\mathrm{N, C_6H_5}$).

Adduct 5: Analogous to **2**. CdS (300 mg, 2.08 mmol), **1** (1495 mg, 5.82 mmol), and α-pinene (37.0 mL, 0.23 mol) in MeOH (180 mL) for 27 h. Yield: 1644 mg (72%) of white solid. M.p. 156–159 °C. IR (KBr): $\tilde{\nu}$ = 3387 (NH), 3033, 3002, 2976, 2949 (CH), 1598, 1502 (C=C); MS: m/z = 393 [M^+]; $\mathrm{C_{29}H_{31}N}$ (393.57): calcd C 88.50, H 7.94, N 3.56; found C 88.15, H 8.05, N 3.56; ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 270 MHz): δ = 0.05 (d, J = 7.9 Hz, 1H, $\mathrm{=C(C)CH(C)}H\mathrm{CH}$), 0.90 (s, 3H, $\mathrm{C}H_3\mathrm{(C)C(C)CH_3}$), 1.21 (s, 3H, $\mathrm{CH_3(C)C(C)C}H_3$), 1.57 (s, 3H, $\mathrm{C}H_3\mathrm{C{=}CH}$), 1.68–1.79 (m, 1H, $\mathrm{=C(C)CH(C)HC}H$), 1.68–1.79 (m, 1H, $\mathrm{=C(C)C}H$), 2.25–2.33 (m, 1H, $\mathrm{=CHCH(C)C}H$), 3.30–3.37 (m, 1H, $\mathrm{C}H\mathrm{CN}$), 4.46 (br, 1H, NH), 5.06–5.12 (s, 1H, $\mathrm{C(C){=}C}H\mathrm{CH(C)}$), 6.26–6.32, 6.47–6.53, 6.82–6.89 (m, 5H, $\mathrm{NC_6}H_5$), 7.08–7.31, 7.48–7.55 (m, 10H, $\mathrm{CC_6}H_5$); ^{13}C NMR ($\mathrm{CDCl_3}$, 67.7 MHz): δ = 20.63 ($C\mathrm{H_3(C)C(C)CH_3}$), 23.27 ($C\mathrm{H_3C{=}CH}$), 25.52 ($\mathrm{=C(C)CH(C)}C\mathrm{H_2}$), 26.52 ($\mathrm{CH_3(C)C(C)}C\mathrm{H_3}$), 42.34 ($\mathrm{=CHCH(C)}C\mathrm{H(C)}$), 42.48 ($\mathrm{=C(C)CH(C)(C)}C\mathrm{(C)}$), 46.60 ($\mathrm{=C(C)}C\mathrm{H(C)CH_2}$), 52.15 ($\mathrm{=CH}C\mathrm{H(C)}$), 68.23 ($C\mathrm{NC_6H_5}$), 115.74 ($\mathrm{C(C){=}}C\mathrm{H}$), 116.36, 117.33, 128.23 ($\mathrm{N}C_6\mathrm{H_5}$), 126.58, 127.36, 127.63, 128.82, 129.70 ($\mathrm{C}C_6\mathrm{H_5}$), 140.72, 142.58 ($C\mathrm{CN, C_6H_5}$), 146.01 ($C\mathrm{N, C_6H_5}$), 147.44 ($C\mathrm{(C){=}CH}$).

Adduct 6: Analogous to **2**. CdS (312.4 mg, 2.16 mmol), **1** (1508 mg, 5.87 mmol), and 2,5-DHF (17.7 mL, 0.23 mol) in MeOH (200 mL) for 5.5 h; recrystallization from diethyl ether/petroleum ether. Overall yield: 1052 mg (55%) of white solid, which, according to HPLC, contained 70% of **6a** and 30% of **6b**, as compared to 55 and 45%, respectively, before crystallization. M.p. 152–156 °C. IR (KBr): $\tilde{\nu}$ = 3415 (NH), 3053, 2941, 2883 (CH), 1599 (-O-C=C-, -C=C-), 1506 (C=C); MS: m/z = 327 [M^+]; $\mathrm{C_{23}H_{21}NO}$ (327.44): calcd C 84.37, H 6.47, N 4.28; found C 84.62, H 6.63, N 4.35.

6a: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 270 MHz): δ = 4.12–4.30 (m, 3 H, $\mathrm{OC}H_2\mathrm{C}H$), 4.77 (br s, 1H, NH), 4.91–4.94 (m, 1H, $\mathrm{C}H\mathrm{{=}CHO}$), 6.41–6.44 (m, 1H, $\mathrm{CH{=}C}H\mathrm{O}$), 6.27–6.32, 6.52–6.61, 6.88–6.97 (m, 5H, $\mathrm{NC_6}H_5$), 7.18–7.37, 7.42–7.61 (m, 10H, $\mathrm{CC_6}H_5$); ^{13}C NMR ($\mathrm{CDCl_3}$, 67.7 MHz): δ = 55.07 ($\mathrm{=CH}C\mathrm{HCH_2}$), 67.14 ($C\mathrm{NC_6H_5}$), 71.92 ($\mathrm{O}C\mathrm{H_2CH}$), 100.36 ($C\mathrm{H{=}CHO}$) 148.72 ($\mathrm{CH{=}}C\mathrm{HO}$), 116.08, 117.35, 128.13 ($\mathrm{N}C_6\mathrm{H_5}$), 126.94, 127.79, 127.89, 128.63, 129.00 ($\mathrm{C}C_6\mathrm{H_5}$), 142.10, 142.40 ($C\mathrm{CN, C_6H_5}$), 145.95 ($C\mathrm{N, C_6H_5}$).

6b: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 270 MHz): δ = 4.12–4.30, 4.52–4.60 (m, 2H, $\mathrm{=CHC}H_2\mathrm{O}$), 4.83 (br s, 1H, NH), 5.47–5.52 (m, 1H, $\mathrm{C}H\mathrm{{=}CHCH}$), 5.71–5.77 (m, 1H, $\mathrm{=CC}H\mathrm{O}$), 5.86–5.90 (m, 1H, $\mathrm{CH{=}C}H\mathrm{CH}$), 6.34–6.39, 6.52–6.61, 6.88–6.97 (m, 5H, $\mathrm{NC_6}H_5$), 7.18–7.37, 7.42–7.61 (m, 10H, $\mathrm{CC_6}H_5$); ^{13}C NMR ($\mathrm{CDCl_3}$, 67.7 MHz): δ = 68.64 ($C\mathrm{NC_6H_5}$), 76.31 ($\mathrm{=CH}C\mathrm{H_2O}$), 93.44 ($\mathrm{=C}C\mathrm{HO}$), 127.02 ($C\mathrm{H{=}CHCH}$), 129.32 ($\mathrm{CH{=}}C\mathrm{HCH}$), 116.08, 117.35, 128.37 ($\mathrm{N}C_6\mathrm{H_5}$), 126.94, 127.34, 127.62, 128.76, 128.86 ($\mathrm{C}C_6\mathrm{H_5}$), 141.07, 141.79 ($C\mathrm{CN, C_6H_5}$), 145.89 ($C\mathrm{N, C_6H_5}$).

Adduct 7: Analogous to **2**. CdS (200 mg, 1.38 mmol), **1** (1500 mg, 5.84 mmol), and 3,4-DHP (10 mL, 0.11 mol) in MeOH (180 mL) for 19 h; recrystallization from diethyl ether/petroleum ether. Yield: 1061 mg (53%) of white solid; 54% of **7a** and 46% of **7b**. M.p. 129–132 °C. MS: m/z = 341 [M^+]; $\mathrm{C_{24}H_{23}NO}$ (341.5); calcd C 84.42, H 6.79, N 4.10; found C 84.30, H 6.93, N 4.12. Separation of the two regioisomers by preparative HPLC.

7a: M.p. 144–146 °C; IR (KBr): $\tilde{\nu}$ = 3392 (NH), 3048, 2965, 2880 (CH), 1641 (OC=C), 1601, 1493 (C=C); ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 270 MHz): δ = 1.79–1.96 (m, 2H, $\mathrm{OCH_2C}H_2$), 3.27–3.36 (m, 1H, $\mathrm{=CHC}H\mathrm{CH_2}$), 3.56–3.66, 3.72–3.82 (m, 2H, $\mathrm{=CHOC}H_2$), 4.42 (m, 1H, $\mathrm{C}H\mathrm{{=}CHO}$), 4.54 (br s, 1H, NH), 6.35–6.39 (m, 1H, $\mathrm{CH{=}C}H\mathrm{O}$), 6.27–6.32, 6.52–6.58, 6.87–6.95 (m, 5H, $\mathrm{NC_6}H_5$), 7.16–7.36, 7.48–7.57 (m, 10H, $\mathrm{CC_6}H_5$); ^{13}C NMR ($\mathrm{CDCl_3}$, 67.7 MHz) δ = 25.30 ($\mathrm{OCH_2}C\mathrm{H_2}$), 43.00 ($\mathrm{=CH}C\mathrm{H(C)}$), 64.87 ($\mathrm{=CHO}C\mathrm{H_2}$), 67.78 ($C\mathrm{NC_6H_5}$), 100.83 ($C\mathrm{H{=}CHO}$) 146.48 ($\mathrm{CH{=}}C\mathrm{HO}$), 115.93, 117.14, 128.28 ($\mathrm{N}C_6\mathrm{H_5}$), 126.87, 126.91, 127.55, 127.76 ($\mathrm{C}C_6\mathrm{H_5}$), 140.52, 141.16 ($C\mathrm{CN, C_6H_5}$), 146.00 ($C\mathrm{N, C_6H_5}$).

7b: M.p. 147–148 °C. IR (KBr): $\tilde{\nu}$ = 3402 (NH), 3048, 2910, 2868 (CH), 1597, 1500 (C=C); ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 270 MHz): δ = 1.82–1.93, 2.07–2.23 (m, 2H, $\mathrm{=CHC}H_2$), 3.58–3.83 (m, 2H, $\mathrm{=CHCH_2C}H_2\mathrm{O}$) 4.87 (m, 1H, $\mathrm{C}H\mathrm{OCH_2}$), 5.27 (br s, 1H, NH), 5.48 (m, 1H, $\mathrm{CHC}H\mathrm{{=}CHCH_2}$), 5.86–5.95 (m, 1H, $\mathrm{CHCH{=}C}H\mathrm{CH_2}$) 6.29–6.36, 6.53–6.60, 6.88–6.97 (m, 5H,

NC_6H_5), 7.22–7.39, 7.57–7.67 (m, 10H, CC_6H_5); ^{13}C NMR ($CDCl_3$, 67.7 MHz): $\delta = 24.92$ (=CH*C*H_2), 63.93 (=$CHCH_2CH_2O$), 68.70 (*C*NC_6H_5), 81.86 (*C*$HOCH_2$), 126.45 (CH*C*H=$CHCH_2$), 127.08 (CHCH=*C*HCH_2) 115.83, 116.91, 128.30 (N*C*$_6H_5$), 126.92, 127.53, 127.73, 129.38, 129.74 (C*C*$_6H_5$), 139.59, 140.92 (*C*CN, C_6H_5), 146.18 (*C*N, C_6H_5).

Adduct 8: Analogous to **2**. CdS (200 mg, 1.39 mmol), **1** (2000 mg, 7.8 mmol), and 2-pentene (*cis/trans*) (10 mL, 0.093 mol) in MeOH (180 mL) for 70 h. After solvent evaporation, the crude product was purified by chromatography (quartz glass column 50 × 2 cm, 100 g of Al_2O_3, activity 3, fluorescence label; eluent: petroleum ether/diethyl ether 5/1); yield: 757.1 mg (30%) of a yellow oil containing 80% (^1H NMR) of **8**. Isolation of the regioisomers could not be achieved by preparative HPLC. IR (CCl_4): $\tilde{\nu} = 3411$ (NH), 3056, 2968 (CH), 1600, 1499 (C=C); MS: $m/z = 328$ [M^+]; $C_{24}H_{25}N$ (327.5): calcd C 88.03, H 7.70, N 4.28; found C 87.53, H 7.90, N 4.54; ^1H NMR ($CDCl_3$, TMS, 270 MHz): $\delta = 0.88$ (d, $J = 6.9$ Hz, 3H, CH(C)C*H*$_3$), 1.58 (d, 3H, =CHC*H*$_3$), 3.06–3.16 (m, 1H, =CHC*H*(C)), 4.69 (br, 1H, NH), 4.88–5.00 (m, 1H, C*H*=$CHCH_3$), 5.46–5.61 (m, 1H, CH=C*H*CH_3), 6.17–6.87 (m, 5H, NC_6H_5), 7.08–7.66 (m, 10H, CC_6H_5); ^{13}C NMR ($CDCl_3$, 67.7 MHz): $\delta = 16.50$ (CH(C)*C*H_3), 18.07 (=CH*C*H_3), 50.20 (=CH*C*H(C)), 67.72 (*C*NC_6H_5), 115.39, 116.76, 128.20 (N*C*$_6H_5$), 126.54, 126.57, 127.23, 127.49, 129.11, 129.77 (C*C*$_6H_5$), 127.31 (*C*H=$CHCH_3$), 132.60 (CH=*C*HCH_3), 139.64, 141.42 (*C*CN, C_6H_5), 145.78 (*C*N, C_6H_5).

Rate dependence on acetic acid concentration in the system 1/cyclopentene: CdS-B (30.0 mg, 0.2 mmol), **1** (51.0 mg, 0.20 mmol), cyclopentene (0.8 mL, 9.1 mmol), and MeOH or THF (20.0 mL) with variable concentrations of acetic acid (0–110 mmol L^{-1}) were sonicated for 15 min under N_2. Irradiation was performed in a quartz cuvette with a cutoff filter ($\lambda > 400$ nm). Small aliquots were taken from the suspension, CdS was filtered off through a micropore filter, and the concentration of **2** was measured by HPLC. The rate of product formation was calculated from the initial slope of a concentration versus time plot.

MeOH:

$c_{HOAc} =$ 0.0 mmol L^{-1}, rate = 2.6×10^{-7} mol $L^{-1}s^{-1}$;
$c_{HOAc} =$ 14.0 mmol L^{-1}, rate = 11.3×10^{-7} mol $L^{-1}s^{-1}$;
$c_{HOAc} =$ 28.0 mmol L^{-1}, rate = 11.5×10^{-7} mol $L^{-1}s^{-1}$;
$c_{HOAc} =$ 55.0 mmol L^{-1}, rate = 12.0×10^{-7} mol $L^{-1}s^{-1}$;
$c_{HOAc} =$ 110.0 mmol L^{-1}, rate = 12.9×10^{-7} mol $L^{-1}s^{-1}$.

THF:

$c_{HOAc} =$ 0.0 mmol L^{-1}, rate = 1.9×10^{-7} mol $L^{-1}s^{-1}$;
$c_{HOAc} =$ 14.0 mmol L^{-1}, rate = 3.7×10^{-7} mol $L^{-1}s^{-1}$;
$c_{HOAc} =$ 28.0 mmol L^{-1}, rate = 4.7×10^{-7} mol $L^{-1}s^{-1}$;
$c_{HOAc} =$ 55.0 mmol L^{-1}, rate = 5.7×10^{-7} mol $L^{-1}s^{-1}$;
$c_{HOAc} =$ 110.0 mmol L^{-1}, rate = 6.7×10^{-7} mol $L^{-1}s^{-1}$.

Influence of the olefinic substrate: General procedure: CdS (239 mg, 1.67 mmol), **1** (257 mg, 1 mmol), olefinic substrate (40 mmol; 3.5 mL cyclopentene; 4.1 mL cyclohexene; 4.7 mL 1-methyl-cyclohexene; 6.4 mL α-pinene; 4.3 mL *cis/trans*-pentene; 5.0 mL 1-hexene; 3.0 mL 2,3- or 2,5-DHF; 3.65 mL 3,4-DHP) and MeOH (90 mL) were irradiated as described for the preparative reactions. Aliquots (2 mL) were withdrawn before and during the reaction, and the concentration of **1** was determined by measuring the absorbance at 330 nm in a quartz cell of 0.1 cm optical path length. Adduct formation was monitored by HPLC analysis.

Influence of the imine substrate: As described above, with CdS (200 mg, 1.38 mmol), cyclohexene (5.0 mL, 49 mmol) and MeOH (90 mL). *N,N'*-dicyclohexyl-1,4-diaza-1,3-butadiene (300 mg, 1.36 mmol), 2,2'-bipyridyl (300 mg, 1.92 mmol), histidine hydrochloride monohydrate (300 mg, 1.38 mmol).

Influence of additives:. As described for the influence of olefinic substrate, with 2,5-DHF (3.0 mL), pyridine (0.5 mL, 0.067 M) or HOAc (1 mL, 0.188 M) or trifluoroacetic acid (1 mL, 0.10 M); all additives were added prior to irradiation.

Benzophenone: standard experiment but omitting CdS. After irradiating for 24 h, benzophenone (104 mg, 0.57 mmol) was added and irradiation was continued for 4 h. Only traces of **6** were detectable by HPLC.

Oxygen: Air was bubbled through the suspension during sonication and for an additional 10 min prior to irradiation.
CdS (239 mg, 1.67 mmol) and **1** (257 mg, 1 mmol) in MeOH, EtOH or *i*PrOH (90 mL) were used for the experiments in the absence of an olefin/ether.

Apparent quantum yields: A suspension of CdS (5.0 mg, 0.0346 mmol) in 3.0 mL of an 10^{-3} M methanolic solution of **1** was sonicated with Ar bubbling in a 4 mL quartz cell for 20 min. 2,5-DHF (0.3 mL, 4.1 mmol) (or 3,4-DHP, cyclohexene, cyclopentene) and HOAc (30 µL, 0.157 M) were added, and evaporated MeOH was replenished. After brief shaking 1 mL of the solution was withdrawn through a micropore filter (pore size ≥0.2 µm), and the concentration of **1** was determined photometrically as described above. After irradiating for 1 h at $\lambda = 437$ nm in the electronically integrating actinometer,[26] the amount of addition product (0.20 to 0.66 µmol) was measured by HPLC. The total reaction volume was obtained by weighing the quartz cell before and after emptying. Typical intensities of absorbed light were in the range of 40×10^{-6} Einstein.

Solar experiment: CdS (151 mg, 1.05 mmol) and **1** (152 mg, 0.59 mmol) in MeOH (50 mL) were sonicated in a two-necked flask for 20 min with Ar bubbling. After addition of 2,5-DHF (1.8 mL, 24 mmol), Ar bubbling was continued for 2 min, the flask was stoppered gastight and left on a windowsill in diffuse sunlight. The concentration of **1**, determined as described above, changed from 12 to 9, 7, and 2 M after 1, 2, and 4 h, respectively.

Variation of the amount of CdS: General procedure as described for influence of additives, using **1** (257 mg, 1 mmol), cyclopentene (3.5 mL, 40 mmol), MeOH (90 mL), and CdS (20.2, 41.5, 74.3, 114.0, 178.3, 238.6, and 347.5 mg).

Use of commercial CdS: According to the general irradiation procedure; CdS Ventron (ultrapure) (239 mg, 1.65 mmol), **1** (257 mg, 1 mmol), and cyclopentene (3.5 mL, 40 mmol) in MeOH (90 mL).

X-ray analyses: Automated four-circle diffractometer (Siemens P4) $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), graphite monochromator, $T = 298$ K, ω-scan speed 3.0–30° min^{-1}. Structure solution by direct methods (SHELXTL-PLUS), anisotropic refinement (SHELXL-93) of non-hydrogen atoms; the positions of all hydrogen atoms were taken from a difference fourier analysis and fixed at these coordinates. Single crystals of **2** and **5** were obtained from CH_2Cl_2/MeOH, **4** from CH_3CN/H_2O.

Adduct 2: $C_{24}H_{23}N$ (325.46): crystal size 0.60 × 0.30 × 0.30 mm, orthorhombic, space group $Fdd2$; $a = 2166.9(10)$ pm, $b = 3924(2)$ pm, $c = 844.2(5)$ pm, $V = 7.178(6)$ nm^3, $\rho_{calcd} = 1.205$ g cm^{-3} ($Z = 16$). 2229 reflections collected, 2229 independent reflections, 681 observed reflections [$F > 4\sigma(F)$]; structure refined against full-matrix least-squares on F^2; $\mu = 0.069$ mm^{-1}; $F(000) = 2784$; $R = 0.0495$, wR (all data) = 0.1267; 225 parameters refined; $2\theta_{max} = 54°$.

Adduct 4: $C_{26}H_{27}N$ (353.51): crystal size 0.5 × 0.4 × 0.4 mm, monoclinic, space group $P2_1/c$, $a = 868.5(3)$, $b = 2167.9(11)$, $c = 1129.8(6)$ pm, $\beta = 107.92(4)°$, $V = 2.024(2)$ nm^3, $\rho_{calcd} = 1.16$ g cm^{-3} ($Z = 4$). 12288 reflections collected, 4455 independent reflections, 1337 observed reflections [$F > 4\sigma(F)$]; structure refined against full-matrix least-squares on F^2; $\mu = 0.066$ mm^{-1}; $F(000) = 760$; $R = 0.0870$, wR (all data) = 0.2853; 244 parameters refined; $2\theta_{max} = 54°$.

Adduct 5: $C_{29}H_{31}N$ (393.58), crystal size 0.8 × 0.4 × 0.4 mm, monoclinic, space group $P2_1/c$, $a = 1632.7(5)$, $b = 827.5(3)$, $c = 1785.9(6)$ pm, $\beta = 108.29(3)°$, $V = 2.2910(1)$ nm^3, ρ_{calcd} 1.141 g cm^{-3} ($Z = 4$). 5647 reflections collected, 5037 independent reflections, 2564 observed reflections [$F > 4\sigma(F)$]; structure refined against full-matrix least-squares on F^2; $\mu = 0.065$ mm^{-1}; $F(000) = 848$; $R = 0.0439$, wR (all data) = 0.1110; 271 parameters refined; $2\theta_{max} = 54°$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100204. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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[1] a) N. Zeug, J. Bücheler, H. Kisch, *J. Am. Chem. Soc.* **1985**, *107*, 1459; b) R. Künneth, G. Twardzik, G. Emig, H. Kisch, *J. Photochem. Photobiol. A.: Chem.* **1993**, *76*, 209; c) S. Yanagida, H. Kawakami, Y. Midori, H. Kizumoto, C. Pac, Y. Wada, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1811.

[2] a) R. Künneth, C. Feldmer, H. Kisch, *Angew. Chem.* **1992**, *104*, 1102; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1039; b) R. Künneth, C. Feldmer, F. Knoch, H. Kisch, *Chem. Eur. J.* **1995**, *1*, 441.

[3] W. Schindler, H. Kisch, *Chem. Ber.* **1996**, *129*, 925.

[4] C. Amatore, A. R. Brown, *J. Am. Chem. Soc.* **1996** , *118*, 1482.

[5] J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, **1992**, p. 21.

[6] M. J. Begley, G. B. Gill, B. Wallace, *J. Chem. Soc. Perkin Trans. 1* **1978**, 93.

[7] R. J. Abraham, M. A. Cooper, J. R. Salmon, D. Whittaker, *Org. Magn. Reson.* **1972**, *4*, 489.

[8] a) W. Offermann, *Org. Magn. Reson.* **1982**, *20*, 203; b) W. Offermann, A. Mannschreck, *ibid.* **1984**, *22*, 355.

[9] C. W. Haigh, R. B. Mallion, *Org. Magn. Reson.* **1972**, *4*, 203.

[10] a) A. Mills, G. Williams, *J. Chem. Soc. Faraday Trans. 1* **1987**, *83*, 2647; b) J. R. Harbour, R. Wolkow, M. L. Hair, *J. Phys. Chem.* **1981**, *85*, 4026; c) M. V. Rao, K. Rajeshwar, V. R. Pal Vernekey, J. Du Bow, *J. Phys. Chem.* **1980**, *84*, 1987, d) J. Cunningham, B. K. Hodnett, *J. Chem Soc. Faraday Trans. 1* **1987**, *77*, 2777.

[11] a) M. Fischer, *Tetrahedron* **1966**, *43*, 5273; b) M. Fischer, *Chem. Ber.* **1967**, *100*, 3599.

[12] H. Lund, J. Simonet, *Bull. Soc. Chim. Fr.* **1973**, *5*, 1843.

[13] a) J. G. Smith, C. D. Veach, *Can. J. Chem.* **1966**, *44*, 2245; b) J. G. Smith, *ibid.* **1968**, *46*, 2271; c) J. G. Smith, R. A. Turle, *J. Org. Chem.* **1972**, *37*, 126; d) J. G. Smith, I. Ho, *ibid.* **1972**, *37*, 653; e) J. G. Smith, G. E. F. Simpson, *ibid.* **1976**, *41*, 2878; f) J. G. Smith, D. J. Mitchell, *J. Am. Chem. Soc.* **1977**, *99*, 5045; g) J. G. Smith, D. C. Irwin, *ibid.* **1980**, *102*, 2757.

[14] K. Harada, *The Chemistry of the Carbon–Nitrogen Double Bond* (Ed.: S. Patai), Interscience, New York, **1970**.

[15] K. Takaki, Y. Tsubaki, S. Tanaka, F. Beppu, Y. Fujiwara, *Chem. Lett.* **1990**, 203.

[16] H. Thies, H. Schönberger, K. H. Bauer, *Arch. Pharmaz.* **1960**, *293*, 67.

[17] a) H. Lund, *Acta Chem. Scand.* **1959**, *13*, 249; b) C. P Andrieux, J. M. Saveánt, *J. Electroanal. Chem.* **1970**, *26*, 223.

[18] a) D. Meissner, R. Memming, B. Kastening, *J. Phys. Chem.* **1988**, *92*, 3476; b) D. Meissner, I. Lauermann, R. Memming, B. Kastening, *ibid.* **1988**, *92*, 3484; c) M. F. Finlayson, B. L. Wheeler, N. Kakuta, K.-H. Park, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber, J. M. White, *ibid.* **1985**, *89*, 5676; d) D. S. Ginley, M. A. Butler, *J. Electrochem. Soc.* **1978**, *125*, 1968; e) A. M. Roy, G. C. De, N. Sasmal, S. S. Bhattacharyya, *Int. J. Hydrogen Energy* **1995**, *30* No. 8, 627.

[19] R. Knorr, K. Ferchland, *Liebigs Ann.* **1995**, 419.

[20] a) W. Schindler, Ph.D. Thesis, Üniversität Erlangen-Nürnberg, **1996**; b) These can be only very rough estimates since for the powders employed the exact redox potentials of the reactive hole and the adsorbed olefin are unknown. For 2,5-DHF ($E_{\text{ox}} = 2.6$ V) an actual potential in solution of 2.3 V was obtained from the Nernst equation by assuming concentrations of 10^{-6} and 10^{-1} M for 2,5-DHF$^{\cdot +}$ and 2,5-DHF, respectively; c) Estimated according to ref. [20d] by using $E_0(H^+/H) = -2.1$ V and a C–H bond dissociation energy of 3.7 eV as obtained from ref. [20e]. The same argument was used to explain the photooxidation of alcohols by ZnS [20d]; d) A. Henglein, M. Gutierrez, Ch.-H. Fischer, *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 170. e) R. T. Sanderson, *Chemical Bond and Bond Energy*. Academic Press, New York, 1976. f) The 2-tetrahydrofuryl adduct of ArCH=NAr, Ar = p-ClC$_6$H$_4$, was isolated in 65% yield [20a].

[21] a) M. Anpo, A. Matsumoto, S. Kodama, *J. Chem. Soc., Chem. Commun.* **1987**, 1038; b) Y. Nakaoka, Y. Nosaka, *J. Phys. Chem.* **1995**, *99*, 9893; c) P. V. Kamat, N. M. Dimitrijevic, R. W. Fessenden, *J. Phys. Chem.* **1987**, *91*, 396. d) L. Lunazzi, G. Placucci, L. Grossi, *Tetrahedron* **1983**, *39*, 159. e) See, for example, A. Nozik, R. Memming, *J. Phys. Chem.* **1996**, 1306. f) A more positive E_{ox} results in a weaker C–H bond of RH$^{\cdot +}$: A. Albini, M. Mella, M. Freccero, *Tetrahedron* **1994**, *50*, 575.

[22] G. Reddelien, *Ber.* **1913**, *46*, 2718.

[23] $E_{1/2}$ is estimated from the ionization potential (IP in eV) according to the relation $E_{\text{ox}} = 0.89 \times \text{IP} - 6.04 + 0.49$; L. Miller, G. D. Nordblom, E. A. Mayeda, *J. Org. Chem.* **1972**, *37*, 916.

[24] a) D. A. Demeo, M. A. El-Sayed, *J. Chem. Phys.* **1970**, *52*, 2622; b) M. Bloch, F. Brogli, E. Heilbronner, T. B. Jones, H. Prinzbach, O. Schweikert, *Helv. Chim. Acta* **1978**, *61*, 1388.

[25] K. Kimura, S. Katsumata, T. Achiba, S. Iwata, *Handbook of Photoelectron Spectra of Fundamental Organic Molecules* Japan Scientific: Tokyo, Halsted Press, New York, **1981**; P. Bischof, E. Heilbronner, *Helv. Chim. Acta* **1970**, *53*, 1677.

[26] J. Amrein, J. Gloor, K. Schaffner, *Chimia* **1974**, *29*, 185.