Semiconductor-Catalysed Photoaddition: γ,δ-Unsaturated Amines from Cyclopentene and Schiff Bases[☆][◇]

Wolfram Schindler, Falk Knoch, and Horst Kisch*

Institut für Anorganische Chemie der Universität Erlangen-Nürnberg,
Egerlandstraße 1, D-91058 Erlangen
Telefax: (internat.) +49(0)9131/857363
E-mail: kisch@anorganik.chemie.uni-erlangen.de

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Irradiation of methanolic cadmium sulfide suspensions in the presence of Schiff bases and cyclopentene opens an easy access to new γ,δ-unsaturated amines. Their formation can be described as a kind of *paired photoelectrolysis* induced by the photogenerated electron-hole pair trapped at reactive surface sites of CdS. At the reductive site the imine is converted to an α-aminobenzyl radical by a proton-coupled electron transfer, while at the oxidative site cyclopentene is transformed to the cyclopentenyl radical through deprotonation of the intermediate radical cation. C–C coupling of these radicals affords the addition products. Competitive dimerisation of the radicals produces hydrodimers of the imines and dehydrodimers of the olefin, as demonstrated in the case of 1-phenylcyclohexene. Using optical active imines, we found no significant diastereoselectivity. In the absence of an olefin the alcoholic solvent was added to the imine. The molecular structure of one hydrodimer was resolved by X-ray analysis. When CdS/Pt was used as photocatalyst, hydrolysis products of the imine were formed, suggesting involvement of an intermediate OH radical.

The mechanism of photoreactions catalysed by semiconductor powder suspensions resembles the function of an electrochemical cell with the difference that reductive and oxidative reactions of adsorbed substrates occur simultaneously at a single catalyst particle[1,2]. This field is still a domain of physical chemistry[3] and applications in synthetic chemistry are very limited. The reactions investigated like the splitting of water[4], reduction of carbon dioxide[5] and dinitrogen[6], and cycloaddition[7] or oxidative fragmentation[8] of olefins afford known products and only in few cases they were performed on a preparative scale. Exceptions are the recently described ZnS and CdS catalysed photodehydrodimerisation of cyclic allyl and enol ethers or olefins[9] and their linear addition to 1,2-diazenes[10] affording new compounds on a gram scale. The latter reaction represents a novel type of semiconductor photocatalysis which can be mechanistically classified as *paired photoelectrolysis*. In the following we report that Schiff bases undergo an analogous addition reaction affording hitherto unknown γ,δ-unsaturated amines. This new method can be a simple alternative to the more complicated synthesis involving the corresponding Grignard reactions[11].

Results and Discussion

Addition of Cyclopentene: Irradiation of a methanolic CdS suspension in the presence of the Schiff bases **1a–1d** and an excess of cyclopentene afforded the addition products **2a–2d** and the hydrodimers **3a–3c** (Scheme 1). HPLC analysis indicated a quantitative transformation of **1a** into **2a** and **3a**, the ratio of **2a** to **3a** being 6:1. After complete disappearance of the imine component the products were isolated in yields of 50–95% by preparative HPLC. **3d** was formed in very low concentrations and no attempts were made for its isolation.

The structure of the γ,δ-unsaturated amines was deduced from their mass spectra and one- and two-dimensional ^{1}H- and ^{13}C-NMR analyses. Since the addition reaction generates two chiral centers, a racemic mixture of four diastereomers was obtained. The two enantiomeric pairs could be identified in the ^{1}H^{1}H COSY and ^{1}H^{13}C COSY NMR spectrum as displayed for **2a** in Figure 1.

The signals of the methylene protons at C-6 and C-5 appear as a multiplet at δ = 1.65–2.20 and 2.20–2.45, respectively. The protons at C-1 and C-2 give rise to two doublets of equal intensities at δ = 4.15 (^3J = 6.5 Hz) and 4.28 (^3J = 4.5 Hz) as well as to two multiplets at δ = 3.08 and 3.16, respectively. This and the four multiplets of the olefinic protons at C-3 (δ = 5.44, 5.52) and C-4 (δ = 5.88, 5.96) clearly indicate the presence of two diastereomers. The presence of a C–C bond between C-1 and the cyclopentenyl group at the allylic carbon atom C-2 is proved by the ^{1}H^{1}H COSY spectrum; the proton 1-H gives rise to an intensive cross peak with 2-H which further couples with 6-H. Whereas in the case of **2a** coupling of 2-H with the olefinic proton 3-H could not be detected, this coupling was observed in the COSY spectra of the other addition products. The appearance of a set of two slightly shifted cross peak patterns is further evidence for the presence of a diastereomeric mixture (Figure 1).

[◇] Heterogeneous Photocatalysis, XIV. – Part XIII: Ref.[10b].

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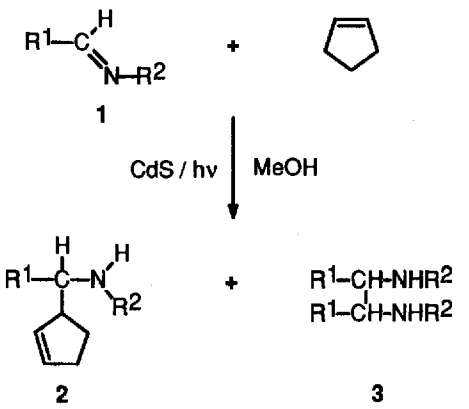
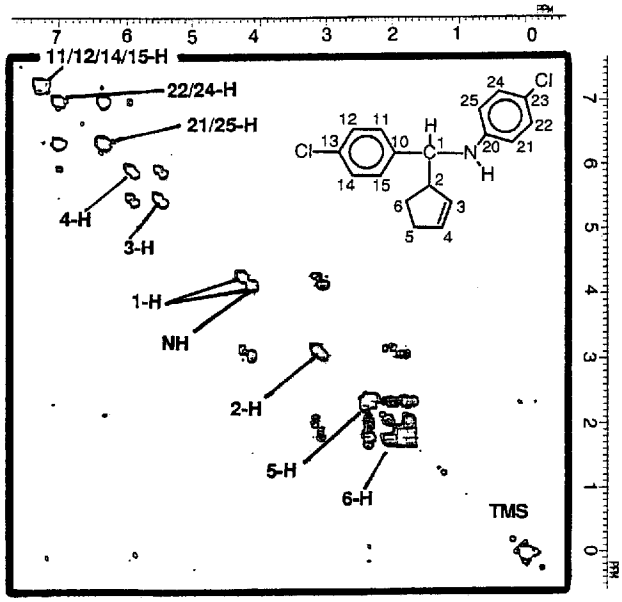
Scheme 1



	a	b	c	d
R^1	4-ClC_6H_4	2,6-$Cl_2C_6H_3$	4-ClC_6H_4	4-$MeOC_6H_4$
R^2	4-ClC_6H_4	C_6H_5	3,5-$Me_2C_6H_3$	4-MeC_6H_4
2 *)	60	40	55	80
3 *)	20	10	40	-

*) yield, [%]

Figure 1. $^1H^1H$ COSY NMR spectrum of **2a** in $CDCl_3$



The ^{13}C-NMR spectra contain a double signal set for the two diastereomers (Table 1). Chemical shifts of the carbon atoms fit well to values estimated from incremental data. On the basis of these ^1H- and ^{13}C-NMR data an alternative bond between C-6 and C-1 or C-2 and the nitrogen atom of the imine can be ruled out.

The hydrodimers **3a–3c** were similarly characterised. Analogous to the electrochemical synthesis of the same type of compounds involving reduction of the imine at metallic mercury electrodes[12], three stereoisomers were obtained. The achiral *meso* isomer was distinguished from the two *d,l* isomers by the chemical shift of the CH protons in the ^1H-NMR spectrum. By analogy with the literature[12] the two doublets of equal intensities for **3a** at $\delta = 4.85$ ($^3J = 7.0$ Hz) and 4.45 ($^3J = 8.5$ Hz) can be assigned to the *meso* and the *d,l* form, respectively (Table 1). While in the case of **3a** and **3c** the two diastereomers are formed in equal amounts, an excess of 85–90% of one isomer, as indicated by HPLC analysis, was obtained for **3b**. The difference in retention time was large enough to isolate the major component **3b′**. Accordingly, in the ^{13}C-NMR spectrum only one set of signals is observed, in contrast to the double set obtained for **3a** and **3c**.

Table 1. Selected NMR data of **2a–2d** and **3a–3c**

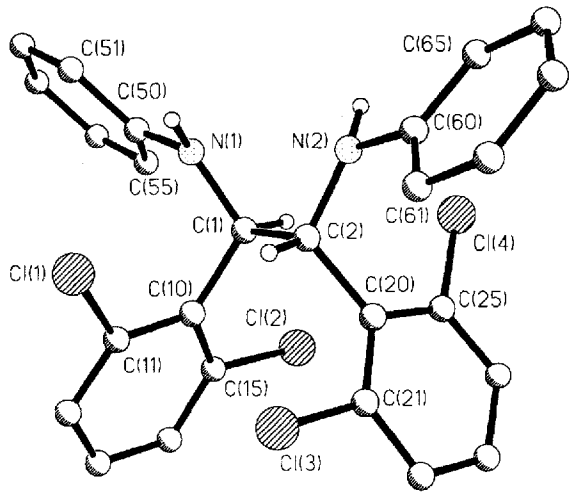
	2a	3a	2b	3b	2c	3c	2d
δ(^{13}C-NMR)[a]							
C-1	60.9 61.8	61.3 63.4	59.0 59.2	55.5	60.0 61.1	61.2 63.3	62.2 62.3
C-2	53.9 54.0	-	49.3 49.4	-	53.3 53.4	-	54.3 54.4
C-3	134.6 136.8	-	130.7 132.3	-	133.5 134.8	-	133.6 134.8
C-4	132.0	-	130.5 130.7	-	129.2 131.6	-	130.6 132.8
C-5	32.7 33.2	-	31.9 32.0	-	32.0 32.6	-	26.0 27.5
C-6	26.2 27.7	-	26.9 28.8	-	25.5 27.0	-	30.2 30.3
δ(^1H-NMR) [b]							
N-H	4.11	4.40 4.55	4.75	5.17	3.99	4.40 4.43	3.98
1-H	4.15 4.28	4.45 4.85	4.95 5.12	6.08	4.18 4.32	4.34 4.88	4.13 4.28

[a] $CDCl_3$, TMS, 67.7 MHz; [b] $CDCl_3$, TMS, 270 MHz

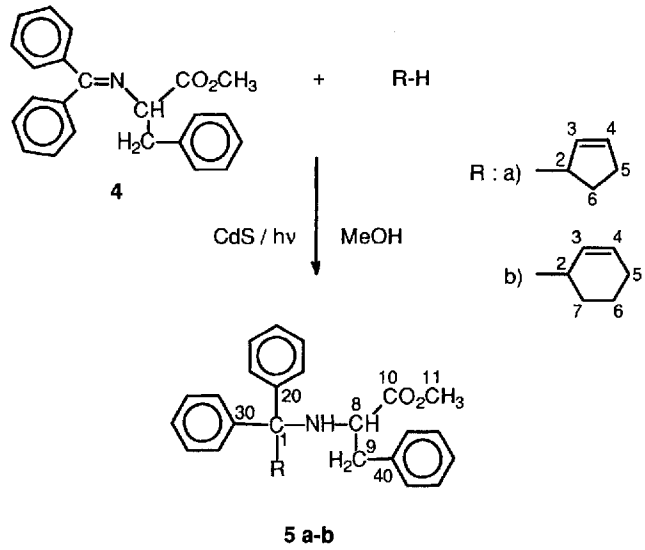
Crystals suitable for X-ray structural analysis could be obtained for the diastereomer **3b′**, the structure of which is shown in Figure 2. The two chiral centers C-1 and C-2 both have the same configuration. Therefore, **3b′** represents the *d,l* form of **3b**. The molecule has a staggered conformation along the C-1–C-2 bond with a torsion angle C-20–C-2–C-1–C-10 of 61.3°. The large torsion angles C-1–C-2–C-20–C-25 (75.1°) and C-2–C-1–C-10–C-11 (75.9°) allow a minimum of steric hindrance between the two 2,6-Cl_2-C_6H_3 groups. The distances C-1–C-2 [156.0(5) pm], C-1–C-10 [152.4(5) pm] and C-1–N-1 [145.4(4) pm] are typical of sp^3-sp^3 bonds. The bond angles at C-1 and C-2 indicate a slight distortion from an ideal tetrahedron as demonstrated by the values for C-1; N-1–C-1–C-2 (109.2°), C-10–C-1–C-2 (110.6°) and C-10–C-1–N-1 (113.9°).

In the ^{13}C-NMR spectrum of **3b′** the presence of six peaks for the 2,6-Cl_2-C_6H_3 group is noteworthy. These are assigned to C-12/C-14 ($\delta = 128.2/129.2$), C-13 (130.4), C-11/C-15 (134.1/135.6), and C-10 (136.8). The splitting of the

Figure 2. Molecular structure of **3b'**



Scheme 2



signals for C-11/C-15 and C-12/C-14 indicates a hindered rotation around the C-1–C-10 (C-2–C-20) bond. In the case of free rotation, molecular symmetry, either a C_2 axis (*d,l* form) or a mirror plane (*meso* form), requires that the two 2,6-Cl_2-C_6H_3 groups should give rise to only four signals. This steric demand of the dichlorophenyl groups seems to be responsible for the preferred formation of the diastereomer **3b'**. No two-electron reduction products of the Schiff bases were detected except in the case of the reaction of **1d** from which 4-methoxybenzyl-4-methylaniline could be isolated in low yields (<5%, see Experimental).

Reactions of Other Substrates: Analogous addition products could also be isolated when cyclopentene was replaced by cyclohexene. But yields were in all cases lower (5–40%) and no pure materials were obtained. However, characterisation was possible by comparison of MS and NMR data with those of the addition products of cyclopentene (see Experimental). In the case of **1a** the corresponding addition product and the hydrodimer were formed in a ratio of 3:1, as estimated on the basis of the ^{1}H-NMR spectral data.

To investigate whether the heterogeneous catalyst may induce some diastereoselectivity, chiral imines were also employed. Camphor-*N*-phenylimine or *N*-(4-methylbenzylidene) alanine methyl ester were not reactive[13] but experiments with easier reducible benzophenone derivatives were successful. The reaction of *N*-diphenylmethylene-L(–)-phenylalanine methyl ester **4**[14] with cyclopentene and cyclohexene afforded the addition products **5a** and **5b** in low yields (estimated < 10%) (Scheme 2). The formation of two diastereomers could be deduced from ^{1}H-NMR spectra. The signal of methoxy group of **5a** is split into two singlets at δ = 3.05 and 3.15. Integration of these peaks afforded a ratio of 1.3:1. For compound **5b** the two isomers were formed in an equimolar ratio. The apparent diastereoselectivity in the case of the cyclopentene adduct could be an artefact of the isolation procedure (see Experimental).

Mechanistic Aspects: The reaction did not take place when CdS was omitted from the complete system under otherwise identical experimental conditions (λ > 400 nm or UV light). Thus, a homogeneous photoreaction, similar to the addition of cyclohexene to an iminium salt[15], is excluded. Attempts to detect a mutual charge-transfer complex in concentrated methanol solutions of **1a** and cyclopentene failed. Accordingly, the mechanism is assumed to be analogous to the addition of olefins to 1,2-diazenes[10]. Light absorption by CdS generates an electron-hole pair which is trapped and separated into reducing (e_{tr}^-) and oxidising (h_{tr}^+) surface sites (eq. 1). Proton-coupled electron transfer to the adsorbed imine affords the corresponding α-aminobenzyl radicals (eq. 2), while electron transfer from the adsorbed olefin RH to h_{tr}^+ and deprotonation of the resulting radical cation produces the allyl radical R• (eq. 3).

$$CdS \xrightarrow{h\nu} CdS\,(e_{tr}^-, h_{tr}^+) \quad (1)$$

$$RCH{=}NR + e_{tr}^- + H_3O^+ \rightarrow R\dot{C}H{-}NHR + H_2O \quad (2)$$

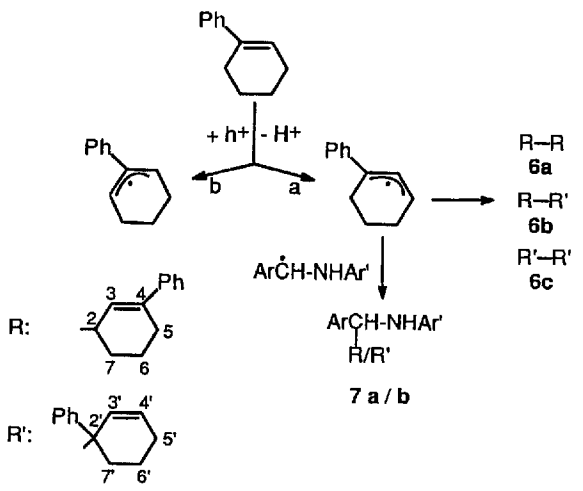
$$RH + h_{tr}^+ + H_2O \rightarrow \dot{R} + H_3O^+ \quad (3)$$

Subsequent C–C coupling of the α-aminobenzyl and allyl radicals leads to the products **2a–2d**. In a competition reaction the amino radicals may dimerise to the hydrodimers **3a–3c**. Their formation parallels the electrochemical synthesis[12] and therefore strongly supports the postulated electron transfer mechanism. An analogous ZnS-catalysed photohydrodimerisation of aromatic ketones has been reported[16].

Similar to the CdS/Pt catalysed dehydrodimerisation of cyclic enol and allyl ethers[9] the oxidatively produced radicals R• should undergo also dimerisation. While no corresponding products could be detected in the case of cyclopentene, this was possible in the system **1a** and 1-phenylcyclohexene. In addition to the expected products **7** and **3a**, the regioisomers **6a** and **6b** were formed (Scheme 3). This points to the unsymmetrical phenylcyclohexenyl radical as intermediate (path a, Scheme 3). The absence of **6c** is prob-

ably due to the expected high steric hindrance to dimerisation.

Scheme 3

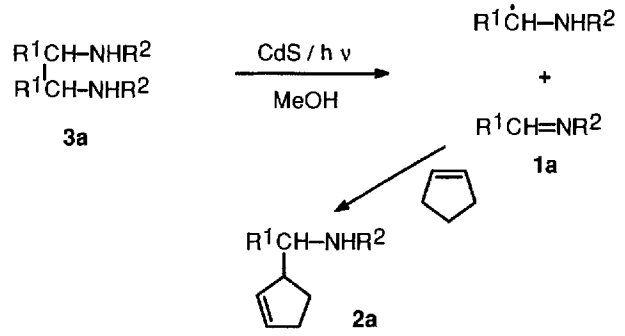


The reaction is fastest in protic solvents and accordingly dehydration of CdS had a negative effect; the reaction rate was lowered by 40–60% and the ratio of **3a** to **2a** was reduced from 1.07 to 0.64. In contrast to this, addition of 2.5% of water accelerated the formation of **2a** and **3a** by the factors of 1.2 and 2.0, respectively, while the ratio **3a** to **2a** of 1.04 was almost the same as for non-dehydrated CdS. Addition of CH_3COOH is disadvantageous due to the fast acid-catalysed hydrolysis of the imines.

From the positive effect of water one may conclude that in the primary oxidative step not RH (eq. 3) but rather water is oxidised to the OH radical[17] which could abstract hydrogen from RH to afford also the intermediate allyl radicals. This can be ruled out because of the following. When the reaction of cyclopentene and **1a** in a methanolic suspension containing 3.5% of H_2O was conducted in the presence of platinised CdS, the rate increased from $1.5 \cdot 10^{-7}$ mol l^{-1} s^{-1}, compared to the reaction of **2a** and **3a** in the presence of the unplatinised powder, to 5.7 and $4.8 \cdot 10^{-7}$ mol l^{-1} s^{-1}, respectively. Simultaneously, 4-chlorobenzaldehyde and 4-chloroaniline were formed in high amounts. Irradiating CdS/Pt in the above system in the absence of added water, we detected only minor amounts of the hydrolysis products and the rate was lowered to 4.1 (**2a**) and $3.3 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**3a**). The appearance of hydrolysis products can be related to the formation of OH radicals at the CdS/Pt particles, which was proved by spin trapping experiments[18]. Addition of OH to **1a** and subsequent H abstraction from RH produce an α-hydroxyamine which decomposes to 4-chlorobenzaldehyde and 4-chloroaniline. This type of reaction is known to occur in the photolysis of hydrogen peroxide in the presence of various imines[19]. From these results it seems very unlikely that in the presence of unplatinised CdS the primary oxidative step is the formation of an OH radical. Further mechanistic details will be discussed elsewhere[20].

When irradiation was continued after all the imine had been converted, decomposition of the hydrodimer occurred. Separate irradiation of CdS in the presence of **3a** and cyclopentene resulted in the formation of **2a** and **1a** in approximately equal amounts. The decomposition of **3a** may take place through H abstraction by the radicals S_X^- or R·, formed by hole (h_{tr}^+) oxidation of S_X^{2-} or cyclopentene. Alternatively, the hydrodimer may be directly oxidised by h_{tr}^+ to afford the radical cation. Subsequent deprotonation and C–C fragmentation produce the imine **1a** and an α-aminobenzyl radical (Scheme 4). C-C coupling of the latter with R· results in the formation of **2a**. In the reductive step cathodic photocorrosion of CdS affords metallic cadmium.

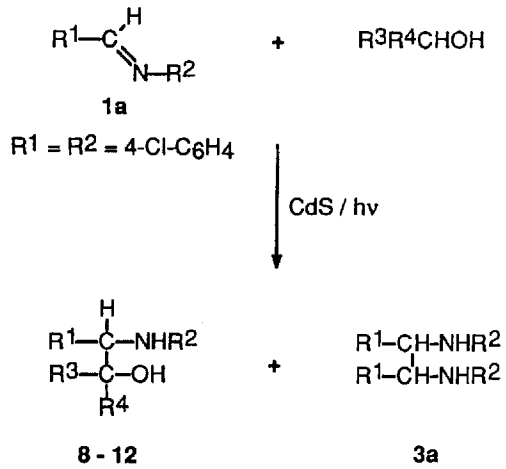
Scheme 4



Control experiments with **1a** showed that in the absence of olefins hydrodimers were also formed but the reaction rate was reduced by about 90%. Either CdS itself (under photocorrosion) or the solvent must therefore be involved in the oxidative step of this reaction. Irradiation of CdS in a solution of **1a** in different alcohols transformed the imine at different rates (Table 2), and the corresponding addition products **8**–**12** were isolated and characterised by mass, ^1H- and ^{13}C-NMR spectra (see Table 2 for selected data). Except for methanol and 2-propanol the products are racemic diastereomeric mixtures and were obtained in low yields (5–20%); they are often mixed with the two-electron reduction product *N*-4-chlorobenzyl-4-chloroaniline as revealed by the signal of the CH_2 group at $\delta = 47.6$ ($CDCl_3$) in the ^{13}C-NMR spectra. The major product in all reactions was the hydrodimer **3a**, obtained in yields of 10% (MeOH), 28% (BuOH), 29% (PrOH), 42% (EtOH), and 60% (*i*PrOH). In all cases the hydrodimer was partially decomposed upon prolonged irradiation. Other by-products were also formed but not isolated. The structure of **8**–**12** indicates that in all cases the α-CH bond of the alcohol adds to the imine in agreement with the preferred formation of α-hydroxyalkyl radicals from oxidation of the alcohols[21,22] (Scheme 5).

The rate of imine disappearance increased from MeOH (relative rate 1.0) to EtOH (2.0) and PrOH (2.0) and *i*PrOH (3.3) (Table 2) in agreement with the easier oxidation of these alcohols. BuOH does not follow this correlation since it induces a relative rate of only 1.8; in addition, more by-

Scheme 5



	8	9	10	11	12
R3	H	CH_3	C_2H_5	C_3H_7	CH_3
R4	H	H	H	H	CH_3

Table 2. Selected NMR data of **8**–**12**

	8	9	10	11	12
ROH	MeOH	EtOH	PrOH	BuOH	iPrOH
δ(^{13}C-NMR)[a]					
-COH	67.1	70.2 71.7	75.9 77.2	74.0 75.5	72.8
-C-NH-	59.4	62.5 63.7	61.2 61.4	61.6 61.7	66.0
$-CH_3$	-	19.5 20.3	10.3 10.4	13.9 14.0	27.0[b] 28.0[b]
$-CH_2-$	-	-	26.8	35.8 36.0	-
$-CH_2-$				19.2	
relativ rate [c]	1.0	2.0	2.0	1.8	3.3

[a] $CDCl_3$, TMS, 67.7 MHz; double peaks are assigned to the different diastereomers; [b] diastereotopic methyl groups; [c] relative to the disappearance rate of **1a** in MeOH ($-d[1a]/dt = 1.7\ 10^{-7}$ mol l^{-1} s^{-1})

products are formed. In the case of *i*PrOH, involvement of the intermediate hydroxyalkyl radical was corroborated by detection of its disproportion product acetone by IR analysis [ν(C=O) = 1707 cm^{-1}] of the reaction mixture. The possibility that the α-hydroxyalkyl radicals are involved as intermediates also in the formation of the of cyclopentene–imine adducts seems very unlikely since for this reaction the relative rate is lowered from 1.0 to 0.2 when methanol is replaced by ethanol, but no alcohol addition products could be detected by HPLC analysis. Even when the alcohol was present in a 500 fold molar excess, only the olefin adducts could be observed by HPLC.

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Experimental

All experiments were performed under N_2. – Solvents were dried according to common procedures and stored under N_2. – Unless noted otherwise all yields correspond to material isolated by preparative HPLC. – Melting points are uncorrected. – Schiff bases were synthesised according to literature[23], all other materials were commercially available and were used as received, except for cyclopentene and cyclohexene, which were distilled and stored under N_2 before use. – NMR: Jeol FT-JNM-EX 270 (TMS as internal standard). – IR: Perkin-Elmer 983. – MS: Varian Mat 212 (70 eV). – HPLC: Analytical set-up: Knauer HPLC pump 64, semipreparative pump head with 20-µl sample loop, column: Eurosphere 100 C18 (250 × 8 mm, 5 µm, Knauer) with precolumn (30 × 8 mm), eluent: CH_3CN/H_2O, 5:1, flow rate: 5.0 ml/min, detection: Knauer UV/Vis filter photometer at λ = 254 nm; Preparative set-up: Knauer HPLC pump 64, preparative pump head with 1000 µl sample loop, column: Nucleosil 120 C18 (250 × 36 mm, 5 µm, Macherey-Nagel) with precolumn (30 × 36 mm), eluent: CH_3CN/H_2O, 5:1, flow rate: 30 ml/min, detection as above. – Preparative irradiations were performed with a 100-W tungsten halogen lamp in a solidex immersion lamp apparatus, mechanistic irradiations in a cylindrical 20-ml quartz cuvette on an "optical train" equipped with XBO 150-W lamp and a cut-off filter of λ ≥ 375 or 400 nm (Schott Glas).

CdS: A solution of 24.0 g (0.1 mol) of $Na_2S \cdot 9\ H_2O$ in 200 ml of H_2O and a solution of 25.7 g (0.1 mol) of $CdSO_4 \cdot 8/3\ H_2O$ in 200 ml of H_2O were added dropwise and simultaneously with stirring to 200 ml of H_2O. Stirring was continued for 12 h and the powder was washed by multiple decantion with H_2O. After separation by suction filtration the residue was dried over P_2O_5 in a desiccator. The ground powder (CdS_{wet}) was heated at 150°C and reduced pressure of $3 \cdot 10^2$ Pa for 5 h (gravimetric weight loss 4–8%), again ground in an agate mortar to an orange powder and stored under N_2. CdS (144.47): found S 21.62, C 0.13, H 0.15, N 0.00; calcd. S 22.19; particle size 1–50 µm[24]; specific surface area 60–80 m^2 g^{-1} (BET method, N_2); – no reflections for cubic or hexagonal CdS were observable in the X-ray powder diffractograms, indicating a highly amorphous structure.

Synthesis of **2a** *and* **3a**: 1.0 g (4.00 mmol) of **1a**, 0.3 g (2.08 mmol) of CdS, 10.0 ml (113 mmol) of cyclopentene, and 70 ml of MeOH were suspended in a Pyrex immersion lamp apparatus by sonication for 15 min. When HPLC analysis indicated that all imine had reacted (48 h), irradiation was stopped, CdS removed by suction filtration and the remaining liquid concentrated under reduced pressure. From the resulting raw material **2a** and **3a** were separated by preparative HPLC; evaporation of the solvent afforded two colourless oils. Elemental analyses of the corresponding hydrochlorides, obtained by adding concentrated hydrochloric acid to a solution in diethyl ether, were performed. The white precipitate was filtered off, recrystallised from tetrahydrofuran/diethyl ether and dried at reduced pressure.

2a: 430 mg (60%). – IR (CCl_4): $\tilde{\nu}$ = 3418 cm^{-1} (NH), 3056, 2946, 2853 (CH), 1600, 1496 (C=C). – MS-FD *m/z*: 318 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 1.65–2.20 (m, 2H, $-CH_2-$), 2.20–2.45 (m, 2H, $-CH_2-CH=$), 3.08–3.16 (m, 1H, $-CH_2-CH-CH=$), 4.11 (br, 1H, -NH-), 4.15, 4.28 (d, 1H, -CH-NH-), 5.44–5.52 (m, 1H, $-CHCH=CH-$), 5.88–5.96 (m, 1H, $-CH-CH=CH-$), 6.34, 6.35 (d, 2H, $-NH-CH=CH-$), 6.98, 7.00 (d, 2H, $-NH-CH=CH-$),

7.18–7.30 (m, 4H, -CH-C_6H_4Cl). – ^{13}C NMR ($CDCl_3$): δ = 26.2, 27.7 (C-6), 32.7, 33.2 (C-5), 53.9, 54.0 (C-2), 60.9, 61.8 (C-1), 114.9, 115.3 (C-21/25), 122.4, 122.8 (C-23), 128.6, 128.8 (C-11/15), 129.3 (C-12/14), 129.5, 129.6 (C-22/24), 132.0 (C-4), 133.2, 133.3 (C-13), 134.6, 136.8 (C-3), 141.7, 141.8 (C-10), 146.3, 146.6 (C-20). – $C_{18}H_{17}Cl_2N \cdot HCl$ (354.68): found C 61.08, H 5.28, N 3.90; calcd. C 60.95, H 5.12, N 3.96; – m.p. 169°C (dec.).

3a: 200 mg (20%), m.p. 105–110°C (dec.). – IR (CCl_4): $\tilde{\nu}$ = 3415 cm^{-1} (NH), 3060, 2955 (CH), 1600, 1493 (C=C). – MS-FD, *m/z*: 502 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 4.45, 4.85 (d, 2H, -C*H*-NH-), 4.40, 4.55 (br, 2H, -NH-), 6.40 (d, 4H, -NH-C*H*=CH-), 6.84, 7.05 (d, 4H, -NH-CH=C*H*-), 6.95–7.25 (m, 8H, -CH-C_6H_4Cl). – ^{13}C NMR ($CDCl_3$): δ = 61.3, 63.4 (C-1/2), 115.0, 115.3 (C-51/55), 123.1, 123.4 (C-53), 128.6, 128.8 (C-11/15), 128.85, 128.9 (C-12/14), 129.1, 129.2 (C-52/54), 133.7, 133.9 (C-13), 135.8, 137.5 (C-10), 144.4, 144.9 (C-50). – $C_{26}H_{20}N_2Cl_4 \cdot 2\,HCl$ (574.99): found C 53.69, H 3.65, N 3.98; calcd. C 54.29, H 3.86, N 4.87.

Synthesis of **2b** *and* **3b′**: Analogous to the preparation of **2a** and **3a** but using 500 mg (2.00 mmol) of **1b**, 5.0 ml (56.5 mmol) of cyclopentene and 75 ml of MeOH. After of irradiation for 44 h HPLC separation afforded two pale white powders.

2b: 250 mg (40%), m.p. 80°C. – IR (CCl_4): $\tilde{\nu}$ = 3430 cm^{-1} (NH), 3057, 3024, 2943, 2851 (CH), 1601, 1579, 1558, 1502 (C=C). – MS-FD *m/z*: 317 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 1.45–2.00 (m, 2H, -CH_2-), 2.15–2.60 (m, 2H, -CH_2-CH=), 3.50–3.65 (m, 1H, -CH_2C*H*-CH=), 4.75 (br, 1H, -NH-), 4.95–5.12 (m, 1H, -C*H*-NH-), 5.12–5.20, 5.88–5.94 (m, 1H, -CH-C*H*=CH-), 5.78–5.84, 5.97–6.04 (m, 1H, -CH-CH=C*H*-), 6.57–6.68, 6.95–7.30 (m, 8H, aryl CH). – ^{13}C NMR ($CDCl_3$): δ = 26.9, 28.8 (C-6), 31.9, 32.0 (C-5), 49.3, 49.4 (C-2), 59.0, 59.2 (C-1), 113.0, 113.2 (C-21/25), 117.4 (C-23), 128.5 (C-12/14), 129.2 (C-22/24), 130.5, 130.7 (C-4), 130.7, 132.3 (C-3), 132.8, 132.9 (C-13), 133.7, 136.4 (C-11/15), 136.6, 136.8 (C-10), 146.9, 146.8 (C-20). – $C_{18}H_{17}Cl_2N$ (318.23): found C 67.79, H 5.46, N 4.43; calcd. C 67.93, H 5.38, N 4.40.

3b′: 50 mg (10%), m.p. 205°C. – IR (CCl_4): $\tilde{\nu}$ = 3410 cm^{-1} (NH), 3057, 2930, 2853 (CH), 1600, 1580, 1561, 1501 (C=C). – MS-FD *m/z*: 502 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 6.08 (dd, 2H, -C*H*-NH-), 5.17 (dd, 2H, -NH-), 6.69 (m, 4H, -NH-C*H*=CH-), 6.72 (s, 2H, -NH-CH=CH-C*H*-), 7.05 (m, 4H, -NH-CH=C*H*-), 7.10–7.25 (m, 6H, -CH-$C_6H_3Cl_2$). – ^{13}C NMR ($CDCl_3$): δ = 55.5 (C-1/2), 113.3 (C-51/55), 118.2 (C-53), 128.2, 129.2 (C-12/14), 129.4 (C-52/54), 130.4 (C-13), 134.1, 135.6 (C-11/15), 136.8 (C-10), 146.2 (C-50). – $C_{26}H_{20}Cl_4N_2$ (502.24): found C 62.08, H 4.12, N 5.64; calcd. C 62.18, H 4.01, N 5.58.

Synthesis of **2c** *and* **3c**: Analogous to the preparation of **2a** and **3a** but using 520 mg (2.10 mmol) of **1c**. After of irradiation for 25 h HPLC separation afforded two yellow waxy oils.

2c: 360 mg (55%), m.p. 200–205°C (dec.). – IR (CCl_4): $\tilde{\nu}$ = 3421 cm^{-1} (NH), 3051, 3027, 2919, 2853 (CH), 1602, 1510, 1488 (C=C). – MS-FD, *m/z*: 311 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 1.70–2.10 (m, 2H, -CH_2-), 2.14, 2.15 (s, 6H, -CH_3), 2.25–2.45 (m, 2H, -CH_2-CH=), 3.05–3.15 (m, 1H, -CH_2-C*H*-CH=), 3.99 (br, 1H, -NH-), 4.18, 4.32 (d, 1H, -C*H*-NH-), 5.44–5.50 (m, 1H, -CH-C*H*=CH-), 5.87–5.94 (m, 1H, -CH-CH=C*H*-), 6.08 (s, 2H, -NH-C*H*=CH-), 6.30, 6.31 [s, 2H, -C(CH_3)=C*H*-], 7.25–7.27 (m, 4H, -CH-C_6H_4Cl). – ^{13}C NMR ($CDCl_3$): δ = 21.4 (CH_3), 25.5, 27.0 (C-6), 32.0, 32.6 (C-5), 53.3, 53.4 (C-2), 60.0, 61.1 (C-1), 110.9, 111.4 (C-21/25), 119.2, 119.6 (C-23), 127.9, 128.1 (C-11/15), 128.5 (C-12/14), 129.2, 131.6 (C-4), 132.1, 132.2 (C-13), 133.5, 134.8 (C-3), 138.7, 138.8 (C-22/24), 141.9, 142.0 (C-10), 147.3, 147.5 (C-20). – $C_{20}H_{22}ClN \cdot HCl$ (348.29): found C 68.54, H 6.81, N 4.08; calcd. C 68.97, H 6.66, N 4.02.

3c: 200 mg (40%), m.p. 85–90°C. – IR (CCl_4): $\tilde{\nu}$ = 3414 cm^{-1} (NH), 3026, 2910, 2859 (CH), 1600, 1507, 1489 (C=C). – MS-FD *m/z*: 491 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 2.14 (s, 12H, CH_3), 4.34, 4.88 (d, 2H, -C*H*-NH-), 4.40, 4.43 (br, 2H, -NH-), 6.12 (s, 4H, -NH-C*H*=CH-), 6.35 [s, 2H, -C(CH_3)=C*H*-], 7.17–7.22 (m, 8H, -CH-C_6H_4Cl). – ^{13}C NMR ($CDCl_3$): δ = 21.4 (CH_3), 61.2, 63.3 (C-1/2), 111.6, 111.9 (C-51/55), 120.2, 120.5 (C-53), 128.6, 128.7 (C-13), 128.65, 128.8 (C-12/14), 133.2, 133.4 (C-13), 136.8, 138.6 (C-10), 138.9, 139.0 (C-52/54), 146.1, 146.6 (C-50). – $C_{30}H_{32}Cl_2N_2$ (491.48): found C 73.87, H 6.55, N 5.37; calcd. C 73.31, H 6.56, N 5.70.

Synthesis of **2d** *and 4-Methoxybenzyl-4-methylaniline:* Analogous to the preparation of **2a** but using 600 mg (2.70 mmol) of **1d**. After irradiation for 40 h HPLC separation afforded two pale yellow oils.

2d: 640 mg (80%), m.p. 115°C (dec.). – IR (CCl_4): $\tilde{\nu}$ = 3417 cm^{-1} (NH), 3051, 3001, 2953, 2936, 2852, 2836 (CH), 1612, 1585, 1510 (C=C). – MS-FD *m/z*: 293 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 1.70–2.25 (m, 2H, -CH_2-), 2.17 (s, 3H, CH_3), 2.25–2.45 (m, 2H, -CH_2CH=), 3.07–3.16 (m, 1H, -CH_2-C*H*-CH=), 3.76, 3.77 (s, 3H, OCH_3), 3.98 (br, 1H, NH), 4.13–4.28 (d, 1H, -C*H*-NH-), 5.46–5.59 (m, 1H, -CH-C*H*=CH-), 5.85–5.92 (m, 1H, -CH-CH=C*H*-), 6.40 (m, 2H, -NH-C*H*=CH-), 6.80–6.90 [m, 4H, -NH-CH=C*H*-, -C*H*=C(OCH_3)-], 7.25 [m, 2H, -C*H*-CH=C(OCH_3)-]. – ^{13}C NMR ($CDCl_3$): δ = 20.5 (CH_3), 26.0, 27.5, (C-6), 30.2, 30.3 (C-5), 54.3, 54.4 (C-2), 55.8 (OCH_3), 62.2, 62.3 (C-1), 114.4 (C-21/25), 113.8, 114.4 (C-12/14), 126.9, 127.4 (C-23), 128.2, 128.5 (C-11/15), 130.1, 130.3 (C-22/24), 130.6, 132.8 (C-4), 133.6, 134.8 (C-3), 135.8, 136.2 (C-10), 146.0, 146.2 (C-20), 158.0, 159.0 (C-13). – $C_{20}H_{23}NO \cdot HCl \cdot H_2O$ (347.87): found C 68.20, H 7.51, N 3.76; calcd. C 69.05, H 7.53, N 4.03.

4-Methoxybenzyl-4-methylaniline: 30 mg (<5%) (no analytically pure material). – MS-FD, *m/z*: 227 [M^+]. – ^{1}H-NMR ($CDCl_3$): δ = 2.22 (s, 3H, CH_3), 3.78 (s, 3H, -OCH_3), 3.80 (br, 2H, -NH-), 4.22 (s, 2H, -CH_2NH-), 6.54 (d, 2H, -NH-C*H*=CH-), 6.86 (d, 2H, -NH-CH=C*H*-), 6.97 [d, 2H, -CH=C*H*-C(OCH_3)-], 7.27 [d, 2H, -C*H*=CH-C(OCH_3)-]. – ^{13}C NMR ($CDCl_3$): δ = 20.2 (CH_3), 49.0 (C-1), 55.2 (-OCH_3), 113.7 (C-12/14), 114.6 (C-21/25), 127.0 (C-23), 129.4 (C-11/15), 130.4 (C-22/24), 131.5 (C-10), 146.0 (C-20), 159.0 (C-13) (atomic numbering as in **2d**).

X-ray Structural Analysis of **3b′**: Single crystals were obtained by slow evaporation of a diethyl ether solution at ambient temperature. For apparatus and method of analysis see literature[25]. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-404512. $C_{26}H_{20}Cl_4N_2$ (502.24): crystal size 0.90 × 0.60 × 0.40 mm, triclinic, space group $P\bar{1}$; *a* = 1034.4(2), *b* = 1448.5(4), *c* = 1722.0(5) pm; α = 84.40(2), β = 77.68(2), γ = 73.55(2)°; *V* = 2.416(1) nm^3; $d_{calcd.}$ = 1.38 g/cm^3 (*Z* = 4); the unit cell contains two independent molecules. Mo-K_α radiation (graphite monochromator). ω-Scan at 3.0 to 30.0°/min. 8767 reflections collected, 7583 independent reflections, 4482 [$F > 4.0\sigma(F)$] observed reflections; μ = 0.507 mm^{-1}, *F*(000) 1032; 577 parameters refined. Final values [$I > 2\sigma(I)$]: *R* = 0.0595, R_w = 0.1740.

Addition of Cyclohexene to Different Imines: Irradiation was performed analogously to the reactions with cyclopentene. 600 mg (2.66 mmol) of **1d** and 10.0 ml (98.6 mmol) of cyclohexene were irradiated for 46 h. HPLC separation afforded a yellow oil. 160 mg (20%) of *(2-cyclohexene-1-yl)(4-methoxyphenyl)(4-methylanilino)-methane.* – IR (CCl_4): $\tilde{\nu}$ = 3420 cm^{-1} (NH), 3021, 2933, 2863, 2836 (CH), 1612, 1584, 1510 (C=C). – MS-FD *m/z*: 307 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 1.35–1.85 (m, 4H, -CH_2-), 2.17 (s, 3H,

CH_3), 1.95–2.05 (m, 2H, -C*H*$_2$-CH=), 2.48–2.60 (m, 1H, -CH$_2$-C*H*-CH=), 3.96 (br, 1H, -NH-), 3.76, 3.77 (s, 3H, -OCH$_3$), 4.20, 4.21 (d, 1H, -C*H*-NH-), 5.47–5.55 (m, 1H, -CH-C*H*=CH-), 5.55–5.65 (m, 1H, -CH-CH=C*H*-), 6.39, 6.40 (d, 2H, -NH-C*H*=CH-), 6.80–6.92 (m, 2H, -NH-CH=C*H*-), 7.22–7.29 (m, 4H, -CH-C$_6$*H*$_4$Cl). – ^{13}C NMR ($CDCl_3$): δ = 21.3 (CH_3), 22.8, 22.9 (C-6), 24.9, 26.2 (C-7), 26.3, 28.6 (C-5), 44.0, 44.3 (C-2), 56.2 (-OCH$_3$), 62.0, 62.6 (C-1), 114.0, 114.6 (C-21/25), 114.6, 114.7 (C-12/14), 126.8, 127.3 (C-23), 128.7, 128.9 (C-11/15), 127.4, 130.3 (C-4), 130.4, 130.6 (C-22/24), 131.2, 131.8 (C-3), 135.4, 135.8 (C-10), 146.4, 146.6 (C-20), 159.3 (C-13).

500 mg (2.04 mmol) of **1c** and 10.0 ml (98.6 mmol) of cyclohexene were irradiated for 26 h. HPLC separation afforded a yellow oil. 260 mg (40%) of *(4-chlorophenyl)(2-cyclohexene-1-yl)(3,5-dimethylanilino)methane.* – IR (CCl_4): $\tilde{\nu}$ = 3422 cm^{-1} (NH), 3023, 2924, 2862, 2839 (CH), 1600, 1508, 1488 (C=C). – MS-FD *m/z*: 325 [M$^+$]. – ^{1}H NMR ($CDCl_3$): δ = 1.35–1.85 (m, 2H, -C*H*$_2$-), 2.13, 2.15 (s, 6H, CH_3), 1.95–2.05 (m, 2H, -C*H*$_2$-CH=), 2.55 (m, 1H, -CH$_2$-C*H*-CH=), 3.98 (br, 1H, -N*H*-), 4.22–4.32 (m, 1H, -C*H*-NH-), 5.43–5.55 (m, 1H, -CH-C*H*=CH-), 5.82–5.94 (m, 1H, -CH-CH=C*H*-), 6.09 (s, 2H, -NH-C*H*=CH-), 6.29, 6.32 [s, 2H, -C(CH$_3$)=C*H*-], 7.26–7.27 (m, 4H, -CH-C$_6$*H*$_4$Cl). – ^{13}C NMR ($CDCl_3$): δ = 21.5 (CH_3), 21.7, 21.8 (C-6), 23.6, 25.2 (C-7), 25.2, 27.7 (C-5), 42.8, 43.1 (C-2), 60.6, 61.2 (C-1), 110.8, 111.4 (C-21/25), 119.2, 119.6 (C-23), 128.1, 128.3 (C-11/15), 128.5 (C-12/14), 125.6, 128.9 (C-4), 132.5, 132.2 (C-13), 128.9, 130.6 (C-3), 138.7, 138.8 (C-22/24), 141.0, 141.5 (C-10), 147.4, 147.7 (C-20).

1b: Product formation was indicated by HPLC, no preparative isolation; **1a**: separation of addition product and hydrodimer was not possible.

Synthesis of **5a** *and* **5b**: Irradiation was performed analogously to the reaction of **1a** with cyclopentene and cyclohexene by using 500 mg (1.46 mmol) of **4**, 10 ml (113 mmol) of cyclopentene and 70 ml of MeOH [40 ml (390 mmol) of cyclohexene and 40 ml of MeOH]. After irradiation for 50 h **5a** and **5b** were isolated by preparative HPLC as two slightly yellow oils which could not be crystallised.

5a: IR (CCl_4): $\tilde{\nu}$ = 3324 cm^{-1} (NH), 3087, 3062, 3031, 2948, 2859, 2838 (CH), 1603, 1493, 1445, 1431 (C=C), 1201, 1166 (C-O-C). – MS-FD *m/z*: 411 [M$^+$] 344 [M – $C_5H_6^+$]. – ^{1}H NMR ($CDCl_3$): δ = 1.05–1.95 (m, 4H, -CH$_2$-), 2.25 (br, 1H, -NH-), 2.65–2.90 (m, 2H, -CH$_2$-), 3.05, 3.15 (s, 3H, OCH$_3$), 3.50 (t, 1H, -C*H*-NH-), 3.75 (m, 1H, -C*H*-CH=CH-), 5.50, 5.50–5.80 (m, 2H, -CH-C*H*=C*H*-), 7.05–7.35 (m, 15H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 25.1, 31.5, 31.7 (C-5/6), 41.8, 41.9 (C-9), 51.2, 51.3 (C-11), 52.3, 52.8 (C-2), 57.7, 57.8 (C-8), 68.9, 69.1 (C-1), 126.15, 126.2, 126.3, 126.5, 126.6, 126.9, 127.0, 127.1, 128.1, 128.2, 129.3, 129.5, 129.6, 129.9 (C-21–23, 31–33, 41–43), 131.3, 131.7 (C-4), 133.3, 133.8 (C-3), 137.55, 137.6 (C-40), 142.1, 143.8, 144.2, 144.4 (C-20/30), 175.2, 175.3 (C-10).

5b: MS-FD, *m/z*: 426 [M$^+$], 344 [M – $C_5H_6^+$]. – ^{1}H NMR ($CDCl_3$): δ = 1.30–2.10 (m, 6H, -CH$_2$-), 2.15 (br, 1H, -NH-), 2.65–2.90 (m, 2H, -CH$_2$-), 3.05, 3.10 (s, 3H, -OCH$_3$), 3.45 (m, 1H, -C*H*-NH-), 3.20 (m, 1H, -C*H*-CH=CH-), 5.55, 5.73, 5.95 (m, 2H, -CH-C*H*=C*H*-), 7.05–7.40 (m, 15H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 21.9, 22.4, 25.1, 25.2 (C-5/6), 42.0, 42.1 (C-9), 41.9, 43.2 (C-2), 51.2, 51.3 (C-11), 57.7, 57.9 (C-8), 68.7, 69.3 (C-1), 126.3, 126.4, 126.45, 126.5, 126.6, 126.7, 127.0, 127.1, 128.0, 128.1, 128.8, 129.1, 129.6, 129.7 (C-21–23, 31–33, 41–43), 127.4, 127.7, 128.2, 128.5 (C-3/4), 137.5, 137.7 (C-40), 141.2, 142.8, 143.3, 143.4 (C-20/30), 175.1, 175.2 (C-10).

The diastereomeric ratio of 1.3:1 as measured by ^{1}H NMR for **5a** may be an artefact since due to weak overlap of the HPLC product peak with neighbour peaks a complete elution was not possible.

Dependence of the Reaction Rates of **1a** *on the Content of Water:* Reaction rates were determined in the system 30 mg (0.2 mmol) of CdS, 0.5 ml (5.7 mmol) of cyclopentene, and 18.5 ml of MeOH suspended in the cylindrical quartz cuvette. In addition to the standard CdS powder (vide supra), CdS_{wet} obtained by omitting the dehydration procedure at 150°C was used. Reaction rates in absolute MeOH [dried over $Mg(OMe)_2$] and MeOH containing 2.5% of water were calculated from the initial slopes of imine concentration vs. time plots. – a) CdS_{wet}/abs. MeOH: $0.89 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**2a**); $0.95 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**3a**); – b) CdS/abs. MeOH: $0.56 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**2a**); $0.36 \cdot 10^{7}$ mol l^{-1} s^{-1} (**3a**); – c) CdS/MeOH containing 2.5% H_2O: $0.69 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**2a**); $0.72 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**3a**).

Reaction of **1a** *with Cyclopentene Using CdS/Pt (1.0%) as Photocatalyst:* Platinisation was performed according to Bönnemann et al. precipitating 1.0% of colloidal platinum by concentration of a THF suspension of tetraalkylammonium stabilised platinum and CdS[26]. 50.0 mg (35 mmol) of CdS or 50.5 mg of CdS/Pt (1.0%), 0.5 ml (5.7 mmol) of cyclopentene, 25.0 mg (0.10 mmol) of **1a**, and 18.5 ml of MeOH or MeOH containing 3.5% of H_2O were suspended in the cylindrical quartz cuvette by sonication for 15 min. The suspension was irradiated on the optical train (λ ≥ 400 nm) with mechanical stirring. Reaction rates were calculated from the initial slope of an imine concentration vs. time plot. – a) CdS, MeOH containing 3.5% H_2O: $1.5 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**2a**); $1.5 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**3a**); ratio **2a**:**3a** = 1.0; – b) CdS/Pt (1.0%)/MeOH containing 3.5% H_2O: $5.7 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**2a**); $4.8 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**3a**); – c) CdS/Pt (1.0%)/absolute MeOH: $4.1 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**2a**); $3.3 \cdot 10^{-7}$ mol l^{-1} s^{-1} (**3a**). 4-Chlorobenzaldehyde and 4-chloroaniline were identified by HPLC.

Reaction of **3a** *with Cyclopentene:* 2.5 mg (0.01 mmol) of **3a**, 30 mg (0.2 mmol) of CdS, 0.5 ml (5.7 mmol) of cyclopentene, and 18.5 ml of MeOH were suspended in the cylindrical quartz cuvette by sonication for 15 min. The suspension was irradiated for 8 h on the optical train (λ ≥ 400 nm) with mechanical stirring. Products were characterised by HPLC analysis. $5 \cdot 10^{-3}$ mmol of **1a**, $6 \cdot 10^{-3}$ mmol of **2a** and $3 \cdot 10^{-3}$ mmol of **3a** were recovered. Metallic cadmium as cathodic photocorrosion product was identified by the reduction of added 1,1′-dimethyl-4,4′-bipyridinium dichloride (MV^{2+}) to the blue radical cation.

Synthesis of **6** *and* **7**: 0.5 g (2.0 mmol) of **1a**, 0.3 g (2.08 mmol) of CdS, 2.0 ml (12.5 mmol) of 1-phenyl-1-cyclohexene, and 75 ml of MeOH were suspended in a Pyrex immersion lamp apparatus by sonication for 15 min. After 30 h irradiation was stopped, CdS removed by suction filtration and the remaining liquid concentrated under reduced pressure. From the resulting raw material **6** and **7** were separated by preparative HPLC; evaporation of the solvent afforded two colourless oils which could not be crystallised. In both cases products were a mixture of diastereomers and regioisomers. **6**: MS-FD, *m/z*: 314 [M$^+$]. – ^{1}H NMR ($CDCl_3$): δ = 1.25–2.05 (m, -CH$_2$-), 2.4 (m, -C*H*-, -C*H*$_2$-CH=), 2.7 (m, -CH-), 5.7–6.0 (**6b**, m, -CH-), 6.0–6.1 (**6a**, m, -C*H*-), 7.2–7.4 (m, Ar-H). – ^{13}C NMR ($CDCl_3$): δ = **6a**: 22.7, 22.8 (-CH$_2$-C*H*$_2$-CH$_2$-), 25.3, 25.6 (-CH$_2$-C*H*$_2$-CH-), 41.2, 41.4 (-C*H*$_2$-CH=), 46.5, 46.8 (-C*H*-). – **6b**: 18.9, 23.1, 24.6, 25.7, 27.7, 31.5 (-CH$_2$-). – **7**: MS-FD, *m/z*: 408 [M$^+$]. – ^{1}H NMR ($CDCl_3$): δ = 1.2–2.6 (m, 6H, -CH$_2$-), 2.75 (**7a**, br, 1H, -C*H*-C*H*$_2$-), 4.10 (**7a**), 4.25 (**7b**) (br, 1H, -N*H*-), 4.35 (**7a**), 4.45 (**7b**) (m, 1H, -C*H*-NH-), 5.95 (**7a**), 6.10 (**7b**) (m, 2H, -NH-CH=C*H*-CH=), 6.95 (m, 2H, -NH-CH=CH-C*H*=), 7.3 (m, 9H, Ar-*H*). – ^{13}C NMR ($CDCl_3$): δ = 19.0, 19.4 (C-6′), 22.8, 23.0

(C-6), 24.1, 28.2 (C-7), 26.1, 26.4 (C-5'), 27.9, 28.2 (C-5), 30.7, 34.0 (C-7'), 44.2, 44.7 (C-2), 49.7, 49.8 (C-2'), 61.8, 62.4 (C-1), 67.8, 65.5 (C-1'). Complete assignment was not possible for all peaks due to the complex diastereomeric and regioisomeric mixture.

Reaction of **1a** *with Alcohols:* 300 mg (1.20 mmol) of **1a**, 300 mg (2.08 mmol) of CdS and 90 ml of the absolute alcohol were suspended in a Pyrex immersion lamp apparatus by sonication for 15 min. When HPLC analysis indicated that all imine had reacted or products started to decompose, irradiation was stopped. CdS was removed by suction filtration and the remaining liquid was concentrated under reduced pressure. The resulting brown oil was analysed by HPLC and **8**–**12** were isolated by preparative HPLC; evaporation of the solvent afforded yellow oils. Estimated yields were about 5–20%. Reaction rates were deduced from the initial slope of an imine concentration versus time plot.

8: MS-FD, *m/z*: 282 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 1.7 (br, 1H, -O*H*), 3.7, 3.9 (m, 2H, -C*H*$_2$-OH), 4.4 (m, 1H, -C*H*-NH-), 6.45 (d, 2H, -NH-C*H*=CH-), 7.05 (d, 2H, -NH-CH=C*H*-), 7.3 (m, 4H, -CH-C$_6$*H*$_4$Cl). – ^{13}C NMR ($CDCl_3$): δ = 59.4 (C-1), 67.1 (CH_2), 114.9 (C-21/25), 122.7 (C-23), 128.1 (C-11/15), 129.0 (C-12/14), 129.1 (C-22/24), 133.5 (C-13), 138.2 (C-10), 145.5 (C-20) (for atomic numbering see **2a**).

9: MS-FD, *m/z*: 295 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 1.10, 1.25 (d, 3H, CH_3), 2.0 (br, 1H, -OH), 3.95, 4.15 (m, 1H, -C*H*-OH), 4.10, 4.30 (m, 1H, -C*H*-NH-), 6.40 (m, 2H, -NH-C*H*=CH-), 7.05 (m, 2H, -NH-CH=C*H*-), 7.3 (m, 4H, -CH-C$_6$*H*$_4$Cl). – ^{13}C NMR ($CDCl_3$): δ = 19.5, 20.3 (CH_3), 62.5, 63.7 (C-1), 70.2, 71.7 (CHOH), 114.7, 114.9 (C-21/25), 122.3, 122.6 (C-23), 128.3, 128.8 (C-11/15), 129.0 (C-12/14), 129.1 (C-22/24), 133.45, 133.5 (C-13), 138.0, 139.3 (C-10), 145.3, 145.7 (C-20).

10: MS-FD, *m/z*: 309 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 0.95 (t, 3H, C*H*$_3$), 1.20–1.70 (m, 2H, -C*H*$_2$-), 1.7 (br, 1H, -OH), 3.70, 3.85 (m, 1H, -C*H*-OH), 4.25, 4.35 (m, 1H, -C*H*-NH-), 6.40 (m, 2H, -NH-C*H*=CH-), 7.00 (m, 2H, -NH-CH=C*H*-), 7.2–7.3 (m, 4H, -CH-C$_6$*H*$_4$Cl). – ^{13}C NMR ($CDCl_3$): δ = 10.3, 10.4 (CH_3), 19.5, 20.3 (CH_2), 62.5, 63.7 (C-1), 70.2, 71.7 (CHOH), 114.7, 114.9 (C-21/25), 122.3, 122.6 (C-23), 128.3, 128.8 (C-11/15), 129.0 (C-12/14), 129.1 (C-22/24), 133.45, 133.5 (C-13), 138.0, 139.3 (C-10), 145.3, 145.7 (C-20).

11: MS-FD, *m/z*: 323 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 0.9 (m, 3H, CH_3), 1.15–1.60 (m, 2H, -C*H*$_2$-C*H*$_2$-), 3.75, 3.95 (m, 1H, -C*H*-OH), 4.20, 4.35 (m, 1H, -C*H*-NH-), 4.7 (br, 1H, -NH-), 6.40 (m, 2H, -NH-C*H*=CH-), 7.00 (m, 2H, -NH-CH=C*H*-), 7.1–7.3 (m, 4H, -CH-C$_6$*H*$_4$Cl). – ^{13}C NMR ($CDCl_3$): δ = 13.9, 14.0 (CH_3), 19.2 (CH_2), 35.8, 36.0 (CH_2), 61.6, 61.7 (C-1), 74.0, 75.5 (CHOH), 113.9, 114.6 (C-21/25), 122.2, 122.3 (C-23), 132.2, 133.4 (C-13), 145.6, 146.3 (C-20).

12: MS-FD, *m/z*: 309 [M^+]. – ^{1}H NMR ($CDCl_3$): δ = 1.10, 1.40 (s, 6H, CH_3), 4.20 (d, 1H, -C*H*-NH-), 4.75 (br, 1H, -N*H*-), 6.40 (d, 2H, -NH-C*H*=CH-), 7.00 (d, 2H, -NH-CH=C*H*-), 7.3 (m, 4H, -CH-C$_6$*H*$_4$Cl). – ^{13}C NMR ($CDCl_3$): δ = 27.0, 28.0 (CH_3), 66.0 (C-1), 72.8 (CHOH), 114.7 (C-21/25), 122.1 (C-23), 128.6 (C-11/15), 128.9 (C-12/14), 129.4 (C-22/24), 133.4 (C-13), 138.3 (C-10), 145.6 (C-20).

☆ Dedicated to Professor *Max Herberhold* on the occasion of his 60th birthday.

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