Semiconductor-Catalysed Photoaddition of Olefins and Enol Ethers to 1,2-Diazenes: A New Route to Allylhydrazines**

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Dedicated to Professor Hans-Dieter Scharf on the occasion of his 65th birthday

Abstract: Suspensions of zinc or cadmium sulfide powders in a protic solvent catalyse the linear addition of enol ethers and olefins to 1,2-diaryl- and 1-aryl-2-alkyl-1,2-diazenes, producing allylhydrazine derivatives. Relative quantum yields decrease sharply when the 1,2-diazene is more difficult to reduce, while their relationship to the oxidation potential of the enol ether/olefin is complicated. Reduction to 1,2-diarylhydrazine and concomitant dehydrodimerization of the enol ether occurs as a side reaction. It is favoured by increasing light intensity and becomes the major reaction path when platinized (5 mol%) photocatalysts are employed. It is proposed that the photogenerated electron–hole pair in a proton-coupled electron transfer reduces the diazene to a hydrazyl radical and oxidizes the olefin/enol ether to a radical cation. The allylic radical obtained from the latter by deprotonation then undergoes C–N coupling with the hydrazyl radical to afford the allylhydrazine. Diarylhydrazine formation occurs by disproportionation of the hydrazyl radical or by a successive proton-coupled reduction. Thus photoaddition can be classified as a 1 e^-/1 h^+ process while 2 e^-/2 h^+ are necessary for the reduction.

Keywords
allylhydrazines · cadmium compounds · catalysis · photochemistry · zinc compounds

Introduction

Inorganic semiconductor powders, such as titanium dioxide and cadmium or zinc sulfide, suspended in a solution of corresponding organic substrates can photocatalyse oxidation, reduction, cycloaddition, and isomerization reactions. These reactions are seldom performed on a preparative scale, since more conventional routes are generally more convenient. An exception is the photodehydrodimerization of cyclic enol ethers catalysed by ZnS and platinized cadmium sulfide (CdS/Pt).[1, 2] The first step in the mechanism of all these reactions involves formation of a surface-trapped electron–hole pair, $e_{tr}^- - h_{tr}^+$, by light absorption followed by heterogeneous electron transfer to and from adsorbed substrates A_{ad} and D_{ad}. This produces the primary products A_{ad}^- and D_{ad}^+ radical ions, which in most cases are separately converted to two final products. One of the very few exceptions is the TiO_2-catalysed oxidative cleavage of olefins in the presence of air.[3] In this case A_{ad}^- is O_2^-, which reacts with $RCH{=}CH_2^+$ to afford RCHO and CH_2O. Thus, although two final products are obtained, they are not formed by separated reactions of A_{ad}^- and D_{ad}^+. Here we report a new type of semiconductor-catalysed photoreaction in which the primary electron transfer intermediates preferentially combine to give a single product. The reaction formally consists of addition of the allylic C–H bond of an olefin or cyclic enol ether across the N=N bond of a 1,2-diazene to afford hitherto unknown allylhydrazines. From a few examples of limited synthetic utility it is known that the same reaction type may occur in homogeneous solution when either the 1,2-diazene[4] or the olefin[5] is substituted by electron-withdrawing groups. Some allylhydrazines have been prepared by more conventional thermal procedures.[6] Some of the following results have been published in preliminary form.[7]

Results and Discussion

1. Synthesis and Structure: Irradiation (tungsten lamp, $\lambda > 350$ nm) of 1,2-diphenyldiazene (**1**) (Scheme 1) and 3,4-dihydro-2*H*-pyran (3,4-DHP, **a**), in the presence of a methanolic suspension of CdS ($\lambda_{bg} = 516$ nm) induced complete bleaching of the orange solution and formation of the trisubstituted allylhydrazine **1a** (HPLC: 70% yield) and 1,2-diphenylhydrazine (HPLC: 25% yield).[7] Likewise, bis-1,2-(4-methylphenyl)-diazene (**2**) and 1-*tert*-butyl-2-phenyldiazene (**3**) afforded **2a** and **3a**. Similarly, retaining (**1**) and replacing 3,4-DHP (**a**) with cyclohexene (**b**), 2,5-dihydrofuran or 2,3-dihydrofuran (**c**) (2,5- or 2,3-DHF), cyclopentene (**d**), 4-methylcyclohexene (**e**), or 2-pentene (**f**) led to the corresponding allylhydrazines **1b–f**. In the case of **1e** a mixture of two isomers was obtained, which we were unable to separate. The difference between isolated (40–10%) and HPLC yields (70–40%) probably stemmed from the similar very poor crystallization properties of major and side products.

The same reaction occurred when CdS was replaced by ZnS ($\lambda_{bg} = 336$ nm) and a mercury lamp ($\lambda \geq 290$ nm) was employed

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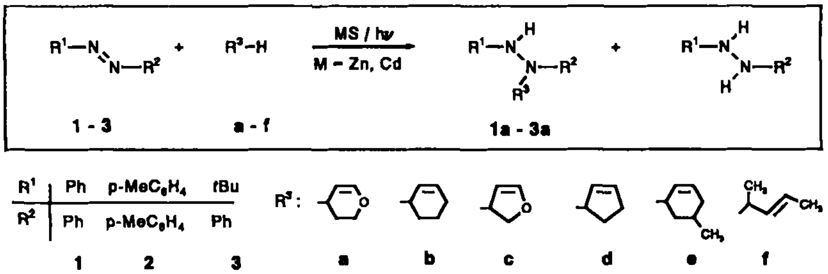

Scheme 1.

rather than a tungsten one. In contrast to photocatalysis by CdS, no hydrazine derivatives were formed initially, but they appeared together with the dehydrodimers of the enol ether after irradiation for 3 h. When irradiation was continued after all 1,2-diazene had been consumed, dehydrodimerization and concomitant hydrogen evolution were observed.[1]

Polychromatic irradiation ($\lambda \geq 290$ nm) in the absence of the metal sulfide resulted in *cis/trans* photoisomerization of the diazene component as major reaction path, although after 24 h the addition product is formed in a yield of 5%. When only 1,2-diphenyldiazene was irradiated in the methanolic solution, very small amounts (1% yield) of 1,2-diphenylhydrazine are produced within 24 h. In contrast to these results, monochromatic irradiation at $\lambda = 405$ nm induced only isomerization and no other products could be detected by HPLC. No reaction at all was observed when the MS/cyclohexene/1,2-diphenyldiazene/MeOH system (M = Zn, Cd) was refluxed in the dark.

We were able to obtain crystals of **1b** suitable for X-ray analysis (Fig. 1). The geometry around N(1) can be described as a flattened pyramid with N(1) located only 31 pm above the C(1), C(10), N(2) plane and bond angles N(2)-N(1)-C(1) = 111.3°, C(1)-N(1)-C(10) = 119.2°, and N(2)-N(1)-C(10) = 115.5°. It is known that large substituents favour a planar arrangement at nitrogen.[8] Around N(2) an almost ideal planarity is reached as indicated by the angles N(1)-N(2)-H(2) = 120.3°, N(1)-N(2)-C(20) = 120.1°, and H(2)-N(2)-C(20) = 119.6°. The torsion angle C(10)-N(1)-N(2)-C(20) is 12.8°, the N–N bond length 141.7 pm. As expected, the bonds N(1)–C(10) and N(2)–C(20), with bond lengths of 141.1 and 140.9 pm, respectively, are somewhat shorter than N(1)–C(1) (147.1 pm). The cyclohexenyl group, in which the atoms C(1), C(2), C(3) and C(4) are located in a plane, is bound to N(1) at C(1). The C(2)–C(3) bond length (130.5 pm) is typical for an sp^2–sp^2 bond, and the C(1)–C(2) (149.2 pm) and C(3)–C(4) (147.0 pm) bond lengths are typical for sp^3–sp^2 bonds. All bond lengths and angles are in good agreement with those reported for 1,2-diphenylhydrazine[9] and tetraphenylhydrazine.[10]

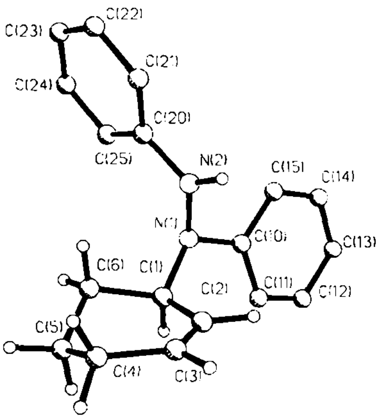

Fig. 1. Crystal structure of **1b** obtained by X-ray analysis.

The structures of **1a** and **1c–3a** follow from comparison of spectroscopic data with those of **1b**. In the IR spectrum of the latter, the N–H stretch appears at 3318 cm^{-1} (KBr) and the mass spectrum contains characteristic fragments at $m/z = 183$ ($M^+ - C_6H_9$) and 77 (C_6H_5) in addition to the molecular ion (m/z = 264). The ^{1}H NMR spectrum exhibits the signals of the protons at C(4), C(5) and C(6) (see Fig. 1) in the range $\delta = 1.5$–2.2 while the broad peaks at δ = 4.65, 5.7 and 5.9 are assigned to the protons at C(1), C(2) and C(3). Addition of D_2O leads to almost complete disappearance of the NH singlet at δ = 5.45. In the ^{13}C NMR spectrum the signals of the secondary C atoms C(4), C(5) and C(6) appear at 24.92, 21.49 and 25.7 (broad) while those of tertiary C(1) and olefinic C(2) and C(3) are found at 57.4, 131.9 and 126.5 (the latter both broad), respectively. The signals of the aromatic C atoms are observed in the range 111–150 (*meta*-atoms of both phenyl rings afford only one common peak). This assignment is based on DEPT and ^{1}H ^{13}C COSY spectra.

On reaction with **a**, the asymmetrical 1-*tert*-butyl-2-phenyldiazene (**3**) regioselectively afforded only the isomer in which the dihydropyranyl group is bound to the phenyl-substituted nitrogen atom. This is shown by the chemical shift δ = 3.17 of the NH proton as compared to δ = 5.30–5.62 observed for the other compounds (Table 1). In the case of **1e** the ^{13}C NMR spectrum indicates the presence of two compounds since all signals are doubled except those of the olefinic atoms C(2) and C(3) and the aromatic *meta*-carbons. In contrast, only the NH group gives rise to two peaks (at δ = 5.39 and 5.42) in the ^{1}H NMR spectrum. Since TLC, HPLC, and FD mass spectrum showed no evidence of an impurity, **1e** seems to be composed of two regioisomers in which a 4- or 5-methyl-2-cyclohexen-1-yl group is connected to N(1).

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

	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**2a**	**2b**	**3a**
IR [cm^{-1}] [a]									
$\tilde{\nu}$(NH)	3328	3318	3290	3338	3323	3305	3288	3317	3286
$\tilde{\nu}$(O-C=C)	1636		1601				1640		1641
$\tilde{\nu}$(CH)	752	750	753	750	754	753	810	809	752
^{1}H NMR (CDCl$_3$, TMS)									
NH	5.62	5.45	5.47	5.33	5.36	5.39 5.42	5.35	5.30	3.17
H-1	4.77	4.65	5.35	5.22	4.57	4.65	4.64	4.57	3.85
^{13}C NMR (CDCl$_3$, TMS)									
C-1	51.2	57.4	64.0	67.0	56.9	54.3 58.6	51.7	57.9	57.7
C-2 [b]	99.2	131.9	[c]	137.1	129.0	132.3	99.8	133.9	102.3
C-3 [b]	148.3	126.5	150.3	127.5	127.4	126.3	148.1	126.7	145.8

[a] In KBr, **3a**: film. [b] Broad. [c] No signal detected.

*Dynamic NMR Spectra of **1b** and **3a***: As mentioned above, the ^{13}C NMR signals of C(2), C(3) and C(6) are very broad at room temperature. At + 45 °C the signal sharpens, while at −30 °C

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all signals except those of *meta* positions of the phenyl rings become doubled as shown for **1b** in Figure 2. Warming up to room temperature restores the original spectrum. The same behaviour is found for **3a**, for which a free activation enthalpy of 13.8 kcal mol^{-1} at 233 K is calculated from coalescence temperatures (293–273 K) and chemical shift differences of the separated signals (95–27 Hz) of the C(1), C(2), C(3), aromatic *ipso* and *ortho* atoms. We suggest that the dynamic process consists of hindered rotation around the N–N bond. Since the C(1) atom is chiral, two diastereomers are present which give rise to two sets of signals at 233 K. A value of 13.2 kcal mol^{-1} was reported for the same process in 1-benzyl-1,2-bis(phenylacyl)hydrazine.[11]

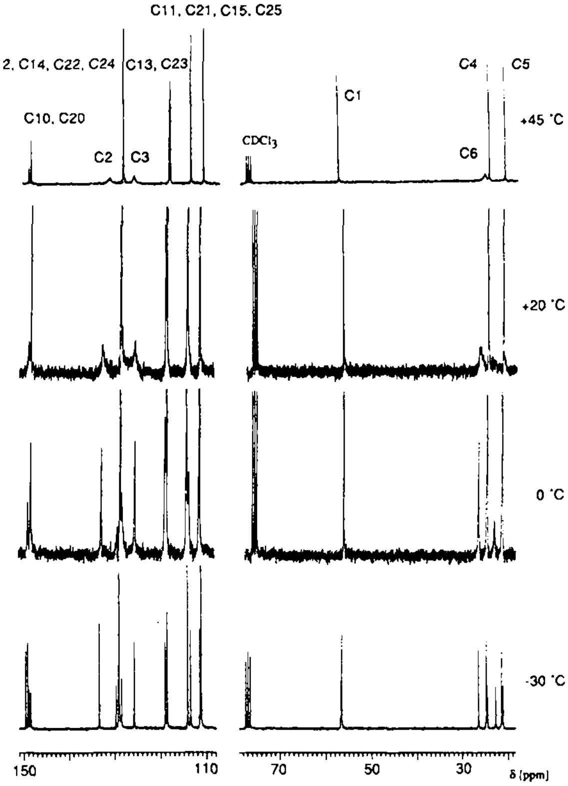

Fig. 2. Temperature-dependent ^{13}C NMR spectra of **1b** in $CDCl_3$.

2. ZnS Photocatalysis:

Influence of ZnS Preparation and Platinization: As reported elsewhere, the relative rate of dehydrodimerization of 2,5-DHF decreases from 1.0 to 0.5 or 0.2 when the specific surface area of the ZnS powder is reduced from about 100 (ZnS-B_1) to 36 (ZnS-C) or 18 m^2 g^{-1} (ZnS-B_2).[1] For the addition of 3,4-DHP to 1,2-diphenyldiazene, the relative rates (1.0, 0.4 and 0.1, respectively) are quite similar, which suggests that the rate-determining step is the same in both reactions. When ZnS-B_1 is stored in air, it loses activity because of the formation of surface ZnO (evidenced by emission spectra).[1] The oxide impurity seems also to be responsible for the inactivity of commercial ZnS.

From the fact that all active samples contain excess sulfur at the surface and exhibit long-wavelength tailing in their diffuse reflectance spectra,[1] it seems likely that the presence of surface states is necessary for the reaction. Thus, a ZnS sample prepared at 0 °C, which contains almost no surface states,[12] induces only a very slow photoaddition reaction.

When platinized zinc sulfide is employed, the rate of consumption of 1,2-diphenyldiazene (**1**) decreases by 70% and 1,2-diphenylhydrazine becomes the major reaction product while only traces of the addition product are formed.

Influence of Solvent: No reaction is observed in the ZnS-B_1/3,4-DHP/PhN=NPh system when 1,4-dioxane or *n*-hexane is employed as the solvent, while in the case of MeCN, *i*PrOH, MeOH, and dioxane/H_2O (5/1, v/v) the relative rate of photoaddition increases from 0.1 to 0.6, 0.9, and 1.0, respectively.

Influence of Substrate Redox Potential: The rate of consumption of 1,2-diphenyldiazene (**1**) was measured in the system ZnS-B_1/PhN=NPh in dioxane/H_2O (5/1, v/v) in order to test the influence of the oxidation potential of the olefin/enol ether. No reaction occurs in the presence of diethyl ether (E_{ox} = 2.9 V vs. NHE, in MeCN, see Experimental Section), MeOH (3.36 V), *i*PrOH (3.13 V) or dioxane (2.8 V), but when 3,4-DHP (1.9 V) is replaced by 2,3-DHF (2.0 V), 2,5-DHF (2.6 V), 3,6-dihydrodioxepine (2.9 V), THF (3.0 V) or cyclohexene (2.6 V), the relative rate decreases from 1.0 to 0.8, 0.7, 0.2, 0.1 or 0.1, respectively. There is no simple relation between rate and redox potential, as is indicated by the relative rates of 0.1 and 0.7 for cyclohexene and 2,5-DHF, respectively, which are both oxidized at 2.6 V. However, in the case of the enol ethers, the rate decrease parallels the increase of E_{ox} although the effect is rather small, as shown by the values of 0.8 and 0.7 for 2,3- and 2,5-DHF, whose potentials differ by 0.6 V. No correlation is observed for the saturated ethers THF, dioxane and diethyl ether. The latter two do not react although their potentials are 0.2 and 0.1 V lower than that of the reactive THF. The inactivity of the two alcohols may be due to their very high oxidation potentials.

When 2-methyl-4,5-dihydrofuran is used, it is oxidized to 2-methylfuran; the photoaddition is completely inhibited in favour of reduction to 1,2-diphenylhydrazine, which is formed in 90% yield as indicated by HPLC.

Methyl and chloro substitution of the 4,4′-positions of 1,2-diphenyldiazene result in a medium and a large decrease in the reaction rate, respectively. No photoaddition is observed when nitro groups are present in these positions.

3. CdS Photocatalysis

Influence of CdS Preparation: The reactivity of two different CdS powders was tested in the system 1,2-diphenyldiazene (**1**)/2,5-DHF in dioxane/H_2O (5/1, v/v). CdS-A_1 and CdS-A_2 were prepared by using a 1:1 and 1:2 ratio of cadmium sulfate to sodium sulfide, respectively. The resulting powders had specific surface areas of 80 and 120 m^2 g^{-1}, respectively.

In the case of CdS-A_1, slow evolution of hydrogen (0.5 mL h^{-1}) began once all the diazene had been consumed. This was accompanied by heavy cathodic photocorrosion [Eq. (1)].[13]

$$CdS + 2e_{tr}^{-} \longrightarrow Cd + S^{2-} \qquad (1)$$

The latter is indicated by darkening of the powder and formation of blue $MV^{+\bullet}$ upon addition of methyl viologen dichloride ($MVCl_2$).[14] When 1,2-diphenyldiazene was omitted, photocorrosion started within a few minutes and hydrogen evolution (1 mL h^{-1}) stayed constant over a period of 24 h. Subsequent addition of 1,2-diphenyldiazene after cessation of the irradiation caused the brown colour of Cd(0) to disappear. No $MV^{+\bullet}$ was produced when $MVCl_2$ was added 10 min thereafter. This clearly demonstrates that the diazene prevents photocorrosion and that it is reduced by Cd(0) in a dark reaction.

When CdS-A_2 was used, some characteristic differences were observed. The reaction was much faster and no photocorrosion was observed after all the 1,2-diphenyldiazene had been consumed. Photocorrosion did not occur even in the absence of 1,2-diphenyldiazene while dehydrodimers of 2,5-DHF and hydrogen (2 $mL\,h^{-1}$, constant rate over a period of 48 h) were formed.[2, 15] This indicates that excess sulfide ions prevent photocorrosion, as has also been reported for CdS colloids[16a] and single crystal electrodes.[16b, c]

In the case of the platinized sample CdS-A_1/Pt, diazene disappearance was much slower, and 1,2-diphenylhydrazine was formed in 80% yield while only traces of **1c** were found. No photocorrosion occurred either after diazene consumption or when the diazene was omitted from the otherwise complete system. In the latter case hydrogen evolution and dehydrodimerization[2] occurred eight times faster than with the nonplatinized photocatalyst. The stabilizing effect of platinization on cadmium sulfide is well known.[13a]

When colloidal CdS[17] was employed in the system 3,4-DHP/1,2-diphenyldiazene/MeOH, no photoaddition but efficient photocorrosion occurred. Apparently the latter cannot be prevented by the diazene, as was observed for the powder CdS-A_1 in aqueous dioxane. This and CdS-A_2 are photostable in methanol suspensions.[18]

Influence of Solvent: In the CdS system, unlike the zinc sulfide system, the relative rate increased only from 0.7 to 1.0 when methanol was substituted for acetonitrile as the solvent. No reaction occurred in absolute *n*-hexane or THF, but addition of sufficient amounts of water was able to induce a reaction as fast as in methanol (Table 2). While the amount of 1,2-diphenylhydrazine produced was zero in acetonitrile it increased to 17% in aqueous acetonitrile.

Table 2. Influence of solvent on yield of **1a** and 1,2-diphenylhydrazine (1,2-DPH) and relative reaction rates in the system CdS/3,4-DHP/1,2-diphenyldiazene.

	1a (%)	1,2-DPH (%)	v_{rel} [a]
$MeOH_{abs}$ [b]	70	25	1.00
THF_{abs} [c]	–	–	–
THF/H_2O (7/1, v/v)	38	60	0.20
THF/H_2O (2/1, v/v)	45	55	1.00
CH_3CN [b]	65	30	0.10
CH_3CN/H_2O (2/1, v/v)[b]	55	25	0.45
petroleum ether [c]	–	–	–

[a] Calculated from t_{MeOH}/t_x where t_{MeOH} and t_x represent times for complete diazene consumption. [b] From ref. [18]. [c] No reaction.

Influence of Substrate Redox Potential: Apparent quantum yields were measured at $\lambda = 366$ nm, the wavelength at which light absorption by the diazene is minimized (see Experimental Section). Φ_{app} of allylhydrazine formation in the system CdS/R^3H/1,2-diphenyldiazene/MeOH varied from 0.04 to 0.05, 0.03 and 0.02 when E_{ox} changed from 1.9 (3,4-DHP) to 2.0 (2,3-DHF), 2.6 (cyclohexene) and 2.6 V (2,5-DHF). As observed for ZnS photocatalysis, in some cases a lower oxidation potential induced a higher quantum yield, as indicated by the values for 2,5-DHF (0.02) and 3,4-DHP (0.04), while in others there was the opposite relation or none. Note that although 3,4-DHP was more readily oxidized than 2,5-DHF by 0.7 V, its quantum yield was only twice as large.

Contrasting with these weak effects, lowering of the reduction potential of the diazene caused a large increase in the relative quantum yield of diazene disappearance. In the series 1,2-bis(*p*-tolyl)diazene, 1,2-diphenyldiazene and 1,2-bis(*p*-chlorphenyl)diazene, E_{red} varies from -0.82 to -0.75 and -0.66 V (in dioxane/H_2O (7/3, v/v), vs. NHE) and Φ_{rel} varied from 0.5 to 1.0 and 5.0, respectively. Thus, although it was only slightly easier to reduce the *p*-chloro derivative than the *p*-methyl (0.16 V), the quantum yield was greater by a factor of ten. In the case of 1,2-bis(4-nitrophenyl)diazene, a multiplicity of products were observed and formation of the photoaddition product could not be confirmed. No photoaddition or reduction was observed in the case of 2,3-diazabicyclo[2.2.1]hept-2-ene either. It is known that aliphatic diazenes are much more difficult to reduce than aromatic ones.[19]

4. Mechanism

Photoaddition: Since the influence of catalyst preparation, solvent, and substrate redox potential is very similar for both metal sulfides, it is likely that the same mechanism operates in both cases. Owing to the ability of CdS to absorb visible light, most experiments were performed with this photocatalyst. Unless otherwise noted, the following discussion applies to a methanolic suspension of CdS-A_1. In this solvent no photocorrosion was observable[18] even in the absence of the substrates; in dioxane/H_2O, CdS-A_1 photocorroded when all the diazene had been consumed while CdS-A_2, precipitated from an excess of sodium sulfide, was photostable. It is likely that adsorbed sulfide ions enable a fast recombination ($1e^-/1h^+$ process)[16] of the electron–hole pair generated by one photon. This prevents photocorrosion, which is a $2e^-/2h^+$ process [Eqs. (1) and (2)] and would therefore require absorption of a second photon before recombination could occur.

$$CdS + 2h_{tr}^+ \longrightarrow Cd^{2+} + S \qquad (2)$$

From the fact that hydrogen evolution occurred only when all the diazene had been consumed, it follows that this substrate is involved in the reductive reaction step. Since the photoaddition proceeded only in protic solvents, electron transfer may be coupled to protonation according to Equation 3.

$$ArN{=}NAr_{ad} + e_{tr}^- + H_{ad}^+ \longrightarrow ArN(H){-}\dot{N}Ar_{ad} \qquad (3)$$

The electrochemical potential of e_{tr}^- at pH 7 is in the range of -1.9 and -0.9 V (vs. NHE) for ZnS and CdS, respectively,[20] while reduction potentials of -0.75 and -1.10 V (vs. NHE) were reported for 1,2-diphenyldiazene[21] in aqueous dioxane and DMF, respectively. Thus, reduction in the non-protic solvent is disfavoured by 0.35 V. An alternative mechanism wherein e_{tr}^- first reduces H_{ad}^+ to an adsorbed hydrogen atom, which is then transferred to the diazene, seems unlikely. In such a case, 2,3-diazabicyclo[2.2.1]hept-2-ene should also react, since in homogeneous solution it abstracts hydrogen from benzhydryl radicals.[22]

From the observation that after a few minutes of irradiation the ratio of *cis*/*trans*-diazene stays constant, one can conclude that both isomers react with the same rate although *cis*-1,2-diphenyldiazene is more easily reduced (by 0.18 V).[21] Hydrazyl radicals derived from 1,2-diaryl- and 1,2-dialkyldiazenes have been postulated[22] and identified in homogeneous solution by ESR[23]. The observation that the product **3a** obtained from 1-*tert*-butyl-2-phenyldiazene consists of only one isomer is in agreement with the expectation that the hydrazyl radical should be more stable when the unpaired electron is localized on the PhN rather than on the *t*BuN group.

By analogy to the ZnS- and CdS/Pt-catalysed photodehydrodimerization[1, 2] the trapped holes may oxidize the donor substrate to the radical cation, which subsequently deprotonates to the allylic radical $R^{3\cdot}_{ad}$ [Eqs. (4) and (5)]. Coupling of the

$$R^3H_{ad} + h^+_{tr} \longrightarrow R^3H^{\cdot+}_{ad} \qquad (4)$$

$$R^3H^{\cdot+}_{ad} + H_2O_{ad} \longrightarrow R^{3\cdot}_{ad} + H_3O^+_{ad} \qquad (5)$$

hydrazyl and allyl radicals affords the allylhydrazine [Eq. (6)]. We cannot exclude the possibility that the adsorbed radicals

$$R^{3\cdot}_{ad} + ArN(H){-}\dot{N}Ar_{ad} \longrightarrow ArN(H){-}N(R^3)Ar_{ad} \qquad (6)$$

desorb before they undergo this final reaction step. Formation of one product molecule is a $1e^-/1h^+$ process, while $2e^-/2h^+$ are necessary in the case of the photodehydrodimerization. Apparently generation of a further radical through absorption of a second photon and subsequent dimerization of $R^{3\cdot}$ is slower than coupling of the initially produced $R^{3\cdot}$ with a hydrazyl radical.

Indirect evidence for the intermediate $R^{3\cdot}$ radicals comes from the formation of two regioisomers when an asymmetrical olefin is employed, as indicated by the NMR spectrum of **1e** (vide supra). In the case of the enol ethers, the isolated material contained only the product in which the carbon atom at the 4-position is bound to nitrogen (Scheme 1), although in the HPLC spectrum obtained after 15 min of irradiation a splitting of the product peak is observed. This is not the case after longer reaction times or when 1 mL of water is added before irradiation.[18] These observations suggest that the peak splitting originates from the regioisomer bound at the 2-position (α to oxygen) since this should be very sensitive to hydrolysis.[18] More direct evidence is obtained when the reaction is performed in the presence of the radical scavenger diphenylpicrylhydrazyl.[24] In the case of cyclohexene, formation of the corresponding addition product is indicated by MS analysis (see Experimental Section). The cyclohexenyl radical was also postulated in the electrochemical oxidation of cyclohexene in methanolic solution.[25] It is also known that MeS radicals in homogeneous solution can abstract allylic hydrogen from 2,3-DHF and 3,4-DHP.[26]

While the reduction potentials of the diazenes are in the range of semiconductor conduction band energy, in some cases the oxidation potentials of the olefins/enol ethers are below the valence band edges, which are located at about 1.8 and 1.5 V (at pH 7, vs. NHE)[27] for zinc and cadmium sulfide, respectively. If the actual potential for 2,5-DHF is estimated as 2.0 V[28], the oxidative reaction step [Eq. (4)] requires an input of 0.5 eV. However, since the deprotonation of radical cations is usually highly exergonic[29], this step may furnish the required energy. Accordingly, using a bond dissociation energy (BDE) of 3.7 eV[30] one may calculate a driving force of 1.6 eV[31] for the overall reaction [Eq. (7), which is the sum of Eqs. (4) and (5)].

$$R^3H + h^+_{tr} \longrightarrow R^{3\cdot} + H^+ \qquad (7)$$

An alternative mechanism involving oxidation of adsorbed water or sulfur species to OH˙ or sulfur radicals and subsequent H-abstraction from R^3H seems unlikely but cannot be completely ruled out at present.[32, 33]

Model experiments in homogeneous solution support the intermediary radical mechanism postulated. Irradiation ($\lambda > 290$ nm) of a *dilute* solution of benzophenone and 1,2-diphenyldiazene (**1**) *in 3,4-DHP* (**a**) affords the addition product in a yield of 30% (HPLC). The yield is negligible when the concentrations of the first two components are increased or when a different solvent is employed. In addition to the more difficult separation of the photosensitizer, this homogeneous reaction is therefore of low synthetic value. For the mechanism we postulate that benzophenone in its excited triplet state abstracts hydrogen from 3,4-DHP[34] producing benzhydryl and dihydropyranyl radicals. The former transfers a hydrogen atom to the diazene[22] to give the 1,2-diphenylhydrazyl radical, which then couples with the latter to form **1a**.[34b] Since it is known that hydrazyl radicals do not abstract hydrogen from C–H bonds,[22, 35] the preference of the coupling reaction becomes understandable. The addition product **1a** is also obtained when the irradiation is performed in the absence of benzophenone, although in the much smaller yield of 5%. In this case, the triplet π,π* state of PhN=NPh abstracts hydrogen from 3,4-DHP. No reaction except isomerization occurs upon monochromatic irradiation at $\lambda = 405$ nm, which affords the triplet n,π* state.[35a, 36a]

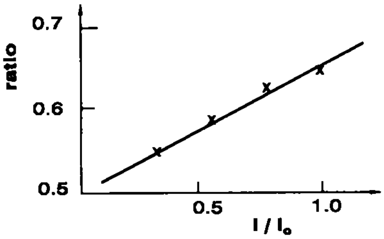

Fig. 3. The ratio of 1,2-diphenyldiazene/**1a** obtained by irradiation ($\lambda \geq 400$ nm) of CdS-A$_1$/PhN=NPh/3,4-DHP in MeOH at different light intensities.

Photoreduction: As mentioned above, the major side-reaction consists of a $2e^-$ reduction of the 1,2-diazene to the corresponding hydrazine derivative with concomitant $2h^+$ dehydrodimerization of the olefin/enol ether. In the system 3,4-DHP/1,2-diphenyldiazene the amount of 1,2-diphenylhydrazine produced increases with increasing light intensity (Fig. 3). These observations suggest that the local hydrazyl radical concentration may become so large that disproportionation according to Equation 8 is favoured over recombi-

$$2\,ArN(H){-}\dot{N}Ar \longrightarrow ArN(H){-}N(H)Ar + ArN{=}NAr \qquad (8)$$

nation with R^3. Thus hydrazine formation should predominate when $2e^-/2h^+$ processes become more favourable. Indeed, the platinized sample (5 mol% Pt) in the system PhN=NPh/2,5-DHF in dioxane/H_2O (5/1, v/v) induces almost exclusive photoreduction owing to the ability of the noble metal to act as electron transfer catalyst.[36b] In this case the hydrazyl radical may be further reduced according to Equation 9. A similar

$$ArN(H){-}\dot{N}Ar + e^-_{tr} + H^+ \longrightarrow ArN(H){-}N(H)Ar \qquad (9)$$

mechanism was proposed for the CdS-assisted photoreduction of methyl orange in the presence of EDTA.[37]

In the zinc sulfide catalysed reaction, 2,3-DHF afforded the addition product while its 2-methyl derivative is oxidized to 2-methylfuran with concomitant formation of 1,2-diphenylhydrazine, possibly as a result of the higher reducing power of the intermediate radical R^3 in the latter case, which should favour oxidation by a second hole. Subsequent deprotonation produces 2-methylfuran. This parallels the observation that THF is dehydrodimerized while 2,5-dimethyltetrahydrofuran is oxidized in the presence of irradiated aqueous ZnS suspensions.[38]

Experimental Section

All experiments were performed under an atmosphere of N_2; solvents were deoxygenated by N_2 bubbling. Unless otherwise noted, all yields correspond to analytically pure isolated material and were not optimized. Symmetric diazenes [39], 1-phenyl-2-*tert*-butyldiazene [40], 1-(4-methoxyphenyl)-2-phenyldiazene [41] and ZnS-B$_1$ [1] were prepared in accordance with the literature; all olefinic substrates were commercially available. Instruments: NMR: Jeol FT-JNM-EX 270 (TMS as internal standard); IR: Perkin–Elmer 983 and FT IR 1600; MS: Varian MAT 212 (70 eV); 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$_3$CN/H$_2$O (5/1, v/v), 1.5 mL min^{-1}, detection by Knauer UV/Vis Filter-Photometer at λ = 254 nm (separation conditions for the enol ether substituted hydrazines); Knauer HPLC pump 64, analytical pump head with 20 µl sample loop, column: Nucleosil 120 C18 (250 × 4 mm, 5 µm, Machery–Nagel) with precolumn (30 × 4 mm), CH$_3$CN/H$_2$O (3/1, v/v), 1.0 mL min^{-1}, detection as above (separation conditions for cycloalkenylsubstituted hydrazines). Preparative irradiations were performed with a tungsten–halogen lamp in a solidex immersion lamp apparatus, mechanistic irradiations in a cylindrical 20 mL quartz cuvette on an optical train equipped with an XBO 150 W lamp and a cut-off filter of $\lambda \geq 400$ nm. All redox potentials are relative to NHE and were taken from ref. [42a], except those of olefins and enol ethers which were calculated from ionization energies according to refs. [42b, c] and [28].

CdS-A$_1$: Na$_2$S · *x* H$_2$O (22.3 g, 35 wt % Na$_2$S, 0.10 mol) dissolved in H$_2$O (100 mL) was added dropwise over 1.5 h to a solution of 25.4 g (0.033 mol) of 3 CdSO$_4$ · 8 H$_2$O in 10 % aqueous NH$_3$. The solution was stirred for 20 h and the powder was washed to neutrality by multiple decanting. The remaining paste was washed with 2 M HOAc and then with H$_2$O to neutrality. After separation by suction filtration the residue was again washed with 50 mL of H$_2$O and dried over P$_2$O$_5$ in a desiccator. After grinding in an agate mortar the yellow powder was stored under N$_2$.

CdS-A$_2$: Analogous to CdS-A$_1$ but double the amount of Na$_2$S · *x* H$_2$O was used (44.59 g, 0.20 mol). Specific surface areas were measured by N$_2$ adsorption. Platinization was performed photochemically in the presence of 5 mol % hexachloroplatinate according to the method of Bard [43].

1-(3,4-Dihydro-2*H*-pyran-4-yl)-1,2-diphenylhydrazine (1 a): 1,2-Diphenyldiazene (500 mg, 2.74 mmol), CdS-A$_1$ (500 mg, 3.46 mmol), 3,4-DHP (3.0 mL, 33.2 mmol) and MeOH (85 mL) were suspended in a Pyrex immersion lamp apparatus by sonicating for 15 min. When TLC analysis indicated that all diazene had reacted (15 h) irradiation was stopped, CdS removed by suction filtration and the remaining liquid evaporated in vacuo. The resulting yellow oil was twice crystallized from MeOH to produce a white solid: 219 mg (30 %), M.p. 68 °C. IR (KBr) [cm^{-1}]: 3328 (NH), 3052, 2968 (CH), 1636 (O–C=C), 1595, 1495 (C=C), 752, 696 (CH); MS *m*/*z*: 266 [*M*$^+$]; C$_{17}$H$_{18}$N$_2$O (266.4 g mol^{-1}): calcd C 76.66, H 6.81, N 10.51; found C 76.98, H 7.20, N 10.44; ^{1}H NMR (CDCl$_3$): δ = 2.20 (br d, 2 H, C*H*$_2$CH$_2$O), 4.15 (m, 2 H, C*H*$_2$O), 4.77 (br s, 2 H, C*H*=CHO and C*H*NR$_2$), 5.62 (s, 1 H, NH), 6.65 (br s, 1 H, =CH–O), 6.75–7.45 (m, 10 H, C$_6$H$_5$); ^{13}C NMR (CDCl$_3$): δ = 26.8 (*C*H$_2$CH$_2$O, 64.4 (*C*H$_2$O), 51.2 (CH$_2$*C*HN), 99.2 (*C*H=CHO), 148.3 (=*C*HO), 111.7, 114.8, 119.2, 119.9, 129.3 (*C*$_6$H$_5$), 149.1, 149.6 (*C*N in C$_6$H$_5$).

1-(2-Cyclohexen-1-yl)-1,2-diphenylhydrazine (1 b): Analogous to **1 a** with CdS-A$_1$ (300 mg, 2.08 mmol), 1,2-diphenyldiazene (300 mg, 1.65 mmol), and cyclohexene (3.0 mL, 29.6 mmol) in MeOH (85 mL). After two crystallizations, each from 5 mL petroleum ether (b.p. 50–60 °C), clusters of white needles were obtained: 155 mg (36 %). M.p. 90 °C; IR (KBr) [cm^{-1}]: 3318 (NH), 3018, 2943 (CH), 1599, 1495 (C=C); MS (% intensity) *m*/*z*: 264 (10) [*M*$^+$], 183 (100) [*M*$^+$ – C$_6$H$_9$], 81 (10) [C$_6$H$_9$], 77 (75) [C$_6$H$_5$]; C$_{18}$H$_{20}$N$_2$ (264.37 g mol^{-1}): calcd C 81.78, H 7.62, N 10.60; found C 81.98, H: 7.79, N 10.26; ^{1}H NMR (CDCl$_3$) δ = 1.5–2.2 (br, 6 H, 3 C*H*$_2$), 4.65 (br s, 1 H, CH$_2$C*H*N), 5.45 (s, 1 H, NH), 5.7 (br, 1 H, CH$_2$C*H*=), 5.9 (br, 1 H, =C*H*CHN), 6.7–7.3 (m, 10 H, C$_6$*H*$_5$); ^{13}C NMR (CDCl$_3$) δ = 21.5 (=CHCH$_2$*C*H$_2$), 24.9 (=CH*C*H$_2$), 25.7 (br, *C*H$_2$CHN), 57.4 (CH$_2$*C*HN), 111.7, 114.5, 118.9, 119.3, 129.3 (*C*$_6$H$_5$), 126.5 (br, CH$_2$*C*H=), 131.9 (br, =*C*HCHN), 149.3, 149.6 (*C*N in C$_6$H$_5$).

1-(2,3-Dihydrofuran-3-yl)-1,2-diphenylhydrazine (1 c): Analogous to **1 a** with 1,2-diphenyldiazene (800 mg, 4.44 mmol), ZnS-B$_1$ (1.2 g, 12.3 mmol) and 2,3-DHF (5.0 mL, 55.3 mmol) in H$_2$O (15 mL) and 1,4-dioxane (70 mL). High-pressure mercury lamp Philips HPK 125 W ($\lambda \geq 290$ nm). Colourless crystals: 220 mg (20 %). IR (KBr) [cm^{-1}]: 3290 (NH), 1601 (CH=CHO), 753 (C$_6$H$_5$); MS: 252 [*M*$^+$], 222 [*M*$^+$ –CH$_2$O], 182 [*M*$^+$ –C$_4$H$_6$O]; C$_{16}$H$_{16}$N$_2$O (252.31 g mol^{-1}): calcd C 76.16, H 6.39, N 11.10; found C 76.38, H 6.54, N 10.78; ^{1}H NMR (CDCl$_3$, TMS extern, 270 MHz) δ = 4.34 (m, 2 H, C*H*$_2$O), 4.98 (m, 1 H, C*H*=CHO), 5.35 (m, 1 H, CH=CHC*H*N), 5.47 (s, 1 H, NH), 6.64 (d, 1 H, CH=C*H*O), 6.75–7.30 (m, 10 H, C$_6$*H*$_5$); ^{13}C NMR (CDCl$_3$, 67.7 MHz) 64.0 (=CH*C*HN), 71.9 (*C*H$_2$O), 150.3 (CH=*C*HO), 111.8, 114.9, 119.2, 120.2, 129.3 (*C*$_6$H$_5$), 149.3, 149.7 (*C*N in C$_6$H$_5$).

1-(2-Cyclopenten-1-yl)-1,2-diphenylhydrazine (1 d): Analogous to **1 a** with 1,2-diphenyldiazene (500 mg, 2.74 mmol), cyclopentene (2.5 mL, 28.4 mmol) and CdS-A$_1$ (300 mg, 2.08 mmol) in MeOH (80 mL). Crystallization from petroleum ether afforded clusters of white needles: 240 mg (34 %). M.p. 95 °C; IR (KBr) [cm^{-1}]: 3338 (NH), 3019, 2979 (CH), 1595, 1496 (C=C); MS (%): 250 (30) [*M*$^+$] 183 (100) [*M*$^+$ – C$_5$H$_7$] 77 (90) [C$_6$H$_5$] 66 (75) [C$_5$H$_6$]; C$_{17}$H$_{18}$N$_2$ (250.34 g mol^{-1}): calcd C 81.56, H 7.25, N 11.19; found C 81.53, H 7.37, N 11.36;. ^{1}H NMR (CDCl$_3$) δ = 1.7–2.5 (m, 4 H, C*H*$_2$C*H*$_2$), 5.22 (m, 1 H, CH$_2$C*H*N), 5.33 (s, 1 H, NH), 5.68 (m, 1 H, CH$_2$C*H*=), 6.05 (br, 1 H, =C*H*CHN), 6.7–7.25 (m, 10 H, C$_6$*H*$_5$); ^{13}C NMR (CDCl$_3$) δ = 26.22 (CH$_2$*C*H$_2$CHN), 31.74 (=CH*C*H$_2$), 66.99 (=CH*C*HN), 127.5 (br, CH$_2$*CH*=), 137.1 (br, =*C*HCHN), 111.59, 114.47 118.93, 119.35, 129.16 (*C*$_6$H$_5$), 149.54, 150.45 (*C*N in C$_6$H$_5$).

1-(Methyl-2-cyclohexen-1-yl)-1,2-diphenylhydrazine (1 e): Analogous to **1 a** with 1,2-diphenyldiazene (500 mg, 2.74 mmol), 4-methylcyclohexene (3.5 mL, 29.1 mmol) and CdS-A$_1$ (700 mg, 4.85 mmol) in MeOH (85 mL). After separation by chromatography through a quartz column (50 × 2 cm, 100 g Al$_2$O$_3$, activity III, fluorescence label: petroleum ether as eluting agent) and crystallization from petroleum ether (2.5 mL), a white powder was obtained: 215 mg (28 %). M.p. 62 °C; IR (KBr) [cm^{-1}]: 3323 (NH), 1601, 1495 (CH), 3018, 2951 (C=C); MS (%): 278 (15) [*M*$^+$] 183 (100) [*M*$^+$ –C$_7$H$_{11}$] 95 (15) [C$_7$H$_{11}$] 77 (90) [C$_6$H$_5$]; C$_{19}$H$_{22}$N$_2$ (278.39 g mol^{-1}): calcd C 81.97, H 7.96, N 10.06; found C 81.92, H 8.10, N 10.20; ^{1}H NMR (CDCl$_3$): = 0.94 (s, 3 H, C*H*$_3$), 1.56–2.20 (m, 5 H, CHC*H*$_2$C*H*$_2$CHN, C*H*$_2$C*H*MeC*H*$_2$CHN), 4.65 (m, 1 H, CHN), 5.39, 5.42 (s, s, 1 H, N*H*), 5.62 (br, 1 H, =C*H*CHN), 5.89 (br, 1 H, C*H*=CHCHN); ^{13}C NMR (CDCl$_3$) δ = 20.58, 22.20 (*C*H$_3$), 25.55, 32.37 (NCHCH$_2$*C*HMeCH$_2$, NCHCH$_2$*C*H$_2$), 28.82, 33.88 (=CH*C*H$_2$, =CH*C*HMeCH$_2$), 33.4, 34.8 (br, *C*HN), 126.3 (br, *C*H=CHCHN), 132.3 (br, =*C*HCHN), 111.68, 111.78, 114.26, 114.49, 118.87, 118.99, 119.27, 129.22 (*C*$_6$H$_5$), 149.16, 149.26 (*C*N in C$_6$H$_5$).

1-(3-Penten-2-yl)-1,2-diphenylhydrazine (1 f): Analogous to **1 a** with 1,2-diphenyldiazene (500 mg, 2.74 mmol), 2-pentene (3.0 mL, 23.2 mmol) and CdS-A$_1$ (700 mg, 4.85 mmol) in MeOH (85 mL). The remaining yellow oil was purified as described for **1 d** but using Al$_2$O$_3$ of activity V. Colourless oil: 350 mg (51 %), part of which gave a white powder after standing for several weeks at –20 °C : 80 mg (12 %). IR (film) [cm^{-1}]: 3305 (NH), 3055, 2971 (CH), 1601, 1495 (C=C); FD-MS 252; C$_{17}$H$_{20}$N$_2$ (252.36 g mol^{-1}): Found C 79.76, H 7.54, N 10.74; Calcd. C 80.91, H 7.99, N 11.10; ^{1}H NMR (CDCl$_3$) δ = 1.28 (d, 3 H, C*H*$_3$), 1.63 (d, 3 H, C*H*$_3$), 4.57 (m, 1 H, =CHC*H*N), 5.36 (s, 1 H, N*H*), 5.57 (m, 2 H, CH=CH), 6.7–7.2 (10 H, C$_6$*H*$_5$); ^{13}C NMR (CDCl$_3$) δ = 17.5 (br, NCH*C*H$_3$), 17.88 (=CH*C*H$_3$), 56.95 (*C*HN), 127.4, 129.0 (br, *C*H=*C*H), 111.90, 114.29, 119.03, 119.09, 129.14, 129.18 (*C*$_6$H$_5$), 149.38, 149.86 (*C*N in C$_6$H$_5$).

1-(3,4-Dihydro-2*H*-pyran-4-yl)-1,2-bis(4-methylphenyl)hydrazine (2 a): Analogous to **1 a** with 1,2-bis(4-methylphenyl)diazene (400 mg, 1.90 mmol), 3,4-DHP (3.0 mL, 33.2 mmol) and ZnS-B$_1$ (600 mg, 6.16 mmol) in MeOH (200 mL). Isolation as described for **1 e** using petroleum ether/Et$_2$O: 10/1 (v/v). The yellow oil (225 mg, 40 %) yielded a white solid on crystallization from petroleum ether: 60 mg (11 %). M.p. 66 °C; IR (KBr) [cm^{-1}]: 3288 (NH), 3021, 2919 (CH), 1640 (OC=C), 1611, 1510 (C=C); MS (FD) *m*/*z*: 294; C$_{19}$H$_{22}$N$_2$O (294.4 g mol^{-1}): calcd C 77.52, H 7.53 N 9.52 ; Found C 77.64, H 8.20, N 9.70; ^{1}H NMR (CDCl$_3$) δ = 2.1 (m, 2 H, OCH$_2$C*H*$_2$), 2.24 (s, 6 H, 2-C*H*$_3$), 4.08 (m, 2 H, OC*H*$_2$), 4.65 (m, 2 H, CH$_2$C*H*N and OCH=C*H*), 6.55 (d, 1 H, OC*H*=), 6.74–7.05 (m, 8 H, 2 C$_6$*H*$_4$); ^{13}C NMR (CDCl$_3$) δ = 20.34, 20.48 (*C*H$_3$), 26.7 (br, OCH$_2$*C*H$_2$), 51.75 (=CH*C*HN), 64.76 (O*C*H$_2$), 99.8 (br, OCH=*CH*), 148.13 (br, O*C*H=), 111.86, 115.05, 129.82 (*C*$_6$H$_4$), 128.22, 129.21 (*C*CH$_3$, C$_6$H$_4$), 146.99, 147.50 (*C*N in C$_6$H$_4$).

1-(2-Cyclohexen-1-yl)-1,2-bis(4-methylphenyl)hydrazine (2 b): Analogous to **1 b**. 1,2-bis(4-methylphenyl)diazene (300 mg, 1.43 mmol), cyclohexene (3.0 mL, 29.6 mmol) and CdS-A$_1$ (300 mg, 2.08 mmol) in MeOH (140 mL). Two crystallizations from petroleum ether afforded white microcrystals: 190 mg (45 %). M.p. 80 °C; IR (KBr) [cm^{-1}]: 3317 (NH), 3021, 2945 (CH), 1611, 1510 (C=C); MS (%): 292 (55) [*M*$^+$], 211 (100) [*M*$^+$ – C$_6$H$_9$], 91 (100) [C$_7$H$_7$], 81 (60) [C$_6$H$_9$]; C$_{20}$H$_{24}$N$_2$ (292.4 g mol^{-1}): calcd C 82.15, H 8.27, N 9.58; found C 81.86, H 8.41, N 9.72; ^{1}H NMR (CDCl$_3$): δ = 1.55–2.05 (m, 6 H, 3 C*H*$_2$), 2.21 (s, 6 H, 2 C*H*$_3$), 4.57 (br m, 1 H, =CHC*H*N), 5.30 (s, 1 H, N*H*), 5.62 (br d, 1 H, CH$_2$C*H*=), 5.89 (br, 1 H, =C*H*CHN), 6.70–7.05 (m, 8 H, 2 C$_6$*H*$_4$); ^{13}C NMR (CDCl$_3$): δ = 20.30, 20.48 (2 *C*H$_3$), 21.55 (=CHCH$_2$*C*H$_2$), 24.96 (=CH*C*H$_2$), 26.2 (br, *C*H$_2$CHN), 57.58 (CH$_2$*C*HN), 126.7 (CH$_2$*C*H=CH), 133.9 (=*C*HCHN), 111.84, 114.59, 128.01, 128.43, 129.38 (*C*$_6$H$_4$), 147.24, 147.62 (*C*N in C$_6$H$_4$).

1-(3,4-Dihydro-2*H*-pyran-4-yl)-1-phenyl-2-tert-butylhydrazine (3 a): Analogous to **1 a**. 1-phenyl-2-*tert*-butyldiazene (500 mg, 3.08 mmol), 3,4-DHP (3.0 mL, 33.2 mmol) and CdS-A$_1$ (500 mg, 3.46 mmol) in MeOH (100 mL). After separation as described for **2 a** a colourless oil was obtained: 210 mg (28 %). IR (film) [cm^{-1}]: 3286 (NH), 3060, 2973 (CH), 1641 (OC=C), 1595, 1489 (C=C); MS FD) *m*/*z*: 246; C$_{15}$H$_{22}$N$_2$O (246.3 g mol^{-1}): calcd C 73.13, H 9.00, N 11.37; found C 73.38, H 9.20, 11,50; ^{1}H NMR (CDCl$_3$) δ = 0.99 (s, 9 H, C(C*H*$_3$)$_3$), 1.82/2.20 (br m, 2 H, C*H*$_2$CHN), 3.17 (br s, 1 H, N*H*), 4.02 (m, 3 H, =CHC*H*N and OC*H*$_2$CH$_2$), 4.61 (br, 1 H, CH=CH), 6.39 (d, 1 H, OC*H*=CH), 6.97 (t, 1 H, *p*-*H*, C$_6$H$_5$), 7.16–7.27 (m, 4 H, C$_6$*H*$_5$); ^{13}C NMR (CDCl$_3$): δ = 26.94 (OCH$_2$*C*H$_2$CHN), 57.66 (=CH*C*HN), 64.58 (O*C*H$_2$CH$_2$), 102.3 (br, OCH=*CH*), 145.75 (OCH=CH), 28.91 (NC(*C*H$_3$)$_3$), 54.23 (N*C*(CH$_3$)$_3$), 122.1 (br, *o*- and *p*-*C*, C$_6$H$_5$), 153.82 (*C*N in C$_6$H$_5$). The coalescence temperatures and peak distances at the lowest temperature ($\Delta\nu$) were 285/88, 288/95 and 273 K/27 Hz for C-1, C-2 and C-3, respectively. From these values free activation energies were calculated by $\Delta G_c^{*} = 4.57\,T_c(9.97 + \log T_c/\Delta\nu)$ [44].

Relative Rates: ZnS (0.2 g, 2.05 mmol) were suspended in a solution of 1,2-diphenyldiazene (0.180 g, 1 mmol) and olefin/enol ether (55 mmol) in a dioxane/water (70/15 mL) mixture and sonicated for 20 min. After irradiating in the solidex immersion lamp apparatus the concentration of 1,2-diphenyldiazene was measured by HPLC. When 2,5-DHF and 1,2-bis(4-methylphenyl)diazene were employed, the diazene was completely consumed in 30 h of irradiation while only 10 h were necessary for the reaction of 1,2-diphenyldiazene. In the case of 1,2-bis(4-chlorophenyl)diazene the reaction was incomplete even after 48 h. No addition product was detected in the case of 1,2-bis(4-nitrophenyl)diazene after irradiating for 48 h.

Dependence on Intensity: A suspension of CdS-A_1 (50 mg, 0.346 mmol) in a solution of 1,2-diphenyldiazene (20 mg, 0.110 mmol) in $MeOH/H_2O$ (17 mL, 15/2 v/v) was sonicated for 15 min while N_2 was bubbled through it. After addition of 3,4-DHP (0.3 mL, 3.3 mmol) the cuvette was sealed by a septum. Different attenuators were placed in the light beam. After 50 min irradiation, the amounts of **1a** and 1,2-diphenylhydrazine were determined as described above.

Dependence on Solvent: A mixture of CdS-A_1 (100 mg, 0.69 mmol), 1,2-diphenyldiazene (100 mg, 0.55 mmol) and 3,4-DHP (3.0 mL, 33 mmol) in 100 mL solvent (see Table 5) was sonicated for 15 min while N_2 was bubbled through it. Irradiation was continued until all the diazene had been consumed; in THF and petroleum ether no reaction occurred even after 24 h, while a very slow one was observable in THF/H_2O (20/1, v/v). Concentrations of **1a** and 1,2-diphenylhydrazine were measured as described above.

Homogeneous Systems: A solution of 1,2-diphenyldiazene (0.01 mmol) and benzophenone (3.6 mg, 0.02 mmol) in 3,4-DHP (15 mL) was irradiated in the cylindrical cuvette (vide supra). After 2 h all the diazene was consumed and **1a** was formed in 30% yield (HPLC).

Apparent Quantum Yields: A suspension of CdS-A_1 (5.0 mg, 0.0346 mmol) in 3.0 mL of an 0.887 $mmol\,L^{-1}$ methanolic solution of 1,2-diphenyldiazene was sonicated for 15 min in a 4 mL quartz cell through which N_2 was bubbled. The enol ether or cyclohexene (3.32 mmol) was added and the sample was transferred to an electronically integrating actinometer [45] and irradiated at $\lambda = 366$ or 436 nm for 1 h. The number of "absorbed and scattered/reflected" light quanta N_{abs} was in the region of 3.1×10^{19} (at 366 nm). Amount of product (typical values are 0.1–0.3 μmol) was determined by filtering through a micropore filter (see above), washing the cuvette three times with MeOH (1 mL × 3), filtering the combined solution again and evaporating to dryness. The residue is dissolved in MeCN (1 mL) and analysed by HPLC. The number of quanta absorbed by the diazene, N_d, (e.g., 1.07×10^{19} at 366 nm) was measured by omitting CdS-A_1 in the experiment described above. The amount of light scattered/reflected, N_{ref}, (e.g., 0.64×10^{19}) was measured by irradiating the complete suspension at $\lambda = 580$ nm. The apparent quantum yield Φ_{app} is given by N_p/N_q, wherein N_p corresponds to the number of product molecules and N_q, the number of apparently absorbed quanta, to $N_{abs} - N_{ref} - N_d$.

Relative Quantum Yields: The influence of 1,2-diazene structure on the relative quantum yield was studied in the presence of cyclohexene. Since consumption of the *trans*-1,2-diazene was measured, the following workup after irradiation was performed in the dark in order to prevent *cis–trans* isomerization. The suspension was quantitatively transferred to a calibrated flask by washing three times with 0.5 mL portions of MeOH and adjusting the volume to 5 mL. Aliquots were withdrawn through the micropore filter and absorbance was measured at the maximum of the n,π* absorption in the range 430–435 nm. From this value, A, the absorbance A_i (obtained by the same procedure but omitting cyclohexene) was subtracted in order to correct for the amount of *cis–trans* isomerization. The value obtained for 1,2-diphenyldiazene was arbitrarily chosen as 1.0. (In the case of 1,2-bis(4-nitrophenyl)diazene the reaction had to be conducted in toluene/MeOH (2/1, v/v) because of solubility problems.) In the photostationary equilibrium, HPLC demonstrates that the ratio of *cis* and *trans*-diazene stays constant after 10 min of irradiation.

Scavenging Experiment: Suspension of CdS-A_1 (0.1 g, 0.69 mmol) in MeOH (15 mL) containing 1,1-diphenyl-2-picrylhydrazyl (DPPH) (20 mg, 0.0051 mmol). Irradiation for 2.5 h on the optical train in the presence of a) of cyclohexene (1 mL, 9.8 mmol) and 1,2-diphenyldiazene (20 mg, 0.11 mmol); b) cyclohexene (1 mL, 9.8 mmol); or c) 1,2-diphenylacetylene (20 mg, 0.11 mmol). The oil obtained after evaporation was analysed by MS. In the cases of a) and b) only, a peak at $m/z = 475$ was observed which corresponds to the addition product of C_6H_9 to DPPH.

X-ray Analysis of 1b: Single crystals were obtained by slow evaporation of a methanolic solution at ambient temperature and pressure. For apparatus and method of analysis see ref. [46]. $C_{18}H_{20}N_2$ (**1b**) 264.4, crystal size 0.80 × 0.40 × 0.40 mm, orthorhombic, space group *Pccn*, $a = 17.797(6)$, $b = 20.824(6)$, $c = 7.994(4)$ Å, $V = 2962.7(16)$ Å^3, $\rho_{calc} = 1.185$ $g\,cm^{-3}$ ($Z = 8$), $R = 5.70$, $R_w = 3.51$, 181 parameters refined, $2\theta_{max} = 54°$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-401417.

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