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PAPER

Visible light mediated homo- and heterocoupling of benzyl alcohols and benzyl amines on polycrystalline cadmium sulfide†

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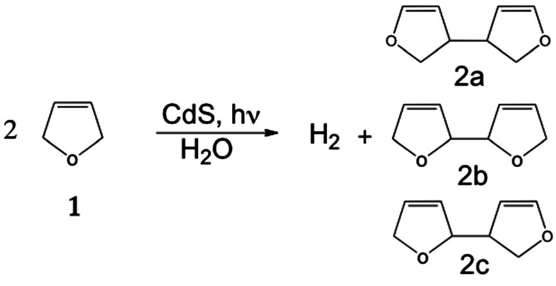
The oxidative coupling of sp^3 hybridized carbon atoms by photocatalysis is a valuable synthetic method as stoichiometric oxidation reagents can be avoided and dihydrogen is the only byproduct of the reaction. Cadmium sulfide, a readily available semiconductor, was used as a visible light heterogeneous photocatalyst for the oxidative coupling of benzyl alcohols and benzyl amines by irradiation with blue light. Depending on the structure of the starting material, good to excellent yields of homocoupling products were obtained as mixtures of diastereomers. Cross-coupling between benzyl alcohols and benzyl amines gave product mixtures, but was selective for the coupling of tetrahydroisoquinolines to nitromethane. The results demonstrate that CdS is a suitable visible light photocatalyst for oxidative bond formation under anaerobic conditions.

Introduction

Visible light photocatalysis uses available and sustainable energy sources to drive chemical processes, reducing synthetic costs and environmental concerns. The visible range of solar irradiation is the most desirable part of the spectrum for photocatalysis, because it is intense and most organic substrates do not absorb in this range, which avoids photochemistry by direct excitation.[1] Recently visible light homogeneous photocatalysis using ruthenium or iridium complexes[2] or various organic dyes[3] was applied for carbon–carbon and carbon–heteroatom bond formation, even with control of the absolute stereochemistry. Heterogeneous inorganic semiconductors can be of advantage compared to homogeneous photocatalysts, as they are easily separated from the reaction mixture and recycled. In addition, oxidation and reduction reactions can be performed simultaneously on one catalyst particle.[4] However, the use of visible light semiconductor photocatalysis for organic synthesis is less investigated, compared to homogeneous catalysis. Typical visible light absorbing semiconductors are dye-sensitized or element-doped titanium dioxide, other transition metal oxides, carbon nitride and cadmium sulfide. They have been applied to visible light water splitting,[5] reduction of nitrate to ammonia,[6] carbon dioxide activation,[7] hydrogen production,[8] oxidation of alcohols to aldehydes,[9] and amines to imines.[10] Photocatalytic C–C bond formations using heterogeneous photocatalysts are rare. A preparative example is the anaerobic dehydrodimerization of cyclic unsaturated ethers photocatalyzed by zinc or cadmium sulfides (Scheme 1).[11] In the proposed mechanism the reactive electrons photogenerated in the conduction band reduce water, while the simultaneously in the valence band formed reactive holes oxidize 2,5-dihydrofuran *via* a dissociative electron transfer to a dihydrofuryl radical. Dimerization of the latter leads to the dehydrodimer, obtained as a mixture of the depicted regioisomers (eqn (1)–(3), RH_2 = 2,5-dihydrofuran).

$$2\,H_2O + 2\,e_r^- \rightarrow H_2 + 2\,OH^- \tag{1}$$



Scheme 1 Photocatalytic dehydrodimerization of 2,5-dihydrofuran (**1**).

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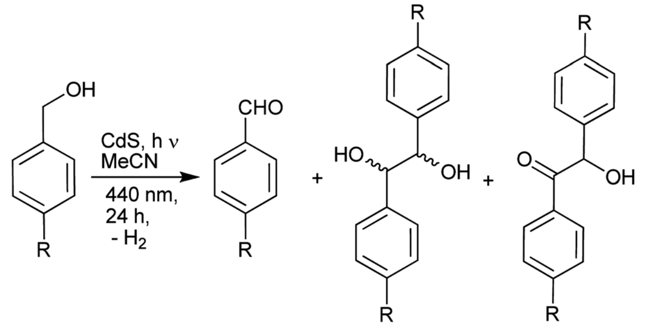


3 **4** **5** **6**

Scheme 2 Photoconversion of benzylic alcohols **3**. R = H, OMe, Cl, Br, I, COOMe.

Table 1 Concentration and temperature dependence of product composition in benzyl alcohol photoconversion

		Products [%]				
	Temp. [°C]	**3-H** [mmol L^{-1}]^a	**4-H**	**5-H**	**6-H**	**3-H**^{b}
1	20	0.04	83	17	0	0
2	20	0.1	51	43	3	0
3	20	0.4	16	38	40	4
4	20	1	5	10	40	43
5	−15	0.1	12	10	54	23
6	−15	0.4	4	6	62	27

[a] Initial benzyl alcohol concentration. [b] Recovered benzyl alcohol.

$$RH_2 + 2\ h_r^+ \rightarrow 2\ RH^{\cdot} + 2\ H^+ \qquad (2)$$

$$2\ RH^{\cdot} \rightarrow HR - RH \qquad (3)$$

Cadmium sulfide is an attractive semiconductor photocatalyst, which in comparison to unmodified TiO_2 absorbs visible light due to its bandgap of 2.4 eV.[4] In water at pH 7 the conduction and valence band edges are located at about −0.4 and +2.0 V (rel. to NHE), respectively. When changing to acetonitrile a cathodic shift of 0.4 V was reported.[12] Thus the reactive holes (h_r^+) will have weaker oxidative power as in water, which may enable some mild oxidations and even C–C couplings. We report here, the visible light catalyzed homo- and cross-coupling of benzyl amines and benzyl alcohols on cadmium sulfide in an oxygen-free atmosphere, studies of the reaction mechanism, the effects of temperature and substrate structure.

Results and discussion

Photoconversions of benzyl alcohols

Irradiation of a benzyl alcohol (**3**) solution in acetonitrile in an oxygen-free atmosphere with light of 440 nm in the presence of cadmium sulfide leads to the formation of three main products: benzaldehyde (**4**), hydrobenzoin (**5**) (as a mixture of diastereomers), and benzoin (**6**) (Scheme 2), as confirmed by GC-MS analyses. Phenylbenzylketone and benzyl were detected in the reaction mixture in trace amounts. The photoconversion of the benzyl alcohols is accompanied by the evolution of dihydrogen gas, which was confirmed by GC-H_2 measurements of the gas phase from the reaction vessels. To the best of our knowledge, this is the first example of photocatalytic hydrogen production from alcohols on unmodified cadmium sulfide. Jiang *et al.* reported the photocatalytic dehydrogenation of aliphatic alcohols in water on platinized CdS, where Pt is suggested to generate dihydrogen by reduction of protons.[13]

Analogous to Scheme 1 and the reactions according to eqn (1)–(3) the formation of compounds **4–6** is rationalized as follows. Reactive holes oxidize the alcohol by a dissociative electron transfer to benzyl radicals and protons (eqn (4)). The latter recombine with the hydroxide ions produced according to eqn (1) forming water, essential for the observed hydrogen evolution. It is noted that the employed CdS contains at least one monolayer of surface water. The produced hydroxybenzyl radicals may undergo homocoupling to the dehydrodimer **5** (eqn (5)) or give benzaldehyde, *via* disproportionation to benzaldehyde and benzyl alcohol (eqn (6)), electron injection into the CdS conduction band (eqn (7)) and hole oxidation according to eqn (8).

$$ArCH_2\text{–}OH + h_r^+ \rightarrow Ar\dot{C}H\text{–}OH + H^+ \qquad (4)$$

$$2\ Ar\dot{C}H\text{–}OH \rightarrow Ar(OH)CH\text{–}CH(OH)Ar \qquad (5)$$

$$2\ Ar\dot{C}H\text{–}OH \rightarrow ArCHO + ArCH_2OH \qquad (6)$$

$$Ar\dot{C}H\text{–}OH \rightarrow ArCHO + e_r^- + H^+ \qquad (7)$$

$$Ar\dot{C}H\text{–}OH + h_r^+ \rightarrow ArCHO + H^+ \qquad (8)$$

The hydrobenzoin **5-H** can eliminate water, and through the keto-enolic equilibrium gives phenylbenzylketone, which was found in the reaction mixtures in amounts of 3–14%. Benzoin **6-H** most likely results from the oxidation of **5-H** and can be further oxidized to benzil, which was observed as a minor byproduct in the case of substituted benzyl alcohols. Accordingly, using *meso*-hydrobenzoine **5-H** as a starting material in acetonitrile under identical irradiation conditions in the presence of CdS gives benzoine **6-H** (60%) and phenylbenzylketone (7%). Although this suggests that **5-H** is an intermediate when benzyl alcohol is the substrate, the concentration dependence of the product composition does not support this possibility.

As noticeable from Table 1 only the percentage of **6-H** strongly increases upon increasing the alcohol concentration (Table 1, entries 1–3). Above concentrations of 0.4 mmol L^{-1} there is no longer any change. In the same sequence the hydrobenzoin yield starts decreasing above 0.1 mmol L^{-1}. The strong increase observed when changing the alcohol concentration from 0.1 mmol L^{-1} to 0.4 mmol L^{-1} occurs at the cost of the aldehyde **4-H**, which decreases from 51% to only 16%. Noteworthy, the same changes are observable, when lowering the temperature to −15 °C (compare entries 2 and 5, Table 1). Furthermore the ratio of **5-H**:**6-H** changes from 14 : 1 to 1 : 5. Obviously, decreasing the temperature disfavors aldehyde and hydrobenzoin formation, but favors benzoin.

The increase of the C–C coupling products **3-H** and **4-H** with increasing alcohol concentration is in accordance with a surface C–C bond formation. Apparently, a maximum surface coverage

Table 2 Dependence of product composition on the nature of the substituent X in p-X-$C_6H_4CH_2OH$

	Product yield [%]		
para-substituent X	**4**	**5**	**6**
–Br	24	25	45
–I	36	64[16]	—
–CO_2Me[a]	5	76	10
–OCH_3[b]	24	11	36

[a] The corresponding 1,2 diketone was obtained in 10%. [b] The corresponding anisil (1,2 diketone) was obtained in 15%.

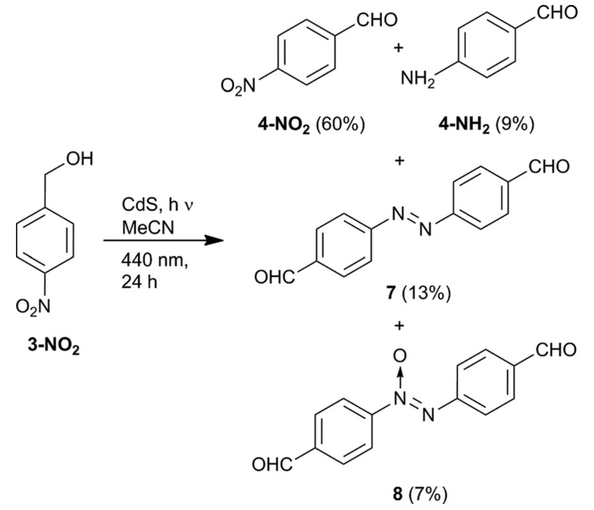
is reached at 0.4 mmol L^{-1} (Table 1, entry 3). On the other hand, aldehyde formation *via* the disproportion pathway should be favored (eqn (6)), since it is also a bimolecular reaction. However, the amount of benzaldehyde decreases, indicating that the aldehyde is not formed according to eqn (6) but rather *via* the electron transfer paths (eqn (7) and (8)). It is also unlikely that the hole oxidation according to eqn (8) is so strongly temperature dependent (Table 1, entries 2 and 5). It seems likely that aldehyde formation is *via* electron injection from the benzyl radical into the CdS conduction band. Such processes are well known in semiconductor photocatalysis. At concentrations between 0.4–1.0 mmol L^{-1} the benzaldehyde pathway is almost suppressed and the major C–C coupling product is dehydrobenzoin obtained as a mixture of diastereomers with a diastereomeric ratio (dr, *rac* : *meso*) of 7 : 3. At these concentrations the benzyl alcohol was not fully converted within 24 h; full conversion required longer irradiation time.

To the best of our knowledge, this is the first example of visible light photocatalytic synthesis of benzoin and hydrobenzoin from benzylalcohol on cadmium sulfide. Photocatalytic reductive coupling of aryl ketones into the corresponding diols by colloidal CdS suspensions with excess of reducing agent triethylamine was reported earlier by the group of Yanagida.[14] The same group also observed the reductive coupling of benzophenone and acetophenone to the corresponding diols during the photocatalytic fixation of CO_2 by ketones in colloidal suspensions of CdS in DMF.[15]

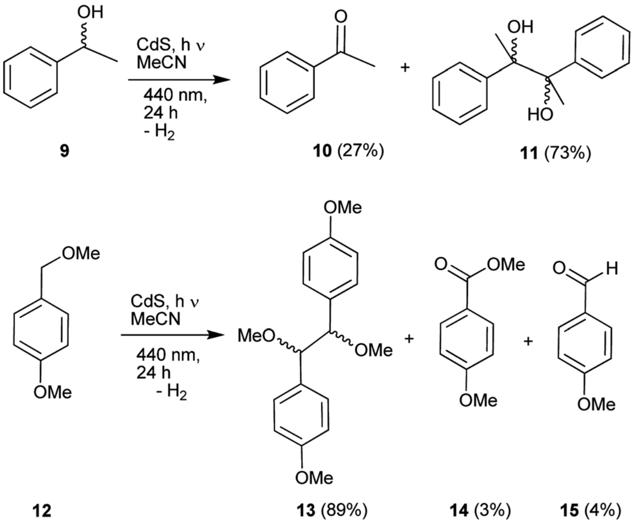
Analogous experiments with substituted benzyl alcohols reveal a clear influence of the *para*-substituent on the product ratio (Table 2). Whereas in the case of unsubstituted benzaldehyde the product mixture contains only 3% of the benzoin, introduction of a bromo or methoxy group affords 36–45%.

para-Nitrobenzyl alcohol (**3-NO$_2$**) displays a different behavior upon visible light irradiation on CdS, as the substrate can undergo a photocatalytic redox process giving *p*-nitrobenzaldehyde (**4-NO$_2$** 60%), *p*-aminobenzaldehyde (**4-NH$_2$**, 9%), 4,4′-diformylazobenzene (**7**, 13%) and 4,4′-diformyl-azoxybenzene (**8**, 7%) (Scheme 3). Small amounts of water ($H_2O : CH_3CN$ = 1 : 14 v/v) favor the nitro group reduction. No C–C-coupling products were observed in these reactions.[17] Cenini reported the formation of similar products, such as azo-, azoxy- and aminobenzene by the photocatalytic anaerobic reaction of nitrobenzene and cyclohexene on CdS in addition to the formation of *N*-(cyclohex-2-enyl)benzeneamine.[18]

The formation of benzoines can be avoided using secondary benzyl alcohol, for example α-methylbenzyl alcohol **9** (Scheme 4). Irradiation of the racemate on CdS gave the diastereomeric mixture of the corresponding 1,2-diols **11** (35% *meso*-diol; 38% *dl*-diol) and acetophenone **10** (27%). Such diols have been obtained in non-photocatalytic conditions by reductive coupling of benzaldehyde or acetophenone using either $NbCl_3(DME)$ or SmI_2.[19]



Scheme 3 Products obtained from 4-nitro benzyl alcohol by CdS visible light photocatalysis.



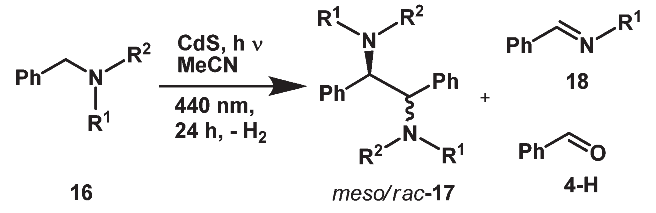
Scheme 4 Visible light photooxidation of a secondary benzyl alcohol (**9**) and *para*-methoxybenzyl alcohol methylether (**12**).

para-Methoxybenzyl alcohol-methylether (**12**) gave in an analogous photoreaction with CdS almost selectively the homocoupling product **13** as a mixture of *dl*-**13** (42%) and *meso*-**13** (47%) as determined by NMR.[20] Ester **14** and *p*-methoxybenzaldehyde **15** were found in trace amounts of 3 and 4%, respectively, in the product mixture .

Photoconversions of benzyl amines

N,*N*-Dimethylbenzyl amine **16a** yields 1,2-diphenyl-*N*,*N*,*N*′,*N*′-tetramethylethylenediamine **17a**[21] as a mixture of the *rac* and

Table 3 Photoconversion of benzyl amines **16**



Amine[a]	R^1	R^2	Product **17** [%][b]	Observed byproducts (%)
16a	CH_3	CH_3	35 (*meso*), 61 (*rac*)[c]	**4-H** (<3)
16b	Bn	*n*Pr	15 (*meso*), 44 (*rac*)[c]	**4-H** (<3)
16c[d]	Bn	H	66	**16c** (34)
16c	Bn	H	16	**18-c** (84)
16d	H	H	20	**16c** (20), **18-c**(21), **17c** (19)

[a] A concentration 0.33 mol L^{-1} of the amine was used. [b] Yields determined by GC and NMR. [c] Ratio of diastereomers determined by NMR. [d] Concentration of **16c** was 0.033 mol L^{-1}.

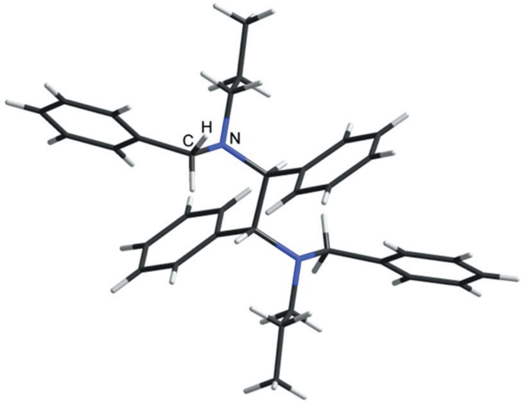


Fig. 1 Molecular structure of the compound *meso*-**17b** in the solid state.

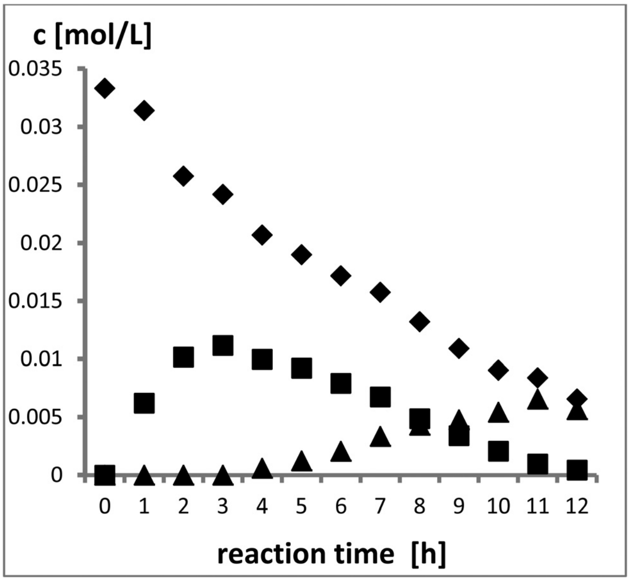


Fig. 2 Substrate consumption and product formation in the photoconversion of *N*,*N*-dibenzyl amine (**16c**, ◆), imin (**18c**, ■), and dehydrodimer (**17c**, ▲).

meso diastereomers upon irradiation on CdS in CH_3CN at room temperature (Table 3). Only very small amounts of benzaldehyde (~3%) are observed in the product mixture, which may result from the side reaction with water adsorbed on the surface of semiconductor. The diasteromeric ratio of *rac* : *meso* 1 : 2 was reproducible in three independent experiments.

N,*N*-Dibenzyl-*N*-(n-propyl) amine **16b** is photocatalytically transformed into diamine **17b**. Under identical conditions less product is obtained and the ratio of product diastereomers reverts to *rac*–*meso* 2 : 1. Compound *meso*-**17b** crystallized from the filtered reaction mixture in large yellow crystals, which were suitable for X-ray single crystal analysis (Fig. 1) confirming the expected connectivity and relative stereochemistry.

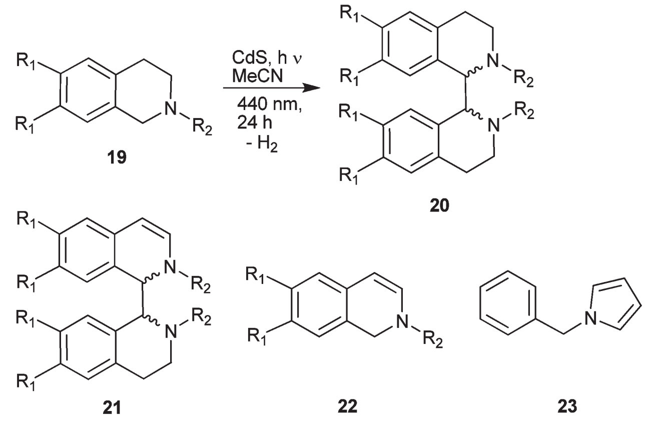
Upon irradiation of CdS in the presence of *N*,*N*-dibenzyl amine (**16c**) for 24 h, benzylidenebenzyl amine **18c**, as the product of intramolecular dehydrogenation, and diamine **17c**[22] are obtained.[23] The ratio between the two products depends on the initial concentration of the substrate and time of irradiation. At an initial concentration of 0.33 mol L^{-1} about 90% of the amine **16c** is converted to imine **18c** and only 10% to diamine **17c**. At a lower concentration of 0.033 mol L^{-1} 75% of the amine **16c** is converted into diamine **17c** as the only observed product.

Kinetic experiments of the dibenzyl amine photoconversion were performed to gain a better insight into the mechanism of the reaction. The measurements were carried out within the first 12 hours of irradiation (Fig. 2). The samples were taken from the reaction mixture every hour, mixed with chlorobenzene solution as standard and analyzed by gas chromatography. The reaction monitoring shown in Fig. 2 reveals that within the first 3 h the concentration of imine **18c** increases, reaches its maximum and then starts to decrease. Significant production of the diamine **17c** begins after approximately 5 h of irradiation and reaches its plateau when imine **18c** is almost totally consumed. These observations suggest that imine **18c** may be an intermediate in the formation of **17c**. Indeed, if imine **18c** is taken as a starting material for the photoreaction, it is converted into diamine **17c** with similar yield (72%) at the same initial concentration (3.33×10^{-2} mol L^{-1}). However, we doubt the role of imine **18c** as a necessary precursor for the formation of diamine **17c**, because in the case of tertiary *N*,*N*-dimethylbenzyl amine **16a** and *N*,*N*-dibenzyl-*N*-(n-propyl) amine (**16b**) imine formation is not possible, but the homocoupling process still proceeds. Irradiation of **16c** over CdS under identical conditions, but at −15 °C yields only imine **18c**.

The conversion of benzyl amine (**16d**) on CdS is less selective and irradiation leads to a product mixture of compounds **16c**, **17c**, **18c** and **17d**.[24] Diamine **17d**, obtained as a mixture of diastereomers, results from dehydrodimerization of **16d** through a possible formation of an aminobenzyl radical, similarly to the above discussed homocoupling of benzyl alcohols and substituted benzyl amines.

The formation of compounds **17c** and **18c** may be rationalized by conversion of **16d** into benzylidene amine **18d**, which

Table 4 Photocatalytic dehydrodimerisation homocoupling of *N*-aryltetrahydroisoquinolines **19a–c**



Tetrahydro-isoquinoline	R^1	R^2	Yield [%] **20** (**22**)
19a	H	Ph	89[a] (3)
19b	H	4-C_6H_4Br	81 (8)
19c	OMe	Ph	52[b] (10)

[a] 53% *meso* product and 36% *rac*. [b] Only *meso* diastereomer detected.

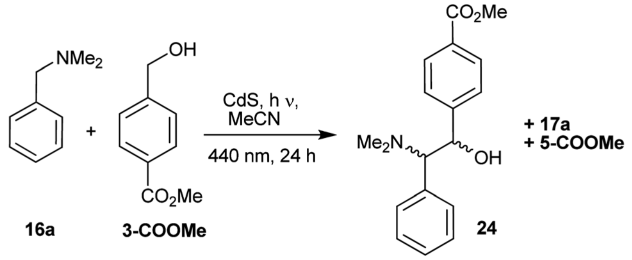
hydrolyses to benzaldehyde (**2-H**) and subsequently reacts with initial benzyl amine **16d** giving **18c**. Diamine **17c** is a product of photodimerization of imine **18c**, as discussed above. The photocatalytic oxidative coupling of benzyl amine **16d** to benzylidene-benzyl amine **17c** in aerobic conditions either mediated by carbon nitride, porphycenes or by TiO_2 was reported earlier.[25]

N-Phenyltetrahydroisoquinoline (**19**) undergoes a similar photocatalytic homo-C–C-coupling yielding diamine **20** as the main reaction product in 52–89% yield with trace amounts of compounds **21** (<1%) and **22** (3–10%, Table 4).[26] The structures of byproducts **21** and **22** were deduced from mass spectrometric data, as obtained very small amounts did not allow for a spectroscopic characterization. *N*-Benzylpyrrole (**23**) does not photoconvert into the corresponding dimer under the same conditions due to its higher oxidation potential.

Photocatalytic cross-coupling reactions

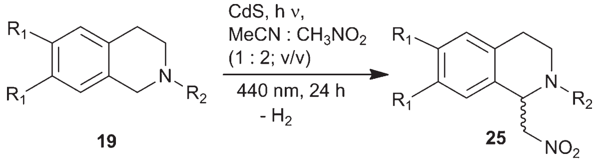
Cross-dehydrogenative couplings are particularly valuable for synthetic organic chemistry.[27] Copper and iron catalysts with hydrogen peroxide as the stoichiometric oxidant have been used,[28] and more recently homogeneous photocatalytic methods using $[Ru(bipy)_3]^{2+}$ and Eosin Y were reported.[29]

The cross-coupling of benzyl alcohols and benzyl amines by CdS photocatalysis was investigated using **16a** and **3-CO$_2$Me**. At equimolar concentrations (0.33 mol L^{-1}) a mixture of amine homocoupling product **17a** and the cross-coupling product **24** was observed (Scheme 5). With a threefold excess of **3-CO$_2$Me** the formation of **17a** is suppressed, but now significant amounts of the homo-dehydrodimer **5-CO$_2$Me** are obtained. The synthesis of 1,2 aminoalcohols by photocatalytic oxidative coupling is possible, but the reaction lacks selectivity and requires optimization for a specific substrate combination to be synthetically useful.



Scheme 5 Photocatalytic cross-coupling of benzyl amine **16a** and benzyl alcohol **3-CO$_2$Me**.

Table 5 Photocatalytic aza-Henry reactions of *N*-aryltetrahydroisoquinolines **19a–c** with nitro-methane



Tetrahydro-isoquinoline	R^1	R^2	Yield [%] **25**
19a	H	Ph	97[a]
19b	H	4-C_6H_4Br	85[b]
19c	OMe	Ph	96[c]

[a] 3% compound **22a**. [b] Traces of compound **22b**. [c] 4% compound **22c**.

In contrast, *N*-aryltetrahydroisoquinolines **19** undergo aza-Henry type reactions with nitromethane upon 440 nm light irradiation on CdS giving **25a–c** as major products in 85–97% yield (Table 4). As a minor byproduct (~3%) is the corresponding substituted 1,2-dihydro-2-phenylisoquinoline **22**, resulting from photocatalytic dehydrogenation of **19** from the second available benzylic position. Use of nitromethane as a co-solvent ($CH_3CN : CH_3NO_2 = 1 : 2$) is necessary to prevent the dimerization of photogenerated benzylic radicals into the dimers **20**. The homo-C–C-coupling process dominates even if CH_3NO_2 is used in a 10-fold molar excess relative to the *N*-aryltetrahydroisoquinolines (Table 5).

Conclusions

Cadmium sulfide catalyzes the visible light homo-C–C coupling of *p*-substituted benzyl alcohols; a competing pathway leads to the formation of aldehydes. The oxidative reactions are accompanied by evolution of dihydrogen gas and proceed *via* hydroxybenzyl radicals. Reaction temperature, concentration of the substrate and the nature of the *para*-substituent (X = H, Br, I, COOMe, OMe) influence the ratio between aldehyde and homocoupling products. *p*-Nitro-substituted benzyl alcohol undergoes an intramolecular redox process giving substituted aniline, azobenzene and azoxybenzene instead of C–C coupling products. Benzyl amines, such as benzyl-*N*,*N*-dimethyl amine and *N*-phenyltetrahydroisoquinoline yield the corresponding 1,2-diamines from oxidative homocoupling as a mixture of diastereomers.

While the CdS photocatalytic cross-coupling reactions of benzyl alcohol and benzyl amine proceed with low selectivity and give product mixtures, *N*-aryltetrahydroisoquinolines undergoes a photocatalyzed aza-Henry reaction with nitromethane as co-solvent giving the cross-coupling products in excellent yields.

Overall, CdS visible light photocatalysis mediates oxidative bond formation of benzylic substrates. The readily available CdS performs equally well in visible light photocatalytic oxidative bond formations as graphitic carbon nitride or titanium dioxide, which requires UV irradiation.[25] Selected for the appropriate substrates and optimized for the specific application, CdS photocatalysis is an efficient synthetic tool for oxidative C–C bond formation under anaerobic reaction conditions.

Acknowledgements

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Notes and references

1 (*a*) F. Teply, *Collect. Czech. Chem. Commun.*, 2011, **76**, 859–917; (*b*) J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102–113; (*c*) K. Zeitler, *Angew. Chem., Int. Ed.*, 2009, **48**, 9785–9789; (*d*) D. Ravelli, D. Dondi, M. Fagnoni and A. Albini, *Chem. Soc. Rev.*, 2009, **38**, 1999–2011.

2 (*a*) T. P. Yoon, M. A. Ischay and J. N. Du, *Nat. Chem.*, 2010, **2**, 527–532; (*b*) M. Rueping, C. Vila, R. M. Koenigs, K. Poscharny and D. C. Fabry, *Chem. Commun.*, 2011, **47**, 2360; (*c*) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2011, **133**, 4160–4163; (*d*) A. G. Condie, J. C. González-Gómez and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2010, **132**, 1464–1465.

3 (*a*) G. Pandey, G. Kumaraswamy and P. Y. Reddy, *Tetrahedron*, 1992, **48**, 8295–8308; (*b*) D. P. Hari and B. Koenig, *Org. Lett.*, 2011, **13**, 3852–3855; (*c*) M. Neumann, S. Fueldner, B. Koenig and K. Zeitler, *Angew. Chem., Int. Ed.*, 2011, **50**, 951–954.

4 H. Kisch, *Adv. Photochem.*, 2001, **26**, 93.

5 (*a*) J. Feng and H. Frei, *Angew. Chem.*, 2009, **121**, 1873–1876; (*b*) W. J. Youngblood, S.-H. A. Lee, K. Maeda and T. E. Mallouk, *Acc. Chem. Res.*, 2009, **42**, 1966–1973.

6 A. Kumar and A. G. Samuelson, *Eur. J. Org. Chem.*, 2011, 951.

7 (*a*) S. Sato, T. Morikawa and S. Saeki, *Angew. Chem., Int. Ed.*, 2010, **49**, 5101–5105; (*b*) U. P. Apfel and W. Weigand, *Angew. Chem., Int. Ed.*, 2011, **50**, 4262–4264.

8 (*a*) F. Wang, W. G. Wang and X. J. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 3193–3197; (*b*) X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76–80.

9 (*a*) R. Lechner and B. König, *Synthesis*, 2010, 1712–1718; (*b*) H. Schmaderer, P. Hilgers, R. Lechner and B. König, *Adv. Synth. Catal.*, 2009, **351**, 163–174.

10 X. J. Lang, H. W. Ji and C. C. Chen, *Angew. Chem., Int. Ed.*, 2011, **50**, 3934–3937.

11 (*a*) N. Zeug, J. Bücheler and H. Kisch, *J. Am. Chem. Soc.*, 1985, **107**, 1459–1465; (*b*) W. Hetterich and H. Kisch, *Chem. Ber.*, 1987, **121**, 15–20.

12 M. A. Fox, *Top. Curr. Chem.*, 1987, **142**, 71.

13 Z. Jin, Q. Li, X. Zheng, C. Xi, C. Wang, H. Zhang, L. Feng, H. Wang, Z. Chen and Z. Jiang, *J. Photochem. Photobiol., A*, 1993, **71**, 85–96.

14 T. Shiragami, H. Ankyu, S. Fukami, C. Pac and S. Yanagida, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1055.

15 H. Fujiwara, M. Kanemoto, H. Ankyu, K. Murakoshi, Y. Wada and S. Yanagida, *J. Chem. Soc., Perkin Trans. 2*, 1997, 317–322.

16 A. Bieging, L. X. Liao and D. V. McGrath, *Chirality*, 2002, **14**, 258–263.

17 P. Wan and K. Yates, *Can. J. Chem.*, 1986, **64**, 2076–2086.

18 A. Maldotti, L. Andreotti, A. Molinari, S. Tollari, A. Penoni and S. Cenini, *J. Photochem. Photobiol., A*, 2000, **133**, 129.

19 J. Szymoniak, J. Besancon and C. Moise, *Tetrahedron*, 1992, **48**, 3867–3876.

20 (*a*) S. H. Goh, S. H. Ong and I. Sieh, *Org. Magn. Reson.*, 1971, **3**, 713–720; (*b*) C.-Y. Tsai, R. Sung, B.-R. Zhuang and K. Sung, *Tetrahedron*, 2010, **66**, 6869–6872.

21 (*a*) H. Fleischer and D. Schollmeyer, *Z. Naturforsch., B: Chem. Sci.*, 2005, **60**, 1083–1087; (*b*) E. A. Mistryukov, *Mendeleev Commun.*, 2002, **12**, 230–231; (*c*) R. Imwinkelried and D. Seebach, *Helv. Chim. Acta*, 1984, **67**, 1496–502.

22 (*a*) R. Annunziata, M. Benaglia, M. Caporale and L. Raimondi, *Tetrahedron: Asymmetry*, 2002, **13**, 2727–2734; (*b*) G. B. Giovenzana, D. Imperio, A. Penoni and G. Palmisano, *Beilstein J. Org. Chem.*, 2011, **7**, 1095–1099.

23 The photocatalytic dehydrodimerization of related imines was previously observed by Kisch as a side process in the CdS-mediated addition of olefins and alcohols to disubstituted imines: (*a*) W. Schindler, F. Knoch and H. Kisch, *Chem. Ber.*, 1996, **129**, 925–932; (*b*) W. Schindler and H. Kisch, *J. Photochem. Photobiol., A*, 1997, **103**, 257–264.

24 I. Lifschitz and J. G. Bos, *Recl. Trav. Chim. Pays-Bas*, 1940, **59**, 173–183.

25 (*a*) F. Su, S. C. Mathew, L. Mühlmann, M. Antonietti, X. Wang and S. Blechert, *Angew. Chem., Int. Ed.*, 2011, **50**, 657–660; (*b*) A. Berlicka and B. Koenig, *Photochem. Photobiol. Sci.*, 2010, **9**, 1359–1366; (*c*) X. J. Lang, H. W. Ji and C. C. Chen, *Angew. Chem., Int. Ed.*, 2011, **50**, 3934–3937; (*d*) P. Zhang, Y. Wang, J. Yao, C. Wang, C. Yan, M. Antonietti and H. Li, *Adv. Synth. Catal.*, 2011, **353**, 1447–1451; (*e*) L. Liu, S. Zhang, X. Fu and C.-H. Yan, *Chem. Commun.*, 2011, **47**, 10148–10150; (*f*) S. Furukawa, Y. Ohno, T. Shishido, K. Teramura and T. Tanaka, *ACS Catal.*, 2011, **1**, 1150–1153.

26 CAS Registry Number: 959575-88-3.

27 (*a*) C. S. Yeung and V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215–1292; (*b*) For an example of C–O bind formation using TiO_2 and UV light, see: X.-H. Ho, M.-J. Kang, S.-J. Kim, E. D. Park and H.-Y. Jang, *Catal. Sci. Technol.*, 2011, **1**, 923–926(*c*) . Photocatalyzed α-oxyamination:.H. Liu, W. Feng, C. W. Kee, Y. Zhao, D. Leow, Y. Pan and C.-H. Tan, *Green Chem.*, 2010, **12**, 953–956.

28 (*a*) Z. Li, D. S. Bohle and C.-J. Li, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 8928; (*b*) Y. Shen, M. Li, S. Wang, T. Zhan, Z. Tan and C.-C. Guo, *Chem. Commun.*, 2009, 953; (*c*) A. Sud, D. Sureshkumarz and M. Klussmann, *Chem. Commun.*, 2009, 3169–3171.

29 (*a*) M. Rueping, C. Vila, R. M. Koenigs, K. Poscharny and D. C. Fabry, *Chem. Commun.*, 2011, **47**, 2360; (*b*) D. P. Hari and B. König, *Org. Lett.*, 2011, **13**, 3852; (*c*) Y. Pan, C. W. Kee, L. Chen and C.-H. Tan, *Green Chem.*, 2011, **13**, 2682–2685; (*d*) Y. Pan, S. Wang, C. W. Kee, E. Dubuisson, Y. Yang, K. P. Loh and C.-H. Tan, *Green Chem.*, 2011, **13**, 3341–3344.