Visible-light Induced Allylation of Benzyl Halide Using CdS Nanocrystallites

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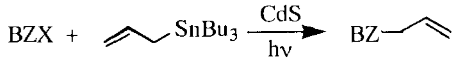
(Received April 20, 1998; CL-980294)

CdS nanocrystallites catalyzed photoallylation of benzyl halide (BZX, X=Br or Cl) with allyltributyltin in N, N–dimethylformamide (DMF) under visible–light irradiation, giving 4–phenyl–1–butene. The reaction proceeds via bimolecular coupling between benzyl radical and allyl radical, which are formed by photo–excited electrons and holes pairs on the surface of quantized CdS nanocrystallites.

Heterogeneous semiconductor photocatalysis has attracted much attention in view of utilization of solar–light energy.[1,2] Relatively efficient photocatalysis in reduction and oxidation are attributed to their characteristics of quantum size effect and high surface to volume ratio of semiconductor nanocrystallites. We previously reported the C–C bond formation from coupling of radicals by photo–formed holes at oxidation sites of ZnS photocatalysts.[3] Recently, we observed the formation of reduced CO_2, i. e. $CO_2^{\cdot-}$, and reduced organic molecules by photo–excited electron at the reduction sites of CdS nanocrystallites, which gives the CO_2–fixed organic molecules through radical coupling.[4]

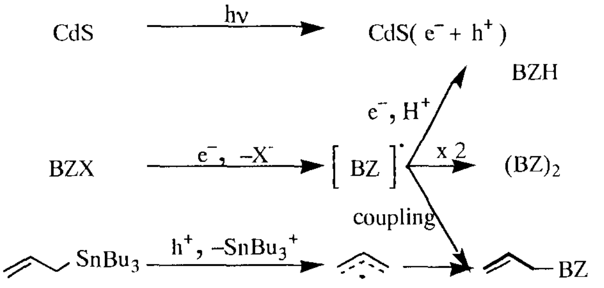
Semiconductor–catalyzed photoreactions proceed through the formation of anion radical and cation radical at the respective adsorption sites on the surface of nanocrystallites. Although this characteristic of the system is expected to apply for various important organic synthetic reactions using both of redox active sites, there are few reports of such reactions on the C–C bond formation.[5]

In this paper, we report allylation of benzyl halide catalyzed by CdS nanocrystallites using allyltributyltin as an electron donor under visible–light irradiation. Normally, allylation of benzyl compounds hardly proceeds.[6] Simultaneous photo–formation of reduced benzyl halide and oxidized allyltin should lead to their coupling. As a result, the allylation proceeded to form 4–phenyl–1–butene as an allylation product.



CdS nanocrystallites (CdS–DMF; hexagonal, mean diameter 4 nm) were prepared from 5 mM of $Cd(ClO_4)_2 \cdot 6H_2O$ and H_2S in DMF.[2b] Photo–reaction was carried out under visible–light irradiation (λ>400 nm) using an aqueous solution filter ($NaNO_2$) and a 300 W halogen–tungsten lamp in Pyrex tube (ϕ=8 mm). Photocatalytic systems (2 mL) consist of CdS nanocrystallites or commercially available bulk CdS (Aldrich) as a photocatalyst, benzyl halide and allyltributyltin as substrates. Conversions of substrates and yields of products were determined by gas chromatography using an OV–1 column (3.7 mm x 2 m) and liquid chromatography using a Cosmosil–ODS column (4.6 mm x 150 mm).

Table 1 summarizes the results of photoreaction between benzyl halide and allyltributyltin. When 2.5 mM of CdS–DMF was used as a photocatalyst, 4–phenyl–1–butene (yield was 15%) was formed from benzyl bromide (BZBr) with bibenzyl (33%), and toluene (5%). Each product formed linearly depending on reaction time. A small amount of H_2 was also detected (run 1). The formation of 4–phenyl–1–butene was not detected without irradiation or CdS–DMF, respectively (run 4, 5). As reported previously,[4] Photo–excited electrons in CdS–DMF can reduce benzyl halide to form benzyl radical ($[BZ]^{\cdot}$). Bibenzyl and toluene form by dimerization and protonation of benzyl radical, respectively. Bibenzyl and toluene was not detected in the system without irradiation or CdS–DMF, suggesting no formation of benzyl radical. These results suggest that allyltributyltin works as an electron donor in photocatalysis. Allyltributyltin oxidized by photo–formed holes forms allyl radical. As a result, the allylation is expected to proceed via bimolecular coupling between benzyl radical and allyl radical on the surface of CdS nanocrystallites. (Scheme 1).[7,8] Increment of yields of 4–phenyl–1–butene in the system containing higher concentration of allyltributyltin (run 2, 3) suggests that the increased formation of allyl radicals should be beneficial for bimolecular coupling on CdS surface.

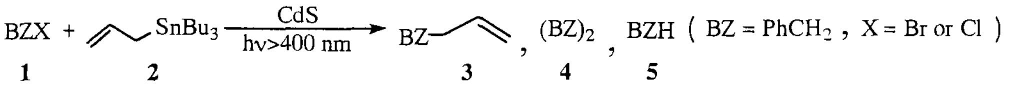


Scheme 1.

The CdS–DMF–catalyzed photoallylation was also extended to benzyl chloride (BZCl). The yield of 4–phenyl–1–butene from BZCl (19%) was higher than that from BZBr (run 6). The effect of higher concentration of allyltributyltin on the yield of 4–phenyl–1–butene was more apparent than that of BZBr system (run 7, 8). We previously revealed that the yield of the CO_2 fixed products depends on the redox potentials of the organic compounds in the CO_2–fixation into organic substrates using CdS nanocrystallites.[4] BZCl (–2.18 V *vs.* SCE[9]) has a more negative redox potential than BZBr (–1.68 V *vs.* SCE[9]), suggesting that electron transfer of the photo–formed electrons on CdS–DMF to BZCl should be slower. Lower surface concentration of benzyl radicals reduced the yield of by–products, leading to higher yield of allylation because of the slow formation of allyl radical. These results may suggest improvement of product selectivity by the choice of substrate and particle size in nanocrystallites.

Allylation of BZBr also proceeded using surface modified CdS nanocrystallites as a photocatalyst[10] (run 9, 10). Commercially available bulk CdS (CdS–Ald), however, did not catalyze the photoallylation (run 10) due to absence of quantum

Table 1. Allylation of benzyl halide under various reaction condition



Run	React. Condition	Cat.	Substrate	Init. Conc. / mM		React. Time / h	Convn.		Product Yield / % [a]		
				1	**2**		**1**	**2**	**3**	**4**[b]	**5**
1	Irradiation	CdS–DMF[c]	BZBr	10	10	24	63	74	15	33	5
2	Irradiation	CdS–DMF[c]	BZBr	10	50	24	85	23	25	34	trace
3	Irradiation	CdS–DMF[c]	BZBr	10	100	24	91	10	28	34	trace
4	Dark[d]	CdS–DMF[c]	BZBr	10	10	24	29	13	0	0	0
5	Blank[e]	none	BZBr	10	10	24	55	2	0	0	0
6	Irradiation	CdS–DMF[c]	BZCl	10	10	48	9	51	19	32	trace
7	Irradiation	CdS–DMF[c]	BZCl	10	50	48	12	6	34	34	12
8	Irradiation	CdS–DMF[c]	BZCl	10	100	48	15	--[h]	41	42	15
9	Irradiation	ϕ^F–CdS[f]	BZBr	10	10	24	89	39	10	63	4
10	Irradiation	ϕ–CdS[f]	BZBr	10	10	24	100	63	12	63	4
11	Irradiation	CdS–Ald[g]	BZBr	10	10	24	40	22	0	0	0

[a] Yields are calculated on the basis of the converted BZBr or BZCl. [b] Yield of 5 was doubled in calculation. [c] 2.5 mM of CdS-DMF (diatmic) was used as a photocatalyst. [d] Under dark condition. [e] Without CdS-DMF as a photocatalyst. [f] 2 mg of ϕ^F–CdS (hexagonal, mean diameter = 3.1 nm) and 2 mg of ϕ– CdS (hexagonal, mean diameter = 2.5 nm) was used as a photocatalyst. See ref. 10. [g] 50 mg of CdS–Ald (hexagonal, mean diameter = 1.5 μm, 99.999 %) was used as a photocatalyst. [h] Not determined.

size effect and lack of surface active sites. These results reveal that the relatively high allylation is an unique property of quantized CdS nanocrystallites.

We presented the photoallylation of benzyl halides using CdS nanocrystallites as a photocatalyst and allyltributyltin as an electron donor and source of allyl group under visible–light irradiation. As a possible mechanism, photoallylation of benzyl halides should proceed via a coupling between intermediary allyl radical by photo–formed hole on oxidation sites and benzyl radical by photo–excited electron on reduction sites of CdS nanocrystallites.

This research was supported in part by a Grant–in–Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan and by a Research Fellowship for Young Scientists from the Japan Society for the Promotion of Science (to H.F.).

References and Note

1 M. A. Fox and M. T. Dulay, *Chem. Rev.*, **93**, 341 (1993).
2 a) M. Kanemoto, T. Shiragami, C. Pac, and S. Yanagida, *J. Phys. Chem.*, **96**, 3521 (1992), b) S. Yanagida, M. Kanemoto, K. Ishihara, Y. Wada, T. Sakata, and H. Mori, *Bull. Chem. Soc. Jpn.*, **70**, 2063 (1997).
3 a) S. Yanagida, H. Kawakami, Y. Midori, H. Kizumoto, C. Pac, and Y. Wada, *Bull. Chem. Soc. Jpn.*, **68**, 1811 (1995).
4 H. Fujiwara, M. Kanemoto, H. Ankyu, K. Murakoshi, Y. Wada, and S. Yanagida, *J. Chem. Soc., Parkin Trans 2*, **1997**, 317.
5 a) R. Kunneth, C. Feldmer, and H. Kisch, *Angew. Chem., Int. Ed. Engl.* **31**, 1039 (1992), b) L. Cermenati, C. Richter, and A. Albini, *J. Chem. Soc., Chem. Comm.*, **1998**, 805.
6 Y. Yamamoto and N. Asao, *Chem. Rev.*, **93**, 2207 (1993).
7 K. Maruyama, H. Imahori, A. Osaka, A. Takuwa, and H. Tagawa, *Chem. Lett.*, **1986**, 1719.
8 Apparent quantum yield of the formation of 4–phenyl–1–butene was calculated to be less than 0.1%.
9 D. A. Koch, B. J. Henne, and D. E. Bartak, *J. Electrochem. Soc.*, **134**, 3062 (1987).
10 H. Hosokawa, T. Ogata, Y. Wada, K. Murakoshi, T. Sakata, H. Mori, and S. Yanagida, *J. Chem. Soc., Faraday Trans.*, **92**, 4575 (1996).