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Photodimerization and photooxygenation of 9-vinylcarbazole catalyzed by titanium dioxide and magnesium perchlorate

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Abstract

Photoreaction of 9-vinylcarbazole in acetonitrile in the presence of titanium dioxide and a catalytic amount of magnesium perchlorate gave 3,6-di(9-carbazolyl)-1,2-dioxane as a photooxygenated product *via* photodimerization of 9-vinylcarbazole. The photoreaction proceeds *via* an electron transfer mechanism, where magnesium perchlorate accelerated formation of the photooxygenated product.

Keywords: Titanium dioxide; Magnesium perchlorate; 9-Vinylcarbazole; Photooxygenation; Photodimerization

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Photoinduced electron transfer reactions by using titanium dioxide (TiO_2) have attracted much attention because TiO_2 has high potential as a clean heterogeneous photocatalyst [1–3]. We have recently developed efficient photooxygenation reactions of alkenes [4], cyclopropanes [5], and carboxylic acids [6], catalyzed by TiO_2 to give the corresponding oxygenated products, respectively. During the course of our study, we investigated the photooxygenation of 9-vinylcarbazole (**1**), a representative enamine having relatively low oxidation potential, and found that photodimerization is a primary step and that a 1,2-dioxane derivative (**3**) is then formed in the presence of a catalytic amount of magnesium perchlorate ($Mg(ClO_4)_2$).

1. Experimental

TiO_2 (ST-01, particle size = 7 nm) was donated by Ishihara Sangyo, Co. Ltd. 9-Vinylcarbazole (**1**), 9,10-dicyanoanthracene (DCA), and $Mg(ClO_4)_2$ were purchased and used without purification. Acetonitrile was distilled from P_2O_5. A 300 W high-pressure mercury lamp (Eikosha, PIH-300) was used as a light source. ^{1}H NMR (300 MHz) was recorded on Varian Mercury 300 spectrometer. Column chromatography was done by using Merck silica gel 60

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Table 1
Photodimerization and photooxygenation of 9-vinylcarbazole (**1**)[a].

Entry	Additive	Atmosphere	Irradiation time (min)	Yields of products[b] (%)			Recovery of **1**[b] (%)	
				2	**3**	**4**	**5**	
1	TiO_2, $Mg(ClO_4)_2$	O_2	20	20	57	20	2	0
2	TiO_2, $Mg(ClO_4)_2$	O_2	1	93	4	0	trace	0
3	DCA[c]	O_2	20	64	21	5	8	0
4	DCA[c], $Mg(ClO_4)_2$	O_2	20	18	54	12	14	0
5	none	O_2	60	76	O	trace	trace	22
6	TiO_2, $Mg(ClO_4)_2$	Ar	60	97	0	0	0	0
7	TiO_2	O_2	30	66	0	3	10	21
8	TiO_2	O_2	60	88	0	5	6	trace

[a] Compound **1** (57 mg, 0.3 mmol), TiO_2 (20 mg), CH_3CN (10 mL), DCA (3 mg), $Mg(ClO_4)_2$ (5 mg), 300 W high-pressure mercury lamp, stirred by a magnetic stirrer.

[b] Determined by ^1H NMR.

[c] DCA = 9,10-dicyanoanthracene.

(70–230 mesh). HPLC separation was conducted by Jasco Megapak GEL 201C (GPC, eluent: $CHCl_3$) equipped with Jasco PU-986 pump and Shodex RI-72 refractometry.

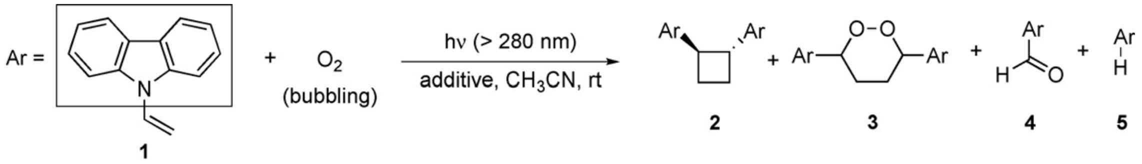
*1.1. General procedure for photoreaction of **1***

Into a Pyrex vessel (12 mmØ × 10.5 cm), **1** (57 mg, 0.3 mmol), TiO_2 (20 mg), $Mg(ClO_4)_2$ (5 mg) acetonitrile (10 mL), and a stirrer bar were placed and sealed with a rubber septum. After bubbling of oxygen injected through a needle for 10 min, the suspension was irradiated by a 300 W high-pressure mercury lamp with continuous stirring and continued bubbling of oxygen for 1–60 min (See Table 1). The temperature of the suspension was kept around room temperature during irradiation by circulated cooling water. TiO_2 was removed by centrifugal separation (3000 rpm, 30 min) and subsequent decantation. The TiO_2 was washed with methanol and precipitated by centrifugal separation again. The combined filtrate was evaporated. Yields of products were determined by ^1H NMR spectra of the crude mixture, comparing with the reported data of **1** [7], **2** [8], **3** [9], **4** [10], and **5** [11]. Data for 9-vinylcarbazole (**1**) [7]: mp 60–65 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 5.17 (d, 1H, $J = 9.2$ Hz), 5.56 (d, 1H, $J = 15.7$ Hz), 7.30 (t, 2H, $J = 7.7$ Hz), 7.32 (dd, 1H, $J = 15.7$, 9.2 Hz), 7.48 (t, 2H, $J = 7.7$ Hz), 7.67 (d, 2H, $J = 7.7$ Hz), 8.08 (d, 2H, $J = 7.7$ Hz). Data for *trans*-1,2-di(9-carbazolyl)-cyclobutane (**2**) [8]: mp 196–198 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 2.67–2.82 (m, 2H), 3.04–3.19 (m, 2H), 6.26–6.36 (m, 2H), 7.20 (t, 4H, $J = 8.0$ Hz), 7.39 (t, 4H, $J = 8.0$ Hz), 7.56 (d, 4H, $J = 8.0$ Hz), 8.05 (d, 4H, $J = 8.0$ Hz). Data for 3,6-di(9-carbazolyl)-1,2-dioxane (**3**) [9]: mp 183–184 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 2.40 (d-like, 2H, $J = 9.0$ Hz), 3.36 (t-like, 2H, $J = 10.6$ Hz), 6.78 (d-like, 2H, $J = 8.6$ Hz), 7.32 (t, 4H, $J = 7.8$ Hz), 7.53 (, 4H t, $J = 7.8$ Hz), 7.78 (d, 4H, $J = 7.8$ Hz), 8.11 (d, 4H, $J = 7.8$ Hz).

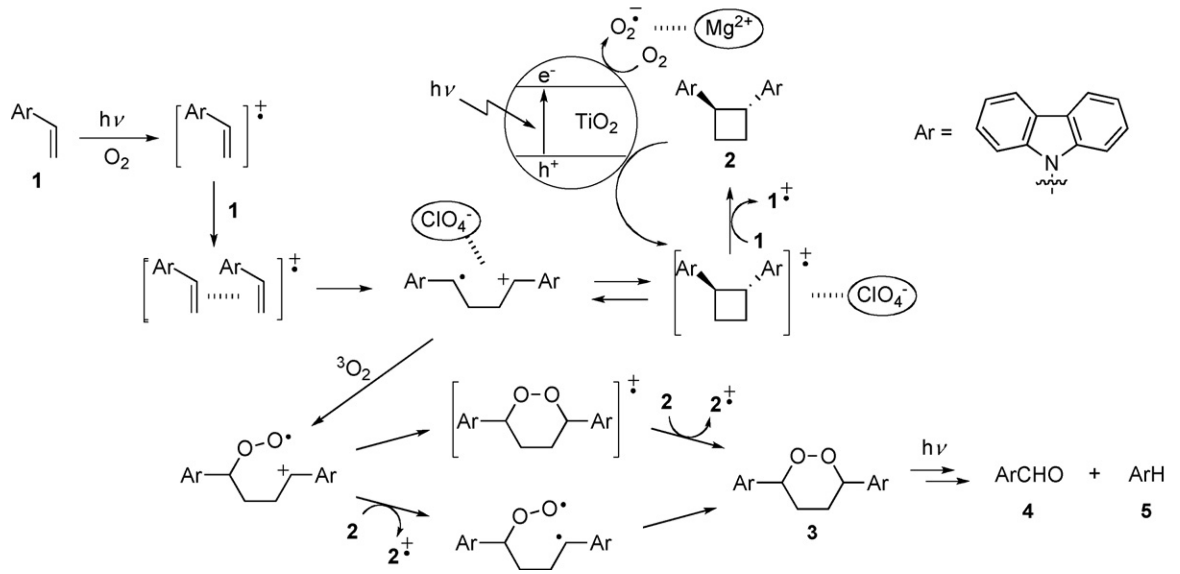
2. Results and discussion

Photoirradiation to a slurry containing 9-vinylcarbazole (**1**), TiO_2, a catalytic amount of $Mg(ClO_4)_2$, and acetonitrile with continuous bubbling of oxygen and stirring for 20 min gave a mixture containing dimerized product *trans*-1,2-di(9-carbazolyl)cyclobutane (**2**, 20%), 3,6-di(9-carbazolyl)-1,2-dioxane (**3**, 57%), 9-formylcarbazole (**4**, 20%) and carbazole (**5**, 2%) (Scheme 1, entry 1 in Table 1). At the early stage of the photoreaction, dimer **2** was obtained as a major product (entry 2). When 9,10-dicyanoanthracene (DCA) was used as a homogeneous photosensitizer, the yield of **3** decreased (entry 3) [12]. When a mixed system of DCA with $Mg(ClO_4)_2$ was employed, the product yield became comparable with the TiO_2/$Mg(ClO_4)_2$ system (entry 4) [9]. The photooxygenated product **3** was not produced in the absence of TiO_2 (entry 5), under Ar atmosphere (entry 6), and in the absence of $Mg(ClO_4)_2$ even in the presence of TiO_2 and oxygen (entries 7 and 8).

Photoirradiation to the isolated **2** under the same irradiation conditions as those of entry 1 gave **3** (51%) and **4** (21%). Photoirradiation to the isolated **3** under the same conditions gave some decomposed products containing **4** and **5** mainly without formation of **1** and **2**.



Scheme 1. Photodimerization and photooxygenation of 9-vinylcarbazole (**1**).



Scheme 2. Reaction mechanism for the photodimerization and photooxygenation of 9-vinylcarbazole (**1**) catalyzed by TiO_2 and $Mg(ClO_4)_2$.

From these results, we propose a reaction mechanism depicted in Scheme 2. It is already reported that the dimerization of **1** proceeds to give **2** by photoirradiation with or without photocatalyst [9,12–16], and by oxidation with metal salts [8,17,18]. The dimerization without photocatalyst proceeds *via* an electron transfer from **1** ($E_{ox} = 0.94$ V vs. SCE [19]) to O_2 ($E_{red} = -0.86$ V vs. SCE [20]) even under the conditions without bubbling of O_2 because the dissolved oxygen is enough to act as an electron acceptor. Photoexcitation of TiO_2 causes the promotion of an electron into the conduction band (−0.8 V vs. SCE) to generate a hole in the valence band (+2.4 V vs SCE). Electron transfer from **2** to the valence band takes place as an exoergonic process to produce the radical cations of **2** ($\mathbf{2}^{+\bullet}$). $Mg(ClO_4)_2$ might act to stabilize $O_2^{-\bullet}$ [20,21] and $\mathbf{2}^{+\bullet}$ or its open form, hence suppresses the back electron transfer to give **2** [22–30]. Another possibility for the effect of $Mg(ClO_4)_2$ is that the magnesium salt may accelerate the desorption of the radical cation from the TiO_2 surface due to the enhanced cationic charge on the surface [31]. When the concentration of O_2 is sufficiently high, open form of $\mathbf{2}^{+\bullet}$ attacks O_2 and the following ring closure and electron transfer from neutral **2** affords **3**. Further photoirradiation causes decomposition of **3** to give **4** and **5**.

In conclusion, photooxygenation of **1** is catalyzed by TiO_2 and $Mg(ClO_4)_2$ to give a 1,2-dioxane derivative **3** *via* the initial formation of dimerized product **2**. In the absence of $Mg(ClO_4)_2$, photooxygenated product was not obtained upon irradiation even in the presence of TiO_2 and O_2. It was demonstrated that TiO_2–$Mg(ClO_4)_2$–O_2 system is a powerful tool for the effective photooxygenation reaction under mild conditions.

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References

[1] M.A. Fox, Acc. Chem. Res. 16 (1983) 314.
[2] M.R. Hoffmann, S.T. Martin, W. Choi, et al. Chem. Rev. 95 (1995) 69.
[3] V. Ramamurthy, K.S. Schanze (Eds.), Molecular and Supramolecular Photochemistry, Semiconductor Photochemistry and Photophysics, vol. 10, Marcel Dekker, Inc., New York, 2003.
[4] H. Maeda, H. Miyamoto, K. Mizuno, Chem. Lett. 33 (2004) 462.
[5] H. Maeda, H. Nakagawa, K. Mizuno, Photochem. Photobiol. Sci. 2 (2003) 1056.
[6] H. Maeda, H. Nakagawa, K. Mizuno, J. Photochem. Photobiol. A: Chem. 189 (2007) 94.
[7] G.N. Kurov, A.V. Afonin, L.I. Svyatkina, et al. Izv. Akad. Nauk SSSR Ser. Khim. 2 (1987) 444.
[8] S. McKinley, J.V. Crawford, C.H. Wang, J. Org. Chem. 31 (1966) 1963.
[9] K. Mizuno, K. Murakami, N. Kamiyama, et al. J. Chem. Soc. Chem. Commun. (1983) 462.
[10] C. Flo, U. Pindur, Liebigs Ann. Chem. 6 (1987) 509.
[11] V. Promarak, M. Ichikawa, T. Sudyoadsuk, et al. Synth. Met. 157 (2007) 17.
[12] K. Gollnick, A. Schnatterer, Tetrahedron Lett. 25 (1984) 2735.
[13] R.A. Carruthers, R.A. Crellin, A. Ledwith, J. Chem. Soc. D Chem. Commun. (1969) 252.
[14] R.A. Crellin, M.C. Lambert, A. Ledwith, J. Chem. Soc. D Chem. Commun. (1970) 682.
[15] Y. Shirota, H. Mikawa, J. Macromol. Sci. Rev. Macromol. Chem. C16 (1977–1978) 129.
[16] A. Tsuchida, M. Yamamoto, J. Photochem. Photobiol. A: Chem. 77 (1994) 17.
[17] F.A. Bell, R.A. Crellin, H. Fujii, et al. J. Chem. Soc. D Chem. Commun. (1969) 251.
[18] P. Beresford, M.C. Lambert, A. Ledwith, J. Chem. Soc. C (1970) 2508.
[19] S.M. Bonesi, R. Erra-Balsells, J. Chem. Soc. Perkin Trans. 2 (2000) 1583.
[20] K. Ohkubo, S.C. Menon, A. Orita, J. Otera, S. Fukuzumi, J. Org. Chem. 68 (2003) 4720.
[21] S. Fukuzumi, K. Ohkubo, Chem. Eur. J. 6 (2000) 4532.
[22] K. Mizuno, N. Ichinose, Y. Otsuji, Chem. Lett. (1985) 455.
[23] K. Mizuno, N. Kamiyama, N. Ichinose, et al. Tetrahedron 41 (1985) 2207.
[24] K. Mizuno, N. Ichinose, T. Tamai, et al. Tetrahedron Lett. 26 (1985) 5823.
[25] T. Tamai, K. Mizuno, I. Hashida, et al. Photochem. Photobiol. 54 (1991) 23.
[26] A. Loupy, B. Tchoubar, D. Astruc, Chem. Rev. 92 (1992) 1141.
[27] K. Mizuno, N. Ichinose, Y. Otsuji, J. Org. Chem. 57 (1992) 1855.
[28] K. Mizuno, Y. Otsuji, Top. Curr. Chem. 169 (1994) 301.
[29] S. Fukuzumi, Bull. Chem. Soc. Jpn. 70 (1997) 1.
[30] K. Mizuno, K. Nire, H. Sugita, et al. Tetrahedron Lett. 42 (2001) 2689.
[31] T. Tachikawa, S. Tojo, M. Fujitsuka, et al. J. Phys. Chem. B 108 (2004) 11054.