Synthesis of 3,3,6,6-Tetraaryl-1,2-Dioxanes via TiO_2-catalyzed Photooxygenation of 1,1-Diarylethenes in the Presence of $Mg(ClO_4)_2$

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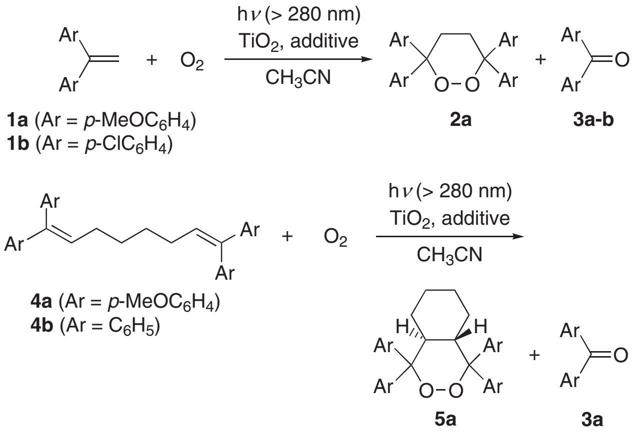
Photooxygenation of methoxy-substituted 1,1-diarylethenes and 1,1,8,8-tetraaryl-1,7-octadienes catalyzed by titanium dioxide proceeded via photoinduced electron transfer to give 3,3,6,6-tetraaryl-1,2-dioxanes in high yields. The photooxygenation was remarkably accelerated by the addition of $Mg(ClO_4)_2$.

Semiconductor-catalyzed photoreactions of organic molecules are of current interest.[1] Semiconductors such as TiO_2, CdS, ZnS are utilized as redox type heterogeneous photocatalysts for various types of photoinduced electron tranfer reactions using photoexcitation from their valence bands to conduction bands.[2] Hitherto various alkenes are exposed to the semiconductor-catalyzed photoreactions in the presence of oxygen, and it is already known that the alkenes are converted to ketones, aldehydes, epoxides, hydroperoxides, and so on.[3] However, the efficiency, selectivity, and chemical yields are not necessarily high in these photoreactions. To explore the synthetic utility for such reactions, we have investigated the photooxygenation of methoxy-substituted 1,1-diarylethenes and found that 3,3,6,6-tetraaryl-1,2-dioxanes were obtained in high yields.

Photoirradiation of an acetonitrile solution containing 1,1-bis(*p*-methoxyphenyl)ethene (**1a**) in the presence of suspended TiO_2 and $Mg(ClO_4)_2$ under a constant stream of dioxygen through a Pyrex filter by a 300 W-high pressure mercury lamp for 40 min afforded 3,3,6,6-tetrakis(*p*-methoxyphenyl)-1,2-dioxane (**2a**) in a 97% isolated yield (Scheme 1, Table 1). In the absence of $Mg(ClO_4)_2$, **2a** was slowly formed accompanying methoxy-substituted benzophenone **3a**. Photoreaction of *p*-chloro derivative **1b** gave a small amount of benzophenone derivative **3b** without any formation of **2b**. Photooxygenation of 1,1,8,8-tetrakis(*p*-methoxyphenyl)-1,7-octadiene (**4a**) in the presence of $Mg(ClO_4)_2$ proceeded intramolecularly to give *trans*-fused 1,2-dioxane derivative **5a** in a 71% isolated yield. In the absence of $Mg(ClO_4)_2$, prolonged photoirradiation was required to obtain **5a**. Addition of other inorganic salts such as $KClO_4$, $NaClO_4$, $LiClO_4$, and $LiBF_4$ also enhanced the rate of the photooxygenation, but their efficiency was lower than that of $Mg(ClO_4)_2$. Photoreaction of unsubstituted 1,1,8,8-tetraphenyl-1,7-octadiene (**4b**) resulted in almost recovery of **4b**.



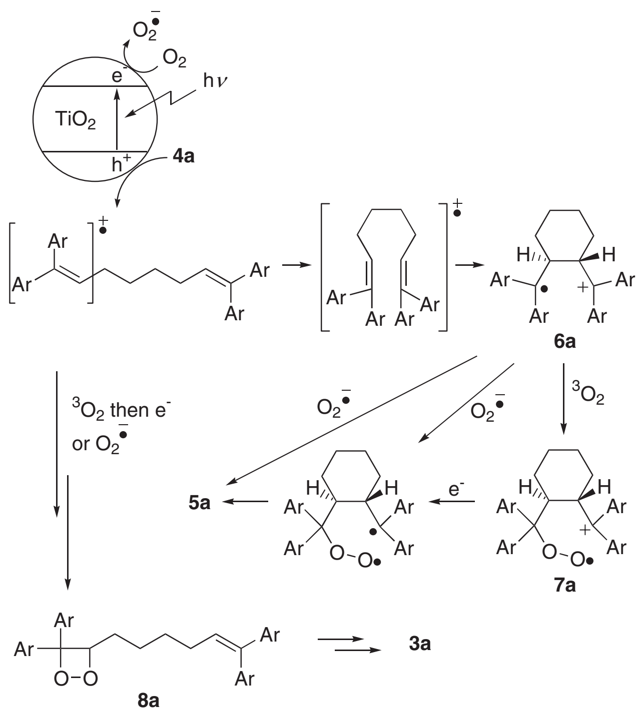
Scheme 1.

Table 1. Photooxygenation of 1,1-Diarylethenes Catalyzed by Titanium Dioxide[a]

Substrate	Additive	Irradiation time/min	Products and yields[b]	Recovery of substrate[b]
1a	none	40	**2a** (6%), **3a** (10%)	56%
1a	$Mg(ClO_4)_2$	40	**2a** (97%)	0%
1b	none	40	**3b** (12%)[c]	88%[c]
1b	$Mg(ClO_4)_2$	40	**3b** (8%)	73%
4a	none	40	**5a** (9%)[c]	91%[c]
4a	none	960	**5a** (75%)[c], **3a** (25%)[c]	0%
4a	$Mg(ClO_4)_2$	40	**5a** (71%)	0%
4a	$KClO_4$	40	**5a** (34%)[c]	66%[c]
4a	$NaClO_4$	40	**5a** (25%)	28%
4a	$LiClO_4$	40	**5a** (41%)	44%
4a	$LiBF_4$	40	**5a** (51%)	40%
4b	none	40	—	97%
4b	$Mg(ClO_4)_2$	40	—	87%

[a] Conditions: Substrate (0.25 mmol), TiO_2 (10 mg), additive (0.125 mmol), CH_3CN (15 mL), oxygen bubbling, rt. [b] Isolated yields. [c] Determined by ^1H NMR.

Irradiation of TiO_2 in acetonitrile 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).[1,4] One electron transfer from **1a** ($E_{ox} = 1.32$ V vs SCE in CH_3CN)[5] and **4a** ($E_{ox} = 0.95$ V vs Ag/Ag^+ in CH_3CN)[6] to the valence band should take place as an exothermic process to produce the radical cations of these alkenes, because their oxidation potentials are sufficiently low.[1a,b] In addition, electron transfer from the conduction band to O_2 ($E^0{}_{red} = -0.86$ V vs SCE in CH_3CN)[7] is thermodynamically permissible process to produce $O_2^{-\bullet}$.[1a,3a,b,g] From these results, we propose a plausible mechanism for the TiO_2-catalyzed photooxygenation of 1,1-diarylethenes as exemplified in Scheme 2 using the photoreaction of **4a**. The initial step is the excitation of TiO_2 followed by one-electron transfer from **4a** to the valence band of TiO_2 to produce monomer radical cation of **4a**. The monomer radical cation of **4a** cyclizes intramolecularly to give distonic radical cation **6a** via dimer radical cation of **4a**. The attack of triplet dioxygen on the 1,4-radical cation **6a** generates 1,6-radical cation **7a** which gives 1,2-dioxane derivative **5a** by one-electron reduction. The other possible pathway for the photooxygenation is the attack of $O_2^{-\bullet}$ to **6a**. Formation of benzophenone derivative **3a** can be explained by the decomposition of dioxetane **8a**, which is produced by the oxygenation of monomer radical cation. The enhancement of the ef-



Scheme 2.

ficiency by the addition of $Mg(ClO_4)_2$ can be explained by the suppression of back electron transfer from TiO_2^- to $\mathbf{4a}^{+\bullet}$ due to the interaction between Mg^{2+} and ionic species such as TiO_2^- and $O_2^{-\bullet}$ or the interaction between ClO_4^- and $\mathbf{4a}^{+\bullet}$.[2r,8–10]

Photooxygenation of **1a** and **4a** to give 1,2-dioxanes under photoinduced electron transfer conditions have already been reported in homogeneous solutions using electron accepting photosensitizers such as 9,10-dicyanoanthracene.[5,6,11] But the present system using TiO_2 as a heterogeneous photocatalyst has a notable advantage; the photocatalyst can be removed only by the filtration of the reaction mixture. For synthetic use, TiO_2 is a clean, low cost, efficient, and facile tool for the synthesis of 3,3,6,6-tetraaryl-1,2-dioxanes.

In conclusion, it was demonstrated that 1,2-dioxane derivatives can be synthesized by the photooxygenation of electron-rich diarylalkenes by use of TiO_2 as a heterogeneous photocatalyst. Scope and mechanisms are now under investigation.

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9 Diffuse reflectance spectrum of suspension of TiO_2 in CH_3CN was not changed by the addition of $Mg(ClO_4)_2$.

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