Tetrahedron Letters 55 (2014) 619–622

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Chemically-induced geometrical isomerization of stilbenes during peroxyoxalate chemiluminescence reaction: revisit to 'photochemistry without light'

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ARTICLE INFO

Article history:
Received 17 July 2013
Revised 11 November 2013
Accepted 18 November 2013
Available online 28 November 2013

Keywords:
Peroxyoxalate chemiluminescence
Geometrical isomerization
Stilbene
Photochemistry without light

ABSTRACT

The chemically-induced isomerization of stilbenes during the peroxyoxalate chemiluminescence (PO-CL) reactions was reinvestigated. The PO-CL reactions using bis(2,4,6-trichlorophenyl) oxalate in the presence of several stilbenes (type A reaction) produced *cis*-stilbenes in 0–4% yields, which was dependent on the singlet excitation energy of the stilbenes. On the other hand, the PO-CL reactions of the oxalates, containing the stilbene moieties in the molecules (type B reaction), produced *cis*-stilbenes 0–9.3% yields, some of which were much more effective than the type A reactions considering the amount of the oxalate moiety as the energy supplier.

Chemiluminescence reactions produce energy for the excitation of the fluorescent molecules to emit light, while the energy can be used for sensitization of the coexisting photochemically reactive molecules instead of the chemiluminescence. A few significant reports documented such a chemical sensitization called 'photochemistry without light',[1] in which some typical photoreactions were induced during the chemiluminescent reactions that included the thermal decomposition of the 1,2-dioxetanes, oxidation of the phthalhydrazides,[2] and the peroxyoxalate chemiluminescence (CL) reactions.[3] One of the representative examples is the *cis*–*trans* isomerization of stilbenes during the peroxyoxalate chemiluminescence (PO-CL) reaction[3a] instead of a light emission as shown in Scheme 1. Although the concept of 'photochemistry without light' is very attractive from the viewpoint of the energy source for the photoreactions without irradiation by a UV lamp, less attention has been paid to such systems and there have been only a few examples.[2,3] As a part of our continuing study of the peroxyoxalate chemiluminescence,[4] we revisited this interesting CL reaction accompanying the geometrical isomerization of stilbenes and investigated the two types of PO reactions without fluorophores, one of which is the PO reaction in the presence of various stilbenes (type A reaction) and the other which is that using the oxalates containing the stilbene unit in the oxalate molecules (type B reaction).

To investigate the type A reactions, the *trans*-stilbenes (**1a**–**h**) bearing various substituents (7.5×10^{-4} M in THF/H_2O = 3/1) were treated with bis(2,4,6-tricholorophenyl) oxalate (TCPO) (3.75×10^{-2} M) and hydrogen peroxide (2.5×10^{-2} M) under alkaline conditions (K_2CO_3, 2.5×10^{-5} M). After work-up the stilbenes were quantitatively obtained and no other product was detected in this reaction. The reactions were repeated at least three times for each stilbene and the ratios of the *cis*- and *trans*-stilbenes were determined by their ^1H NMR spectra. The results are summarized in Table 1. Although the ratio varied below 10%, some *trans*-stilbenes (**1c**, **1d**, **1e**, **1g**, and **1h**) isomerized to the *cis*-stilbenes during the peroxyoxalate (PO) reactions of TCPO, while three stilbenes (**1a**, **1b**, and **1f**) did not isomerize at all.

To compare the isomerization efficiency for the above PO reactions to that for the photochemical reactions, the *trans*-stilbenes were treated in aqueous THF (THF/H_2O = 3/1) by irradiation using a high pressure mercury lamp for 2 min. and the ratios determined by ^1H NMR spectra are shown in Table 1. The tendency of the substituent-depending *cis*-isomer ratio in the chemiluminescent reactions was roughly similar to that in the direct photoisomerization as shown in Figure 1, and thus the peroxyoxalate chemiluminescent reaction provides the situation similar to the direct photoexcitation of the stilbenes. These ratios of the *cis*-stilbenes obtained in the present study are lower than that previously reported in which *trans*-4-methoxy-4′-nitrostilbene was treated with bis(2,4-dinitrophenyl) oxalate (DNPO) (5 equiv to the stilbene) and hydrogen peroxide in dimethoxyethane under anhydrous conditions to afford a 9% yield of the *cis*-isomer as the

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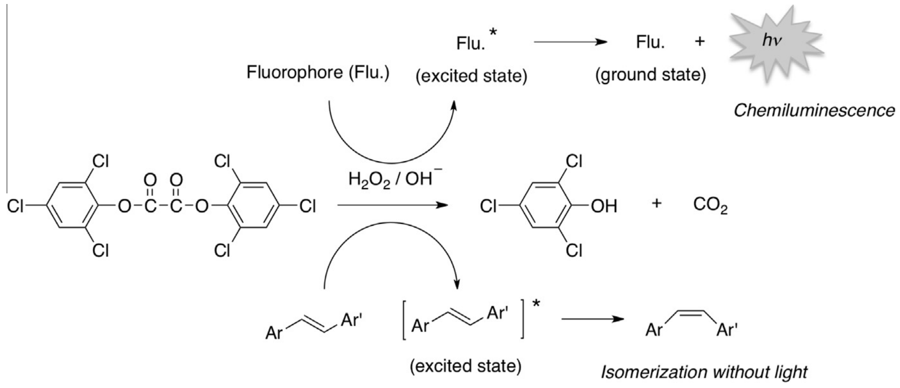
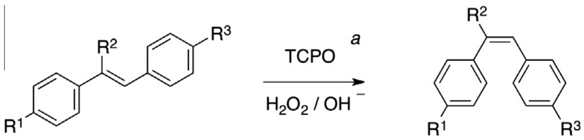
0040-4039/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2013.11.094



Scheme 1. Chemiluminescence and isomerization without light.

Table 1
Isomerization of stibenes (**1a**–**i**) in the PO reactions of TCPO (Type A reaction)



trans-Stilbene	R^1	R^2	R^3	*cis*-Stilbene[b] (%)				Ratio of *cis*-isomer in photoirradiation[c]	
				Entry 1	Entry 2	Entry 3	Average		Abs.[d] (nm)
1a	H	H	H	0	0	0	0	0	297
1b	H	H	OMe	0	0	0	0	12.1	320
1c	OMe	H	OMe	1.6	0.8	1.2	1.2	10.3	323
1d	OBu	H	OMe	0.8	0.6	0.6	0.7	29.7	328
1e	^{t}Bu	H	OMe	0.5	0.4	0.8	0.6	11.7	322
1f	H	Me	OMe	0	0	0	0	7.2	287
1g	CN	H	OMe	7.9	7.9	6.2	7.3	46.1	338
1h	COOEt	H	OMe	1.6	1.1	0.6	1.1	2.7	338

[a] [Stilbenes (**1a**–**i**)] = 7.5×10^{-3} M, [TCPO] = 3.75×10^{-2} M, [H_2O_2] = 2.5×10^{-1} M, [K_2CO_3] = 2.5×10^{-5} M.
[b] Determined by ^{1}H NMR after the work-up.
[c] Direct photoisomerization of *trans*-stilbenes under irradiation by a high pressure mercury lamp for 2 min in THF/H_2O_2 (3/1). [*trans*-stilbene] = 1.0×10^{-4} M.
[d] Absorption with the longer wavelength of two large peaks around 300 nm.

maximum value.[3a] The lower ratios in the present study, in spite of the high amount of TCPO (50 equiv to the stilbenes), would be due to the different reaction conditions, i.e., the reactions were carried out in aqueous media and the use of TCPO instead of more reactive DNPO. We examined the concentration effect under the conditions changing the ratios of stilbene/oxalate (1/10, 1/20, 1/50) and found that the higher ratio than 1/50 gave no *cis*-isomer. In the type A reactions, **1g** with the cyano group was transformed into the *cis*-isomer the most effectively of all. This would be due to the lower singlet excitation energy of **1g** than the others, because it showed the maximum absorption at 338 nm in the solvents the same as used for the reactions and the emission at 559 nm, which was the longest wavelength of all except for **1h** with the absorption and emission at 338 nm and 422 nm, respectively. The difference in the isomerization ratio between **1g** and **1h** can be explained by the rapid loss of the excitation energy of **1h**, because the excited **1h** decays faster than **1g** due to the hydrogen bonding in the aqueous media due to the very weak emission of **1h** in the aqueous media.[6]

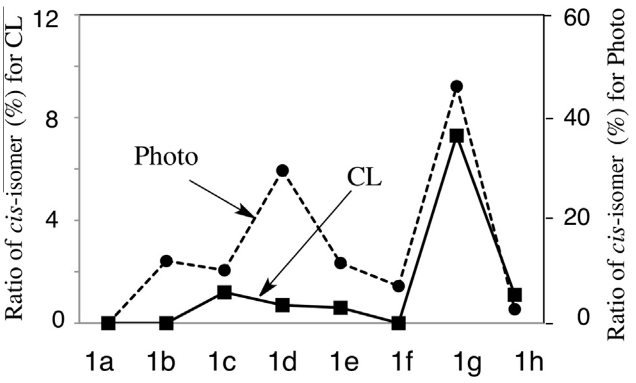
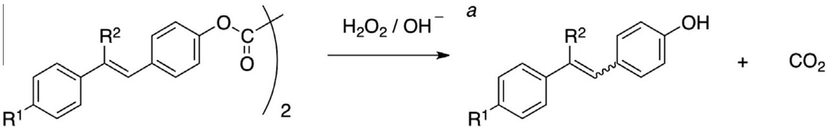


Figure 1. Ratios of *cis*-stilbenes (%) for the chemiluminescent reaction (CL) and direct photoisomerization (Photo).

Next, for the type B reactions, the PO reactions of the oxalates (**2b**, **2d**, **2e**, **2f**, **2g,** and **2h**),[4b,5] containing the stilbene moieties were reacted with aqueous hydrogen peroxide under weak alkaline conditions. After a work-up similar to the above type A reactions, the *cis*/*trans* ratios of the stilbenes were determined by their ^{1}H NMR spectra. As shown in Table 2, the ratios of the *cis*-stilbenes increased compared to the type A reactions except for **2g** and **2h**. To explore the photochemical behavior of **2g** and **2h**, we examined the photoirradiation of the corresponding phenolic stilbenes such as 4-cycno-4′-hydroxystilbene (**3**) and 4-carboethoxy-4′-hydroxystilbene (**4**) under the neutral and basic conditions. The *cis*-isomers were formed in 4.1% for **3** and 5.1% for **4**, respectively, after 5 min. irradiation under the neutral condition, and 32% for **3** under the basic condition. These results show that the *cis*-isomers formed during the type B reactions can exist

Table 2
Peroxyoxalate reaction of the oxalates bearing the stilbene moiety (Type B reaction)



Oxalate	R[1]	R[2]	*cis*-Stilbene[b] (%)				Ratio of *cis*-isomer in photoirradiation of corresponding phenolic stilbenes[c] (%)
			Entry 1	Entry 2	Entry 3	Average	
2b	H	H	7.3	5.9	4.8	6.0	0
2d	OBu	H	2.2	2.2	1.8	2.1	14.2
2e	*tert*-Bu	H	6.5	6.2	4.2	5.6	11.7
2f	H	Me	8.8	10.0	8.9	9.3	3.0
2g	CN	H	0	0	0	0	4.1
2h	COOEt	H	0	0	0	0	5.1

[a] [Oxalate] = 7.5 × 10^{-2} M, [H_2O_2] = 2.5 × 10^{-1} M, [K_2CO_3] = 2.5 × 10^{-5} M in THF/H_2O_2 (3/1).

[b] Determined by ^{1}H NMR after the work-up.

[c] Direct photoisomerization of *trans*-stilbenes under irradiation by a high pressure mercury lamp for 2 min in THF/H_2O_2 (3/1). [*trans*-stilbene] = 1.0 × 10^{-4} M.

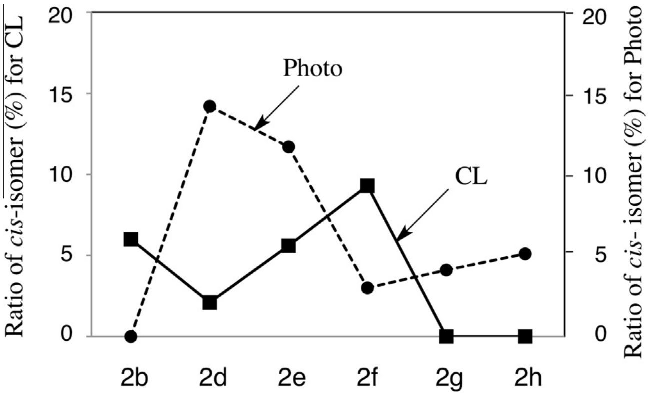
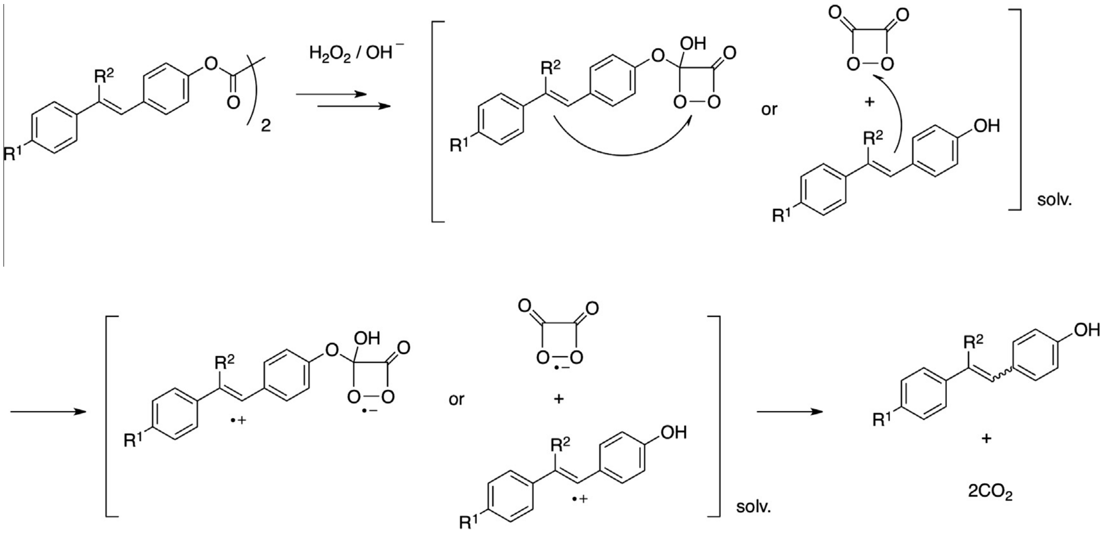


Figure 2. Ratios of *cis*-stilbenes (%) for the chemiluminescent reaction (CL) and direct photoisomerization of the corresponding phenolic stilbenes (Photo).

in their forms under the reaction conditions and not isomerize to the *trans*-isomers. Considering the amount of the oxalate moiety as an energy supplier, the type B reactions are much more effective than the type A reactions except for the push–pull type stilbenes **2g** and **2h**. In Figure 2 the ratios of the *cis*-isomers generated during the type B reaction and the photoirradiation are illustrated. The reason that **2g** and **2h** gave no *cis*-stilbenes might be due to the poor *trans* to *cis* isomerization of donor–acceptor type stilbenes in the protic solvents as previously reported.[7] It is also noteworthy that when perylene was added as a fluorophore to the PO reactions of **2d** and **2f**, no or less isomerization was observed due to the consumption of the excitation energy forming the excited perylene, namely, the ratios of the *cis*-stilbenes were reduced from 2.1% to 0% and from 9.3% to 3.8% for **2d** and **2f**, respectively.

There is a remarkable difference in the isomerization efficiency between the type A and B reactions as described above. The PO-CL reaction is believed to involve the 1,2-dioxetanone bearing one stilbene moiety or the 1,2-dioxetanedione as the high-energy intermediates,[4d,8] the former of which is the precursor of the latter and formed by the initial acyl substitution of the hydroperoxide anion to the oxalate followed by the intramolecular nucleophilic addition of the peroxide end, and the latter of which contains no stilbene moiety and is ready to decompose to two moles of carbon dioxide. The type B reactions provided the interesting result as mentioned above, namely, the appearance in Figure 2 shows an opposite tendency between two excitation ways. There might be an excitation process in the type B reactions different from the energy transfer as in the type A reaction. A plausible explanation



Scheme 2. A plausible electron transfer process for the chemically induced isomerization of the oxalates 2.

is that an intramolecular charge transfer or an electron exchange process is involved in the type B reactions as can be seen in some bioluminescence[9] or as proposed during the CIEEL process for the PO-CL,[8,10] respectively. In this assumed mechanism the isomerization of the formed radical cations of the stilbenes might occur as shown in Scheme 2.[11] The intramolecular charge transfer or an electron transfer would take place between the 1,2-dioxetanedione still bearing the stilbene moiety or the 1,2-dioxetanedione and the liberated stilbenes, once they are formed in the solvent cage. In contrast, the electron deficient cyano and carboethoxy groups of **2g** and **2h** prevented the electron transfer from the stilbene unit to the 1,2-dioxetane moiety, resulting in no isomerization.

The isomerization efficiency of this electron transfer system is comparable or higher comparing the fumaronitrile or 9,10-dicyanoanthracene sensitized isomerization of *trans*-stilbene whose Φ_{cs} were reported to be 0.011–0.31,[9a,b] because Φ_{cs} for **2b** was calculated to be 0.24 from the equation, $\Phi_{\text{PO-cs}}$ = (yield of *cis*-stilbene) × [initial *trans*-stilbene]/([oxalate] × $\Phi_{trans \to cis}$) defined for the stilbene's *trans*–*cis* isomerization during the peroxyoxalate chemiluminescence reaction, using 0.50 for $\Phi_{trans \to cis}$ as the tentative value of *trans*-stilbene.[7] However, this mechanism is based on a little evidence and more detailed study is necessary, which will make the peroxyoxalate chemiluminescence reaction clearer.

In conclusion, the chemically-induced geometrical isomerization of the stilbenes during the peroxyoxalate chemiluminescent reactions was investigated again and some new results were obtained. The isomerization efficiency was dependent upon the singlet excitation energy of the stilbenes for the type A reactions, while the isomerization occurred much more effectively in the type B reactions in which an intramolecular or quasi-intramolecular electron transfer might take place.

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5. *Compound **2b**:* To a solution of (*E*)-4-hydroxystilbene (0.37 g, 1.90 mmol) in benzene (50 ml) and triethylamine (0.23 g, 2.30 mmol) was added oxalyl chloride (0.14 g, 1.10 mmol) dropwise under an argon atmosphere. After being stirred at room temperature for 2 h, the precipitation was filtered and washed with THF. The washing containing the product was concentrated under a reduced pressure to give a white crystal, which was recrystallized from ethyl acetate. Yield: 84% (0.38 g); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.28–7.43 (m, 14H), 7.63 (d, 4H), 7.74 (d, 4H); HRMS (ESI): Calcd for $C_{30}H_{22}O_4Na$ ($[M+Na]^+$): 469.1410, found 469.1411. *Compound **2d**:* This compound was prepared by the procedure as described above using (*E*)-butoxy-4′-hydoxystilbene (0.8 g, 3.00 mmol), triethylamine (0.30 g, 3.00 mmol), and oxalyl chloride (0.19 g, 1.50 mmol) in THF (50 ml). Yield 86% (0.76 g); ^{1}H NMR (400 MHz, $CDCl_3$) d 0.99 (t, 6H), 1.50 (m, 4H), 1.78 (m, 4H), 4.00 (t, 4H), 6.90 (d, 4H), 6.97 (d, 2H), 7.06 (d, 2H), 7.24 (d, 4H), 7.44 (d, 4H), 7.56 (d, 4H). HRMS (ESI): The molecular ion peak was not observed. *Compound **2e**:* This compound was prepared by the procedure as described above using (*E*)-*tert*-butyl-4′-hydoxystilbene (0.40 g, 1.60 mmol), triethylamine (0.16 g, 1.6 mmol), and oxalyl chloride (0.10 g, 0.79 mmol) in THF (30 ml). Yield 84% (0.38 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 18H), 7.06 (d, 2H), 7.11 (d, 2H), 7.26 (d, 4H), 7.40 (d, 4H), 7.47 (d, 4H), 7.58 (d, 4H); HRMS (ESI): Calcd for $C_{38}H_{38}O_4Na$ ($[M+Na]^+$): 581.2662, found 581.2664. *Compound **2f**:* This compound was prepared by the procedure as described above using (*E*)-1-(4′-hydoroxyphenyl)-2-phenylpropene (0.30 g, 1.30 mmol), triethylamine (0.16 g, 1.60 mmol), and oxalyl chloride (0.10 g, 0.80 mmol) in benzene (10 ml). Yield 80% (0.25 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (br s, 6H), 6.82 (s, 2H), 7.28–7.32 (m, 6H), 7.38 (t, 4H), 7.44 (d, 4H), 7.53 (d, 4H); HRMS (ESI): Calcd for $C_{32}H_{26}O_4Na$ ($[M+Na]^+$): 497.1723, found 497.1724. *Compound **2g**:* This compound was prepared according to the established procedure.[4b] *Compound **2h**:* This compound was prepared by the procedure as described above using (*E*)-4-carbethoxy-4′-hydroxystilbene (0.80 g, 3.00 mmol), triethylamine (0.30 g, 3.00 mmol), and oxalyl chloride (0.19 g, 1.50 mmol) in THF (30 ml). Yield 72% (0.64 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (t, 6H), 4.38 (q, 4H), 6.84 (d, 1H), 7.13 (d, 2H), 7.22 (d, 2H), 7.30 (d, 3H), 7.43 (d, 1H), 7.53 (d, 1H), 7.59 (m, 6H), 8.01 (d, 1H), 8.05 (d, 3H). HRMS (ESI): Not measured because of thermal lability.
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