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Unique Thia-Baeyer–Villiger-Type Oxidation of Dibenzothiophene Sulfoxides Derivatives

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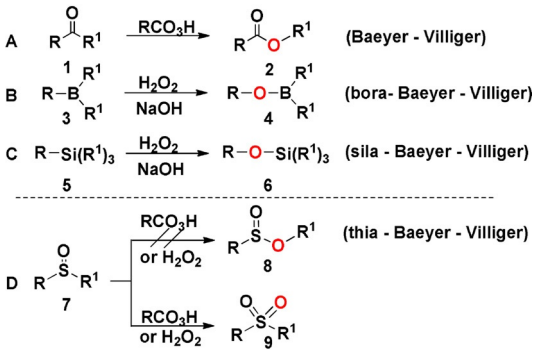
In memory of Prof. Dr. István E. Markó

Abstract: The present research has demonstrated that selective C–S bond cleavages of dibenzothiophene and its derivatives are feasible by thia-Baeyer–Villiger type oxidation, i. e. the oxygen insertion process within a sulfoxide-carbon linkage, in the presence of porphyrin iron (III) and by ultraviolet irradiation originating from sunlight, high pressure Hg-lamp or residentially germicidal ultraviolet lamp under very mild conditions. This reaction with *tert*-butylhydroperoxide at 30.0 °C leads to dibenzo[1,2]oxathiin-6-oxide (**PBS**) in 83.2% isolated yield or its hydrated products, 2-(2-hydroxyphenyl)-benzenesulfinic derivatives (**HPBS**) in near 100% yield based HPLC data. **PBS** and **HPBS** are a type of biological products detected on the C–S bond cleavage step through various oxidative biodesulfurization (**OBDS**) pathways, and are useful synthetic intermediates and fine chemicals. These observations may contribute on understanding delicately molecular aspect of **OBDS** in the photosynthesis system, expanding the C-S cleavage chemistry of S-heterocyclic compounds and approaching toward biomemic desulfurization with respect to converting sulfur contaminants to chemically beneficial blocks as needed and performing under the ambient conditions.

Introduction

Various pathways proposed for **OBDS** of dibenzothiophene **(DBT)** were reported,[1] wherein typically including one step of C–S cleavage reaction that is just challenging the artificial or biomemic methodology potential. **ODS** at presence normally leads to **DBT** sulfoxide (**DBTO**) or **DBT** sulfone (**DBTO$_2$**) that both of them keep C–S bonds[2] A few reports involved C–S cleavage but had to performe under the harsh conditions[3a] or using strong oxidant like persulfate oxidant,[3b] therefore the products had neither selectivity nor biological activity. Since scission desulfurization of **DBT** and its derivatives (**DBTs**), abundant and refractory compounds in the fossil fuels, under the mild condition are extremely necessary for the atom-economic desulfurization, to learn C–S bond cleavage from **OBDS** and understand the molecular aspect of this reaction is paramount. The C–S incision reaction in **OBDS** can be considerated as oxygen insertion reaction, and that simlar reactions were discovered like the insertion of an oxygen atom in one of the acyl-carbon bonds of aldehydes or ketones **1** (Scheme 1 A) named as Baeyer–Villiger oxidation is a particular important transformation leading to the corresponding ester derivatives



Scheme 1. Examples of Baeyer–Villiger oxidation represented by the insertion of an oxygen atom.

2. The Baeyer–Villiger oxidation can be promoted by a variety of oxidants, including peracids and hydroperoxides. Its regioselectivity can be controlled by the judicious choice of the reaction parameters and its mechanism has been thoroughly investigated. In a related transformation, Brown[4] has reported that the treatment of boranes **3** by basic hydrogen peroxide afforded the corresponding borate esters **4** via a *bora*-analog of the Baeyer–Villiger rearrangement (Scheme 1 B). Subsequent hydrolysis generated the corresponding alcohols; the whole process being the famous hydroboration reaction. Tamao[5] and Fleming[6] subsequently described the silicon version of the *bora*-Baeyer–Villiger oxidation. Depending upon the structure of the silane substrates **5**, either hydrogen peroxide or peracids can be employed to promote this rearrangement leading to the corresponding silylethers **6** (Scheme 1 C). The versatility of these transformations coupled with their enormous synthetic potential account for their popularity and their use in numerous synthetic ventures. In stark contrast, attempted insertion

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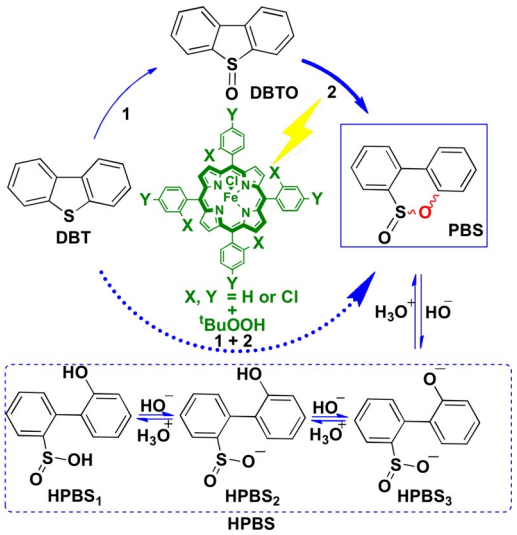
of an oxygen atom within a sulfoxide carbon bond, to selectively generate the corresponding sulfinate ester **8** has, to the best of our knowledge, been considered a hopeless endeavor and has not been reported in the literature (Scheme 1 D). Evidently, a much lower energy pathway is available to the sulfoxide **7** in the form of its conversion into the sulfone **9**, the major or exclusive products observed in various oxidation reactions.[2]

In this context, we wish to report some of our preliminary results on the establishment of selective C–S bond cleavage reaction of **DBTs**. It has been demonstrated that C–S bond incision is feasible via *thia*-Baeyer–Villiger type oxidation, *i. e.* the oxygen insertion hydrated products, **HPBS** (Scheme 2), a type



Scheme 2. Present obervation of **DBT** oxidation oxidation generating **PBS** or **HPBS** via C-S bond incision reaction.

of biological products detected on the C–S bond cleavage step through various oxidative biodesulfurization (**OBDS**) pathways and they are also useful synthetic intermediates and fine chemicals. These observations may contribute on understanding delicately molecular aspect of **OBDS** in the photosynthesis system, expanding the C–S cleavage chemistry of S-heterocyclic compounds and approaching toward biomemic desulfurization with respect to converting sulfur contaminants to chemically beneficial blocks as needed and performing under the ambient conditions.

Results and Discussion

DBT and its derivatives oxidation has been extensively investigated for its potential application in ultra-deep desulfurization of diesel fuels.[2] Mechanistic investigation reveals that oxidative reactions generally undergoes two stages: slow sulfoxidation and fast sulfonation, which, respectively generating **DBTO** and **$DBTO_2$**. Although various oxidants such as ozone, nitrogen oxides, oxygen, nitric acid, sulphuric acid and hydroperoxides were tested, the final product of these reactions mostly liked to be **$DBTO_2$**. **$DBTO_2$** is inert under our reaction conditions and also most of other conditions, which resisting from higher than 400 °C temperature in the absence of catalysts.[8] Alternatively, **DBTO** is flexible and ready to develop many reactions. Thus, our initial interest was on the selective oxidation of **DBT** to **DBTO**.[9] In this regard, the mimetic oxidation system using H_2O_2 or ***t*BuOOH** in the presence of porphyrin iron(III) was established. At near natural conditions, the results found **DBT** uniquely converted to **DBTO**. Further mechanistic study revealed that a low-valent hydroperoxy porphyrin iron(III) (**Int0 so**) complex was involved, which proved to be highly selective for sulfoxide production. **Int0 so** is formed by the coordination of **DBTO** bound to iron ion through axial dimension. Metal porphyrins were directly employed as the chlorophyll model harvesting light for the artificial photosynthesis.[10] Inspired by these successes, we tested **DBTO** oxidation reaction in the presence of ***o*-TCPPFeCl** under natural sunlight at ambient temperature, surprisingly led to an unknown compound in 27.3 % yield based HPLC data (ESI, S1). Various attempts at improving the yield of unknown compound by varying the reaction's parameters met with complete failure in the dark, which leading exclusively to **$DBTO_2$**. It thus transpired that light was a prerequisite for the successful conversion of **DBTO** into unknown product. Taking the consideration of **Int0 so** and **DBTO** light absorbance bands typically in the range of UV, 250 W high-pressure mercury lamp (light wavelength is intensive in the range of 220–450 nm) was employed. Irradiation of the reaction solution as the general procedure afforded the unknown product with high selectivity as shown in HPLC spectra (ESI, S2). Repeating this reaction on the three times larger scale allow us to obtain a definite amount of the unknown compound in 88.1 % isolated yield after column chromatography on silica gel. Spectroscopic analysis with ^{1}H NMR, ^{13}C NMR (ESI, S17-1) indicated that this product was non-symmetrical and tentatively attributed to **PBS**. Fortunately, **PBS** had been prepared earlier by Crich,[11] via a different synthetic route, and the data reported perfectly matched ours, confirmed the structure of this product. Infrared absorption spectrum found the necessary absorbance peaks related to the functional groups in **PBS** molecule (ESI, S18). The structure of **PBS** was further confirmed by high resolution mass spectrum, which found the molecular ion at *m/z* 216.0239 (ESI, S19); calcd for $C_{12}H_8O_2S$: 216.0245.

The importance of the catalyst was verified first by performing the photoreaction of **DBTO** in the absence of porphyrin iron(III) under identical conditions. In this case, **DBTO** converted to mixtures of **DBT** (major) and **PBS** (minor) whether the oxidant ***t*BuOOH** was used or not (Figure 1, sky blue and purplish blue curves), obviously photo deoxygenation of **DBTO** was dominated that agrees well with the research results reported, *i. e.* irradiation of **DBTO** in absence of catalyst afforded no or rare **PBS** but **DBT** and oxidized solvent via generation of oxygen atom resulting from the cleavage of the sulfoxide S–O bond.[12] Similarly, Yasuhiro Shiraishi and co-workers revealed that UV irradiation of **DBT** in the presence of oxidant but no catalyst resulted in the mixture of **DBTO**, **$DBTO_2$**, aromtic sulfonate and a trace of **PBS**, wherein **$DBTO_2$** was the major product.[13] The experimental results demonstrate that porphyrin iron(III) are important and efficient for the reaction. The sub-

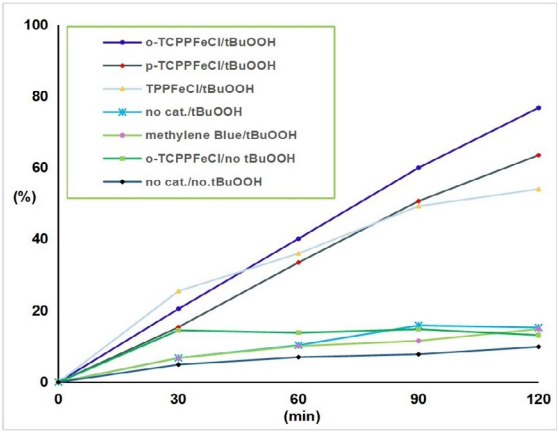
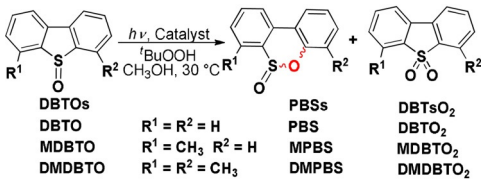


Figure 1. PBS yield-time diagram based on HPLC spectra monitoring DBTO photoreaction under various conditions. Note: yields of PBS are represented by peak area percent based on correspounding HPLC data. The above reactions follow the general photoreaction procedure while changed conditions are explained in the note box of curves.

stituent effect on porphyrin ring was next tested. It is well-known that porphyrins commonly undergo the degradation in oxidative system, and the solution for resisting it is to introduce the electron-withdrawing substituents.[14] This strategy was applied in our experiments and the observation discovered the success. Unsubstituted porphyrin iron(III), *meso*-tetrakisphenylporphine iron(III) chloride (**TPPFeCl**), color bleached faster than chloric substituted porphyrins iron(III), ***o*-TCPPFeCl** and ***p*-TCPPFeCl**; its corresponding reaction rate was vanishing in the range of 30–120 min. The beginning activity of **TPPFeCl** might be contributed by less steric effect on the axial dimension. Activity of ***o*-TCPPFeCl** is higher than ***p*-TCPPFeCl**, possibly due to the electron-withdrawing effect on the *ortho* position is stronger than on the *para* position, which overwhelms the steric effect. Other potential catalysts, such as, Methylene Blue, was tested, which provided **PBS** only in 14.9% yield being similar with no catalyst, indicating that singlet oxygen was not likely involved in this oxidative rearrangement. Test experiment also revealed that oxidant ***t*BuOOH** is mandatory for the conversion of **DBTO** into **PBS** with the result that in the absence of ***t*BuOOH**, **DBTO** mostly deoxygenated to **DBT**. Inorganic catalysts like Ti_2O used in photooxidation of **DBT** and its derivatives have been reported, these photoreactions produced **DBTO** and **$DBTO_2$**, the same as the thermodynamic products.[15] Thus, four key components, **DBTO** substrate, porphyrin iron(III) catalyst, ***t*BuOOH** oxidant and ultraviolet light, are indispensable for this photoreaction success.

With the optimized conditions, various substrates and different light sources were examined; some relevant results are presented in Table 1. As can be seen in Table 1, the reaction tolerates a variety of substituents. Whilst placing the methyl substituents at the 4,6-position had little impact on the yield of the reaction. The non-symmetrical nature of **MDBTO** resulted in the formation of two isomeric **MPBS** (ESI, S17-3 (NMR), S4 (HPLC)). It is worth noting that **DMDBT** is a particularly inert substrate against stringent conditions in hydrodesulfurization, the desired product **DMPBS** could be formed in 82.3% yield

Table 1. Test of applicable scope of substrates and light sources for the present C–S cleavage reactions.



Entry	DBTOs	Catalyst	*t*BuOOH [Equiv.]	*hv* λ[nm]/Watt	*T* [h]	PBSs Yield [%]	$DBTsO_2$ Yield [%]
1	**DBTO**	***o*-TCPPFeCl**	2.4	Sunlight[a]	7	10.0	12.0
					14	27.4	38.7
2	**DBTO**	***o*-TCPPFeCl**	3.2	Hg-lamp[b]	2	76.8	5.9
			4.8	220–450/250	3	89.4	10.6
3	**DMDBTO**	***o*-TCPPFeCl**	3.2	Hg-lamp	2	57.0	≈[c]
			4.8	220–450/250	3	82.3	≈
4	**MDBTO**	***o*-TCPPFeCl**	3.2	Hg-lamp	2	65.5	≈
			4.8	220–450/250	3	82.2	≈
5	**DBTO**	***o*-TCPPFeCl**	4.0[d]	Xe-lamp	3	1.5	40.9
			6.4	450–800/	7	2.4	48.7
			6.4	250	14	3.7	55.7
6	**DBTO**	**TPPFeCl**	2.4	UV-Lamp	3	≈	≈
			3.2	365/6	7	≈	2.8
			4.8		14	2.1	3.9
7	**DBTO**	**TPPFeCl**	2.4	UV-Lamp	3	4.1	1.1
			3.2	254/6	7	7.9	1.3
			4.0		14	**17.7**	2.8

Note: [a] Photoreaction irradiated by the sunlight follow the procedure for DBTO sunlight photoreaction in Experimental Section while others follow the genaral procedure under artificial lights in Experimental Section. [b] high-pressure mercury lamp. [c] ≈ = not detected. [d] The normal molar ratio of ***t*BuOOH** on substrate was 4.8 but in some case, the less molar ratios were used when ***t*BuOOH** was detected by iodometry method and then no more eq. was added at the regular period (see the general procedure). [e] Original HPLC spectra and data are in ESI (S1–S7).

(Table 1, entry 3) is a clear testimony to the power of this C–S cleavage reaction. The limitation of the light sources involves Xe-lamp and UV-Lamp-365. Xe-lamp motivated DBTO predominantly to $DBTO_2$ (Table 1, entry 5); while UV-Lamp-365 didn't afford the desired product at all (Table 1, entry 6). However, UV-Lamp-254 (6 W, Table 1, entry 7) provided an inspiring result by **DBTO** to **PBS** in 17.7% yield, which was further investigated and improved remarkbly by introducing buffer.

Since **DBTO** was synthesized in the same reaction system, conversion of **DBTO** into **PBS** photoreaction started directly from **DBT** instead of **DBTO** by employing an excess of the peroxide. In the event, the peak of **DBTO** generated from sulfoxidation was detected initially by HPLC (Figure 2, 1 h and 2 h) and then vanished after C–S bond cleavage reaction eventually dominated. According to HPLC analyses **PBS** provided the highest yield of 91.9% in 2.5 h. Pure **PBS** in 83.2% isolated yield was obtained by column chromatography on silica gel. Encouraged by the preliminary observation, pure water or phosphate buffer (pH 7.8) was introduced for approaching toward the nature as far as possible. Buffer or pure water

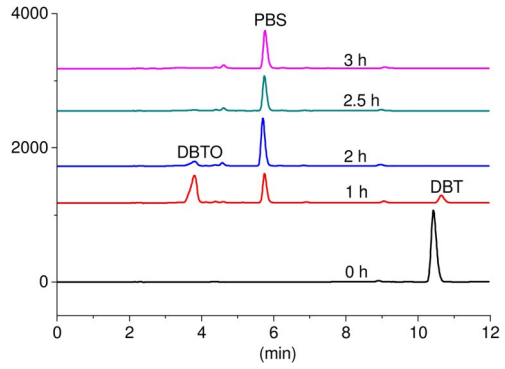
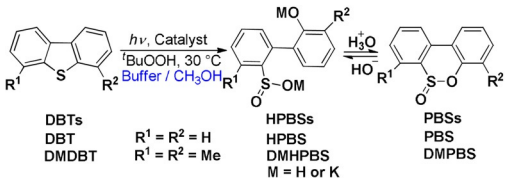


Figure 2. HPLC spectra monitoring **DBT** photoreaction following the general procedure. Note: HPLC data are in ESI (S8).

mixed with CH_3OH were the best solvents for all of starting materials being in one homogeneous phase, which allows HPLC etc analysis to monitor the reaction process that is important for thermoynamic and mechanistic investigation. In this case **DBT** smoothly afforded **HPBS** near in 100% yield and no trace of **$DBTO_2$** was detected (Table 2, entry 1). The most impressive result arises from UV-Lamp-254 (6 W), which promoted **DBT** and **DMDBT** to give outstanding selectivity and good yield, 91.3% and 87.2% respectively for each (Table 2, entry 2 and 3). **HPBSs** peaks in HPLC spectra were recognized by the standard substances, which were synthesized from **PBSs** hydrolysis according to the reference[16] and then confirmed by NMR (ESI, S17-4–S17-6). Indeed, it was expected that pure water instead of phosphatic buffer would deliver the same, but this was proved not to be the case. **DBT** photoreaction (Table 2, entry 4) only afforded **PBS** in 15.8% yield and no **HPBS** was detected by HPLC. This result indicated that phosphatic salts are the hydrolysis catalyst for **PBS** leading to **HPBS**, which agrees well with the results reported,[16] and removal of **PBS** from the reaction solution could facilitate C-S bond cleavage photoreaction. **HPBS** has extremely high water-solubility that provides more favors of the separation from the oil phase than **DBTO** and **$DBTO_2$**. Another important advantage of UV-Lamp-254 (6 W) for the present reaction should be near zero heat release. Therefore, UV-Lamp-254 generating a definite wavelengh at 254 nm displayed practically energy-saving, generally efficient, commercially cheap and available characters.

HPBS reversibly dehydrated to **PBS** under the acidic condition has been evidenced also by HPLC spectra (ESI, S9*) that **PBS** peak appearing strongly based on the sample taken from the reaction solution (Table 2, entry 1) and kept for 3 weeks after adjusted its pH to 6. Since the numerous **HPBS** (**$HPBS_1$**, **$HPBS_2$** and **$HPBS_3$**) appeared in acid-base equilibrium (Scheme 2), UV/Vis spectroscopy was used to obtain a more precise view of the competition among **HPBS** components (Figure 3). By adjusting pH value of product solution with adding aqueous dilute HCl or NaOH, each of them was identified according to the reference data reported, *i. e.* 302 nm (pH 12, **$HPBS_3$**), 278 nm (pH 7, **$HPBS_2$**) and 280 nm (pH 1, **$HPBS_1$**).[17]

Table 2. DBTs photoreaction in CH_3OH mixed with buffer (pH 7.8) or pure water.



Entry	DBTs	Catalyst	*t*BuOOH [Equiv.]	*Hv* λ[nm]/Watt	*T* [h]	HPBSs Yield [%]	PBSs Yield [%]	$DBTsO_2$ Yield [%]
1[a]	**DBT**	***o*-TCPPFeCl**	4.8	Hg-lamp 250–450 /250	3	≈**100**	0	0
2[a]	**DBT**	**TPPFeCl**	2.4	UV-Lamp	3	3.0	0	0
			3.2	254/6	7	12.7	0	0
			5.6		14	**91.3**	0	0
3[a]	**DMDBT**	**TPPFeCl**	2.4	UV-Lamp	3	12.8	0	0
			3.2	254/6	7	48.8	0	4.4
			4.0		15	**87.2**	0	4.9
4[b]	**DBT**	**TPPFeCl**	4.0	UV-Lamp	3	0	1.47	0
			4.8	254/6	7	0	4.01	0
			5.6		15	0	15.8	0

Note: 1) Photoreactions following the general procedure (in the experiemntal section) 2) [a] phosphatic buffer (pH 7.8)/ CH_3OH (1/2 volume ratio) [b] pure water/CH_3OH (1/2 volume ratio). 2) Original HPLC spectra are shown as ESI S9–12.

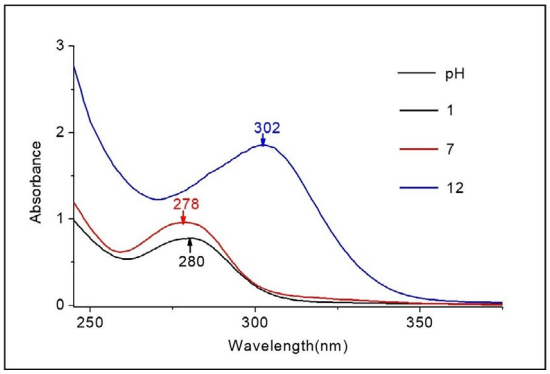
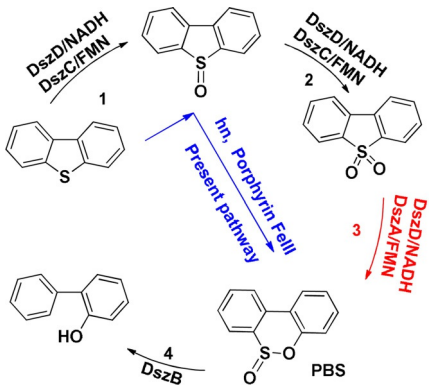


Figure 3. UV/Vis spectra of aquous **HPBS** solution at different pH values.

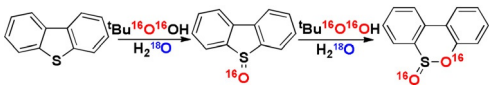
Thus, **DBT** cascading to generate **PBS** as well as water-, salt- and pH-dependent products, various **HPBS**, in one chlorophyll-biomimetic photocatalysis system has been experimentally demonstrated. It is important note that except the same taking the oxidants, this reaction pathway is very distinguished from well-known 4S pathway,[1a,d,e] a catabolizing **DBT** pathway most scientifically evidenced until now, from basic and key points: 1) C–S cleavage in 4S needs expensive chemical energy like obtained from NADH, while the presence concerned only needs a little light energy; 2) the key intermedaite for C-S cleavage of 4S is **DBTs** sulfone, extremely stable compounds resisting most of ractions including the present reaction, while the key intermediate for the present C-S cleavage reaction is more flexible intermedaite, **DBTs** sulfoxide; 3) obviously the present procedure from **DBT** to **PBS** is one step shorter than



Scheme 3. 4S pathway and present observation.

the corresponding procedure in 4S (Scheme 3), hence the energy needed is reduced further; 4) the active site of DszA, an enzyme catalyst motivate the third step in 4S is flavin-type,[18] while the present catalysts are porphyrin iron related with chlorophyll wildly and widely existing in cyanobacteria. Extraordinary cyanobacteria, which were found in the petrolum contianminate coast or similar place exposed to the sunlight and in the saltine, which survived from the caustic conditions and evolved the degrading **DBT** ability.[19] Their natural strategy resisting caustic conditions may solve or moderate the **OBDS** shortcoming, but little have been paid on their molecular aspects at present. The functional and supplymentary coincidence between the present reaction system and cyanobacteria degrading **DBT** is motivating us to pursuit further understanding the mechanistic insights for developing an efficient and applicable biomimetic **ODS**.

The isotopic exchange experiment following the general procedure wherein employing **DBT**, ***o*-TCPPFeCl** and high-pressure Hg-lamp but adding ^{18}O-labeled water (10 wt%) in CH_3OH (Scheme 4), showed that no PBS product incorpor ated an ^{18}O



Scheme 4. Isotopic exchange experiment adding ^{18}O-labeled water.

atom, as demonstrated by GC-LRMS detection (molecular ion at *m/z* 216.0; calcd for $C_{12}H_8{}^{16}O_2S$: 216.0, ESI, S20). This experiment result supports the postulated mechanism that the C-S bond cleavage is an oxidative incision reaction by an intra oxygen rearrangement and insertion within sulfoxide-carbon bond like Baeyer–Villiger oxidation. **Int0so** complex importance in diverting the reaction pathway and leading to the *thia*-Baeyer–Villiger product was emphasized by the designed experiment. UV/Vis spectroscopic detection indicated the formation of **Int0so** complex established by our previous research,[9] according to the typical signal at 412 nm of *o*-TCPPFeCl shifting to 392 nm upon irradiation (Figure 4, left), and PBS was generated. Addition of 0.1 equiv. imidazole on DBT to the catalytic system results in the disappearance of this

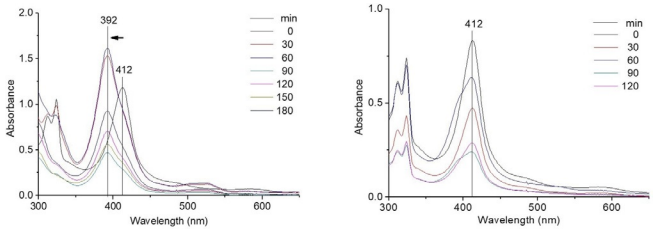
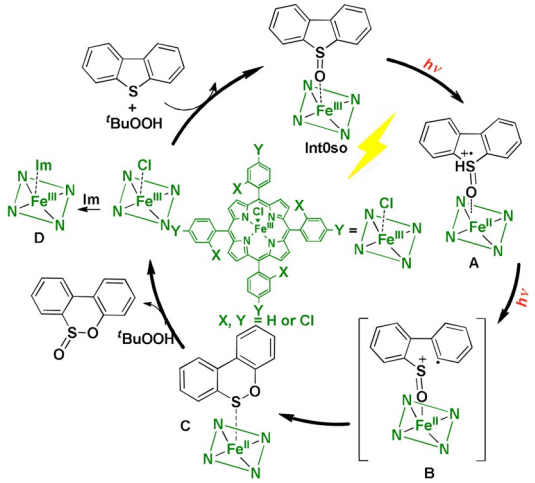


Figure 4. UV/Vis spectra monitoring the **DBT** photoreaction (left). UV/Vis spectra monitoring **DBT** photoreaction adding imidazole (right). Note: DBT photoreaction following the general procedure wherein employing ***o*-TCPPFeCl** and high-pressure Hg-lamp.

peak shifting (Figure 4, right), and only a trace of **PBS** was produced (ESI S13, 14). Imidazole is a good axial ligand for ***o*-TCPPFeCl** and it displaces rapidly **DBTO** from porphyrin iron(-III). The lack of photo reaction in the presence of imidazole demonstrates that the formation of **Int0so** complex is a compulsory step in the successful generation of **PBS**. The radical trap experiment was conducted under the typical procedure but adding 4-hydroxy-2,2,6,6-tetramethylpiperidine1-oxyl (**HTEMPO**, a wide and rapid radical trapper). The rates represented by the slopes of yield$_{PBS}$/time fit lines (ESI, S15 and 16) are, respectively 0.67 and 0.27 when adding no and 0.1 equiv. **HTEMPO** on **DBTO**. Photoreaction of **DBTO** was retarded with 59.7% yield by 0.1 equiv. radical trapper, which suggests that radical intermediate was involved in the photoreaction.

A plausible mechanism is proposed according to the present results (Scheme 5). **DBT** is selectively oxidized to **DBTO** by ***t*BuOOH** in the presence of porphyrin iron(III), which acts as the axial ligand of porphyrin iron(III) to form complex **Int0so** based the previous research.[9] Irradiation of **Int0so** leads to photo-induced electron transfer from sulfur atom to anti-π orbital of S=O, and further delocalized to conjugated tetrapyrrole ring through axial bond to form intermedaite **A**. Consequently, porphyrin catalyst appears to be the stabilization of S–O bond (in the absence of porphyrin catalyst, deoxygenation S–O bond was dominated in Figure 1 related), hence homolytic



Scheme 5. A plausible mechanism is proposed according to the present results. Note: Im = Imidazole.

cleavage happens on neighbor S–C bond to generate **B**, which conduct O-rearrangement to carry out **C**. Oxidation of **C** via this oxidative system affords **PBS** (or **HPBS** in buffer) and regenerates porphyrin iron (III) that re-enters a new catalytic cycle. **A** can be trapped by **HTEMPO** to afford corresponding intermediate (ESI, S21), and Imidazole as a good axial ligand **D** can resist **DBTO** from porphyrin iron (III), both of them can end this catalytic cycle.

Conclusions

In conclusion, we have uncovered a dibenzothiopenic C-S bond incision reaction via regioselective insertion of an oxygen atom within sulfoxide-carbon linkage, a *thia*-analog of the Baeyer–Villiger oxidation. The reaction led to cyclic sulfinate ester **PBS**, and subsequent hydrolysis generated the correspounding **HPBS**. Porphyrin iron(III) catalyst, hydroperoxide oxidant and ultraviolet light are indispensable for this reaction success. Using high-pressure mercury lamp in the presence of ***o*-TCPPFeCl** and ***t*BuOOH**, photoreaction of **DBT** at 30.0 °C in 2.5 h lead to 100% conversion of **DBT** and 91.9% yield of **PBS** based on the HPLC analysis, and 83.2% isolated yield obtained by column chromatography on silica gel. Placing the methyl substituents at the 4,6-position of **DBT** had a little impact on the yield of correspounding **PBS**, although **DMDBT** is a particularly inert substrate against stringent conditions in hydrodesulfurization. The impressive result was emphasized by residentially germicidal UV-Lamp-254 (6 W) irradiation reaction performed in mixed solvent of the phosphatic buffer (pH 7.8) and methanol, which promoted **DBT** and **DMDBT** to completey convert and to give outstanding yields, 91.3% and 87.2% respectively for each desired **HPBS**. The isotopic exchange experiment supports that the present photoreactions is an oxidative incision reaction by an intra oxygen rearrangement and insertion within sulfoxide-carbon bond. **Int0 so** complex importance in diverting the reaction pathway and leading to the *thia*-Baeyer–Villiger product was emphasized by the axial ligand replacement experiment. The radical trap experiment suggests that radical intermediate was involved in the photoreaction by 0.1 equiv **HTEMPO** on **DBTO** retarded the photoreaction of **DBTO** upon 59.7%. A plausible mechanism is proposed according to the present results.

Experimental Section

General information

All experiments using artificial lights were performed in the built-in lamp photoreactor with magnetic stirrer and cooling water condenser. **DBTs** and **TPPFeCl** were used as received. Solvents were redistilled. *tert*-butylhydroperoxide (***t*BuOOH**, 80% in water) was titrated by iodometry method before used. *meso*-tetrakis(*o*-chlorophenyl)porphine iron (III) chloride (***o*-TCPPFeCl)** and *meso*-tetrakis(*p*-chlorophenyl)porphine iron (III) (***p*-TCPPFeCl)** were synthesized according to the references reported.[7] High-pressure mercury lamp (Giguang, 250 Wt), residentially germicidal ultraviolet lamp (UV-Lamp-254, Philips TUV-TL, $\lambda = 254$ nm, 6 W) and insect trap ultraviolet lamp (UV-Lamp-365, Philips TUV-TL, $\lambda = 365$ nm, 6 W) were obtained commercially. The visualization of spots on TLC plates was effected by exposure to UV. Column chromatography was performed over Silica gel (200 mesh) using the relevant eluent. High Performance Liquid Chromatography (HPLC) was performed on an Agilent HP1100 chromatograph equipped with a DAD detector detector using a fused XB-C18 capillary column (Welch Ultimate, 25.0 cm × 4.6 mm × 5.0 μm). A standard program was used for all HPLC analysis: eluent concentration of acetonitrile water solution was increased from the initial concentration 70% to 95% with 2.5% per minute, eluent flow rate was 1 mL min^{-1}, and monitoring wavelength was at 254.4 nm. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR-spectra were recorded on Bruker UltraShield spectrometers at ambient temperature in $CDCl_3$ or $[D_6]$DMSO. Chemical shifts are reported in ppm downfield to tetramethyl silane. Coupling constants are reported and expressed in Hz, splitting patterns are designated as s (singlet), d (doublet), t (triplet) and m (multiplet). NMR Fourier transform, integration and peak picking were done with MestReNova software. Infrared absorption spectra were recorded on Nicolet-20DXB spectrometer and the absorption bands are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra (HRMS) were recorded at Micromass GCT-TOF, and Ultraviolet-Visible (UV/Vis) spectra were recorded at Ultraviolet-Visible Absorption Spectroscopy, PerkinElmer Lambda 35 (190–1100 nm).

Procedure for DBTO sunlight photoreaction

To a 100 mL round-bottomed quartz flask fitted with a water condenser, introduced **DBTO** (10.0 mg, 50.0 μmol), ***t*BuOOH** (3.2 equiv. on **DBTO**) and ***o*-TCPPFeCl** (2 mg, 2.4 μmol) in CH_3OH (10 mL). Irradiating this mixture for 14 h was proceeded at ambient temperature under the sunlight without stirring.

General procedure for DBTs or DBTs sulfoxides photoreaction irradiated by artificial lights

In a 200 mL three-necked and round-bottomed flask, added a solution of **DBT** sulfoxide or **DBT** (150.0 μmol) and catalyst (7.2 μmol) in CH_3OH (30.0 mL). Light lamp was carefully set in a quartz tube (length: 28 cm, diameter: 3.8 cm) and then together installed in the middle of the round-bottomed flask. The reactor was equipped with the water condenser on the one neck of the flask and 2/3 flask immersed in the 30.0 °C water bath with integrated temperature control. Initial 0.8 equiv. ***t*BuOOH** (2.4 equiv. if **DBT** serviced as the substrate) was dropwised into the solution after switched on magnetic stirring and water recycling. The reactor was covered with tinfoil before turn on the lamp. After irradiating the reaction mixture for 0.5 h, turned off the lamp, rapidly took a sample (150.0 μL) and added ***t*BuOOH** (0.8 equiv.) into reaction solution only if examined no ***t*BuOOH** left by iodometry method and restarted the lamp to irradiate reaction solution for another 0.5 h. Repeat the last step until the designed time, wherein catalyst (2.4 μmol) was added at 2 h if reaction time is more than 2 h. After evaporating the solvent, the crude product was purified by column chromatography on silica gel.

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Conflict of interest

The authors declare no conflict of interest.

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