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Oxidative cleavage of α -substituted styrenes using excited dibenzothiophene *S*-oxide and DMSO

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Visible-light-induced oxidative cleavage of α -substituted styrenes has been achieved using a photocatalyst, dibenzothiophene *S*-oxide, and DMSO. The reaction proceeds via an addition of a methyl radical to the styrenic double bond, representing a mechanistically distinct pathway compared with conventional methods for oxidative cleavage that rely on toxic and/or explosive oxidants. This unique radical mechanism enables interesting chemoselectivities such as preferential oxidation of electron-deficient alkenes over electron-rich ones as well as provides an environmentally benign alternative for oxidative cleavage.

The oxidative cleavage of alkenes is a fundamental transformation in organic synthesis, providing straightforward access to carbonyl compounds from readily available alkenes. Conventional methods for the cleavage utilize toxic and/or explosive oxidants such as ozone,¹ heavy-metal oxides,² and peroxides,^{2*h,i*,3} which often raise concerns regarding safety and environmental impact (Fig. 1A). Recently, photocatalytic oxidative cleavage of alkenes using safe and easy-to-handle molecular oxygen has been reported.⁴ However, overoxidation and poor site-selectivity remain major limitations. Consequently, the development of new oxidation methods that are safe, mild, and highly selective remains an important topic, particularly for molecules bearing multiple olefinic moieties. In this context, Parasram^{4*g*,5} and Leonori⁶ independently reported oxidative cleavage of alkenes employing nitroarenes as stoichiometric oxidants (Fig. 1B). Upon photoexcitation, nitroarenes transfer oxygen atoms in an electrophilic manner via a radical pathway, which is a mechanistically distinct process that enables selective oxidation of more electron-rich alkenes. Accordingly, the development of oxidative cleavage that operates through mechanisms fundamentally different from conventional approaches is crucial for achieving site-selective alkene oxidation.

We have recently reported that dibenzothiophene *S*-oxide (DBTSO) can be excited via triplet energy transfer using visible

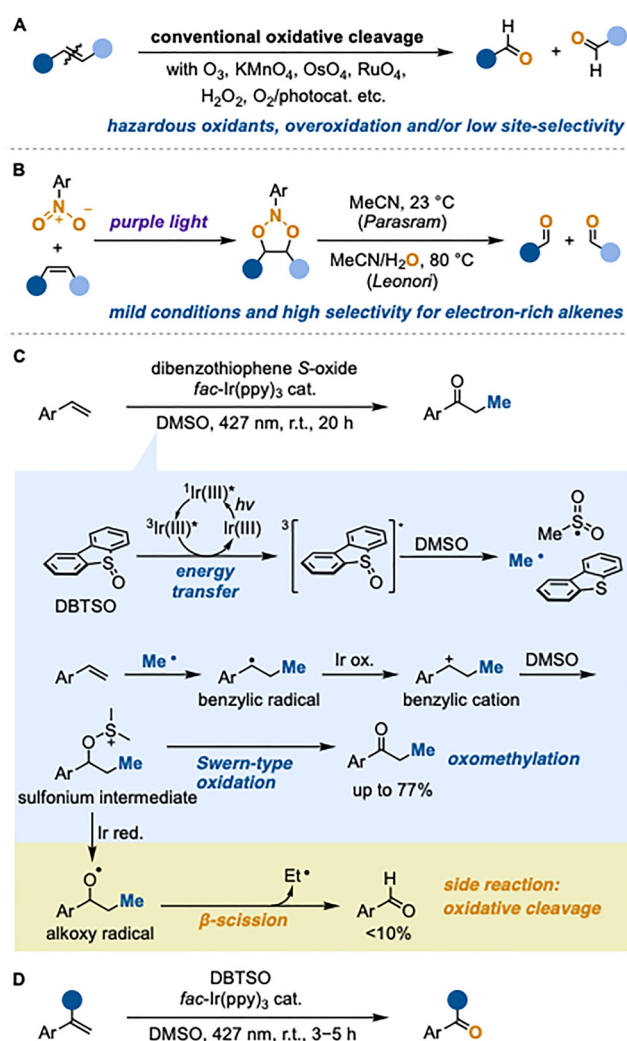


Fig. 1 (A) Conventional oxidative cleavage. (B) Oxidative cleavage of alkenes using photoexcited nitroarenes. (C) Our previous work. Oxomethylation of styrenes using photoexcited DBTSO. (D) This work. Oxidative cleavage of α -substituted styrenes using photoexcited DBTSO.

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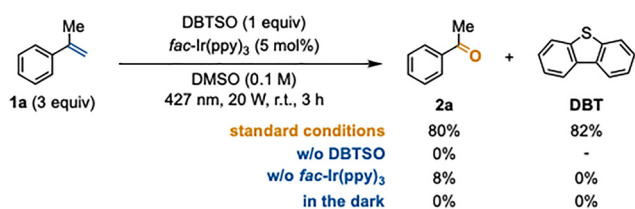


light and an Ir photocatalyst, enabling oxomethylation of styrenes *via* methyl radical generation (Fig. 1C).⁷ Mechanistic investigations revealed that the excited DBTSO undergoes rapid fragmentation in DMSO to produce a methyl radical, which adds to the styrene to generate a benzylic radical intermediate. Subsequent oxidation of this radical by the excited Ir photocatalyst affords the corresponding benzylic cation, which is trapped by DMSO to form a sulfonium intermediate. This intermediate then undergoes Swern-type oxidation to afford propiophenone.

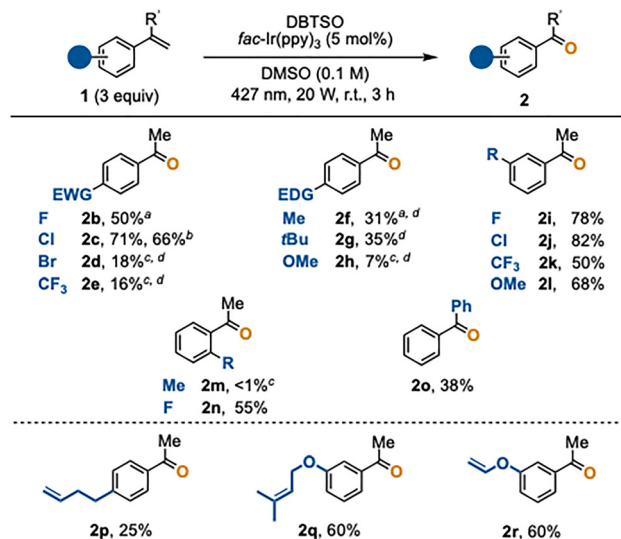
Notably, benzaldehyde was detected as a minor side product (<10%). We presumed that this aldehyde arises from β -scission of the alkoxy radical generated by single-electron reduction of the sulfonium intermediate by the Ir photocatalyst. On this basis, we envisioned that applying the excited DBTSO/DMSO system to α -substituted styrenes would enable exclusive formation of alkoxy radicals, ultimately leading to oxidative cleavage (Fig. 1D). Herein, we report a new oxidative cleavage process initiated by methyl radical addition, utilizing the DBTSO/DMSO system.

Under similar conditions to the oxomethylation reaction,⁷ a solution of DBTSO ($E_T = 54.4 \text{ kcal mol}^{-1}$), α -methylstyrene (**1a**, 3 equiv.), and *fac*-Ir(ppy)₃ photocatalyst (5 mol%, $E_T = 58.1 \text{ kcal mol}^{-1}$) in DMSO (0.1 M) was irradiated with blue LED (427 nm, 20 W) for 3 h (Scheme 1). The expected oxidative cleavage proceeded smoothly to give acetophenone (**2a**) in 80% yield. We confirmed that none or a small amount of **2a** was observed in the absence of DBTSO, *fac*-Ir(ppy)₃, or light irradiation.

We next investigated the scope of the oxidative cleavage of various α -substituted styrenes **1** (Scheme 2). α -Methylstyrenes **1b–1d** bearing a halogen substituent at the *para*-position afforded the corresponding acetophenones **2** in moderate to high yields, except for *p*-bromo- α -methylstyrene (**1d**). The reaction also proceeded smoothly on a 1-mmol-scale to afford **2c** in 66% yield. Strongly electron-withdrawing *p*-CF₃ group markedly lowered the yield of **2e**. Substrates **1f** and **1g** having an electron-donating group at the *para*-position gave the corresponding products **2f** and **2g** in moderate yields. Unfortunately, the reaction of *p*-methoxy- α -methylstyrene (**1h**) provided acetophenone **2h** in only 7% yield. These results suggest that pronounced electronic perturbations relative to unsubstituted α -methylstyrene (**1a**) adversely affect the efficiency of the oxidative cleavage.⁸ For reactions that afforded moderate to low yields, one-carbon-homologation products, including 2-aryl-2-butenes and α -ethylstyrenes, were observed as side products in approximately 10–30% yields. These side products likely arose from deprotonation of the corresponding benzylic cations.



Scheme 1 Oxidative cleavage of α -methylstyrene using excited DBTSO. Conditions: DBTSO (0.10 mmol, limiting agent), **1a** (0.30 mmol), *fac*-Ir(ppy)₃ (0.0050 mmol), DMSO (1.0 mL), blue LED (427 nm, 20 W), r.t., 3 h.



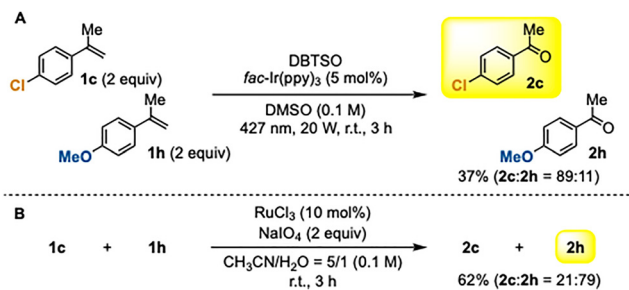
Scheme 2 Oxidative cleavage of various α -substituted styrene **1**. Standard conditions: DBTSO (0.20 mmol, limiting agent), **1** (0.60 mmol), *fac*-Ir(ppy)₃ (0.010 mmol), DMSO (2.0 mL), blue LED (427 nm, 20 W), r.t., 3 h. ^aPerformed on half the scale of the standard conditions with the same reaction time of 3 h. ^bPerformed on a 1 mmol scale (5 \times standard scale) with two LED lamps and the reaction time of 5 h. ^cNMR yield. ^d2-Aryl-2-butenes and α -ethylstyrenes were observed as side products (ca. 10–30% yields).

In the case of *meta*-substituted substrates, where electronic perturbation of the C=C bond is minor, the oxidative cleavage proceeded smoothly to afford the corresponding acetophenones **2i–2l** in good yields (50–82%). On the other hand, *o*-methyl- α -methylstyrene (**1m**) did not react, probably because the conjugation between the C=C bond and the phenyl group is hindered. In contrast, *o*-fluoro- α -methylstyrene (**1n**), which imposes less steric demand, underwent the reaction smoothly to give **2n** in 55% yield. Benzophenone (**2o**) was obtained in 38% yield when 1,1-diphenylethylene (**1o**) was used.

Remarkably, substrates **1p**, **1q**, and **1r**, each bearing two distinct olefinic moieties, selectively gave acetophenones **2p**, **2q**, and **2r**, leaving the non-arylated C=C bonds intact. This high site-selectivity is due to the higher reactivity of the phenylated C=C bonds toward the radical addition of a methyl radical (Fig. 1C). It is worth mentioning that, based on a survey of the literature, research on conventional oxidative cleavage lacks general information on site-selectivity and that one could suffer from poor selectivity in performing site-selective oxidative cleavage. The present methyl-radical-based approach therefore offers unique selectivity,^{4g–6,9} being complementary to or advantageous over established oxidative cleavage.^{2–4}

As shown in Scheme 2, the yields were strongly influenced by the electronic properties of the α -methylstyrenes. To further clarify the site-selectivity of this transformation, we conducted a competition experiment using two α -methylstyrenes with contrasting electronic properties (Scheme 3A). When a mixture of electron-deficient *p*-chloro- α -methylstyrene (**1c**) and electron-rich *p*-methoxy- α -methylstyrene (**1h**) was subjected to our photo-induced DBTSO/DMSO system, oxidative cleavage occurred





Scheme 3 Competition experiments. (A) Oxidative cleavage by our photoinduced DBTSO/DMSO system. (B) Oxidative cleavage using ruthenium tetroxide.

preferentially at **1c**, affording an 89:11 selectivity in favor of the electron-deficient alkene. This result is consistent with the substrate scope shown in Scheme 2 and demonstrates that the present method selectively oxidizes electron-deficient C=C bonds. For comparison, the same substrate mixture was oxidized using ruthenium tetroxide^{2f} (Scheme 3B). In line with the well-established behavior of conventional oxidative cleavage reactions,² the more electron-rich alkene of **1h** was preferentially oxidized (2c:2h = 21:79). Thus, the DBTSO-based photoinduced system exhibits a clear reversal of selectivity relative to traditional oxidative cleavage methods. These results suggest that the site-selectivity of the present oxidative cleavage is governed by the preferential addition of a nucleophilic methyl radical to the more electron-deficient C=C bond, highlighting a mechanistic origin distinct from that of conventional electrophilic oxidation processes.

To further validate our mechanistic working hypothesis, several control experiments were performed. Addition of 1 equivalent of TEMPO completely suppressed the oxidative cleavage, affording methylated TEMPO **3** in 18% yield (Fig. 2A). This result is consistent with our previous study,⁷ supporting the essential role of the generation of methyl radicals. When ¹⁸O-labeled DBTSO was employed in the oxidative cleavage of **1a** (Fig. 2B), only negligible incorporation of ¹⁸O into **2a** was observed (¹⁸O:¹⁶O = 6:94) as previously noted in the previous oxomethylation.⁷ Given that the reaction was conducted entirely under an inert atmosphere, the oxygen atom in **2a** most reasonably originated from DMSO. To determine whether the reaction proceeds *via* a radical chain or a non-chain process, a light on/off experiment was performed (Fig. 2C), wherein irradiation was alternately turned on and off every 10 min. No changes in the amounts of **2a**, DBTSO, and DBT were observed during the light-off periods, which indicates that the oxidative cleavage reaction does not proceed *via* a radical chain mechanism.

When 2-phenyl-1-hexene (**1s**) was subjected to the standard conditions (Fig. 2D), valerophenone (**2s**) and propiophenone (**2s'**) were formed in 30% and 12% yields, respectively. This product distribution supports the generation of a tertiary alkoxy radical *via* single-electron reduction of the corresponding sulfonium intermediate (also depicted in Fig. 1C) and subsequent β -scission of the alkoxy radical intermediate. Importantly, elimination of an ethyl radical was slightly favored over that of a butyl radical, in agreement with the previous report.¹⁰

Based on these mechanistic experiments, the site-selectivity observed in Schemes 2 and 3, and our previous report,⁷ we propose the reaction mechanism illustrated in Fig. 2E. Following a pathway

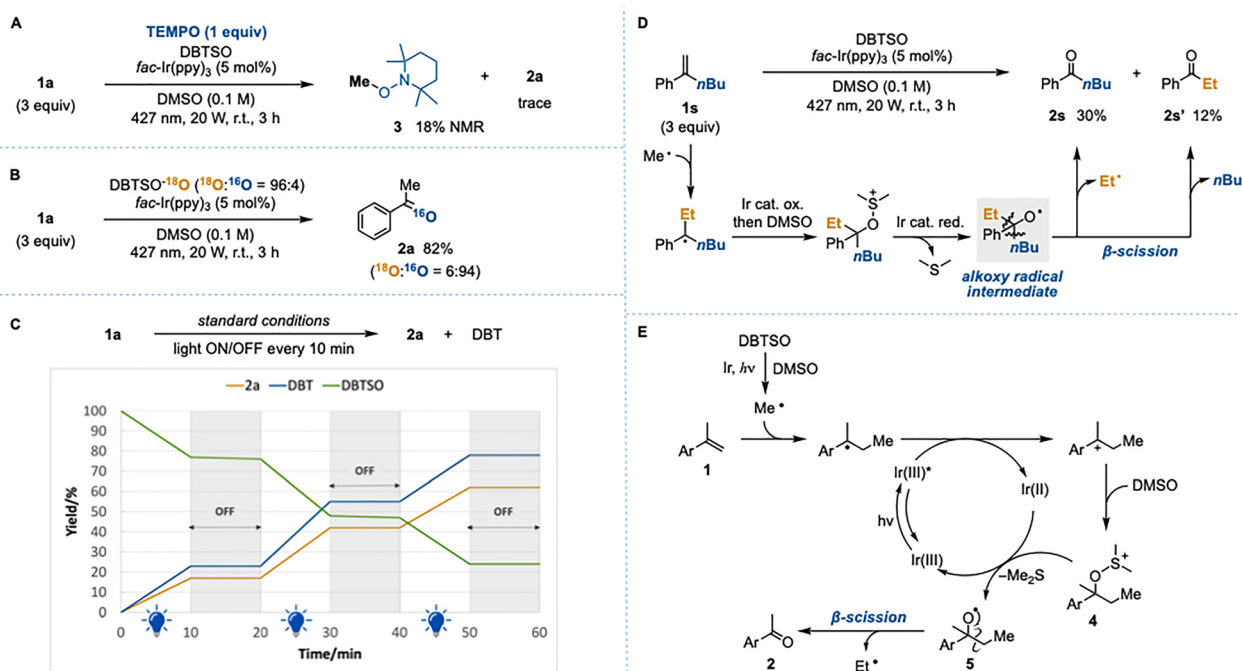


Fig. 2 (A) Trapping of methyl radical. (B) ¹⁸O-labeling experiment using DBTSO-¹⁸O. (C) Light on/off experiment. (D) Investigation of the selectivity of β -scission. (E) Plausible mechanism.



analogous to that described in Fig. 1C, the reaction should proceed *via* the formation of the corresponding sulfonium intermediate **4**. This intermediate is then reduced by the Ir(II) species *via* single-electron transfer to form alkoxy radical **5**,¹¹ which subsequently undergoes β -scission to afford acetophenone **2** with predominant release of the much more stable ethyl radical over a methyl radical.

In summary, we have developed photoinduced oxidative cleavage of α -substituted styrenes mediated by excited DBTSO. The reaction proceeds through generation of a methyl radical from the reaction between excited DBTSO and DMSO, followed by selective addition of the radical to the more electron-deficient styrenic C=C bond, thereby enabling site-selective oxidative cleavage. This selectivity contrasts with conventional oxidative cleavage methods, which typically oxidize electron-rich alkenes preferentially. The distinct methyl-radical-based mechanism underlying this transformation provides a new strategy for controlling site-selectivity in alkene oxidation and is expected to be applicable to the selective functionalization of complex molecules bearing multiple olefinic moieties.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: general information, experimental procedure, characterization data, NMR spectra, together with References. See DOI: <https://doi.org/10.1039/d6cc00617e>.

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