

A comparison of hydrogen bonding solvent effects on the singlet oxygen reactions of allyl and vinyl sulfides, sulfoxides, and sulfones

Kristina L. Stensaas,^{*} Brent V. McCarty, Natacha M. Touchette and James B. Brock

Department of Chemistry, Millsaps College, 1701 N. State Street, Jackson, MS 39210-0001, United States

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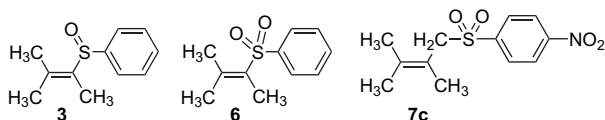
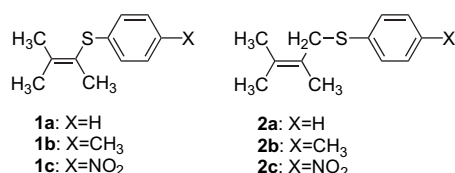
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Abstract—The singlet oxygen ($^1\Delta_g$) photooxidations of 2-methyl-3-phenylthio-2-butene (**1a**), 1-[(4-nitrophenyl)thio]-2,3-dimethyl-2-butene (**2c**), 2-methyl-3-phenylsulfinyl-2-butene (**3**), 2-methyl-3-phenylsulfonyl-2-butene (**6**), and 1-[(4-nitrophenyl)sulfonyl]-2,3-dimethyl-2-butene (**7c**) were conducted in the following deuterated solvents: acetonitrile, benzene, chloroform, methanol, or methanol/water mixture. In each case the ene allylic hydroperoxide products and/or the [2+2] cycloaddition products were quantified and inspected for possible hydrogen bonding induced differences in product selectivity and regiochemistry. After comparison to literature values for related substrates, the results indicate that only photooxidations of vinyl sulfides are susceptible to hydrogen bonding solvent effects.

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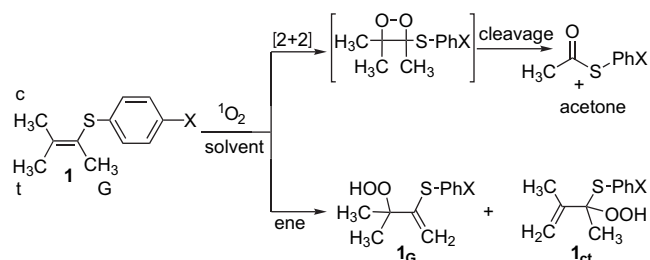
1. Introduction

Hydrogen bonding and specifically aqueous solvent effects have recently been reported^{1,2} for the singlet oxygen ene reactions of α,β -unsaturated esters, acids, and sodium salts. As part of our continued interest in hydrogen bonding solvent effects on the singlet oxygen reactions of substituted alkenes, we have conducted a comparative study of the effects of hydrogen bonding solvents on the photooxidations of 2-methyl-3-phenylthio-2-butene (**1a**), 1-[(4-nitrophenyl)thio]-2,3-dimethyl-2-butene (**2c**), 2-methyl-3-phenylsulfinyl-2-butene (**3**), 2-methyl-3-phenylsulfonyl-2-butene (**6**), and 1-[(4-nitrophenyl)sulfonyl]-2,3-dimethyl-2-butene (**7c**).



The possible reaction modes available to sulfides **1** and **2** certainly make these substituted substrates interesting to study. Vinyl sulfide **1** can conceivably undergo reaction with singlet

oxygen at the alkene double bond via the ene reaction³ to form regioisomeric allylic hydroperoxides **1_G** and **1_{ct}** or a [2+2] cycloaddition to form the dioxetane product (Scheme 1).⁴ Oxidation at sulfur to form a sulfoxide is also a possibility. In conjunction with literature values for previous photooxidations of vinyl sulfides,⁴ allyl sulfides,^{5,6} allyl sulfoxides,^{5,6,14} and allyl sulfones⁶ conducted in a variety of solvents, we will systematically investigate the possibility of hydrogen bonding induced changes in product formation, product distributions, and implications for the mechanisms of these reactions.



2. Results and discussion

2.1. Singlet oxygen photooxidations of vinyl and allyl sulfides

In a typical experiment, 2-methyl-3-phenylthio-2-butene (**1a**, 0.5 M) in benzene-*d*₆ was irradiated at 0 °C with a 500 W tungsten–halogen lamp. Tetraphenylporphine (TPP, 2 × 10^{−4} M) was used as the photosensitizer and dry oxygen

Keywords: Singlet oxygen; Ene reactions; Hydrogen bonding; Sulfides; Sulfoxides; Sulfones.

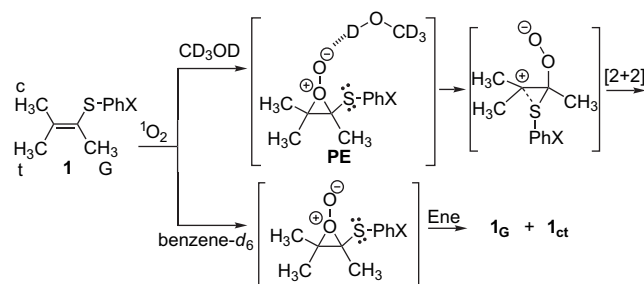
^{*} Corresponding author. Tel.: +1 601 974 1402; fax: +1 601 974 1401; e-mail: stenskl@millsaps.edu

was continuously purged through the system. The photo-oxidation products and their distributions were determined using ^1H NMR. Table 1 lists the quantified products of vinyl sulfides **1a–c** and allyl sulfides **2a–c** in various deuterated solvents.

The results indicate that for **1a** reaction at 0°C occurs at the alkene double bond producing exclusively [2+2] cycloaddition products in CD_3OD and a mixture of ene product and [2+2] product in benzene- d_6 . Clearly a solvent effect is occurring, but initially it was unclear whether hydrogen bonding was involved because Adam⁴ and co-workers previously reported that in CDCl_3 at -25°C only [2+2] products were formed with **1a** and **1b** (Table 1). Furthermore, they reported that the electronic character of the *p*-substituent influences the mode selectivity for vinyl sulfides. Photooxidation of **1c** containing the electron-withdrawing NO_2 group resulted in 70% ene reaction and 30% [2+2] products.

Ando⁷ and co-workers previously suggested that the mode selectivity for vinyl sulfides depends on several factors including solvent and temperature. Protic solvents and low temperatures appear to accelerate the dioxetane mode for vinyl sulfides. Ando indicated that protic solvents would stabilize the proposed perepoxide intermediate (**PE** Scheme 2) by hydrogen bonding with the negatively charged pendant oxygen, thereby allowing the sulfur to attack and form the zwitterion intermediate, which would lead to the [2+2] product. Aprotic solvents would not stabilize **PE** and therefore the ene mode would be expected to predominate.

The different mode selectivity observed in benzene- d_6 and CDCl_3 for **1a** could be attributed to the different temperatures utilized to run these reactions, 0°C in benzene- d_6 and -25°C in CDCl_3 . Again, lower temperatures have been shown⁷ to favor the dioxetane mode. However, as a reviewer indicated, the fact that such a substantial temperature dependence is observed in aprotic solvents indicates that the structure of the transition state leading to products is also important.⁸ Therefore, another contributing factor to the mode selectivity could be the activation entropy leading to a transition state, which resembles the perepoxide. Clearly the structure and subsequent stabilization of the perepoxide is very important in determining the reaction mode with vinyl sulfides.



Scheme 2. Proposed hydrogen bonding stabilization of perepoxide **PE**.

It is interesting to note that when the ene mode does operate with **1** the well-established phenomenon of geminal^{9,10} selectivity, preferential abstraction of the allylic hydrogen geminal to the sulfur group, does not determine the regiochemistry. In benzene- d_6 , 44% *cis*+*trans* hydrogen abstraction was observed with **1a** and in CDCl_3 Adam and co-workers reported 60% *cis*+*trans* hydrogen abstraction with **1c**. Perhaps this regiochemistry can be explained by a favorable interaction between the incoming electrophilic singlet oxygen and the electron rich sulfur. Frimer et al.¹¹ suggested the importance of an initial interaction between the incoming oxygen and the enol ether in their study of the photooxidations of 2,3-dihydro- γ -pyrans. Sulfur may be inducing the same type of directing 'cis' effect with vinyl sulfides **1**.

Geminal selectivity is slightly favored with allyl sulfides **2**. These substrates appear to be unaffected by polarity or hydrogen bonding solvent effects as the ene product distributions are fairly stable over a wide range of dielectric constants. Under our conditions, neither the [2+2] cycloaddition nor sulfide oxidation was competitive with the ene reaction for **2c**. Methylene hydrogen abstraction was not observed either. Clennan¹² previously reported that only at temperatures below -29°C does the oxidation at sulfur become important for **2b**.

Geminal selectivity has been reported⁵ as preferential for the ene reactions of allylic sulfides, sulfoxides, and sulfones. Several reasons have been suggested for this preference including: (1) electronic repulsions between the lone pairs on the sulfur substituent and the negatively charged pendant

Table 1. Ene product ratios resulting from geminal (G)/*cis*+*trans* (ct) hydrogen abstraction or [2+2] cycloaddition products for vinyl sulfides **1a–c** and allylic sulfides **2a–c** where X=H (a), CH_3 (b), and NO_2 (c)

Solvent	Vinyl sulfide 1			Allylic sulfide 2		
	H (1a)	CH_3 (1b)	NO_2 (1c)	H (2a)	CH_3 (2b)	NO_2 (2c)
Benzene- d_6	0/44, 56	—	—	—	—	—
CDCl_3	100 ^a	—	10/60, 30 ^b	—	—	56/44
Acetone- d_6	—	—	—	^d	52/48 ^{b,c}	52/48 ^b
CD_3OD	100	—	—	—	—	54/46
CD_3CN	—	—	—	—	—	54/46

^a Ref. 4.

^b Ref. 5.

^c Ref. 6.

^d Ref. 6. Note only ene products form.

oxygen, which favor the perepoxide intermediate **A** (Fig. 1) that places these groups on opposite sides, and (2) substituted tetramethylethylenes exist in conformations where the geminal hydrogens achieve the perpendicular geometry necessary for abstraction easier than the cis/trans allylic hydrogens.

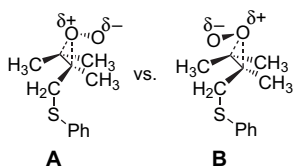


Figure 1. Perepoxide **A** is preferred for allyl sulfides, sulfoxides, and sulfones.

2.2. Singlet oxygen photooxidations of vinyl and allyl sulfoxides

The photooxidation products of vinyl sulfoxide **3**, allyl sulfonides **4a–c**, and the related α,β -unsaturated ester **5d** and acid **5e** are reported in Table 2. Under our conditions only the geminal ene product was formed during photooxidation of **3** in benzene- d_6 ¹³ and CD₃OD. Solvent effects have previously² been reported for **5d** and **5e**; specifically, as the polarity of the solvent increases, geminal selectivity decreases. It has been suggested that the perepoxide leading to **5_G** is somewhat less stabilized in a polar solvent. Therefore, we were surprised to discover that vinyl sulfoxide **3** only forms geminal product, regardless of solvent polarity. Clearly perepoxide **I** leading to **3_G** is more stabilized than the perepoxide intermediate leading to **5_G** (Fig. 2). These results appear to indicate that hydrogen bonding with the solvent is not important in determining the ene product ratio for **3** because only one ene product is formed regardless of solvent choice.

Clennan⁶ and Chen previously reported that the ene product distribution of allyl sulfoxides **4a–c** did not show solvent effects or electronic effects due to the *p*-substituent, and

Table 2. Ene product ratios resulting from geminal (**G**)/cis+trans (**ct**) hydrogen abstraction for vinyl sulfoxide **3**, allylic sulfoxides **4a–c** where X=H (**a**), CH₃ (**b**), and NO₂ (**c**), and **5d,e** where Y=OCH₃ (**d**) and OH (**e**)

Solvent	ϵ^a	Allylic sulfoxides 4			Vinyl sulfoxide 3	
		H (4a)	CH ₃ (4b)	NO ₂ (4c)	t (3)	G (3)
Benzene- <i>d</i> ₆	2.3	—	—	—	100/0	—
CDCl ₃	4.8	—	75/25 ^d	—	—	—
Acetone- <i>d</i> ₆	20.7	74/26 ^c	75/25 ^c	75/25 ^c	—	—
CD ₃ OD	33	—	75/25 ^d	—	100/0	—
CD ₃ CN	36.6	—	—	—	—	—
CD ₃ OD/D ₂ O ^b	51.8	—	—	—	—	—

Solvent	ϵ^a	Allylic sulfones 7			Vinyl sulfones 6	
		H (7a)	CH ₃ (7b)	NO ₂ (7c)	t (6)	G (6)
CDCl ₃	—	—	—	81/19	—	—
Acetone- <i>d</i> ₆	—	83/17 ^b	83/17 ^b	—	—	—
CD ₃ OD	100/0	—	—	73/27	—	—
CD ₃ OD/D ₂ O ^a	100/0	—	—	—	—	—

^a Dielectric constants (ϵ) were taken from Ref. 16.

^b A mixture of 90% CD₃OD and 10% D₂O.

^c Ref. 5.

^d Ref. 6.

^e Ref. 14.

^f Ref. 1.

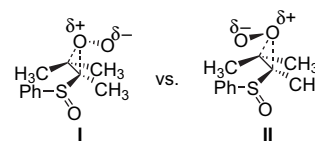


Figure 2. Perepoxide **I** is preferred for vinyl sulfoxides.

only minimal temperature effects were noted with **4b**; at -77°C a 75/25 ratio of **G/ct** was reported but at 20°C a 67/33 ratio of **G/ct** resulted. It is clear that geminal selectivity is overwhelming with all of these substrates.

2.3. Singlet oxygen photooxidations of vinyl and allyl sulfones

Table 3 lists the photooxidation products for vinyl sulfone **6** and allyl sulfones **7a–c**. Under our conditions only ene products were formed from photooxidation of **6** and **7c**. Again, overwhelming geminal selectivity was observed. Neither the *p*-substituent nor choice of solvent affected the product ratios for **7a–c**. Clennan⁵ suggested that the conformational arrangement of the geminal hydrogens in the allylic substrates favors the abstraction of the geminal hydrogens.

Table 3. Ene product ratios resulting from geminal (**G**)/cis+trans (**ct**) hydrogen abstraction for vinyl sulfone **6** and allylic sulfones **7a–c** where X=H (**a**), CH₃ (**b**), and NO₂ (**c**)

Solvent	Allylic sulfones 7			Vinyl sulfones 6	
	H (7a)	CH ₃ (7b)	NO ₂ (7c)	t (6)	G (6)
CDCl ₃	—	—	81/19	—	—
Acetone- <i>d</i> ₆	83/17 ^b	83/17 ^b	—	—	—
CD ₃ OD	100/0	—	73/27	—	—
CD ₃ OD/D ₂ O ^a	100/0	—	—	—	—

^a Solvent mixtures of CD₃OD/D₂O (95/5 and 90/10) were used.

^b Ref. 6.

3. Conclusions

Several interesting conclusions can be drawn from this work:

- (1) The singlet oxygen mode selectivity for vinyl sulfides are susceptible to a combination of factors including the solvent, reaction temperature, and the electronic character of the *p*-substituent. In particular, hydrogen bonding stabilization of the peroxide by a protic solvent favors formation of the dioxetane.
- (2) The overall trend for geminal selectivity in allyl sulfides, sulfoxides, and sulfones increases with increasing size of the allyl substituent; allyl sulfide **2b** produced 52%, allyl sulfoxide **4b** produced 75%, and allyl sulfone **7b** produced 83% of the ene hydroperoxide resulting from geminal hydrogen abstraction.
- (3) Vinyl sulfoxides and sulfones show no solvent effects, which is unexpected when compared to their solvent dependent α,β -unsaturated ester and acid counterparts.

4. Experimental

4.1. General

¹H NMR spectra were recorded on a 60 MHz Varian EM 360-L spectrometer and referenced internally to tetramethylsilane. Melting points were taken in open capillaries on a Mel-Temp II apparatus and are uncorrected. Thin layer chromatography was carried out on 250 μ m layer silica gel flexible plates and column chromatography was carried out with SilicAR CC-4 silica gel obtained from Mallinckrodt. Methyl isopropyl ketone and thiophenol were obtained from Eastman and used as received. Anhydrous HCl, *m*-chloroperoxybenzoic acid, 2,3-dimethyl-2-butene, *N*-bromosuccinimide, benzoyl peroxide, and *p*-nitrothiophenol were purchased from Aldrich and used without further purification. Hydrogen peroxide (30%) and dichloromethane were obtained from Fisher and used as received. Sodium methoxide from Mallinckrodt and formic acid from JT Baker were also used without further purification. Deuterated solvents (benzene, methanol, chloroform, acetonitrile, and deuterium oxide) and photosensitizers (rose bengal, methylene blue, and tetraphenylporphine) were used as received.

4.1.1. 2-Methyl-3-phenylthio-2-butene (1a). It was synthesized according to literature procedures¹⁵ from the reaction of methyl isopropyl ketone (6.55 g, 0.076 mol) and thiophenol (6.06 g, 0.055 mol). After the reaction was cooled to 0 °C, anhydrous HCl was bubbled through the system as thiophenol (10.69 g, 0.097 mol) was added from an addition funnel dropwise for 40 min. After the solution warmed to room temperature, the excess ketone was distilled off at atmospheric pressure (bp 94–95 °C). The crude product then underwent reduced pressure distillation to yield 6 mL of distillate; this was then dissolved in ether, extracted with 2 M NaOH to remove excess thiophenol, and dried with NaSO₄. Lit. bp: 49.5–50 °C (0.03 mm Hg), ¹H NMR (C₆D₆): δ 1.6 (s, 3H), 1.95 (s, 3H), 2.01 (s, 3H), 7.05–7.35 (m, 5H).

4.1.2. 2-Methyl-3-phenylsulfinyl-2-butene (3). Compound **1a** (1.77 g, 0.0099 mol) was oxidized with 30% hydrogen

peroxide (1.127 g, 0.0374 mol) by literature procedures¹⁵ in methanol (39.76 mL) with a formic acid catalyst (0.994 mL). The reaction mixture was extracted with 50 mL of distilled water and 35 mL fractions of ethyl ether, and the organic layer was dried with MgSO₄. Compound **3** was recrystallized with petroleum ether. Lit. mp: 75–76.5 °C, ¹H NMR (CDCl₃) δ 1.6 (s, 3H), 1.8 (s, 3H), 2.2 (s, 3H), 7.2–7.5 (m, 5H).

4.1.3. 2-Methyl-3-phenylsulfonyl-2-butene (6). It was synthesized by the oxidation of **1a** (1 g, 0.0056 mol) with 2.5 molar equiv of *meta*-chloroperoxybenzoic acid (2.42 g, 0.014 mol). Compound **1a** was dissolved in dichloromethane with 1 equiv of sodium bicarbonate. *m*-CPBA was dissolved in dichloromethane in an addition funnel and added dropwise to the sulfide solution for 15 min. The solution was then stirred and cooled over ice for an additional 45 min. The product was washed with 2 \times 20 mL portions of distilled water, 3 \times 20 mL portions of 2 M NaOH, and 20 mL portions of distilled water. The organic layer was dried over MgSO₄ and purified on a silica gel column using 7:3 hexane/ethyl acetate ¹H NMR (CDCl₃) δ 1.93 (s, 3H), 2.08 (s, 3H), 2.28 (s, 3H), 7.4–8.0 (m, 5H).

4.1.4. 1-Bromo-2,3-dimethyl-2-butene. It was prepared using literature procedures¹⁴ by the reaction of 2,3-dimethyl-2-butene (40.4 mmol) and *N*-bromosuccinimide (41.1 mmol) in a solution of carbon tetrachloride (25 mL) with benzoyl peroxide (0.129 mol). The product mixture was distilled under reduced pressure at 65 °C (24 mm Hg). ¹H NMR (CDCl₃) δ 1.7 (s, 3H), 1.77 (s, 6H), 4.08 (s, 2H).

4.1.5. 1-[(4-Nitrophenyl)thio]-2,3-dimethyl-2-butene (2c). It was synthesized from the reaction⁶ of 1-bromo-2,3-dimethyl-2-butene (1.0 g, 6.13 mmol) with *p*-nitrothiophenol (1.18 g, 6.20 mmol) in a solution of absolute ethanol (45 mL) and sodium methoxide (0.335 g, 6.22 mmol). The product was extracted using diethyl ether and water, dried with MgSO₄, and purified through recrystallization from hexanes. Mp: 67–69 °C (lit. mp: 67–68 °C), ¹H NMR (CD₃OD) δ 1.65–2.0 (m, 9H), 3.85 (s, 2H), 7.6 (d, 2H, *J*=9 Hz), 8.3 (d, 2H, *J*=9 Hz).

4.1.6. 1-[(4-Nitrophenyl)sulfonyl]-2,3-dimethyl-2-butene (7c). Compound **2c** (0.217 mmol) was oxidized with 2 equiv of *m*-chloroperoxybenzoic acid (0.434 mmol) in a solution of dichloromethane (5 mL) as per literature procedure.¹⁴ The *m*-CPBA was extracted using saturated NaHCO₃, the products were washed with ether and a saturated NaCl solution, and dried with MgSO₄ before undergoing reduced pressure distillation to remove the solvent. ¹H NMR (CD₃OD) δ 1.2–1.65 (m, 9H), 3.9 (s, 2H), 8.05 (d, 2H, *J*=6 Hz), 8.35 (d, 2H, *J*=6 Hz).

4.2. Singlet oxygen photooxidation procedure for 1a

Samples of **1a** (0.5 M) immersed in an ice bath were photooxidized in benzene-*d*₆ using 2 \times 10⁻⁴ M tetraphenylporphine (TPP) as the photosensitizer and a sodium nitrite filter solution (75 g NaNO₂/100 mL H₂O). After 4 h of photooxidation, all the starting material reacted to form either **1a_{ct}** [¹H NMR (C₆D₆) δ 1.63 (s, 3H), 1.77 (s, 3H), 5.35 (s, 1H, *J*=8 Hz), 5.47 (s, 1H, *J*=8 Hz), 6.92–7.57 (m, 5H)] or

the cleavage products (Scheme 1) of the dioxetane, the thioester [$^1\text{H NMR}$ (C_6D_6) δ 1.12 (s, 3H)] and acetone [$^1\text{H NMR}$ (C_6D_6) δ 1.93 (s, 6H)].

Compound **1a** was completely converted in 12 h by the photooxidation in CD_3OD using 2×10^{-4} M methylene blue as the photosensitizer and a sodium dichromate filter solution (50.25 g $\text{Na}_2\text{Cr}_2\text{O}_7/50$ mL H_2O). The only products observed were the cleavage products of the dioxetane (Scheme 1) the thioester [$^1\text{H NMR}$ (CD_3OD) δ 1.32 (s, 3H)] and acetone [$^1\text{H NMR}$ (CD_3OD) δ 2.5 (s, 6H)].

4.3. Singlet oxygen photooxidation procedure for **3**

Samples of **3** (0.5 M) immersed in an ice bath were photooxidized in both benzene- d_6 using 2×10^{-4} M tetraphenylporphine (TPP) photosensitizer and a sodium nitrite filter solution (75 g $\text{NaNO}_2/100$ mL H_2O). After 2 h of reaction time, **3_G** was the only product. $^1\text{H NMR}$ (C_6D_6) δ 1.0 (s, 3H), 1.32 (s, 3H), 5.39 (s, 1H), 5.77 (s, 1H), 7.0–7.7 (m, 5H), 9.67 (s, 1H).

For the photooxidation of **3** in CD_3OD , a 2×10^{-4} M solution of methylene blue photosensitizer and a sodium dichromate filter solution (50.25 g $\text{Na}_2\text{Cr}_2\text{O}_7/50$ mL H_2O) were used. After 6 h of photooxidation, the only product was **3_G**. $^1\text{H NMR}$ (CD_3OD) δ 1.02 (s, 3H), 1.42 (s, 3H), 6.04 (s, 1H), 6.25 (s, 1H), 7.23–7.8 (m, 5H).

4.4. Singlet oxygen photooxidation procedure for **6**

Samples of **6** (0.25 M) immersed in an ice bath were photooxidized in deuterated methanol and 95/5 and 90/10 mixtures of CD_3OD and D_2O using a 5×10^{-4} M solution of rose bengal photosensitizer and a potassium dichromate filter solution (1.0001 g $\text{K}_2\text{Cr}_2\text{O}_7/200$ mL H_2O). After 18 h of photooxidation, **6_G** formed as the only product. $^1\text{H NMR}$ (CD_3OD) δ 1.42 (s, 6H), 6.4 (s, 1H), 6.62 (s, 1H).

4.5. Singlet oxygen photooxidation procedures for **2c** and **7c**

Compound **2c** was photooxidized in deuterated chloroform, acetonitrile, and methanol, while **7c** was reacted in both deuterated chloroform and methanol. A 2×10^{-4} M solution of methylene blue photosensitizer and a 0.2% w/v filter solution of rhodamine B were used in these photooxidations and all were conducted in an ice bath. Ratios of **2c_G**/**2c_{ct}** and **7c_G**/**7c_{ct}** were produced for each reaction.

2c_G: $^1\text{H NMR}$ (CD_3CN) δ 1.40 (s, 6H), 3.9 (s, 2H), 5.3 (s, 1H), 5.4 (s, 1H), 7.5 (d, 2H), 8.2 (d, 2H), 9.3 (s, 1H).

2c_{ct}: $^1\text{H NMR}$ (CD_3CN) δ 1.42 (s, 3H), 1.80 (s, 3H), 3.5 (s, 2H), 5.1 (s, 2H), 7.5 (d, 2H), 8.2 (d, 2H), 9.3 (s, 1H).

7c_G: $^1\text{H NMR}$ (CD_3OD) δ 1.26 (s, 6H), 4.18 (s, 2H), 5.5 (s, 2H), 8.1 (d, 2H), 8.4 (d, 2H).

7c_{ct}: $^1\text{H NMR}$ (CD_3OD) δ 1.57 (s, 3H), 1.72 (s, 3H), 3.84 (s, 2H), 4.80 (s, 2H), 8.1 (d, 2H), 8.4 (d, 2H).

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