Spectral and Chemical Properties of Dimethyldioxirane as Determined by Experiment and ab Initio Calculations

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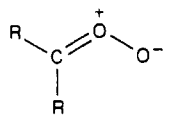
Dimethyldioxirane (**2b**), prepared by the reaction of potassium monoperoxy sulfate with acetone under buffered conditions as a yellow acetone solution, exhibits a ^{13}C resonance at 102.30 ppm. Ab initio calculations are in good agreement with this experimental value. At room temperature the dioxirane **2b** persists for ca. 7 h. The unexpected stability of this most strained cyclic peroxide is rationalized in terms of *gem*-dimethyl substitution, imparting thermodynamic as well as kinetic stabilization, as suggested by ab initio calculations. Oxygen transfer by dioxirane **2b** to thianthrene 5-oxide (SSO) reveals a dominating nucleophilic character, causing mainly oxidation of the sulfoxide sulfur.

Among the reaction intermediates, the carbonyl oxides **1** and the dioxiranes **2** have received much attention from



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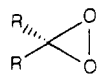
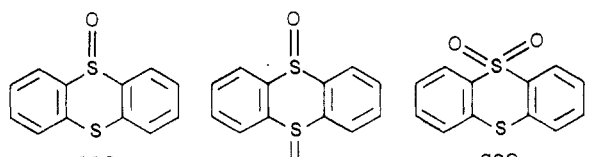


2a, R=H
b, R=CH_3

the experimental and theoretical point of view, especially during the last few years.[1-3] Although carbonyl oxides have been invoked some 35 years ago as key species in the mechanism of ozonolysis,[4] only recently was it possible to provide spectral data on these elusive entities by means of matrix isolation.[1] Dioxiranes, on the other hand, have a much later history, the parent system **2a** having been spectroscopically detected in the gas phase.[5] In fact, the relatively stable dimethyldioxirane (**2b**) was recently isolated in acetone solution and a number of oxygen-transfer reactions reported.[6]

In the interest of differentiating the nucleophilic character of these distinct chemical species in their oxygen transfer (epoxidation, sulfoxidation, etc.), we developed thianthrene 5-oxide (SSO) as a convenient mechanistic probe.[7] Indeed, the carbonyl oxides **1** with their nucleophilic pendant oxygen produced proportionally more sulfone SSO_2 than disulfoxide SOSO compared to the dioxiranes **2**. However, in those experiments[7] the dimethyldioxirane (**2b**) was prepared in situ from acetone and potassium monoperoxy sulfate, and the possibility that the "true" electronic character of the dioxirane could be obscured by oxygen transfer from unknown intermediary oxidants in that reaction could not be rigorously excluded.



SSO SOSO SSO_2

It seemed to us, therefore, advisable to check our previous oxygen-transfer results[7] with the thianthrene 5-oxide (SSO) probe by employing the recently isolated[6] dimethyldioxirane (**2b**). We used this opportunity to reinvestigate the spectroscopic properties of **2b** and to compare these with the results of ab initio calculations carried out for **1**, **2a,b**, and appropriate reference compounds.

Results and Discussion

We found it convenient and advantageous to simplify the published[6a] procedure. For large-scale preparations (more than 300 mL of 0.1 M solutions of **2b** in acetone), best results were obtained when vigorous mechanical stirring was used, a carrier gas (argon or nitrogen), moderately reduced pressure (ca. 150–200 Torr; water aspirator), an efficient double-jacketed spiral condenser, a reaction temperature of ca. 20 °C, and addition of the potassium monoperoxy sulfate in ca. 100-g portions over a period of 15 min. Under these operations, besides the dry ice cooled receiving flask, only one additional trap was necessary. The pale yellow dioxirane solution could be concentrated maximally to ca. 0.10 M by means of frac-

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Table I. ^{13}C NMR Chemical Shifts of Dimethyldioxirane (2b) and Appropriate Reference Compounds Relative to Me_4Si

molecule	carbon	ppm	ref
dimethyldioxirane (**2b**)	CH_3	22.69	this work,
	C	102.30	and 6d, e
1,2-dioxetane	CH_2	76.14	9
acetone	CH_3	30.71	this work
	CO	206.52	
cyclopropane	CH_2	−6.2	*a*
oxirane	CH_2	37.4	*a*
n-propane	CH_2	12.5	*a*
dimethoxymethane	CH_2	109.9	*b*
1,3-dioxane	$C(O-)_2$	94.8	*b*
1,1-dimethylcyclopropane	$C(CH_3)_2$	11.3	*b*
tetramethyl-1,2,4,5-tetroxane	$C(CH_3)_2$	106	6d

[a] Breitmaier, E.; Voelter, W. *^{13}C NMR Spectroscopy*, 2nd ed.; Verlag Chemie: Weinheim, West Germany, 1978. [b] Kalinowski, H.-O.; Berger, S.; Braun, S. ^{13}C NMR Spektroskopie; Thieme Verlag: Stuttgart, West Germany, 1984.

tional distillation (bath temperature ca. 0 °C and ca. 35 Torr). Either the dioxirane **2b** and acetone form an azeotrope at this concentration or the dioxirane decomposes about at the same rate as it is being concentrated.

The yellow acetone solutions of **2b** could be stored in the freezer (ca. −20 °C) for weeks, but at room temperature (ca. 22 °C) the dioxirane content was consumed within ca. 7 h, as monitored by UV spectrometry. Its decomposition kinetics was not first order as expected but exhibited a pronounced inhibition period.

For small-scale preparation of dioxirane **2b** (ca. 10–15 mL of ca. 0.10 M solutions), we found it more practical to use efficient magnetic stirring, no external carrier gas (sufficient oxygen gas is self-produced during the reaction), and to add the potassium monoperoxy sulfate all at once, but to maintain otherwise the same reaction conditions as in the large-scale preparation.

For the quantitative determination of the dioxirane **2b** in these acetone solutions, three methods were utilized. These consisted of iodometric titration for peroxide content, comparison of the methyl proton resonance (1.65 ppm) vs. the C-13 satellite signal of acetone, and oxidation of methyl phenyl sulfide to its sulfoxide with subsequent electronic integration of the phenyl proton resonances of the sulfoxide vs. sulfide. All three methods gave within experimental error consistently ca. 0.10–0.11 M dioxirane **2b** as maximum concentration.

The following characteristic spectral data were obtained for the dimethyldioxirane (**2b**) solutions in acetone. The pale yellow solution exhibited a maximum UV absorption of λ 335 nm (ϵ 10), with broad tailing out to 450 nm, similar to that reported.[6a] A freshly distilled solution showed only tailing to 390 nm, but on standing in the freezer overnight the tailing extended to 450 nm.

The proton NMR spectrum reveals only one singlet at 1.65 ppm, as previously observed[6a] for the dioxirane **2b**. The carbon NMR spectrum (100 MHz) at −15 °C showed absorptions at 22.69 and 102.30 ppm (relative to Me_4Si), respectively, for the methyl (q) and ring carbons (s).[6a,d] The 102.30 and 22.69 ppm signals disappeared on reduction with methyl phenyl sulfide. Meanwhile, similar results were obtained by using ^{13}C-enriched dioxirane.[6d,e]

Because of the large discrepancy between our results and those reported[6a] for the ring carbon resonance of dioxirane **2b**,[8] we felt obliged to back up our observations with theoretical estimates for this critical value. In Table I, known ^{13}C shift values are listed that provide a basis to estimate the position of this signal. Extrapolating the ^{13}C shift values for cyclopropane and oxirane to the one of **2a**, a shift value of ca. 80 ppm can be predicted. A somewhat higher value is obtained when comparing $^{13}C(H_2)$ shifts for propane, dimethoxymethane, and 1,3-dioxane (Table I). The difference in the ^{13}C absorptions of cyclopropane and 1,1-dimethylcyclopropane (Table I) suggests that geminal methyl groups lead to a downfield shift of ca. 20 ppm for a substituted ring carbon. Hence, the signal for the ring carbon of **2b** should appear between 100 and 110 ppm.

Table II. Ab Initio NMR Chemical Shifts[a]

molecule	^{13}C		^{1}H		^{17}O
dioxirane (**2a**)	CH_2	82.6	CH_2	4.32	250
dimethyldioxirane (**2b**)	C	99.2	H_i	0.31	330
	CH_3	17.0	H_o	0.73	
dioxetane	CH_2	65.5	CH_2	3.82	268
acetone	CO	23.5	H_i	1.16	680
	CH_3	209.7	H_o	1.01	

[a] All values in ppm relative to Me_4Si (^{13}C, ^{1}H) or H_2O (^{17}O). Subscripts i and o denote in-plane and out-of-plane protons with the reference plane given by the positions of the three C atoms. MP2/6-31G* geometries have been used for **2a**[3a] and **2b** (see Figure 1). Dioxetane geometry: Schmidt, T.; Cremer, D.; unpublished results. Acetone geometry: ref 3d.

Table III. Isodesmic Stabilization Enthalpies (cf. eq 1)[a]

molecule H_2CXY	$\Delta\Delta H(1)$	molecule H_2CXY	$\Delta\Delta H(1)$
n-propane	8.5	cyclopropane	10.0[b]
dimethoxymethane	13.9	oxirane	16[c]
ethene	12.0	oxirane (O-protonated)	25[c]
formaldehyde	21.2	dioxirane	21.4[d]

[a] $\Delta\Delta H(1)$ in kcal/mol. $\Delta H_f°(298)$ values from Cox and Pilcher [Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970]. [b] $\Delta H_f°$ of 1,1-dimethylcyclopropane from Fuchs et al. [Fuchs, R.; Hallman, J. H.; Perlman, M. O. *Can. J. Chem.* **1982**, *60*, 1832–1835]. [c] Estimated from ab initio reaction energies $\Delta E(1)$. Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800–3810. [d] MP2/6-316* value of $\Delta\Delta E(1)$.

In Table II, ab initio values of the NMR chemical shifts for **2a**, **2b**, the parent dioxetane, and acetone obtained with the IGLO approach (see Experimental Section) are listed. These values refer to isolated molecules in their equilibrium geometries at 0 K. Thus, neither a temperature dependence of the NMR signals nor effects of intermolecular interactions are considered in the calculations. As a consequence, ab initio shift values differ from experimental shifts measured in liquid or solution phases. For example, the theoretical ^{13}C shift value of the parent dioxetane is 10.6 ppm lower than the reported experimental shift[9] (Table I). On the other hand, calculated ^{13}C shift values of **2b** (99.2 and 17.0 ppm, Table II) deviate by just 3 and 5.7 ppm, respectively, from the experimental ones (102 and 22.7 ppm, Table I), suggesting a ^{13}C shift of ca. 86 ppm for the parent dioxirane **2a**. (**Note added in proof**: After completion of this work we were informed[6e] that the experimental ^{17}O shift value is 302 ppm (relative to external $H_2{}^{17}O$). In view of the large sensitivity of ^{17}O NMR resonance signals on experimental conditions, the agreement with our theoretical value (330 ppm, Table II) is satisfactory. Hence, the dioxirane structure **2b** for the product of the monoperoxy sulfate–acetone reaction is confirmed.)

(8) While this work was in progress (cf. ref 3d), Prof. R. W. Murray has informed[6d] us that the 214 ppm ^{13}C resonance is an artifact.

(9) Adam, W.; Baader, W. J. *Angew. Chem.* **1984**, *96*, 156–157; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 166–167. See also: Adam, W. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; pp 828–920.

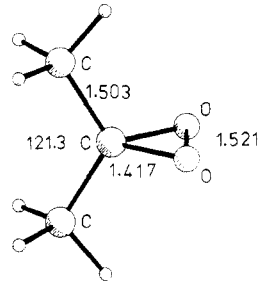

Figure 1. Ab initio geometry of dimethyldioxirane (**2b**); bond lengths in Å and bond angles in degrees.

In view of the labile nature of **2a** (decomposition at −60 °C),[5] it is surprising that the dimethyl derivative **2b** can be kept at room temperature for several hours. We attribute this increase in stability to the electronic and steric effects of the geminal methyl groups. Such stabilization of *gem*-dimethyl substitution can be estimated by the isodesmic reaction of eq 1. Changes in reaction enthalpies

$$(CH_3)_2CXY + 2CH_4 \rightarrow H_2CXY + 2CH_3CH_3 \quad (1)$$

$\Delta\Delta H(1)$ for appropriate reference compounds are listed in Table III. They are all positive, thus indicating that geminal methyl groups always lead to stabilization of the H_2CXY molecule. The degree of stabilization depends on both the hybridization of the quarternary carbon atom and the electronegativity of its X and Y substituents. Ethylene is more stabilized by two methyl groups than propane, while cyclopropane takes an intermediate position (Table III). For X = Y = OCH_3, the stabilizing effect of methyl substitution is larger than that for X = Y = CH_3 (Table III). Methyl acts as an electron-releasing substituent that is more effective the larger the electron deficiency at the substituted carbon is. The isodesmic reaction energy calculated for **2a**, i.e., $\Delta E(1)$ = 20 kcal/mol (Table III), nicely fits into these trends and explains the increase in the *thermodynamic* stability of dialkyl dioxiranes.

Ab initio calculations reveal that the breaking of the oxygen–oxygen bond of **2** requires considerably less energy than that of a carbon–oxygen bond.[10] We expect that decomposition of **2a** or **2b** will be initiated by oxygen–oxygen bond lengthening (widening of the COC angle). This causes a rehybridization of the ring carbon and a subsequent decrease of the exocyclic angle. The latter is 117° in **2a**[3a,5b] but 120° in **2b** (Figure 1). Clearly, enhanced steric interactions between the methyl groups upon decrease of the CCC angle will hinder any decomposition of **2b** that is initiated via oxygen–oxygen bond rupture. We suggest that *gem*-dialkyl substitution leads also to increased *kinetic* stability of dioxiranes, enabling the impressive feat of isolating[6] acetone solutions of this to date most strained cyclic peroxide.

The data on the oxygen transfer by dioxirane **2b** to thianthrene 5-oxide (SSO) are collected in Table IV. Clearly, the nucleophilicity parameter (X_{Nu}) for the dioxirane **2b** depends on the medium. When the isolated authentic dioxirane **2b** is added to a spent solution from the in situ oxygen transfer (entry 5 in Table IV), within experimental error (±0.03), nearly the same X_{Nu} value is obtained as in the in situ oxygen transfer (entry 4 in Table IV), i.e., 0.74 vs. 0.71. In methylene chloride X_{Nu} = 0.77 (entry 2 in Table IV) and in acetone X_{Nu} = 0.85 (entry 1 in Table IV). However, it is gratifying that in the same medium (biphasic phosphate buffer and methylene chloride system) the nucleophilic character of the isolated authentic and of the in situ generated dioxirane **2b** are the same, i.e., $X_{Nu} \sim 0.70$. Consequently, the same molecular species, namely dioxirane **2b**, serves as donor in the oxygen transfer to SSO,[2d] irrespective of whether in situ generated[2d] or isolated dioxirane **2b**[6a] is used. This high nucleophilicity of the genuine dimethyldioxirane (**2b**) is unexpected, especially in view of its chemical behavior such as oxidizing pyridine to its N-oxide, primary amines (aliphatic and aromatic) to their nitro compounds, aromatic hydrocarbons to arene oxides, alkenes to epoxides, or alkanes to alcohols.[6]

Table IV. Nucleophilic Character (X_{Nu}) of Dimethyldioxirane (2b) in the Oxygen Transfer to Thianthrene 5-Oxide (SSO)

medium[a]	convn[b] (%)	product composition[b] (%)			X_{Nu}[c] (±0.03)
		SSO_2	SOSO	$SOSO_2$	
1. acetone	33	84.9	15.1		0.85
2. CH_2Cl_2	16	77.2	22.8		0.77
3. phosphate buffer,[d] CH_2Cl_2	40	54.6	17.9	27.5	0.68
4. phosphate buffer, CH_2Cl_2, $KHSO_5$[e]	26	61.0	17.3	21.7	0.71
5. spent solution[f]	36	58.8	10.4	30.8	0.74

[a] Concentration of SSO (acetone or CH_2Cl_2) ca. 0.008 M. [b] % conversion of SSO into SSO_2, SOSO, and $SOSO_2$, determined by HPLC on a silica gel column, using *p*-nitrophenyl sulfone as internal standard. [c] Cf. ref 7. [d] To phosphate buffer (3 mL) and CH_2Cl_2 (3 mL) was added 0.092 M dioxirane–acetone (0.1 mL) and SSO (0.02 mmol). [e] Dioxirane generated in situ; in all other entries authentic dioxirane was used. [f] To a spent solution of in situ generated dioxirane (after 19 h at room temperature) without SSO was added subsequently first SSO and then the dioxirane in acetone.

Experimental Section

Instrumentation. ^1H NMR and ^{13}C NMR were recorded on a Bruker WM 400-MHz spectrometer. Samples were measured in acetone, with deuteriated acetone (15%) being added for deuterium lock. UV spectra were obtained on a Perkin-Elmer 330 UV–vis spectrophotometer. Analytical HPLC was performed on a Kontron HPLC Model, with a silica gel column (25 cm × 4 mm) purchased from the Bischoff Co., Leonberg, West Germany.

Materials. Commercially available reagents were used directly without purification. Potassium monoperoxy sulfate ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was obtained as a generous gift from Peroxid-Chemie GmbH. Acetone (C.P.) was used in all experiments.

Preparation of Dimethyldioxirane Solution. (a) Large Scale. A 4-L, four-necked, round-bottomed flask, containing a mixture of water (440 mL), acetone (320 mL, 4.35 mol), and sodium bicarbonate (240 g), was equipped with a mechanical stirrer, an addition funnel for solids, containing potassium monoperoxy sulfate (500 g, 0.813 mol), a gas inlet tube, and an air condenser, loosely packed with glass wool. The exit of the air condenser was connected to the top entry of a high-efficiency double-jacketed spiral condenser, supplied with methanol coolant (−78 °C to −85 °C) from a Colora Ultra Cryostat, Model KT 290S. The bottom exit of the high-efficiency condenser was attached in succession to a receiving flask (500 mL) and three cold traps, all being kept at dry ice–acetone temperature. Argon was passed through the reaction flask, while the solid potassium monoperoxy sulfate was added in five portions at 3-min intervals, stirring the mixture vigorously at room temperature (20 °C) and applying simultaneously a slight vacuum (ca. 180 Torr, water aspirator). The effluent was collected as a yellow solution consisting of dimethyldioxirane and acetone, mainly in the receiving flask (300 mL, ca. 0.100 M in dioxirane), an appreciable amount (26 mL, 0.090 M) in the first trap and negligible amounts in the second trap (8 mL, 0.088 M) and third trap (5 mL, 0.094 M). The

(10) For example, in the presence of an electrophile (H^+) carbon–oxygen bond rupture requires five times more energy than oxygen–oxygen rupture. Gauss, J.; Cremer, D., unpublished results.

combined yellow solutions were stored in the freezer for subsequent use.

(b) Small Scale. A 250-mL, three-necked, round-bottomed flask, containing a mixture of water (20 mL), acetone (13 mL, 0.177 mol), sodium bicarbonate (12 g), and a magnetic stirring bar, was equipped with an addition funnel for solids containing potassium monoperoxy sulfate (25 g, 0.041 mol) and an air condenser (set up as described above), except only a receiving flask (25 mL), cooled by means of dry ice–acetone, was required. While applying a slight vacuum (ca. 180 Torr, water aspirator), the solid potassium monoperoxy sulfate was added in one portion, stirring vigorously at room temperature (ca. 20 °C). The yellow dioxirane–acetone solution (11 mL, 0.099 M) was collected in the receiving flask.

(c) Fractionation. A 50-mL, round-bottomed flask, containing 25 mL of 0.096 M dimethyldioxirane–acetone solution, was equipped with a 25-cm Vigreux fractionation column, whose top exit was connected to the top entry of a high-efficiency double-jacketed, spiral condenser, supplied with methanol coolant (−78 °C) from a cryostat, and bottom exit to a receiving flask (25 mL), which was cooled by means of dry ice–acetone. At an ice–water bath temperature and an intermediate vacuum of 32–37 Torr (mechanical pump), during the first 60 min, 14 mL of a yellow solution of the dimethyldioxirane in acetone (ca. 0.11 M) distilled, and during the next 30 min another 7 mL (ca. 0.092 M). All efforts to concentrate the dioxirane solution in acetone beyond ca. 0.11 M by vacuum fractionation under a broad range of pressure, temperature, and speed of distillation failed.

Spectroscopic Measurements on Dimethyldioxirane. (a) Ultraviolet. The UV spectrum of dimethyldioxirane was measured by using 1-cm quartz cells and acetone as reference solvent: λ_{max} = 335 nm (ϵ 10) with a tail extending to 450 nm.[6a]

(b) NMR. The ^{13}C NMR spectrum of a freshly prepared solution of dimethyldioxirane (ca. 0.11 M) was recorded in acetone by using acetone-d_6 (15%) lock. The proton-decoupled spectrum was accumulated at −15 °C for 1 h, exhibiting absorptions at 22.69 (q) and 102.30 (s) ppm respectively for the methyl and dioxirane carbons.[6d,e] An additional singlet at 125.63 ppm was also detected (carbon dioxide),[6d] which decreased in intensity on long accumulation or on warming up to 40 °C. Strong acetone absorptions were also observed at 30.71 (q) and 206.52 (s) ppm for the methyl and carbonyl carbons (relative to Me_4Si).

The ^1H NMR spectrum of dioxirane in acetone solution showed besides the solvent signal a single absorption at δ 1.65 (s) for the methyl protons.[6a]

Assays for Dioxirane Content. (a) Phenyl Methyl Sulfide. A solution of dimethyldioxirane (1.00 mL) in acetone was mixed with a acetone-d_6 solution of phenyl methyl sulfide (0.4 mL, 0.55 M). The solution was allowed to stand at room temperature for 5 min and the ^1H NMR spectrum was taken. Signal integration of the sulfoxide phenyl protons (δ 7.6–7.9) vs. those of the sulfide (δ 7.1–7.3) gave a 1:1 ratio. Assuming all dioxirane had reacted, the concentration of dioxirane solution in acetone was calculated to be 0.11 M.

(b) Iodometric Titration. A solution of dimethyldioxirane in acetone (1.00 mL) was added to a 3:2 mixture of acetic acid–acetone solution (2 mL). Saturated aqueous KI solution (2 mL) was then added together with some dry ice to deaerate and the resulting mixture was stored in the dark at room temperature (ca. 20 °C) for 10 min. The sample was diluted with water (5 mL) and three aliquots (1.00 mL) were titrated with aqueous $Na_2S_2O_3$ (0.001 N) solution, affording a dioxirane concentration of 0.11 M.

(c) ^1H NMR. The height of the methyl proton signal of the dioxirane (at δ 1.65) was compared with the ^{13}C satellite peak to the right of acetone (0.5%), resulting in a 1% or 0.1 M dioxirane solution.

Oxidation of Thianthrene 5-Oxide. (a) Authentic Dioxirane. To 4.60 mg (0.0200 mmol) of thianthrene 5-oxide (SSO) in 2.5 mL of acetone or 2.5 mL of CH_2Cl_2 was added 0.1 mL of a 0.092 M (0.0092 mmol) freshly distilled dioxirane solution in acetone and the resulting mixture was allowed to stand at ca. 20 °C for 20 min. The acetone was removed, and the residue taken up in 1 mL of CH_2Cl_2 and dried over anhydrous $MgSO_4$. The reaction mixture was analyzed by HPLC for thianthrene 5,5-dioxide (SSO_2), thianthrene 5,10-dioxide (SOSO), and thianthrene 5,5,10-trioxide ($SOSO_2$), by eluting with a 96:4:0.4 mixture of petroleum ether (64–68 °C)–ethyl acetate–methanol, at a flow rate of 3.0 mL/min, using *p*-nitrophenyl sulfone as standard.[11] The quantitative results are given in Table IV.

(b) In Situ Generated Dioxirane.[11] A solution of potassium monoperoxy sulfate (408 mg, 1.61 mmol) and EDTA (ca. 20 mg), dissolved in doubly distilled water (10 mL), was added to a biphasic system of 0.60 M KH_2PO_4/Na_2HPO_4 buffer solution (20 mL, pH 7.5), CH_2Cl_2 (30 mL), acetone (0.83 mL, 11.3 mmol), 18-crown-6 (250 mg, 0.946 mmol), and SSO (180 mg, 0.775 mmol). The resulting mixture was stirred at 0 °C for 1 h and then at 23 °C for 19 h. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL), and the combined CH_2Cl_2 solutions were dried over anhydrous $MgSO_4$ and analyzed by HPLC as above. The results are shown in Table IV.

Ab Initio Calculations. The geometry of **2b** has been computed at the MP2 level of theory,[12] employing the 6-31G* basis set.[13] Previous investigations[3a] have revealed that peroxides are fairly well described at the MP2/6-31G* level. NMR chemical shifts have been determined with the IGLO (individual gauge for localized orbitals) method[14] using a (9s5p1d/5s1p) Huzinaga basis[15] contracted to [51111, 2111, 1/311, 1]. The exponents of the polarization functions of this basis are 1.0 for d(C) and d(O), respectively, and 0.65 for p(H).

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Registry No. **2a**, 157-26-6; **2b**, 74087-85-7; SSO, 2362-50-7; SSO_2, 2362-53-0; SOSO, 951-02-0; $SOSO_2$, 2362-54-1; acetone, 67-64-1; 1,2-dioxetane, 6788-84-7.

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