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Singlet oxygen generation from poly[4-diacetoxyiodo]styrene and hydrogen peroxide

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Abstract: Treatment of hydrogen peroxide with a polymer-supported hypervalent iodine compound, poly[4-diacetoxyiodo] styrene (PDAIS), generates singlet molecular oxygen ($^1O_2$). Singlet oxygen generation was proved by trapping with typical organic compounds such as conjugated dienes, aromatic dienes, and electron-rich alkene. When compared to monomer analogue, the use of PDAIS in peroxidation of substrates gave slightly better yields (45%–96%). Regeneration and reuse of PDAIS showed similar activity. The mechanism underlying generation of singlet oxygen and reaction scope was examined.

Key words: Hydrogen tetroxide, oxidation, peroxyiodane, polymer-supported hypervalent iodine, singlet oxygen

1. Introduction

Singlet molecular oxygen ($^1O_2$), an unstable, energy-rich active oxygen species, was first reported in the 1960s. Since then, peroxidation of organic molecules to endoperoxides or alkyl hydroperoxides by singlet oxygen has received much attention because of its unique reactivity and high selectivity toward organic substrates such as olefins, conjugated dienes, heterocyles, sulfides, and phenols.[1,2] $^1O_2$ also plays diverse, important roles in intracellular signaling mechanisms, in reactions leading to cell death,[3–5] and, remarkably, in photodynamic therapy, which is a noninvasive procedure used for the cure of malignant tumors and age-related macular degeneration.[6–9] Among the various methods available for the production of $^1O_2$, the photochemical method involving the irradiation of oxygen gas in the presence of an organic dye such as rose bengal, methylene blue, or porphyrins is the most commonly used.[10,11] In addition, a number of chemical methods for singlet oxygen generation from hydrogen peroxide have been reported.[12–14] For example, disproportionation of hydrogen peroxide catalyzed by molibdate ions affords $^1O_2$ in aqueous alkaline media.[15,16] However, this method is restricted to low-molecular-weight substrates or substrates bearing hydrophilic groups.[17,18]

Hypervalent iodine reagents are reactive, highly selective, and compatible with a range of functional groups, because of which they are popular in natural product synthesis. These reagents are suitable alternatives to heavy metal-based reagents used in industry.[19] In particular, *bis*(trifluoroacetoxy)iodobenzene **1a**, (diacetoxy)iodobenzene **1b**, iodosylbenzene **1c**, iodylbenzene **1d**, and Dess–Martin periodinane **1e** have been extensively used in a variety of useful oxidative transformations (Figure).[20–22] However, oxidation of organic substrates with these reagents results in a stoichiometric amount of iodobenzene as waste, which is troublesome to recover and reuse because it is volatile and more soluble in typical organic solvents.[23] On the other hand,

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polymer-supported reagents are generally easy to regenerate, less toxic, and pose a reduced risk of explosion. For this reason, a number of research groups have attempted to develop iodobenzene-based polymer-supported hypervalent iodine reagents having (diacetoxy)iodo groups (**2b**),[24–27] hydroxy(tosyloxy)iodo groups (**2c**),[27] and 1,2-benziodoxol-3-one groups (**2d**)[28] (Figure). PDAIS (**2b**) was successfully used in several organic transformations including oxidation of alcohols,[29] α-hydroxylation of ketones,[29] oxidative 1,2-aryl migration of alkyl aryl ketones,[30] oxidative esterification of primary alcohols,[31,32] and oxidative ligand-directed acetoxylation of arene and alkane C–H bonds.[33] Togo showed that reactivity of PDAIS (**2b**) is similar to that of their monomeric compound **1b**.[30]

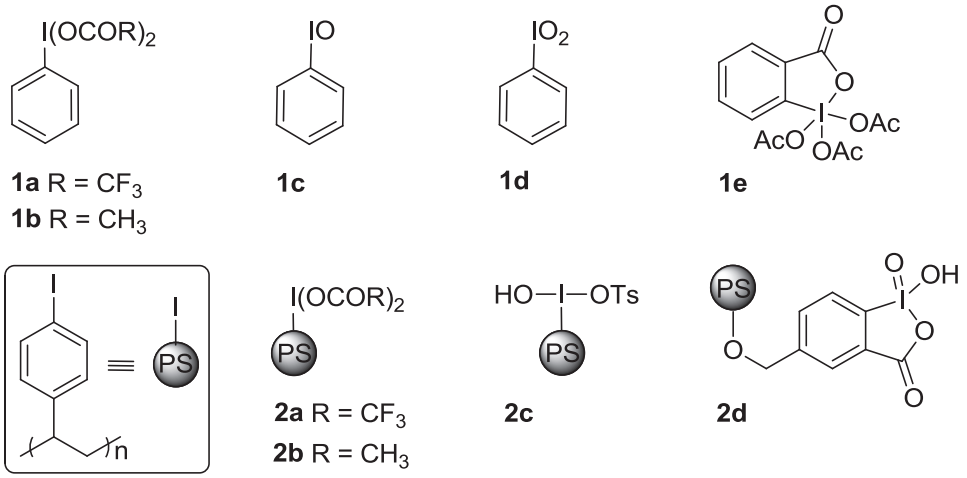
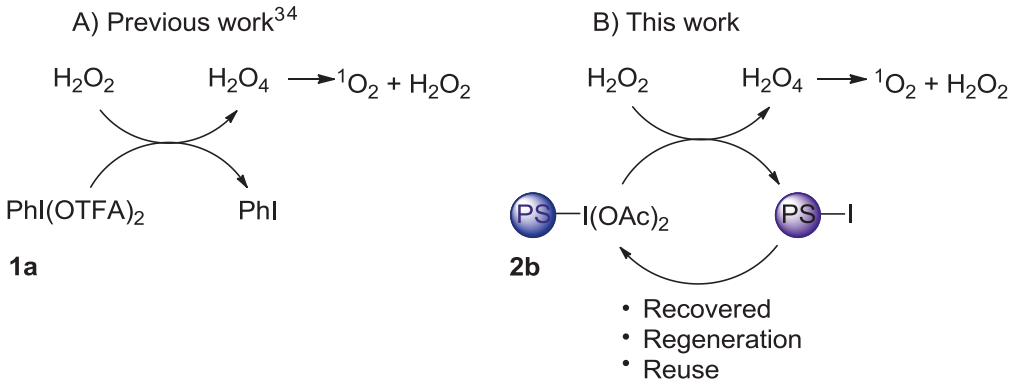


Figure. Examples of hypervalent and polymer-supported hypervalent iodine compounds.

We previously described the decomposition of hydrogen peroxide by hypervalent aryl-λ^3-iodane PIFA **1a** to generate singlet oxygen, which can be trapped by the addition of singlet oxygen acceptors.[34,35] Recently, we reported a new method for the generation of $^1O_2$ in which iodosylarene (ArIO) is generated in situ from an iodoarene (ArI) and H_2O_2 in the presence of methyltrioxorhenium as a catalyst. Further reaction of ArIO with H_2O_2 produced singlet oxygen.[36] Herein, I introduce the first example of poly[4-diacetoxyiodo]styrene (PDAIS-**2b**)-induced activation of hydrogen peroxide to generate singlet oxygen for the peroxidation of organic substrates, regeneration and reuse of **2b** for the same reactions, and comparison of the product yield with that obtained using our previously reported PIFA/H_2O_2 system (Scheme 1).[34]



Scheme 1. Generation of singlet oxygen in organic media.

2. Results and discussion

2.1. Preparation of PDAIS (2b)

Polymer-supported hypervalent(III) reagent PDAIS (**2b**) was synthesized by the oxidation of commercially available iodopolystyrene (PS-I) with peracetic acid, which was freshly prepared from acetic anhydride and hydrogen peroxide.[37,38] The results of IR spectroscopy, elemental analysis, and iodometry analysis[33] performed on **2b** suggested that most of the iodine atoms in the polystyrene ring were oxidized to the corresponding (diacetoxy)iodo groups, which is in agreement with the literature yield (83%).[37]

2.2. Peroxidation of organic substrates by PDAIS and H_2O_2

Treatment of a suspension of PDAIS in dichloromethane with 35% hydrogen peroxide led to the release of oxygen bubbles and yielded a solid, which was filtered off from the reaction medium and washed with ether. IR spectroscopy confirmed that the product was iodopolystyrene. To determine whether the PDAIS/H_2O_2 system could generate singlet oxygen or not, α-terpinene **3a** was selected as the singlet oxygen acceptor. Compound **3a** can be aromatized by PDAIS to give *p*-cymene **5** or peroxidized with $^1O_2$ to form ascaridole **4a**, rendering it a good diagnostic tool for product distribution. Oxidation of **3a** with the PDAIS-hydrogen peroxide system was first studied as the model reaction in CH_2Cl_2 at room temperature for 3 h. The decreasing of **3a** and the appearance of the signals belonging to **4a** and **5** were observed by the ^{1}H NMR spectra of the reaction mixture that was separated from the polymer by filtration, providing evidence for the generation of singlet oxygen. To examine the solvent effect on the peroxidation of model substrate **3a** and the product ratio, tetrahydrofuran (THF), ether, acetone, dichloromethane (DCM), 1,2-dichloroethane, and carbon tetrachloride were selected for solvent screening. Two equivalents of PDAIS were sufficient for the full conversion of the starting reactant **3a** in all the tested solvents, although the yields of **4a** and the product ratios (**4a**:**5**) varied according to the solvent (Table 1). The results presented in Table 1 indicate that, while the best product ratio (**4a**:**5**) was observed in DCM or ether, the optimum yield of **4a** was obtained in DCM (Table 1, entry 2). The poor solubility of hydrogen peroxide and excellent dispersion of PDAIS in DCM allowed for controllable singlet oxygen production with the use of the PDAIS/H_2O_2 system. Therefore, DCM was selected as the optimal reaction solvent and the optimal reaction conditions were determined to be as follows: ratio of PDAIS/H_2O_2 to **3a**, 2:10; room temperature; reaction time, approximately 3 h. In the control experiments, **4a** was not observed in the absence of PDAIS or H_2O_2, while the reaction of **3a** with PDAIS in the absence of H_2O_2 afforded **5**. Thus, it was confirmed that the use of both PDAIS and H_2O_2 is essential to generate singlet oxygen.

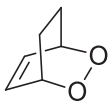
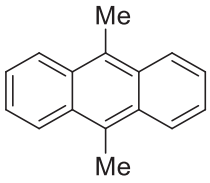
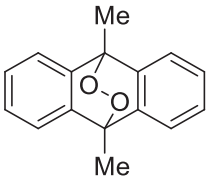
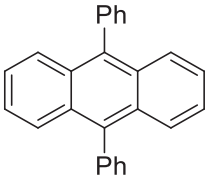
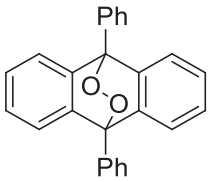
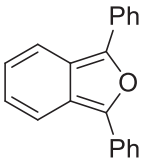
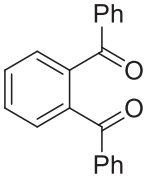
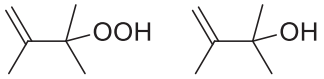
Table 1. Peroxidation of **3a** with the PDAIS/H_2O_2 system in various solvents[a].

Entry	Solvent	Conv. [%][b]	Yield 4a [%][c]	(4a:5)[b]
1	CCl_4	> 98	40	73:27
2	CH_2Cl_2	> 98	**80**	**85:15**
3	$(CH_2)_2Cl_2$	> 98	40	54:56
4	CH_3CN	> 98	49	72:28
5	Et_2O	> 98	63	86:14
6	THF	> 98	51	77:23

[a] Conditions: **3a** (0.3 mmol), PDAIS (0.6 mmol), 35% H_2O_2 (3 mmol). [b] Conversions and product ratios were determined by ^{1}H NMR spectra of the reaction mixture. [c] NMR yields determined with 4-methoxyacetophenone as internal standard.

To demonstrate the utility of this method for the peroxidation of different types of organic substrates, two conjugated dienes **3b** and **3c**; three aromatic hydrocarbons **3d**, **3e**, and **3f**; and one electron-rich alkene **3g** were oxidized using the PDAIS/H_2O_2 system under the optimal reaction conditions. The results are given in Table 2. 1,3-Cyclohexadiene **3b** afforded the desired endoperoxide **4b** in 45% chemical yield and 90% conversion,

Table 2. Peroxidation of various substrates (**3b**–**g**) by the PDAIS/H_2O_2 system[a].

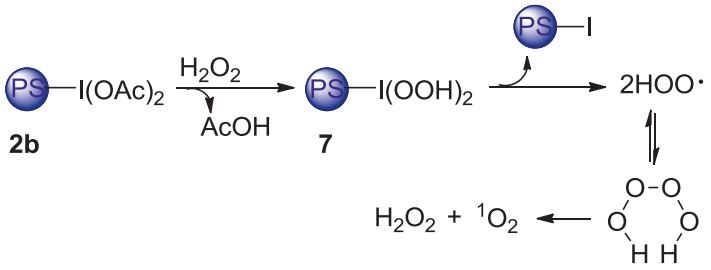
Entry	Substrate	Product(s)	Conv. %][b,c]	Yield [%][a]	Lit. Yield [%][f]
1	 **3b**	 **4b** **5b**	90 (75:25)	45[d] 49[b,e]	40[d]
2	 **3c**	 **4c**	>98	73[d] 80[b,e]	30[d]
3	 **3d**	 **4d**	>98	93[d] 96[e]	90[d]
4	 **3e**	 **4e**	65	61[d]	85[d,g]
5	 **3f**	 **4f**	>99	88[d]	80[d]
6	 **3g**	 **4g** **6**	75 (95:5)	48[d] 63[b,e]	30[d]

[a] Conditions: Substrate (0.5 mmol), PDAIS (1 mmol) and 35% H_2O_2 (5 mmol); [b] The conversions, product ratios, and yields were determined by ^{1}H NMR analysis with 4'-methoxyacetophenone as internal standard; [c] Values in parentheses correspond to product ratios obtained in $CDCl_3$ as a solvent; [d] Isolated yields after column chromatography; [e] $CDCl_3$ was used as solvent; [f] Previously reported yields obtained from the PIFA-H_2O_2 system: Substrate/PIFA/H_2O_2 (1/2.5/6); [g] Substrate/PIFA/H_2O_2 (1/4/10).

along with benzene as the byproduct in 15% NMR yield (Table 2, entry 1). Similarly, 1,3-cycloheptadiene **3c** afforded endoperoxide **4c** in good isolated yield (73%) (Table 2, entry 2). The reaction of dimethylanthracene **3d** under identical reaction conditions provided the corresponding endoperoxide **4d** in a high yield of 93% (Table 2, entry 3). The relatively less reactive diphenylanthracene **3e** was also oxygenated to **4e**, albeit with a slightly lower conversion of 65% (Table 2, entry 4). Oxygenation of **3f** proceeded smoothly to produce **4f** in 88% yield (Table 2, entry 5). The electron-rich alkene 2,3-dimethyl-2-butene **3g** participated in the ene reaction with singlet oxygen. Oxygenation of **3g** resulted in the formation of allylic hydroperoxide **4g** and allylic alcohol **6** in a 95:5 ratio (Table 2, entry 6). Hydroperoxide **4g** was isolated as a colorless oil in 48% yield at 75% conversion. The formation of **6** was attributed to the reaction of a small amount of **4g** with PDAIS under the given reaction conditions. The oxidation products obtained using the present system were purified by short column chromatography and characterized by ^{1}H and ^{13}C NMR spectroscopy. The spectra of the products were identical to the literature data.[36]

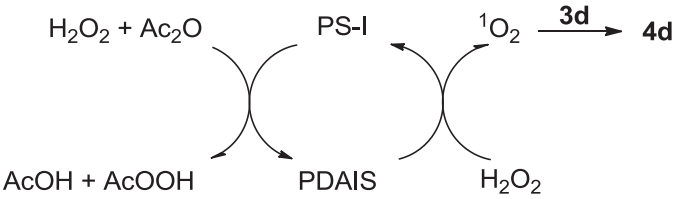
For all the reactions considered, PDAIS **2b** as the hypervalent iodine(III) source slightly outperformed its previously reported monomer analogue PIFA **1a** in terms of reactivity and peroxidation yield.[34] Probably because of the relatively poor solubility of PDAIS in the solvent its slow reaction with hydrogen peroxide prevents loss of singlet oxygen through bubbles. An exception was 9,10-diphenylanthracene **3e**, which required a greater amount of **1a** for full conversion (Table 2, footnote g). Poly(4-iodostyrene) (PS-I) generated after the reaction with PDAIS could easily be recovered in quantitative yield, and PDAIS could be regenerated by the reaction of PS-I in acetic anhydride with hydrogen peroxide in the usual manner. The regenerated PDAIS showed no loss of activity, as was confirmed by its use in the oxygenation of **3a** and **3d**; endoperoxides **4a** and **4d** were isolated in 78% and 93% yield, respectively.

Based on the above-mentioned experimental results and our previous reports, a plausible mechanism for the generation of $^{1}O_2$ from the PDAIS/H_2O_2 system is proposed (Scheme 2). First, PDAIS reacts with H_2O_2 to give reactive intermediate peroxyiodane **7** via the exchange of two acetyl groups for two hydroperoxyl groups. Homolytic cleavage of the iodine(III)-peroxy bonds in **7** generates PS-I and hydroperoxyl radicals, which undergo coupling to form hydrogen tetroxide (H_2O_4). Homolytic dissociation of the H_2O_4 intermediate generates singlet oxygen and hydrogen peroxide.



Scheme 2. Proposed mechanism of $^{1}O_2$ generation from the PDAIS/H_2O_2 system.

To confirm the assumption that PDAIS was synthesized from the reaction of iodopolystyrene (PS-I) with hydrogen peroxide and acetic anhydride, a catalytic amount of PS-I (10% mol) was used in the control experiment for the oxidation of DMA **3d** to endoperoxide **4d** in the presence of acetic anhydride and hydrogen peroxide. After stirring the reaction mixture for 48 h, **4d** was isolated in 65% yield. In this catalytic process, peracetic acid oxidizes PS-I to **2b**, which then reacts with hydrogen peroxide to generate singlet oxygen and PS-I (Scheme 3).



Scheme 3. Proposed mechanism for catalytic oxidation of **3d** to **4d** with the PDAIS/H_2O_2 system.

In conclusion, this report presents a convenient method for chemical singlet oxygen generation in organic media for the oxygenation of organic substrates using the PDAIS/H_2O_2 system. PDAIS can be regenerated quantitatively from the iodopolystyrene formed after the peroxidation reaction and reused without loss of activity, thus making this system both synthetically practical and environmentally benign.

3. Experimental

3.1. General

All reagents used were commercially available unless otherwise stated, and all solvents were used as received. Compound **2b** was prepared according to the method reported in the literature. Varian 400 and Bruker 400 spectrometers were used to acquire 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectra. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) and chloroform-d. All the peroxidation products are known and were confirmed by comparison with the previously reported NMR data.[39–44]

3.2. Preparation of poly[4-diacetoxyiodo]styrene (2b)[33]

To an acetic anhydride (23 mL, 243 mmol) was slowly added hydrogen peroxide (35%, 5.34 mL, 58.7 mmol) at 0 °C. The solution was left to warm to ambient temperature and stirred overnight. Iodopolystyrene (PS-I) (920 mg, 4 mmol) was then added to this solution. The mixture was stirred for 16 h at 40 °C. At the end of the reaction, the crude mixture was cooled to room temperature and diethyl ether (60 mL) was added to the solution to precipitate the polymer. The collected polymer was washed with ether (3 × 20 mL) and ether was removed under reduced pressure to afford PDAIS-**2b** (1.16 g, 3.36 mmol) as an off-white solid. IR (KBr, cm^{-1}): 1628, 1571, 1481, 1448, 1405, 1270, 1183, 1004, 766. Anal. calcd for PDAIS: C, 36.33; H, 3.66, found: C, 34.84; H, 3.37.

3.3. General procedure for oxygenation of substrates (3a–g) with the 2b/H_2O_2 system

To a suspension of substrates (**3a**–**g**, 0.5 mmol) and 35% hydrogen peroxide (443 μL, 5 mmol) in dichloromethane (4 mL) was added PDAIS (**2b**) (348 mg, 1 mmol) dropwise within 1 h at room temperature. The mixture was further stirred for 2 h. After removal of the solvent, ether was added to the reaction mixture to precipitate iodopolystyrene (PS-I). The formed PS-I was recovered by washing with ether (2 × 15 mL). After the addition of 4-methoxyacetophenone as an internal standard, the organic phase was washed with water (2 × 10 mL) and brine, dried over Na_2SO_4, and concentrated. The conversion of **3a**–**g**, formation of **4a**–**g**, and product distribution were determined directly by ^{1}H NMR analysis of the crude mixture. Then the resulting mixture was chromatographed on a short column (silica gel, 13–15 g) using a mixture of hexane and Et_2O (90:10) as an eluent to afford the desired oxygenated products.

3.3.1. 1-Methyl-4-(propan-2-yl)-2,3-dioxabicyclo[2.2.2]oct-5-ene (4a)[39]

Colorless oil, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.50 (d, J = 8.6 Hz, A part of AB system, 1H), 6.41 (d, J = 8.6 Hz, B part of AB system, 1H), 2.05–1.98 (m, 2H), 1.96–1.87 (m, 1H), 1.57–1.51 (m, 2H), 1.37 (s, 3H), 1.0 (d, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.6, 133.3, 80.0, 74.6, 32.3, 29.7, 25.8, 21.6, 17.5, 17.4.

3.3.2. 2,3-Dioxabicyclo[2.2.2]oct-5-ene (4b)[40]

Colorless oil, 45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.69 (dd, J = 4.4, 3.3 Hz, 2H), 4.69–4.66 (m, 2H), 2.33–2.27 (m, 2H, AA′ part of AA′BB′ system), 1.53–1.47 (m, 2H, BB′ part of AA′BB′ system). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.2, 70.9, 21.6.

3.3.3. 6,7-Dioxabicyclo[3.2.2]non-8-ene (4c)[41]

Colorless oil, 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.39 (dd, J = 4.9, 3.2 Hz, 2H), 4.76 (m, 2H), 2.01–1.87 (m, 4H), 1.62–1.56 (m, 1H), 1.46–1.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.9, 77.4, 31.7, 18.5.

3.3.4. 9,10-Dimethyl-4a,9,9a,10-tetrahydro-9,10-epidioxyanthracene (4d)[42]

Recrystallized from DCM-hexane, white powder, 93%, mp 217–219 °C, lit. 218.5–220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.36 (m, 4H, AA′ part of AA′BB′ system), 7.29–7.24 (m, 4H, BB′ part of AA′BB′ system), 2.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 127.6, 120.9, 79.7, 13.9.

3.3.5. 9,10-Diphenyl-9,10-dihydro-9,10-epidioxyanthracene (4e)[42]

Recrystallized from DCM-hexane, white powder, 61%, mp 193–195 °C (decomposition), lit. 194–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.75 (m, 4H), 7.71–7.67 (m, 4H), 7.61–7.56 (m, 2H), 7.26–7.19 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2, 133.0, 128.4, 128.3, 127.7, 127.6, 123.5, 84.1.

3.3.6. Benzene-1,2-diylbis(phenylmethanone) (4f)[43]

Recrystallized from ether-hexane, white powder, 88%, mp 143.5–145 °C, lit. 144–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.35 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6, 140.0, 137.2, 133.0, 130.3, 129.8, 129.7, 128.3.

3.3.7. 2,3-Dimethylbut-3-en-2-yl hydroperoxide (4g)[44]

Isolated as a colorless oil, 48%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 1H), 5.01–5.00 (m, 1H), 4.97–4.95 (m, 1H), 1.81–1.80 (m, 3H), 1.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.9, 111.9, 84.4, 23.9, 18.7.

3.3.8. 2,3-Dimethylbut-3-en-2-ol (6)[44]

Colorless oil, 2%–3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.00 (m, 1H), 4.77 (m, 1H), 1.81 (m, 3H), 1.54 (bs, 1H), 1.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 108.4, 73.1, 28.8, 19.2.

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