

Calcium Peroxide Diperoxohydrate as a Storable Chemical Generator of Singlet Oxygen for Organic Synthesis

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Calcium peroxide diperoxohydrate ($\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$) is an environmentally friendly generator of singlet oxygen ($^1\text{O}_2$, $^1\Delta_g$) that can be used in organic synthesis as an alternative to the regular photochemical method. This compound produces $^1\text{O}_2$ in various solvents and can be easily recovered by filtration for further regeneration. Both monitoring of $^1\text{O}_2$ luminescence at 1270 nm and specific trapping have shown that $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ can be stored for several days at -80°C and that the yield of $^1\text{O}_2$ is equal to 25%. Oxidation of typical organic substrates in methanol or THF through [4 + 2] or [2 + 2] cycloaddition and ene reaction have been carried out on a preparative scale with total conversion and selectivity.

Introduction

Singlet oxygen ($^1\text{O}_2$, $^1\Delta_g$), a powerful although selective oxidant toward many types of electron-rich substrates, is usually produced by photosensitization. This method requires photochemical reactors that are not always available in research laboratories or in industrial plants. On the other hand, chemical sources of $^1\text{O}_2$ involving readily available oxidants such as H_2O_2 have been reported as attractive alternatives to the photochemical process. As an example, MoO_4^{2-} is known to catalyze the disproportionation of H_2O_2 into H_2O and $^1\text{O}_2$ in water,^{1–3} in aqueous methanol,^{1,4,5} or in w/o microemulsions.⁶ The two first reaction media exhibit poor solubilizing properties toward typical organic compounds; therefore, only substrates with low molecular weight or bearing hydrophilic groups^{7,8} can be oxidized in these solvents. Moreover, side reactions can occur between substrates and H_2O_2 itself or with peroxomolybdates.⁷ The third microheterogeneous system requires high quantities of surfactant and cosurfactant and, consequently, makes the recovering of the oxidized product from the media troublesome.

Chemical generation of $^1\text{O}_2$ in organic media without addition of H_2O_2 can be also achieved by thermolysis of isolable organic⁹ or inorganic¹⁰ peroxides. For example, singlet oxygen can be produced by warming triphenyl phosphite ozonide,^{11,12} but this method is only used for mechanistic studies since it involves the costly triphenyl phosphite, the handling of hazardous chemicals, and the separation of the reduced phosphorus compound from the products after completion of the oxidation. Singlet oxygen can also be produced beside other reactive oxygen species during the base-catalyzed disproportionation of peracids.¹⁵ The same phenomenon occurs with K_3CrO_8 ^{16,17} that induces radical side reactions. Pure singlet oxygen can be generated in organic media from naphthalenic endoperoxides^{18,19} that decompose thermally in solution to the parent hydrocarbon and molecular oxygen, half of which in a singlet state. The oxidation of organic substrates on the preparative scale would require the

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preparation of a great amount of the endoperoxide and the removing of the naphthalene derivative from the reaction medium. However, water-soluble endoperoxides have found valuable applications in biochemistry when the releasing of a known amount of pure $^1\text{O}_2$ was necessary.^{9,20–26}

Recently, Ca^{2+} has been found to be the most environmentally friendly catalyst to generate $^1\text{O}_2$ by disproportionation of hydrogen peroxide. The precursor of $^1\text{O}_2$ has been identified as the isolable solid calcium peroxide diperoxyhydrate $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ which was described as unstable for temperature higher than 25 °C.²⁷ This oxidizing agent offers the advantage to generate singlet oxygen in pure organic solvent without addition of aqueous hydrogen peroxide. In this paper, we show that calcium peroxide diperoxyhydrate can be used as a simple heterogeneous source of $^1\text{O}_2$ for the oxidation of organic compounds in MeOH or in THF through the typical [4 + 2] and [2 + 2] cycloadditions and the ene-reaction.

Results and Discussion

Synthesis and Characterization of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$.

Although numerous calcium peroxides are reported in the literature,^{28,29} Gladysheva³⁰ has established that only two well-defined compounds may be obtained by reaction of H_2O_2 with $\text{Ca}(\text{II})$ in aqueous solution: the stable octahydrate peroxide $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ and the thermolabile diperoxyhydrate peroxide $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$. This last compound can be prepared from $\text{Ca}(\text{OH})_2$,^{30–33} $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$,^{30,33} CaO_2 ,^{29,34} or CaCl_2 ²⁹ by addition of concentrated hydrogen peroxide, followed by separation of the precipitate on a glass filter at –15 °C. In this work, $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ was synthesized from crystal of $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ with a 95% yield. To avoid partial disproportionation of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$, the wet peroxide obtained was rapidly and carefully deshydrated by filtration and used immediately or stored at –80 °C. Chemical titrations and thermogravimetric analysis of the precipitate show the absence of free water and the presence of three peroxide groups per atom of calcium.

Heating $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ in methanol at 50 °C leads to the release of 1 molar equiv of oxygen and leaves an in-

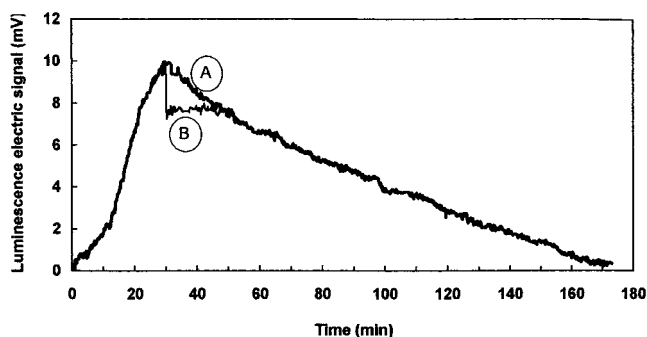
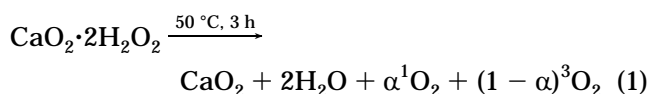
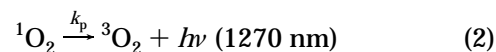


Figure 1. Luminescence electric signal of $^1\text{O}_2$ at 1270 nm versus time during the thermolysis of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ (4 mmol) in CH_3OH (20 mL) at 50 °C without (A) and with (B) addition of α -terpinene (0.02 mmol).

soluble cream-colored residue, which was shown to be the anhydrous calcium peroxide, CaO_2 , as reported by Gladysheva (eq 1).³³



Formation of $^1\text{O}_2$ during the thermolysis of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ was proved unambiguously by detection of its monomol emission at 1270 nm (eq 2).



Kinetics of $^1\text{O}_2$ formation during the thermolysis at 50 °C of a suspension of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ in methanol was studied by monitoring the luminescence signal at 1270 nm. Figure 1A shows a steep increase of the intensity during the first 30 min, and then the signal slowly decreases during 2.5 h. Finally, all the available $^1\text{O}_2$ was released within 3 h at 50 °C.

Yield of $^1\text{O}_2$. The yield (α) of $^1\text{O}_2$ produced by thermolysis of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ (eq 1) can be defined by the expression (3) where $[\text{}^1\text{O}_2]_{\text{cumul}}$ and $[\text{}^3\text{O}_2]_{\text{cumul}}$ are, respectively, the cumulated concentrations of singlet and triplet oxygen.

$$\alpha = \frac{[\text{}^1\text{O}_2]_{\text{cumul}}}{[\text{}^3\text{O}_2]_{\text{cumul}} + [\text{}^1\text{O}_2]_{\text{cumul}}} = \frac{[\text{}^1\text{O}_2]_{\text{cumul}}}{[\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2]} \quad (3)$$

Two different methods were used to determine $[\text{}^1\text{O}_2]_{\text{cumul}}$. The first one (Figure 1) is based on the calibration of the luminescence signal with an internal trap added to the suspension.^{26,35–37} α -Terpinene **3** was the chosen trap because it reacts quickly and selectively with $^1\text{O}_2$ through a [4 + 2] cycloaddition with negligible physical quenching.^{38,39} The addition of α -terpinene **3** to a warmed suspension of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ in MeOH leads to a decrease of the underlying area in Figure 1B). By comparing this missing area with the total underlying area (Figure 1A),

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Table 1. Yield of $^1\text{O}_2$ Produced by Thermolysis of 4 mmol $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ in CH_3OH at 50 °C for 3 h^a

α -terpinene (mmol)	ascaridole (mmol)	α (%)
1	0.94	24 ^a
2	1.04	26 ^{a,b}
4	0.94	24 ^a
16	1.00	25 ^a

^a All experiments were analyzed by HPLC (a) and the second entry was also studied by luminescence (b).

Table 2. Influence of Time and Temperature of Storage on the Yield of $^1\text{O}_2$ Generated during the Thermolysis of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ at 50 °C in Methanol

T (°C)	time (days)	α (%)
	0	25
-80	6	25
-18	6	17
4	6	0
20	6	0

it was found that the cumulated amount of $^1\text{O}_2$ arising from $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ corresponds to a yield of 26%.

$[\text{O}_2]_{\text{cumul}}$ can also be determined by measurement of the quantity of ascaridole **8** formed by oxidation of an excess of α -terpinene with a given amount of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$. Table 1 shows that whatever the concentration of α -terpinene is, the amount of ascaridole **8** formed is always equal to a quarter of the concentration of calcium peroxide. Hence, the four experiments lead to an average yield of 25% for the production of singlet oxygen (Table 1). This yield, based on chemical trapping, is probably an underestimated value of the total yield of $^1\text{O}_2$ since a part of the $^1\text{O}_2$ released inside the crystals of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ is deactivated before reaching the solution.

It is noteworthy that a higher yield of 50% was reported previously by Nardello et al.²⁷ This discrepancy could arise from the different procedure used to prepare calcium peroxide diperoxohydrate.³³ In this previous work, calcium peroxide was isolated by centrifugation and was still moistened with aqueous H_2O_2 , which generates extra $^1\text{O}_2$ through disproportionation by $\text{Ca}(\text{II})$. Another explanation could be the larger specific area of the crystals, which could increase the available $^1\text{O}_2$.

Calcium peroxide diperoxohydrate is stable only in the presence of concentrated hydrogen peroxide.²⁸ Little detailed information on the stability is available except the storage experiments carried out by Gladysheva.³³

To determine the evolution of the oxidative power of the calcium peroxide with the time of storage, we have measured the total underlying area of the luminescence intensity during thermolysis of calcium peroxide at 50 °C in methanol. This area can be converted into $^1\text{O}_2$ yield since for freshly prepared peroxide, it corresponds to a 25% yield.

Table 2 presents the yields of $^1\text{O}_2$ as a function of time and temperature of storage. It is clear that $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ is unstable above 4 °C. The higher the temperature of storage is, the higher the rate of singlet oxygen loss is. At -18 °C, 32% of the available $^1\text{O}_2$ is lost after 6 days, whereas at -80 °C no loss could be observed during the storage in agreement with previous work.³³ Finally, to avoid oxygen loss, the time elapsed between filtration and use or storage should be minimized. Otherwise, the peroxide should be kept frozen before run.

Oxidation of Organic Substrates. Seven typical organic substrates including three conjugated dienes **1**, **2**, and **3**, two aromatic hydrocarbons **4** and **5**, and two

Table 3. Solvent Effect on the Oxidation of Rubrene **4 (0.05 M) with $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ (0.2 M) Warmed for 3 h at 50 °C**

solvent	τ_{Δ}^{41} (μs)	conversion (%)	α (%)
acetonitrile	67	0	0
anisole	9	0	0
dichloromethane	97	18	5
chloroform	120	17	4
1,1-dichloroethane	67	15	4
dioxane	25	18	5
THF	22	85	21

olefins **6** and **7** were oxidized by $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ on the preparative scale. These substrates illustrate three standard types of $^1\text{O}_2$ reactions, namely, the [4 + 2] cycloaddition, the [2 + 2] cycloaddition, and the ene reaction.

The solvents were selected in order to allow the oxidation of high concentrations of substrates ($C \geq 0.1$ M) and to be readily removed at the end of the reaction. Moreover, to minimize the quenching of $^1\text{O}_2$ by the solvent, a minimal $^1\text{O}_2$ lifetime (τ_{Δ}) of 10 μs was chosen. At last, solvents should lead to a fine dispersion of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ under stirring to permit the release of $^1\text{O}_2$ in the media.

Although dipolar aprotic solvents such as DMSO, *N,N*-dimethylformamide and *N*-methylformamide exhibit both good solubilizing and dispersion properties toward organic and inorganic compounds, they were not retained because of their high boiling point and of the quenching of $^1\text{O}_2$ by the sulfoxide group of DMSO.

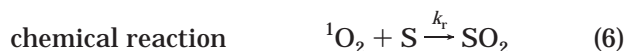
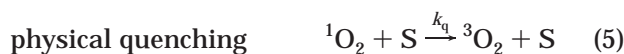
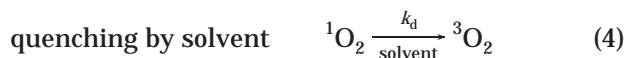
On the basis of these criteria, seven potential solvents (Table 3) were selected and compared through the peroxidation of rubrene **4**, a highly reactive substrate able to trap the total amount of available $^1\text{O}_2$. For solubility reasons, methanol could not be examined by this method. A concentration of 0.05 M of **4** is sufficient for the complete scavenging of $^1\text{O}_2$ and, in this case, chemical quenching (eq 7) predominates over other pathways of $^1\text{O}_2$ quenching (eqs 5 and 6). Table 3 presents the yields for the conversion of **4** into the endoperoxide in the different solvents after 4h of reaction at 50 °C with $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ (0.2 M). NMR analysis have confirmed the formation of the expected 5,12-endoperoxide as the sole oxidation product. The low yields of conversion (15–17%) obtained with chlorinated solvents show that a long lifetime of singlet oxygen is not a sufficient condition to get a high yield of conversion.^{38,40} Anisole and acetonitrile were found to be unsuitable for our purpose since **4** remains unchanged after thermolysis of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$. Finally, experiments reported in Tables 1 and 3 show that THF and methanol are the most efficient solvents. The poor solubility of **1**, **2**, **4**, and **6** in MeOH compelled us to resort to THF for their oxidations. The conversions of **3**, **5**, and **7** are less dependent on the solvent effect, but comparative studies have shown that THF leads to a better yield for the conversion of **7** into the corresponding hydroperoxides, whereas methanol was more adapted to the conversion of α -terpinene **3** into ascaridole **8**.

Determination of the Amount of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ Required for Total Conversion of a Given Substrate. The peroxidation of a given substrate is considered as complete when more than 99% of the starting material is consumed. This goal may be achieved only when a sufficient amount of $^1\text{O}_2$ is generated from the thermal decomposition of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ through reaction 1. The different pathways of decay of $^1\text{O}_2$ are presented

Table 4. Reactivity Indexes (γ , β) of Studied Substrates and Theoretical Amounts of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ Required for a 99% Oxidation in MeOH and THF

substrate		$\log(k_r + k_q)$	$\gamma = k_r/(k_r + k_q)$	$\beta = k_d/(k_r + k_q)$ (M)		[$\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$] (M)	
no.	M			MeOH	THF	MeOH	THF
1	0.1	9.0	1	1.0×10^{-4}	4.5×10^{-5}	0.40	0.40
2	0.05	8.6	0.8	2.5×10^{-4}	1.1×10^{-4}	0.26	0.25
3	0.1	7.5	1	3.2×10^{-3}	1.4×10^{-3}	0.46	0.43
4	0.1	7.5	1	3.2×10^{-3}	1.4×10^{-3}	0.46	0.43
5	0.1	6.3	0.34	5.0×10^{-2}	2.2×10^{-2}	3.89	2.36
6	0.1	6.8	0.4	1.6×10^{-2}	7.2×10^{-3}	1.74	1.33
7	0.2	5.8	0.87	1.6×10^{-1}	7.2×10^{-2}	4.31	2.44

through eq 4 to eq 6, where k_d is the pseudo-first-order constant of singlet oxygen decay in the solvent whereas k_q and k_r are the bimolecular rate constants for the physical and the chemical quenching of singlet oxygen by a substrate S.



The overall rate constants ($k_r + k_q$) have been determined for many organic compounds by flash photolysis, whereas the reported rate constants k_r are quite scarce.⁴¹ Once generated by the reaction 1, singlet oxygen decays mainly according to physical (eqs 4 and 5) and to chemical (eq 6) quenching. Under pseudostationary-state conditions ($d[{}^1\text{O}_2]/dt = 0$), and after integration between zero time and infinite time, we obtain the expression (7), where the infinite time refers to the complete decomposition of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$.

The ratio $\gamma = k_r/(k_r + k_q)$ expresses the contribution of the chemical quenching in the overall quenching whereas $\beta = k_d/(k_r + k_q)$ corresponds to the minimum concentration of substrate required so that the interaction of ${}^1\text{O}_2$ with the substrate (eq 5 and 6) predominates over the deactivation of ${}^1\text{O}_2$ by the solvent (eq 4).

As we searched for experimental conditions permitting a conversion of 99% of the substrate, $[\text{S}]_\infty$ is equal to $[\text{S}]_0/100$. Moreover, we know that the yield of ${}^1\text{O}_2$ generated from $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ is 25%, therefore the cumulative amount of ${}^1\text{O}_2$ generated in the medium is related to the concentration of calcium peroxide ($[{}^1\text{O}_2]_\infty = 0.25[\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2]$).

By introducing these expressions of $[\text{S}]_\infty$ and $[{}^1\text{O}_2]_\infty$ into (7) we can calculate the concentration of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ necessary to oxidize a substrate S of known reactivity (eq 8).

$$\frac{k_d}{k_r + k_q} \text{Ln} \frac{[\text{S}]_0}{[\text{S}]_\infty} + [\text{S}]_0 - [\text{S}]_\infty = \frac{k_r}{k_r + k_q} [{}^1\text{O}_2]_\infty \quad (7)$$

$$[\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2] = \frac{4}{\gamma} (\beta \text{Ln} 100 + [\text{S}]_0) \quad (8)$$

Tables 4 and 5 present the studied substrates and their characteristic reactivity indexes γ and β calculated from the known overall quenching rate constants ($k_r + k_q$)

and the k_d values in MeOH ($k_d = 1.0 \times 10^5 \text{ s}^{-1}$) and THF ($k_d = 4.5 \times 10^4 \text{ s}^{-1}$).^{6,38,41} Table 4 shows that the starting concentrations of substrates were always higher than their β values so that during most of the oxidation the quenching of ${}^1\text{O}_2$ by the substrates predominates over the deactivation of ${}^1\text{O}_2$ by the solvents. It is noteworthy that for the most reactive substrates 1–4 theoretical quantities of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ required for a 99% conversion are the same for both solvents. On the contrary, for less reactive substrates 5–7 greater amounts of peroxide are needed in methanol, due to the faster deactivation of ${}^1\text{O}_2$ in methanol compared with THF.

Peroxidation of Organic Substrates on the Preparative Scale. Control experiments have shown that the solvents (MeOH and THF) remained unchanged after heating with $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ for 3 h at 50 °C. Furthermore, no reaction was observed when sodium hydroxide was added to a mixture of H_2O_2 and substrate in the two studied solvents, leading to the conclusion that ${}^1\text{O}_2$ arises from the thermolysis of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ and not from a possible base-catalyzed disproportionation of H_2O_2 .

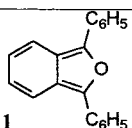
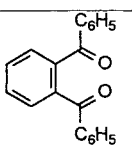
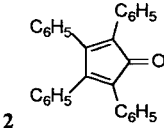
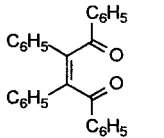
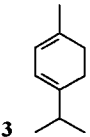

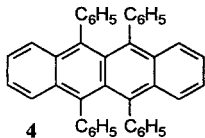
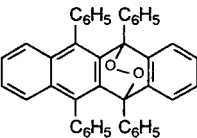
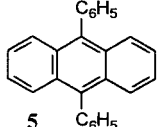
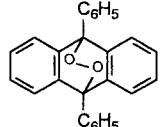
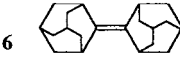
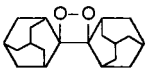
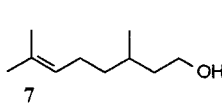
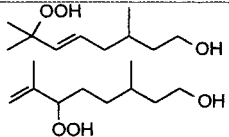
To illustrate the potentiality of this method in preparative organic synthesis, the concentration of the substrates was always higher than 0.1 M except for tetraphenylcyclopentadienone **2** (0.05 M) because of its poor solubility in methanol and THF. Despite the well-known thermal instability of peroxides and hydroperoxides, no secondary reaction was observed during the peroxidation of compounds 1–7 at 50 °C. However, considering the low persistence of many peroxidic products at this temperature, this method has to be validated with small quantity of a new substrate and the stability of the oxidation product under the required experimental conditions should be checked carefully. All oxidations were carried out according to experimental conditions indicated in Table 5. In all cases, the amount of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ was sufficient to achieve the total oxidation of the starting material, the sole exception was for adamantylideneadamantane **6**, which was converted up to 95%.

It is noteworthy that lower concentrations of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ lead to incomplete conversion of the substrates. This observation validates eq 8 and shows that the availability of released singlet oxygen from the insoluble peroxide is similar to the one obtained from homogeneous chemical sources of ${}^1\text{O}_2$. Thus, even with huge concentrations of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ (2.5 M), its dispersion in methanol and THF is sufficient to permit the diffusion of ${}^1\text{O}_2$ from the inorganic particles up to the reaction medium. Moreover, oxidation products were easily separated from the catalyst by filtration and washing, giving a high yield ($\geq 75\%$) of isolated products (Table 5).

Although a very high conversion rate (95%) of **6** could be achieved with excess of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ (2.5 M), it is

(41) Wilkinson, F.; Hellman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 603–1021.

Table 5. Oxidation of Substrates 1–7 with $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ in THF^a or in CH_3OH ^b at 50 °C for 3 h

Substrate	[S] ₀ M	[CaO ₂ ·2H ₂ O ₂] M	Product	Yield %
	0.1 ^a	0.4		88 ^d
	0.05 ^a	0.4		95 ^d
	0.1 ^b	0.4		90 ^c 40 ^d
	0.1 ^b	0.5		82 ^d
	0.1 ^b	2.5		98 ^d
	0.1 ^b	2.5		95 ^c 75 ^d
	0.2 ^{a,b}	2.4		54 ^c 41 ^c

^a In methanol. ^b In THF. ^c Assessed from ¹H NMR. ^d Isolated.

significantly lower than the theoretical yield of 99% calculated from eq 8. This discrepancy could be explained by an incorrect value of γ underestimating the consumption of ¹O₂ through physical quenching by **6**. Actually, lower values of γ (0.12 and 0.15) can be calculated from eq 8 using experimental results obtained with 2.5 and 1.3 M $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ which lead to 95% and 30% transformation, respectively.

The ¹H NMR spectrum recorded after the oxidation of α -terpinene proves the disappearance of **3** and confirms the formation of ascaridole **8** as the major product (>90%). This rather stable endoperoxide was then purified by distillation (78 °C, 3 mmHg) with a moderate yield of 40%. ¹H NMR spectrum of the residue of distillation exhibits two large patterns corresponding to polymeric compounds as described by Crivello.⁴²

Conclusions

Calcium peroxide diperoxohydrate ($\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$) is an environmentally friendly generator of ¹O₂ that can be easily prepared from calcium chloride and hydrogen peroxide and stored for several weeks at low temperature. Preparative scale oxidation of hydrophobic substrates in THF or in methanol can be achieved within 3 h at 50 °C, the oxidized product can be recovered in high yields by simple filtration. It has been shown that sufficiently reactive substrates ($\log(k_r + k_t) \geq 6$ and $\gamma \geq 0.3$) can be completely oxidized by this method. For less reactive compounds, this method is inappropriate since it would require an important amount of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ which would hinder the stirring of the reaction mixture. Temperature of thermolysis can be lower than 50 °C to avoid further reduction of thermosensitive products but, in this case, the reaction time will be longer than 3 h.

(42) Crivello, J. V.; Yang, B. J. *Polymer Sci.: Part A, Polymer Chem.* **1995**, *33*, 1881–1890.

Experimental Section

Reagents. 1,3-Diphenylisobenzofuran **1**, tetraphenylcyclopentadienone **2**, α -terpinene **3**, rubrene **4**, 9,10-diphenylanthracene **5**, and β -citronellol **7** were purchased from Aldrich and used as received. Potassium permanganate, calcium chloride, ammonium hydroxide (28–30%), and hydrogen peroxide (50%, rectapur) were obtained from Prolabo. Adamantylideneadamantane **6** was prepared according to a known procedure⁴³ from phosphorus pentabromide and adamantane (Aldrich). **Luminescence intensity at 1270 nm:** Infrared emission of $^1\text{O}_2$ was detected with a liquid nitrogen cooled germanium photodetector similar to the one described previously by Di Mascio and Sies.²⁶

Quantitative Analysis of Singlet Oxygen. The areas of the total curve of luminescence electric signal (Figure 1A) during thermolysis of 0.2 M $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ are 1594 mV min^{-1} . The chemical quenching induced by 1 mM of α -terpinene led to a difference (Figure 1A,B) of 31 mV min^{-1} . Therefore, the yield of singlet oxygen is equal to $(1594/31)(10^{-3}/0.2) = 0.26\%$.

Analysis. High-performance liquid chromatography (HPLC) was carried out with a Waters pump model 600 using a $4.6 \times 250 \text{ mm}$ column packed with Nova-Pack C18 4 mm. A mixture of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (10/90) was used as eluent, and the detection was performed both by a UV-multiwavelength detector (Waters 490 E) and by a refractive index detector (Waters 2410). Carbon and proton NMR were recorded on a Bruker AC-200 spectrometer. Reactions were monitored by thin-layer chromatography (TLC) using Merck precoated silica gel plates.

Calcium Peroxide Octahydrate: $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$.⁴³ An Erlenmeyer flask (250 mL) was half-filled with an homogeneous solution prepared by dissolving 6.71 g (61 mmol) of CaCl_2 into a mixture of H_2O_2 50% (17.6 mL, 300 mmol) and water (232 mL). The Erlenmeyer was covered with perforated Parafilm and placed into a closed vessel containing 200 mL of aqueous ammonia (14%). After 1 week at 4 °C, the crystalline precipitate was collected by filtration and washed twice with water and acetone giving 10.14 g (47 mmol, 77%) of $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ as colorless crystals.

Calcium Peroxide Diperoxohydrate: $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$.⁴⁴ A 5.0 g (23 mmol) portion of ground $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ was added to 30 mL of hydrogen peroxide (17 M) at $-15 \text{ }^\circ\text{C}$. The turbidity of the suspension rapidly decreased in a first step and then increased while a new precipitate was formed. After 1 h of stirring, the precipitate was filtered and stirred once again

in 30 mL of hydrogen peroxide (17 M) at $-15 \text{ }^\circ\text{C}$ for 1 h and rapidly filtered under suction and stored at $-80 \text{ }^\circ\text{C}$ ($m = 3.1 \text{ g}$, 22 mmol, 95%).

Analysis of Calcium Peroxides.^{32,45–46} The peroxide groups bound to each calcium ion are released through hydrolysis with aqueous H_2SO_4 , and the H_2O_2 thus obtained was titrated with potassium permanganate. The total calcium content was measured by complexometric titration with EDTA (Calcium-Test from Merck). Thermogravimetric analysis of the samples were performed with a Setaram TAG-SR12 setup (France) which includes a derivatograph and a PC/TX computer with a program from the Setaram software. Small samples (10–50 mg) were studied under argon atmosphere with a heating rate of $1 \text{ }^\circ\text{C}/\text{min}$ from 20 to $200 \text{ }^\circ\text{C}$ and $10 \text{ }^\circ\text{C}/\text{min}$ from 200 to $1000 \text{ }^\circ\text{C}$.

Caution: Peroxides are potentially dangerous. $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ should not be kept at room temperature, due to its instability

Oxidation of Tetraphenylcyclopentadienone (2). To a solution of 0.148 g (0.4 mmol) of **2** in 8 mL of THF was added 0.448 g (3.2 mmol) of freshly prepared $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$. After being stirred for 3 h at $50 \text{ }^\circ\text{C}$, the suspension was filtered and washed under suction through a sintered glass funnel to eliminate the inorganic solid. The filtrate was rotatory evaporated at $50 \text{ }^\circ\text{C}$ in a vacuum, and 10 mL of methylene chloride was added to the residue. The organic layer was washed successively with NaHCO_3 5% (10 mL), distilled water (10 mL), and water saturated with NaCl (10 mL) and then dried over MgSO_4 . Evaporation of solvent gave 142 mg (95%) of pure 1,2,3,4-tetraphenyl-2-butene-1,4-dione **9**.

Oxidation of Other Substrates. The other substrates **1** and **3–7** were oxidized according to the same procedure under initial conditions of concentrations reported in Table 4. All the ^1H and ^{13}C NMR spectra were in agreement with the published spectra⁴ or with those of authentic samples prepared by photo-oxygenation in the presence of methylene blue or tetraphenylporphyrine as photosensitizers.

Acknowledgment. This work was in part supported by Rhodia and by the Centre National de Recherche Scientifique (CNRS) within the program "Catalyseurs pour l'industrie et l'environnement".

Supporting Information Available: Luminescence spectrum of $^1\text{O}_2$ obtained by thermolysis of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ (2.5 M) in D_2O at $80 \text{ }^\circ\text{C}$ for 1 min. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO010766X

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