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A New Methodology for the Bis(oxocyclohexadienyl) Peroxide Formation

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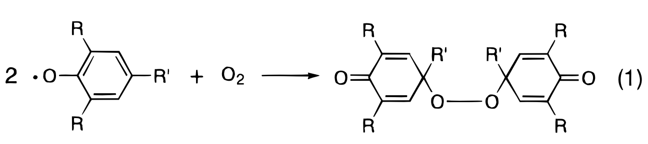
Symmetrically substituted bis(4-oxocyclohexa-2,5-dienyl) peroxide **5** ($R = R'$) as well as unsymmetrically substituted **5** ($R \neq R'$) can be prepared efficiently by treating 4-halogenocyclohexa-2,5-dienone **3** with 4-hydroperoxycyclohexa-2,5-dienone **4** in the presence of an appropriate positive halogen compound such as *N*-iodosuccinimide. Acetonitrile is a suitable solvent for the reaction. The formation of **5** is suggested to take place via electrophilic attack by the positive halogen species upon **3** generating the 4-oxocyclohexa-2,5-dienyl cation (or the phenoxy cation), followed by nucleophilic attack by **4** upon the cation. It is emphasized that some of the peroxides obtained by this means have not been prepared by the classical method, coupling of phenoxy radicals with O_2.

Bis(oxocyclohexadienyl) peroxides such as **2** can be prepared by coupling of stable or relatively stable phenoxy radicals such as **1** with O_2 (eq 1).[1] Unfortunately, the majority of phenoxy radicals have short lives. Hence, the number of peroxides obtainable by this means is limited. The thermochemical nature of the peroxides is unique in that homolytic fission of not only O−O but also C−O bonding is possible.[2] Addition of new and varied bis(oxocyclohexadienyl) peroxides may contribute to getting deeper insight into their chemical nature. In this paper, we report an entirely new principle for the formation of bis(oxocyclohexadienyl) peroxides, which appears to proceed through an ionic process.



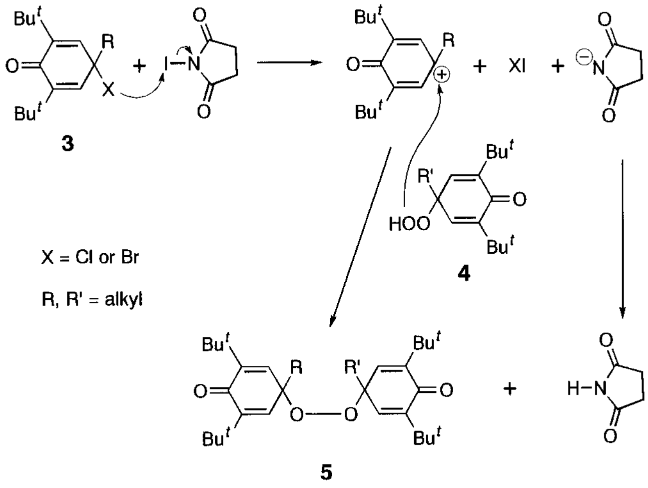
1 **2**

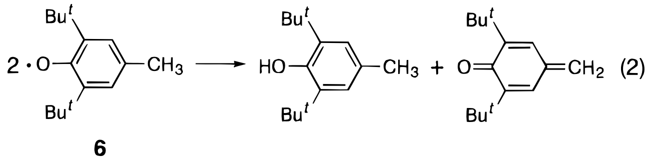
R = *t*-Bu or *t*-Amyl

R' = *i*-Pr, *t*-Bu, O-Alkyl, OPh, or Aryl

Results and Discussion

Scheme 1





In a recent investigation on the mechanism of the reaction of 2,6-di-*tert*-butylphenol with an iodinating agent, I_2 and H_2O_2, in MeOH, it has been proposed that the reaction involves electrophilic assistance by I_2 of deiodination of the intermediary 4-iodocyclohexa-2,5-dienone, generating the 4-oxocyclohexa-2,5-dienyl cation (or the phenoxy cation).[3] In accordance with this postulation, it has been more recently proved that nucleophilic displacement of 4-halogeno-4-alkyl-2,6-di-*tert*-butylcyclohexa-2,5-dienones **3** with alcohols affording 4-alkoxy-4-alkyl-2,6-di-*tert*-butylcyclohexa-2,5-dienones can be strongly accelerated by an electrophilic halogen species such as *N*-iodosuccinimide (NIS).[4] It seemed reasonable to us to anticipate that in the presence of a positive halogen compound **3** would react analogously with 4-hydroperoxy-4-alkyl-2,6-di-*tert*-butylcyclohexa-2,5-dienone **4**, giving rise to bis(oxocyclohexadienyl) peroxide **5**, as illustrated in Scheme 1. This was found to be the case. 4-Chloro-4-methyl-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**3a**) was allowed to react with an excess (3 molar equiv) of 4-hydroperoxy-4-methyl-2,6-di-*tert*-butylcyclohexa-2,5-dienone (**4a**) in MeCN containing NIS (1 molar equiv). The reaction was complete within 5 min at 35 °C. After workup, bis(1-methyl-3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienyl) peroxide (**5a**) was isolated in 74% yield (run 2, Table 1). It is noteworthy that **5a** cannot be formed from coupling of 4-methyl-2,6-di-*tert*-butylphenoxy radicals (**6**) with O_2 (cf. eq 1) since it cannot compete with extremely rapid disproportionation of **6** (eq 2).[5,6] It is clear that NIS plays an essential role in the formation

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(4) The results will be published separately.

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Table 1. Peroxide 5a from Reaction of Chloro Dienone 3a and Hydroperoxy Dienone 4a[a]

run	positive halogen	solvent	time (min)	recovery of **3a** (%[b])	yield of **5a**[c] (%[d])
1		MeCN	60	85	trace
2	NIS	MeCN	5	0	74
3	NIS[e]	MeCN	30	0	58
4	NBS	MeCN	5	98	2
5	I_2	MeCN	5	10	36
6	Br_2	MeCN	5	35	23
7	NIS	DME	60	40	1
8	NIS	PhH	60	0	14

[a] A mixture of **3a** (1 mmol), **4a** (3 mmol), and a positive halogen reagent (1 mmol) in a solvent (15 mL) was stirred at 35 °C for the time indicated in the table. [b] Estimated from the ^{1}H NMR spectrum of the crude reaction product. [c] Isolated product. [d] (Mol/mol **3a** employed) × 100. [e] With 0.33 mmol of NIS.

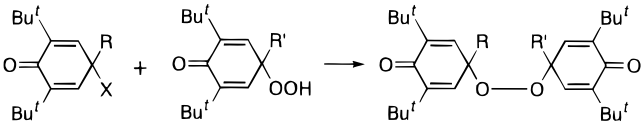
of **5a**, since if NIS is omitted, little **5a** was yielded and a large quantity of **3a** was recovered unchanged despite an extended reaction time (run 1, Table 1). However, it is questionable whether employment of a stoichiometric amount (1 molar equiv) of NIS is mandatory for completing the reaction, as explained below. The reaction of NIS with **3a** may produce an equivalent amount of ICl (cf. Scheme 1), which may be also active as an electrophilic halogen species. Thus, the ICl may also react with more of **3a** (hereby generating fresh ICl) and contribute toward forming **5a**. When the reaction of **3a**, **4a**, and NIS was started, the originally light yellow or light brown mixture soon turned brownish orange, indicative of rapid formation and persistence of a molecular halogen (ICl). As the result, employment of a catalytic amount of NIS may in principle suffice to complete the reaction between **3a** and **4a** (eq 3). The reaction of **3a** with **4a** in MeCN in the

$$\mathbf{3a} + \mathbf{4a} \xrightarrow{\text{NIS (catalyst)}} \mathbf{5a} + \text{HCl} \qquad (3)$$

presence of 0.33 molar equiv of NIS was complete within 30 min and afforded 0.58 molar equiv (58% yield) of **5a** (run 3, Table 1).[7] This yield was appreciably lower than that with 1 molar equiv of NIS. In this regard, it is pointed out that different products accompany **5a** depending on by which positive halogen compound the reaction is mediated. When mediated by NIS, practically neutral and presumably inactive succinimide may be generated (Scheme 1), but when mediated by ICl, an acid, HCl, is formed (eq 3), which might cause a reaction(s) disadvantageous to the formation or preservation of **5a**. In our present study, all the reactions of **3** and **4** other than run 3, Table 1, were carried out with a stoichiometric amount (1 molar equiv) of positive halogen species.

The effect of electrophilic halogen compounds other than NIS was also investigated on the formation of **5a** from the reaction between **3a** and **4a** in MeCN, and the results were compared (see also Table 1). *N*-Bromosuccinimide (NBS) was far less effective than NIS, and only a very small amount of **5a** was obtained, the rest having been unreacted **3a** (run 4, Table 1). The reaction with I_2 or Br_2 proceeded considerably fast, but **5a** was furnished in an unsatisfactory yield (runs 5 or 6, Table 1). The effect of solvent was also studied. Nonpolar solvents were found to be much less suitable than MeCN. Thus, the reaction of **3a**, **4a** and NIS in DME was quite slow and gave little **5a** (run 7, Table 1). The reaction in benzene for an extended time could complete the consumption of **3a**, but **5a** was obtained only in a limited amount (run 8, Table 1). It deserves mentioning that MeCN is also the most appropriate solvent for the aforementioned positive-halogen assisted nucleophilic displacement of **3** with alcohols.[4]

Table 2. Peroxides 5 from NIS-Induced Reactions of Chloro Dienones 3 and Hydroperoxy Dienones 4 in MeCN[a]



3

a: R = Me
X = Cl
b: R = Me
X = Br
c: R = *t*-Bu
X = Br
d: R = *t*-Bu
X = Cl
e: R = Et
X = Cl

4

a: R' = Me
b: R' = *t*-Bu
c: R' = Et

5

a: R = R' = Me
b: R = R' = *t*-Bu
c: R = R' = Et
d: R = Me
R' = *t*-Bu
e: R = Et
R' = *t*-Bu
f : R = Et
R' = Me

run	3	4	5[b] (yield, %[c])
1[d,e]	**3a**	**4a**	**5a** (74)
2[e]	**3b**	**4a**	**5a** (57)
3[e,f]	**3b**	**4a**	**5a** (48)
4	**3c**	**4b**	**5b** (26)
5[g,h]	**3d**	**4b**	**5b** (0)
6	**3e**	**4c**	**5c** (61)
7	**3a**	**4b**	**5d** (61)
8	**3b**	**4b**	**5d** (49)
9	**3c**	**4a**	**5d** (58)
10[h]	**3d**	**4a**	**5d** (0)
11	**3e**	**4b**	**5e** (37)

[a] A mixture of **3** (1 mmol), **4** (3 mmol), and NIS (1 mmol) in MeCN (15 mL) was stirred for 10 min at 35 °C. Consumption of **3** was complete or essentially complete. [b] Isolated product. [c] (Mol/mol **3** employed) × 100. [d] Identical with run 2, Table 1. [e] Reaction for 5 min. [f] NBS was employed in place of NIS. [g] Reaction for 60 min. [h] Compound **3d** was recovered quantitatively.

The NIS-induced reactions in MeCN of various combinations of halogenodienones **3** and hydroperoxy dienones **4** deserved investigation. The results are summarized in Table 2. Peroxide **5a** was also obtained by the rapid reaction of 4-bromo-4-methylcyclohexa-2,5-dienone (**3b**) with **4a**, although the yield was moderate (run 2, Table 2). Replacement of NIS by NBS in this reaction also afforded **5a** rapidly (run 3, Table 2). Exposure of 4-bromo-4-*tert*-butylcyclohexa-2,5-dienone (**3c**) to 4-hydroperoxy-4-*tert*-butylcyclohexa-2,5-dienone (**4b**) produced bis(1,3,5-tri-*tert*-butyl-4-oxocyclohexa-2,5-dienyl) peroxide (**5b**) in a relatively small yield (run 4, Table 2). Complete lack of the reaction was observed between 4-chloro-4-*tert*-butylcyclohexa-2,5-dienone (**3d**) and **4b** despite an extended reaction time (run 5, Table 2). There appears to be little interaction between **3d** and NIS. The new methodology successfully afforded a new peroxide, bis(1-ethyl-3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienyl) peroxide (**5c**) in a fair yield. This was accomplished when 4-chloro-4-ethylcyclohexa-2,5-dienone (**3e**) and 4-hydroperoxy-4-ethylcyclohexa-2,5-dienone (**4c**)

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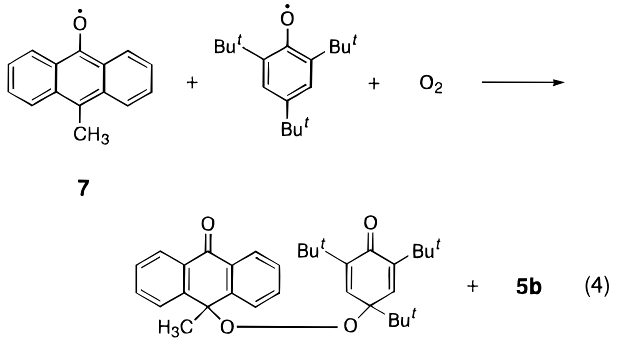
(6) However, peroxide **5a** has been isolated in an unspecified yield among other products from the reaction of 4-hydroxy-4-methyl-2,6-di-*tert*-butylcyclohexa-2,5-dienone with performic acid. See: Benjamin, B. M.; Raaen, V. F.; Hagaman, E. W.; Brown, L. L. *J. Org. Chem.* **1978**, *43*, 2986.

(7) Since ICl can play the role that NIS does in the peroxide formation, it is possible that not all of NIS employed initially in runs 2 or 3 was consumed.

were employed as the reactants (run 6, Table 2). Synthesis of **5c** by coupling of 4-ethyl-2,6-di-*tert*-butylphenoxy radicals with O_2 (cf. eq 1) has not been feasible due to rapid disproportionation of the radical.[5a]

As exemplified above, symmetrically substituted bis(oxocyclohexadienyl) peroxides **5** (R = R′) including ones unobtainable by the classical procedure (eq 1) can be synthesized by our new method.

The concept of the new method predicts that preparation of unsymmetrically substituted bis(oxocyclohexadienyl) peroxides **5** ($R \neq R'$) may likewise be possible. It should be emphasized that, as Altwicker has previously pointed out, formation of a "mixed peroxide" such as **5** ($R \neq R'$) from a competition of two different phenoxy radicals for O_2 is difficult,[1a] possibly owing to different stability and/or different reactivity toward O_2, of the different radicals. As far as we are aware, a very rare example of an isolated "mixed peroxide" is **8**.[8] Peroxide **8** is formed during thermal decomposition of a transannular ozonide of an anthracene derivative in the presence of 2,4,6-tri-*tert*-butylphenol. This decomposition is suggested to generate phenoxy radical **7**, 2,4,6-tri-*tert*-butylphenoxy radical and O_2. Peroxide **5b** is formed simultaneously, as may be anticipated (eq 4). It was proved that our procedure can indeed make "mixed peroxides", **5** ($R \neq R'$). For instance, with the assistance of NIS in MeCN, **3a** successfully coupled with **4b**, forming a new "mixed peroxide", 1-methyl-3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienyl 1,3,5-tri-*tert*-butyl-4-oxocyclohexa-2,5-dienyl peroxide (**5d**) in 61% yield (run 7, Table 2). As expected, the same peroxide (**5d**) was obtainable also from combination of **3b** with **4b** (run 8, Table 2) or of **3c** with **4a** (run 9, Table 2). From runs 7−9, Table 2, neither symmetrically substituted bis(oxocyclohexadienyl) peroxide **5a** nor **5b** was detectable, which is compatible with our originally proposed mechanism (Scheme 1). Allowing **3d** to react with **4a** for a long period, however, did not produce **5d** at all, again supporting the assumed lack of interaction between **3d** and NIS (run 10, Table 2). Another new "mixed peroxide", (1-ethyl-3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienyl) 1,3,5-tri-*tert*-butyl-4-oxocyclohexa-2,5-dienyl peroxide (**5e**) was furnished from the reaction of **3e** with **4b** (run 11, Table 2). Finally, the NIS-induced reaction of **3a** with **4c** or of **3e** with **4a** gave a crystalline product, presumed to be "mixed peroxide" **5f**, in a good yield (70% or less). Unfortunately, stubborn contamination by an impurity (impurities) has prevented purification of the product.



It is our feeling that a bulky 4-alkyl substituent in halogeno dienone **3** or hydrperoxy dienone **4** tends to decrease the yield of bis(cyclohexadienyl) peroxide **5** in the NIS reaction in MeCN, but the data accumulated above may not be enough to make a conclusive statement. In general, bis(oxocyclohexadienyl) peroxides **5** obtained in this study were isolated simply by passing the crude reaction product through neutral alumina (Activity II) with petroleum ether. Products other than **5** were not investigated in detail.

By our new method, synthesis of a variety of fresh bis(oxocyclohexadienyl) peroxides may be expected when it is taken into account that diverse methods are available for preparing 4-(or 6-)halogeno-[9] and 4-(or 6-)hydroperoxycyclohexa-2,5-(or 2,4-)dienones[10] as the starting materials.

Experimental Section

^1H (90 MHz) and ^{13}C (22.6 MHz) NMR and IR spectra were taken in $CDCl_3$ and in $CHCl_3$, respectively. TLC was run on SiO_2.

Starting Materials. Halogeno dienones **3a**,[9d] **3b**,[5b] **3c**,[5b] and **3d**[9d] were synthesized according to the reported methods. Compound **3e** was prepared in a nearly quantitative yield by adaptation of the reported method for the preparation of **3a** and **3d**,[9d] using 4-ethyl-2,6-di-*tert*-butylphenol (0.1 mol), sulfuryl chloride (0.12 mol), and trimethyl phosphate (190 mL in total) at ca. 3 °C. Light yellow crystals from hexane: mp 46−47 °C; ^1H NMR δ 6.54 (s, 2H), 2.08 (q, J = 7.4 Hz, 2H), 1.25 (s, 18H), 0.86 (t, J = 7.4 Hz, 3H); IR 1659, 1640 cm^{-1}. Anal. Calcd for $C_{16}H_{25}OCl$: C, 71.49; H, 9.37; Cl, 13.19. Found: C, 71.21; H, 9.64; Cl, 13.33.

Hydroperoxy dienones **4a** and **4b** were synthesized according to the reported procedure.[10g] Employment of a mixture of EtOH and H_2O (20:1) in place of EtOH alone as the solvent made completion of the reaction appreciably faster. Compound **4c** was obtained in 70% yield by adaptation of the method reported for the preparation of **4a** and **4b**[10g] by using 4-ethyl-2,6-di-*tert*-butylphenol (50 mmol), KOH (0.6 mol), a mixture of EtOH (400 mL) and H_2O (20 mL), and O_2. Colorless crystals from petroleum ether: mp 89−91 °C; ^1H NMR δ 7.79 (s, 1H), 6.51 (s, 2H), 1.70 (q, J = 7.5 Hz, 2H), 1.25 (s, 18H), 0.76 (t, J = 7.5 Hz, 3H); IR 3520, 3300 (br), 1665, 1642 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 72.09; H, 10.08.[11]

Other reagents were used as received.

Peroxide 5a from Chloro Dienone 3a and Hydroperoxy Dienone 4a As Assisted by Positive Halogen Reagents (Table 1). To **3a** (255 mg, 1 mmol) and a positive halogen compound (1 mmol) placed in a bottle was added in one portion a solution of **4a** (756 mg, 3 mmol) in a solvent (15 mL). In run 1, Table 1, a positive halogen reagent was omitted. In run 3, Table 1, 0.33 mmol (75 mg) of NIS was employed as the positive halogen compound. The mixture in the stoppered bottle was stirred at 35 °C for the time indicated

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in Table 1. The mixture was poured into a stirred, cold solution of $NaHSO_3$ (0.9 g) in water (150 mL). The stirring was continued for 2 min. The mixture was extracted with ether (150 mL × 2). The extract was washed with water, dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was chromatographed on neutral Al_2O_3 (Merck, 70−230 mesh, Activity II, 130 g) with petroleum ether, affording **5a** as nearly colorless crystals. Colorless crystals from hexane: mp 124 °C (lit.[6] mp 125 °C); IR 1665, 1642 cm^{-1}. The ^1H and ^{13}C NMR spectra were compatible with those reported for **5a**.[6] Anal. Calcd for $C_{30}H_{46}O_4$: C, 76.55; H, 9.85. Found: C, 76.35; H, 9.94. The highest amount of **5a** (347 mg, 74%) was obtained from run 2, Table 1.

In runs 5 or 6, Table 1, a solution of **4a** (3 mmol) in MeCN (10 mL) and a solution of I_2 (254 mg, 1 mmol) (run 5, Table 1) or Br_2 (160 mg, 1 mmol) (run 6, Table 1) in MeCN (5 mL) was added successively to **3a** (1 mmol). The mixture in a stoppered bottle was stirred at 35 °C for the time indicated in Table 1.

Treatment of **5a** (100 mg) in MeCN (15 mL) with a stirred, cold solution of $NaHSO_3$ (0.9 g) in water (150 mL) for 2 min resulted in quantitative recovery of unreacted **5a**. Replacement of **5a** in this reaction by **3a** (100 mg) gave nearly quantitative recovery of unreacted **3a**, while that by **4a** (100 mg) provided 4-hydroxy-4-methyl-2,6-di-*tert*-butylcyclohexa-2,5-dienone in ca. 90% yield as colorless crystals with mp 111−113 °C (lit.[10a] mp 112−113 °C).

Peroxides 5 from NIS-Induced Reactions of Halogeno Dienones 3 and Hydroperoxy Dienones 4 in MeCN (Table 2). To **3** (1 mmol) and NIS (225 mg, 1 mmol) placed in a bottle was added in one portion a solution of **4** (3 mmol) in MeCN (15 mL). The mixture in the stoppered bottle was stirred at 35 °C for the time indicated in Table 2. The reaction mixture was worked up and the crude product mixture was analyzed in the manner described above for the runs in Table 1.

Peroxide **5b** (143 mg, 26%) was obtained from run 4, Table 2, by using **3c** (341 mg) and **4b** (881 mg). Colorless crystals from hexane, identical with an authentic sample[12] (^1H NMR and TLC): mp 138−139 °C (lit.[12] mp 139−140.5 °C).

Treatment of a solution of **5b** (100 mg) in MeCN (15 mL) with a stirred, cold solution of $NaHSO_3$ (0.9 g) in water (150 mL) for 2 min resulted in quantitative recovery of unreacted **5b**. Replacement of **5b** in this reaction by **3c** (100 mg) resulted in quantitative recovery of unreacted **3c**, while that by **4b** (100 mg) gave 2,6-di-*tert*-butyl-*p*-benzoquinone in ca. 90% yield as deep yellow crystals, identical with an authentic sample[13] (^1H NMR and TLC): mp 64−67 °C (lit.[13] mp 65−68 °C).

Peroxide **5c** (303 mg, 61%) was obtained from run 6, Table 2, by using **3e** (269 mg) and **4c** (798 mg). Light yellow crystals from hexane: mp 132−133 °C; ^1H NMR δ 6.47 (s, 4H), 1.57 (q, $J = 7.4$ Hz, 4H), 1.26 (s, 36H), 0.71 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR δ 186.6, 148.3, 140.3, 80.2, 34.9, 30.1, 29.6, 7.8; IR 1662, 1639 cm^{-1}. Anal. Calcd for $C_{32}H_{50}O_4$: C, 77.06; H,10.10. Found: C, 76.96; H, 10.38.

Peroxide **5d** (313 mg, 61%) was obtained from run 7, Table 2, by using **3a** (255 mg) and **4b** (882 mg). Colorless crystals from MeOH: mp 122.5−124 °C; ^1H NMR δ 6.63 (s, 2H), 6.53 (s, 2H), 1.26 (s, 36H), 1.21 (s, 3H), 0.83 (s, 9H); ^{13}C NMR δ 186.4, 148.6, 147.2, 141.7, 140.4, 83.2, 76.8, 41.1, 35.1, 34.7, 29.6, 29.5, 25.9, 23.6; IR 1663, 1640 cm^{-1}. Anal. Calcd for $C_{33}H_{52}O_4$: C, 77.28; H, 10.23. Found: C, 77.00; H, 10.25.

Peroxide **5e** (196 mg, 37%) was obtained from run 11, Table 2, by using **3e** (269 mg) and **4b** (883 mg). Light yellow crystals from hexane: mp 107−108 °C; ^1H NMR δ 6.65 (s, 2H), 6.50 (s, 2H), 1.54 (q, $J = 7.9$ Hz, 2H), 1.27 (s, 36H), 0.84 (s, 9H), 0.72 (t, $J = 7.7$ Hz, 3H); ^{13}C NMR δ 186.7, 186.4, 148.5, 148.3, 140.8, 140.4, 83.1, 80.1, 40.9, 35.1, 34.9, 29.6, 25.9, 7.7; IR 1663, 1640 cm^{-1}. Anal. Calcd for $C_{34}H_{54}O_4$: C, 77.52; H, 10.33. Found: C, 77.50; H, 10.58.

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[11] Compound **4c** appears in the literature, but its physical and spectral data do not appear to have been cited. Cf. (a) Nishinaga, A.; Nakamura, K.; Matsuura, T. *Tetrahedron Lett.* **1978**, 3557. (b) Wand, M. D.; Thompson, J. A. *J. Biol. Chem.* **1986**, *261*, 14049. (c) Reference 10j.

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