

Thermal Decomposition Mechanisms of *tert*-Alkyl Peroxypivalates Studied by the Nitroxide Radical Trapping Technique

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The thermolysis of a series of *tert*-alkyl peroxy-pivalates **1** in cumene has been investigated by using the nitroxide radical-trapping technique. *tert*-Alkoxy radicals generated from the thermolysis underwent the unimolecular reactions, β -scission, and 1,5-H shift, competing with hydrogen abstraction from cumene. The absolute rate constants for β -scission of *tert*-alkoxy radicals, which vary over 4 orders of magnitude, indicate the vastly different behavior of alkoxy radicals. However, the radical generation efficiencies of **1** varied only slightly, from 53 (R = Me) to 63% (R = Bu), supporting a mechanism involving concerted two-bond scission within the solvent cage to generate the *tert*-butyl radical, CO₂, and an alkoxy radical. The thermolysis rate constants of *tert*-alkyl peroxy-pivalates **1** were influenced by both inductive and steric effects [Taft–Ingold equation, $\log(\text{rel } k_d) = (0.97 \pm 0.14)\Sigma\sigma^* - (0.31 \pm 0.04)\Sigma E_s^c$, was obtained].

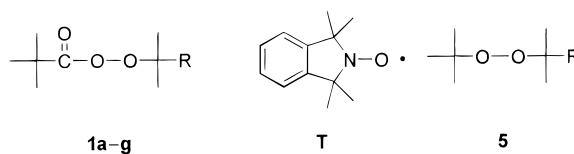
Introduction

Peroxyesters are among the most commonly used free radical initiators for the radical polymerization of olefinic compounds such as styrene and (meth)acrylates.¹ They are also useful radical sources for kinetic studies in radical chemistry.² *tert*-Alkyl peroxy-pivalates, such as *tert*-butyl peroxy-pivalate **1a**, are some of the most useful peroxyesters in polymer manufacturing, and there have been several reports concerning their decomposition mechanisms.^{3,4} Peroxyesters **1** thermolyze homolitically via a concerted two-bond scission with no cage return ($k_{-1} = 0$ in Scheme 1), as demonstrated by the quantitative formation of carbon dioxide and the independence of the decomposition rate on solvent viscosity.^{3a}

The decomposition involves a proportion of cage reaction, in which stable compounds are formed directly from the transition state **2**, e.g., isobutylene and *tert*-butyl alcohol formed by disproportionation and di-*tert*-butyl ether by radical recombination (eqs 2 and 3 in Scheme 1) for peroxyester **1a**.^{3b} However, there has been one report suggesting a transition state **4** involving a concerted “three-bond” scission for the thermolysis of **1** (Scheme 2).⁴ This decomposition mechanism was based

on the product ratio of acetone to the corresponding alcohol RCM₂OH without any consideration of the production of the alcohol by other reactions.⁵ It was concluded that the thermolysis rates of **1** were enhanced by both hyperconjugative and inductive stabilizing effects and that steric effects did not contribute to the rate enhancement. Recently, Hendrickson et al. have reported⁶ that both steric and electronic factors influence the decomposition rate constants of *t*-alkyl *tert*-butyl peroxides **5**.

In this study, the thermolysis of a series of *tert*-alkyl peroxy-pivalates **1a–g** in cumene has been investigated by using the radical trapping technique employing 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yl-oxyl (**T**), focusing on the detailed behavior of *tert*-alkoxy radicals and the decomposition mechanism. The technique was developed by the CSIRO and has been mostly used to investigate initiation mechanisms in free radical polymerization.⁷ The aminoxyl **T** reacts with carbon-centered radicals (but not oxygen-centered radicals) at close to diffusion-



a : R = Me e : R = Prⁱ
 b : R = Et f : R = C₆H₁₁^{cyclo}
 c : R = Pr^f g : R = Bu^t
 d : R = Me₃CCH₂

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(1) Sheppard, C. S. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Klingsberg, A., Piccininni, R. M., Salvatore, A., Baldwin, T., Eds.; Wiley-Interscience: New York, 1988; Vol. 11, pp 1–21.

(2) For example, see: Busfield, W. K.; Jenkins, I. D.; Monteiro, M. *J. Polymer* **1997**, *38*, 165–171.

(3) (a) Bartlett, P. D.; Simons, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 1753–1756. (b) Koenig, T.; Wolf, R. *J. Am. Chem. Soc.* **1967**, *89*, 2948–2952. (c) Lorand, J. P.; Chodroff, S. D.; Wallace, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 5266–5267. (d) Pryor, W. A.; Morkved, E. H.; Bickley, H. T. *J. Org. Chem.* **1972**, *37*, 1999–2005. (e) Ernst, J. E.; Thankachan, C.; Tidwell, T. T. *J. Org. Chem.* **1974**, *39*, 3614–3615.

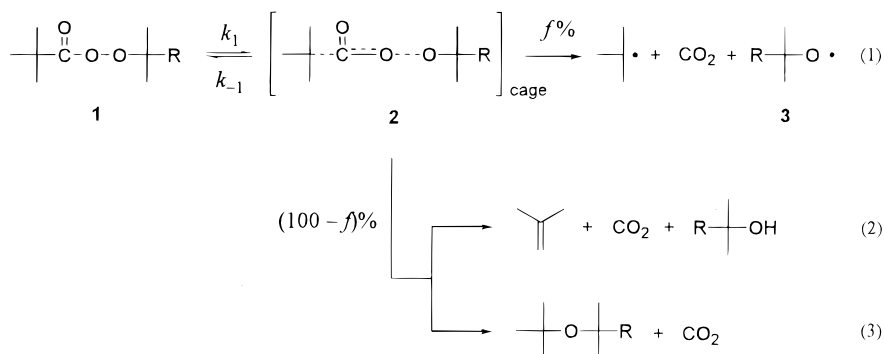
(4) Komai, T.; Matsuyama, K.; Matsushima, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1641–1646.

(5) The production of the *tert*-alcohol via intramolecular hydrogen abstraction by *tert*-alkoxy radicals also has to be considered.

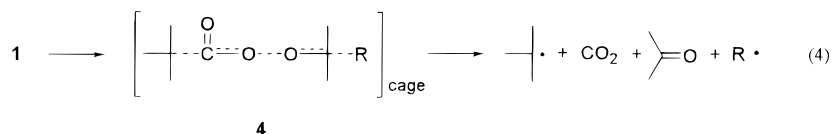
(6) Hendrickson, W. H.; Nguyen, C. C.; Nguyen, J. T.; Simons, K. T. *Tetrahedron Lett.* **1995**, *36*, 7217–7220.

(7) Busfield, W. K.; Jenkins, I. D.; Nakamura, T.; Monteiro, M. J.; Rizzardo, E.; Suyama, S.; Thang, S. H.; Le, P. V.; Zayas-Holdsworth, C. I. *Polym. Adv. Tech.* **1998**, *9*, 94–100 and references contained therein.

Scheme 1



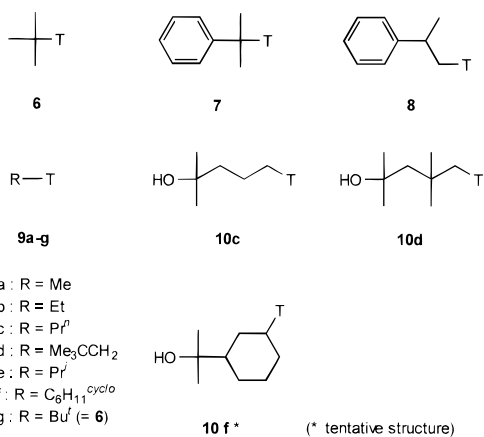
Scheme 2



controlled rates to produce stable alkoxyamines.⁸ In our previous work,⁹ we have shown that the thermolysis of *tert*-alkyl peroxy-pivalates is not affected by the presence of **T** and equimolar amounts of *tert*-butyl and *tert*-alkoxy radicals **3** are generated.

Results and Discussion

Thermal Decomposition Products of 1 in the Presence of T. *tert*-Alkyl peroxy-pivalates **1a–g** were prepared by the reaction of pivaloyl chloride with the corresponding *tert*-alkyl hydroperoxides in alkaline solution according to the literature procedure.^{4,9} The thermal decomposition of **1** (0.040 M) in cumene as solvent in the presence of **T** (0.040 M) was carried out in vacuo at 60 °C for 3.0 h.¹⁰ Alkoxyamines formed by trapping of the carbon-centered radicals derived from the peroxide or of the radicals resulting from the reactions of the primary radicals with cumene were analyzed by HPLC, HPLC–MS, and NMR.



tert-Butyl radicals generated from the thermolysis of **1** were immediately trapped by **T** to form *tert*-butoxyamine **6** [$k_T(\text{Bu}^\cdot) = \text{ca. } 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$].⁸ On the other hand, a variety of products were formed from the reaction

of *tert*-alkoxy radicals. Alkoxyamines **7** and **8** were derived from hydrogen abstraction from cumene by *tert*-alkoxy radicals (it is unlikely that any of the alkyl radicals are involved in significant H-abstraction from cumene under these reaction conditions, since the rate of trapping is extremely fast). No other cumene-derived products were detected. Phenylalkyl radicals such as 2-phenylpropyl radicals could rearrange via 1,2-phenyl migration; however, this reaction is too slow ($<10^4 \text{ s}^{-1}$)¹¹ to compete with trapping under the reaction conditions. Alkoxyamines **9** and **10** were derived from the alkyl radicals formed by β -scission and by rearrangement of *tert*-alkoxy radicals, respectively. Unfortunately, an insufficient amount of **10f** was available for complete characterization by NMR. The tentative structure of **10f** is proposed on the basis of the MS and ¹H NMR. A tiny amount of an isomer of **10f** was also detected. The relative yields of *tert*-alkoxy radical-derived products **7–10** to the yield of *tert*-butoxyamine **6** (taken as 100%) are shown in Table 1, and a postulated reaction mechanism for the decomposition of *tert*-alkoxy radicals is shown in Scheme 3.

It can be seen from Table 1 that the total yields of alkoxyamines **7–10** were entirely comparable to the yield of **6** in all runs, showing that the thermolysis of **1** generates an equimolar amount of *tert*-butyl and *tert*-alkoxy radicals.⁹ A slightly lower yield of alkoxyamine

(9) (a) Nakamura, T.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *J. Am. Chem. Soc.* **1996**, *118*, 10824–10828. (b) Nakamura, T.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *Macromolecules* **1997**, *30*, 2843–2847. (c) Nakamura, T.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *J. Org. Chem.* **1997**, *62*, 5578–5582. (d) Nakamura, T.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *J. Am. Chem. Soc.* **1997**, *119*, 10987–10991. (e) Nakamura, T.; Watanabe, Y.; Tezuka, H.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *Chem. Lett.* **1997**, 1093–1094. (f) Nakamura, T.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *Chem. Lett.* **1998**, 965–966. (g) Nakamura, T.; Busfield, W. K.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H.; Suyama, S. *Polymer* **1999**, *40*, 1395–1401.

(10) A relatively low concentration of **T** was used in order to try to study the (competitive) reaction of alkyl radicals such as 1,2-phenyl migration. However, under the condition of the reaction, **T** is still present in excess because of the low conversion (<40%) and <65% efficiency of generation of radicals from **1**.

(11) The absolute rate constant for the neophyl rearrangement has been estimated to be $6 \times 10^3 \text{ s}^{-1}$ at 60 °C (Lindsay, D. A.; Luszyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 7078–7093).

(8) Beckwith, A. L. J.; Bowry, V. W.; Moad, G. *J. Org. Chem.* **1988**, *53*, 1632–1641.

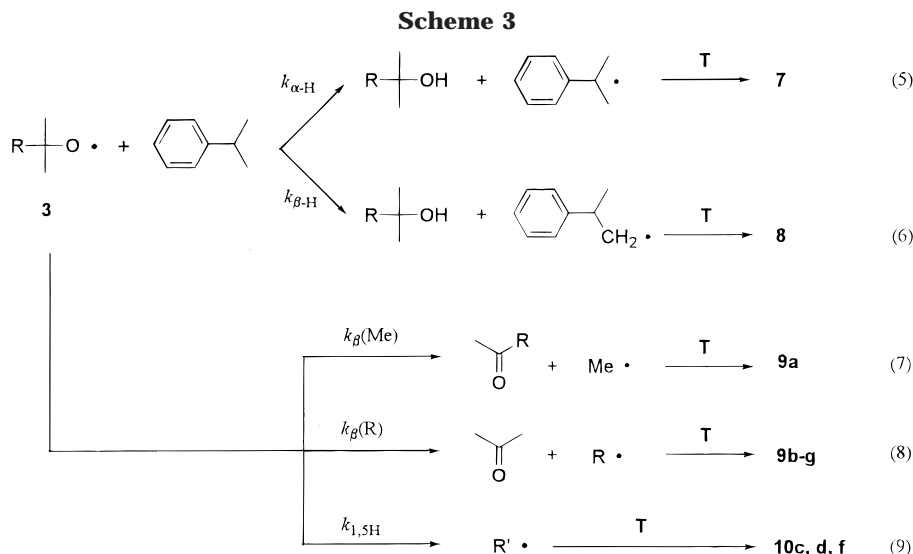


Table 1. Relative Yields of *tert*-Alkoxy Radical-Derived Products in the Thermolysis of **1 in Cumene in the Presence of T at 60 °C^a**

run	<i>tert</i> -alkoxy radicals (3)	R in 3	relative product yields (%)				
			7	8	9a	9b–g	10
1	3a	Me	94.0	4.3	1.7		
2^b	3a	Me	92.8	4.3	1.7		
3	3b	Et	38.8	1.6	0.9	58.7	
4	3c	Pr ⁿ	22.4	0.8	0.6	32.8	43.3
5	3d	Me ₃ CCH ₂	2.7	0.1	0.7	43.1	53.5
6	3e	Pr ⁱ	4.8	0.2	0.5	94.5	
7	3f	<i>c</i> -C ₆ H ₁₁	0.6	trace	0.1	96.8	2.5 ^c
8	3g	Bu ^t	0.2	trace	0.1	99.7	

^a [1]₀ = 0.040 M, [T]₀ = 0.040 M, reaction time: 3.0 h. ^b Reaction time: 65 h. ^c The total yield of two isomers (2.3% + 0.2%).

7 was observed in a longer reaction time (run 2 in Table 1), which might be due to lower stability of **7** under the reaction conditions.¹² The major reaction with *tert*-butoxy radicals **3a** was hydrogen abstraction from cumene. β -Scission to form methyl radicals was a very minor process. On the other hand, *tert*-alkoxy radicals **3b–g** underwent significant β -scission, generating alkyl radicals to form the corresponding alkoxyamines **9b–g**. In addition, alkoxy radicals **3c**, **3d**, and **3f** underwent intermolecular hydrogen abstraction (1,5-H shift) to form **10c**, **10d**, and **10f**, respectively.

Hydrogen Abstraction from Cumene by *tert*-Alkoxy Radicals. Cumene underwent hydrogen abstraction by *tert*-alkoxy radicals, resulting in alkoxyamines **7** and **8** (eqs 5 and 6 in Scheme 3). The overall reactivity of cumene toward hydrogen abstraction by *tert*-alkoxy radicals was estimated by using the competing fragmentation reaction to form methyl radicals (eq 7) as a “free radical clock”¹³ From the ratio of the product yield (**7** + **8**)/**9a** in run 1 and taking the concentration of cumene as 7.2 M, the value of $k_{\text{H}}/k_{\beta}(\text{Me})$ for *tert*-butoxy radicals **3a** was calculated to be 8.0 M⁻¹, where k_{H} is an overall reaction rate constant for hydrogen abstraction from cumene (per molecule). Our value is in good agreement

Table 2. Relative Rates of 1,5-Hydrogen Shift versus β -Scission of *tert*-Alkoxy Radicals (3c**, **3d**, and **3f**) in Cumene at 60 °C**

<i>tert</i> -alkoxy radical (3)	R in 3	δ -hydrogen		
		no.	type	$k_{1,5\text{H}}/k_{\beta}(\text{R})$
3c	Pr ⁿ	3	primary	1.3
3d	Me ₃ CCH ₂	9	primary	1.2
3f	<i>c</i> -C ₆ H ₁₁	2	secondary	0.03

with the literature value of 6.3 M⁻¹ at 60 °C in benzene.¹⁴ Similarly, the individual reactivities of the α - and β -hydrogens of cumene toward abstraction by **3a** were determined. The values, corrected for the statistical factor, were $k_{\alpha\text{-H}}/k_{\beta}(\text{Me}) = 7.7$ and $k_{\beta\text{-H}}/k_{\beta}(\text{Me}) = 0.060$ M⁻¹ (per C–H bond), respectively, and the relative reactivity of β -H to α -H of cumene was $k_{\beta\text{-H}}/k_{\alpha\text{-H}} = 0.008$ (per C–H).¹⁵ Thus, the reactivity of the β -H of cumene seems to be very comparable to that of *tert*-butylbenzene [$k_{\beta\text{-H}}/k_{\beta}(\text{Me}) = 0.050$ M⁻¹ at 60 °C (per C–H bond)].¹⁹

β -Scission of *tert*-Alkoxy Radicals. In contrast to the *tert*-butoxy radical, other *tert*-alkoxy radicals **3b–g** underwent significant β -scission to form alkoxyamines **9b–g** as the major reaction pathway (eq 8 in Scheme 3). For **3c** and **3d** other pathways are equally important (i.e., 1,5-hydrogen shift) as shown in Table 2. The relative rates of β -scission to hydrogen abstraction from cumene, $k_{\beta}(\text{R})/k_{\text{H}}$, for *tert*-alkoxy radicals **3** were obtained from the ratio of **9**/(**7** + **8**). Assuming that k_{H} for any *tert*-alkoxy radical has approximately the same value,²⁰ the absolute rate constants for β -scission of *tert*-alkoxy

(14) Dulog, L.; David, K.-H. *Makromol. Chem.* **1976**, *177*, 1717–1724.

(15) Although Walling and Jacknow¹⁶ have obtained a much higher value ($k_{\beta\text{-H}}/k_{\alpha\text{-H}} = 0.038$) from the yields of 2-chloro-2-phenylpropane **11** (81.3%) and 1-chloro-2-phenylpropane **12** (18.7%) in the photochlorination of cumene by *t*-BuOCl at 40 °C, it was later shown that the reaction involved a chlorine atom chain,¹⁷ which would lead to a product distribution of **11**:**12** = ca. 70:30.¹⁸

(16) Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6108–6112.

(17) Walling, C.; McGuinness, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2053–2058.

(18) Russell, G. A.; Brown, H. C. *J. Am. Chem. Soc.* **1955**, *77*, 4578–4582.

(19) The value was calculated from the Arrhenius equation [$\log [A(\beta\text{-H abstraction})/A(\beta\text{-scission})] = -4.22 \text{ M}^{-1}$, $E_{\alpha}(\beta\text{-H abstraction}) - E_{\alpha}(\beta\text{-scission}) = -24.7 \text{ kJ mol}^{-1}$]. Howard, J. A.; Scaiano, J. C. *Landolt-Börnstein, New Series, Radical Reaction Rates in Solution*; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, Part d, pp 107–108.

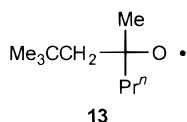
(20) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593–1597.

(12) The half-life of the analogue alkoxyamine to **7**, 1-(2-methyl-2-phenylethoxy)-2,2,6,6-tetramethyl-4-oxopiperidine, has been reported to be ca. 3.6 h at 100 °C in degassed *tert*-butylbenzene (Howard, J. A.; Tait, J. C. *J. Org. Chem.* **1978**, *43*, 4279–4283).

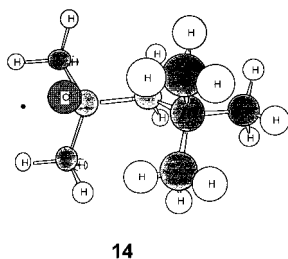
(13) Griller, D. G.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323.

radicals, $k_{\beta}(R)$, were estimated from the concentration of cumene (7.2 M) and the reported value of k_H for **3a** ($= 8.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).²¹ The resulting values of $k_{\beta}(R)$ increased in the following order: **3a** ($1.1 \times 10^5 \text{ s}^{-1}$) < **3c** ($8.9 \times 10^6 \text{ s}^{-1}$), **3b** ($9.1 \times 10^6 \text{ s}^{-1}$) < **3d** ($9.6 \times 10^7 \text{ s}^{-1}$) < **3e** ($1.2 \times 10^8 \text{ s}^{-1}$) < **3f** ($1.0 \times 10^9 \text{ s}^{-1}$) < **3g** ($3.1 \times 10^9 \text{ s}^{-1}$)

It is obvious that the rate constants depend greatly on the nature of the R group in *tert*-alkoxy radicals, varying by 4 orders of magnitude over the series **3a–g**. Kochi has mentioned that the rates for β -scission depend on the stability of the leaving alkyl radicals.²² Our value of k_{β} for **3a** was very similar to the literature value of $0.7 \times 10^5 \text{ s}^{-1}$ at 60 °C.²³ However, it seems unlikely that the rate constant for neopentyl radical elimination from **3d** is significantly higher (more than 10 times) than that of *n*-propyl radical elimination from **3c** and that of ethyl radical elimination from **3b**. The elimination rates to produce neopentyl and *n*-propyl radicals in the β -scission of the alkoxy radical **13** have been reported to be the same at 0 °C.²⁴



This contradiction could be caused by the above assumption of the same values of k_H . We have previously reported that the lower reactivity of alkoxy radical **3d** is due to the steric hindrance around the oxygen radical caused by the methyl groups on the γ -carbon as shown in the preferred conformer **14** of **3d**.^{9d}



Similarly, if there is significant steric hindrance around the oxygen in other *tert*-alkoxy radicals (although with the exception of **3g**, it is expected to be less than that in **3d**), the above k_H values become smaller correspondingly.

It is also worth noting that the rate constants for β -scission of **3a–g** are less than the rate constant for diffusion of a radical from a solvent cage (estimated to be of the order of 10^{10} s^{-1}).^{3d,25} Therefore, it is unlikely that β -scission occurs via the transition state **4** in the solvent cage as shown in Scheme 2. Further evidence against the transition state **4** is provided by radical efficiencies (see the following text).

1,5-Hydrogen Shift of *tert*-Alkoxy Radicals. *tert*-Alkoxy radicals **3c**, **3d**, and **3f** underwent the alternative unimolecular reaction, a 1,5-H shift, in addition to

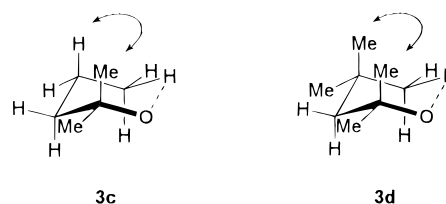


Figure 1. 1,3-Diaxial interaction in the transition states for 1,5-H shift in *tert*-alkoxy radicals **3c** and **3d**.

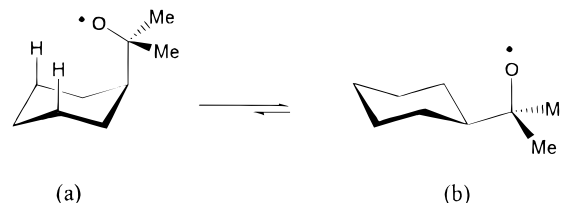


Figure 2. Axial (a) and equatorial (b) conformer of *tert*-alkoxy radical **3f**.

Table 3. Radical Generation Efficiency (*f*) for *tert*-Alkyl Peroxypivalates **1** in Cumene at 60 °C^a

	Me	Et	Pr ⁿ	Me ₃ CCH ₂	Pr ⁱ	<i>c</i> -C ₆ H ₁₁	Bu ^t
peroxypivalates	1a	1b	1c	1d	1e	1f	1g
<i>f</i> (%)	53	53	54	61	55	56	63

^a [**1**]₀ = 0.050 M, [**T**]₀ = 0.110 M.

β -scission, resulting in the corresponding alkoxyamines **10**. The relative rates, $k_{1,5H}/k_{\beta}(R)$, for these *tert*-alkoxy radicals are listed in Table 2 as well as the numbers and types of δ -position hydrogen.

Since the absolute rate constants of β -scission, $k_{\beta}(R)$, for both alkoxy radicals **3c** and **3d** are comparable as discussed above, the rate constants of $k_{1,5H}$ for both alkoxy radicals are also comparable, even though a 1,5-H shift in 1,1,2,2-tetramethylpropoxyl radicals **3d** has a 3-fold statistical advantage (**3d** has three times more δ -hydrogens than *tert*-hexyloxy radicals do). We have previously suggested that the relatively low rate for the 1,5-H shift observed in **3d** is a result of the steric repulsion between the two methyl groups attached to the α - and γ -carbons (see Figure 1),^{9d} which may disfavor a chair conformation of the six-membered ring as the transition state for a 1,5-H shift.

The 1,5-H shift in **3f** was a very minor reaction, although **3f** has secondary hydrogens at the δ -position. This must be due to the large steric repulsion (1,3-diaxial interactions) in the conformer (a) required for internal H-abstraction (see Figure 2).

Radical Generation Efficiency of the Thermolysis of **1.** The radical generation efficiency (*f*) of **1** was measured by a trapping experiment. Thus, peroxyester **1** (0.050 M) in cumene was completely decomposed at 60 °C for 10 half-lives in the presence of excess **T** (0.110 M). *tert*-Butyl radicals generated from the thermolysis of **1** were immediately trapped by **T** to form *tert*-butoxyamine **6** [$k_T(\text{Bu}^t) = \text{ca. } 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$].⁸ In a separate experiment, alkoxyamine **6** was found to be stable under the reaction conditions (see the Experimental Section). The value of *f* was determined from the yield of *tert*-butoxyamine **6** on the basis of peroxyester consumed. The results are shown in Table 3. Each value was the average from several experiments. The observed value for **1a** is close to that given in previous reports, in which the extent

(21) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

(22) Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 1193–1197.

(23) The value was calculated from the Arrhenius equation ($\log A = 13.4 \text{ s}^{-1}$, $E_a = 54.4 \text{ kJ mol}^{-1}$) in ref 3d.

(24) Greene, F. D.; Savitz, M. L.; Osterholtz, F. D.; Lau, H. H.; Smith, W. N.; Zanet, P. M. *J. Org. Chem.* **1963**, *28*, 55–64.

(25) Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, p 173.

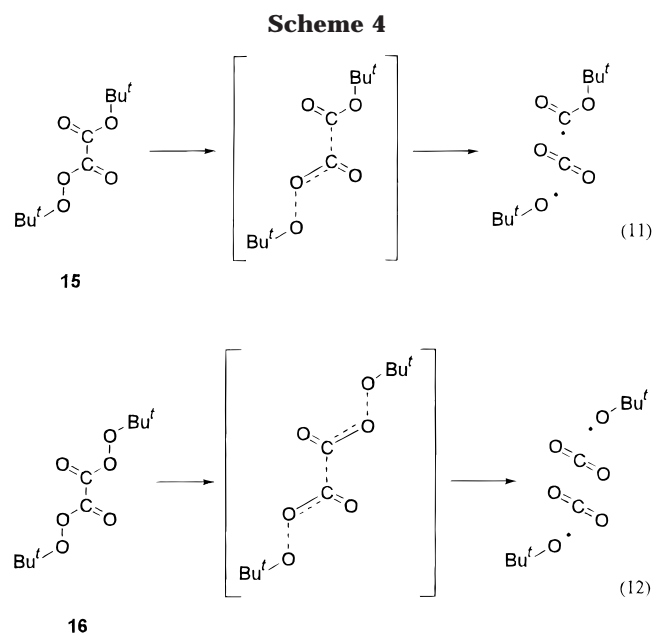
Table 4. Decomposition Rate Constants and Activation Parameters for the Thermolysis of *tert*-Alkyl Peroxypivalates **1 in Cumene^a**

1	R	T(°C)	$k_d \times 10^5$ (s ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	rel k_d^b	$\Sigma\sigma^*{}^c$	$\Sigma E_s^c{}^d$
1a	Me	60	2.95	118.3 ± 1.1	22.7 ± 6.7	≡ 1.00	-0.300	-2.10
1b	Et	60	3.51	114.9 ± 1.2	14.5 ± 7.2	1.19	-0.315	-2.35
1c	Pr ⁿ	60	3.37	116.3 ± 0.8	18.0 ± 4.8	1.14	-0.330	-2.54
1d	Me ₃ CCH ₂	60	6.18	112.4 ± 1.3	11.6 ± 8.1	2.09	-0.344	-3.43
1e	Pr ^t	60	5.14	114.3 ± 1.4	15.8 ± 8.7	1.74	-0.325	-2.80
1f	c-C ₆ H ₁₁	40	0.356	116.8 ± 0.7	23.6 ± 4.0	1.94	-0.260	-3.01
		50	1.57					
		60	5.72					
		70	20.0					
1g	Bu ^t	40	0.689	109.4 ± 1.1	5.1 ± 7.0	3.08	-0.365	-3.70
		45	1.36					
		50	2.51					
		55	5.01					
		60	9.10 ^e					
1h	PhCH ₂	60	6.91	116.5 ± 0.4	24.4 ± 2.7	2.34	-0.120	-2.55
1i	Ph	60	10.32	114.8 ± 0.2	22.5 ± 1.3	3.50	+0.025	-2.94

^a [1]₀ = 0.05 M. See ref 4 for **1a–e,h** and ref 30 for **1i**. ^b The relative thermolysis rate at 60 °C. ^c The sum of the substituent constant of σ^* .^{6,31,32} ^d Hancock's corrected steric constant³² calculated by eq 8 in ref 33. ^e Extrapolated.

of the cage reaction (100 - *f*%) for **1a** in cumene was estimated to be ca. 50%.^{3b,d}

It is noteworthy that the efficiency does not change very much by changing the alkyl group R in **1** despite the very different behavior of these alkoxy radicals. Kiefer et al.²⁶ and Leffler²⁷ have studied radical efficiency and mentioned that in a concerted decomposition, more intervening molecular fragments between the caged radicals cause higher radical generation efficiency because the reaction of caged radicals is hindered by such molecules, thus allowing more of the radicals to escape.



The value of *f* for di-*tert*-butyl mono-peroxyoxalate **15**, which decomposed via a concerted two-bond scission and in which the caged radicals are separated by one CO₂ molecule, was reported to be ca. 0.50.²⁸ By contrast, the decomposition of di-*tert*-butyl peroxyoxalate **16**, which forms two intervening molecules of CO₂, resulted in 93–

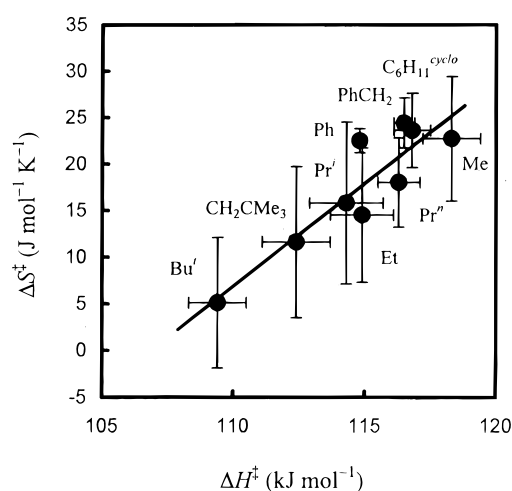


Figure 3. ΔS^\ddagger plotted against ΔH^\ddagger for the thermolysis of *tert*-alkyl peroxy-pivalates **1** in cumene.

99% radical efficiency.^{26,29} Thus, in the thermal decomposition of peroxy-pivalates **1**, the transition state **4** (which would result in two intervening molecules) can probably be excluded; i.e., the extent of C–R bond cleavage is not advanced in the transition state. The small but significant increase of *f* for **1d** and **1g** compared to the *tert*-butyl analogue **1a** might be attributed to the correspondingly longer distance between radical pairs (*tert*-butyl and *tert*-alkoxy radicals) caused by steric repulsion, i.e., radical combination should be slightly less for **1d** and **1g**.

Decomposition Mechanism of *tert*-Alkyl Peroxy-pivalates in Cumene. The decomposition rate constants and the activation parameters of the series of **1** [six electron-donating alkyl substituents studied above, one weaker electron-donating (R = PhCH₂) and one electron-withdrawing substituent (R = Ph)] in cumene are summarized in Table 4. It can be seen from Figure 3 that a linear free energy relationship was observed in a plot of ΔS^\ddagger versus ΔH^\ddagger , which suggests that the fragmentation mechanism does not change across the series.³⁴ The

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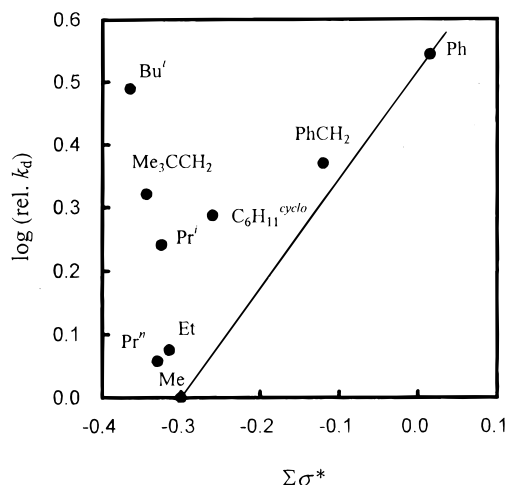
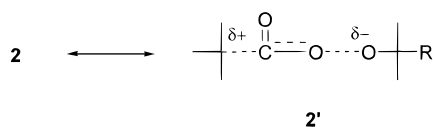


Figure 4. Taft plot for the thermolysis of *tert*-alkyl peroxy-pivalates **1** in cumene.

thermolysis rates of peroxy-pivalates **1** increased in the order **1a** < **1c** < **1b** < **1e** < **1f** < **1d** < **1h** < **1g** < **1i**. The fact that peroxyester **1i** decomposes 3.5 times faster than **1a** can be explained by a polarized transition state **2'**.^{30,35} However, it is clear from Figure 4 that the Taft equation



does not fully explain the rate acceleration of all the peroxides. A small deviation of **1h** (R = PhCH₂) from a linear line passing through the points of **1a** and **1i** indicates that the resonance effects on the alkyl group stabilities are not important, which can be understood by little possibility of the transition states **4** as mentioned above.

It is worthy of note that the values of ΔH^\ddagger and ΔS^\ddagger for two peroxy-pivalates with bulky alkyl groups [R = Me₃CCH₂ (**1d**) and Bu^t (**1g**)] are lower than those of others. The trend in ΔH^\ddagger and ΔS^\ddagger has been explained in terms of frozen bond rotations in the transition state.³⁶ That is, in the concerted two-bond scission of peroxyesters, both of the σ bonds to the CO₂ moiety need to be approximately *antiperiplanar*, which results in the loss of rotational freedom in the carbonyl to oxygen bond and, hence, in a lower entropy (Figure 5).

It is very important to note that in the antiperiplanar conformer the steric repulsion between oxygen in carbonyl group and RMe₂ groups becomes significant due to the reduced distance between carbonyl oxygen and

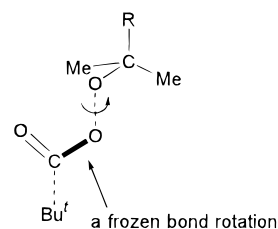


Figure 5. Antiperiplanar conformer of **1**.

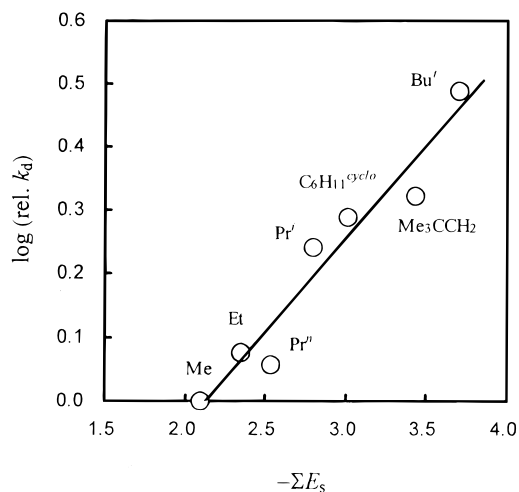


Figure 6. Correlation between relative rate constants for the thermolysis of **1** and Hancock corrected steric constants (ΣE_s^c).

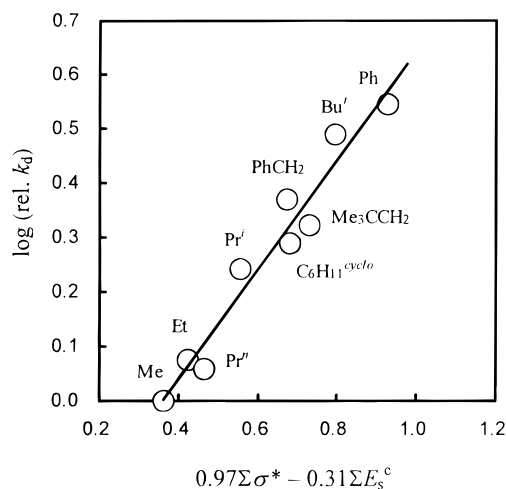


Figure 7. Correlation of $\log(\text{rel } k_d)$ with $0.97\Sigma\sigma^* - 0.31\Sigma E_s^c$.

(31) $\Sigma\sigma^*$ for R(CH₃)₂C group was obtained by adding each substituent constant of RCH₂ and two CH₃CH₂. (a) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 4231–4238. (b) Richardson, W. H.; Yelvington, M. B. Andrist, A. H.; Ertley, E. W.; Smith, R. S.; Johnson, T. D. *J. Org. Chem.* **1973**, *38*, 4219–4225.

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oxygen in alkoxy groups and may cause the loss of rotational freedom in an additional bond. We suggest that the lower values of ΔS^\ddagger for peroxy-pivalates are a result of the correspondingly restricted O–O bond rotation caused by the steric hindrance around the oxygen in alkoxy groups as mentioned above. This may indicate that the steric factors control the thermolysis rates of **1**.

Hancock's corrected steric constants (E_s^c),³² which separate the hyperconjugation effect from Taft's steric substituent constant E_s , were employed for the study of the influence of steric effects on the thermolysis rate of **1**. The values of E_s^c were calculated by a method developed by Fujita.³³ The plots of the logarithm of the thermolysis constants of peroxy-pivalates with electron-donating alkyl substituents **1a**–**1g** versus E_s^c of R(CH₃)₂C

groups as shown in Figure 6 give a good correlation with a slope of -0.29 ($r = 0.968$). These results indicate that steric effects are a major contributor to the rate acceleration for **1**. Utilization of the Taft–Ingold equation [$\log(\text{rel } k_d) = \rho^* \Sigma \sigma^* + \delta \Sigma E_s^c$] gives $\rho^* = 0.97 \pm 0.14$ and $\delta = -0.31 \pm 0.04$ ($r = 0.974$) for the thermolysis of peroxyesters **1** (Figure 7). The positive value of ρ^* shows that an electron-withdrawing substituent R in the *tert*-alkoxy group accelerates the decomposition. Thus, the thermolysis rate of *tert*-alkyl peroxyphthalates **1** are influenced by both polar (i.e., electronic) and steric effects, although a previous report has excluded any contribution from steric effects to the rate enhancement.⁴

Conclusions

In this study, the reactions of *tert*-alkoxy radicals and the thermolysis mechanism of **1** were studied by the nitroxide trapping technique. The absolute rate constants for β -scission of *tert*-alkoxy radicals, which vary over 4 orders of magnitude, indicate the vastly different behavior of alkoxy radicals. However, even 1,1,2,2-tetramethylpropoxy radicals **3g** are relatively stable in the solvent cage, with a k_β less than the rate constant for diffusion from the cage. The radical generation efficiencies of a series of peroxyesters **1** varied slightly, from 53 (R = Me) to 63% (R = Bu^t). These values are not sufficiently high to support the notion that β -scission occurs in the solvent cage. Moreover, for R groups such as R = Me₃CCH₂ or Prⁿ, the major reaction observed is a 1,5-H shift, not β -fragmentation. Thus, the data presented here support a homolysis mechanism involving concerted two-bond scission within a solvent cage (Scheme 1), not three-bond scission (Scheme 2), as has been suggested previously. This work has clearly shown that the thermolysis rates of a series of *tert*-alkyl peroxyphthalates **1** correlate with $\rho^* \Sigma \sigma^* + \delta \Sigma E_s^c$, which indicates that the thermolysis rates are accelerated by an electron-withdrawing substituent in the *tert*-alkoxy group, i.e., both inductive effects and steric effects are important in the thermolysis reaction. Among the *tert*-alkyl peroxyphthalates **1** studied here, **1d** (R = Me₃CCH₂) and **1g** (R = Bu^t) showed the highest decomposition rates and radical generation efficiencies, mainly as a result of steric effects.

Experimental Section

Materials. Cumene was washed with concentrated H₂SO₄ and water, dried over anhydrous Na₂SO₄, distilled at atmospheric pressure, and stored in a refrigerator (-20 °C). *tert*-Alkyl peroxyphthalates **1**^{4,9} and nitroxide **T**³⁷ were prepared by the literature procedure. 3-Phenylbutyryl chloride was obtained from the chlorination of 3-phenylbutyric acid by thionyl chloride. Spectroscopic data of 3-phenylbutyryl chloride: δ_{H} (CDCl₃) 1.39 (d, 3H, CH₃, $J = 6.9$ Hz), 3.1–3.5 (m, 3H, CH and CH₂), 7.2–7.4 (m, 5H, ArH); δ_{C} (CDCl₃) 21.4 (CH₃), 36.7 (CH), 55.1 (CH₂), 126.7, 127.0 (C-2, C-4), 128.9 (C-3), 144.0 (C-1), 172.4 (C=O).

Preparation of Di(3-phenylbutyryl) Peroxide. 3-Phenylbutyryl chloride (9.13 g, 0.05 mol) in toluene (15 mL) was added dropwise over a period of 25 min with stirring at 0 – 5 °C to a mixture of 30% hydrogen peroxide (3.40 g, 0.03 mol) and 15% KOH (20.57 g, 0.055 mol). Stirring was continued for 30 min at 0 – 5 °C, and then toluene was added to the mixture. The organic layer was washed with water and dried over anhydrous Na₂SO₄ and MgSO₄. After the evaporation of

the solvent under vacuum, a product of 6.1 g was obtained. The purity was determined by iodometric titration using isopropyl alcohol and acetic acid as the solvent and saturated sodium iodide as the source of iodide. The purity and yield of the hydroperoxide were 98.8% and 74.0%, respectively. The structure was consistent with its NMR: δ_{H} (CDCl₃) 1.42, (d, 6H, $2 \times \text{CH}_3$, $J = 7.0$ Hz), 2.6–2.8 (m, 4H, $2 \times \text{CH}_2$), 3.3–3.5 (m, 2H, $2 \times \text{CH}$), 7.2–7.4 (m, 10H, $2 \times \text{ArH}$); δ_{C} (CDCl₃) 21.5 (CH₃), 36.5 (CH), 38.6 (CH₂), 126.7, 126.9 (C-2, C-4), 128.8 (C-3), 144.8 (C-1), 167.9 (C=O). The half-lives of the analogous peroxides, 3-phenylpropionyl peroxide and 3-methyl-3-phenylbutyryl peroxide, were reported to be ca. 28 h at 55.8 °C and ca. 30 h at 55.0 °C, respectively.³⁸

General Method. The general procedure for carrying out the radical trapping experiments and for the quantitative analysis of the reaction products has been described previously.⁹ The products of the trapping experiments were in each case isolated by preparative HPLC and characterized by spectroscopic methods.

Kinetic Experiment. The thermolysis of **1** (0.05 M), which was carried out in degassed cumene at several temperatures (40 – 70 °C), was measured by monitoring its disappearance by iodometric titration and was found to satisfy first-order kinetics at all of the temperatures. The decomposition rate constants and the activation parameters at 60 °C were calculated from Arrhenius plots.

Trapping Experiments. In a typical reaction, a solution of **1** (0.040 M) and **T** (0.040 M) in cumene was degassed by three successive freezing–pump–thaw cycles to 10^{-4} mmHg. The reaction vessel was then sealed under vacuum and heated at 60 ± 0.1 °C for 3.0 h. The majority (ca. 90%) of excess cumene was then removed under reduced pressure prior to analysis by reversed-phase HPLC with methanol/water mixtures as the eluent.

Radical Generation Efficiency. A solution of **1** (0.050 M) and excess **T** (0.110 M) in cumene was degassed. The reaction vessel was then sealed under vacuum and heated at 60 °C for 65 h (>10 half-lives of **1**). The majority (ca. 90%) of excess cumene was removed under reduced pressure, which was followed by the analysis of the residue by HPLC. Several runs were carried out for each peroxyester, and the value of f was determined from the average yield of *tert*-butoxyamine **6** based on peroxyester consumed. A blank experiment was carried out in order to test the stability of **6**. Thermolysis of **6** (0.050 M) in cumene in the presence of **T** (0.050 M) indicated no significant decomposition of **6** after 65 h at 60 °C.

Products and New Compounds. The HPLC-separated products were identified by electrospray mass spectrometry. Products **6**, **7**, **9**, and **10** (except for **10f**) were also identified by co-chromatography with authentic samples.^{7,39–41}

The new compound **8** was isolated by preparative HPLC and characterized by NMR. An authentic sample of alkoxyamine **8** was prepared by the thermolysis of di(3-phenylbutyryl) peroxide in the presence of **T** in benzene. Thus, a solution of di(3-phenylbutyryl) peroxide (97.9 mg, 0.30 mmol) and **T** (95.1 mg, 0.50 mmol) in benzene (6 mL) was degassed and heated at 60 °C for 89 h. After evaporation of the solvent under vacuum, alkoxyamine **8** was isolated from the residue by preparative HPLC.

The tentative structure of **10f** was proposed by means of the MS and ¹H NMR, and it is the most likely on the basis of the other products observed in the reaction of other *tert*-alkoxy radicals **3c** and **3d**. However, the ¹H NMR spectrum of alkoxyamine **10f** was complex, and an insufficient amount of **10f** was available for complete characterization by NMR, which usually requires proton decoupling experiments, DEPT, and

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COSY relay experiments to confirm assignments. The four strong methyl signals of the isoindoline moiety had chemical shifts that overlapped those of the cyclohexyl ring protons, so that determination of coupling constants and connectivity were difficult. Another isomer of **10f** was detected by HPLC and HPLC-MS, but in lower yield (0.2%) than **10f** (2.3%). It ran slightly faster on HPLC (90% methanol/water mixture as eluent).

Spectroscopic data for new compounds and some known compounds are listed below [ring CH₃ refers to methyl substituents on the isoindole and primed carbon numbers refer to the monosubstituted phenyl ring (for **7** and **8**) or the cyclohexyl ring (for **9f**).

2-(1-Methyl-1-phenylethoxy)-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole 7:^{9f} $\delta_{\text{C}}(\text{CD}_3\text{OD})$ 26.3, 29.2 and 30.6 [4 × ring CH₃ and 2 × (CH₃)₂CO], 67.0 (C-1, C-3), 80.3 [(CH₃)₂CON], 122.6 (C-4, C-7), 127.4 (C-2'), 127.9 (C-4'), 128.2 (C-5, C-6), 128.8 (C-3'), 146.6 (C-3a, C-7a), 149.5 (C-1').

2-(2-Phenylpropoxy)-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole 8: $\delta_{\text{H}}(\text{CDCl}_3)$ 1.43, 1.44 and 1.48 (3 × br s, 15H, 4 × ring CH₃ and CH₃CH), 3.05–3.15 [m, 1H, CH₃CH], 4.0–4.2 [m, 2H, CH₂ON], 7.10–7.15 (m, 2H, ArH), 7.22–7.32 (m, 2H, ArH), 7.34–7.40 (m, 5H ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 18.7 (CH₃CH), 24–31 (br hump, 4 × ring CH₃), 39.8 (CH₃CH), 67.3 (C-1, C-3),

83.3 (CH₂ON), 121.5 (C-4, C-7), 126.3 (C-2', C-4'), 127.2 (C-5, C-6), 128.3 (C-3'), 144.9 (C-1'), 145.4 (C-3a, C-7a); m/z 332 (M + Na)⁺, 310 (M + H)⁺.

2-Cyclohexyloxy-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole 9f:⁴¹ $\delta_{\text{H}}(\text{CDCl}_3)$ 1.1–2.2 (m, 22H, aliphatic H), 3.72 (m, 1H, CHON), 7.05–7.15 (m, 2H, ArH), 7.20–7.28 (m, 2H, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 24.6 (C-3'), 25.3 and 30.5 (2 × br s, 4 × ring CH₃), 26.0 (C-4'), 32.6 (C-2'), 67.4 (C-1, C-3), 81.8 (CHON), 121.6 (C-4, C-7), 127.1 (C-5, C-6), 145.5 (C-3a, C-7a); m/z 296 (M + Na)⁺, 274 (M + H)⁺.

2-cis-[3-(1-Hydroxy-1-methylethyl)cyclohexyloxy]-1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindole 10f: $\delta_{\text{H}}(\text{CDCl}_3)$ 1.24 and 1.26 [2 × s, 2 × 3H, (CH₃)₂COH], 1.35 and 1.51 (2 × br s, 2 × 6H, 4 × ring CH₃), 0.8–2.4 [m, 10H, 4 × CH₂ and CH (cyclohexyl) and OH], 3.95–4.15 (m, 1H, CHON), 7.04–7.15 (m, 2H, ArH), 7.18–7.30 (m, 2H, ArH); m/z 354 (M + Na)⁺, 332 (M + H)⁺.

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