isomerized to nitrone IVa in 40% H_2SO_4 in aqueous MeOH by standing overnight at room temperature: uv (EtOH) 305 nm (ε 16,000) [lit.[37] 304 nm (15,900) in MeOH); picrate, mp 138–141° (lit.[41] 141–142°).

3,4-Dihydro-1-methylisoquinoline 1,2-Oxide (IIIb). Imine IIb (3.75 mmol) was oxidized by peracetic acid (3.85 mmol) in benzene (27 ml)–EtOH (3 ml) at 25° for 4 hr. A treatment similar to that of IIIa gave crude oxazirane IIIb (86.9% purity by iodometry). This oxazirane was also difficult to purify and identified similarly to the case of IIIa: uv (EtOH) 207 nm (ε ~7000); nmr (CCl_4 *vs.* TMS) δ 6.9–7.7 (4 H, m, aromatic proton), 2.70 (2 H, t, *J* = 10.5 Hz, 3 $-CH_2-$), 2.40 (2 H, t, *J* = 10.5 Hz, 4 $-CH_2-$), 1.78 (3 H, s, 1 $-CH_3$).

On standing, IIIb was gradually converted to 1-methylisoquinoline, which was identified by the characteristic uv spectra, tlc, and nmr in comparison with the authentic sample.

3,4-Dihydro-1-methylisoquinoline 2-Oxide (IVb). Crude IIIb (0.835 g) was converted to nitrone IVb by H_2SO_4 catalyzed isomerization (40% H_2SO_4 in aqueous MeOH for 7 hr at room temperature). The reaction mixture was neutralized with aqueous Na_2CO_3, extracted with ether, washed with aqueous KH_2PO_4, and dried over Na_2SO_4; after evaporation of solvent, crystallization from petroleum ether gave crystals of IVb: mp below 0°; uv (EtOH) 218 nm (ε 11,200), 296 (13,500);[42] nmr (CCl_4 *vs.* TMS) δ 8.2–6.9 (m, aromatic proton), 3.82 (t, *J* = 8.5 Hz, 3 $-CH_2-$), 2.93 (t, *J* = 8.5 Hz, 4 $-CH_2-$), 2.40 (s, 1 CH_3). Nitrone IVb may be isolated as picrate: 1.2 (60% yield); mp 176–178° (from EtOH); nmr (DMSO-d_6 *vs.* TMS) δ 8.43 (2 H, s, aromatic proton of picric acid), 7.75–7.30 (4 H, m, aromatic proton), 4.15 (2 H, t, *J* = 8.5 Hz, 3 $-CH_2-$), 3.15 (2 H, t, *J* = 8.5 Hz, 4 $-CH_2-$), 2.55 (3 H, 2, 1 CH_3).

Anal. Calcd for $C_{16}H_{14}N_4O_8$: C, 49.23; H, 3.62; N, 14.4. Found: C, 48.5; H, 3.77; N, 14.8.

2-Cyclohexyl-3-phenyl-3-methyloxazirane. Acetophenonecyclohexylimine (3.24 mmol) was oxidized by peracetic acid in 30 ml of benzene at 25° for 3 hr. The benzene solution was washed twice with aqueous Na_2CO_3 and aqueous KH_2PO_4 and the solvent was evaporated. Crystallization from petroleum ether afforded the titled oxazirane: mp 45.3–46.5° (96.0% pure by iodometry); uv (EtOH) 208 nm (ε 4400), 252 (130), 257 (160), 263 (130); nmr (CCl_4 *vs.* TMS) δ 8.1–7.8 (4 H, m, aromatic proton), 2.44 (1 H, q, *J* = 14 Hz, N–CH), 1.67 (3 H, s, 3 CH_3), 1.9–1.1 (10 H, m, pentamethylene).

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[41] J. Thesing and H. Mayer, *Justus Liebigs Ann. Chem.*, **609**, 46 (1957).

[42] The molar absorptivity of IVb was estimated from the uv spectra of the picrate (10^{-4} *M*) in EtOH. The uv spectra of picric acid was unaffected by addition of IVb or triethylamine, suggesting no acid–base interaction at these concentrations.

Phenolic Peresters. I. Radical and Base-Induced Decomposition

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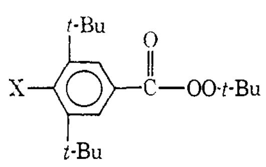
Abstract: The phenolic perester **1a** is prevented from giving the usual bimolecular reaction between phenols and acyl peroxides by its hindering *tert*-butyl groups. Although the spontaneous decomposition of **1a** shows only the normal substituent effect, removal of the phenolic hydrogen to give either the oxygen radical *or the anion* induces a rapid *radical* decomposition reaction. This perester is sensitive to base even at room temperature and below. The evidence suggests that the expected α-lactone intermediate **2** exists as a diradical **2a** and gives typical radical reactions. CIDNP signals are observed from the ring protons of the carboxylic acid produced in the base-initiated reaction in ethers and from the vinyl protons of unsaturated ethers corresponding to the solvent.

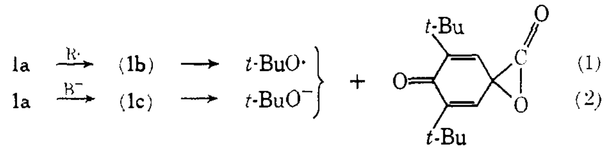
The synthesis of the perester **1a** was motivated by an interest in the interactions of the perester functional group with oxygen radical or anionic substituents.



1a, X = OH
b, X = O·
c, X = O⁻
d, X = OD

Generation of a radical substituent in an aliphatic peroxide gives α- or γ-lactones[1] or alkenes[2] depending on the structure of the peroxide. Similar experiments with aromatic acyl peroxides, in which an atom was removed from a carbon atom of the ring or of a benzylic substituent, had only negative results.[3] The radicals reacted without any decomposition of the peroxide function.

Removal of the phenolic hydrogen from **1a** either as an atom or as a proton was expected to give the lactone **2**, a process that would provide a driving force for the decomposition of the perester. A further reason for interest in the reactions of **1a** is the re-



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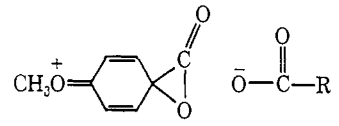
[1] (a) P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963); (b) L. B. Gortler and M. D. Saltzman, *J. Org. Chem.*, **31**, 3821 (1966); (c) H. Hart and F. J. Chloupek, *J. Amer. Chem. Soc.*, **85**, 1155 (1963); (d) C. Rüchardt and H. Schwarzer, *Chem. Ber.*, **99**, 1861 (1966).

[2] (a) L. M. Bobroff, L. B. Gortler, D. J. Sahn, and H. Wiland, *J. Org. Chem.*, 31, 2678 (1966); (b) E. N. Cain, R. Vukov, and S. Masamune, *Chem. Commun.*, 243 (1969).

[3] (a) M. M. Schwartz and J. E. Leffler, *J. Amer. Chem. Soc.*, **90**, 1368 (1968); (b) *ibid.*, **93**, 919 (1971); (c) A. I. Dalton and T. T. Tidwell, *J. Org. Chem.*, 37, 1504 (1972).

semblance of **2** to the hypothetical cationic intermediate **3** of the carboxy inversion reaction.[4–6]



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Spontaneous Decomposition of 1a. In degassed benzene at 100°, at low initial concentrations (0.005–0.01 *M*), the first-order rate constant for the decomposition of **1a** is $(3.18 \pm 0.1) \times 10^{-5}\ \mathrm{sec}^{-1}$ (Table I).

Table I. Rates of the Uncatalyzed Decomposition at 100° [a]

Concn, *M*	10^5k, sec^{-1} **1a** in C_6H_6	 **1d** in C_6H_6	 **1a** in CCl_4
0.005	3.18		3.60
0.010	3.18[d]	2.88[b]	4.80
0.030	3.99		
0.050	6.37	2.77[b]	5.30
0.100	27	1.95[c]	

[a] Initial rate constants. For runs in C_6H_6 at initial concentrations greater than 0.01 *M*, *k* usually increased during the run. For runs in CCl_4 at initial concentrations greater than 0.005 *M*, *k* decreased during the run. [b] 78% OD. [c] 96% OD. The rate constant increased during the run, presumably because OD groups exchanged hydrogen with reaction products. [d] In C_6H_5Cl the rate constant was $3.15 \times 10^{-5}\ \mathrm{sec}^{-1}$.

Since this is very close to the predicted value,[7] there is no unusual intramolecular interaction between the *unmodified* phenolic hydroxyl and the perester group of **1a**.

Radical-Induced Process. In the case of ordinary *tert*-butyl perbenzoates in aromatic solvents, a tenfold increase in initial concentration produces a less than 10% increase in the decomposition rate constant.[8] The much larger effect seen for **1a** (Table I) is therefore a consequence of the *p*-hydroxyl substituent. The failure of the deuterium compound **1d** to show a similar sensitivity to increased concentration supports a mechanism in which the attacking radicals remove hydrogen from the OH group.

One of the attacking radicals is undoubtedly *tert*-butoxy, and indeed the yield of *tert*-butyl alcohol is higher in the more concentrated runs. However, any chains involving *tert*-butoxy radicals must be quite short. Thus, when di-*tert*-butyl peroxyoxalate[9] was added to 0.01 *M* **1a** in benzene at 55°, the yield of induced decomposition per mole of externally supplied *tert*-butoxy radicals was only 0.3 for 0.028 *M* DTBPO.[10]

Manganese dioxide, a commonly used reagent for converting hindered phenols to the phenoxy radical, decomposes **1a** in benzene solution rapidly at room temperature, giving 2,6-di-*tert*-butylbenzoquinone (0.40 mol/mol) and 3,5,3′,5′-tetra-*tert*-butyldiphenoquinone (0.29 mol/mol). *tert*-Butyl alcohol and traces of isobutylene were also present. No acid (**4**) was found, but a control experiment showed that MnO_2 rapidly oxidizes **4** to the diphenoquinone **10** (0.36 mol/mol) and a polymer identical with that from the thermal decomposition of 0.10 *M* **1a** in benzene. An epr spectrum, consisting of three lines of relative intensities 1:2:1 and 1 G apart was observed in a benzene solution of **1a** freshly exposed to MnO_2. This spectrum agrees with that reported for 2,6-di-*tert*-butyl-4-*tert*-butoxyphenoxy radical.[11] The spectrum of **1b** should have about a 2-G splitting.[12]

trans-Stilbene and iodine were tested as possible inhibitors of the decomposition in benzene. Neither had any very significant effect on the initial rate constant at 0.05 *M* initial concentration of **1a**. Iodine prevented the increase in rate constant ordinarily observed in the second half-life of runs at this initial concentration. It also prevented the formation of 3,5-di-*tert*-butyl-4-hydroxybiphenyl while very much increasing the yield of 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (Table II). We suggest that iodine traps 3,5-di-*tert*-butyl-4-hydroxybenzoyloxy radicals as the hypoiodite, but that the hypoiodite oxidizes **1a** to **1b** with about the same efficiency as the radical-induced

Table II. Products from the Decomposition of **1a** in C_6H_6 at 100°

Product	Yields, mol/mol of **1a** 0.01 *M*[h]	 0.05 *M*[h]	 0.10 *M*[h]
ArCOOH[a] (**4**)	0.44	0.09 1.00[b] 0.71[c]	0.10 0.44[d]
ArC_6H_5 (**5**)	0.32	0.01	Trace 0.38[a]
ArCOOAr	0.01	0.11	0.07
ArCOOAr′[e]	0.00	0.03	0.05
3,5,3′,5′-Tetra-*tert*-butyldiphenoquinone (**10**)	0.01	0.01	0.03
2,6-Di-*tert*-butylbenzoquinone	Trace		
tert-Butyl alcohol	0.32	0.60 0.97[b]	0.59
Acetone	0.73	0.41	0.32
Isobutylene		0.17[f]	
CO_2		0.51	
Toluene	0.39	0.11	0.04
3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde			Trace
Polymer[g]			Present

[a] Ar is 3,5-di-*tert*-butyl-4-hydroxyphenyl. [b] In the presence of 0.25 *M* 2,6-di-*tert*-butyl-4-methylphenol. [c] In the presence of 0.25 *M* I_2. [d] From **1d**. [e] Ar′ is 3-methyl-5-*tert*-butyl-4-hydroxyphenyl. [f] Note that this product has to come from aromatic *tert*-butyl because the aliphatic *tert*-butyl is accounted for. [g] Shows HO but no C=O in the ir. [h] Initial concentration of **1a**.

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(4) J. E. Leffler, *J. Amer. Chem. Soc.*, 72, 67 (1950).

(5) C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *ibid.*, 92, 4927 (1970).

(6) J. E. Leffler and A. A. More, *ibid.*, 94, 2483 (1972).

(7) Using the rate constant reported for *tert*-butyl perbenzoate in *p*-chlorotoluene at 110° and the activation energy and Hammett ρ value reported for the same solvent [A. T. Blomquist and I. A. Berstein, *ibid.*, 73, 5546 (1951)], the rate constant predicted for **1a** in *p*-chlorotoluene at 100° is $3.3 \times 10^{-5}\ \mathrm{sec}^{-1}$. The solvent effect is expected to be small.

(8) A. T. Blomquist and A. F. Ferris, *ibid.*, 73, 3408 (1951).

(9) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *ibid.*, 82, 1762 (1960).

(10) The products from a solution of **1a** (0.05 *M*) and DTBPO (0.026 *M*) in benzene were biphenyl (0.03 mol/mol), 2,6-di-*tert*-butylbenzoquinone (0.20 mol/mol), 3,5,3′,5′-tetra-*tert*-butyldiphenoquinone (0.10 mol/mol), and an unidentified polymer like that from the reaction of **1a** alone in benzene (ir). Excess DTBPO converts 3,5-di-*tert*-butyl-4-hydroxybenzoic acid to the tetra-*tert*-butyldiphenoquinone, and the latter reacts further to give other quinonoid products.

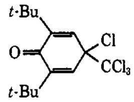
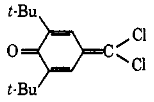
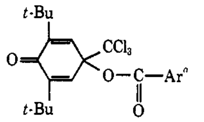
(11) E. Müller, K. Ley, and K. Scheffler, *Chem. Ber.*, 91, 2682 (1958).

(12) The esr spectrum obtained by treating a benzene solution of 2,6-di-*tert*-butyl-4-carbomethoxyphenol with MnO_2 had a main splitting of 2.15 G, each member of the triplet being split further into a quartet by the ester CH_3 group.

decomposition that would otherwise occur. The addition of 0.25 *M* 2,6-di-*tert*-butyl-4-methylphenol effectively diverted all of the radicals from 0.05 *M* **1a** to the acid and *tert*-butyl alcohol, as shown in Table II. There was no significant effect on the rate, presumably because of a balance between radical trapping and chain transfer.

Chain Transfer. Besides the dependence of the first-order rate constant on the initial concentration, there are deviations from first-order kinetics within the run, at least for runs at the higher concentrations. In benzene the rate constant increases later in the run, in CCl_4 it decreases. The autocatalysis in benzene is associated with the accumulation of certain phenolic products (Table II). The products from the reaction in CCl_4 include fewer phenols and more quinonoid compounds that might act as chain inhibitors (Table III).

Table III. Products from the Decomposition of **1a** in CCl_4 at 100°

Product	Yields, mol/mol of **1a** 0.10 M^c	 0.05 M^c
ArCOOH[a]	0.16	0.29
	0.34	0.08
	0.07	0.13
	0.09	0.10
10		0.04
tert-Butyl chloride	0.26	0.23
Methyl chloride	0.71	0.23
Acetone	0.33	0.23
tert-Butyl alcohol	0.0	0.15
Isobutylene	0.0[b]	0.19[b]
CO_2	0.78	0.50

[a] Ar is 3,5-di-*tert*-butyl-4-hydroxyphenyl. [b] There was no isobutane. [c] Initial concentration of **1a**.

The effects of added phenols on the initial rate of decomposition of **1a** in benzene at 100° are shown in Table IV. As can be seen from the table, phenols capable of forming long-lived phenoxy radicals accelerate the decomposition of **1a** whereas 4-methyl-2,6-di-*tert*-butylphenol does not. We attribute the effect of phenols in the stable radical category to a rapid transfer of hydrogen atoms from the hydroxyl group of **1a** to the oxygen of the stable radical. Rapid transfer of hydrogen from hindered phenols to equally hindered phenoxy radicals is a well-known phenomenon.[13] A solution of 2,6-di-*tert*-butyl-4-carbomethoxyphenoxy radical in degassed benzene is completely decolorized by **1a** in minutes at room temperature.

Table IV. Effect of Added Phenols on the Initial Rates in Benzene at 100°

Initial concn of **1a**, *M*	Additive, concn (*M*)	% increase
0.01	ArCOOH,[a] 0.0021	3
0.03	Ar-Ar,[a] 0.0194	27
	2,6-Di-*tert*-butyl-4-*tert*-butoxyphenol, 0.0070	7.5
0.05	Solvent from a run at 0.05 *M*	33
	2,4,6-Tri-*tert*-butylphenol, 0.22	260
	4-Methyl-2,5-di-*tert*-butylphenol, 0.25	0[b]

[a] Ar is 3,5-di-*tert*-butyl-4-hydroxyphenyl. [b] Accelerated after the first half-life.

On the other hand, a direct bimolecular reaction of the perester function of **1a** with hindered phenols is unlikely to be important. Such reactions are very slow for sterically hindered phenols and are also decelerated by electron-withdrawing substituents in the phenol.[14] Our control experiments with 0.05 *M* *tert*-butyl perbenzoate (a more reactive perester than **1a**) and 0.05 *M* 2,4,6-tri-*tert*-butylphenol (a more reactive phenol than **1a**) showed no decomposition of that perester in excess of the rate in the absence of the phenol.[15] Added 2,6-di-*tert*-butyl-4-carbomethoxyphenol also had no effect on the rate of decomposition of *tert*-butyl perbenzoate.

We therefore conclude that the acceleration by added phenols is due to chain transfer to give a long-lived aryloxy radical which then abstracts a hydrogen atom from **1a**. In summary, the high rate constants at high initial concentrations of **1a** and in the presence of certain phenols are due to a reaction whose first step gives the aryloxy radical **1b** or a related transition state.

Base-Initiated Reaction. The perester **1a** is extremely sensitive to traces of base, especially in solvents capable of radical chain transfer such as alcohols or ethers. For example, when a cold solution of **1a** in tetrahydrofuran containing a few drops of pyridine is allowed to warm to −20°, a transient deep green color appears for about 0.5 min and then the usual yellow color of the base-catalyzed products appears.

The base-catalyzed reaction, like the spontaneous and radical-initiated processes, takes an obviously radical course. For example, the products incorporate moieties of the solvent and are altered by the presence of 4-methyl-2,6-di-*tert*-butylphenol (DTBC) as a radical trap. The kinetic behavior is also different in the presence of oxygen or DTBC. CIDNP signals are observed when the reaction is run in ethers.

Kinetics. The kinetics of the pyridine catalyzed reaction are difficult to interpret because of pronounced autocatalysis and a sensitivity to traces of oxygen. In degassed benzene at 26°, the rate expressed as a second-order rate constant (without any implications as to the actual order) is initially about 6×10^{-3} M^{-1} sec^{-1}, increasing by an order of magnitude or more after the first 20 min. A similar run, not de-

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[13] For example, the equilibrium reaction between 2,6-di-*tert*-butyl-4-*tert*-butoxyphenol and 2,4,6-tri-*tert*-butylphenoxyl radical is fast in both directions at room temperature: C. D. Cook, C. B. Depatie, and E. S. English, *J. Org. Chem.*, 24, 1356 (1959). See also R. W. Kreilick and S. I. Weissman, *J. Amer. Chem. Soc.*, **84**, 306 (1962).

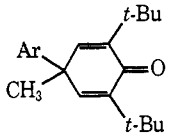
[14] (a) C. Walling and R. Hodgdon, Jr., *ibid.*, **80**, 228 (1958); D. B. Denney and D. Z. Denney, *ibid.*, **82**, 1389 (1960); (c) J. J. Batten and M. F. R. Mulcahy, *J. Chem. Soc.*, 2948 (1956); (d) S. L. Cosgrove and W. A. Waters, *ibid.*, 3189 (1949).

[15] The distinctive color of the stable phenoxy radical was observed to appear and eventually disappear during the reaction.

Table V. Products from 0.01 *M* **1a** in C_6H_6 at 26°

Conditions	Yields in mol/mol of **1a** Ar-COOH[a]	DPQ[c]	BQ[d]	*t*-BuOH	Acetone	ArC[e]	ArO-*t*-Bu	Biphenyl
0.04 *M* pyridine	0.22	0.32	0.04	0.71	0.20			
0.04 *M* pyridine and 0.03 *M* DTBC[b]	0.73	0.0	0.0	0.88	Trace	0.18[f]		
10% saturated KO-*t*-Bu	0.26	0.26	0.10					0.03
15% saturated KO-*t*-Bu and 0.15 *M* DTBC[b]	0.26	0.0	0.0			0.49	0.29	

[a] Ar is 3,5-di-*tert*-butyl-4-hydroxyphenyl. [b] 4-Methyl-2,6-di-*tert*-butylphenol. [c] 3,5,3′,5′-Tetra-*tert*-butyldiphenoquinone. [d] 2,6-Di-*tert*-butyl-1,4-benzoquinone. [e] ArC has structure I. [f] 0.41 mol/mol of II also formed.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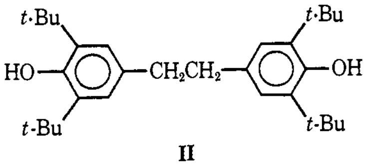
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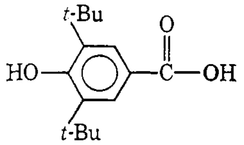
gassed, has about the same initial rate constant but it decreases rather than increases later in the run. Added 4-methyl-2,6-di-*tert*-butylphenol reduces the amount of autocatalysis and delays its onset. In the presence of this reagent, the initial rate, expressed as a second-order rate constant, is about $0.3 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$.

In degassed solutions of pyridine in CCl_4 at 26°, first-order plots for the disappearance of **1a** are linear for at least the first half-life. The rate, expressed as a second-order rate constant, is about $10^{-4}\ M^{-1}\ \text{sec}^{-1}$.

The rate of the uncatalyzed reaction in C_6H_6 and in CCl_4 at 26° is negligible.

Products. The products from the base-catalyzed decomposition of **1a** in degassed benzene at 26° are shown in Table V. These of course must be assigned in some substantial but unknown proportion to radical-induced processes as well as to the initiating base-induced reaction.

There are several differences from the results of the uncatalyzed reaction at 100° that should be noted. First of all, there is less acid **4** and no 4-phenyl-2,6-di-*tert*-butylphenol (**5**) in the products of the base-catalyzed reaction. We also find that **5** is absent from the products of photolysis at 3500 Å. A third difference is that in the low-temperature, base-catalyzed reaction the intermediate trapped in the presence of DTBC appears as an aryl derivative **6** rather than as the acid **4**.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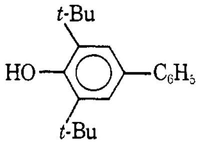
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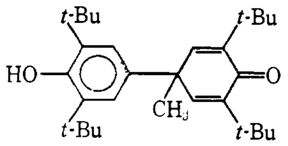
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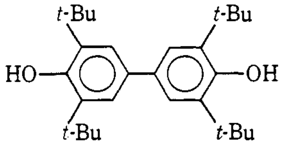
The products of reactions in THF with various bases at 26° were the acid **4** (0.5–0.8) (yields, mol/mol of **1a**), 2,6-di-*tert*-butylphenol (0.01–0.08), the hydroquinone **7** (0.01–0.17), 4-*tert*-butyoxy-2,6-di-*tert*-butylphenol (**8**) (0.01–0.05), and compound **9** (0.18–0.32).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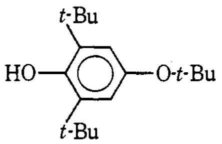
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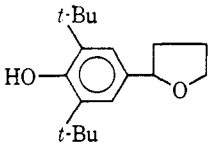
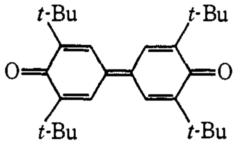

9

Added DTBC reduced the yield of **9** to 0.12, diverting this product to **6**.

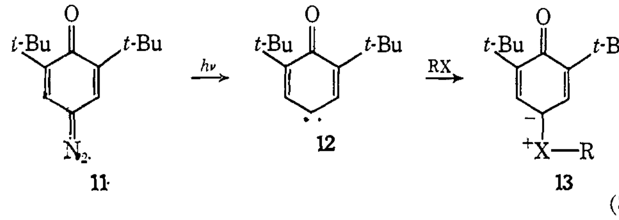
The products of the decomposition in 90% methanol with KOH at 26° included the acid, the diphenoquinone **10** (0.04 mol/mol), 4-hydroxymethyl-2,6-di-*tert*-butylphenol (0.05), 4-*tert*-butoxy-2,6-di-*tert*-butylphenol (**8**) (0.06–0.09), and *tert*-butyl alcohol (0.67–0.81). No 4-methoxy-2,6-di-*tert*-butylphenol was obtained.


10

The yields of **8** are higher when more viscous reaction media and/or lower temperature are used. In 97% butyl alcohol–3% CCl_4, for example, with sodium butoxide as the catalyst, the yield of **8** was 0,09 mol/mol when the reagent solutions were mixed at room temperature and 0.33 when they were mixed at −90°. A yield of 0.34 was also obtained in a reaction in benzene heterogeneously catalyzed by basic Al_2O_3 at room temperature.

CIDNP. Decomposition ot **1a** by pyridine in ethers at room temperature in the probe of an A-60 nmr spectrometer gave strong CIDNP signals. In diethyl ether a pattern of enhanced emissions at δ 4.30, 4.05, and 3.93 was accompanied by enhanced absorptions at δ 6.68, 6.57, 6.43, and 6.31. These are attributed to the β- and α-vinyl protons, respectively, of vinyl ethyl ether. Similar CIDNP signals attributable to the vinyl protons of 2,3-dihydrofuran were observed when THF was used as the solvent. In both solvents the ortho protons of 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (**4**) gave strongly enhanced absorption at δ 8.17. The aromatic carboxylic acids from ordinary acyloxy radicals never exhibit enhanced absorption or emission by the ortho protons because the hyperfine coupling constant is too small. No CIDNP was observed from the uncatalyzed reaction of **1a** in various solvents at 140–200°.

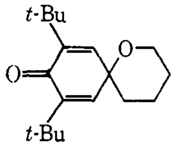
Behavior of the Carbene. Pirkle and Koser[16] have studied the reactions of both the singlet and triplet ground state of the carbene **12**. Singlet **12** gives an



(3)

insertion reaction with cyclohexane and adds stereoselectively to double bonds. Dilution of the reaction mixture with hexafluorobenzene facilitates relaxation of **12** to its triplet ground state and diminishes the stereoselectivity.

In benzene the product was mainly 2,6-di-*tert*-butyl-4-phenylphenol (**5**), and we have confirmed this for mixtures of benzene and C_6F_6 as well. The diphenoquinone **10** is formed only in the presence of alkyl bromides or iodides, presumably *via* the halonium ylide **13**.[16] Photolysis of **11** in THF at wavelengths greater than 4800 Å gave 2,6-di-*tert*-butylphenol (2 mol %), **9** (14 mol %), and a compound tentatively identified as **14** (47 mol %). Again, none of the diphenoquinone **10** was found.



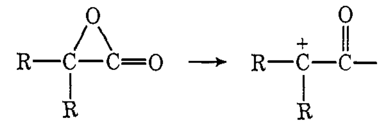
14

Photolysis of **11** in CCl_4[16b] gave 2,6-di-*tert*-butyl-4-chloro-4-trichloromethyl-2,5-cyclohexadien-1-one and no **10**.

Discussion

In the thermal decomposition of **1a** in benzene, added DTBC diverts the aromatic moiety of **1a** quantitatively to the acid **4** while leaving the rate at a high level indicative of considerable induced decomposition. Hence the first intermediate after the cleavage of the peroxide bond retains the CO_2 moiety not only in the spontaneous decomposition but also in the induced decomposition. To account for the latter reaction, we propose that driving force is provided by a species closely related to the α-lactone **2**. Before describing this intermediate more specifically, it is desirable to review briefly what is already known about α-lactones.

α-Lactones. Although no α-lactone has ever been isolated, nmr[17] and infrared[18] spectra have been obtained, and at least in several instances there can be no doubt about their existence. Most of the reactions of α-lactones can be explained in terms of a zwitterionic structure **15** which undergoes either rearrangement or reaction with nucleophiles at its carbonium ion center. Other reactions are the formation of

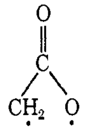


(4)

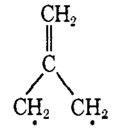
15

polyesters,[17] thermal or photochemical decarboxylation to the carbene,[19] and photolytic decarbonylation to the ketone.[18]

Molecular orbital calculations on acetolactone[20] suggest that an open diradical form **16** analogous to trimethylenemethane should at least be quite stable if not the ground state. The ground state of trimethylenemethane is the triplet **17**.[21,22]



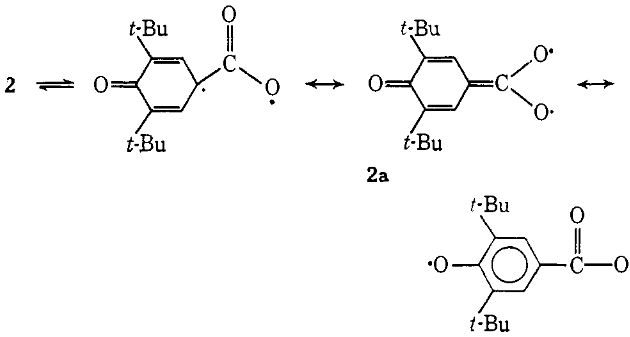
16



17

The Undecarboxylated Intermediate. The lactone **2** proved not to be isolable,[23] and we were also unable to detect any transient infrared absorptions assignable to it. Polyester and solvolysis products analogous to those formed by zwitterion-like α-lactones were also absent.

The conjugated carbonyl group of **2** is unfavorable for a carbonium zwitterion but at the same time is favorable for a diradical (**2a**). It is therefore not surprising that the reaction products and kinetics, as discussed in the following sections, indicate radical intermediates.



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[16] (a) W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 3959 (1968); (b) *J. Amer. Chem. Soc.*, **90**, 3598 (1968).

[17] R. Wheland and P. D. Bartlett, *ibid.*, **92**, 6057 (1970).

[18] O. L. Chapman, P. W. Wojtkowski, W. Adam, O. Rodriquez, and R. Rucktäschel, *ibid.*, **94**, 1365 (1972).

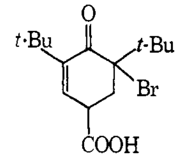
[19] C. Walling and Z. Čekovič, *ibid.*, **89**, 6681 (1967).

[20] T. Koenig and T. Barklow, *Tetrahedron*, **25**, 4875 (1969).

[21] P. Dowd, *Accounts Chem. Res.*, **5**, 242 (1972).

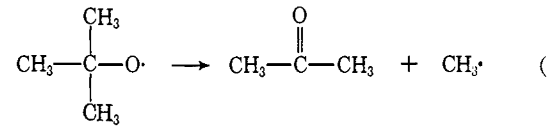
[22] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **51**, 1672 (1969).

[23] The reaction of bromine with 4-hydroxy-3,5-di-*tert*-butylbenzoic acid gives **18** [V. V. Ershov and A. A. Volod'kin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 893 (1963)]. Reaction of **18** with bases gave the parent acid, 4-bromo-2,6-di-*tert*-butylphenol, 2,6-di-*tert*-butylbenzoquinone, and 3,5,3′,5′-tetra-*tert*-butyldiphenoquinone.

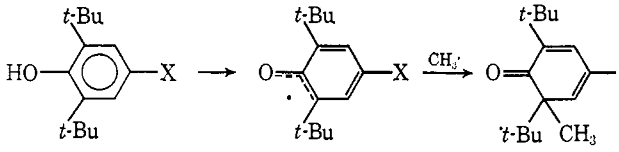


18

Radical-Induced Processes in C_6H_6 and in CCl_4. In benzene at low initial concentrations of **1a**, both the acyloxy radical and the diradical **2a** can abstract hydrogen from suitable donors to give the acid **4**. At higher concentrations, however, the yield of acid (Table II) declines because of secondary reactions. Among the latter must be reactions like those leading to isobutylene and 3-methyl-5-*tert*-butyl-4-hydroxyphenyl 3,5-di-*tert*-butyl-4-hydroxybenzoate. We suggest a radical displacement reaction as in (eq 5–8) to explain this result and also the formation of $t\text{-}C_4H_9Cl$ in CCl_4.



$$(CH_3)_3C\text{—}O\cdot \longrightarrow CH_3\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3 + CH_3\cdot \qquad (5)$$



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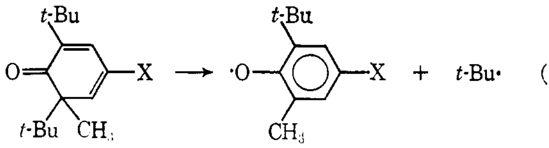

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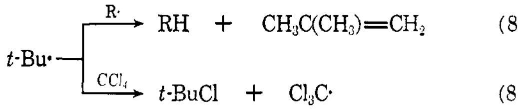
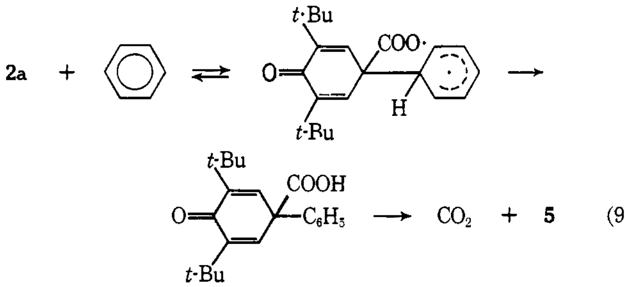


$$t\text{-Bu}\cdot \xrightarrow{R\cdot} RH + CH_3C(CH_3)\text{=}CH_2 \qquad (8a)$$

$$t\text{-Bu}\cdot \xrightarrow{CCl_4} t\text{-BuCl} + Cl_3C\cdot \qquad (8b)$$

The 2,6-di-*tert*-butyl-4-phenylphenol (**5**) from the decomposition in benzene could in principle arise from any of several intermediates. These include the carbene, 3,5-di-*tert*-butyl-4-hydroxyphenyl radical, and **2a** (eq 9). The yields of **5** are higher at lower initial concentrations of the perester and with the deuterated perester **1d** as compared with **1a**. This may merely reflect secondary reactions of **5** at the phenolic functional group, or a larger proportion of reaction of **2a** with 3,5-di-*tert*-butyl-4-hydroxyphenyl radical to give the ester.



(9)

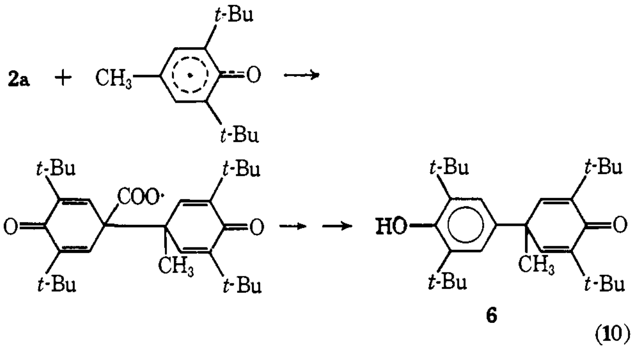
The various quinonoid products incorporating parts of the CCl_4 molecule (Table III) can plausibly be assigned to the carbene intermediate. The diphenoquinone **10**, however, cannot come from the carbene in view of the control experiments already described. A plausible explanation for **10** is dimerization of **2a** followed by decarboxylation.

The trace of 2,6-di-*tert*-butylbenzoquinone formed in benzene may be due to decarbonylation of **2**[18] or to oxidation of the *tert*-butyl ether **8**.

Base-Initiated Reaction. It is clear from the products and the effects of radical traps that the base-initiated reaction involves radicals as well as the formation of **2** (or **2a**) and $t\text{-BuO}^-$.

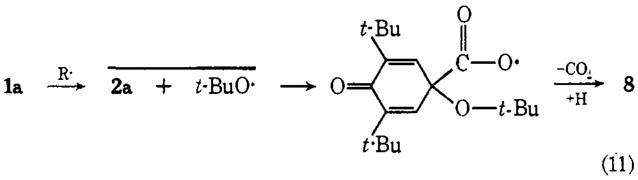
One difference from the thermal or radical-initiated reaction is the absence of **5** from the products of the reaction initiated by pyridine in benzene at 26° (Table V). The yield of acid **4** is also lower, perhaps because **2a** is diverted to the diphenoquinone **10**.

In the presence of DTBC the diphenoquinone product is replaced entirely by the acid and **6** (eq 10).



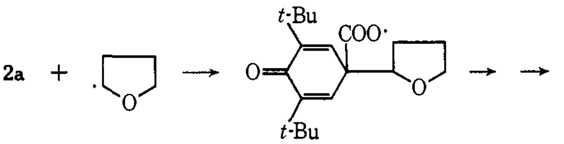
(10)

Because of the temperature and medium effects on its yield, we suggest that the ether 4-*tert*-butoxy-2,6-di-*tert*-butylphenol (**8**) is a cage product. External combination is probably ruled out, since DTBC failed to suppress the formation of **8**. Formation from the carbene and *tert*-butyl alcohol is also unlikely since no methyl ether is formed in CH_3OH solution.



(11)

The absence of the major product **14** of the control experiment with the carbene makes the latter an unlikely precursor of the substituted tetrahydrofuran **9**. We suggest instead that **9** results from the combination of the solvent-derived radical either with 3,5-di-*tert*-butyl-4-hydroxyphenyl radical or with **2a**, or with the phenoxyl radical corresponding to the acid **4**, followed by decarboxylation.



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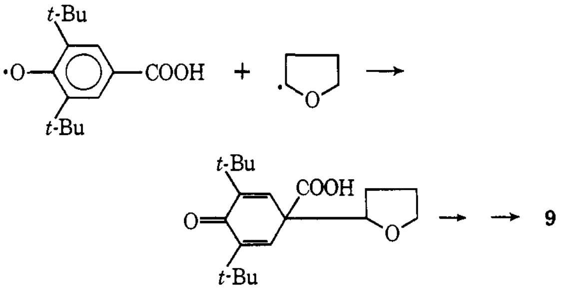
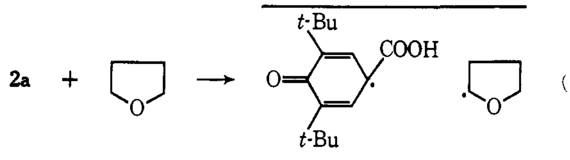


(13)

CIDNP in the Base-Induced Reaction. In ethers such as diethyl ether, dioxane, or tetrahydrofuran-, plus pyr idine, there is enhanced absorption of the ortho protons of the acid **4** and A/E multiplets from the vinyl protons of the unsaturated ether corresponding to the solvent. One explanation for this result is polarization in a radical pair **19** (eq 14). Geminate reaction of **19** gives the unsaturated ether and the acid **4**.



(14)

19

The polarization of the acid may be predicted from eq 15,[24] in which our assumptions about the signs

$$\begin{array}{ccccccc} \Gamma_{\mathrm{ne}} & = & \mu & \epsilon & \Delta g & a & = + \\ & & + & + & & + & = +\mu \end{array} \qquad (15)$$

have been placed below each symbol. The observed enhanced absorption requires a positive value for Γ_{ne}, which in turn requires a positive value for μ, implying that **2a** is a triplet.

As can be seen from eq 16,[24] the A/E observed for the ether multiplets again implies that **2a** is a triplet.

$$\begin{array}{cccccccccc} \Gamma_{\mathrm{me}} & = & \mu & \epsilon & a_\alpha & a_\beta & J_{\alpha\beta} & \sigma_{\alpha\beta} & = - \\ & & + & - & + & + & + & & = -\mu \end{array} \qquad (16)$$

Experimental Section

tert-Butyl 3,5-Di-_tert_-butyl-4-hydroxyperbenzoate (1a). To a mixture of 350 ml each of pentane and cylohexane was added 28.15 g (0.106 mol) of 3,5-di-*tert*-butyl-4-hydroxybenzoyl chloride.[25] After this mixture was cooled to 5° in an ice bath, *ca.* 50 ml of $CHCl_3$ was added to effect total solution of the acid chloride. *tert*-Butyl hydroperoxide (11.5 g, 0.127 mol) was then added in one portion, followed by a 10.1 g (0.127 mol) of pyridine added dropwise with stirring over a period of 1 hr. After stirring for an additional 3 hr at 0°, the mixture was washed twice with 100-ml portions of 10% HCl and with H_2O. The organic solvent was then stripped off with a rotary evaporator and the oily residue treated with pentane to induce crystallization. After three recrystallizations from 2:1 *n*-pentane–*n*-heptane, the perester was obtained as a white crystalline solid (10.1 g, 29%): mp 92–92.5° dec; ir (C_6H_6) 1755 cm^{-1}; nmr (CCl_4) δ 7.83 (s, 2 H), 5.67 (s, 1 H), 1.66 (s, 18 H), 1.39 (s, 9 H). *Anal.* Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 71.01; H, 9.37.

The compound deuterated in the hydroxyl group (**1d**) was prepared as follows. A solution of 1.0 g of **1a** in a few milliliters of C_6H_6 (dried over a 4Å molecular sieve) was prepared in a drybox and stirred for 2 hr with 10 ml of 99.8% D_2O in a stoppered flask. The supernatant liquid, transferred to an ir cell in the drybox, showed no OH band and had a sharp OD band at 2670 cm^{-1}.

Kinetics.[26] Kinetic and product isolation experiments were carried out with reaction mixture decomposed in glass ampoules or bombs degassed by freeze–thaw pumping cycles. The disappearance of the perester was followed by means of the ir band at 1755 cm^{-1}. In the experiments in C_6H_6 or CCl_4 (at 100°), each ampoule was quenched thermally before analysis. In the pyridine catalyzed experiments at 26°, the solution was made up from degassed benzene and benzene–pyridine stock solution in an inert atmosphere box under argon. Aliquots of the solution were transferred to a 0.5-mm NaCl ir cell also in the inert atmosphere box after which the cell was passed out of the box for reading the $\%T$ at the perester carbonyl frequency.

Products from the Reaction in Benzene.[26] Nonvolatile products were determined after stripping off the solvent by molecular distillation through a side arm attached to the bomb. After solution in ether and treatment with CH_2N_2 to convert the acid to its methyl ester, the various yields were determined by gl chromatography on Carbowax and SE-30 columns. Nonvolatile products were also isolated for identification by liquid–solid elution chromatography on Florisil. Unless otherwise specified, reaction products were compared with samples synthesized by methods in the literature.

Volatile products (acetone, *t*-BuOH, and toluene) were determined by adding an aliquot of methanol in benzene and chromatography on a Poropak Q column.

Condensable gases were collected in a liquid N_2 trap after removal of other volatiles by condensation in Dry Ice–isopropyl alcohol traps. After measuring the pressure of the gases, samples were removed for glc or mass spectral analysis.

3,5-Di-_tert_-butyl-4-hydroxyphenyl 3,5-Di-_tert_-butyl-4-hydroxybenzoate. This compound was synthesized for comparison with the decomposition product as follows: 0.26 g (1.2 mmol) of 2,6-di-*tert*-butylhydroquinone was heated with 0.31 g (1.2 mmol) of 3,5-di-*tert*-butyl-4-hydroxybenzoyl chloride in petroleum ether. After removal of solvent, the crude ester was recrystallized from methanol: yield 0.4 g (73%); mp 210–213°; ir (reflectance) 3610 cm^{-1} (hindered OH), 1718 cm^{-1} (C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.18 (s, 2.15, ArH), 7.07 (s, 2.00, ArH), 5.81 (s, 1.00, OH), 5.16 (s, 0.90, OH), 1.51 (s, –, *t*-Bu), 1.46 (s, –, *t*-Bu).

3-_tert_-Butyl-5-methyl-4-hydroxyphenyl 3,5-Di-_tert_-butyl-4-hydroxybenzoate. This compound was isolated by elution chromatography from Florisil of the decomposition products of **1a** in benzene after replacement of the solvent with hexane: mp (after recrystallization from hexane) 241–244°; ir ($CHCl_3$) 1722, 3630 cm^{-1}; nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.17 (s, 2, ArH), 7.00 (m, 2, ArH), 5.83 (s, 1, OH), 4.86 (s, 1, OH), 2.27 (s, 3, CH_3), 1.53 (s, ~18, *t*-Bu), 1.44 (s, ~9, *t*-Bu); *m/e* (70 V) *ca.* 410–420 (molecular), 233 (base), 57, 41, 29. The ir and nmr spectra of this material were similar to those, of 3,5-di-*tert*-butyl-4-hydroxyphenyl 3,5-di-*tert*-butyl-4-hydroxybenzoate. It elutes before the latter on 3.5% SE-30 and after it on Florisil.

Unidentified polymer was eluted from a Florisil column with methanol. The benzene–heptane insoluble fraction decomposes at 301°. The benzene–heptane soluble fraction was colorless: mp 244–250° dec; nmr $\delta_{\mathrm{TMS}}^{\mathrm{D_3CCOCD_3}}$ 8.08 (s), 3.33 (s), 1.44 (s), peak at 3.33 shifts and narrows on dilution; ir (either fraction) 3670 cm^{-1} (sharp OH), 3410 (broad OH), no C=O.

2,6-Di-_tert_-butyl-4-methyl-4-(3,5-di-_tert_-butyl-4-hydroxyphenyl)-2,5-cyclohexadien-1-one (6). This substance was isolated from the base catalyzed decomposition products of **1a** in benzene in the presence of 2,6-di-*tert*-butyl-*p*-cresol by elution chromatography: mp 146–150°; ir (film) 3700 (hindered OH) and 1657 and 1640 cm^{-1} (carbonyl doublet); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.03 (s, 2, ArH), 6.5 (s, 2, vinyl H), 5.12 (s, 1, HO), 1.60 (s, not resolved, CH_3), 1.42 (s, not resolved, *t*-Bu), 1.25 (s, not resolved, *t*-Bu); *m/e* 424 (molecular ion).

1,2-Bis(3,5-di-_tert_-butyl-4-hydroxyphenyl)ethane. This compound is formed when **1a** is decomposed in the presence of di-*tert*-butyl-*p*-cresol and pyridine: ir (film) 3630 cm^{-1}; nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 6.75 (s, 4.0, Ar H), 4.76 (s, 2.0, OH), 2.71 (s, 4.0, CH_2), 1.38 (s, –, *t*-Bu).

Products from the Decomposition of 1a in CCl_4.[26] **2,6-Di-_tert_-butyl-4-chloro-4-trichloromethyl-2,5-cyclohexadien-1-one.** This product was identified by pmr, ir, and mass spectra and melting point.[16b]

2,6-Di-_tert_-butyl-4-dichloromethylene-2,5-cyclohexadien-1-one. This product was isolated in crude form (mp 73–80°) as a light yellow waxy solid by elution chromatography: ir 1615 cm^{-1}, 940, 908, 885, no OH peaks; nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 7.41 (s, 2, Ar H), 1.31 (s, 18, *t*-Bu); *m/e* 286 (molecular) with P + 2 and P + 4 present. Reaction with $LiAlH_4$ gave 2,6-di-*tert*-butyl-*p*-cresol.

1-Trichloromethyl-3,5-di-_tert_-butyl-2,5-cyclohexadien-4-on-1-yl 3,5-di-_tert_-butyl-4-hydroxybenzoate was isolated by elution chromatography from Florisil and crystallization from pentane: yellow crystals; mp 204–209°; ir 1735 (C=O), 1670 and 1650 (C=O doublet), 3620 (sharp, OH), 1225, 1120, 800 cm^{-1}; nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.11 (s, 2, Ar H), 6.71 (s, 2, vinyl H), 5.83 (s, 1, OH), 1.50 (s, 18, *t*-Bu), and 1.29 (s, 18, *t*-Bu).

Products from the Base-Catalyzed Decomposition of 1a in Tetrahydrofuran.[26] **2,6-Di-_tert_-butyl-4-(1-tetrahydrofuranyl)phenol (9)** was isolated by elution chromatography from Florisil: ir (film) 3500 (hindered OH), 1105, 1060, 950, and 875 cm^{-1} (all broad); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.23 (s, 2.0, Ar H), 5.20 (s, 1.0, OH), 4.81 (t, 0.92, H_1 of THF moiety), 4.02 (m, 2.28, H_4 of THF moiety), 2.00 (m, 5.11, 2, 3 H of THF moiety), 1.45 (s, –, *t*-Bu); *m/e* 276 (molecular).

Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.35; H, 10.28.

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[24] R. Kaptein, *Chem. Commun.*, 732 (1971); Dissertation, Leiden, 1971, Chapter VIII.

[25] E. Müller, A. Rieker, R. Mayer, and K. Scheffler, *Justus Liebigs Ann. Chem.*, **645**, 36 (1961).

[26] For further details, see A. M. Hucek, Dissertation, Florida State University, 1970.

This product was also found in the thermal decomposition of **1a** in THF and in the photolysis of **11**.

Products from the Photolysis of 11 in THF. A 0.026 *M* solution of **11** in THF was degassed and irradiated at wavelengths ≥480 nm.

1-Oxa-8,10-di-*tert*-butylspiro[5.5]undeca-7,10-dien-9-one (14). This product and those already described were isolated by elution chromatography on Florisil: mp 51–54°; ir (film) 1665 and 1650 (carbonyl doublet); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 6.63 (s, 2.12, vinyl H), 3.71 (t, 2.00, CH_2), 1.61 (m, 6.72, CH_2), 1.20 (s, –, *t*-Bu); *m/e* 276 (molecular). Compound **14** is recovered unchanged after heating in CH_3OH with 10% HCl.

Photolysis of 1a in C_6H_6. A degassed 0.01 *M* benzene solution of **1a** was irradiated in Pyrex at a temperature of about 45° with RPR-3500 Å uv lamps for 5 days. After complete photolysis of **1a**, the decomposition products were worked up by extraction by $NaHCO_3$ and by glc (10% Carbowax on 20M TPA). No 2,6-di-*tert*-butyl-4-phenylphenol (**5**) was present. The yield of acid **4** was 0.41 mol/mol.

Acknowledgments. The authors wish to acknowledge support of this work by the National Science Foundation Grant GP 15991 and in part by U. S. Public Health Service Grant No. AM 10498 from the National Institute of Arthritis and Metabolic Diseases.

Polar Radicals. VI. Bromination Reactions with Molecular Bromine and *N*-Bromosuccinimide. Apparent Anomalies and Similarities[1]

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Abstract: The relative rates of bromination of a number of alkanes and substituted alkanes have been determined. A comparison of the relative rates of bromination with high concentrations of *N*-bromosuccinimide (NBS) and with molecular bromine shows significant differences. These differences can be attributed, in part, to the polar effects on the transfer reactions between the substituted and unsubstituted alkyl radicals with hydrogen bromide. The differences observed between the two reagents are found to disappear when the brominations with molecular bromine are carried out at very high bromine concentrations where the transfer reaction with hydrogen bromide cannot compete effectively with the transfer reaction with molecular bromine. This observation further substantiates, at least at high concentrations of NBS in acetonitrile, the mechanism which has been proposed for NBS bromination reactions. The relative rates observed demonstrate the retarding effect of a neighboring bromine or chlorine atom on the hydrogen abstraction reactions of a bromine atom.

Free radical hydrogen abstraction reactions on electronegatively substituted alkanes by intermediates other than hydrogen atoms or carbon-centered radicals (eq 1) would be predicted to proceed at a slower rate than those of similar reactions carried out on the unsubstituted parent alkanes.[3,4] Polar repulsion between the incipient polar molecule YH and the new polar

$$\mathrm{Y\cdot} + \mathrm{RH} \text{—} [\cdot\mathrm{Y\ H{-}R} \longleftrightarrow \mathrm{Y{-}H\ R\cdot}]^{\ddagger} \longrightarrow \mathrm{YH} + \mathrm{R\cdot} \quad (1)$$

radical R· would be reflected by an increase in the energy requirements of the transition state and thereby a decrease in the rate of this reaction compared to the rate of the reaction of the unsubstituted alkane, where the new radical formed is not polar.

This precept could possibly be challenged if one considers the abstraction reactions on selected brominated and chlorinated alkanes, where neighboring group participation by the halogen atom has been proposed as being responsible for increased rates of reaction of the hydrogen atoms located on carbon atoms *β* to the halogen.[5,6] If the assistance were large enough to overcome the normal polar effects, the resulting rates of abstraction found for the substituted alkanes could be predicted to be faster than those of the parent hydrocarbon.

Some evidence can be found in the literature to rationalize the concept that bromination of halogenated alkanes proceeds at a rate faster than that of the parent alkane or of a less highly halogenated derivative.

Recently, Skell has reported results obtained from the competitive bromination of a number of halogenated alkanes *vs.* their unsubstituted analogs.[7] In all cases that he has reported, although the experimental conditions were not given, the brominated alkanes apparently reacted at a faster rate than their parent hydrocarbons. It is of interest to note that although *cis*- and *trans*-4-bromo-*tert*-butylcyclohexane should show a very similar polar effect, the relative rate of bromination has been reported to be $k_{\mathrm{cis}}/k_{\mathrm{trans}} > 15$.[8] In his more recent publication the cis isomer was reported to undergo bromination 19.2 times faster than cyclo-

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