In addition we are grateful to Prof. S. Huzinaga and D. M. Klobukowski for performing Gaussian 80 calculations and to Prof. S. Pons. and Dr. B. Speiser for electrochemical studies.

Registry No. 2, 498-66-8; 3, 73321-28-5; 4, 73679-39-7; 5, 86954-77-0; 7, 4233-18-5; 8, 765-83-3; 9, 57984-32-4; 10, 7125-60-2; 12, 591-48-0; 4,5-dihydroxy-4,5-dipropyloctane, 86954-78-1; 5-methyl-1,4,4a,5,6,7,8,8a-octahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylic anhydride, 86954-79-2; 5-methyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylic anhydride, 86954-80-5; 5-methyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylic acid, 86954-75-8; methyl hydrogen 5-methyl-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4-*exo*-methanonaphthalene-4a,8a-dicarboxylate, 86954-76-9.

Peroxy Esters. 8. Base-Catalyzed Rearrangement of Peroxy Esters: Formation of Alkoxyacetic Acid Derivatives[1]

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p-Peroxyquinol esters derived from base-catalyzed oxygenation of 4-alkyl-2,6-*tert*-butylphenols followed by Schotten–Baumann acylation undergo a novel base-catalyzed rearrangement with *t*-BuOK in *N,N*-dimethylformamide to give *p*-quinoxyacetic acid derivatives in excellent yield. The same base-catalyzed rearrangement was also observed with *tert*-butyl peroxy esters. The base-catalyzed reaction of peroxy esters depended strongly on the nature of the acyl group in the esters and the base used and is suggested to involve homolysis of the peroxy bond.

Reactions of organic peroxides have received intensive study because knowledge of their properties and reactivity is of the highest importance in a wide range of organic chemistry.[2] Reactions of peroxy esters with bases have been demonstrated to result in fragmentation through an ionic cleavage of the peroxy bond either by direct attack of bases on the peroxy bond[3-6] or by deprotonation from a C–H bond in the α-position to the peroxy group followed by concerted ionic decomposition.[7] Hydroxy anion is known to attack the carbonyl group in peroxy esters, leading to hydrolysis.[8]

The present paper deals with a novel base-catalyzed rearrangement of peroxy esters **1** derived from 4-alkyl-2,6-di-*tert*-butylphenols (**4**) to give *p*-quinoxyacetic acid derivatives **2** in excellent yield. Similar rearrangement was also observed in the base-catalyzed reaction of *tert*-butyl peroxy esters. A mechanism involving homolysis of the peroxy bond is discussed.

Results

Base-Catalyzed Reaction of 4-Alkyl-2,6-di-*tert*-butyl-4-(acylperoxy)-2,5-cyclohexadienones (*p*-Quinol Peroxy Esters) (1).

Peroxy esters **1** were readily obtained by the Schotten–Baumann acylation of 4-alkyl-2,6-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadienones, which were derived quantitatively from base-catalyzed oxygenation of 4-alkyl-2,6-di-*tert*-butylphenols.[9] Peroxy esters **1** except **1b** and **1f** (see Chart I) were not obtained as crystals, but TLC and NMR analyses of their reaction mixture showed the quantitative formation of **1**. The peroxy esters **1** were thermally stable, could be stored at 5 °C without decomposition for a year, but were susceptible to light. It is noted that compound **1a** could be purified by a vacuum distillation at 105 °C.

When a solution of **1** in *N,N*-dimethylformamide (DMF) containing *t*-BuOK was stirred at −60 °C under nitrogen atmosphere, the starting material disappeared normally in 2 h. Acidic workup followed by TLC separation of the

Table I. *t*-BuOK-Catalyzed Reaction of Peroxy Esters 1[a]

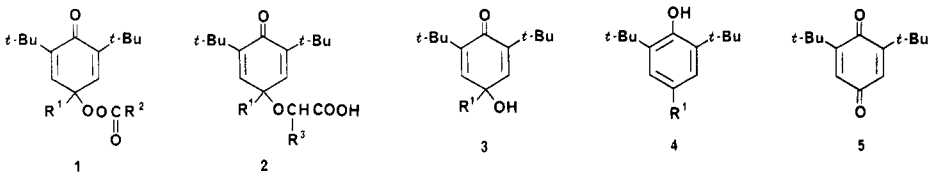
	product yield,[b] %			
1	2	3	4	5
1a	81	3	4	0
1a (MeOH)	19	60	21	0
1b	91	1	0	0
1c	94	0	4	1
1d	53	15	2	17
1e	38	35	9	0
1f	34	0	7	0
1g	0	77	0	0
1h[c]	0		54	

[a] 1 (4 mmol), *t*-BuOK (16 mmol), DMF (15 mL) at −60 °C. [b] Determined by ^{1}H NMR. [c] In addition to phenol 4a, a hydrolyzed product, 2,6-di-*tert*-butyl-4-(hydroperoxy)-4-methyl-2,5-cyclohexadienone, was obtained in 12% yield.

(1) Preliminary communication: Nishinaga, A.; Nakamura, K.; Matsuura, T. *Chem. Lett.* **1977**, 303. Part 7: Nishinaga, A.; Nakamura, K.; Matsuura, T. *J. Org. Chem.* **1982**, *47*, 1431.
(2) Mageli, O. L.; Sheppard, C. S. "Organic Peroxides"; Swern, D., Ed.; Wiley-Interscience: New York, London, Sydney, Toronto, 1970; Vol. 1, Chapter 1.
(3) Ball, R. E.; Edward, J. O.; Haggett, M. L.; Jones, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2331.
(4) Koukek, E.; Welson, J. E. *J. Org. Chem.* **1968**, *33*, 445.
(5) Lawesson, S.-O.; Yang, N. C. *J. Am. Chem. Soc.* **1959**, *81*, 4231.
(6) Lawesson, S.-O.; Friesell, C.; Denney, D. Z.; Denney, D. B. *Tetrahedron* **1963**, *19*, 1229.
(7) Pincock, R. E. *J. Am. Chem. Soc.* **1964**, *86*, 1820.
(8) Anonovoski, V. L.; Buzlanova, M. M.; Frolova, Z. S. *Kinet. Katal.* **1967**, *8*, 671.
(9) Nishinaga, A.; Itahara, T.; Shimizu, T.; Matsuura, T. *J. Am. Chem. Soc.* **1978**, *100*, 1820.

0022-3263/83/1948-3696$01.50/0

Chart I



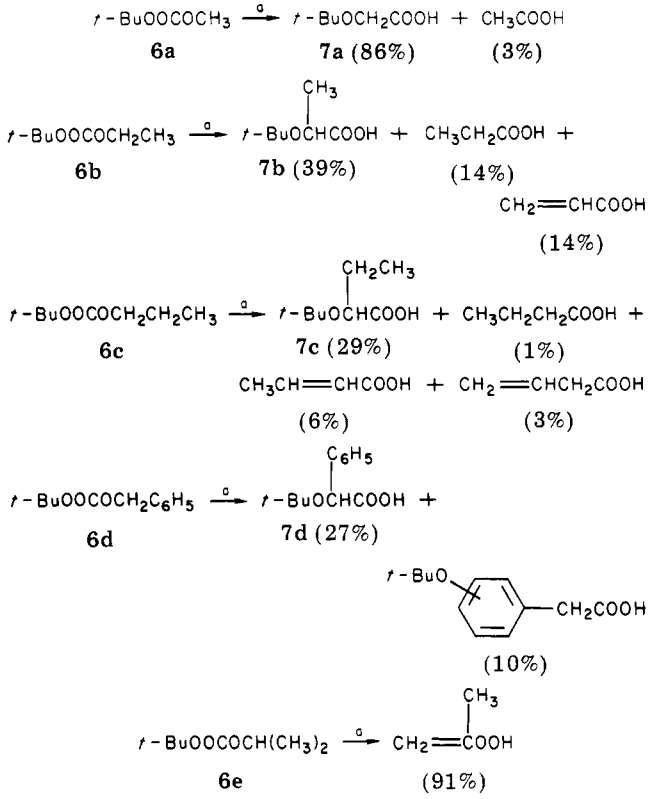
	a	b	c	d	e	f	g	h	i
R^1	Me	Et	*i*-Pr	*t*-Bu	Me	Me	Me	Me	Me
R^2	Me	Me	Me	Me	Et	CH_2Ph	*i*-Pr	Ph	*t*-Bu
R^3	H	H	H	H	Me	Ph			

reaction mixture gave *p*-quinoxyacetic acid (**2**) as a main product, 4-alkyl-2,6-di-*tert*-butyl-*p*-quinol (**3**), 4-alkyl-2,6-di-*tert*-butylphenol (**4**), and 2,6-di-*tert*-butyl-*p*-benzoquinone (**5**). The results are summarized in Table I. All the products were isolated as crystals. Characteristic spectra of the new compounds **2** are structurally correlated to each other. Values of ν_{CO} (1645–1660 cm^{-1}) and olefinic proton signals (δ 6.35–6.51) are typical for 2,5-cyclohexadienones.[10] Compound **2** also shows ν_{OH} 2500–2700 cm^{-1} and ν_{CO} 1720–1730 cm^{-1}, attributable to the carboxyl group. The structure of **2** was further confirmed by the chemical reactions of **2a** and **2f**. Thus, reduction of **2a** and **2f** with Zn–HCl in ethanol gave 2,6-di-*tert*-butyl-4-methylphenol (**4a**) in nearly quantitative yield. Ethyl mandelate was also obtained in 70% yield from the reduction of **2f**. The reduction is analogous to that of *p*-quinols, giving rise to the corresponding phenols as reported by Rieker and Scheffler.[11] Methylation of **2a** with diazomethane afforded the corresponding methyl ester quantitatively. The ^1H NMR spectra of **2e** and **2f** show two signals for nonequivalent *t*-Bu groups and a pair of doublets (J = 3.0 Hz) in the olefinic region. However, their IR and UV data are quite similar to those of **2a**, indicating that the same *p*-quinoid chromophore exists in these products. The nonequivalent NMR data of the *tert*-butyl and the olefinic protons in **2e** and **2f** may be due to the asymmetric induction at the quinoxyacetic moiety in these products.

Yield of the migration product **2** depended on the nature of the substituents R^1 and R^2 in **1** and the base used. The strong steric interaction of R^1 with R^2 and strong nucleophilicity of the base are unfavorable to the migration (Table I). Thus, no reaction took place with amine (pyridine, diethylamine) or with sodium hydride. With **1d–f** the yield of migration product **2** decreased remarkably, and compound **1g** underwent no migration but only decomposition. The reaction of **1a** with NaOMe in DMF at 0 °C gave *p*-quinol **3a** predominantly, which results probably from nucleophilic attack by the methoxy anion on the carbonyl group of the acyl moiety in **1a**. Such a nucleophilic reaction was demonstrated by the reaction of **1h** with *t*-BuOK, where the formation of **4a** (54%), **3a** (12%), and *tert*-butyl benzoate (ca. 30%) was observed. Compound **1i** was found to be unsusceptible to the *t*-BuOK-catalyzed reaction at –60 °C. This may be due to steric hindrance in the nucleophilic attack by *tert*-butoxy anion on the acyl group in **1i**.

Base-Catalyzed Reaction of *tert*-Butyl Peroxy Esters (6a–e). *tert*-Butyl peroxy esters (**6a–e**) were prepared by the Schotten–Baumann reaction of *tert*-butyl hydroperoxide with acyl chloride in light petroleum in the presence of pyridine at 0 °C in nearly quantitative yield.

Scheme I[a]



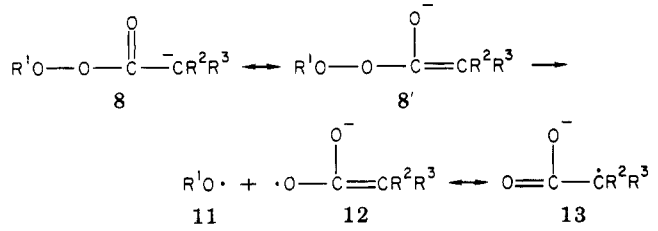
[a] *t*-BuOK/DMF, –60 °C, N_2, 4 h.

Since the peroxy esters were decomposed to some extent under a vacuum distillation (although some of them could be purified by the distillation), they were employed for the succeeding reaction without further purification. When the peroxy esters (**6a–e**) were treated with *t*-BuOK in DMF at –60 °C under nitrogen atmosphere, they underwent cleavage of the peroxy bond to give the corresponding 2-*tert*-butoxyalkanoic acids (**7a–7d**) and decomposition products (Scheme I).[12] With **6e**, only a decomposition product was obtained.

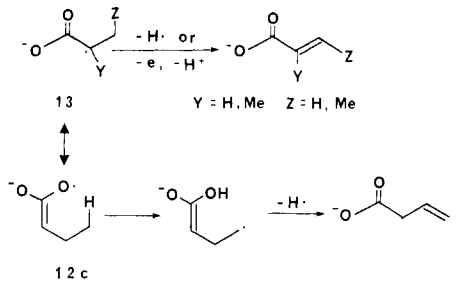
Compound **7a** was isolated by distillation from the reaction mixture, whereas **7b–d** were isolated as methyl esters. Direct distillation of the reaction mixture including these products did not give good results. Interestingly, the reaction of **6d** gave a mixture (ca. 1:1) of *o*- and *p*-*tert*-butoxyphenylacetic acids in 10% yield, as determined by ^1H NMR and combustion analyses of the esterified mixture. Attempts for chromatographic separation of these acids or methyl esters were not successful. The ^1H NMR and combustion analyses of **7b–d** and their methyl esters are in good agreement with the structures.

(10) Rieker, A.; Rundel, K.; Kessler, H. *Z. Naturforsch. B* **1969**, *24B*, 547.
(11) Rieker, A.; Scheffler, K. *Justus Liebigs Ann. Chem.* **1965**, *689*, 78.
(12) In the present work, products other than carboxylic acids were not investigated.

Scheme II



Scheme III



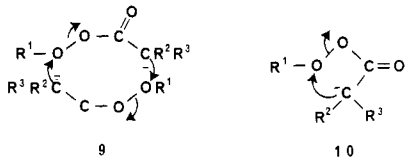
Discussion

Although base-catalyzed rearrangement reactions of organic peroxides accompanying cleavage of the peroxy bond has been known with the acetate anion catalyzed reaction of diacetyl peroxide to give acetoxyacetic acid,[13] the present work provides the first example of base-catalyzed rearrangement of peroxy esters to alkoxyacetic acid derivatives.

The migration reactions **1** → **2** and **6** → **7** result from the formation of carbanion **8** by deprotonation with *t*-BuO⁻. Initiation of the attack by the *t*-BuO⁻ anion on the

$$R^1O\text{-}OCOCHR^2R^3 \xrightarrow{t\text{-}BuO^-} \underset{8}{R^1O\text{-}OCO^-CR^2R^3}$$

peroxy bond can be reasonably ruled out, because a hindered ester (**1i**) was quite stable against the base-catalyzed reaction. The known reactions of carbanions with peroxy esters involving heterolysis of the peroxy bond and giving rise to ethers and carboxylates[3-6] seem to suggest an intermolecular (**9**) or intramolecular (**10**) mechanism for the

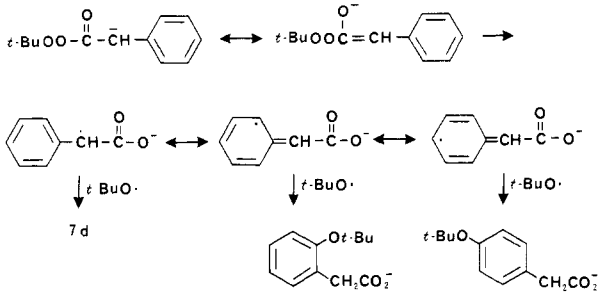


formation of **2** and **7**. The intermolecular mechanism (**9**) is, however, ruled out, because treatment of a mixture (1:1) of **1a** and **6b** with *t*-BuOK in DMF gave **2a** (96%), **7b** (18%), acrylic acid (23%), and propionic acid (16%) but no cross reaction products **2e** and **7a**. On the other hand, the intramolecular mechanism (**10**) does not provide reasonable interpretation for the formation of **5** from **1d**, phenols (**4**) from **1a–f**, and unsaturated acids from **6b–c**. The results in the present work may be rationalized by assuming homolysis of the O–O bond in **8** (Scheme II). The anion **8** can exist in its enolate form though resonance and readily undergoes homolysis to give alkoxy radical (**11**) and carboxyl radical (**12**), which in turn gives a carbon radical (**13**). The recombination of **11** with **13** gives migration products **2** and **7**. This recombination was strongly

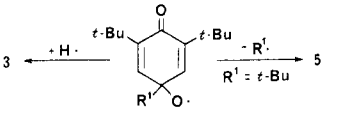
$$11 + 13 \rightarrow 2, 7$$

(13) Koenig, T.; Wielesek, R. *J. Am. Chem. Soc.* **1969**, *91*, 2551.

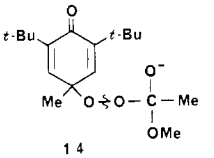
Scheme IV



dependent on the size of the groups R^2 and R^3 in **13**. With $R^2 = R^3 = H$, the recombination took place most efficiently. The case with **1d** was rather exceptional, because the migration reaction was hindered by the *t*-Bu group in the quinoxy moiety and the corresponding quinoxy radical (**11a**) underwent β-scission[14] to give *p*-benzoquinone **5** and

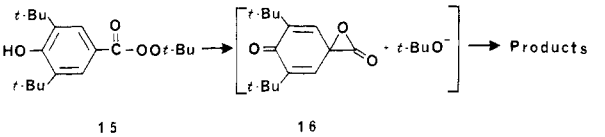


reduction to give *p*-quinol **3d**. The formation of phenol (**4**) was the result of attack by the base on the carbonyl group in **1** to give peroxy *p*-quinolate anions, which are known to liberate oxygen, giving rise to the parent phenols.[15] The predominant formation of quinol **3a** in the reaction of **1a** with NaOMe suggests that intermediate **14**



also readily undergoes homolysis of the peroxy bond. The formation of the olefinic acids from **6** can also be reasonably elucidated in terms of radical anion **12** (**13**) as shown in Scheme III. Hydrogen abstraction probably by *tert*-butoxyl radical from **13** or oxidation followed by deprotonation produced the conjugated olefinic acids as obtained from **6b**, **6c**, and **6e**. The intramolecular hydrogen abstraction from the δ-position in **12** ($R^2 = H$, $R^3 = CH_2CH_3$) followed by oxidation gave 3-butenoic acid as obtained from **6c**. The homolysis mechanism (Scheme II) is well demonstrated in the base-catalyzed reaction of **6d** (Scheme IV).

Hucek et al.[16] investigated the base-catalyzed decomposition of phenolic peroxy ester **15** and proposed a mechanism involving α-lactone intermediate **16**. A similar



α-lactone mechanism, however, may not be applicable to our present results, especially the highly selective formation of **2** from **1** and 2-methylpropionic acid from **6e**. As stated in the following paper, the base-catalyzed reaction of **15** may also be rationalized by homolysis of the peroxy bond.

(14) Starnes, W. H., Jr.; Neureiter, N. P. *J. Org. Chem.* **1967**, *32*, 333.
(15) Nishinaga, A.; Shimizu, T.; Matsuura, T. *J. Org. Chem.* **1979**, *44*, 2983.
(16) Hucek, A. M.; Barbas, J. T.; Leffler, J. E. *J. Am. Chem. Soc.* **1973**, *95*, 4698. Barbas, J. T.; Leffler, J. E. *Ibid.* **1975**, *97*, 7270.

It is noted that generation of a carbanion in the α-position of an acyl group of peroxy esters weakens markedly the peroxy bond, resulting in homolysis even at −60 °C.

Experimental Section

All melting points were uncorrected. Elemental analyses were performed by the Analytical Center of the Pharmaceutical Department, Kyoto University. Infrared spectra were recorded on a JASCO IRA-1 spectrophotometer. Ultraviolet spectra were determined with a Shimazu UV-200 spectrophotometer. Proton magnetic resonance spectra were determined with a Varian T-60 spectrometer.

4-Alkyl-2,6-di-*tert*-butyl-4-(acylperoxy)-2,5-cyclohexadienones (*p*-Quinol Peroxy Esters) (1). A solution of an appropriate acyl chloride (12.1 mmol) in dry petroleum ether was added dropwise in 3 min to a stirred solution of the corresponding peroxy *p*-quinol (12 mmol) prepared by the base-catalyzed oxygenation of phenol **4a–d** in dry petroleum ether containing pyridine (0.99 mL, 12.1 mmol) at 0 °C. After being stirred for 30 min at 0 °C, the mixture was warmed up to room temperature and kept stirring for 2 h. The resulting pyridine hydrochloride precipitated and was removed by filtration through a Celite layer (1.5 cm, 7 g). The filtrate was washed with dilute HCl, water, and an aqueous $NaHCO_3$ solution and dried (Na_2SO_4). Evaporation of the resulting solution gave *p*-quinol peroxy ester 1 quantitatively. Peroxy ester **1a** was purified by distillation. Esters **1b**, **1f**, and **1h** were crystallized. Physical and analytical data of 1 are given below.

1a: yellow oil; bp 105 °C (5 mmHg); ^1H NMR (CCl_4) δ 1.22 (s, 18 H), 1.43 (s, 3 H), 1.83 (s, 3 H), 6.49 (s, 2 H); IR (film) 1780, 1630 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found: C, 69.28; H, 8.90.

1b: colorless cubes from petroleum ether; mp 46–48 °C; ^1H NMR (CCl_4) 1.23 (s, 18 H), 0.84 (t, 3 H, J = 7.5 Hz), 1.78 (q, 2 H, J = 7.5 Hz), 1.84 (s, 3 H), 6.41 (s, 2 H); IR (Nujol) 1780, 1630 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 68.94; H, 9.41.

1c: yellow oil; ^1H NMR (CCl_4) 1.22 (s, 18 H), 0.91 (d, 6 H, J = 7.5 Hz), 2.04 (sep, 1 H, J = 7.5 Hz), 1.81 (s, 3 H), 6.50 (s, 2 H); IR (film) 1790, 1665 cm^{-1}.

1d: yellow oil; ^1H NMR (CCl_4) 1.21 (s, 18 H), 1.03 (s, 9 H), 1.84 (s, 3 H), 6.64 (s, 2 H); IR (film) 1800, 1665 cm^{-1}.

1e: yellow oil; ^1H NMR (CCl_4) 1.24 (s, 18 H), 1.44 (s, 3 H), 1.08 (t, 3 H, J = 7.5 Hz), 2.09 (q, 2 H, J = 7.5 Hz), 6.49 (s, 2 H); IR (film) 1790, 1650 cm^{-1}.

1f: colorless cubes from petroleum ether; mp 88–90 °C; ^1H NMR (CCl_4) 1.17 (s, 18 H), 1.41 (s, 3 H), 3.39 (s, 2 H), 6.48 (s, 2 H), 7.17 (s, 5 H); IR (Nujol) 1785, 1645 cm^{-1}. Anal. Calcd for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16. Found: C, 74.39; H, 8.18.

1g: yellow oil; ^1H NMR (CCl_4) 1.21 (s, 18 H), 1.43 (s, 3 H), 1.08 (d, 6 H, J = 7.5 Hz), 2.29 (sep, 1 H, J = 7.5 Hz), 6.55 (s, 2 H); IR (film) 1780, 1645 cm^{-1}.

1h: colorless cubes from petroleum ether; mp 121–123 °C; ^1H NMR (CCl_4) 1.16 (s, 18 H), 1.52 (s, 3 H), 7.50 (s, 2 H), 7.25–7.80 (m, 5 H); IR (Nujol) 1760, 1640 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.37; H, 8.10.

1i: yellow oil; ^1H NMR (CCl_4) 1.22 (s, 18 H), 1.24 (s, 9 H), 1.45 (s, 3 H), 6.48 (s, 2 H); IR (film) 1790, 1650 cm^{-1}.

***t*-BuOK-Catalyzed Reaction of *p*-Quinol Peroxy Esters 1.** A solution of 1 (4 mmol) in dry petroleum ether (15 mL) was added dropwise in 30 min to a vigorously stirred solution of *t*-BuOK (1.79 g, 16 mmol) in a mixture of DMF (15 mL) and petroleum ether (5 mL) at −60 °C under nitrogen atmosphere. After being stirred at −60 °C for 2 h, the mixture was acidified with dilute HCl, extracted with ether, dried (Na_2SO_4), and evaporated. Trituration of the resulting residue from **1a–c** with petroleum ether gave **2a–c** as crystals. The residue from **1d–g** was subjected to silica gel layer chromatography with a mixture of petroleum ether and dichloromethane (1:1) as eluant. The results are given in Table I. Compounds **3–5** are known and were identified with authentic samples. Physical and analytical data of **2** are given below.

2a: colorless needles from petroleum ether; mp 84–86 °C; ^1H NMR (CCl_4) δ 1.22 (s, 18 H), 1.45 (s, 3 H), 3.79 (s, 2 H), 6.43 (s, 2 H); IR (Nujol) 1730, 1650 cm^{-1}; UV (EtOH) λ 235 nm (log ε, 4.53). Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found: C, 69.10; H, 9.11.

2b: colorless prisms from petroleum ether; mp 93–95 °C; ^1H NMR (CCl_4) δ 0.77 (t, 3 H, J = 7.5 Hz), 1.20 (s, 18 H), 1.79 (q, 2 H, J = 7.5 Hz), 3.82 (s, 2 H), 6.35 (s, 2 H); IR (Nujol) 1725, 1650 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_4$: C, 69.83; H, 9.45. Found: C, 69.10; H, 9.15.

2c: colorless needles from petroleum ether; mp 94–96 °C; ^1H NMR (CCl_4) δ 0.93 (d, 6 H, J = 7.5 Hz), 1.23 (s, 18 H), 2.04 (sep, 1 H, J = 7.5 Hz), 3.94 (s, 2 H), 6.47 (s, 2 H); IR (Nujol) 1720, 1660 cm^{-1}. Anal. Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 70.54; H, 9.51.

2d: colorless needles from petroleum ether; mp 110–112 °C; ^1H NMR (CCl_4) δ 0.91 (s, 9 H), 1.22 (s, 18 H), 3.84 (s, 2 H), 6.51 (s, 2 H); IR (Nujol) 1725, 1645 cm^{-1}. Anal. Calcd for $C_{20}H_{32}O_4$: C, 71.39; H, 9.59. Found: C, 71.16; H, 9.71.

2e: colorless prisms from petroleum ether; mp 75–77 °C; ^1H NMR (CCl_4) δ 1.13 (s, 9 H), 1.21 (s, 9 H), 1.28 (d, 3 H, J = 7.5 Hz), 1.39 (s, 3 H), 3.66 (q, 1 H, J = 7.5 Hz), 6.26 (d, 1 H, J = 3.0 Hz), 6.47 (d, 1 H, J = 3.0 Hz); IR (Nujol) 1720, 1660 cm^{-1}; UV (EtOH) λ 235 nm (log ε, 4.52). Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.05; H, 9.05.

2f: colorless prisms from petroleum ether; mp 114–116 °C; ^1H NMR (CCl_4) δ 1.08 (s, 9 H), 1.17 (s, 9 H), 1.46 (s, 3 H), 4.52 (s, 1 H), 7.30 (s, 5 H), 6.13 (d, 1 H, J = 3.0 Hz), 6.53 (d, 1 H, J = 3.0 Hz); IR (Nujol) 1725, 1660 cm^{-1}; UV (EtOH) λ 234 nm (log ε, 4.52). Anal. Calcd for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16. Found: C, 74.76; H, 8.23.

Reduction of *p*-Quinoxyacetic Acid (2a, 2f) with Zn/HCl. Hydrochloric acid (35%, 3 mL) was added dropwise to a vigorously stirred solution of **2a(2f)** (0.54 mmol) containing Zn powder (0.71 g) in ethanol (4 mL) at 50 °C. After being stirred for 1 h, the remaining Zn was removed by filtration through a Celite layer (2 cm) and washed with ether. The filtrate was poured into water, acidified with an ice-cooled dilute HCl, and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. The ^1H NMR spectrum of the resulting residue from **2a** showed only the signals for **4a**, which was isolated quantitatively. The residue obtained from **2f** was subjected to silica gel plate chromatography and developed with dichloromethane to give **1a** (quantitative yield) and ethyl mandelate (69% yield), which were identified by comparison with authentic samples.

Methylation of *p*-Quinoxyacetic Acid 2a. A solution of diazomethane (3 mmol) in ether was added to a solution of **2a** (1 mmol) in ether (10 mL). The mixture was allowed to stand at room temperature for 30 min and evaporated to give the methyl ester of **2a** quantitatively, which was isolated as colorless prisms; mp 52–54 °C; ^1H NMR ($CDCl_3$) δ 1.22 (s, 18 H), 1.49 (s, 3 H), 3.76 (s, 3 H), 3.88 (s, 2 H), 6.48 (s, 2 H); IR (Nujol) 1740, 1660 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.30; H, 9.15.

***tert*-Butyl Peroxy Esters 6.** A solution of acyl chloride (6.1 mmol) in dry penatane (15 mL) was added dropwise in 30 min to a stirred solution of *tert*-butyl hydroperoxide (commercial grade, 6 mmol) in dry pentane (20 mL) containing dry pyridine (6.1 mmol) at 0 °C. After being stirred at 0 °C for 1 h, the mixture was warmed up to 40 °C and stirred for 10 min. For the formation of **6d**, the mixture was stirred at 0 °C for 3 h, because **6d** was decomposed at 40 °C. The resulting pyridine hydrochloride precipitate was removed by filtration through a Celite layer (7 cm, 10 g) and washed with pentane. The filtrate was dried (Na_2SO_4) and evaporated below 40 °C to give **6** as colorless oil in quantitative yield, as judged by NMR. The product **6** thus obtained was employed without further purification for the following base-catalyzed reaction. The spectral data of **6** are as follows.

6a: ^1H NMR (CCl_4) δ 1.27 (s, 9 H), 1.98 (s, 3 H); IR (film) 1780 cm^{-1}.

6b: ^1H NMR (CCl_4) δ 1.28 (s, 9 H), 1.16 (t, 3 H, J = 7.5 Hz), 2.23 (q, 2 H, J = 7.5 Hz); IR (film) 1780 cm^{-1}.

6c: ^1H NMR (CCl_4) δ 0.99 (t, 3 H, J = 6.6 Hz), 1.22 (t, 2 H, J = 6.0 Hz), 1.29 (s, 9 H), 1.70 (q, t, 2 H, J = 6.6, 6.0 Hz); IR (film) 1780 cm^{-1}. Anal. Calcd for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 59.79; H, 10.17.

6d: ^{1}H NMR (CCl_4) δ 1.20 (s, 9 H), 3.50 (s, 2 H), 7.20 (s, 5 H); IR (Nujol) 1780 cm^{-1}.

6e: ^{1}H NMR (CCl_4) δ 1.19 (d, 6 H, J = 7.5 Hz), 1.29 (s, 9 H), 2.62 (sep, 1 H, J = 7.5 Hz); IR (film) 1780 cm^{-1}.

***t*-BuOK-Catalyzed Reaction of *tert*-Butyl Peroxy Esters 6.** A solution of **6** (5 mmol) in dry pentane (10 mL) was added dropwise in 30 min to a vigorously stirred solution of *t*-BuOK (20 mmol) in dry DMF (20 mL) containing dry pentane (6 mL) at −60 to −78 °C under nitrogen atmosphere. The mixture was stirred at the same temperature for 4 h and neutralized with dilute HCl (pH ca. 8). The resulting mixture was then evaporated under a reduced pressure at 40 °C to dryness. The residue was further acidified with dilute HCl and extracted with ether. The extract was dried (Na_2SO_4) and evaporated to givbe a colorless oily residue. Products were isolated by the following workup. Compound **7a** was obtained by direct distillation of the residue. The residues from **6b–e** were treated with diazomethane, and **7b–e** and other carboxylic acids were isolated as their methyl esters by means of gas chromatography followed by distillation. The methyl esters of the C_3 and C_4 carboxylic acids were identified with authentic samples. Acetic acid from **6a** was not isolated, but its formation was confirmed by ^{1}H NMR spectrum of the reaction mixture obtained from **6a**.

7a: bp 95 °C (4 mmHg); ^{1}H NMR (CCl_4) δ 1.20 (s, 9 H), 3.96 (s, 2 H); IR (film) 1735 cm^{-1}. Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.42; H, 9.25.

Methyl ester of 7b: colorless oil; bp 100 °C (6 mmHg); ^{1}H NMR (CCl_4) δ 1.17 (s, 9 H), 1.26 (d, 3 H, J = 7.0 Hz), 3.71 (s, 3 H), 4.13 (q, 1 H, J = 7.0 Hz); IR (film) 1755 cm^{-1}. Anal. Calcd for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 59.83; H, 9.88. **7b**: ^{1}H NMR (CCl_4) δ 1.21 (s, 9 H), 1.34 (d, 3 H, J = 7 Hz), 4.09 (q, 1 H, J = 7 Hz).

Methyl ester of 7c: colorless oil; bp 55 °C (4 mmHg); ^{1}H NMR (CCl_4) δ 0.95 (t, 3 H, J = 7 Hz), 1.13 (s, 9 H), 1.55 (q, d, 2 H, J = 7, 6 Hz), 3.66 (s, 3 H), 3.77 (t, 1 H, J = 6 Hz); IR (film) 1755 cm^{-1}. Anal. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 61.79; H, 10.49. **7c**: ^{1}H NMR (CCl_4) δ 0.95 (t, 3 H, J = 7.5 Hz), 1.20 (s, 9 H), 1.60 (q, d, 1 H, J = 7.5, 6 Hz), 3.88 (t, 1 H, J = 6 Hz).

Methyl ester of 7d: colorless oil; bp 95 °C (3 mmHg); ^{1}H NMR (CCl_4) δ 1.26 (s, 9 H), 3.70 (s, 3 H), 5.11 (s, 1 H), 7.2–7.6 (m, 5 H); IR (film) 1755 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.98; H, 8.21. **7d**: ^{1}H NMR (CCl_4) δ 1.20 (s, 9 H), 4.97 (s, 1 H), 7.0–7.5 (m, 5 H).

Methyl (*o*-*tert*-butoxyphenyl)acetate: colorless oil; ^{1}H NMR (CCl_4) δ 1.37 (s, 9 H), 3.45 (s, 2 H), 3.56 (s, 3 H), 6.6–7.2 (m, 4 H). Anal. Calcd for $C_{13}H_{18}O_3$ (as a mixture with the *p*-isomer): C, 70.24; H, 8.16. Found: C, 70.24; H, 8.41.

Methyl (*p*-*tert*-butoxyphenyl)acetate: colorless oil; ^{1}H NMR (CCl_4) δ 1.32 (s, 9 H), 3.48 (s, 2 H), 3.65 (s, 3 H), 6.7–7.3 (m, 4 H).

Registry No. **1a**, 62926-71-0; **1b**, 62926-72-1; **1c**, 62926-73-2; **1d**, 62926-74-3; **1e**, 62926-75-4; **1f**, 62926-76-5; **1g**, 62955-68-4; **1h**, 62926-77-6; **1i**, 87100-48-9; **2a**, 62926-78-7; **2a** methyl ester, 87100-49-0; **2b**, 62926-79-8; **2c**, 62926-80-1; **2d**, 62926-81-2; **2e**, 62926-82-3; **2f**, 62926-83-4; **4a**, 128-37-0; **4b**, 4130-42-1; **4c**, 5427-03-2; **4d**, 732-26-3; **6a**, 107-71-1; **6b**, 14206-05-4; **6c**, 18072-84-9; **6d**, 3377-89-7; **6e**, 109-13-7; **7a**, 13211-32-0; **7b**, 87100-50-3; **7b** methyl ester, 87100-51-4; **7c**, 87100-52-5; **7c** methyl ester, 87100-53-6; **7d**, 66667-02-5; **7d** methyl ester, 87100-54-7; acetyl chloride, 75-36-5; propanoyl chloride, 79-03-8; benzeneacetyl chloride, 103-80-0; 2-methylpropanoyl chloride, 79-30-1; benzoyl chloride, 98-88-4; 2,2-dimethylpropanoyl chloride, 3282-30-2; 4-methyl-2,3-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadienone, 6485-57-0; 4-ethyl-2,6-di-*tert*-butyl-4-(hydroxperoxy)-2,5-cylcohexadienone, 87013-27-2; 4-isopropyl-2,6-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadienone, 87013-28-3; 2,4,6-tri-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadienone, 33919-05-0; *tert*-butyl hydroperoxide, 75-91-2; butanoyl chloride, 141-75-3; methyl (*o*-*tert*-butyoxyphenyl)acetate, 87100-55-8; methyl (*p*-*tert*-butoxyphenyl)acetate, 87100-56-9.

Peroxy Esters. 9. Base- and Radical-Induced Decomposition of 1-Alkyl-3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienyl 3,5-Di-*tert*-butyl-4-hydroxyperbenzoates[1]

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The title peroxy esters **1**, when deprotonated with *t*-BuOK in DMF to the corresponding phenolate anions, decompose even at −78 °C to give compounds **2–10**. These compounds result undoubtedly from homolysis of the peroxy bond in **1**, indicating that the generation of a carbanion at the α-position of the acyl group in peroxy esters (via resonance in the present case) induces ready homolysis of the peroxy bond. The oxidation of **1** with one-electron oxidizing agents gives rise to the corresponding phenoxy radicals, which also induce homolysis of the peroxy bond.

In the preceding paper,[1] we reported that 1-alkyl-3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienyl and *tert*-butyl peroxy acetates underwent base-catalyzed rearrangement at −60 °C or below to give the corresponding alkoxyacetic acid derivatives resulting from cleavage of the peroxy bond. The proposed mechanism involves homolysis of the peroxy bond, which is accelerated when a carbanion is generated in the α-position of the acyl group of the peroxy esters. On the other hand, Leffler et al.[2] have argued a heterolytic cleavage of the peroxy bond for the base-catalyzed decomposition of *tert*-butyl 3,5-di-*tert*-butyl-4-hydroxyperbenzoate. However, an insufficient search for the fate of the *tert*-butoxy moiety of the ester has made their argument uncertain. We have therefore investigated the base-catalyzed reaction as well as the oxidation of 1-al-

(1) Preliminary communication: Nishinaga, A.; Nakamura, K.; Matsuura, T. *Tetrahedron Lett.* **1978**, 3557. Part 7: Nishinaga, A.; Nakamura, K.; Matsuura, T. *J. Org. Chem.*, preceding paper in this issue.

(2) Hucek, A. M.; Barbas, J. T.; Leffler, J. E. *J. Am .Chem. Soc.* **1973**, *95*, 4698.

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