Tetrahedron Vol. 35, pp. 2493 to 2499
© Pergamon Press Ltd., 1979. Printed in Great Britain

0040-4020/79/1101 2493/$02.00/0

PEROXY ESTERS—III[1]

ACID-CATALYZED REACTION OF 4-HYDROPEROXY-2,5-CYCLOHEXADIENONES AND THEIR DERIVATIVES[2]

AKIRA NISHINAGA,* KOICHI NAKAMURA, and TERUO MATSUURA
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

and

ANTON RIEKER,* DIETER KOCH, and RAINER GRIESSHAMMER
Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 7400 Tübingen, Germany

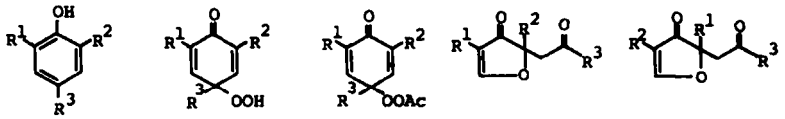
(*Received in Japan* 10 *April* 1979)

Abstract—Acid-treatment of 4-hydroperoxy-2,5-cyclohexadienones (peroxy-*p*-quinols) and their acetates leads to the corresponding quinoxy cations through a protonation at the peroxy group, giving rise to different types of products depending on the structure of the peroxy esters. 2,4,6-Trialkyl-*p*-quinoxy cations undergo a rearrangement with ring opening to give 4-oxa-2-cyclopentenone derivatives, except for *p*-quinoxy cations with t-butyl or benzyl groups at the 4-position where 2,6-di-t-butyl-*p*-benzoquinone is exclusively obtained. *p*-Quinoxy cations with aromatic substituents at the 4-position undergo migration of this substituent to the cationic oxygen. In the case of peroxy-*p*-quinols (even peroxy-*p*-naphthoquinols) with 4-aryl substituents the protonation occurs at either O atom of the peroxy bond. Peroxy-*p*-quinols and their acetates with an unhindered dienone system are quite stable towards acid treatment, probably due to a competitive protonation of the peroxy and the dienone CO group. In solvents containing an oxygen function the reaction proceeds slowly.

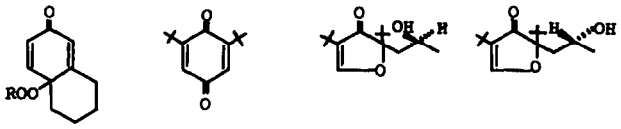
Highly regioselective oxygenation products of 2,6-di-t-butyl-phenols display an interesting chemical behavior under strongly basic conditions, being efficiently utilised for the syntheses of hydroquinones,[3] *o*-benzoquinones,[4] cyclopentadienones,[5-7] 3-hydroxyphenylacetic acids,[8] cyclopentenones,[9] and quinoxyacetic acids.[1] These investigations have revealed the chemical reactivities of *p*-quinolate anions and *p*-quinoxy radicals derived from 2,6-di-t-butylphenols: *p*-quinolate anions readily undergo ketonisation in an aprotic solvent such as DMF to give hydroquinone derivatives, and *p*-quinoxy radicals are involved in the base-catalysed rearrangement of peroxy-*p*-quinol acetates giving *p*-quinoxyacetic acids. *p*-Quinoxy radicals are also found to undergo an intramolecular rearrangement with ring expansion.[1] As a part of investigations in the chemistry of *p*-quinoxy species—since the reaction of *p*-quinoxy cations is not yet known—we have investigated the chemical reactivity of *p*-quinoxy cations which are expected to result from protonation of the peroxy bond in peroxy-*p*-quinols, their esters and ethers. Thus, the present paper deals with the acid-catalysed reaction of 4-hydroperoxy-2,5-cyclohexadienones **2** and **11**, their acetates **3** and alkyl derivatives **12**. It is found that the reactivity of **3** is strongly dependent on the structure of the peroxide used. Compounds **3a–h** are susceptible to the acid-catalysed reaction leading to the corresponding *p*-quinoxy cations, whereas **3i, j** are unreactive.

RESULTS

When the peroxy ester **3a** was treated with trifluoroacetic acid (TFA) in methylene chloride at 0° for 30 min, product **4a** resulting from the ring opening was obtained in quantitative yield. The structure of **4a** is in good agreement with its spectral and analytical data. Further evidence for the structure of **4a** was provided by its chemical reactions. The compound displays a positive haloform reaction, indicating the presence of the acetyl group. The reduction of **4a** with $NaBH_4$ quantitatively yields a mixture of diastereomeric alcohols **7**



	1	2		3		4		5	
	a	b	c	d	e	f	g	h	i
R^1	t-Bu	t-Bu	t-Bu	t-Bu	t-Bu	t-Bu	t-Bu	t-Bu	t-Bu
R^2	t-Bu	t-Bu	t-Bu	t-Bu	t-Bu	t-Bu	Et	Me	H
R^3	Me	Et	i-Pr	t-Bu	CH_2Ph	4-MeOPh	Me	Me	Me



2j; R=H
3j; R=Ac

6 7 7'

Table 1. Acid-catalysed reaction of 3 in CH_2Cl_2

3	Reaction temperature (°C)	Reaction time (h)	Yield of product (%) 4	5	6	IR (Nujol) $\nu_{C=O}$ cm^{-1} 4	5	^{1}H-NMR ($CDCl_3$) δ[b] 4	5	λ_{max}(EtOH) 4	(log ε)[c] 5
a	0	0.5	100	—	—	1730, 1690	—	7.71	—	271(3.79)	—
b	0	0.5	78	—	22	1710, 1685	—	7.72	—	270(3.81)	—
c	0	0.5	53	—	47	1715, 1685	—	7.72	—	271(3.78)	—
d	0	0.5	—	—	100	—	—	—	—	—	—
e	0	1.0	—	—	100	—	—	—	—	—	—
g	20	10	31	47	—	1725, 1695	1725, 1690	7.78	7.79	267(3.84)	270(3.81)
h	20	10	36	44	—	1725, 1690	1725, 1685	7.75	7.84	266(3.82)	270(3.83)

[a] For other data see Experimental. [b] Olefinic proton. [c] Data of log ε reported in a preliminary communication[2] should be revised to those reported here.

and 7', which were separated by tlc as colorless needles (mp 78–81°) and colorless prisms (mp 130–132°). All spectral data of these compounds are consistent with the structures. It is not determined which product corresponds to which structure, but both products are quantitatively reoxidised to **4a**.

The acid-catalysed reaction of **3b** and **3c** also takes place at 0° to give the corresponding **4** and 2,6-di-t-butyl-*p*-benzoquinone (**6**). The yield of **4** decreases with increase in size of the substituent R^3, whilst the amount of **6** increases simultaneously. Peroxy esters **3g** and **3h** were not susceptible to the acid-catalysis at 0° (no reaction in 72 h), but at 20° these esters reacted to give a mixture of the corresponding **4** and **5** (Table 1). They were separated by tlc: **5g** and **5h** were crystalline, whereas **4g** and **4h** were obtained as oily products. A characteristic sharp absorption around 3100 cm^{-1} may be assigned to ν_{C-H} of the enone system bearing the ether bond. All compounds **4** and **5** show a ^{1}H-NMR signal around δ 7.7, reasonably assigned to the vinyl proton. Peroxy esters **3d** and **3e** gave only the benzoquinone **6**. With **3e** benzyl trifluoroacetate was detected (by NMR) in the mixture, from which benzyl alcohol was isolated by means of silica gel chromatography. No such reaction took place with **3i, j** even at elevated temperatures (see, Table 2).

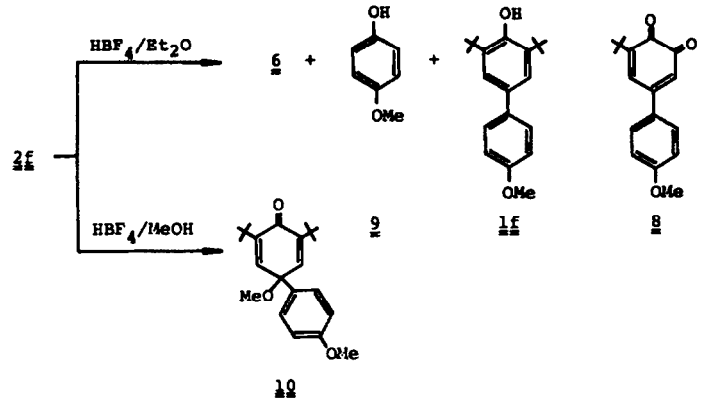
The acid catalysis is much affected by the nature of the solvent used. In ethers and alcohols at 0° the reaction proceeded slowly (Table 2). In methanol at 40°, **3a** gave hydrolysed products **2a** (96%) and **4a** (4%). The acid-catalysed hydrolysis of the ester group in **3** was generally observed in methanol. Thus, **3i** gave only **2i** and **3e** gave **2e** (40%) and **6** (60%).

The acid-treatment of the hydroperoxides **2a–d** led to results comparable to those found when **3a–d** were similarly treated in methylene chloride, although the reaction is more complicated. To the contrary, the reaction of **2f** with acids led to quite different results. When **2f** was treated with TFA at room temperature, a complex mixture was obtained, in which 3-t-butyl-5-(4-methoxyphenyl)-*o*-benzoquinone (**8**)[4] was identified. The treatment of **2f** with HBF_4 in ether at 0° or at room temperature gave *p*-benzoquinone **6** (91%), 4-methoxyphenol (**9**) (67%), and **1f** (9%). Similar results were obtained in the reaction of **2f** with acetic anhydride containing sulfuric acid at room temperature. In methanol the hydroperoxy group was replaced by a

Table 2. Solvent effect on the TFA-catalysed reaction of 3.[a]

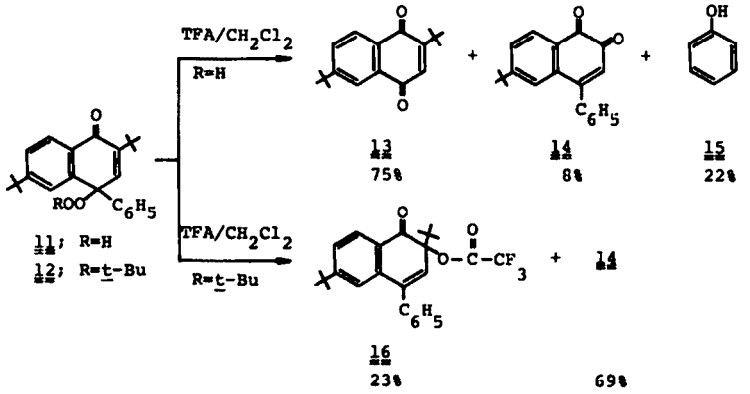
3	Solvent	TFA/solvent (ml/ml)	Reaction temperature (°C)	Reaction time (h)	Conversion (%)	Product (%) 2	4	6
a	MeOH	0.5	0	0.5	0	—	—	—
a	MeOH	0.5	40	15	100	96	4	—
a	MeOH	3	0	0.5	0	—	—	—
a	t-BuOH	3	0	0.5	53	—	100	—
a	Et_2O	3	0	0.5	33	—	94	—
a	THF	0.5	0	15	0	—	—	—
a	DMF	0.5	0	15	0	—	—	—
e	MeOH	0.5	40	15	100	40	—	60
i	MeOH	3	40	15	100	100	—	—

[a] A solution of **3** (1 mmol) in the appropriate solvent containing TFA (3 ml) was allowed to react.



OMe group to give the quinol ether **10** in about 80% yield. Hydrogen peroxide thus liberated was detected by a color reaction with $K_2Cr_2O_7$ (Experimental).

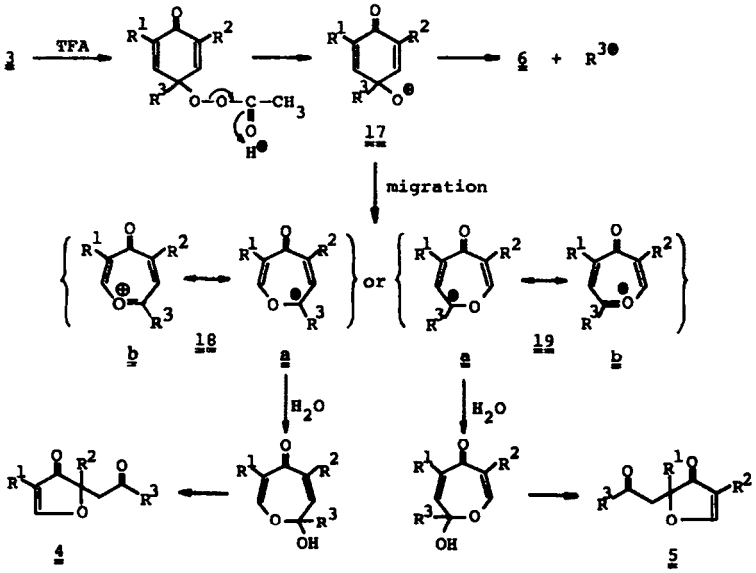
The naphthoquinol hydroperoxide **11**[10] revealed the same reaction pattern as **2f**: in CH_2Cl_2 with TFA *p*-quinone **13**, *o*-quinone **14**, and phenol **15** could be isolated. The corresponding t-butylperoxide **12** with TFA in CCl_4 formed the *o*-quinol trifluoroacetate **16** and *o*-quinone **14**. The acetate **16** was easily de-t-butylated and oxidised in the acidic medium to **14**.



DISCUSSION

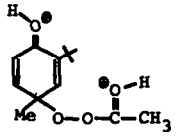
The formation of the 4-oxa-2-cyclopentenones **4** and **5** was reasonably interpreted in terms of the quinoxy cation intermediate **17** which resulted from the heterolysis of the peroxy bond by protonation:

Subsequent reactions of **17** depended on the nature of the substituent R^3. Alkyl substituents susceptible to β-scission resulted in the formation of **6** from **17**. Thus, **3d** and **3e** gave **6** quantitatively. With **3e** the resulting benzyl cation led to benzyl trifluoroacetate. The formation of **6** also resulted quantitatively



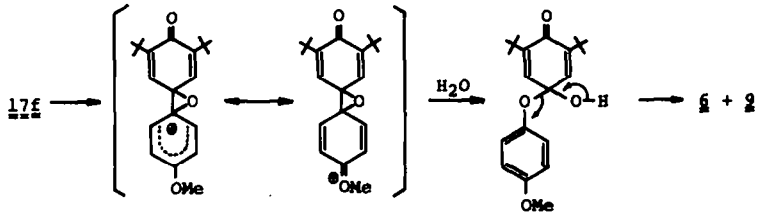
from **2d** by acid catalysis or by treatment with acetic anhydride in the presence of pyridine. The formation of **4** and **5** was realised by assuming the migration of the ring carbon to the cationic oxygen to give a ring expanded cation **18** or **19** (resonance structures **a** and **b**) followed by hydration during working-up, as depicted in the Scheme. The fact that **4** and **5** were formed in nearly equal amounts indicated that the migration of the ring carbon did not depend on the nature of the alkyl substituent on the dienone system. For **3b** and **3c** quinoxy cation **17** either resulted in loss of R^3 or ring carbon migration, as expected. When **3a** was dissolved in acetic anhydride containing sulfuric acid, an intense purple color appeared. This was probably due to the formation of a carbenium–oxonium system (**18** resp. **19**).

The unexpected stability of **3i** and **3j** towards acid catalysis may be rationalised by assuming a diprotonated species **20**, which could stabilise the peroxy bond. For **3a–d** the protonation at the CO group in the dienone system was hindered by the bulky t-Bu groups on both *ortho*-positions resulting in the protonation only at the peroxy group, which accelerated the heterolysis of the peroxy bond. The slow reaction of **3g** and **3h** was also interpreted in terms of the protonation ability of the dienone system. The less reactivity in ethers and alcohols was attributed to a lowering of the acidity of TFA.



20

The formation of **6** and **9** from **2f** was interpreted as migration of the aromatic substituent to the cationic oxygen of **17f** presumably *via* the intramolecular σ-complex **21** as depicted in the following Scheme:



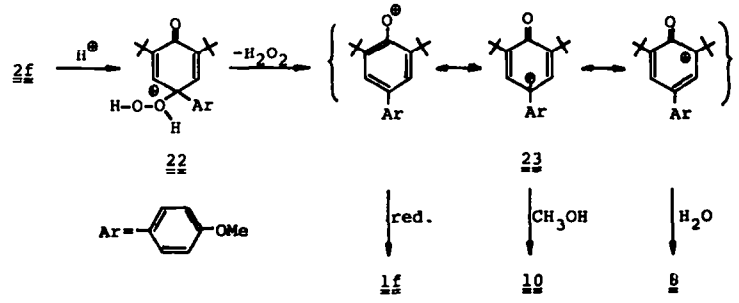
21

Protonation at the other O atom of the peroxy group in **2f** may also occur (**22**) to form the corresponding phenoxy cation (**23**) which would give **1f** after reduction. In methanol this phenoxy cation was trapped by the solvent: the quinol ether **10** could be isolated in 80% yield.

The formation of **8** by treating **2f** with TFA could be interpreted in terms of the hydration of the phenoxy cation **23** at the *ortho* position. The resulting *o*-quinol was susceptible to an acid-catalysed fragmentation of isobutene to give 3-t-butyl-5-(4-methoxyphenyl)-catechol, which could be further oxidised by a second phenoxy cation to **8** and **1f**.

Since the quinoxy cation **17f** led to the exclusive migration of R^3 giving the cation **21**, the behavior of hydroperoxide **11** towards acid catalysis was of great interest. Here, in principle, the 4-phenyl ring and/or the anellated t-butyl-phenyl ring could migrate to the quinoxy oxygen. In fact, only the phenyl ring migrated to form **13** and **15**. To a smaller extent, cleavage of the H_2O_2 group (analogous to **22** → **23**) also occurred to give *o*-naphthoquinone **14**. In the case of the peroxide **12** the last mentioned reaction occurred predominantly: **14** was formed in 69% yield. In water-free TFA, the reaction proceeded via direct addition of TFA to the intermediate naphthoxy cation (analogous to **23**) in the *o*-position. Such a reaction would give **16**, which, indeed, could be isolated in 23% yield besides **14**. The *o*-quinol ester **16** was very sensitive towards acid and was easily transformed into **14** upon addition of TFA in the air.

Thus, the acid-catalysed reaction of peroxy-*p*-quinols and their derivatives seemed to depend on the site of protonation, which was influenced by steric effects of the substituents present.



22 **23** **1f** **10** **8**

EXPERIMENTAL

M.ps are not corrected. Elemental analyses were performed by the Analytical Center of Kyoto University or the Analytical Laboratory of the Chemical Institutes of the University of Tübingen. IR spectra were recorded on a JASCO IRA-1 or Perkin-Elmer 221 spectrophotometer. PMR spectra were determined on a Varian T-60, A-60A, or EM-360 spectrometer with Me_4Si as an internal standard. Carbon-13 magnetic resonance spectra were obtained with a Bruker HFX-90 multi-nucleus spectrometer (22.63 MHz; spectrum width 6024 Hz, pulse width 3.5 μs).

4-Benzyl-2,6-di-t-butylphenol (**1e**). The phenol **1e** was prepared according to the method described by Rieker, *et al.*,[11] from 2,6-di-t-butyl-*p*-benzoquinone and benzyl magnesium chloride followed by the reduction of the resulting *p*-quinol derivative with Zn–HCl in EtOH, colorless prisms (petroleum ether), 55% yield from 2,6-di-t-butyl-*p*-benzoquinone. m.p. 59–61°; lit.[12] 60–61°. ^{1}HNMR ($CDCl_3$) δ 1.42 (s, 18H), 3.89 (s, 2H), 5.02 (s, 1H, OH), 6.98 (s, 2H), 7.15–7.30 (m, 5H). (Found: C, 84.86; H, 9.52. Calcd for $C_{21}H_{28}O$: C, 85.08; H, 9.52.)

2-t-Butyl-6-ethyl-4-methylphenol (**1g**).[13] A soln of 2-ethyl-4-methylphenol (0.1 mol), prepared from the reduction of 2-hydroxy-5-methylacetophenone with Zn—HCl in EtOH, phosphoric acid (80 ml), and P_2O_5 (10 g) in t-BuOH (94 ml) in a sealed bottle was kept at 50° for a week. The mixture was poured into ice-cooled water and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated. The resulting residue was distilled to give **1g** as colorless liquid (20 g, 100% yield); bp 85°/2 mm Hg. ^{1}HNMR ($CDCl_3$) δ 1.41 (s, 9H), 1.23 (t, 3H, J = 7.5 Hz), 2.25 (s, 3H), 2.53 (broad q, 2H, J = 7.5 Hz), 4.63 (s, 1H, OH), 6.88–7.03 (m, 1H), 7.07 (d, 1H, J = 2 Hz). (Found: C, 81.33; H, 10.73. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48.).

2-t-Butyl-4,6-dimethylphenol (**1h**).[14] The phenol **1h** was prepared as described above from 2,4-xylenol. Colorless liquid (90% yield); b.p. 77°/1 mm Hg. ^{1}HNMR ($CDCl_3$) δ 1.39 (s, 9H), 2.16 (broad s, 3H), 2.23 (broad s, 3H), 4.54 (s, 1H, OH), 6.85–7.00 (m, 1H), 7.00–7.15 (m, 1H). (Found: C, 81.02; H, 10.47. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18).

Hydroperoxides **2a–d**. These compounds were prepared by the base-catalysed oxygenation of **1a–d**, respectively, as reported previously.[1]

Hydroperoxides **2e, 2g–i**. These hydroperoxides were prepared according to the method involving oxidation of the corresponding phenols with sodium molybdate—H_2O_2 in MeOH described by Hayashi, *et al.*[15] All these hydroperoxides were purified by recrystallisation from petroleum ether. Spectral and analytical data are given below.

Compound **2e**: colorless needles (94% yield); m.p. 140–142°; IR (Nujol) 3400, 1670, 1630 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.16 (s, 18H), 2.98 (s, 2H), 6.54 (s, 2H), 6.8–7.4 (m, 5H), 7.79 (s, 1H, OOH). (Found: C, 76.55; H, 8.77. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59).

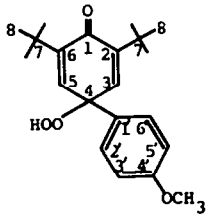
Compound **2g**: colorless prisms (88% yield); m.p. 88–90°; IR (Nujol) 3280, 1670, 1620 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.06 (t, 3H, J = 7.3 Hz), 1.24 (s, 9H), 1.37 (s, 3H), 2.32 (broad q, 2H, J = 7.3 Hz), 6.4–6.6 (m, 1H), 6.62 (d, 1H, J = 3 Hz), 7.79 (s, 1H, OOH). (Found: C, 69.86; H, 9.17. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99).

Compound **2h**: colorless prisms (92% yield); m.p. 78–80°; IR (Nujol) 3400, 1670, 1625 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.25 (s, 9H), 1.36 (s, 3H), 1.88 (broad s, 3H), 6.5–6.7 (m, 2H), 8.39 (s, 1H, OOH). (Found: C, 68.68; H, 8.78. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63).

Compound **2i**: colorless prisms (90% yield); m.p. 99–101°; IR (Nujol) 3300, 1660, 1620 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.24 (s, 9H), 2.38 (s, 3H), 6.15 (d, 1H, J = 10 Hz), 6.63 (d, 1H, J = 3 Hz), 6.79 (d, d, 1H, J = 10, J = 3 Hz), 8.52 (s, 1H, OOH). (Found: C, 67.28; H, 8.37. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22).

Compound **2j**: colorless needles; ^{1}HNMR ($CDCl_3$)[16] δ 0.9–3.2 (m, 8H), 6.10 (d, 1H, J = 2 Hz), 6.21 (d, d, 1H, J = 2, J = 9.5 Hz), 6.84 (d, 1H, J = 9.5 Hz), 10.10 (s, 1H, OOH).

2,6-Di-t-butyl-4-hydroperoxy-4-(4-methoxyphenyl)-2,5-cyclohexadienone (**2f**). Percarbamide (H_2O_2/urea adduct of Degussa AG) (9.4 g) was treated with absolute ether (200 ml) in a separatory funnel by rapid shaking for 10 min to extract H_2O_2 into the organic phase. The ether soln was filtered from unsoluble urea. To the filtrate 2,6-di-t-butyl-4-hydroxy-4-(4-methoxyphenyl)-2,5-cyclohexadienone[17] (3.28 g, 10 mmol) and conc H_2SO_4 (2 drops) were added. The mixture was then stirred at room temp for 18 hr and poured into $NaHCO_3$ aq. The ether phase was separated and the aqueous phase was extracted with ether several times. The combined organic phases were dried (Na_2SO_4) and evaporated *in vacuo* to dryness. Treatment of the residue with petroleum ether (60/90°) at about 0° furnished **2f** as colorless, wadding-like crystals (recrystallisation from petroleum ether): 2.71 g, 79% yield; m.p. 108–109° (dec). IR (KBr) 3460, 2930, 1658, 1635 cm^{-1}. ^{1}HNMR ($CDCl_3$) δ 1.28 (s, 18H), 3.80 (s, 3H), 6.77 (s, 2H), 6.75–7.5 (m, 4H), 7.89 (s, 1H, OOH). ^{13}C NMR ($CDCl_3$) δ 186.6 (C-1), 148.3 (C-2, 6), 138.8 (C-3, 5), 81.7 (C-4), 35.0 (C-7), 29.4 (C-8), 130.6 (C-1'), 127.2 (C-2', 6'), 114.3 (C-3', 5'), 159.7 (C-4'), 55.3 (OCH_3).



MS 344 (M^+), 327, 312, 311, 272, 271, 255 *m/e*. (Found: C, 73.09; H, 7.79. Calcd for $C_{21}H_{28}O_4$: C, 73.22; H, 8.19).

2,6-Di-t-butyl-4-hydroperoxy-1-oxo-4-phenyl-1,4-dihydronaphthalene (**11**) was prepared according to lit.[10]

Peroxy esters **3a–e, g–j**. The peroxy esters were prepared according to the described method.[1] A soln of acetyl chloride (1.73 g, 22 mmol) in dry pentane (15 ml) was added dropwise into a stirred soln of **2** (20 mmol) in dry pentane (40 ml) containing pyridine (1.78 ml, 22 mmol) at 0° in 30 min. The mixture was stirred at 0° for 1 hr, then warmed at 40° for 10 min. The resulting ppt of pyridine hydrochloride was filtered off through a celite layer (7 cm) and washed with pentane and ether. The combined organic solns were evaporated to give **3** in quantitative yield. The crystalline products were purified by recrystallisation from petroleum ether, otherwise the products were used for the acid-catalysed reaction without further purification. Analytical and spectral data for **3** are given below. For **3a–d** the physical data are available in a previous paper.[1]

Compound **3e**: colorless prisms; m.p. 99–101°; IR (Nujol) 1785, 1675, 1640 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.14 (s, 18H), 1.94 (s, 3H), 3.08 (s, 2H), 6.51 (s, 2H), 6.8–7.3 (m, 5H). (Found: C, 74.55; H, 8.44. Calcd for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16).

Compound **3g**: colorless liquid; IR (Film) 1790, 1675, 1645 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.07 (t, 3H, J = 7.5 Hz), 1.25 (s, 9H), 1.49 (s, 3H), 1.94 (s, 3H), 2.34 (broad q, J = 7.5 Hz), 6.35–6.55 (m, 1H), 7.57 (d, 1H, J = 3 Hz).

Compound **3h**: colorless liquid; IR (Film) 1785, 1670, 1640 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.24 (s, 9H), 1.47 (s, 3H), 1.90 (broad s, 3H), 1.94 (s, 3H), 6.4–6.6 (m, 2H).

Compound **3i**: colorless prisms; m.p. 41–42°; IR (Nujol) 1790, 1670, 1640 cm^{-1}; ^1HNMR ($CDCl_3$) δ 1.24 (s, 9H), 1.50 (s, 3H), 1.94 (s, 3H), 6.11 (d, 1H, J = 9.5 Hz), 6.59 (d, 1H, J = 3 Hz), 7.73 (d, d, 1H, J = 9.5, J = 3 Hz). Found: C, 65.55; H, 7.70. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61).

Compound **3j**: colorless liquid; IR (Film) 1785, 1665, 1635 cm^{-1}; ^1HNMR ($CDCl_3$) δ 1.0–3.0 (m, 8H), 1.93 (s, 3H), 6.17 (d, 1H, J = 2 Hz), 6.23 (d, d, 1H, J = 10, J = 2 Hz), 6.78 (d, 1H, J = 10 Hz).

2,6-Di-t-butyl-4-t-butylperoxy-1-oxo-4-phenyl-1,4-dihydronaphthalene (**12**). 2,6-Di-t-butyl-4-phenyl-1-naphthol[10] (500 mg, 1.5 mmol) and cerium(IV) oxide[18] (350 mg) were stirred under reflux for 4 days in a mixture of t-BuOH (10 ml) and t-butyl-hydroperoxide (10 ml). The cerium(IV) oxide was filtered off, the filtrate evaporated *in vacuo*. The residue was treated with ether and the ethereal extract washed with NaCl aq and water. After drying (Na_2SO_4) the solvent was evaporated and the residue separated by preparative layer chromatography (silica gel, Macherey and Nagel P/UV 254+366; petroleum ether/ether/acetone 7:1:0.25 to give two compounds:

(1) 450 mg (71.5%) **12**; colorless crystals (from petroleum ether), m.p. 87–88°. IR (KBr) 2960, 1656, 1608 cm^{-1}; ^1HNMR (CCl_4) δ 1.21 (s, 9H), 1.26 (s, 9H), 1.28 (s, 9H), 6.81 (s, 1H), 7.1–8.2 (m, 8H); MS M^+, not observable, 348, 332, 275 *m/e*. (Found: C, 79.74; H, 8.73. Calcd for $C_{28}H_{36}O_3$: C, 79.96; H, 8.63).

(2) 120 mg (19%) 2,6-Di-t-butyl-2-t-butylperoxy-1-oxo-4-phenyl-1,2-dihydronaphthalene; decomposable oil. IR (CCl_4) 2950, 1690, 1660, 1595 cm^{-1}; ^1HNMR (CCl_4) δ 1.03 (s, 9H), 1.24 (s, 18H), 6.20 (s, 1H), 7.0–8.1 (m, 8H); MS, M^+, not observable, 348, 347, 331, 291 *m/e*.

Acid treatment of peroxy esters **3**. A soln of **3** (3 mmol) in CH_2Cl_2 (1 ml) was added dropwise in 30 s into TFA (3 ml) at 0°. The mixture was stirred at 0° for 30 min. In the case of **3g** and **3h**, the reaction was carried out at 20° for 10 h. The resulting mixture was then poured into ice-cooled water (50 ml) and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to give an oily residue. The product from **3a** was crystallised from petroleum ether and that from **3d** crystallised on standing. The oily residue from **3b**, **3c** and **3h** was chromatographed on tlc plates developing with CH_2Cl_2 and that from **3e** with a mixture of petroleum ether and CH_2Cl_2 (2:1). The products from **3g** were similarly separated developing with a mixture of petroleum ether and CH_2Cl_2 (1:2) three times. The quinone **6** obtained was identical with an authentic sample (tlc, IR, and NMR). Spectral and analytical data for **4** and **5** are given below.

Compound **4a**: 100% yield, colorless prisms (petroleum ether); m.p. 68–70°; IR (Nujol) 3100, 1730, 1690 cm^{-1}; ^1HNMR ($CDCl_3$) δ 0.96 (s, 9H), 1.21 (s, 9H), 2.06 (s, 3H), 2.97 (s, 2H), 7.71 (s, 1H). (Found: C, 71.21, H, 9.58. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59).

Compound **4b**: 78% yield, colorless prisms (petroleum ether); m.p. 58–60°; IR (Nujol) 3100, 1710, 1685 cm^{-1}; ^1HNMR ($CDCl_3$) δ 0.95 (t, 3H, J = 7 Hz), 0.97 (s, 9H), 1.22 (s, 9H), 2.40 (q, 2H, J = 7 Hz), 2.98 (s, 2H), 7.72 (s, 1H). (Found: C, 71.93; H, 9.55. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84).

Compound **4c**: 53% yield, colorless prisms (petroleum ether); m.p. 65–66°; IR (Nujol) 3115, 1715, 1685 cm^{-1}; ^1HNMR ($CDCl_3$) (at 31°C) δ 0.96 (s, 9H), 1.02 (d, 3H, J = 7 Hz), 1.04 (d, 3H, J = 7 Hz), 1.21 (s, 9H), 2.54 (sep, 1H, J = 7 Hz), 2.99 (d, 1H, J = 15 Hz), 3.04 (d, 1H, J = 15 Hz), 7.77 (s, 1H). (Found: C, 72.78; H, 10.17. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.07).

Compound **4g**: 31% yield, colorless liquid; b.p. 93°/2 mm Hg; IR (Nujol) 3090, 1725, 1695 cm^{-1}; ^1HNMR ($CDCl_3$) δ 0.78 (t, 3H, J = 7 Hz), 1.24 (s, 9H), 1.76 (q, 2H, J = 7 Hz), 2.10 (s, 3H), 2.86 (s, 2H), 7.77 (s, 1H). (Found: C, 69.63; H, 9.16. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99).

Compound **5g**: 47% yield, colorless prisms (petroleum ether); m.p. 52–54°; IR (Nujol) 3090, 1725, 1690 cm^{-1}; ^1HNMR ($CDCl_3$) δ 0.99 (s, 9H), 1.11 (t, 3H, J = 7.5 Hz), 2.10 (s, 3H), 2.18 (d, q, 2H, J = 0.8, J = 7.5 Hz), 3.03 (s, 2H), 7.79 (t, 1H, J = 0.8 Hz). (Found: C, 69.36; H, 8.52. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99).

Compound **4h**: 36% yield, colorless liquid; b.p. 84°/1.5 mm Hg; IR (Nujol) 3080, 1725, 1690 cm^{-1}; ^1HNMR ($CDCl_3$) δ 1.23 (s, 9H), 1.32 (s, 3H), 2.09 (s, 3H), 2.86 (s, 2H), 7.75 (s, 1H). (Found: C, 68.26; H, 8.63. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63).

Compound **5h**: 44% yield, colorless prisms (petroleum ether); m.p. 106–108°; IR (Nujol) 1725, 1685 cm^{-1}; ^1HNMR ($CDCl_3$) δ 0.99 (s, 9H), 1.71 (d, 3H, J = 1.3 Hz), 2.09 (s, 3H), 3.04 (s, 2H), 7.84 (q, 1H, J = 1.3 Hz). (Found: C, 68.31; H, 8.78. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63).

Reduction of **4a** *with* $NaBH_4$. To a stirred soln of $NaBH_4$ (0.17 g, 4.5 mmol) in MeOH (4 ml) was added a soln of **4a** (0.505 g, 2 mmol) in MeOH (5 ml) at 0°. The mixture was stirred at room temp for 30 min. A tlc analysis of the mixture showed the completion of the reaction with the formation of two products. The mixture was then poured into an ice-cooled NH_4Cl aq and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to leave a solid residue, whose ^1HNMR showed the quantitative formation of a mixture of alcohols **7** and **7'**. Both products were separated by silica gel chromatography on a tlc plate eluting with CH_2Cl_2 and crystallised from petroleum ether.

Compounds **7** (or **7'**): 63% yield, colorless needles; m.p. 78–81°; IR (Nujol) 3440, 3080, 1675, 1600 cm^{-1}; ^1HNMR ($CDCl_3$) δ 0.96 (s, 9H), 1.12 (d, 3H, J = 3 Hz), 1.23 (s, 9H), 2.07 (d, 2H, J = 2.8 Hz), 2.18 (s, 1H, OH), 3.46–3.74 (m, 1H), 7.98 (s, 1H).

Compounds **7'** (or **7**): 37% yield, colorless prisms; m.p. 130–132°; IR (Nujol) 3400, 3080, 1675, 1600 cm^{-1}; ^1HNMR ($CDCl_3$) δ 0.96 (s, 9H), 1.17 (d, 3H, J = 3 Hz), 1.21 (s, 9H), 1.58 (s, 1H, OH), 2.02 (d, 2H, J = 2.8 Hz), 3.55–3.82 (m, 1H), 7.93 (s, 1H); UV (EtOH) λ_{max} 268 (log ε = 3.81)nm. (Found: C, 70.61; H, 10.30. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30).

Oxidation of a mixture of **7** *and* **7'**. To a soln of a 1:1 mixture of **7** and **7'** (0.1 g) was added a soln of CrO_3 (0.1 g) in water (0.3 ml) containing one drop of conc H_2SO_4 at 0°. The mixture was allowed to stand at room temp overnight. The tlc analysis of the mixture showed the formation of only **4a**. The mixture was then diluted with water and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to give **4a** (99 mg, 100% yield), which was identical with an authentic sample.

Benzyl trifluoroacetate. To a soln of benzyl alcohol (0.114 g, 1 mmol) and dicyclohexylcarbodiimide (0.413 g, 3 mmol) in CH_2Cl_2 (1 ml) was added TFA (1 mmol) at 0° and the mixture was allowed to stand at 30° for 1 hr. The ppt of dicyclohexylurea was filtered off through a celite layer and the filtrate was evaporated to give benzyl trifluoroacetate as colorless liquid in nearly quantitative yield. IR (Film) 1790 cm^{-1}; ^1HNMR ($CDCl_3$) δ 5.22 (s, 2H), 7.32 (s, 5H).

Acid treatment of **2i**. (a) Hydroperoxide **2i** (500 mg, 1.45 mmol) in absolute ether (100 ml) was stirred at room temp for 12 hr after a 54% soln of HBF_4 in ether (5 drops) had been added. The mixture was poured into $NaHCO_3$ aq for neutralisation. The phases were separated; the aqueous layer was extracted several times with ether. After drying of the combined organic phases (Na_2SO_4), the solvent was completely evaporated *in vacuo*. The residue was chromatographed on silica gel

(Macherey and Nagel, 60) with CH_2Cl_2 to give 3 products: (1) **1f**[11]: 40 mg (9% yield); (2) **6**: 290 mg (91% yield); (3) **9**: 120 mg (67% yield). These compounds were identified by NMR (comparison with authentic samples).

(b) Hydroperoxide **2f** (500 mg, 1.45 mmol) was dissolved in abs MeOH (200 ml). After addition of a 54% soln of HBF_4 in ether (5 drops) the soln was stirred at room temp for 4 hr. The mixture was neutralised by stirring for 1 hr with a small amount of water-free Na_2CO_3. The MeOH was evaporated almost completely *in vacuo* and the residue treated with ether. The insoluble material was filtered off and the soln—after concentration—was again treated with MeOH. On cooling colorless crystals precipitated. Further material was obtained by preparative layer chromatrography (silica gel; Macherey and Nagel, P/UV 254+366; petroleum ether/CH_2Cl_2, 2:1) of the mother liquor: 400 mg (81% yield) **10**, identified by comparison with an authentic sample[19] (IR, NMR).

(c) Detection of H_2O_2. $K_2Cr_2O_7$ (20 mg) in water (5 ml) was treated with conc H_2SO_4 (5 drops) and covered with a layer of ether (1 ml). To this reagent a few drops of a soln of **2f** (50 mg) in abs MeOH (1 ml)/conc H_2SO_4 (1 drop) was added. The ether phase immediately attained a deep-blue color (CrO_5). If **2f** was directly added to the reagent (blank test), no color occurred.

Acid treatment of **11**. (a) Hydroperoxide **11** (180 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (0.6 ml) and treated with TFA (0.1 ml) at 10° for 10 days. Phenol **15** was separated from the mixture after extraction with NaOH aq: 10 mg (22% yield). Its identity was proved by transformation into 2,4,6-tribromophenol. The organic layer was evaporated to dryness and separated by preparative layer chromatography (silica gel, Macherey and Nagel, P/UV 254, 366; petroleum ether/ether/acetone 7:1:0.25): 100 mg (75% yield) **13**; 10 mg (8% yield) **14**. The IR spectrum of **13** and **14** were identical with those of authentic samples.[10,20]

(b) Hydroperoxide **11** (90 mg, 0.025 mmol) was stirred with TFA (5 drops) in benzene (5 ml) at 25° for 24 hr. By column chromatography (silica gel, Macherey and Nagel 60), petroleum ether/ether/acetone 7:1:0.25) 50 mg (75% yield) of quinone **13** were isolated.

Acid treatment of **12**. Peroxide **12** (210 mg, 0.5 mmol) was dissolved in CCl_4 or abs ether (2 ml) and treated with TFA (20 drops) at room temp for 48 hr. The mixture was separated by preparative layer chromatography (silica gel, Macherey and Nagel, P/UV 254+366; petroleum ether/ether/acetone 7:1:0.25) to give:

(1) 50 mg (23% yield) of **16**, which decomposed and could not be obtained in crystalline form. IR (CCl_4) 2920, 2850, 1792, 1695, 1665, 1597 cm^{-1}. ^{1}HNMR (CCl_4) δ 1.10 (s, 9H), 1.30 (s, 9H), 5.98 (s, 1H), 7.2–8.1 (m, 8H). MS 444 (M^+) *m/e*.

(2) 100 mg (69% yield) **14**.

Acknowledgement—Support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education and by the Fonds der Chemischen Industrie is greatly acknowledged.

REFERENCES AND NOTES

[1]Part I. A. Nishinaga, K. Nakamura, K. Yoshida, and T. Matsuura, Chem. Lett., 303 (1977). Part II. A. Nishinaga, K. Nakamura, and T. Matsuura, *Tetrahedron Letters* 3557 (1978).

[2]Preliminary communication: A. Nishinaga, K. Nakamura, T. Matsuura, A. Rieker, and D. Koch, *Ibid.* 3597 (1978).

[3]A. Nishinaga, T. Itahara, T. Matsuura, S. Berger, G. Henes, and A. Rieker, *Chem. Ber.* **109**, 1530 (1976).

[4]A. Nishinaga, K. Nishizawa, H. Tomita, and T. Matsuura, *Synthesis* 270 (1977).

[5]A. Nishinaga, T. Itahara, T. Matsuura, A. Rieker, and D. Koch, *Angew. Chem.* **88**, 154 (1976); Int. Ed. Engl., **15**, 160 (1976).

[6]A. Nishinaga, T. Itahara, T. Matsuura, A. Rieker, D. Koch, K. Albert, and P. B. Hitchcock, *J. Am. Chem. Soc.* **100**, 1826 (1978).

[7]A. Nishinaga and A. Rieker, *Ibid.* **98**, 4667 (1976).

[8]A. Nishinaga, T. Itahara, M. Hibi, and T. Matsuura, *Synthesis* 533 (1976).

[9]A. Nishinaga, T. Itahara, and T. Matsuura, *Ibid.* 604 (1976).

[10]R. Griesshammer, H.-P. Schneider, W. Winter and A. Rieker, *Tetrahedron Letters*, in press.

[11]A. Rieker and K. Scheffler, *Liebigs Ann.* **689**, 78 (1965).

[12]G. H. Stillson and D. W. Sawyer, *U.S. Patent*, 2, 248, 831 (1941); *Chem. Abstr.* **35**, 7176 (1941).

[13]See, e.g. B. Miller and H. Margulies, *J. Org. Chem.* **30**, 3895 (1965).

[14]See, e.g. *Beilsteins Handbuch der Organischen Chemie*, 4th Edition, Suppl. 3, Vol. VI, 3, p. 2020, Springer Verlag Berlin, Heidelberg, New York (1966).

[15]Y. Hayashi, S. Shioi, M. Togami, and T. Sakan, *Chem. Lett.* 651 (1973).

[16]The ^{1}HNMR data are in agreement with those for **2j** obtained by Hayashi *et al.*,[15] private communication.

[17]A. Rieker and S. Berger, *Org. Magn. Reson.* **4**, 857 (1972).

[18]Analogous to: D. H. R. Barton, P. D. Magnus, and J. C. Quinney, *J. Chem. Soc.* Perkin I, 1610 (1975).

[19]J. Bracht, Dissertation, Univ. Tübingen 1977.

[20]H. M. Crawford, *J. Am. Chem. Soc.* **36**, 3533 (1971).