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Unusual Inhibition Effect of 1-(1-Naphthyl)-1-methylethylhydroperoxide on the Liquid-Phase Oxidation of Isopropylarenes. GC−MS and Theoretical Studies of the Thermal Decomposition of 1-Naphthyl- and 1-Anthryl-1-methylethylhydroperoxides

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Abstract:

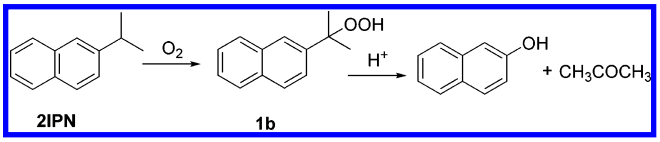
All five possible 1-aryl-1methylethylhydroperoxides derived from naphthalene and anthracene were synthesized and their thermal decomposition in GC−MS conditions was investigated to explain the unusual inhibition effect of 1-(1-naphthyl)-1-methylethylhydroperoxide on the liquid-phase oxidation of isopropylarenes. 2-(1-Aryloxy)propenes were identified as the main decomposition products of 1-(1-naphthyl)-1-methylethylhydroperoxide and 1-(1-anthryl)-1-methylethylhydroperoxide. The relatively unstable 2-aryloxypropenes have thus far never been described as thermal decomposition products of 1-aryl-1-methylethylhydroperoxides. The plausible mechanism of the formation of 2-(1-aryloxy)propenes was proposed on the basis of AM-1 calculations of the possible rearrangement paths of the alkoxy radicals derived from the investigated hydroperoxides. The mechanism explains the inhibition effect of 1-(1-naphthyl)-1-methylethylhydroperoxide on the oxidation of isopropylarenes.

Introduction

The method of 2-naphthol synthesis from 2-isopropylnaphthalene (2IPN) (Scheme 1), analogous to that used to produce phenol from cumene (Hock's process),[1−6] in comparison to the conventional fusion method, is environmentally friendly and offers the advantage of consuming less energy and producing acetone as coproduct.

Free-radical oxidation of 2IPN with oxygen to 1-(2-naphthyl)-1-methylethylhydroperoxide **1b** is a key stage of this synthesis. The technical 2IPN used in oxidation process as a raw material is contaminated by a small amount (5−10%) of 1-isopropylnaphthalene (1IPN), which is difficult to remove. The 1IPN present in the raw material, after oxidation to 1-(1-naphthyl)-1-methylethylhydroperoxide **1a**, reduces the reaction rate and results in a lower yield and poorer selectivity in the production of hydroperoxide **1b**.

Scheme 1. **2-Naphthol synthesis by Hock's method**



The reported data on oxidation of 1IPN are controversial. Some investigators claim that 1IPN fails to undergo oxidation with oxygen,[7,8] whereas others maintain that it undergoes oxidation but at a rate about 5−10 times lower than that of the oxidation of 2IPN.[9,10]

Our kinetic measurements of the rates of oxidation of 1IPN and 2IPN in the presence of 2,2′-azo-bis-isobutyrylnitrile and 1,1′-azo-bis-(1-cyclohexanecarbonitrile) as initiators at 75, 100, and 110 °C showed that 1IPN undergoes free-radical oxidation with oxygen, but the reaction rate was 10−12 times lower than that of 2IPN. On the other hand, long-duration trials of oxidizing 1IPN with oxygen were a complete failure.[11]

Free-radical chain oxidation of hydrocarbons is well-known to be affected by the resulting hydroperoxides. As a result of the thermal decomposition of hydroperoxides into free radicals, the process becomes autocatalytic in its nature. We have demonstrated that hydroperoxide **1b** really acts as an initiator of free-radical oxidation of isopropylarenes. We have also shown that, in contradistinction to **1b**, hydroperoxide **1a** inhibits the free-radical oxidation of isopropylarenes with oxygen.[11]

The inhibition effect of hydroperoxide **1a** on the oxidation of isopropylarenes and the low oxidizability of 1IPN are

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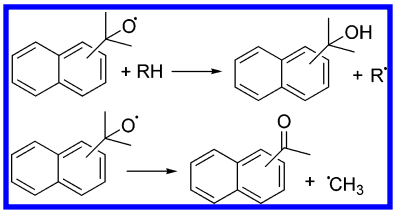
Scheme 2. **Typical reaction of 1-methyl-1-naphthylethyloxy radical**



untypical for isopropylarenes and the corresponding hydroperoxides. To find out the reasons of essential differences in the chemical behaviour of hydroperoxides **1a** and **1b**, their thermal stabilities as well as products of their decomposition were compared.

The differential scanning calorimetry experiments showed that their thermal stabilities are similar; the temperatures of maximum rates of decomposition (T_{max}) of the **1a** and **1b** are close to each other (197.5 and 193.6 °C, respectively).[11] On the other hand, the composition of products of the thermal decomposition of hydroperoxides **1a** and **1b** in liquid phase (120 °C, 30 h, cumene solution, analysis by HPLC) exhibits essential differences: hydroperoxide **1b** undergoes decomposition to 2-(2-naphthyl)-2-propanol (78%) and 2-acetylnaphthalene (22%), whereas **1a** decomposes to the corresponding alcohol and ketone in yields of only 44 and 6%, respectively (Scheme 2), the other part of hydroperoxide **1a** (about 50%) being converted to an unidentified dark tarry substance.[11] We assume that the tarry substance is probably formed as the result of the polymerization of some primary product of decomposition of hydroperoxide **1a**.

This result suggests that alkoxy radicals formed by thermal decomposition of **1a** also entered into reactions other than the well-known reactions: hydrogen abstraction and β-scission (Scheme 2). We also assume, that the other products can affect disadvantageously the course of free-radical oxidation process.

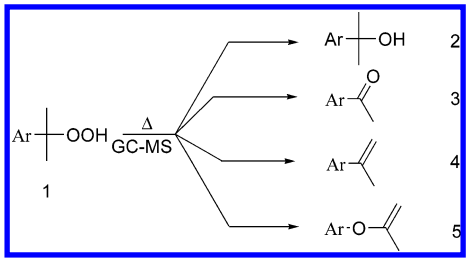
To get a more clear picture of the thermal decomposition of hydroperoxides **1a** and **1b** and to avoid consecutive transformations of primary decomposition products we decided to investigate the thermal decomposition of these hydroperoxides in GC−MS conditions. To acquire more information on the dependence between the structure and properties of hydroperoxides, we extended our investigations on 1-(1-anthryl)-, 1-(2-anthryl)-, and 1-(9-anthryl)-1-methylethylhydroperoxides (**1c**, **1d**, and **1e**, respectively). We also carried out semiempirical calculations of a few possible rearrangement paths of the corresponding alkoxy radicals.

Results and Discussion

The results of the thermal decomposition of hydroperoxides in GC−MS conditions have been gathered in Table 1.

The following three kinds of common products of thermal decomposition of 1-aryl-1-methylethylhydroperoxides were detected by means of the GC−MS method: 2-aryl-2-propanols **2**, acetylarenes **3**, and 2-arylpropenes **4**. They were identified by comparing their MS spectra with the spectra of synthesized authentic samples of the corresponding compounds.

Table 1. **Thermal decomposition of hydroperoxides in GC−MS conditions**



Ar	hydroperoxides **1a−e**	yield of decomposition products [%][a] alcohol **2a−e**	ketone **3a−e**	alkene **4a−e**	aryloxypropene **5a−e**
1-naphthyl	**1a**	23.5	19.7	9.2	45.6
2-naphthyl	**1b**	39.0	40.0	21.0	-
1-anthryl	**1c**	18.8	-	-	81.2
2-anthryl	**1d**	77.7	-	13.5	-
9-anthryl	**1e**	-	18.3	79.7	2.0

[a] Estimated from the area of the corresponding signals on GC.

In the case of hydroperoxide **1a** we also detected some unidentified compound with a plausible molecular ion at *m*/*z* 184 as the main product (Tables 1 and 2). We suspected that the unidentified compound might be 2-(1-naphthyloxy)-propene **5a**. To verify this hypothesis we obtained this compound by means of an independent synthesis (Scheme 3), and we stated that the MS spectrum of the synthesized sample of aryloxypropene **5a** was identical with the spectrum of the decomposition product (Table 2).

A large amount of analogous 2-(1-anthryloxy)propene **5c** we also identified as the main product of the thermal decomposition of hydroperoxide **1c**; a small amount of analogous compound was also detected in the decomposition products of hydroperoxide **1e**. 2-Anthryloxypropenes **5c** and **5e** were identified by comparing their MS spectra with the spectrum of 2-(1-naphthyloxy)propene **5a**; the spectra of anthracene derivatives were very similar to the spectrum of **5a**; the masses of all the prominent ions, however, were higher by 50 Da, which corresponds exactly to the difference between the molecular mass of anthracene and naphthalene derivatives (Table 2).

It should be stressed, that, according to our best knowledge, relatively unstable 2-aryloxypropenes **5** have thus far not been described as thermal decomposition products of 1-aryl-1-methylethylhydroperoxides.

To find out the reasons for the essential differences in the chemical behaviour of hydroperoxides **1a** and **1b**, we carried out semiempirical AM-1 calculations of possible rearrangement paths of alkoxy radicals derived from **1a** and **1b**.[12] In this paper we extended such calculations for alkoxy radicals derived from hydroperoxides **1c**, **1d**, and **1e** (Table 3, Scheme 4).

Considering several possible rearrangement paths of alkoxy radicals which may lead to 2-aryloxypropanes **5**, we noticed that in the case of the 1-(1-naphthyl)-1-methylethoxy radical the most energetically favoured transformation, with

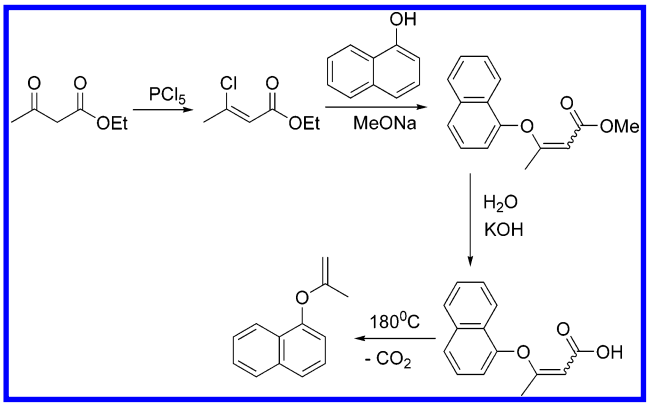
(12) Fiedorow, P.; Koroniak, H.; Mazurkiewicz, R.; Zawadiak, J.; Orlińska, B.; Stec, Z.; Grymel, M. *Cent. Eur. J. Chem.* **2006**. In press.

Table 2. **Prominent peaks in the GC−MS spectra of 2-aryloxypropenes (EI, 70 eV)**

	$M^{+\bullet}$	$[M-C_3H_4]^{+\bullet}$	$[M-C_3H_4-CO]^{+\bullet}$	$[M-C_3H_5-CO]^{+}$	$[M-C_3H_5-CO-C_2H_2]^{+}$	other peaks of relative abundance >10%
5a[a]	184 (40.1%)	144 (60.3%)	116 (82.9%)	115 (100%)	89 (26.5%)	169 (24.5%); 141 (29.2%); 63 (20.2%)
5a[b]	184 (33.6%)	144 (63.9%)	116 (47.9%)	115 (100%)	89 (22.9%)	169 (10.0%); 141 (25.0%); 63 (22.9%)
5c[a]	234 (34.4%)	194 (40.9%)	166 (35.2%)	165 (100%)	139 (19.3%)	219 (10.2%); 205 (29.1%); 191 (56.1%); 138 (19.3%); 114 (22.5%); 87 (18.0%); 75 (33.2%); 62 (36.1%);
5e[a]	234 (60.9%)	194 (95.1%)	166 (13.0%)	165 (100%)	139 (18.4%)	218 (10.8%); 203 (11.7%); 115(13.4%)

[a] Product of decomposition of the corresponding hydroperoxide. [b] The synthesized sample.

Scheme 3. **Synthesis of 2-(1-naphthyloxy)propene 5a**



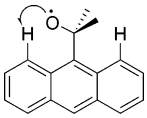
an energy barrier of only 75 kJ/mol, consists of the abstraction of hydrogen from the *peri* position of the naphthyl group.[12] A similar abstraction of hydrogen from *ortho* positions in the cases of both the 1-(1-naphthyl)- and 1-(2-naphthyl)-1-methylethoxy radicals is much more difficult (energy barrier 130.7−138.2 kJ/mol). Very similar results have been obtained for analogous alkoxy radicals with 1-anthryl and 2-anthryl substituents; also in this case the abstraction of hydrogen from the *peri* position of the neighbouring ring is strongly favoured (energy barrier only 54.9 kJ/mol compared with 112.3−126.8 kJ/mol for the abstraction of hydrogen from *ortho* positions). This kind of abstraction, involving the six-membered transition state, seems to be generally more favourable compared with the analogous transformation involving the five-membered transition state. Similar transformations of alkoxy radicals by hydrogen abstraction involving the six-membered transition state are known in the literature.[13]

Unfortunately, we were not able to find a stable structure with all positive normal modes for the alkoxy radical derived from hydroperoxide **1e**.

Assuming that the first stage of the hydroperoxide **1a** rearrangement consists of the abstraction of hydrogen from the *peri* position of the corresponding alkoxy radical, two plausible pathways of its transformation to 2-(1-naphthyloxy)propene can be formulated as presented at Scheme 5.

The first pathway involves a 1,2-aryl migration from carbon to oxygen via a three-membered oxirane-like intermediate as the key step. This kind of rearrangement of alkoxy radicals is well-known in free-radical chemistry.[14] The second pathway involves formation of a naphthofurane derivative as an intermediate followed by its rearrangement to 2-(1-naphthyloxy)propene **5a**.

Both discussed pathways account for the formation of 2-(1-aryloxy)propenes **5** and 2-aryl-2-propanols **2** as the main products of the decomposition of hydroperoxides **1a** and **1c** in GC−MS conditions. The formation of only trace amounts of 2-(9-aryloxy)propene **5e** from hydroperoxide **1e** can be explained by assuming the following two reasons: (i) already in the course of the synthesis and purification of **1e** we observed its proclivity to decompose to 2-(9-anthryl)propene **4e**, probably caused by a steric hindrance around the 2-hydroperoxypropyl group, and (ii) formation of a planar six-membered transition state for abstraction of hydrogen from the *peri* position is, in the case of **1e**, probably difficult because of the steric interaction between two methyl groups and the hydrogen atom at the second *peri* position.



In case of the thermal decomposition of hydroperoxide **1a** carried out in liquid phase (in cumene as a solvent) 2-aryloxypropene **5a** was also detected. A small amount of **5a** was isolated by preparative thin-layer chromatography. It suggests that, in the liquid phase as well as under GC−MS conditions, the thermal decomposition products of 1-aryl-1-methylethylhydroperoxides contain 2-aryloxypropenes. However, when decomposition is carried out in liquid phase, 2-aryloxypropene probably undergoes radical polimerization or hydrolysis, and therefore, its detection is difficult.

The inhibition effect of hydroperoxide **1a** in the oxidation of isopropylarenes may consist in terminating a free-radical chain as a result of catching the $RO^{\bullet}$ radicals in the intermolecular hydrogen abstraction reaction (Scheme 5). The inhibition effect of hydroperoxide **1a** may also be a result of hydrolysis of 2-(1-naphthyloxy)propene **5a** to 1-naphthol by trace amount of water. 1-Naphthol is a well-known

(13) Walling, Ch.; Padwa, A. *J. Am. Chem. Soc.* **1961**, *83*, 2207.

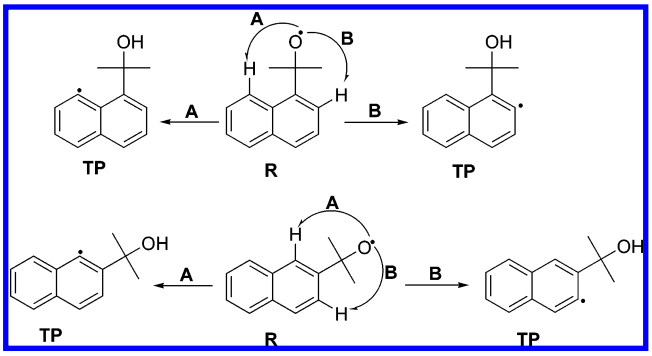
(14) Studer, A.; Bossart, M. *Tetrahedron* **2001**, *57*, 9667.

Table 3. **Hydrogen abstraction from *ortho* and *peri* positions of alkoxy radicals derived from 1-aryl-1-methylethylhydroperoxides (heat of formation of species in kJ/mol; AM1, RHF for openshell system)**

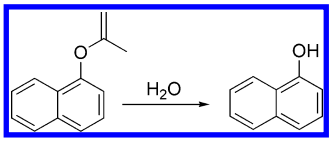
derivative	1-naphthyl[12]		2-naphthyl[12]		1-anthryl		2-anthryl	
position of hydrogen abstraction	peri	ortho	ortho	ortho	peri	ortho	ortho	ortho
and reaction path	(A)	(B)	(A)	(B)	(A)[a]	(B)[a]	(A)[a]	(B)[a]
substrate (**R**)	198.6	198.6	189.4	189.4	312.7	312.7	295.2	295.2
transition state	273.6	330.6	327.6	320.1	367.6	425.0	422.0	411.6
transition product (**TP**)	178.5	183.1	171.0	169.3	279.7	278.0	263.3	263.3

[a] The reaction path analogous to the corresponding reaction path for naphthyl derivatives (cf Scheme 4).

Scheme 4. **Hydrogen abstraction from *ortho* and *peri* positions of alkoxy radicals derived from 1-naphthyl-1-methylethylhydroperoxides**



inhibitor of free-radical oxidation processes. We have isolated a small amount of 1-naphthol from the decomposition product of hydroperoxide **1a** in liquid phase by extraction with NaOH.



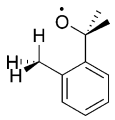
Conclusions

The unusual inhibition effect of hydroperoxide **1a** on the free-radical chain oxidation of isopropylarenes was elucidated. The results described above strongly suggest that the disadvantageous effect may consist of the following: (i) termination of a free-radical chain as a result of the recombination of radicals, which is necessary for the formation of 2-(1-naphthyloxy)propene **5a** and (ii) hydrolysis of **5a** to 1-naphthol. The explanation of the inhibition mechanism may be essential, in case of starting the production of 2-naphthol from technical 2IPN contaminated by 1IPN.

Other 1-aryl-1-methylethylhydroperoxides having the hydrogen atom at the *peri* position to the substituent at the 1-position, e.g., 1-(1-anthryl)-1-methylethylhydroperoxide, may also exhibit inhibition properties.

It was also demonstrated that GC−MS is a valuable method for investigations of the thermal decomposition of hydroperoxides. GC−MS allows observation of the formation of relatively unstable 2-(1-aryloxy)propenes as the primary products of the thermal decomposition of some 1-aryl-1-methylethylhydroperoxides. 2-Aryloxypropenes are formed as the main products from the corresponding hydroperoxides with hydrogen at the *peri* position in relation to the 2-hydroperoxypropyl group, excluding **1e**.

It seems, that the described low oxidizability of *o*-methylisopropylarenes, e.g., *o*-cymene,[15] can be explained in a similar way. Also in this case, one of the hydrogens of the methyl group can be transferred to the oxygen of the alkoxy radical via a six-membered transition state. A verification of this hypothesis requires, however, further investigations. The explanation of this may be very important for production of cresols by the cumene method.



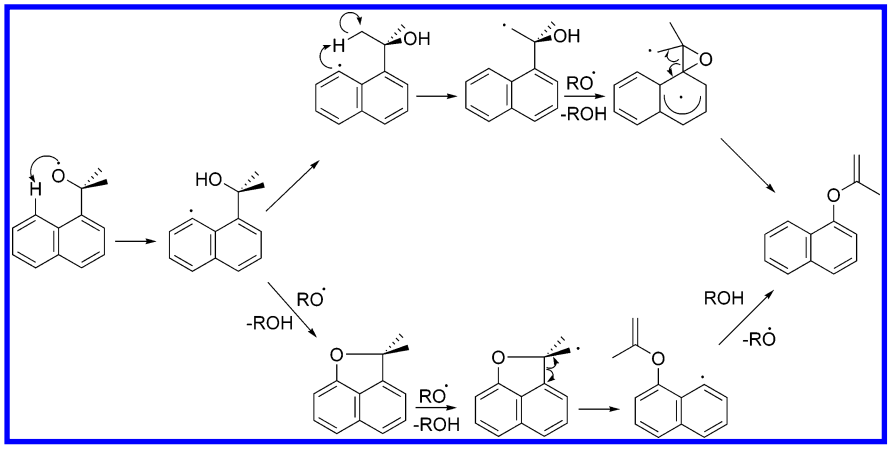
Experimental Section

General. The experiments of thermal decomposition of hydroperoxides were performed using a Varian 3300 gas chromatograph conjugated with a SSQ 700 Mat Finnigan mass spectrometer with EI ionization (70 eV). A solution of hydroperoxides in $CHCl_3$ at a concentration of 0.001 mg/cm^3 was introduced to the GC injector at 60 °C, and the injector temperature was gradually raised with a rate of 25 °C/min up to 270 °C. Decomposition products were separated on the DB5 capillary column (30 m, φ= 0.25 μ helium, 30 cm^3/min). Melting points of synthesized compounds were determined in capillary tubes on SMP 3 (Stuart Scientific) apparatus. High-resolution mass spectra (HRMS) were recorded on an AMD 604 spectrometer with EI ionization. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Unity Inova-300 spectrometer using TMS as an internal standard. IR spectra were recorded on a Zeiss Specord M 80 spectrometer. Kiesegel 60 (Merck 0.063−0.200 mm) was used for column chromatography. TLC analyses were performed using Merck's plastic plates coated wit silica gel 60 F254. The computations were performed with MOPAC-7 program using AM1 (RHF for openshell systems) semiempirical Hamiltonian. Geometries of all the species taken into consideration were optimised, and heats of formation of the molecules were calculated. The optimisation was performed with the Eigenvector Following algorithm.[16] The transition states were obtained by the reaction path method and then were optimised.

Materials. 1-(1-Naphthyl)-1-methylethylhydroperoxide **1a** and 1-(2-naphthyl)-1-methylethylhydroperoxide **1b** were

(15) Heinze, A.; Lauterbach, G. *J. Prakt. Chem.* **1987**, *329*, 439.
(16) Baker, J. *J. Comput. Chem.* **1986**, *1*, 385.

Scheme 5. **Proposed mechanisms of the transformation of 1-(1-naphthyl)-1-methylethyloxy radical to 2-(1-naphthyloxy)propene, where R = 1-(1-naphthyl)-1-methylethyl**



synthesized as previously described.[17,18] Ethyl-3-chloro-2-butenoate was synthesized as described by Holy.[19]

1-Acetyl- and 2-Acetylanthracene (3c and 3d). 1-Acetyl- and 2-acetylanthracene were synthesized by acetylation of anthracene (64 g, 0.36 mol) with acetyl chloride (34.6 g, 0.44 mol) in nitrobenzene (300 cm^3) in the presence of $AlCl_3$ (48 g, 0.36 mol) according to the procedure described by Luttringhaus and Kacer.[20] After purification of the crude products by column chromatography (benzene−ethyl acetate, 10:1), the following pure products were obtained:

3c: yield 6.8 g (8.6%), mp 105−107 °C (lit.,[20] 103−105 °C); (Found: C, 87.15; H, 5.43. $C_{16}H_{12}O$ requires C, 87.25; H, 5.49); ν_{max} cm^{-1} 1680; δ_H 9.47 (1 H, s, Ar, 9-H), 8.43 (1 H, s, Ar, 10-H), 8.15 (1 H, d, $J = 8.4$, Ar), 8.05−8.09 (1 H, m, Ar), 7.97 (2 H, dd, $J = 6.3, 5.7$, Ar), 7.47−7.52 (3 H, m, Ar), 2.79 (3 H, s, C*H*$_3$); δ_C 201.5 (*C*OCH$_3$), 134.8, 133.9, 133.0, 131.9, 131.5, 129.6, 129.2, 127.7, 127.6, 123.9, 126.1, 125.9, 125.8, 123.4 (Ar), 29.7 (*C*H$_3$).

3d: yield 10.9 g (13.8%), mp 191−192 °C (lit.,[20] 183−185 °C); (Found: C, 87.06; H, 5.42. $C_{16}H_{12}O$ requires C, 87.25; H, 5.49); ν_{max} cm^{-1} 1680; δ_H 8.59 (1 H, s, Ar, 1-H or 9-H), 8.52 (1 H, s, Ar, 1-H or 9-H), 8.38 (1 H, s, Ar, 10-H), 7.94−8.02 (4 H, m, Ar), 7.46−7.55 (2 H, m, Ar), 2.73 (3 H, s, C*H*$_3$); δ_C 197.9 (*C*OCH$_3$), 133.9, 133.2, 132.6, 131.9, 131.6, 130.3, 128.9, 128.4, 128.3, 128.1, 126.6, 126.2, 125.9, 122.6 (Ar), 26.5 (*C*H$_3$).

2-(1-Anthryl)-2-propanol 2c. Methylmagnesium iodide was synthesized in the usual manner[21] from magnesium turnings (1.02 g, 42 mmol) and methyl iodide (5.96 g, 42 mmol) in ethyl ether (30 cm^3). The solution of methylmagnesium iodide was diluted with diethyl ether (20 cm^3), and pulverized 1-acethylanthracene (9.3 g, 42 mmol) was added. The reaction mixture was stirred and refluxed for 2 h and then poured into a mixture of ice (12 g) and sulphuric acid (7 cm^3, 27%). The mixture was extracted with diethyl ether, and the organic layers were collected, washed with water, a water solution of $NaHCO_3$ (10%), and again water, and dried with $MgSO_4$. After evaporation of the ether, the pure product was isolated from the residue by column chromatography (benzene−ethyl acetate, 10:1) as a brown oil 6.74 g (67.9%). After recrystallization from benzene, orange crystals were obtained, mp 41−43 °C; (Found: C, 86.41; H, 6.70. $C_{17}H_{16}O$ requires C, 86.40; H, 6.82); ν_{max} cm^{-1} 3600; δ_H 9.39 (1 H, s, Ar, 9-H), 8.38 (1 H, s, Ar, 10-H), 8.02−8.05 (1 H, m, Ar), 7.87−7.95 (2 H, m, Ar), 7.48−7.50 (1 H, m, Ar), 7.42−7.45 (3 H, m, Ar), 2.11 (1 H, s, O*H*), 1.89 [6 H, s, C(C*H*$_3$)$_2$]; δ_C 143.1 [*C*-C(CH$_3$)$_2$OH], 133.1, 131.1, 130.8, 129.1, 128.9, 128.3, 127.5, 127.1, 126.6, 125.6, 125.2, 124.2, 122.1 (Ar), 74.3 [*C*(CH$_3$)$_2$OH], 31.5 (*C*H$_3$).

2-(2-Anthryl)-2-propanol and 2-(2-Anthryl)propene (2d and 4d). The synthesis was carried out as described above for 2-(1-anthryl)-2-propanol using magnesium turnings (0.43 g, 18 mmol) and methyl iodide in diethyl ether (30 cm^3) and 2-acetylanthracene (3.74 g, 17 mmol). The reaction mixture was poured into a mixture of ice (8 g) and sulphuric acid (3 cm^3, 27%); the precipitated crystalline substance was filtered off, and the pure product (2.61 g) was isolated by crystallization from benzene. After evaporation of benzene additional amounts of 2-(2-anthryl)-2-propanol (0.36 g) and 2-(2-anthryl)propene (0.48 g) were isolated from the residue by column chromatography (benzene−ethyl acetate, 50:1).

The properties of the obtained compounds:

2d: yield 2.97 g (74.0%), mp 157−158 °C (after recrystallization from benzene) (lit.,[22] 152−154 °C); (Found: C, 86.22; H, 6.68. $C_{17}H_{16}O$ requires C, 86.40; H, 6.82); ν_{max} cm^{-1} 3600; δ_H 8.38 (1 H, s, Ar, 9-H or 10-H), 8.37 (1 H, s, Ar, 9-H or 10H), 8.04 (1 H, s, Ar, 1-H), 7.94−7.99 (3 H, m, Ar), 7.57 (1 H, dd, $J = 9.0, 1.8$, Ar), 7.42−7.46 (2 H, m, Ar); 1.95 (1 H, s, O*H*), 1.69 [6 H, s, C(C*H*$_3$)$_2$]; δ_C 145.6 [*C*-C(CH$_3$)$_2$], 131.9, 131.6, 131.4, 130.7, 128.3, 128.13, 128.08, 126.4, 125.8, 125.3, 125.2, 123.7, 121.9 (Ar), 72.7 [*C*(CH$_3$)$_2$OH], 31.3(*C*H$_3$).

4d: yield 0.30 g (7.5%), mp 161−162 °C (after recrystallization from benzene) (lit.,[22] 150−152 °C); (Found: C, 93.16; H, 6.35. $C_{17}H_{14}$ requires C, 93.54; H, 6.46); ν_{max} cm^{-1} 1620 and 1460; δ_H 8.38 (1 H, s, Ar, 9-H or 10-H), 8.34 (1 H, s, Ar, 9-H or 10-H), 7.96−7.98 (2 H, m, Ar), 7.68 (1 H,

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d, $J = 1.8$, Ar), 7.65 (1 H, d, $J = 1.8$, Ar), 7.42−7.45 (2 H, m, Ar), 7.35−7.39 (1 H, m, Ar), 5.59 (1 H, s, CH_2), 5.23 (1 H, dq, $J = 1.5$, 1.5, CH_2), 2.30 (3 H, s, CH_3); δ_C 142.7 [*C*-C(CH_3)$_2$], 131.7, 131.6, 128.15, 128.10, 127.9, 126.6, 125.8, 125.4, 125.3, 125.1, 124.98, 124.90, 124.2, 123.7 (Ar), 113.2 (*C*H_2), 21.7 (*C*H_3).

2-(9-Anthryl)-2-propanol and 2-(9-Anthryl)-2-propene (2e and 4e). To a stirred suspension of magnesium turnings (1.53 g, 63 mmol) in dibutyl ether (120 cm^3) was added 9-bromoanthracene (15.2 g, 59 mmol). The reaction mixture was heated under argon to 135−141 °C for 1 h. When the temperature of the reaction mixture reached 130 °C, an iodine crystal and methyl iodide (0.2 cm^3) were added to start the reaction. After the reaction mixture cooled to about 7 °C, a solution of dry acetone (6.7 g 115 mmol) in dibutyl ether (14 cm^3) was added dropwise, the stirring was continued at room temperature for 1.5 h, and the reaction mixture was poured into a mixture of ice (280 g) and hydrochloric acid (63 cm^3, 10%). The precipitated crystalline substance was filtered off, the ethereal layer was separated, and the water layer was extracted with dibutyl ether. The combined ethereal layers were washed with a water solution of $NaHCO_3$ (10%) and then with water, and dried over $MgSO_4$, and the solvent was evaporated. The residue was combined with the crystalline substance, the mixture was dissolved in benzene (30 cm^3), and the solved part of the mixture was separated by column chromatography (benzene−ethyl acetate, 50:1, 700 cm^3 of silica gel) to get 2-(9-anthryl)-2-propanol and 2-(9-anthryl)propene with the following properties:

2e: yield 2.60 g (18.7%), mp 132−134 °C (orange crystals after recrystallization from benzene) (lit.,[23] 138−140 °C); (Found: C, 86.02; H, 6.51. $C_{17}H_{16}O$ requires C, 86.40; H, 6.82); ν_{max} cm^{-1} 3600; δ_H 8.73−8.78 (2 H, m, Ar), 8.29 (1 H, s, Ar, 10-H), 7.91−7.94 (2 H, m, Ar), 7.31−7.40 (4 H, m, Ar), 2.14 [7 H, s, O*H*, C(CH_3)$_2$]; δ_C 141.0 [*C*-C(CH_3)$_2$], 132.1, 129.0, 128.9, 128.2, 127.0, 124.2,123.8 (Ar), 76.8 [*C*(CH_3)$_2$OH], 33.5 (*C*H_3).

4e: yield 1.17 g (8.4%), resin; (Found: C, 92.67; H, 6.78. $C_{17}H_{14}$ requires C, 93.54; H, 6.46); ν_{max} cm^{-1} 1640 and 1620; δ_H 8.35 (1 H, s, Ar, 10-H), 8.13−8.17 (2 H, m, Ar), 7.94−7.99 (2 H, m, Ar), 7.41−7.47 (4 H, m, Ar), 5.74 (1 H, s, CH_2), 5.13 (1 H, s, CH_2), 2.25 (3 H, s, CH_3); δ_C 142.9 [*C*-C(CH_3)$_2$], 138.9, 131.5, 128.5, 126.2, 125.7, 125.3, 125.1 (Ar), 117.9 (*C*H_2), 25.5 (*C*H_3).

Oxidation of 2-Anthryl-2-propanols to 1-Anthryl-1-methylethylhydroperoxides (General Procedure). To the intensively stirred mixture of 2-anthryl-2-propanol (2.36 g, 10 mmol) in 1,2-dichloroethane (20 cm^3) was added at 50 °C a solution of H_2SO_4 (96%, 0.09 cm^3, 0.16 g, 1.6 mmol) in H_2O_2 (67%, 4.8 cm^3, 4.06 g, 80 mmol). The reaction progress was controlled by the TLC method using the CH_2Cl_2/acetone, 35:1 (v/v) mixture as the eluent and a saturated solution of NaI in acetic acid for developing the hydroperoxide spots. The reaction times for 1-(1-anthryl)-, 1-(2-anthryl)-, and 1-(9-anthryl)-1-methylethylhydroperoxide were 3.5, 3, and 2.5 h, respectively. The reaction mixture was cooled to room temperature and washed with a water solution of $NaHCO_3$ (5%, 15 cm^3); the water layer was extracted two times with 1,2-dichloroethane (10 cm^3), and the combined organic layers were washed with a saturated solution of $(NH_4)_2SO_4$ (5 cm^3) and water (5 cm^3) and dried with $MgSO_4$. After evaporation of the solvent the pure hydroperoxide was isolated from the residue by column chromatography using CH_2Cl_2 as the eluent. The properties of the obtained hydroperoxides:

1-(1-Anthryl)-1-methylethylhydroperoxide 1c: yield 0.73 g (29.1%), orange resin; (Found: C, 80.65; H, 6.67. $C_{17}H_{16}O_2$ requires C, 80.93; H, 6.39); ν_{max} cm^{-1} 3520; δ_H 9.41 (1 H, s, Ar, 9-H), 8.45 (1 H, s, Ar, 10-H), 7.94−8.09 (3 H, m, Ar), 7.46−7.51 (3 H, m, Ar), 7.36−7.38 (1 H, m, Ar), 7.41 (1 H, s, OO*H*), 1.92 [6 H, s, C(CH_3)$_2$]; δ_C 139.2 [*C*-C(CH_3)$_2$OOH], 133.2, 132.1, 131.3, 129.8, 129.4, 129.2, 127.83, 127.82, 126.1, 125.8, 125.3, 124.9, 124.6 (Ar), 86.8 [*C*(CH_3)$_2$OOH], 27.2 (*C*H_3).

1-(2-Anthryl)-1-methylethylhydroperoxide 1d: yield 1.25 g (49.6%), yellow resin; (Found: C, 82.15; H, 6.44. $C_{17}H_{16}O_2$ requires C, 80.93; H, 6.39); ν_{max} cm^{-1} 3520; δ_H 8.42 (1 H, s, Ar, 9-H or 10-H), 8.40 (1 H, s, Ar, 9-H or 10-H), 8.00 (1 H, s, Ar, 1-H), 7.98−8.04 (3 H, m, Ar), 7.62 (1 H, dd, $J = 2.1$, 9.0, Ar), 7.41−7.48 (2 H, m, Ar), 7.40 (1 H, s, OO*H*), 1.74 [6 H, s, C(CH_3)$_2$]; δ_C 144.4 [*C*-C(CH_3)$_2$-OOH], 141.2, 138.9, 131.9,131.6, 131.3, 130.9, 128.8, 128.1, 126.6, 125.9, 125.4, 124.4, 123.3 (Ar), 84.1 [*C*(CH_3)$_2$OOH], 25.8 (*C*H_3).

1-(9-Anthryl)-1-methylethylhydroperoxide 1e: yield 0.54 g (21.1%), resin. (Found: C, 81.08; H, 6.46. $C_{17}H_{16}O_2$ requires C, 80.93; H, 6.39); ν_{max} cm^{-1} 3520; δ_H 7.39−7.51 (5 H, m, Ar), 7.28−7.34 (2 H, m, Ar), 7.19−7.25 (2 H, m, Ar), 5.78 (1 H, s, OO*H*), 2.13 [6 H, s, C(CH_3)$_2$]; δ_C 129.6 [*C*-C(CH_3)$_2$OOH], 128.6, 128.4, 127.5, 127.1, 127.0, 125.8, 125.3 (Ar), 85.7 [*C*(CH_3)$_2$OOH], 23.5 (*C*H_3).

Methyl 3-(1-Naphthyloxy)-2-butenoate. To stirred methanol (8 cm^3) was slowly added sodium (0.46 g, 20 mmol) under nitrogen. After dissolution of sodium, 1-naphthol (2.88 g, 20 mmol) was added, the reaction mixture was refluxed for 1 h, and then ethyl 3-chloro-2-butenoate (1.48 g, 10 mmol) was added; the reaction mixture was refluxed for 7 h. The reaction mixture was poured on ice, the product was extracted with diethyl ether, and the ethereal solution was dried with $MgSO_4$. After evaporation of the solvent the pure methyl 3-(1-naphthyloxy)-2-butenoate (1.38 g, 57%) was isolated from the residue by column chromatography using a mixture of toluene and ethyl acetate, 5:1 (v/v) as the eluent. ν_{max} cm^{-1} 1710 and 1140; δ_H 7.10−7.93 (7 H, m, Ar), 4.81 (1 H, s, C*H*), 3.56 (3 H, s, OCH_3), 2.65 (3 H, s, CH_3); δ_C 172.8 (*C*HO), 168.0 (*C*═O), 149.1, 134.9, 128.0, 126.7, 126.5, 125.9, 125.6, 121.4, 117.8 (Ar), 95.9 (*C*H), 50.8 (O*C*H_3), 18.2 (*C*H_3).

3-(1-Naphthyloxy)-2-butenoic Acid. To a solution of KOH in ethanol (10%, 28 cm^3) was added methyl 3-(1-naphthyloxy)-2-butenoate (1.38 g, 5.7 mmol), and the mixture was refluxed for 4 h. After evaporation of the solvent the residue was dissolved in water (3 cm^3), made slightly acidic with H_2SO_4 (10%), and extracted three times with diethyl ether (6 cm^3). The ethereal solution was dried with

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$MgSO_4$, the solvent was evaporated, and the crystalline residue was recrystallized from benzene to get pure product (1.01 g, 78%), mp 155−157 °C; ν_{max} cm^{-1} 3200−2800, 1680, 1618, and 1155; δ_H 7.12−7.94 (7 H, m, Ar), 4.79 (1 H, s, C*H*), 2.62 (3 H, s, CH_3); δ_C 174.8 (*C*HO), 173.0 (*C*O), 149.0, 135.0, 128.1, 126.7, 126.6, 126.1, 125.6, 121.4, 117.9 (Ar), 95.7 (*C*H), 18.6 (*C*H_3); HRMS (EI): Found: 228.0782; $C_{14}H_{13}O_3$ requires: 228.0786.

2-(1-Naphthyloxy)propene 5a. A glass test tube with a capillary neck containing 3-(1-naphthyloxy)-2-butenoic acid (1.01 g, 4.45 mmol) was heated at 180 °C for 2 h. The product (0.39 g, 48%) was isolated from the residue by column chromatography using toluene as the eluent; ν_{max} cm^{-1} 1635, 1255, and 1160; δ_H 7.06−8.08 (7 H, m, Ar), 4.16 (1 H, s, CH_2), 3.88 (1 H, s, CH_2), 2.13 (3 H, s, CH_3); δ_C 159.7 (*C*HO), 150.6, 134.7, 128.2, 127.7, 126.1, 126.0, 125.6, 122.7, 122.4, 115.4 (Ar), 89.7 (*C*H_2), 19.9 (*C*H_3); HRMS (EI): Found: 184.0881; $C_{13}H_{12}O$ requires: 184.0888.

Thermal Decomposition of 1-(1-Naphthyl)-1-methylethylhydroperoxide 1a in Liquid Phase. The hydroperoxide **1a** was thermally decomposed in closed glass test tube. Each test tube was filled with about 1 cm^3 of a solution of **1a** in cumene (5 cm^3; 5 mol/dm^3; 2.55 mmol), flushed with argon, closed and immersed in an oil bath at 140 °C for 15 h. Hydroperoxide **1a** was completely decomposed. The product contained a large amount of tarry substances and, apart from that, alcohol **2a** and ketone **3a**, which were obtained with 44% and 17% selectivity, respectively (HPLC analysis[24]). The product was diluted with diethyl ether (40 cm^3) and extracted with an aqueous solution of NaOH (15%). The inorganic layer was neutralized with diluted HCl and extracted with diethyl ether. The etheral solution was dried with $MgSO_4$, and ether was evaporated; 0.016 g of acidic substance was obtained. 1-Naphthol (0.008 g) was isolated from this mixture by preparative TLC (CH_2Cl_2−acetone, 20:1).

Column chromatography (hexane−acetone, 20:1) was used to isolate 2-aryloxypropene **5a** from the decomposition product after extraction with NaOH. Unfortunately, aryloxypropene **5a** underwent subsequence reactions, e.g. hydrolysis to 1-naphthol. The additional amount of 1-naphthol was obtained (0.0139 g). The obtained 1-naphthol (0.0147 g) was characterized by ^{1}H NMR, IR and MS.

The small amount of aryloxypropene **5a** (0.0215 g) was isolated only by preparative TLC (benzene as eluent). Its structure was confirmed by ^{1}H NMR and IR.

Thermal decomposition of 1-(1-naphthyl)-1-methylethylhydroperoxide **1b** was also carried out under the same conditions (140 °C, 0.5 mol/dm^3 in cumene, 15 h). The obtained product contained only alcohol **2b** and ketone **3b** (76 and 24% selectivity, respectively).

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