The Oxidation of 3,6-Di-*tert*-butyl-2-naphthol. — X-Ray Analysis of 2,5,8,11-Tetra-*tert*-butyl-*peri*-xanthenoxanthene

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The oxidation of 3,6-di-*tert*-butyl-2-naphthol (**9**) with 2,4,6-tri-*tert*-butylphenoxyl in benzene leads to 3,3′,6,6′-tetra-*tert*-butyl-1,1′-binaphthyl-2,2′-diol (**5b**) or 2,5,8,11-tetra-*tert*-butyl-*peri*-xanthenoxanthene (**8b**). The structure of **8b** has been determined by X-ray analysis. In the presence of methanol/KOH **5b** is oxidized by $K_3[Fe(CN)_6]$ to the *ortho*-quinol ether **17b**, derived from 2,5,8,11-tetra-*tert*-butyldibenzo[*a,kl*]xanthen-1-ol (**12b**). The latter can be obtained from **17b** by reduction *via* the corresponding aryloxenium cation **15b**. The presence of the monovalent dehydrogenation product of **12b**, the aryloxyl **14b**, in the oxidation mixtures of **9** was demonstrated by ESR spectroscopy. The expected spirobenzoxete **7** could not be detected.

Die Oxidation von 3,6-Di-*tert*-butyl-2-naphthol. — Röntgenstrukturanalyse von 2,5,8,11-Tetra-*tert*-butyl-*peri*-xanthenoxanthen

Die Oxidation von 3,6-Di-*tert*-butyl-2-naphthol (**9**) mit 2,4,6-Tri-*tert*-butylphenoxyl in Benzol führt zu 3,3′,6,6′-Tetra-*tert*-butyl-1,1′-binaphthyl-2,2′-diol (**5b**) oder 2,5,8,11-Tetra-*tert*-butyl-*peri*-xanthenoxanthen (**8b**). Die Struktur von **8b** wurde röntgenographisch bestimmt. In Gegenwart von Methanol/KOH führt die Oxidation von **5b** mit $K_3[Fe(CN)_6]$ zum *ortho*-Chinolether **17b**, der sich vom 2,5,8,11-Tetra-*tert*-butyldibenzo[*a,kl*]xanthen-1-ol (**12b**) ableitet. Letzteres ist aus **17b** durch Reduktion über das entsprechende Aryloxenium-Kation **15b** zugänglich. Das monovalente Dehydrierungsprodukt von **12b**, das Aryloxyl **14b**, läßt sich in den Oxidationsgemischen aus **9** ESR-spektroskopisch nachweisen. Das erwartete Spirobenzoxet **7** wurde nicht entdeckt.

In previous publications[2] we demonstrated that the oxidation of sterically hindered biphenyl-2,2′-diols **1** (Scheme 1) leads, presumably *via* 2,2′-diphenoquinones **2**[3], to

Scheme 1
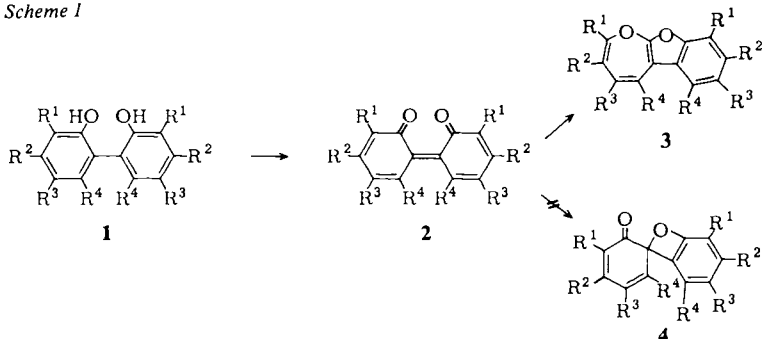
oxepinobenzofurans **3** instead of spirobenzoxetes **4** as had been originally assumed by us[4] as well as by other authors[5]. If we pass over to 1,1'-binaphthyl-2,2'-diols **5**, the formation of the corresponding oxepinobenzofurans **6** is much less probable, due to a certain steric strain between the annelated benzo rings in **6** or in the corresponding arene oxide lying on the reaction path between **6** and the dibenzo analogues of **2**. The latter (*E* and *Z* forms) in turn, are ruled out by similar arguments. This type of steric hindrance should be much less for the benzoxete structure **7**. As a consequence, the bivalent oxidation of **5** might lead to the desired **7**, as long as a completely different structure is not favoured. Oxidation of a 1,1'-binaphthol **5** may indeed open a different reaction path. This has been postulated for the unsubstituted **5a** and 2-naphthol itself[6]. The final product of this sequence, *peri*-xanthenoxanthene ("binaphthylene-dioxide") **(8a)**[7] as well as several derivatives[6,8] have been known for a long time.
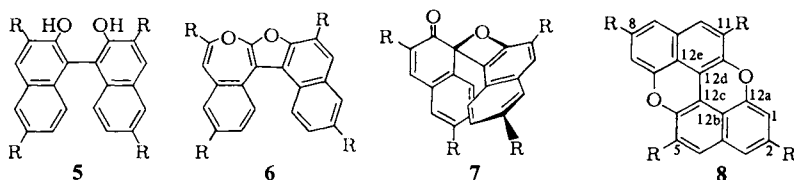

a: R = H
b: R = *t*-Bu

Therefore we decided to investigate the oxidation of **5b** (R = *t*-Bu) − the *tert*-butyl groups were expected to stabilize the reaction products − and to determine whether its bivalent oxidation product has structure **6b**, **7b**, or **8b**. In addition, we were interested whether intermediates of the oxidation process could be detected.

Some features of the oxidation of **5b** and of its parent naphthol **9** have already been reported. This was done, however, in the belief that the di-*tert*-butylation product of 2-naphthol was 1,6-di-*tert*-butyl-2-naphthol **(10)**[9−11]. The binaphthol isolated from the oxidation mixture was consequently thought to be **11**[6,11,12].
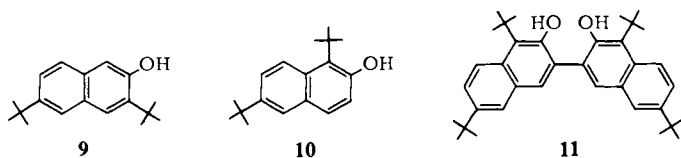
Meanwhile, *Carnduff* et al. [13] recognized that the second *tert*-butyl group must have occupied position 3 (instead of 1) in 2-naphthol. As a consequence, earlier considerations about the oxidation of **10** (actually **9**)[11] and about the product of further oxidation of **11** (actually **5b**)[12] were erroneous. This gave rise to another stimulus for the present work. Elucidation of the structure of the oxidation product of **5b** would provide further proof of structure **9** for the di-*tert*-butyl-2-naphthol under discussion.

The Structure of the Bivalent Oxidation Product of Binaphthol 5b

A) Physical and Spectroscopic Data

1,1'-Binaphthol **5b** was prepared from **9** by dehydrogenation with 2,4,6-tri-*tert*-butylphenoxyl in benzene[6]. By further oxidation with Ag_2O or two equivalents of 2,4,6-tri-*tert*-butylphenoxyl a yellow, crystalline product **A** of m.p. $\geq 365\,°C$ was obtained in 26% yield. The elemental analysis corresponded to $(C_{18}H_{21}O)_n$.

The mass spectrum showed M^+ ($m/e = 506$, relative intensity 100) with few fragment peaks (of relative intensities ≤ 10) characteristic of the fragmentation pattern of the *tert*-butyl groups.

UV spectra of **A** resemble those of **8a**, which we prepared according to the litera-ture[6, 7b]. However, this does not necessarily support the *peri*-xanthenoxanthene nature of **A**, since **8b** and the alternative structures **6** and **7** show some common structural units. The IR absorption between 1600 and 1700 cm^{-1} would be a criterion to differen-tiate between structures **7b** and **8b**, since *o*-quinolide compounds like **7b**, as a rule, exhibit $v_{C=O} > 1675$ cm^{-1}. However, exceptions are also known ($v_{C=O} = 1650-1670$ cm^{-1})[14]. The absorption of **A** at 1634 cm^{-1} therefore does not allow an unequivocal decision against structure **7b**, especially since the influence of an oxete ring on the frequency of the $C=O$ vibration is unknown.

The simple ^1H NMR spectrum indicates a symmetrical structure of **A**. There are two signals of the *tert*-butyl groups, an AB type spectrum ($J = 1.5$ Hz) of aromatic (or eventually quinolide[14]) protons and a singlet of aromatic protons, in the intensity ratio of 9:9:2:1, respectively. Structures **6b** and **7b** are excluded by this pattern. Structure **8b**, on the other hand, is compatible with the observed spectrum. Since coupling between protons in *peri*-position often cannot be observed, protons 4 and 10 might give rise to a singlet, whereas protons 1,3 and 7,9 would be responsible for the AB pattern.

Structure **8b** is further supported by the ^{13}C NMR spectrum. All fourteen signals can be observed in the decoupled spectrum; there is no signal in the carbonyl region, again ruling out structure **7**. Further assignments, given in the Experimental Part, were made on the grounds of chemical shifts (as compared with shift-data of **12b** and 2,7-di-*tert*-butylnaphthalene[15]), intensities, and single-frequency $\{^{13}C, {}^1H\}$ decoupling experiments in the case of the assignable ring protons (see above).

B) X-Ray Analysis

In order to finally prove the structure of **A** we carried out an X-ray study (see Figures 1 and 2, Table 1).

Please, note that for practical reasons the numbering system of Figure 1 is different from the IUPAC system. Atoms which are related to numbered ones by the symmetry operation $-x$, $1 - y$, $2 - z$ are denoted by a dash.

The X-ray analysis decided in favour of **8b**. Consequently, the parent naphthol and binaphthol definitely have structures **9** and **5**, and the structure of **8a** for "binaphthyl-enedioxide" itself gains further support.

The molecule **8b** has a crystallographically imposed center of symmetry (point group C_i) between C 1 and C 1'. The flat shape of the molecule is demonstrated by the small deviations of the atoms from a least-squares plane through the naphthalene system (C 1

through C10). Moreover, there is no twist between the two naphthalenic systems, because symmetry requires parallel least-squares planes through C1 to C10 and C1' to C10'. The possibility of electron delocalization within the entire ring system, already suggested by the yellow colour of **8b** (and **8a**), is further substantiated by the bond lengths given in Figure 2, especially with respect to the central C1 – C1' bond.
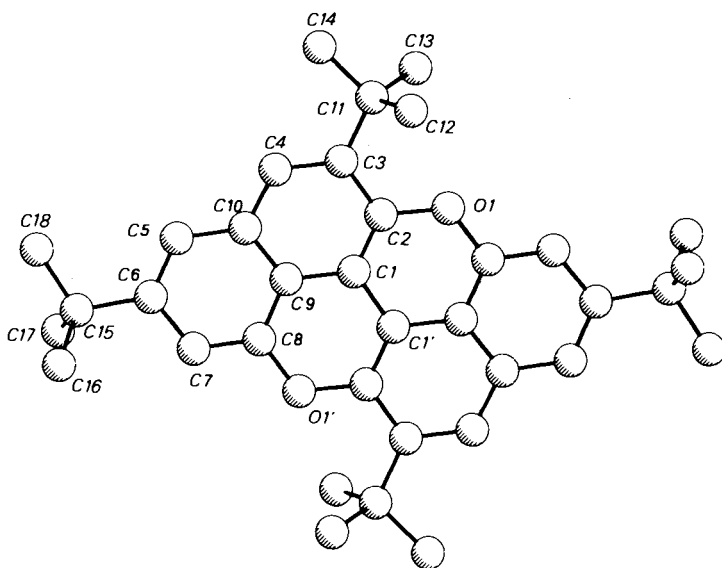

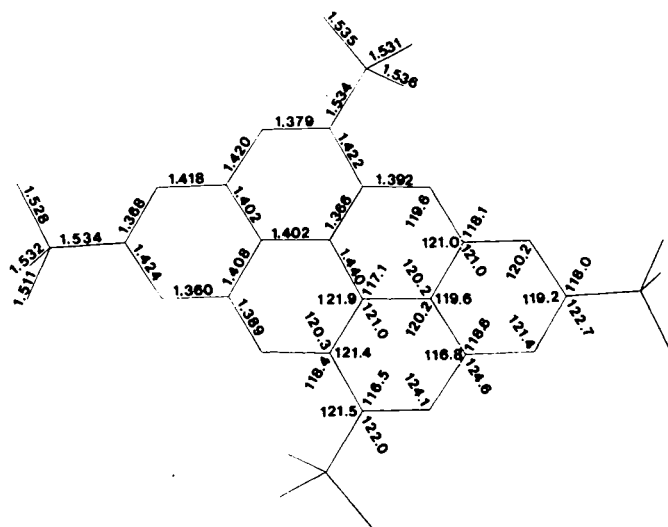Figure 1. Single molecule of **8b** and numbering scheme for the discussion of the X-ray results

Figure 2. Bond lengths (Å) and angles (°) in **8b**. Standard deviations: 0.004 Å for C15 – C16 and C15 – C17, and 0.003 Å for all other bonds; 0.3° for ∢ C16 – C15 – C17, and 0.1 – 0.2° for all other angles

Table 1. Atomic coordinates with e.s.d.'s in parenthesis

	x/a	y/b	z/c	U_{eq}
C1	-0.0178(2)	0.4377(2)	0.9851(2)	0.032(1)
C2	0.0528(2)	0.3611(2)	0.9273(2)	0.033(1)
C3	0.0173(2)	0.2377(2)	0.8995(2)	0.039(1)
C4	-0.0916(2)	0.2001(2)	0.9338(2)	0.035(1)
C5	-0.2770(2)	0.2364(2)	1.0350(2)	0.038(1)
C6	-0.3437(2)	0.3135(2)	1.0965(2)	0.040(1)
C7	-0.3025(2)	0.4363(2)	1.1200(2)	0.039(1)
C8	-0.1980(2)	0.4762(2)	1.0816(2)	0.039(1)
C9	-0.1278(2)	0.3969(2)	1.0197(2)	0.034(1)
C10	-0.1670(2)	0.2757(2)	0.9956(2)	0.033(1)
C11	0.0968(2)	0.1512(2)	0.8352(2)	0.036(1)
C12	0.2149(2)	0.1305(3)	0.9007(3)	0.040(1)
C13	0.1180(3)	0.2084(3)	0.7229(2)	0.055(2)
C14	0.0391(3)	0.0232(2)	0.8161(3)	0.055(2)
C15	-0.4621(2)	0.2734(3)	1.1419(2)	0.053(2)
C16	-0.4523(4)	0.2761(4)	1.2659(3)	0.047(2)
C17	-0.5598(3)	0.3630(3)	1.1002(4)	0.073(2)
C18	-0.4998(3)	0.1433(3)	1.1037(3)	0.087(3)
O1	0.1623(1)	0.4027(1)	0.8945(1)	0.069(2)

If one compares the central bond lengths (in Å) between identical aromatic subunits in other known structures, a systematic shortening of these bonds with an increasing size of the aromatic subunits can be observed: Biphenyl $1.496 - 1.507$[16–18], 1,1'-binaphthyl 1.475[19], perylene 1.471[20], **8b** 1.440 (this work), and tetrabenzoperylene $1.408 - 1.417$[21]. However, it is open to question whether or not the clamping oxygen atoms O1 and O1' play a significant role in (a) the participation in electronic delocalization and (b) the shortening of the bond $C1 - C1'$ for geometrical reasons.

Mechanistic Aspects

A) Preparative Search for Intermediates

The formation of **8b** from **5b** necessarily involves several reaction steps. In analogy to the mechanism discussed for the formation of **8a** from 1,1'-binaphthol **5a**[6,7b,22], dibenzo[a,kl]xanthen-1-ol ("hydroxybinaphthyleneoxide") **12b** (Scheme 2) should be the key intermediate, regardless of whether it is produced *via* the biradical **13b** or by a sequence of consecutive oxidation steps. All efforts to isolate **12b** from the reaction mixture obtained by oxidation of **5b** with Ag_2O followed by immediate reduction (in order to reduce naphthoxyl **14b**, eventually formed by over-oxidation of **12b**) were in vain.

Surprisingly, with $K_3[Fe(CN)_6]$ in methanol/KOH neither **12b** nor **8b** were the main products. Instead, the methyl quinol ether **17b** was obtained in medium yields[23]. This compound can even be obtained starting with **9** instead of **5b** and using an excess of $K_3[Fe(CN)_6]$ in methanol/KOH, although the yields are lower in this case.

The structure of **17b** is in close agreement with its chemical reactivity (vide infra) and spectroscopic properties. The IR spectrum shows an *o*-quinolide[14] carbonyl absorption (1712 cm^{-1}) and the ^{1}H NMR spectrum displays a methoxy group signal, which appears

to be shifted to high field (δ = 2.77, [D_6]benzene) by the diamagnetic anisotropy of the surrounding π-system. For the analogous **17a**, $v_{C=O}$ = 1700 cm^{-1} and δ_{OCH_3} = 2.78 have already been reported[22]. Assignment of the signals of the ring protons 3-H through 13-H of **17b** (Figure 3) is straightforward in the 400 MHz spectrum (CS_2), which can be treated almost according to first order assuming that $J_{3,4}$, $J_{9,10}$, and $J_{10,13}$ are not resolved.

Scheme 2

a: R = H
b: R = *t*-Bu

17: R^1 = Me
18: R^1 = H
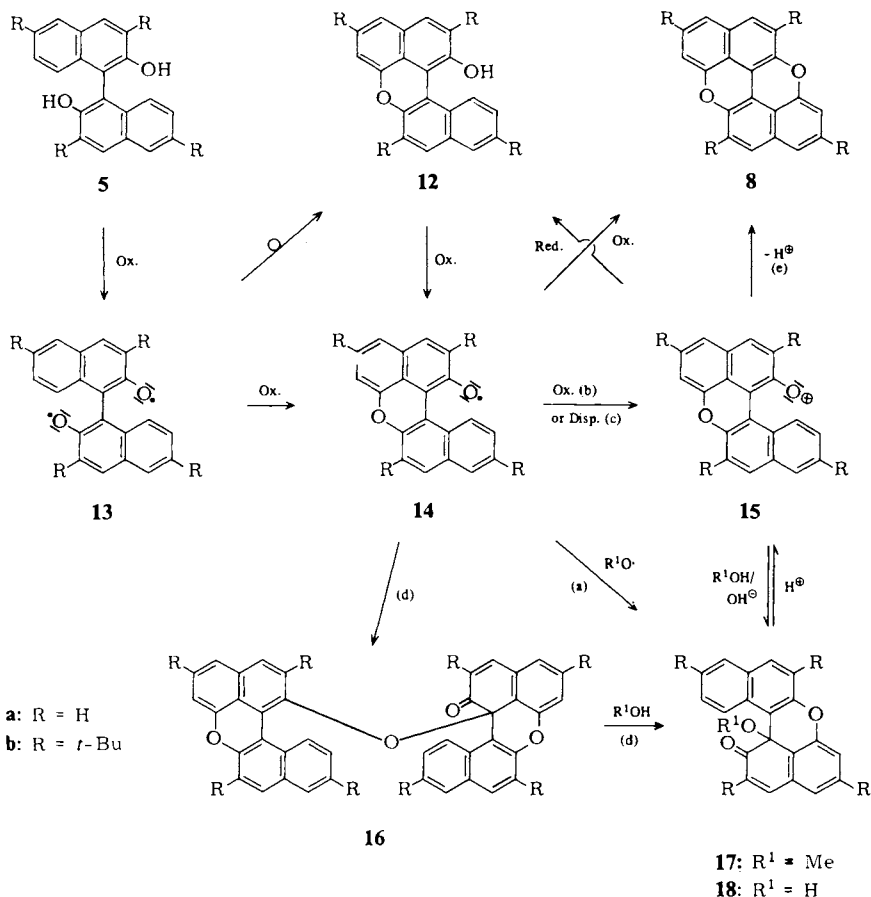
Using the above proton shift-values for $\{^1H\text{-}^{13}C\}$ single frequency decoupling, the signals of the tertiary ring-carbon atoms in the ^{13}C NMR spectrum can be assigned unequivocally (see Experimental Part). The signals of the sp^3-quinol carbon C-13c (δ = 76.8) and of the carbonyl carbon C-1 (δ = 201.9, d, $^3J_{CH}$ = 9.2 Hz) are also easily recognized. The shift position and coupling constant of the latter signal system are again characteristic of an *o*-quinolide structure[14]. The assignment of the other

quaternary ring-carbon and of the *tert*-butyl-carbon signals is not without problems; comparison with the ^{13}C NMR spectrum of **9** is of some help in determining the signals of the naphthalene substructure in **17b**.

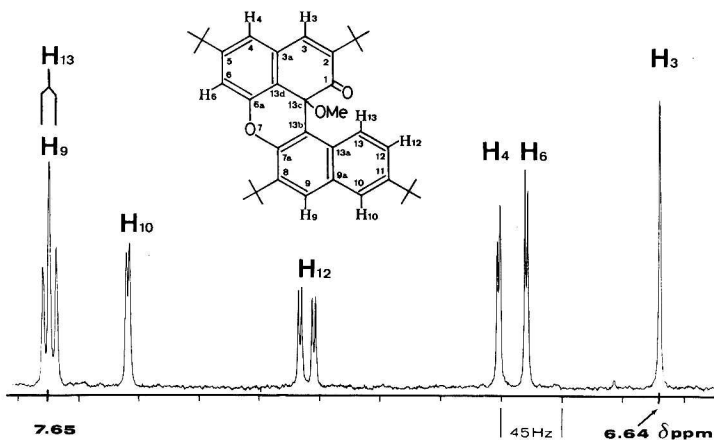Figure 3. 400 MHz ^{1}H NMR spectrum of the ring protons of **17b**

The formation of the quinol ether **17b** on the oxidation of **5b** with K$_3$[Fe(CN)$_6$], a typical one-electron oxidant for phenols in basic media[24], provides several mechanistic problems. It is, however, reasonable to assume that **12b** is the intermediate[25], since **17b** is structurally derived from **12b**. Monovalent oxidation of this phenol would give rise to the radical **14b**. A simple combination of **14b** with methoxyl (*path a*, Scheme 2) is unlikely, since alkoxy radicals would not be formed under our reaction conditions, and, moreover, phenoxy radicals comparable to **14b** do not react with methanol or methanolate[27]. There is also strong evidence against *paths b* or *c* which would involve nucleophilic attack of methanol or methanolate on the cation **15b**, formed by further oxidation (b) or disproportionation (c) of **14b**.

Thus, the half-wave potential of the transition 2,6-di-*tert*-butyl-4-phenylphenoxyl → ...phen-oxenium (i.e. +1100 mV[28] *vs* SCE, acetonitrile) is much higher than the E_0-value of K$_3$[Fe(CN)$_6$] (i.e. +116 mV *vs* SCE[29], water). Furthermore, the equilibrium of disproportionation of aryl-oxyls (as **14b**) is shifted almost completely in favour of the aryloxyl in basic medium[30].

Consequently, *path d* (dimerization[6,22] of **14b** to give **16b**, followed by nucleophilic displacement of the "left" part of **16b**, corresponding to **12b**, by methanol) seems to be the only one consistent with the experiment, although it could not be proven directly. Since oxidation of **12b** (for the synthesis, vide infra) with K$_3$[Fe(CN)$_6$] in alkaline methanol yields also **17b** (54%), "trimers"[6,22] (from **14b** and the hypothetical **13b**) apparently do not play a role in the formation of **17b**.

Next, we have to find out whether **17b** can act as an intermediate in the path **5b** → **8b** or whether it is only a trapping product of **14b** (or **13b**) with methanol. Thermolysis of **17b** (without solvent) at 200°C (0.1 Torr) for 5 hours indeed produces 43% of **8b**. However, the oxidation of **5b** was performed at ambient temperature at which

17b is thermally stable. Hence, this quinol ether cannot be a real intermediate in the formation of **8b** from **5b**.

It was therefore essential to synthesize phenol **12b** and subject it to our oxidation conditions. All efforts to prepare it by direct reduction of **17b** with $LiAlH_4$, $NaBH_4$, or NaH proved unavailing. On the other hand, treatment of **17b** with zinc in acetic acid led to **12b** in more than 90% yield. During this reaction a violet colour emerges, which is also observed when mineral acids are added to **17b**. We ascribe the cation structure **15b** to the corresponding species. Only the aryloxenium ion resonance structure is shown in Scheme 2; an oxonium structure with the positive charge on the second oxygen will significantly contribute to the resonance.

Cation **15b** could be precipitated and isolated as the perchlorate or tetrafluoroborate. The perchlorate notoriously included various amounts of perchloric acid and did not give satisfactory elementary analyses. However, IR and ^1H NMR spectra (see Experimental Part) are in agreement with the cation structure **15b**.

In the dry, solid state the perchlorate of **15b** slowly reacts to give *peri*-xanthenoxanthene **8b**; the reaction can be monitored by IR spectroscopy (KBr disk). It also resisted all efforts to recrystallize it and decomposed in the presence of water plus organic solvents, especially in the presence of a base, to give mainly the quinol **18b**. In methanol (with or without base) **17b** is recovered. Reduction of **15b** with zinc or hydroiodic acid in acetic acid again produces **12b** in over 90% yield.

The oxidation of **12b** with $K_3[Fe(CN)_6]$ under the conditions of the oxidation of **9** and **5b** does indeed produce **8b**, which is in agreement with the assumption that **12b** is an intermediate in the oxidation process.

B) ESR Investigations

Dehydrogenation of **9** and **5b** produced a paramagnetic species giving rise to a doublet ESR signal ($a = 0.227$ mT)[6,11,12]. We repeated the measurement starting with **5b** which was oxidized with PbO_2 in benzene or toluene in a sealed double Schlenk tube. The observed ESR spectrum (Figure 4) reveals a doublet ($a = 0.227$ mT) showing
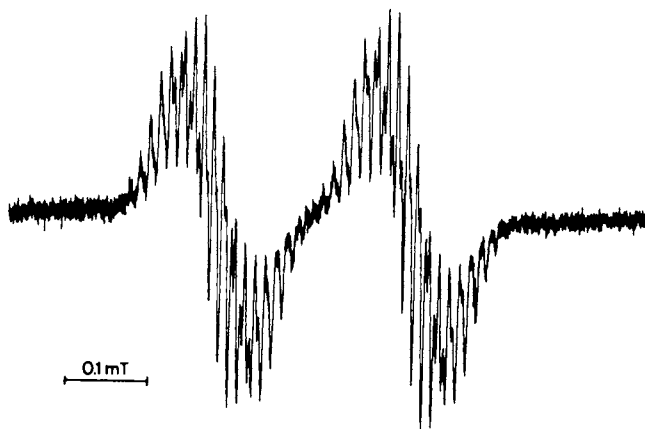

0.1 mT

Figure 4. ESR spectrum obtained during oxidation of **5b** with PbO_2 in toluene

a further hyperfine structure. This is confirmed by ENDOR which gives several a-values $\leqslant 0.041$ mT besides the large coupling (here $a = 0.229$ mT). The g-value was determined as 2.0039: apparently the value 2.0096, reported by *Razuvaev* et al.[11], has to be corrected. Although a detailed interpretation of the ESR spectrum will be given elsewhere, two facts are evident:

(1) *Hewgill* et al.[31] assume that monovalent dehydrogenation of alkoxybiphenols gives 2-(2-hydroxyphenyl)phenoxy radicals. Accordingly, in our case of the oxidation of binaphthol **5b** the aryloxyl **19** could be formed. This possibility can be ruled out, however, since isolated **12b** on dehydrogenation produced a species giving the same ESR spectrum as shown in Figure 4. Hence, there is little doubt that this species is **14b**.

(2) For **14a** a triplet ESR spectrum with $a = 0.25$ mT was observed, corresponding to coupling of the free electron with two nearly equivalent protons[6,7f,32,33]. It was then assumed[6] that these were protons H^2 and H^5. In agreement with this assignment, **14c** causes a doublet ESR spectrum with $a = 0.25$ mT[6], since H^5 is replaced by bromine. **14b** should therefore give rise to a singlet, because H^2 *and* H^5 are now replaced by *tert*-butyl groups, whereas a doublet appears in reality. Comparison with the 2-naphthoxyls **20**[6,34] shows that with these radicals, the highest spin density occurs in position 1 and 6. As a consequence, we may assume that in **14** protons H^5 and H^9 show the largest coupling constants. Then, for **14b** a doublet would result, due to coupling of the free electron with H^9.
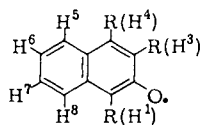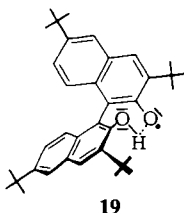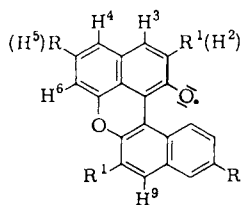
14	R	R¹
a	H	H
b	t-Bu	t-Bu
c	Br	H

19

20a: R = H
b: R = Cl

Conclusion

Aryloxyl **14b** is the first detectable (ESR) oxidation product of binaphthol **5b**, using $K_3[Fe(CN)_6]$ or Ag_2O as oxidants. In the presence of methanol, **14b** is transformed into methyl quinol ether **17b**, presumably *via* nucleophilic exchange in its dimer **16b**. In the absence of methanol, **14b** reacts slowly to give *peri*-xanthenoxanthene **8b** (X-ray analysis). Although the aryloxenium ion **15b** (prepared by a separate route) also forms a second oxygen bridge[35] leading to **8b** (path e, Scheme 2), the transition **14b** → **8b** must be *free-radical* in nature[36] since further monovalent oxidation or disproportionation of **14b** to give **15b** is unlikely under our pH conditions.

The expected spirobenzoxete **7b** could not be observed. In all probability, the dinaphthoquinone (2-analogue) as a forerunner either does not exist or is more easily transformed into **12b** and/or **8b**.

Experimental Part

IR spectra: Perkin Elmer 21 spectrometer. − ^{1}H and ^{13}C NMR spectra: Bruker WP 80, HFX 90, WH 90, and WM 400 spectrometers (^{1}H NMR spectra also with Varian A 60 and EM 360 instruments); tetramethylsilane as internal standard. The assignment of the ^{13}C NMR signals was achieved using chemical shift arguments (comparison with 2,7-di-*tert*-butylnaphthalene[15], 2-naphthol[37]), ^{13}C,^{1}H coupling, off-resonance, or single-frequency decoupling. Shift values wich could not be assigned unambiguously are marked by asterisks. − Mass spectra: AEI MS 9 and Varian MAT 711 spectrometers (inlet temperature 200 − 250 °C, ionisation energy 70 eV). − ESR spectra: Varian E 12 spectrometer. For *g*-value determinations 4-*tert*-butoxy-2,6-di-*tert*-butylphenoxyl ($g = 2.004627$)[38] was used as a standard. − Melting points were obtained by using a Tottoli apparatus and are reported uncorrected. − Microanalyses were performed by the microanalytical laboratory of the Chemical Institutes of the University of Tübingen on a Perkin Elmer C,H,N-analyzer.

The yields given refer to purified compounds if not stated otherwise. Solvents of crystallization were freshly distilled before use; petroleum ether had b.p. 60 − 90 °C.

Analytical TLC work was done with Merck sheets (silica gel on aluminum, fluorescence indicator 254 nm). For preparative layer chromatography glass plates were coated with silica gel (Macherey-Nagel, PUV$_{254}$) of 1 mm layer thickness. For column chromatography silica gel, 70 − 230 mesh (Macherey-Nagel, silica gel 60), and alumina (Macherey-Nagel, alumina neutral, acitvity 1) were used.

3,6-Di-tert-butyl-2-naphthol (**9**): The procedure suggested by *Contractor*[9] was used essentially, employing *tert*-butyl chloride/AlCl$_3$ as butylating agent. Mono-*tert*-butylated 2-naphthol could be removed by boiling with sodium hydroxide solution (5%). Thus, 40.0 g (0.28 mol) of 2-naphthol afforded 8.9 g (16%) of mono-*tert*-butylated product and 31.4 g (44%) of crude **9**; m.p. 135 °C (lit.[10] m.p. 139 °C). − ^{13}C NMR (CDCl$_3$): δ = 29.8* and 31.4* (*t*-Bu), 34.6* and 35.1* (*t*-Bu), 110.4 (C-1), 122.9 (C-5), 124.8 (C-7), 125.0 (C-4), 126.1 (C-8), 129.0 (C-4a), 131.2 (C-8a), 138.3 (C-3), 146.2 (C-6), 153.0 (C-2).

3,3′,6,6′-Tetra-tert-butyl-1,1′-binaphthyl-2,2′-diol (**5b**): Compound **5b** was prepared from **9** by oxidation with 1 equivalent of 2,4,6-tri-*tert*-butylphenoxyl in benzene or toluene[6]. Thus, 10.0 g (39 mmol) of **9** yielded 6.3 g (63%) of **5b**; m.p. 322 − 323 °C (lit.[6] m.p. 331 − 333 °C). − ^{13}C NMR (CDCl$_3$): δ = 29.8* and 31.4* (*t*-Bu), 34.6* and 35.5* (*t*-Bu), 111.6 (C-1), 123.45*, 123.52*, 125.4*, and 127.4* (C-4, C-5, C-7, C-8), 129.1 (C-4a), 130.2 (C-8a), 138.3 (C-3), 146.5 (C-6), 152.3 (C-2).

2,5,8,11-Tetra-tert-butyl-peri-xanthenoxanthene (**8b**)

a) *From* **9**: Naphthol **9** (4.0 g, 15.6 mmol), dissolved in benzene (100 ml), was treated under nitrogen as inert gas with 2 equivalents[39] of a solution of 2,4,6-tri-*tert*-butylphenoxyl[40, 41] in benzene. At the beginning of the addition of the phenoxyl its blue colour disappeared in the reaction mixture. After addition of about 1 equivalent, the colour changed to a deep red violet. This solution showed an ESR spectrum identical with that of Figure 4. After 3 d at room temperature

(day-light) the mixture was deep "dirty" red, after about 1 week a deep blue-green fluorescence occurred and after 14 d the colour did not change further. Concentration of the solution deposited 0.72 g of yellow crystals of **8b**. The filtrate was evaporated and the residue subjected to LC (Al_2O_3,deactivated with 10% of water; benzene) which afforded 2,4,6-tri-*tert*-butylphenol in nearly quantitative yield and an additional 0.3 g of the yellow crystals: overall yield 1.02 g (26% [42]), referring to **9**; 39%, referring to 2,4,6-tri-*tert*-butylphenoxyl [39]); m.p. > 365 °C; low solubility in benzene, petroleum ether, tetrahydrofuran, dioxane, or camphene, but soluble in concentrated sulfuric acid with evolution of a blue colour. – IR (KBr disk): 770, 1598, 1634 cm^{-1} (aromatic CC-bond). – ^{1}H NMR ($CDCl_3$): δ = 1.33 (s; 9H, *t*-Bu), 1.47 (s; 9H, *t*-Bu), 6.69 (d, J = 1.5 Hz; 1H, 1-H, 7-H), 7.02 (d, J = 1.5 Hz; 1H, 3-H, 9-H), 7.21 (s; 1H, 4-H, 10-H). – ^{13}C NMR ($CS_2/[D_6]$acetone): δ = 30.3* and 31.7* (4 C-*t*-Bu), 35.3* and 35.4* (4 C-*t*-Bu), 107.0 (C-1, C-7), 112.4 (C-12c, C-12d), 116.0 (C-3, C-9), 118.9 (C-12b, C-12e), 123.4 (C-4, C-10), 131.5 (C-3a, C-9a), 139.3 (C-5, C-11), 144.1 (C-2, C-8), 150.8* (C-5a, C-11a), 152.2* (C-6a, C-12a). – MS (70 eV): m/e = 506 (100%, M$^+$), 491 (8%, M$^+$ – 15), 476 (10%, M$^+$ – 15 – 15), 450 (10%, M$^+$ – 56).

$C_{36}H_{42}O_2$ (506.7)   Calc. C 85.33 H 8.36   Found C 85.33 H 8.29

b) *From* **5b**: To **5b** (1.0 g, 1.96 mmol), dissolved in warm benzene (50 ml), 2 mmol of 2,4,6-tri-*tert*-butylphenoxyl [41]) (corresponding to 1 equivalent with respect to each hydroxy group [43])) in benzene were added. The colour changed slowly from blue through yellow to deep violet. On standing for several weeks, the colour effects described under a) were observed; however, no precipitation occurred. Considerable concentration of the solution under nitrogen produced yellow crystals: yield 0.15 g (15%, referring to **5b**); m.p. > 365 °C. Evaporation of the mother liquor and digeration of the residue with methanol gave a further 0.45 g (46%, referring to **5b**) of a yellow powder which was deteriorated by **5b**. The methanol fraction afforded 2,4,6-tri-*tert*-butylphenol after evaporation and LC (acidic alumina) in nearly quantitative yield (with respect to 2,4,6-tri-*tert*-butylphenoxyl).

The oxidation of **5b** was also carried out with an excess of silver oxide in toluene to give **8b** in a yield of about 25%.

c) *From* **12b**: 2,4,6-Tri-*tert*-butylphenoxyl (83 mg, 0.32 mmol) in benzene was added to a solution of **12b** (80 mg, 0.16 mmol) in 5 ml of benzene in an atmosphere of nitrogen. The colour changed immediately from blue to red-violet and gradually *via* brown to a final yellow. After 6 weeks the benzene was evaporated *in vacuo*, and the resulting residue was digested twice with petroleum ether to remove 2,4,6-tri-*tert*-butylphenol formed in the oxidation process. Yield 48 mg (60%) of **8b** (IR spectrum), after drying *in vacuo*.

d) *From* **17b**: *o*-Quinol ether **17b** (100 mg, 0.186 mmol) was heated to 200 °C (0.1 Torr). After 5 h, the resulting powder was dissolved in a mixture of petroleum ether (b.p. 60–90 °C) and benzene (1:1) and chromatographed over alumina (deactivated with 5% water) with the same solvent mixture. After evaporation the product was dissolved in pure petroleum ether (b.p. 60–90 °C) and filtered speedily through a short column of silica gel. The resulting product showed a strong fluorescence even in highly diluted solution and was obtained as a lemon-yellow powder after evaporation of the solvent. Yield 40 mg (43%); m.p. > 365 °C.

2,5,8,11-Tetra-tert-butyl-13c-methoxydibenzo[a,kl]xanthen-1(13cH)-one (**17b**)

a) *By oxidation of* **5b**: Binaphthol **5b** (0.5 g, 0.98 mmol) was suspended in a small amount of ether and dissolved after the addition of methanolic potassium hydroxide solution (1%, 100 ml). Then, $K_3[Fe(CN)_6]$ (10.0 g, 30.4 mmol) was added, the flask stoppered and the mixture shaken or stirred for about 12 h with the exclusion of light. The supernatant brownish liquid produced a short-lived violet colour on contact with a DC-plate (silica gel [44]). After filtration through a short

column filled with Na_2SO_4, the ether was evaporated and the residue added to NH_4Cl solution. Yield 0.2 g (38%); decomposition at 320–350°C. Further purification was accomplished by suspending the material in methanol or recrystallizing it from acetone/water. – IR (KBr): 1712 (CO), 2960 cm^{-1} (aliphatic CH). – ^{1}H NMR (CS$_2$, 400 MHz, see Figure 3): δ = 1.33 (s; 9H, *t*-Bu), 1.35 (s; 9H, *t*-Bu), 1.38 (s; 9H, *t*-Bu), 1.56 (s; 9H, *t*-Bu), 2.65 (s; 3H, OCH$_3$), 6.64 (s; 1H, 3-H), 6.86 (d, J = 1.8 Hz; 1H, 6-H), 6.90 (d, J = 1.7 Hz; 1H, 4-H), 7.22 (dd, J = 9.0, 2.1 Hz; 1H, 12-H), 7.52 (d, J = 2.1 Hz; 1H, 10-H), 7.65 (d, J = 9.0 Hz; 1H, 13-H), 7.65 (s; 1H, 9-H). – ^{13}C NMR (CDCl$_3$)[45]: δ = 29.7*, 30.5*, 31.1*, and 31.3* (4 C-*t*-Bu), 34.6*, 34.9*, 35.0*, and 35.4* (4 C-*t*-Bu), 51.4 (OCH$_3$), 76.8 (C-13c), 108.7* and 111.7* (C-13b, C-13d), 110.9 (C-6), 120.8 (C-4), 123.5 (C-10), 123.8 (C-12), 127.0 (C-13), 128.1 (C-9), 129.4 (C-3), 129.6*, 130.2*, and 133.7* (C-3a, C-9a, C-13a), 137.0 (C-8), 146.7 (C-11), 148.8 (C-2), 151.49*, 151.54*, and 154.7* (C-5, C-6a, C-7a), 201.9 (C-1). – MS (70 eV): m/e = 538 (100%, M$^+$), 507 (100%, M$^+$ – 31).

$$C_{37}H_{46}O_3 \ (538.7) \quad Calc. \ C \ 82.48 \ H \ 8.61 \quad Found \ C \ 82.61 \ H \ 8.73$$

b) *By oxidation of* **12b**: Xanthenol **12b** (70 mg, 0.14 mmol) in ether (6 ml) was treated with KOH (0.15 g) in methanol (15 ml) and oxidized with K$_3$[Fe(CN)$_6$] (1.5 g, 4.5 mmol) as described under a). The originally brown solution turned yellow after 15 h. TLC showed that **12b** had been completely consumed. After filtration of the reaction mixture, the ether was evaporated *in vacuo* and the remaining methanolic solution poured into saturated NH$_4$Cl solution (30 ml) to give a precipitate of **17b** which was washed with water and dried in the presence of P$_2$O$_5$: 40 mg (54%). The product was purified by precipitation from benzene with methanol containing 10% of water; the IR spectrum was identical with that of a sample prepared according to a).

2,5,8,11-Tetra-tert-butyldibenzo[a,k]xanthen-1-ol (12b)

a) *From quinol ether* **17b**: Glacial acetic acid (10 ml) was added to quinol ether **17b** (50.0 mg, 0.093 mmol) upon which a deep dark-blue colour immediately emerged. Subsequently, zinc dust (0.5 g) was added and the mixture stirred vigorously for 10 min. After filtration, the yellow solution was treated with water (20 ml). The resultant precipitate was filtered, extensively washed with water, and dried *in vacuo* in the presence of P$_2$O$_5$ to give 42 mg (90%) of **12b**; m.p. ≈ 170°C (red-violet melt). – IR (KBr): 2960 (aliphatic CH), 3552 cm^{-1} (OH). – ^{1}H NMR (CDCl$_3$, numbering as in **17b**): δ = 1.40 (s; 9H, *t*-Bu), 1.43 (s; 9H, *t*-Bu), 1.58 (s; 9H, *t*-Bu), 1.62 (s; 9H, *t*-Bu), 4.89 (s; 1H, OH), 6.95 (d, J = 1.2 Hz; 1H, 6-H), 7.29 (d, J = 1.2 Hz; 1H, 4-H), 7.55 (d, J = 9.2 Hz; 1H, 13-H), 7.56 (s; 1H, 3-H), 7.61 (dd, J = 9, 2 Hz; 1H, 12-H), 7.74 (s; 1H, 9-H), 7.77 (d, J = 1.8 Hz; 1H, 10-H). – ^{13}C NMR ([D$_4$]methanol): δ = 30.6*, 30.8*, 31.8*, and 31.9* (4 C-*t*-Bu), 35.4*, 35.6*, 36.1*, and 36.6* (4 C-*t*-Bu), 105.7 (C-6), 111.9 (C-13b), 116.1 (C-4), 116.2 (C-13c), 124.4 (C-13d), 126.7 (C-13a), 120.0*, 124.4*, 124.7*, 126.8*, and 127.5* (C-3, C-9, C-10, C-12, C-13), 130.6* and 132.8* (C-3a, C-9a), 138.9* and 144.1* (C-2, C-8), 147.9* and 148.7* (C-5, C-11), 148.9*, 150.7*, and 154.3* (C-1, C-6a, C-7a). – MS (70 eV): m/e = 508 (100%, M$^+$), 493 (10%, M$^+$ – 15).

$$C_{36}H_{44}O_2 \ (508.7) \quad Calc. \ C \ 84.98 \ H \ 8.72 \quad Found \ C \ 84.76 \ H \ 8.85$$

b) *From oxenium perchlorate* **15b**: Zinc powder (1.0 g) was added (water cooling) to **15b** (170 mg, 0.28 mmol) in acetic acid (10 ml). After 30 s the yellow solution was filtered by suction. The filtrate was treated with twice its volume of water, whereby a lemon-yellow precipitate was formed which was filtered by suction shortly afterwards. Yield 130 mg (91%); identical (IR spectrum) with a sample prepared according to a).

Oxidation of **12b** in benzene with PbO$_2$ in an atmosphere of N$_2$ gave a solution of **14b** ready for ESR measurement (see Figure 4).

(2,5,8,11-Tetra-tert-butyldibenzo[a,kl]xanthen-1-yl)oxenium perchlorate (**15b**): To *o*-quinol ether **17b** (750 mg, 1.39 mmol) in benzene (30 ml) 70% perchloric acid (1.5 ml) was slowly added while stirring. After 5 min the black-violet precipitate was filtered by suction, traces of benzene were removed in a high vacuum. Afterwards, the product was elutriated in water (30 ml) for 10 min, filtered by suction, and washed with water until the wash water was neutral. The product was dried *in vacuo* in the presence of P_2O_5. Yield 770 mg (91%).

If the benzene was not removed completely before starting the washing procedure, various amounts of the quinol **18b** were formed. The product still seemed to contain small amounts of excess perchloric acid, as may be judged from its elemental analysis. — IR (Nujol): 1090 (ClO), 1646 cm^{-1} (CO). — ^{1}H NMR (CDCl$_3$, immediately after dissolution): δ = 1.44 (s; 9H, *t*-Bu), 1.52 (s; 18H, *t*-Bu), 1.72 (s; 9H, *t*-Bu), 7.6—8.7 (m; 7H, aromatic ring protons).

$$C_{36}H_{43}ClO_6 \ (607.2) \quad \text{Calc Cl } 5.84 \quad \text{Found Cl } 6.25$$

The reaction with NaI/CH$_3$CO$_2$H can be used for quantitative determination of **15b**, if the liberated I_2 is titrated by adjusted Na$_2$S$_2$O$_3$ solution, provided that **18b** is absent. The perchlorate of **15b** is gradually converted into **8b**, which can be monitored by the IR absorption band of **8b** at 770 cm^{-1}.

Crystal structure determinations of **8b**[*]

One of the twinned crystals obtained by vapor diffusion of acetone into a benzene solution of **8b** could be cut to a specimen (0.7 × 0.5 × 0.1 mm^3), suitable for all further experiments. According to the diffraction symmetry and the systematic extinctions, the space group proved to be $P2_1/c$. The crystal data (CAD 4 Enraf Nonius diffractometer) are: a = 11.291(3), b = 10.748(3), c = 12.193(3) Å, β = 92.83(2)°, V = 1477.9 Å^3, $P2_1/c$, Z = 2, $C_{36}H_{42}O_2$, M^r = 506.7, μ = 0.45 mm^{-1}.

Intensities were collected within a 2Θ-range of 6—130° (Cu-K_α, graphite monochromator, ω/Θ-scan). After the usual Lp-correction, 2321 independent reflexions with F > 0 were used for further calculations.

With SHELX and MULTAN 80, we obtained phase sets which showed hexagons with central peaks in the subsequent E-maps ("chicken-wire-solution"). However, it was possible to trace out a correct fragment and with Fourier- and least squares techniques all atoms could be located. The hydrogen atoms were refined together with the corresponding carbon atoms as rigid groups (d_{C-H} = 0.96 Å) and a commonly refining isotropic temperature factor. With anisotropic temperature factors for the nonhydrogen atoms refinement converged at R = 0.05 and R_G = 0.048 (R_G = $[\sum w\Delta^2/\sum wF_0^2]^{1/2}$; unit weights proved to give a good analysis variance). A final difference Fourier synthesis was featureless. Scattering factors were taken from tables of *Cromer* and *Mann*[46] and *Cromer* and *Liberman*[47]. All calculations were performed with the programs SHELX (*G. M. Sheldrick*), MULTAN 80 (*P. Main*), PLUTO (*W. S. Motherwell*), and XANADU (*P. Roberts* and *G. M. Sheldrick*) on Telefunken TR 440 and UNIVAC 1100/80 computers at the Zentrum für Datenverarbeitung of the University of Tübingen. Atomic coordinates for the nonhydrogen atoms according to the numbering scheme in Fig. 1 are listed in Table 1.

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[*] Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany), by specifying registry number CSD 50741 and author with reference to this publication.

[1] X-ray analysis performed by these authors.
[2] [2a] *H. Meier, H. P. Schneider, A. Rieker,* and *P. B. Hitchcock,* Angew. Chem. **90**, 128 (1978); Angew. Chem., Int. Ed. Engl. **17**, 121 (1978). – [2b] *H. P. Schneider, W. Winter,* and *A. Rieker,* J. Chem. Res. (S) **1978**, 337; (M) **1978**, 3901.
[3] At present, the mechanism leading from **2** to **3** is virtually unknown. In any case, the *cis* form seems to be involved, although the normal configuration of **2** is *trans*; see also *F. R. Hewgill, B. La Greca, F. Legge,* and *P. E. Roga,* J. Chem. Soc., Perkin Trans. 1 **1983**, 131.
[4] *E. Müller, R. Mayer, B. Narr, A. Rieker,* and *K. Scheffler,* Liebigs Ann. Chem. **645**, 25 (1961).
[5] See literature quoted in ref. [2a]. For some more recent cases see: [5a] *M. Tashiro, H. Yoshiya,* and *G. Fukata,* J. Org. Chem. **46**, 3784 (1981). – [5b] *M. Tashiro, H. Yoshiya,* and *G. Fukata,* Synthesis **1980**, 495. – [5c] *F. R. Hewgill* and *G. B. Howie,* Aust. J. Chem. **31**, 907 (1978).
[6] *A. Rieker, N. Zeller, K. Schurr,* and *E. Müller,* Liebigs Ann. Chem. **679**, 1 (1966).
[7] [7a] *H. Bünzly* and *H. Decker,* Ber. Dtsch. Chem. Ges. **38**, 3268 (1905). – [7b] *R. Pummerer* and *F. Frankfurter,* Ber. Dtsch. Chem. Ges. **47**, 1472 (1914). – [7c] *R. Pummerer, E. Prell,* and *A. Rieche,* Ber. Dtsch. Chem. Ges. **59**, 2159 (1926). – [7d] *R. Pummerer* and *A. Rieche,* Ber. Dtsch. Chem. Ges. **59**, 2161 (1926). – [7e] *G. R. Clemo* and *R. Spence,* J. Chem. Soc. **1928**, 2815. – [7f] *A. Rieche, B. Elschner,* and *M. Landbeck,* Angew. Chem. **72**, 385 (1960). – [7g] *M. Landbeck,* Monatsber. Dtsch. Akad. Wiss. Berlin **3**, 657 (1961) [Chem. Abstr. **58**, 3382d (1963)].
[8] [8a] *A. Corbellini* and *A. Pasturini,* Gazz. Chim. Ital. **60**, 843 (1930). – [8b] *A. Corbellini* and *F. Vietti,* Gazz. Chim. Ital. **58**, 766 (1928). – [8c] For industrial interests see lit. quoted in ref. [8a] or: *Beilstein,* Handbuch der Organischen Chemie, Vol. 19/II, pp. 52, Springer, Berlin, Göttingen, Heidelberg 1952; Vol. 19/III/IV, pp. 448, Springer, Berlin, Heidelberg, New York 1977.
[9] *R. B. Contractor, A. T. Peters,* and *F. M. Rowe,* J. Chem. Soc. **1949**, 1995.
[10] *N. P. Buu-Hoi, H. LeBihan, F. Binon,* and *P. Rayet,* J. Org. Chem. **15**, 1060 (1950).
[11] *G. A. Razuvaev, M. L. Khidekel,* and *V. B. Berlina,* Dokl. Akad. Nauk SSSR, Ser. Khim. **145**, 1071 (1962) [Chem. Abstr. **58**, 3022h (1963)].
[12] *K. Schurr,* Doctoral Thesis, University of Tübingen 1964.
[13] *P. A. Brady, J. Carnduff,* and *D. G. Leppard,* Tetrahedron Lett. **1972**, 4183.
[14] *A. Rieker,* in Methoden der organischen Chemie (*Houben-Weyl-Müller*), 4. Edit., Vol. VII/3b, p. 765, Thieme, Stuttgart 1979.
[15] *S. P. Srivastava, A. K. Bhatnagar,* and *G. C. Joshi,* Spectrochim. Acta, Part A **37**, 797 (1981).
[16] *G.-P. Charbonneau* and *Y. Delugeard,* Acta Crystallogr., Sect. B **32**, 1420 (1976).
[17] *J. Trotter,* Acta Crystallogr. **14**, 1135 (1961).
[18] *A. Hargreaves* and *S. H. Rizvi,* Acta Crystallogr. **15**, 365 (1962).
[19] *A. Kerr* and *J. M. Robertson,* J. Chem. Soc. B **1969**, 1146.
[20] *A. Camerman* and *J. Trotter,* Proc. R. Soc. London, Ser. A **279**, 129 (1964).
[21] *Y. Kohno, M. Konno, Y. Saito,* and *H. Inokuchi,* Acta Crystallogr., Sect. B **31**, 2076 (1975).
[22] *A. Rieche, K. Kirschke,* and *M. Schulz,* Liebigs Ann. Chem. **711**, 103 (1968).
[23] The ether **17b** was also obtained in nearly quantitative yield by the anodic oxidation of **5b** in methanol/KOH; *E. Streich, H. P. Schneider,* and *A. Rieker,* to be published.
[24] *W. A. Waters,* J. Chem. Soc. B **1971**, 2026.
[25] Whether biradical **13** or the corresponding diamagnetic dinaphthoquinone[26] is an additional intermediate, and whether oxidation of **13** can directly lead to **14** is not discussed here, since our experiments were not designed to clarify this problem.
[26] *A. Rieche* and *W. Rudolph,* Ber. Dtsch. Chem. Ges. **73**, 335 (1940).
[27] *E. Streich* and *A. Rieker,* unpublished results.
[28] *B. Speiser* and *A. Rieker,* J. Chem. Res. (S) **1977**, 314; (M) **1977**, 3601.
[29] *G. H. Aylward* and *T. J. V. Findlay,* Datensammlung Chemie in SI-Einheiten, Verlag Chemie, Weinheim 1975. The potential of the SCE *vs* the SHE was taken as + 0.244 V at 25°C.
[30] *B. Speiser* and *A. Rieker,* J. Electroanal. Chem. **110**, 231 (1980).
[31] *F. R. Hewgill* and *F. Legge,* Tetrahedron Lett. **1977**, 1075; J. Chem. Soc., Perkin Trans. 2 **1983**, 653; c. f. *A. Tkáč, L. Omelka, L. Jiráčkova,* and *J. Pospíšil,* Org. Magn. Reson. **14**, 171 (1980).
[32] *J. B. Farmer, Y. Matsunaga,* and *C. A. McDowell,* Can. J. Chem. **37**, 634 (1959).
[33] *M. B. Neiman* and *A. A. L. Buchachenko,* Izv. Akad. Nauk SSSR, Otd. Khim. Nauk **1961**, 1742 [Chem. Abstr. **58**, 8879d (1963)].
[34] *W. T. Dixon, W. E. J. Foster,* and *D. Murphy,* J. Chem. Soc., Perkin Trans. 2 **1978**, 779; and literature cited therein.

[35] *Via* intramolecular electrophilic aromatic substitution.

[36] Addition of the oxyl oxygen to the aromatic system of the adjacent naphthalene ring at C-13 might be the starting step. The resulting cyclohexadienyl radical needs further monovalent dehydrogenation to give **8b**[6].

[37] *P. E. Hansen*, Org. Magn. Reson. **12**, 109 (1979).

[38] *K. Scheffler*, University of Tübingen, unpublished results; see also *K. Scheffler* and *H. B. Stegmann*, Ber. Bunsenges. Phys. Chem. **67**, 864 (1963).

[39] Although 3 equivalents of 2,4,6-tri-*tert*-butylphenoxyl for 1 equivalent of **9** are necessary to form **8b**, only two equivalents of the phenoxyl were used for two reasons: (1) we were mainly interested in isolating **7**, a twovalent oxidation product of **9**; (2) a test experiment with 3 equivalents did not improve the yield of **8b**, apparently because, due to the long reaction time, more decomposition products of 2,4,6-tri-*tert*-butylphenoxyl were formed.

[40] [40a] *E. Müller* and *K. Ley*, Chem. Ber. **87**, 922 (1954). – [40b] *E. Müller*, *K. Ley*, and *W. Kiedaisch*, Chem. Ber. **87**, 1605 (1954).

[41] The contents of active phenoxyl were determined by reduction of ca. 5 ml of the benzene solution with NaI/acetic acid and titrating of the formed iodine by 0.1 N $Na_2S_2O_3$[40]. Typical preparations contained ca. 90 mg (0.34 mmol) of 2,4,6-tri-*tert*-butylphenoxyl in 1 ml.

[42] In one experiment, working up after 4 weeks, the yield amounted to 35% (relative to **9**). Evaporation of the mother liquor and treating of the residue with methanol yielded another 600 mg (30%), which contained **5b** (IR spectrum).

[43] Two equivalents would be necessary to form **8b** completely, see however the arguments given[39].

[44] Such a colour is not produced by a solution of pure **17b**.

[45] For the numbering of the ring carbon atoms of **17** see Figure 3.

[46] *D. T. Cromer* and *J. B. Mann*, Acta Crystallogr., Sect. A **24**, 321 (1968).

[47] *D. T. Cromer* and *D. L. Liberman*, J. Chem. Phys. **53**, 1891 (1970).

[339/83]