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BASE-CATALYZED OXYGENATION OF 2,6-DI-t-BUTYLANILINES

X-RAY ANALYSIS OF 2,4,6-TRI-t-BUTYL-4,5-EPOXY-6-HYDROXY-2-CYCLOHEXEN-1-IMINE

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Abstract—Oxygenation of 2,4,6-tri-t-butylaniline (**1a**) catalyzed by t-BuOK in hexamethylphosphoric triamide (HMPA) at 75° leads to the incorporation of molecular oxygen into the aromatic ring giving rise to 2,4,6-tri-t-butyl-4,5-epoxy-6-hydroxy-2-cyclohexen-1-imine (**2a**). A similar result is obtained in the oxygenation of 2,6-di-t-butyl-4-phenylaniline (**1b**). The oxygenation of **1a** in toluene containing n-BuLi gave exclusively 2,4,6-tri-t-butylnitrosobenzene. The oxygenation of 2,6-di-t-butyl-4-methoxyaniline (**1d**) in tetrahydrofuran with n-BuLi gave dimeric products in fairly good yields. The structure of **2a** has been confirmed by X-ray analysis. The crystals are monoclinic ($P2_1/a$) with a = 9.99, b = 23.16, c = 8.70 Å, β = 116.19°; Z = 4. The structure was determined by direct methods and refined to R = 0.089.

In the base-catalyzed oxygenation of anilines, molecular oxygen normally attacks the N atom to give the corresponding azobenzenes.[1–3] In contrast to those anilines, t-butylated anilines are expected to behave differently towards the base-catalyzed oxygenation as judged from the results obtained in the base-catalyzed oxygenation of t-butylated phenols.[4–7] We have, therefore, investigated the base-catalyzed oxygenation of 4-substituted 2,6-di-t-butylanilines.

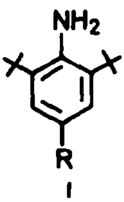
In these experiments, we have found that 2,4,6-tri-t-butyl- and 2,6-di-t-butyl-4-phenyl- anilines undergo the oxygenation at 70° in hexamethylphosphoric triamide (HMPA) containing t-BuOK, giving rise to 4,5-epoxy-6-hydroxy-2-cyclohexen-1-imine derivatives, which resulted from the incorporation of molecular oxygen into the aromatic ring. The reaction path in the oxygenation is affected by the substituent at the para position and by the base used.

RESULTS AND DISCUSSION

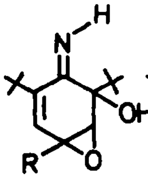
1. *Oxygenation of* 2,4,6-*tri*-*t*-*butylaniline* (**1a**) *and* 2,6-*di*-*t*-*butyl*-4-*phenylaniline* (**1b**). The oxygenation was carried out by bubbling oxygen through the solutions of anilines **1** in appropriate solvents containing t-BuOK or n-BuLi. 2,4,6-Tri-t-butylaniline (**1a**) is not susceptible to the oxygenation in t-BuOK/t-BuOH or in $NaNH_2$/HMPA even at elevated temperatures. When the oxygenation of **1a** was carried out in t-BuOK/HMPA at 75°, a product (**2a**) in which molecular oxygen is incorporated into the starting aniline was obtained in 61% yield.

Similar results are observed in the oxygenation of **1b** in t-BuOK/HMPA, although complete separation of **2b** was not successful. The NMR spectrum of the reaction mixture, however, clearly shows the formation of **2b** in about 60% yield. The difficulty of the separation of **2b** may be due to contamination with a side product that behaves similarly on tlc.

Structure of **2a**. The ^1H *NMR spectrum* shows two characteristic signals for the olefinic proton H-3 (1 H, d, J = 0.6 Hz) and the methine proton H-5 (1 H, d, J = 0.6 Hz) attached to the carbon bearing the oxirane C–O bond. From the ^1H NMR spectrum, two possible structures (**2a** and **2a'**) may be deduced.



1



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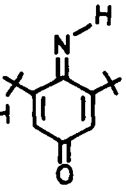

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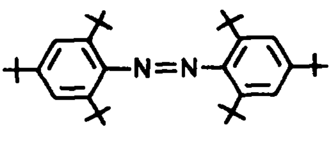

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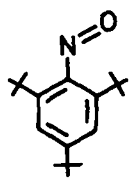

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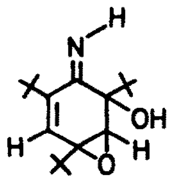
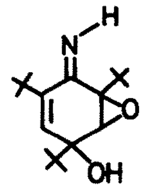
a: R = t-Bu; **b**: R = Ph; **c**: R = Me; **d**: R = OMe



2a



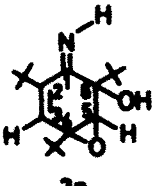
2a'

As can be seen from a comparison of the ^{1}H NMR data of the product with those of the epoxy-quinols[4,5] obtained in the regioselective oxygenation of 2,4,6 - tri - t - butyl - phenol, chemical shifts do not allow any distinction between **2a** and **2a'**. However, the coupling constants of H-3 and H-5 suggest that the structure is analogous to that of the epoxy-*o*-quinol, i.e. **2a** (Table 1). The structure **2a** is further supported by *^{13}C NMR spectroscopy* (Table 2).

This shows 3 signals in the double bond region at $\delta = 175.1$, 149.2 and 129.5 ppm. The signal at $\delta = 129.5$ is tertiary (off-resonance spectrum) and is, therefore, attributed to C-3. The signal at $\delta = 149.2$ is relatively broad and was originally thought to belong to carbon 1 attached to the nitrogen atom. However, the coupled spectrum shows the broad multiplet typical for C atoms bearing a t-Bu group indicating that the signal at δ 149.2 belongs to C-2. The signal at the lowest field ($\delta = 175.1$) shows a coupling pattern of 4 lines. There is no doubt that this signal is caused by C atom 1. In the corresponding epoxy-*o*-quinols[8] C-1 is coupled to H-3 and H-5 with different coupling constants (a doublet of doublets). A model system **3** shows coupling of C-1 with H-3, H-5 ($^3J_{C-H}$) and N-H ($^2J_{C-H}$) of about equal size (*ca.* 9 Hz). Therefore, one would expect that C-1 in **2a** also couples with H-3, H-5 *and* N–H. However, the intensities of the C-1 signal correspond more to a doublet of doublets (2 unequal protons) than to a quartet (3 equal protons). A final decision can be made only by single frequency decoupling. The remarkably low shift value of the imino group carbon (C-1) seems to be a consequence of the H-bond between OH and N (*vide infra*).

The 3 signals of the aliphatic ring C atoms are located at $\delta = 59.3$, 64.6 and 79.4 ppm. C atom 5 can easily be recognized from the off-resonance spectrum. Its shift value is typical for an unsubstituted oxirane-ring C atom in epoxy-*o*- and epoxy-*p*-quinols.[8] As in the case of epoxy-*o*-quinols C-5 is weakly coupled to H-3 (about 2.5 Hz), whereas such a coupling is not observed for C-3/H-5.[8] The signals of C-4 and C-6 cannot be distinguished by coupling experiments. However, the signal at higher field ($\delta = 64.6$ ppm) should belong to the C atom 4 of the oxirane ring. This assignment is in good agreement with the shift sequence in epoxy-*o*-quinols.[8]

Table 2. ^{13}C NMR spectrum of **2a**



2a

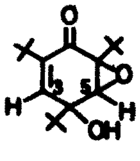
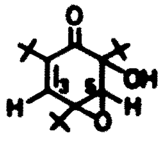
Carbon atom	δ_{ppm} (from TMS, CDCl$_3$)
C-1	175.1
C-2	149.2
C-3	129.5
C-4	64.6
C-5	59.3
C-6	79.4

The signals of the t-butyl C atoms at $\delta = 32.9$, 35.6 and 36.8 ppm (quaternary) and $\delta = 23.7$, 26.2 and 30.6 ppm (Me groups) cannot be assigned definitely since compounds for comparison are missing. However, the pattern is similar to that of tri - t - butyl - epoxy - *p* - quinol.[8]

The results of the *X-ray analysis* confirm the structure of **2a** (Fig. 1).[9] Bond lengths, bond angles and the dihedral angles in the 6-membered ring are collected in Fig. 2. The conformation of the 6-membered ring is similar to that of Δ^3-norcarene[10a] and 1,3-cyclohexadiene[10b] with C-1 and C-2 having the greatest deviations from the plane of the ring (0.20 and −0.20 Å). This conformation leads to a non planar *trans* - 1 - aza - butadiene moiety with a (C-3)–(C-2)–(C-1)–(N-16) dihedral angle of 154° and an axial position of the t-Bu group on C-6 relieving the strain in the molecule. Bond angles and bond lengths are in the expected range except the quite long bond length (C-1)–(C-6) (1.59 Å) and the bond angles on C-1. Both deviations from normal values may be caused by the t-Bu groups at C-2 and C-6. The positions of the H atoms bound to C-3, C-5, N-16 and O-17 are too uncertain to be discussed in detail; the big deviations from usual bond angles may also be due to the steric effect of the t-Bu groups. In the crystal two molecules related by the symmetry operation $\bar{x}, \bar{y}, \bar{z}$ are connected by an intermolecular H-bond (O-7)–(O-17) with a distance O–O of 2.773 Å. The same effect is reported for an epoxy-*p*-quinol.[11] In solution, intramolecular H-bonds (O-7)–(O-17) and (O-17)–(N-16) via H-16 may also be possible.

Mechanistic considerations. Taking the observations on the base-catalyzed oxygenation of 2,4,6 - tri - t - butylphenol into account, the product **2a** should result

Table 1. Comparison of the ^{1}H NMR data of **2a** with those of epoxy-quinols (δ_{ppm} from TMS, CDCl$_3$)

			**2a**
H-3	5.98 (d, J=3.2 Hz)	6.98 (d, J=1 Hz)	6.40 (d, J=0.6 Hz)
H-5	3.65 (d, J=3.2 Hz)	3.80 (d, J=1 Hz)	3.70 (d, J=0.6 Hz)

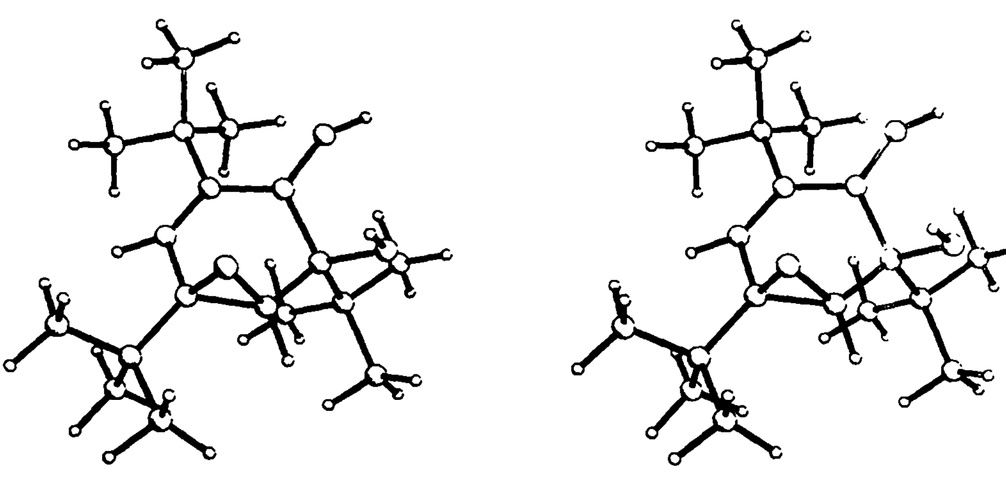
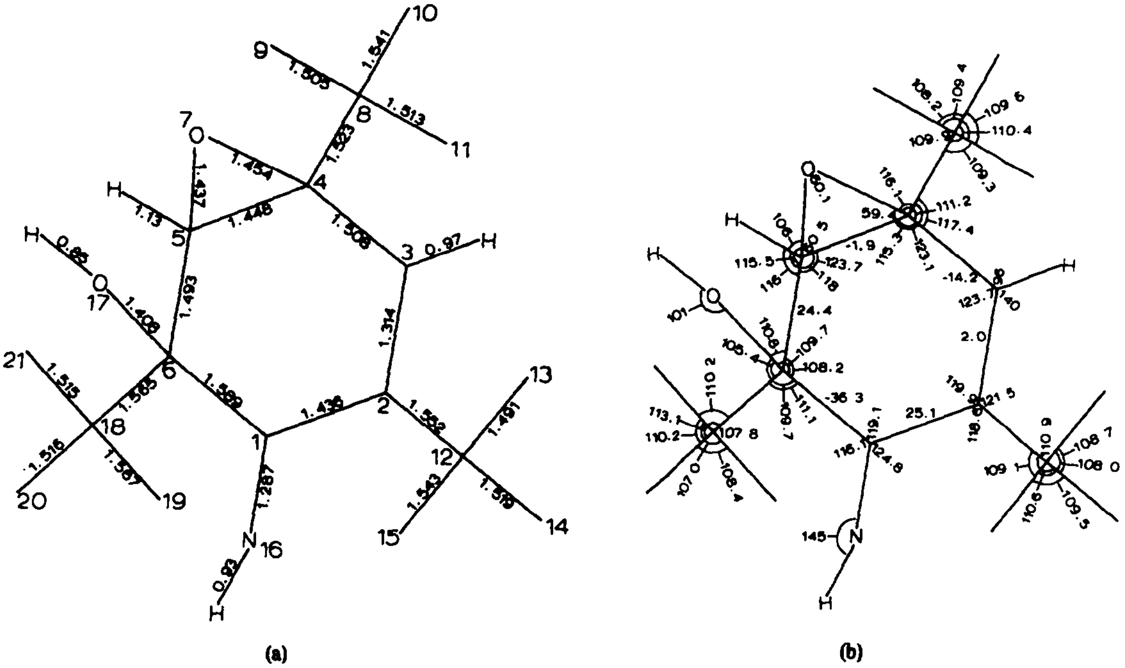


Fig. 1. Molecular structure of 2a.



(a) (b)

Fig. 2. Bond lengths in Å (a), bond angles and dihedral angles in the six membered ring in degrees (b); standard deviations: $\sigma_{XX} = 0.009$ Å, $\sigma_{XH} = 0.08$ Å, $\sigma_{XXX} = 0.4°$, $\sigma_{XXH} = 4°$; $\sigma_{XXXX} = 0.8°$; X = C, N, O.

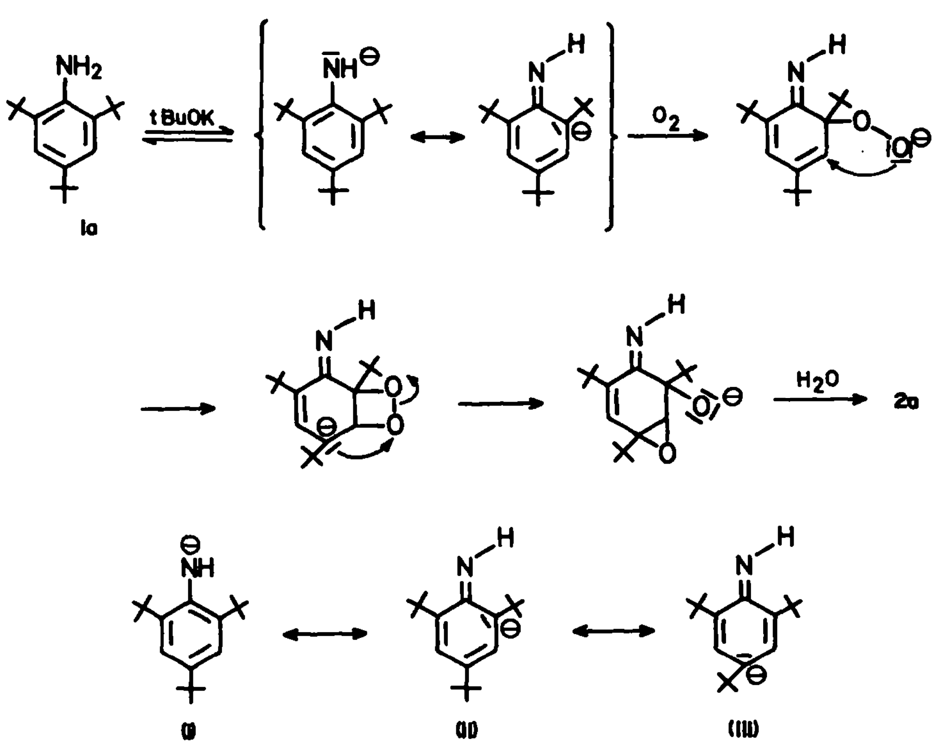
from the *ortho* hydroperoxylation of the anionic form of **1a** (Scheme 1).

Molecular oxygen attacks exclusively the *para* position of 2,4,6 - tri - t - butylphenol in t-BuOK/HMPA.[4] Contrary to this, molecular oxygen attacks predominantly the *ortho* position of **1a** in t-BuOK/HMPA. The difference may be rationalized by considering that the ring carbanion structure of **1a** will arise on the *ortho* position (ii) due to the steric repulsion between imino group and the adjacent t-Bu groups in the resonance structure (iii). Another possibility that the potassium ion is associated with the anion close to the N-(C-2)-(C-6) area can also be considered.

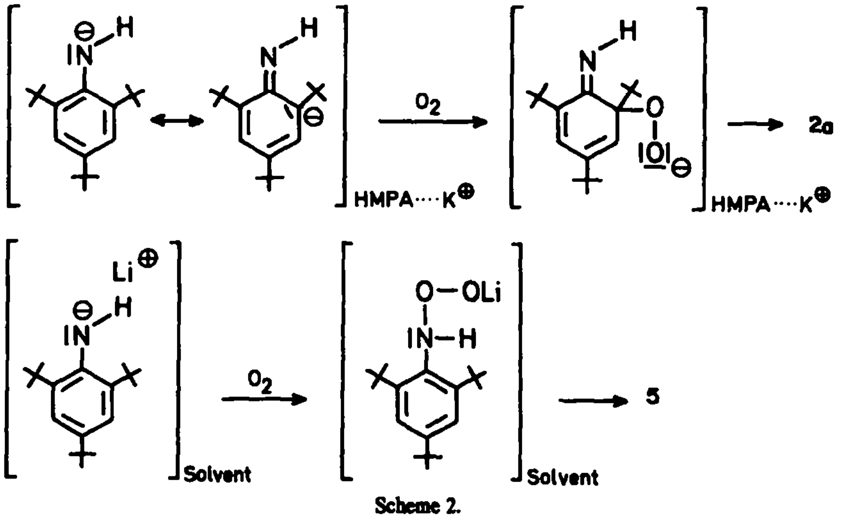
A second product in the oxygenation of **1a** was 2,2',4,4',6,6' - hexa - t - butyl - azobenzene **4** (8% yield), which has been obtained also in the electrochemical oxidation of **1a**.[12]

The yields of the oxygenation products from **1a** are extremely dependent on the base employed. When **1a** was oxygenated in the presence of n-BuLi in toluene, tetrahydrofuran or hexane, no epoxy product **2a** was formed. Instead, 2,4,6 - tri - t - butylnitrosobenzene (**5**) was formed predominantly (58%). The results are rationalized by means of the different structure of the anionic species of **1a**. With *t*-BuOK in HMPA the amount of anionic species present must exist as a free anion form which shows a strong carbanion character on the aromatic ring by resonance, whereas with n-BuLi in aprotic solvents the anion must be located just on the N atom, associated with $Li^{\oplus}$. Oxygen will then attack the "carbanion" in the former and the N atom in the latter (Scheme 2).

Since the azobenzene **4** was not formed when **5** was treated with **1a** in t-BuOK/HMPA at 75°, **4** would not be



Scheme 1.



Scheme 2.

formed by the reaction between them, which is not compatible with the mechanism suggested for the base-catalyzed oxygenation of aniline giving rise to azobenzene.[1] The mechanism of the formation of 4 is still obscure, although a radical process may be relevant (Scheme 3).[13] A radical chain autoxidation mechanism can also be applied for the present oxygenation.

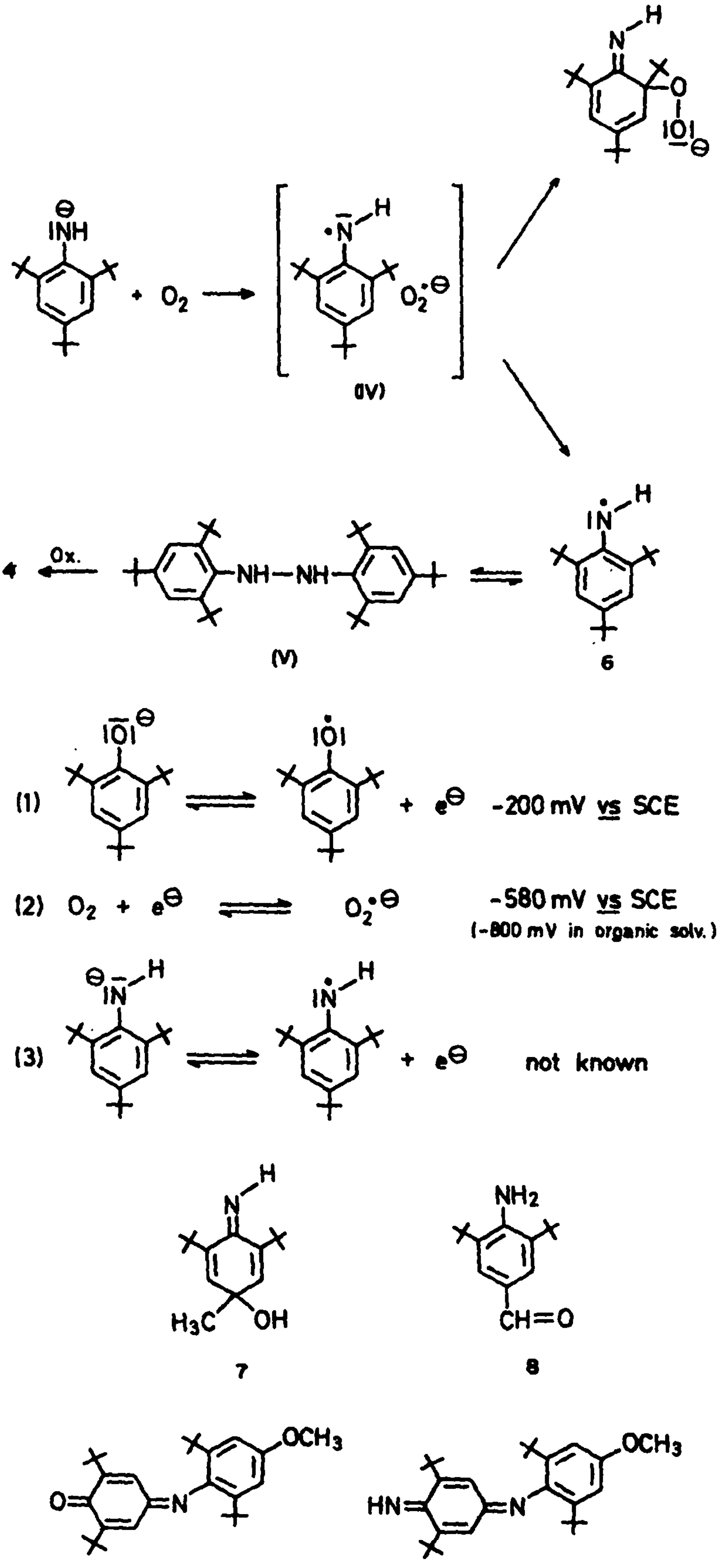
The formation of a cage radical pair analogous to iv can be excluded for the case of the base-catalyzed oxygenation of 2,4,6 - tri - t - butylphenol,[14] which is reasonable since the formal potentials for the two processes (1)[15] and (2)[16] are very different. In the case of the reactions (2) and (3), however, they might be of the same order of magnitude.[17]

Moreover, chemical oxidation of 1a with alkaline $K_3[Fe(CN)_6]$ or PbO_2 leads to the aminyl radical 6,[18–20] which dimerizes to give the azo derivative 4, although the yield of the latter is also moderate.

If the intermediate formation of the aminyl radical 6 in the oxygenation of 1a is accepted, the above mentioned formation of 5 can also be explained by a reaction of 6 with molecular oxygen.

2. *Oxygenation of* 1c *and* 1d. The oxygenation of anilines 1c and 1d in t-BuOK/HMPA gave a complex mixture. Attempts to isolate the products were not successful. At 0° in t-BuOK/HMPA 1c affords after 15 min of oxygenation 50% of the quinol imine 7 and 16% of the aldehyde 8. On this reaction we will report separately.

The oxygenation of 1d in n-BuLi/THF at 60°, on the other hand, gave dimeric products 9 and 10 in 47 and 30% yields, respectively. The structures 9 and 10 are assigned from the analytical and spectral data of these



(IV)
Ox.
4
(V)
6
(1)
+ e⊖ -200 mV vs SCE
(2) O2 + e⊖ ⇌ O2•⊖ -580 mV vs SCE
(-800 mV in organic solv.)
(3)
+ e⊖ not known
H3C OH
CH=O
NH2
OCH3
HN
7
8
9
10

Scheme 3.

products and comparison with other sterically hindered quinone anils[21] (see Experimental). Compound 9 has also been obtained by electrochemical oxidation of 1d in methanol ($E_{1/2} = 570$ mV vs SCE[12b]).

When the oxygenation of 1d was carried out at −70°, conversion was 73% and chromatographic separation of the products gave 9 (30% yield) and 2,6 - di - t - butyl - *p* - benzoquinone monoimine (3, 27% yield), yellow prisms from petroleum ether (IR, NMR, and elemental analysis). This imine is the main reaction product in the electrochemical oxidation of 1a in the presence of water.[12a,22] The product 9 seems to arise from 10 during the work-up of the reaction mixture. In fact, 9 is formed quantitatively upon treatment of 10 with dil. HCl solution. This assumption is further supported by the fact that no formation of 9 is observed when the work-up is carried out using NH_4Cl instead of HCl. The formation of 10 is reasonably explained by coupling between 3 primarily formed and the anionic form of 1d (Scheme 4). Indeed, the reaction of 3 with the anionic form of 1d gave 10 in about 50% yield. However, another mechanism by which 10 is formed via N–C_{para} dimerization of the corresponding aminyl radical of 1d followed by elimination of MeOH cannot be entirely excluded.

The mechanism for the formation of 3 is obscure. One possibility, partial hydrolysis of 10, is not probable since the acid catalyzed hydrolysis normally leads to 9 (*vide supra*).

EXPERIMENTAL

General. All m.ps are uncorrected. Elemental analyses were performed by the Analytical Center of Kyoto University. IR spectra were recorded with a JASCO IRA-1 spectrometer. ^1H NMR spectra were recorded with a Varian T-60 or Bruker HFX 90 spectrometer using TMS as the internal reference. ^{13}C NMR spectra were obtained on a Bruker HFX 90 spectrometer connected to a Bruker–Nicolet BNC 12 computer. A radio-frequency pulse of 3.5 μs was applied up to 60,000 times (for non-decoupled spectra) with a repetition time of 0.68 s over the spectrum width of 6024 Hz.

X-ray analysis of 2a

Crystal data. Colourless prisms, recrystallized from hexane, m.p. 144–145°, $C_{18}H_{31}NO_2$, M = 293.5; space group $P2_1/a$, a = 9.99 (1), b = 23.16 (1), c = 8.70 (1) Å, $\beta = 116.19$ (5)°, V = 1805.3 Å^3, z = 4; $D_{exp} = 1.08$ g cm^{-3}, $D_X = 1.080$ g cm^{-3}.

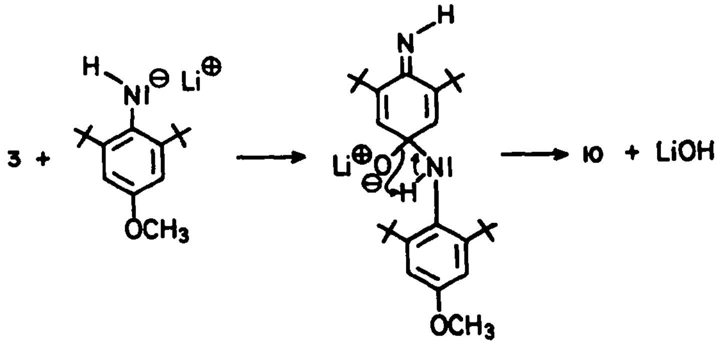
Intensities were collected on a two-circle diffractometer ($Cu_{K\alpha}$ radiation) equipped with a graphite monochromator; the crystal was oriented along *c*. 2455 reflexions with $3° < \theta < 62.5°$ hk0–hk5 were measured. 1835 reflexions with $|F| > 2\sigma_F$ were used for structure determination and refinement.

The structure was solved by direct methods with SHELX-76[23] which uses scattering factors from *International Tables for X-ray Crystallography*.[24] Anisotropic refinement of all C, O and N atoms with calculated positions for the H atoms of the t-Bu groups and positions of the four H atoms from a difference synthesis dropped the R-factor to 0.089. The final parameters are listed in Tables 3 and 4.

Preparation of the starting materials. Compound 1a was prepared according to the recorded procedure.[25] Compounds 1b and 1c were prepared by the reaction of 3 with phenyllithium and methyllithium, respectively, followed by the reduction of the resulting iminoquinols[22] with Zn/HCl. Compound 1d was prepared by modification of the method given by Cauquis *et al.*;[12a]

Table 3. Positional parameters of 2a

Atom	x	y	z
C 1	0.6765(4)	0.6073(2)	0.1470(8)
C 2	0.6839(4)	0.6143(2)	0.3146(8)
C 3	0.5649(4)	0.6047(2)	0.3388(6)
C 4	0.4178(4)	0.5844(2)	0.1998(8)
C 5	0.4026(5)	0.5890(2)	0.0267(9)
C 6	0.5199(5)	0.6137(2)	-0.0163(6)
O 7	0.4374(3)	0.5340(1)	0.1119(4)
C 8	0.2850(4)	0.5828(2)	0.2416(6)
C 9	0.3177(6)	0.5430(3)	0.3908(8)
C10	0.1451(6)	0.5603(3)	0.0869(8)
C11	0.2558(6)	0.6430(2)	0.2873(8)
C12	0.8356(4)	0.6310(2)	0.4652(8)
C13	0.8172(5)	0.6449(3)	0.6223(8)
C14	0.9021(5)	0.6832(2)	0.4183(7)
C15	0.9439(5)	0.5795(2)	0.5067(7)
N16	0.7886(4)	0.5955(2)	0.1170(6)
O17	0.5234(4)	0.5844(1)	-0.1563(4)
C18	0.4871(4)	0.6783(2)	-0.0738(6)
C19	0.3286(5)	0.6811(2)	-0.2298(6)
C20	0.4881(5)	0.7176(2)	0.0659(6)
C21	0.5975(6)	0.6996(2)	-0.1369(8)
H 3	0.531(6)	0.608(3)	0.427(8)
H 5	0.288(7)	0.585(3)	-0.083(8)
H16	0.843(7)	0.607(3)	0.059(8)
H17	0.524(7)	0.549(3)	-0.126(8)



Scheme 4.

Table 4. Anisotropic temperature factors in the form $T = \exp - 2\pi^2(a^{+}U_{11}h^2 + b^{+}U_{22}k^2 + c^{+}U_{33}l^2 + 2a^{+}b^{+}U_{12}hk + 2a^{+}c^{+}U_{13}hl + 2b^{+}c^{+}U_{23}kl)$, all hydrogen atoms: $U = 0.10\ \text{Å}^2$

Atom	U11	U22	U33	U23	U13	U12
C 1	0.032(3)	0.039(3)	0.044(5)	-0.003(3)	0.021(3)	0.002(2)
C 2	0.031(2)	0.040(3)	0.010(4)	-0.005(3)	0.012(2)	0.006(2)
C 3	0.023(2)	0.040(3)	0.013(4)	-0.005(2)	0.003(2)	0.002(2)
C 4	0.032(2)	0.031(2)	0.020(4)	-0.007(3)	0.011(3)	-0.001(2)
C 5	0.036(3)	0.034(3)	0.033(5)	0.000(3)	0.013(3)	-0.005(2)
C 6	0.039(2)	0.034(3)	0.018(4)	-0.003(2)	0.012(2)	0.003(2)
O 7	0.054(2)	0.034(2)	0.045(3)	-0.008(2)	0.018(2)	-0.006(1)
C 8	0.029(2)	0.052(3)	0.027(4)	-0.007(3)	0.009(2)	-0.006(2)
C 9	0.058(3)	0.090(5)	0.080(6)	0.032(4)	0.044(4)	-0.001(3)
C10	0.035(3)	0.150(7)	0.066(5)	-0.035(5)	0.013(3)	-0.032(4)
C11	0.051(3)	0.069(4)	0.101(6)	-0.007(4)	0.044(4)	0.010(3)
C12	0.025(2)	0.057(3)	0.033(4)	-0.007(3)	-0.003(2)	-0.001(2)
C13	0.039(3)	0.093(4)	0.058(5)	-0.021(4)	-0.011(3)	-0.014(3)
C14	0.038(3)	0.078(4)	0.074(5)	0.011(4)	-0.002(3)	-0.018(3)
C15	0.034(3)	0.080(4)	0.080(5)	0.001(4)	-0.003(3)	0.017(3)
N16	0.048(3)	0.101(4)	0.075(5)	0.009(3)	0.043(3)	0.015(2)
O17	0.075(2)	0.049(2)	0.036(3)	-0.008(2)	0.028(2)	0.003(2)
C18	0.034(2)	0.042(3)	0.041(4)	0.007(3)	0.010(3)	0.002(2)
C19	0.061(3)	0.064(3)	0.040(4)	0.011(3)	-0.006(3)	0.007(3)
C20	0.060(3)	0.036(3)	0.050(4)	-0.006(3)	0.013(3)	0.006(2)
C21	0.084(4)	0.067(4)	0.077(5)	0.025(3)	0.058(4)	0.006(3)

i.e. a soln of **1a** (6.5 g, 25 mmol) and MeOH (10 ml) in acetonitrile (500 ml) was anodically oxidized in the presence of sodium perchlorate (8.0 g) as supporting electrolyte. The material of the electrodes was graphite (anode) and stainless steel (cathode). The electrolysis was performed at constant current (200 mA; anodic potential *ca.* + 1 V vs SCE; voltage between cathode and anode: *ca.* 3 V) for about 8 hr. Afterwards, the solvent was removed *in vacuo* and the residue was extracted with petroleum ether. The extract, which contained 2,4,6 - tri - t - butyl - 4 - methoxy - 2,5 - cyclohexadienimine, was chromatographed on a silica gel column eluting with a mixture of petroleum ether and benzene to give **1d**, yield: 70–80%; m.p. 85°.

Oxygenation of 2,4,6 - *tri - t - butylaniline* (**1a**) *in* HMPA/t-BuOK. O_2 was bubbled through a soln of **1a** (1.0 g) and t-BuOK (2.0 g) in HMPA (30 ml) at 75° for 8 hr. The resulting yellow soln was poured into ice-cooled water, and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to leave a yellow semicrystalline residue. Trituration of the residue with hexane gave **2a** (0.35 g), colourless prisms from hexane, m.p. 144–145°; IR (Nujol) 3460 (OH), 1605 (C=N–) cm^{-1}; NMR ($CDCl_3$) δ 0.97 (s, 9 H), 1.04 (s, 9 H), 1.30 (s, 9 H), 3.70 (d, J = 0.6 Hz, 1 H), 6.40 (d, J = 0.6 Hz, 1 H), 10.2 (broad s, 1 H, NH). (Found: C, 73.78; H, 10.66; N, 4.87. Calc. for $C_{18}H_{31}NO_2$: C, 73.67; H, 10.65; N, 4.77%).

The filtrate, after removal of **2a**, was chromatographed on a column of neutral alumina. Elution with petroleum ether gave **4** (0.06 g), orange prisms from MeOH, m.p. 245–247°, lit.[15] 237–238°; IR (Nujol) 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.27 (s, 36 H), 1.33 (s, 18 H), 7.30 (s, 4 H). (Found: C, 83.17; H, 11.57; N, 5.53. Calc. for $C_{36}H_{58}N_2$: C, 83.33; H, 11.27; N, 5.40%).

Subsequent elution with petroleum ether gave the starting aniline **1a** (0.25 g) and with benzene gave additional amount of **2a** (0.23 g).

Oxygenation of **1a** *in toluene containing* n-BuLi. A soln of **1a** (0.26 g) in anhyd toluene (10 ml) was cooled at −78° under N_2. To this soln n-BuLi soln (15% in hexane, 1 ml) was added at once. O_2 was then bubbled through the resulting mixture (exothermic!). The soln turned red-violet, then green, and finally yellow-brown. O_2 bubbling was continued at 90° for 2 hr. The mixture was poured into ice-cooled water, acidified with dil. HCl acid and extracted with ether. The extract was dried (Na_2SO_4) and evaporated to leave a crystalline residue. Tlc of the residue showed 5 spots including the starting aniline. The residue was chromatographed on a silica gel column. Elution with petroleum ether gave **5** (0.08 g, 29%), blue-green needles from MeOH, m.p. 164–166°, lit.[26] 167–168°; IR (Nujol) 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.19 (s, 18 H), 1.31 (s, 9 H), 7.34 (s, 2 H). (Found: C, 78.39; H, 10.90; N, 4.89. Calc. for $C_{18}H_{29}NO$: C, 78.49; H, 10.61; N, 5.09%).

Attempts to isolate the other products detected by tlc were not successful. No compound **2a** was detected by NMR.

Oxygenation of 2,6 - *di - t - butyl - 4 - phenylaniline* (**1b**) *in* HMPA/t-BuOK. O_2 was bubbled through a soln of **1b** (0.15 g) and t-BuOK (0.30 g) in HMPA (10 ml) at 75° for 8 hr. The mixture was poured into ice-cooled water and extracted with ether. The extract was washed with water, dried (Na_2SO_4) and evaporated to leave a yellow oily residue. Separation of the residue by means of neutral alumina tlc developing with benzene afforded the starting aniline **1b** (0.02 g) and crude **2b** (0.11 g). Further attempts to purify the crude **2b** were not successful, but the NMR spectrum of the latter product confirms the presence of **2b** (about 60% yield) from the characteristic signals for H-3 [δ 6.47 (d, J = 0.6 Hz, 1 H)] and H-5 [δ 3.57 (d, J = 0.6 Hz, 1 H)] as well as of the other groups in **2b**.

Oxygenation of 2,6 - *di - t - butyl - 4 - methoxyaniline* (**1d**) *in THF containing* n-BuLi. A soln of **1d** (0.46 g) in THF (10 ml) was cooled at −78° under N_2. To this soln was added n-BuLi soln (15% in hexane, 2.5 ml) at once. O_2 was then bubbled through the resulting mixture (exothermic!). The soln turned brown. O_2 bubbling was continued at 60° for 30 min. The mixture was evaporated, treated with HCl aq, and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to leave an oily residue (violet-brown), which was chromatographed on a silica gel column. Elution with CH_2Cl_2 gave **9** (0.2 g), violet prisms from methanol, m.p. 128–130°; IR (Nujol) 1640 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.07 (s, 9 H), 1.20 (s, 18 H), 1.34 (s, 9 H), 3.84 (s, 3 H), 6.17 (d, J = 3.0 Hz, 1 H), 6.92 (s, 2 H), 7.13 (d, J = 3.0 Hz, 1 H). (Found: C, 79.43; H, 9.86; N, 3.15. Calc. for $C_{29}H_{43}NO_2$: C, 79.58; H, 9.90; N, 3.20%).

Further elution with CH_2Cl_2 gave **10** (0.13 g), red-brown prisms from MeOH, m.p. 148–150°; IR (Nujol) 3360 (NH), 3400 (broad, NH_2), 1600, 1570 (Ar, C=N–) cm^{-1}; NMR ($CDCl_3$) δ 1.17 (s, 9 H), 1.22 (s, 18 H), 1.43 (s, 9 H), 3.82 (s, 3 H), 5.87 (d, J = 2.4 Hz, 1 H), 6.81 (d, J = 2.4 Hz, 1 H), 6.86 (s, 2 H). (Found: C, 79.40; H, 10.48; N, 6.39. Calc. for $C_{29}H_{44}N_2O$: C, 79.76; H, 10.16; N, 6.42%).

Acid hydrolysis of **10** *to* **9**. A soln of **10** (10 mg) in THF (1 ml) was shaken with a small amount of 10% HCl aq at room temp. for a few min. A usual work-up of the mixture gave **9** quantitatively (tlc, NMR). In a separate experiment, where **1d** (0.45 g) was oxygenated at −78° for 30 min, the mixture was acidified with NH_4Cl aq and extracted with ether. The extract was dried (Na_2SO_4) and evaporated to dryness. The residue was chromatographed on a silica gel column. Elution with a mixture of CH_2Cl_2 and petroleum ether (1:1) gave the starting aniline **1d** (0.13 g). Elution with CH_2Cl_2 gave **10** (0.15 g). Further elution with CH_2Cl_2 gave **3** (0.11 g), which was identified with an authentic sample (m.p. 78–80°; IR and NMR). No compound **9** was obtained in this procedure.

Reaction of **3** *with the anionic form of* **1d**. A soln of **1d** (0.47 g, 2 mmol) in abs THF (5 ml) was mixed with 2 N n-BuLi in hexane (1.2 ml) at −60°. To the resulting soln was added a soln of **3** (0.44 g, 2 mmol) in abs THF (5 ml). The mixture showed intense violet color instantaneously. After 10 min, the mixture was poured into excess of NH_4Cl aq and extracted with ether. The extract was dried (Na_2SO_4) and evaporated to give a redviolet residue, whose ^1H NMR spectrum showed the formation of **10** (50% yield). The starting materials were recovered in 30% yield (estimated by NMR).

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