Tetrahedron Letters Vol. 21, pp 1265 - 1268 0040-4039/80/0322-1265$02.00/0
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NEW 1,1-AMINO HYDROPEROXIDES FROM REGIOSELECTIVE OXYGENATION OF 4-(N-ARYLMETHYLENEAMINO)-2,6-DI-t-BUTYLPHENOLS.

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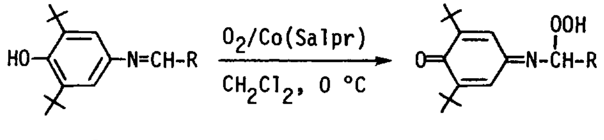
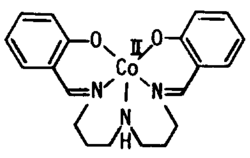
The oxygenation of 4-(N-arylmethyleneamino)-2,6-di-t-butylphenols with Co(Salpr), a five coordinate Co(II) Schiff base complex, in CH_2Cl_2 results in the regioselective hydroperoxylation at the imino carbon to give N-(1-aryl-1-hydroperoxymethyl)-3,5-di-t-butyl-p-benzoquinone monoimines, which give exclusively the corresponding amides and 2,6-di-t-butyl-p-benzoquinone in an aerobic solution of KOH in 90% EtOH.

The regioselective dioxygen incorporation into t-butylated phenols is efficiently mediated by five coordinate Co(II) Schiff base complexes, Co(Salpr) and its derivatives: 4-alkyl-2,6-di-t-butylphenols are exclusively oxygenated at the para position whereas only the ortho position is attacked by dioxygen with 4-aryl-2,6-di-t-butylphenols leading to the corresponding peroxyquinolato Co(III) complexes.[1,2] The same regioselectivity has been observed in the base-catalyzed oxygenation of these phenols,[3,4] strongly suggesting the same mechanism being operated in both the oxygenations. We have recently reported that the base-catalyzed oxygenation of 4-(N-arylmethyleneamino)-2,6-di-t-butylphenols (1) effectively obtained by the condensation of 2,6-di-t-butyl-p-benzoquinone with arylmethylamines provides a new route to amides from amines.[5]
It is now found that the oxygenation of 1 with Co(Salpr) in CH_2Cl_2 gives new 1,1-amino hydroperoxides 2 resulting from the selective dioxygen incorporation into the imino carbon in 1.



1 2

a; R = Ph b; R = 4-MePh c; R = 4-MeOPh
d; R = 4-ClPh e; R = 2-Furyl



Co(Salpr)

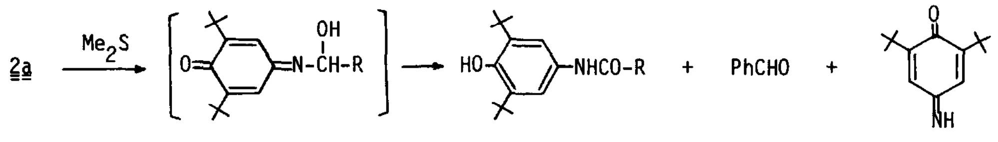
Little has been known about secondary 1,1-amino hydroperoxide formation by oxygenation.[6]

Oxygen was bubbled through a solution of **1** (1 mmol) in CH_2Cl_2 (20 ml) containing Co(Salpr) (1.1 mmol) at 0 °C. The reaction was normally complete within 1 h. The TLC analysis of the reaction mixture showed only one product being formed, which was isolated by filtration of the resulting reaction mixture through a short column of silica gel (5 g) at -78 °C and evaporation of the filtrate *in vacuo* at 0 °C. Triturating the resulting residue with pentane gave N-(1-aryl-1-hydroperoxymethyl)-3,5-di-*t*-butyl-*p*-benzoquinone monoimines (**2**)[10] as crystals in excellent yield (Table 1). In the IR spectra of **2**, the ν_{OH} band for the OOH group appears at around 3100 cm^{-1}, the low frequency being due to a strong hydrogen bonding to the imino group.[7] The ^1H NMR spectra of **2** (Table 1) are all in good agreement with the structures. Two olefinic protons in the quinoid ring are nonequivalent except for **2d**, the assignment, chemical shift values, and coupling constants are quite similar to those observed in other quinone monoimines.[11] The unusual low field shift of the hydroperoxy group corresponds to its IR band shift. The compounds **2** liberate I_2 quantitatively from an acidic solution of iodide. The reduction of **2a** with Me_2S at 0 °C gave 4-(N-benzoylamino)-2,6-di-*t*-butylphenol (**4**) (24% yield),[12] benzaldehyde (76% yield), and 3,5-di-*t*-butyl-*p*-benzoquinone monoimine (**5**) (76% yield).[13] No corresponding 1,1-amino alcohol **3** was not detected in the reaction mixture, indicating that **3** is quite unstable to undergo

Table 1. Synthesis and Physical Data of **2**

2	Yield[a] (%)	mp(dec)[b] (°C)	IR(KBr), cm^{-1} ν_{OH}	$\nu_{C=O}$	$\nu_{C=N}$	^1H NMR($CDCl_3$), δ t-Bu	C-H	C=CH[c]	C=CH[d]	OOH
2a	89	115	3070	1653	1638	1.19 1.20	6.62	6.89[e]	6.94[e]	11.65
2b	74	80	3100	1653	1636	1.20	6.60	6.90[f]	6.95[f]	11.58
2c	85	76	3110	1653	1638	1.19	6.58	6.89[f]	6.95[f]	11.20
2d	71	78	3100	1655	1638	1.20	6.59	6.88		11.27
2e	74	67	3080	1653	1637	1.20 1.23	6.60	6.86[g]	6.93[g]	10.75

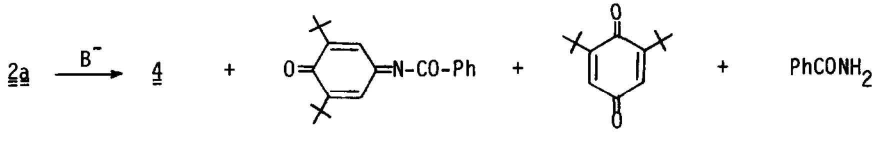
[a] Yields by isolation. [b] All products show satisfactory analytical results: C, ± 0.20%; H, ± 0.25%; N, ± 0.27%. [c] *syn* to R, a doublet. [d] *anti* to R, a doublet. [e] J = 1.5 Hz. [f] J = 2.5 Hz. [g] J = 2.0 Hz.



3 **4** **5**

isomerization to 4 as well as decomposition to benzaldehyde and 5. These results also support the structure 2. In the present oxygenation, peroxy cobalt(III) complexes corresponding to 2 should be formed taking into account the results obtained in the Co(Salpr) mediated oxygenation of 2,6-di-t-butylphenols.[1,2] Attempts to isolate such peroxy cobalt(III) complexes, however, were not successful.

The hydroperoxides 2 are readily decomposed by acid- and base-catalyses. In an aerobic solution of KOH in 90% EtOH at 0 °C, 2a gave 2,6-di-t-butyl-p-benzoquinone (6) and benzamide in nearly quantitative yields. This strongly suggests that the excellent formation of benzamide in the oxygenation of 1a in the KOH-EtOH system[5] involves the anionic form of 2a as the intermediate. In order to clarify the mechanism of this interesting decomposition of 2 to the corresponding amides, the base-catalyzed decomposition of 2a under water and oxygen free conditions has been investigated. Under these conditions, 2a gave a mixture of 4, N-benzoyl-3,5-di-t-butyl-p-benzoquinone monoimine (7),[14] 6, and benzamide. The ratio of these products depends on the reaction conditions employed (Table 2). The quinone imine 7 is quite unstable in an aqueous alkaline solution (KOH in 90% EtOH) imidiately to give $PhCONH_2$ and 6. The phenol 4a is easily oxidized to 7 in an aerobic nonaqueous basic solution.



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6

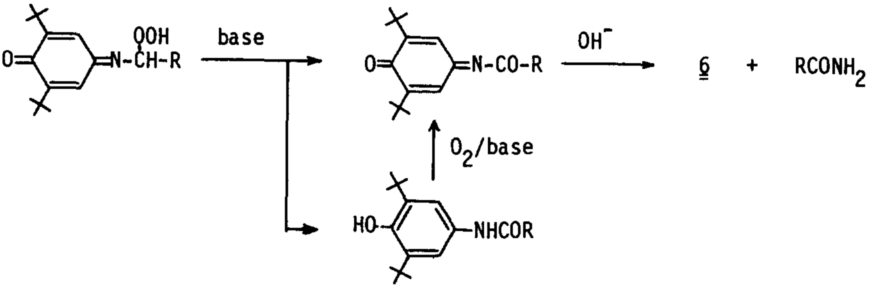
Table 2. Base-Catalyzed Reaction of 2a.[a]

Solvent	Base	Product Yield (%) 4a	6	7	$PhCONH_2$
DMF	t-BuOK	40	25	20	-[b]
THF	t-BuOK	30	15	50	-[b]
t-BuOH	t-BuOK	15	50	15	-[b]
90% EtOH[c]	KOH (0 °C)	0	95	0	95

[a] Reaction conditions: 2a (0.5 mmol), Base (1.5 mmol), Solvent (10 ml), 30 min at 25 °C under nitrogen unless otherwise noted. Yields were determined by NMR. [b] Not determined. [c] An aerobic solution.

The following mechanism can, therefore, be depicted for the quantitative conversion of 2 to

6 and benzamide, which may also implicated in the base-catalyzed oxygenation of 2 leading to the new amide synthesis.[5] An acid-catalyzed reaction of 2 gave a complex reaction mixture.



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

(5) A. Nishinaga, T. Shimizu, and T. Matsuura, J. Chem. Soc. Chem. Commun., in press

(6) Tertiary 1,1-amino hydroperoxides are known for photooxygenations of heterocycles[7] but only two examples of secondary 1,1-amino hydroperoxides have been reported for addition of H_2O_2 to imines[8] and autoxidation of amides.[9]

(7) R. Ramasseul and A. Rassat, Tetrahedron Lett., 1337 (1972) and references cited therein.

(8) Hoeft and A. Rieche, Angew. Chem., 77, 548 (1965).

(9) B. F. Sager, J. Chem. Soc. (B), 428 (1967).

(10) The hydroperoxides 2 are fairly stable but decompose upon standing at room temperature for several days.

(11) A. Rieker and H. Kessler, Tetrahedron, 23, 3723 (1967); J. Bracht and A. Rieker, Synthesis, 708 (1977).

(12) Colorless prisms: mp 212-214 °C: ^{1}H NMR ($CDCl_3$); δ 1.43 (s, 18 H, *t*-Bu), 5.03 (s, 1 H, OH), 7.33 (s, 2 H, C=CH), 7.3-7.9 (m, 5 H, Ph): IR (Nujol); 3650 (OH), 3300 (NH), 1640, 1545 (CON-) cm^{-1}. Anal: C, ± 0.27%; H, ± 0.15%; N, ± 0.07%.

(13) *p*-Benzoquinone monoimine 5 could not be isolated but the TLC and NMR spectrum of the reaction mixture showed that only the three products were formed. A signal at δ 6.77 (s, 2 H, C=CH) along with δ 1.28 (s, 18 H, *t*-Bu) should be assigned for 5. The silica gel chromatography of the reaction mixture, however, gave only the quinone 6 [δ 6.47 (C=CH), 1.28 (*t*-Bu)] except for 4 and PhCHO, indicating that 5 is quite unstable under the chromatographic conditions.

(14) Yellow liquid: bp ca. 130 °C/10^{-2}mmHg: ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 18 H, *t*-Bu), 6.77 (s, 2 H), 7.3-8.1 (m, 5 H, Ph): IR (film); 1650, 1625, 1585 cm^{-1}: UV; $\lambda_{max}^{C_6H_{12}}$(log ε) 280 (4.43), 234 (4.07) nm. Anal: C, ± 0.12%; H, ± 0.09%; N, ± 0.01%.

(Received in Japan 28 December 1979)