3 ml of CCl_4 and a solution of 0.35 g (3.3 mmol) of benzylamine in 2 ml of CCl_4 was added. After several minutes a yellow precipitate, 0.9 g (88%), was filtered. Recrystallization of the product from EtOAc gave white crystals: mp 145–147°; uv max (95% EtOH) 280 (shoulder), 314 mμ (ϵ 10,300); nmr ($CDCl_3$) δ 1.33 (s, 9), 3.82 (d, 2, J = 5 Hz), 4.97 (broad, 1), 7.05–7.4 (unresolved, 10), 8.8 (s, 1), 10.7 (broad, 1).

Anal. Calcd for $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.09. Found: C, 78.06; H, 7.99; N, 9.13.

N-*t*-Butyl-N′-phenyl-2-benzoylpropionamidine (29).—A solution of 1.0 g (3 mmol) of the salt **16**[19] in 100 ml of MeCN was added slowly to a stirred solution of 0.73 g (10 mmol) of *t*-butylamine in 150 ml of MeCN. The reaction was allowed to stand overnight, and the solvent was evaporated. The solid residue was partitioned between 50 ml of water and 75 ml of ether. The organic phase was dried ($MgSO_4$) and filtered, and the solvent was evaporated, giving 0.9 g (97%) of yellow solid. Recrystallization from 95% EtOH gave white crystals: mp 100–101°; uv max (95% EtOH) 242 mμ (ϵ 21,000); nmr ($CDCl_3$) δ 1.3 (s, 9), 1.42 (d, 3, J = 7 Hz, CH_3–), 4.52 (q, 1, J = 7 Hz, CH–), 4.63 (broad, 1), 6.7–7.84 (unresolved, 10).

Anal. Calcd $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.09; O, 5.19. Found: C, 77.75; H, 7.90; N, 9.15; O, 5.05.

N,N-Diethyl-N′-phenyl-2-benzoylpropionamidine (30).—A solution of 2.0 g (6 mmol) of **16** in 150 ml of MeCN was added to a solution of 0.88 g (12 mmol) of diethylamine in 100 ml of MeCN. The reaction mixture was allowed to stand overnight and the solvent was evaporated giving a solid residue. The solid was dissolved in 75 ml of ether and washed with 25 ml of 5% $NaHCO_3$. The aqueous phase was extracted with 25 ml of ether. The organic phase was dried (K_2CO_3) and filtered, and the solvent was evaporated, giving 1.8 g (99%) of solid. Recrystallization from 95% EtOH gave white crystals: mp 77–78°; uv max (95% EtOH) 245 mμ (ϵ 23,000); nmr (CCl_4) δ 0.87 (t, 6, J = 7 Hz, CH_3–), 1.45 (d, 3, J = 7 Hz, CH_3–), 3.12 (q, 4, J = 7 Hz, CH_2–), 4.15 (q, 1, J = 7 Hz, CH–), 6.5–7.7 (unresolved, 10).

Anal. Calcd for $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.09. Found: C, 77.75; H, 7.63; N, 9.19.

Registry No.—**6**, 21554-99-4; **7**, 21555-00-0; **8**, 21555-01-1; **9**, 21555-02-2; **10**, 21555-03-3; **11**, 21555-04-4; **13**, 21555-05-5; **14**, 21555-06-6; **18**, 21555-07-7; **19**, 21555-08-8; **20a**, 21543-43-1; **20b**, 21543-44-2; **23** (*cis*), 21543-45-3; **24**, 21555-09-9; **26**, 21555-10-2; **29**, 21620-41-7; **30**, 21555-11-3; **23** (*trans*), 21543-46-4.

The Oxidation of Amines with Peroxy Radicals. N-Phenyl-2-naphthylamine[1]

D. F. BOWMAN,[2] B. S. MIDDLETON,[3] AND K. U. INGOLD

Division of Applied Chemistry, National Research Council of Canada, Ottawa, Canada

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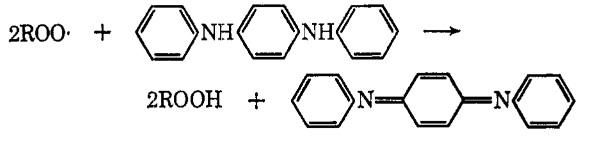
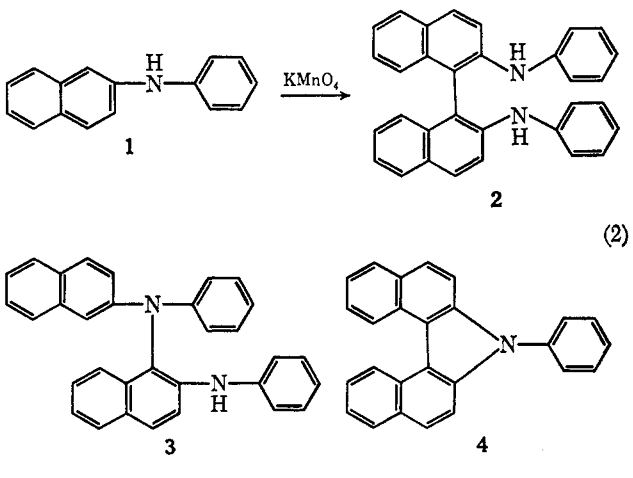
Six products have been identified in the oxidation of N-phenyl-2-naphthylamine by peroxy radicals. Three of the products, 1,1-bis(N-phenyl-2-naphthylamine) (**2**), N,N′-diphenyl-N-(2-naphthyl)-1,2-naphthylenediamine (**3**), and 7-phenyl-dibenzo[*c*,*g*]carbazole (**4**), are formed by the coupling of amino radicals. The remaining products, 2-anilino-1,4-naphthoquinone (**5**), 2-anilino-1,4-naphthoquinone-4-anil (**6**), and 4-(N-phenyl-2-naphthylamino)-1,2-naphthoquinone (**7**), are believed to be formed by the attack of various nucleophiles on 1,2-naphthoquinone-2-anil (**10**). This *o*-quinone imine was not identified among the products, but it is probably formed in the reaction of amino radicals with peroxy radicals.

Aromatic amines are widely used to inhibit the autoxidation of organic materials. Our own work on amine antioxidants has so far been entirely kinetic in nature.[4–7] However, a proper understanding of inhibition requires a knowledge of the products formed in the reactions of the antioxidants with peroxy radicals. Surprisingly little information on this subject is available for amines. Boozer, *et al.*,[8] have shown that N,N′-diphenyl-*p*-phenylenediamine reacts with peroxy radicals to give N,N′-diphenyl-*p*-quinone diimine in high yield (eq 1).



(1)

Bickel and Kooyman[9] have reported that N-phenyl-2-naphthylamine (**1**) reacts with peroxy radicals to give a small amount of a colorless substance, mp 167–167.5°, $C_{16}H_{13}NO$. The oxidation of **1** with potassium permanganate yields a mixture of 1,1′-bis(N-phenyl-2-naphthylamine) (**2**, 63%), N,N′-diphenyl-N-(2-naphthyl)-1,2-naphthylenediamine (**3**, 32%), and 7-phenyldibenzo[*c*,*g*]carbazole (**4**, 0.5%) (eq 2).[10]



(2)

A compound assumed to be **3** (but which is more probably **2**)[10] has been reported to be formed during the atmospheric aging of **1** containing rubber vulcanisates.[11,12] Since 1957, Thomas and coworkers have

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(1) Issued as NRCC No. 11,031.

(2) NRCC Fellow, 1968–1969.

(3) NRCC Fellow, 1965–1967.

(4) D. V. Gardner, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **42**, 2847 (1964).

(5) (a) I. T. Brownlie and K. U. Ingold, *ibid.*, **44**, 861 (1966); (b) *ibid.*, **45**, 2419 (1967); (c) *ibid.*, **45**, 2427 (1967).

(6) K. Adamic, M. Dunn, and K. U. Ingold, *ibid.*, **47**, 287 (1969).

(7) K. Adamic and K. U. Ingold, *ibid.*, **47**, 295 (1969).

(8) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Amer. Chem. Soc.*, **77**, 3233 (1955).

(9) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2217 (1957).

(10) R. F. Bridger, D. A. Law, D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, **33**, 4329 (1968).

(11) P. Schneider, *Proc. Rubber Technol. Conf., 3rd, London*, 309 (1954).

(12) M. A. Salimor, L. G. Angert, A. S. Kuz'minskii, and V. M. Tatevskii, *Chem. Abstr.*, **52**, 775 (1958).

shown in a brilliant series of papers[13] that nitroxide radicals are intermediates in the peroxy radical oxidation of both aromatic and aliphatic amines. However,

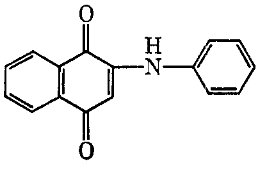
$$\mathrm{ROO\cdot} + \mathrm{R'R''NH} \longrightarrow \mathrm{ROOH} + \mathrm{R'R''N\cdot} \qquad (3)$$

$$\mathrm{ROO\cdot} + \mathrm{R'R''N\cdot} \longrightarrow \mathrm{RO\cdot} + \mathrm{R'R''NO\cdot} \qquad (4)$$

the importance of the nitroxide as an intermediate with respect to the proportion of the amine which is oxidized *via* its nitroxide received only slight attention.[13a,d] We have recently investigated this aspect of amine oxidations using esr spectroscopy.[6,7] At 65° with *t*-butylperoxy radicals, the efficiency of nitroxide formation (per molecule of amine oxidized) reaches as high as 50–60% with diphenylamine and ring-substituted diphenylamines. That is, with these antioxidants, the initial rate of nitroxide formation is 50–60% of the rate of formation of peroxy radicals. In contrast, the efficiency of nitroxide formation from **1** was only 1.5% and from **2** was 12% under similar conditions.[7] The present paper reports a study of the products formed by the oxidation of **1** with peroxy radicals.

Results and Discussion

Peroxy radicals were generated both by the cobalt-catalyzed decomposition of *t*-butyl hydroperoxide at 20°[14–16] and by the thermal decomposition of α,α'-azobisisobutyronitrile (AIBN) in the presence of oxygen at 65°.[8,15,16] N-Phenyl-2-naphthylamine is oxidized by peroxy radicals to a complex mixture of products in which compounds **2**, **3**, **4**, 2-anilino-1,4-naphthoquinone (**5**), 2-anilino-1,4-naphthoquinone-4-anil (**6**), and 4-(N-phenyl-2-naphthylamino)-1,2-naphthoquinone (**7**) have been identified.



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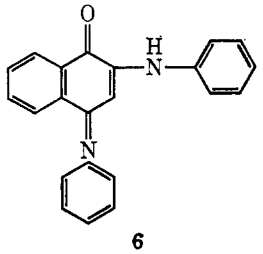

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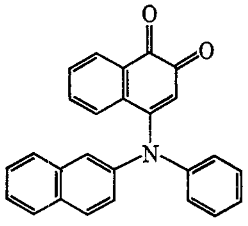

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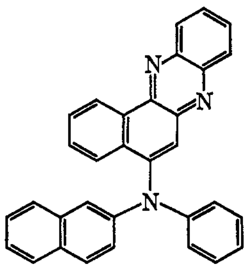
As has been already mentioned, **2**, **3**, and **4** are formed by the oxidation of **1** with $\mathrm{KMnO_4}$. The identities of **5** and **6** were confirmed by their synthesis by known methods.[17,18] Compound **7** has not previously been reported. That it is an *o*-quinone was demonstrated by the formation of a phenazine, **8**, on reaction with



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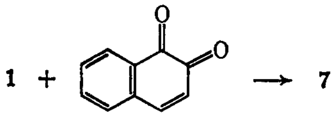
o-phenylenediamine. The structure of **7** was confirmed by a simple synthesis involving the nucleophilic addition of **1** to 1,2-naphthoquinone (**9**) in aqueous alcohol, followed by oxidation with air.



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The percentage yields of the various products obtained under different experimental conditions are summarized in Table I. In general, yields were determined by a technique involving thin layer chromatography and ultraviolet absorption (see Experimental Section). Quantitative isolation of the products, which was carried out in only one case, gave results in good agreement with the general procedure.

Table I

Product Yields in the Oxidation of N-Phenyl-2-naphthylamine with Peroxy Radicals

Reaction[a]	[ROOH]/[1]	Product yield, %[b] 1	2	3	4	5	6	7
A	3.0	0	0	0	8.8[c]	11.3[c]	29.4[c]	28.8[c]
A	3.0	0	0	0	8.4	10	28	27
A	2.0	26	1.9	1.4	6.3	10	21	24
B	2.0	24	2.8	1.3	5.3	8.1	25	27
B	1.0	57	3.4	1.8	5.8	4.0	9.9	15
C	~0	18	24	13	25	1.2	10	0
C	1.0[d]	22	8.6	3.9	9.5	23	10	0
C	3.0[d]	28	4.1	2.5	5.7	41	3.4	0

[a] A = cobalt toluate added in small portions to *t*-butyl hydroperoxide and **1** in benzene at 20°; B = *t*-butyl hydroperoxide added dropwise to cobalt toluate and **1** in benzene at 20°; C = decomposition for 2 half-lives of 2 mol of AIBN per mol of **1** in *n*-decane at 65°: $[\mathrm{ROO\cdot}]/[\mathbf{1}] = 2.0$, assuming a radical generating efficiency of 0.7. [b] Based on the initial concentration of amine and calculated with the assumption that 2 mol of **1** is required to form 1 mol of **2**, **3**, **4**, **6**, and **7**. [c] Isolated; all other yields based on tlc and uv absorption. [d] *t*-Butyl hydroperoxide added to reactants.

As we might expect, product yields depend on the experimental conditions. This is partly due to the fact that some of the products are fairly reactive toward free radicals. A measure of their relative reactivity toward the radicals present in these systems was provided by rate measurements on the AIBN-initiated oxidation of styrene at 65° in the presence of the products **2**–**7** (Table II). Rate measurements at different oxygen pressures provide a comparatively simple method for distinguishing between compounds which react with R· radicals and the more usual types of chain-breaking antioxidants which react only with ROO· radicals.[5,19] Under ideal conditions, the rate of

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(13) (a) O. L. Harle and J. R. Thomas, *J. Amer. Chem. Soc.*, **79**, 2973 (1957); (b) J. R. Thomas, *ibid.*, **82**, 5955 (1960); (c) J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, **35**, 1507 (1961); (d) J. R. Thomas and C. A. Tolman, *J. Amer. Chem. Soc.*, **84**, 2930 (1962); (e) J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966).

(14) T. W. Campbell and G. M. Coppinger, *J. Amer. Chem. Soc.*, **74**, 1469 (1952).

(15) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

(16) E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 263, 269 (1966).

(17) A. Inoue, N. Kuroki, and K. Konishi, *Yuki Gosei Kagaku Kyokai Shi*, **17**, 711 (1959); *Chem. Abstr.*, **54**, 4505 (1960).

(18) A. Euler and H. Euler, *Ber.*, **39**, 1042 (1906).

oxidation of a substrate such as styrene in the presence of an inhibitor which traps only R· radicals (*e.g.*, an aliphatic nitroxide)[5c] is directly proportional to the oxygen partial pressure and is independent of the substrate concentration. In contrast, the rate for an inhibitor which traps only ROO· radicals (*e.g.*, **1**)[5a] is proportional to the first power of the substrate concentration and is independent of the oxygen pressure. A nonintegral dependence on both oxygen and substrate concentrations suggests that the inhibitor can react with both types of radicals.

Table II

Rate[a] of AIBN-Initiated Oxidation of Styrene at 65°

Inhibitor	Rate × 10^6, M sec^{-1} $[O_2]$ = 760 mm	$[O_2]$ = 200 mm
None	93	91
1	1.3	1.3
N-Methyl-**1**	74	70
2	9	9
3	12	12
4	90	92
5	69	47
6	54	39
7	47	27
9	48	27

[a] [AIBN] = 8.67×10^{-3} M; [inhibitor] = 4.33×10^{-3} M; [styrene] = 7.25 M in dichlorobenzene.

The dimeric secondary amines **2** and **3** are moderately active inhibitors for which the inhibited rates are independent of the oxygen pressure. They are therefore fairly reactive toward peroxy radicals and it is not surprising that their yields decrease as the number of peroxy radicals generated per mole of **1** is increased. At [peroxy radical]/[**1**] ratios required to ensure the complete consumption of **1**, compounds **2** and **3** are also consumed.

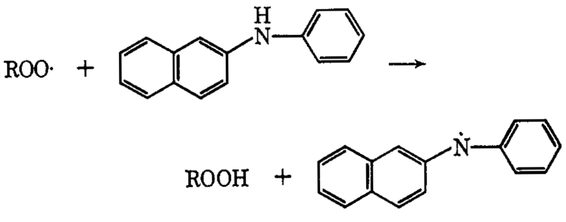
The tertiary amine **4** is a completely ineffective inhibitor of the oxidation of styrene and it is therefore not consumed as the reaction progresses; incidentally, **4** is not formed in the oxidation of **2** with peroxy radicals.

The *p*-quinone **5** and *p*-quinon imine **6** are both rather weak retarders of styrene oxidation and they are therefore fairly stable under our experimental conditions. The dependence of the styrene-inhibited oxidation rates on oxygen pressure implies that these compounds can trap R· radicals. However, the rates are increased by only about 40% when the oxygen pressure is increased by a factor of almost 4, and therefore these compounds must owe most of their inhibiting activity to their ability to trap ROO· radicals.

The 1,2-quinone **7** could not be detected in the reaction of **1** with the peroxy radicals from AIBN. Although **7** is only partly decomposed at 65° in the absence of AIBN in the length of time required for an AIBN experiment (16 hr), it is completely destroyed in the presence of 2 mol of AIBN under the same conditions. These facts suggest that **7** is relatively unreactive toward RO· and ROO· radicals (present in the cobalt-catalyzed decomposition of hydroperoxide) but is reactive toward R· radicals (present together with ROO· in the AIBN-initiated oxidations). The inhibited rates for **7** (and also for 1,2-naphthoquinone, **9**) increase by 70–80% on increasing the oxygen pressure from 200 to 760 mm. These 1,2-quinones are therefore more efficient than **5** and **6** at trapping R· radicals. However, because the inhibited rates show a less than integral dependence on the oxygen pressure, these 1,2-quinones probably have some ability to trap ROO· radicals.

The ratio of the yields [**2**]/[**3**] is about 1.8, as was found previously in the $KMnO_4$ oxidation of **1**.[10] This ratio also corresponds approximately to the value of 1.4 ± 0.2 that has been found for the coupling of N-phenyl-2-naphthylamino radicals.[20] The yield of **4** relative to **2** and **3** is, however, much greater in peroxy radical oxidation than in the other two reactions.

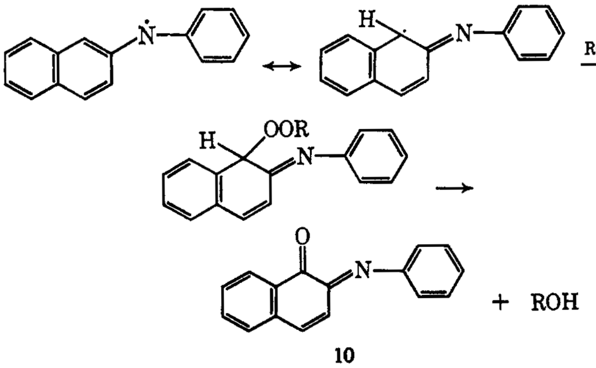
The formation of amino radicals in the present systems is in full accord without knowledge of the inhibition process. Thus, kinetic deuterium isotope studies have shown that the amino hydrogen is abstracted by a peroxy radical in the rate-determining step of inhibition.[5,21] At 65°, $k_H/k_D = 3.0 \pm 0.5$ with $k_H = 5 \times 10^4\ M^{-1}\ sec^{-1}$, assuming that each molecule of **1** stops two oxidation chains.[5] Equation 5 almost certainly



(5)

represents a reversible reaction.[5,6,22] The importance of the amino hydrogen for the inhibition of oxidation is also confirmed by the inability of the tertiary amines **4** and N-methyl-N-phenyl-2-naphthylamine to significantly inhibit oxidations[23] (Table II).

Products **5** and **6** are difficult enough to account for if the amino hydrogen is removed in the first step (eq 5), since it must subsequently be replaced. These two products would be even more difficult to explain if a significant fraction of **1** was oxidized to its nitroxide. However, as already mentioned, our esr studies have shown that only 1–2% of **1** is oxidized to a nitroxide by peroxy radicals. This result implies that the second step in the reaction involves the attack of a peroxy radical on the amino radical at a site other than the nitrogen—presumably at the 1 position of the naphthyl group. The resultant addition product would be extremely unstable and would probably break down to give the *o*-quinone imine **10** as in eq 6. Compounds **5** and **6**



(6)

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[19] K. U. Ingold, Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968, p 296.

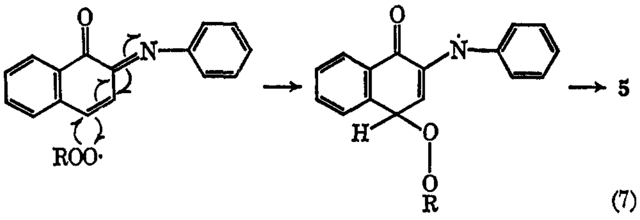
[20] R. F. Bridger, private communication.

[21] J. R. Shelton and D. N. Vincent, *J. Amer. Chem. Soc.*, **85**, 2433 (1963).

[22] J. R. Thomas, *ibid.*, **85**, 2166 (1963).

[23] L. G. Angert and A. S. Kuzminskii, *J. Polym. Sci.*, **32**, 1 (1958).

might then be formed by the addition to **10** of free radicals or of nucleophiles. For example, the 1,4-quinone **5** might be formed by peroxy radical attack on **10** (eq 7) or by nucleophilic addition of hydroperoxide (eq 8).



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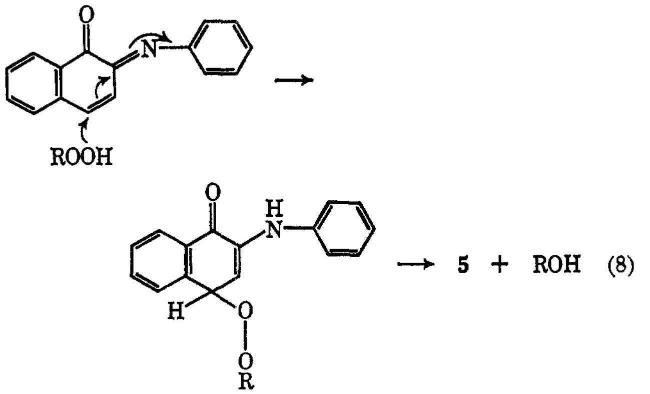

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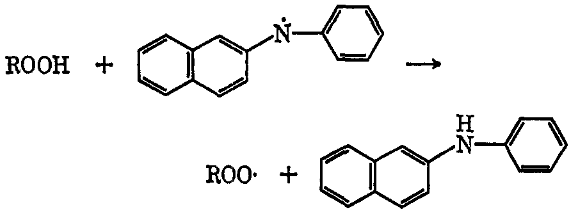
In the AIBN-initiated oxidation of **1**, the product yields are highly dependent on the amount of hydroperoxide present in the reaction mixture (Table I). Increasing the hydroperoxide concentration increases the yield of **5** markedly, but it decreases the amount of **1** actually consumed and the amounts of those products presumed to be formed by the direct coupling of N-phenyl-2-naphthylamino radicals (*i.e.*, **2**, **3**, and **4**). These results can be explained by the reversibility of the reaction represented by eq 5.[5,6,22] An increase in the hydroperoxide concentration will increase the steady-state concentration of peroxy radicals and will decrease the steady-state concentration of amino radicals. The coupling of amino radicals therefore becomes relatively less important than the reaction between amino and peroxy radicals which is presumed to give **10** (eq 6) and hence **5**.[24] The amount of **1** consumed will, of course, decrease, even though the amount of initiator decomposed and the number of radicals produced is unchanged.



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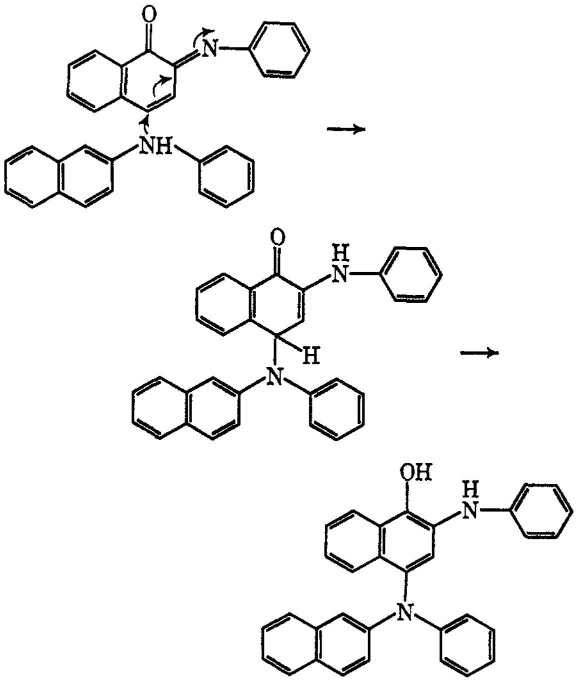
Compounds **6** and **7** were generally formed in approximately equal yields in the cobalt toluate–hydroperoxide oxidation of **1**, which suggests that they may be formed from a common intermediate. A possible intermediate is the aminophenol **11**, formed by rearrangement of the product of nucleophilic addition of **1** to **10** (eq 9). The oxidation of **10** could give a phenoxy radical,[25] which, on reaction with a peroxy radical, might give the cyclohexadienone **12**. The loss of O-*t*-butyl-N-phenylhydroxylamine from **12** would form the 1,2-quinone **7** (eq 10). Nucleophilic attack of the hydroxylamine



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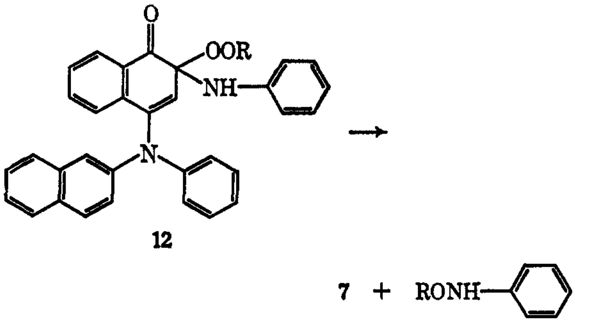

(10)

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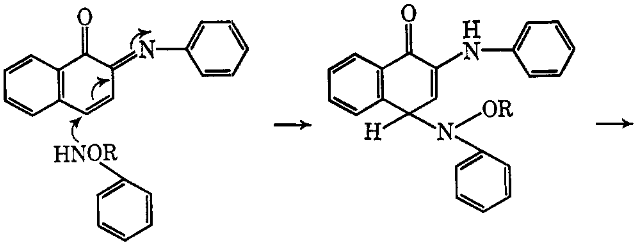
[24] In principle, it should be possible to estimate the average concentrations of amino and peroxy radicals from the product yields in these reactions. That is, if **2**, **3**, and **4** are formed by the coupling of amino radicals, the relative concentrations of amino radicals should be proportional to $([\mathbf{2}] + [\mathbf{3}] + [\mathbf{4}])^{1/2}$. Similarly, if **10** is the precursor of **5**, **6**, and **7** and is formed by the reaction of peroxy and amino radicals, then the relative average peroxy radical concentration should be proportional to $([\mathbf{5}] + [\mathbf{6}] + [\mathbf{7}])/[\text{amino radical}]$. However, our results do not tell us whether **7** is absent from the AIBN reactions, because it is not formed or because it is consumed as rapidly as it is formed. For this reason, it is not possible to decide whether the variations in the conversion of **10** to **5** parallel the variations in [ROOH] or in [ROO·]. That is, our data cannot be used to distinguish between the reactions represented by eq 7 and 8.

[25] Even if the amino hydrogen is initially abstracted, the phenoxy radical could be formed by intramolecular hydrogen transfer. Similar intermolecular hydrogen transfer reactions are well established.[26]

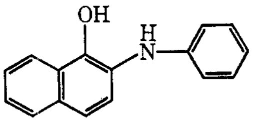
[26] (a) G. V. Karpukhina, Z. K. Maizus, and N. M. Emanuel, *Dokl. Akad. Nauk SSSR*, **160**, 158 (1965); *Neftekhimiya*, **5**, 394 (1965); (b) G. V. Karpukhina, Z. K. Maizus, and L. I. Matienko, *ibid.*, **6**, 603 (1966); (c) G. V. Karpukhina and Z. K. Maizus, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **5**, 957 (1968).

ether on the quinone imine **10** could give the anil **6** and *t*-butyl alcohol (eq 11).



6 + ROH (11)

In an attempt to check the validity of this reaction scheme, 2-anilino-1-naphthol (**13**) was synthesized by the reaction of **1** with benzoyl peroxide and hydrolysis of the N-benzoate. It was hoped that the oxidation of this compound would provide a useful source of the quinone imine **10**.



13

Under basic conditions in aqueous alcohol, **13** reacted with oxygen to give the 1,4-quinone **5** in high yield. In the absence of air, the oxidation of **13** with silver oxide in ether gave mainly amorphous material with a small amount of **6**, the yield of which could be increased by the addition of aniline.[27] The oxidation of a mixture of **1** and **13** with silver oxide in benzene did not yield the 1,2-quinone **7**. The oxidation of **13** with cobalt and *t*-butyl hydroperoxide did not give any **5** or **6**. The absence of **5** suggests that **13** is not oxidized to **10** by peroxy radicals. This surprising result can only be explained if the radical initially formed from **13** couples with a second radical more readily than it donates hydrogen to the second radical.

Although **1** couples readily with 1,2-naphthoquinone (**9**) in alcohol to give the 1,2-quinone **7**, this reaction is not responsible for the formation of **7** in the cobalt–hydroperoxide oxidations. Under the solvent conditions prevailing in these reactions, the condensation was extremely slow, no **7** being detected after 4 hr. The oxidation of a mixture of **1** and **9** with silver oxide in benzene gave only **2**, **3**, and **4**, proving that **7** is not formed by the attack of the N-phenyl-2-naphthylamino radical on **9**. Both of these experiments provide support for the view that **7** is formed by the nucleophilic attack of **1** on **10**, followed by the elimination of the anilino residue, rather than by the attack of **1** on **9** already formed in the reaction.[29]

In summary, six products have been identified in the oxidation of N-phenyl-2-naphthylamine by peroxy radicals. Three of these products are probably formed by the coupling of N-phenyl-2-naphthylamino radicals. Reaction of the amino radical with a peroxy radical appears to give an unstable *o*-quinoneimine. Although this compound could not be identified in the reaction mixture, it is believed to be the precursor of the three oxygen-containing products isolated. These products are probably formed by reaction of the quinone imine with different nucleophiles. The yields of the various products depend on the experimental conditions.

It is hoped that our identification of the products formed in the peroxy radical oxidation of N-phenyl-2-naphthylamine will help in the development of effective nonstaining aromatic amine antioxidants (*i.e.*, antioxidants giving colorless oxidation products).

Experimental Section

Thin layer chromatograms on silica gel sheets ("Chromagram," Eastman Corp.) were developed in carbon tetrachloride for compounds **1–4** and in benzene–chloroform (1:1) for **5–7**. Spots were visualized with ultraviolet and visible light. Yields were determined by streaking a known volume of the reaction mixture onto a 2 × 8 in. sheet, developing in one of the above solvents, extracting the excised sheet with hot 95% alcohol, and comparing the absorption in the ultraviolet or visible spectrum with that of solutions of the pure substances. The semidine **3** and the carbazole **4** could not be adequately resolved by thin layer chromatography. In this case, the absorption at 365 mμ was attributed to the carbazole **4** and those at 272 and 305 mμ to **3** and **4**. In this way, the contribution of **3** could be assessed and its concentration calculated. Analysis of reconstituted mixtures of **3** and **4** showed this method to be valid.

Woelm neutral alumina of activity grade I was used for column chromatography.

Microanalyses were carried out by Mr. G. Weiler and Mr. F. B. Strauss, Oxford, England, or by Mr. J. R. H. Seguin of these laboratories. The rates of oxidation of styrene were measured with a Dynisco (DPT 85-2) pressure transducer. Values of *m/e* were determined by mass spectrometry at 70 eV.

1,2-Naphthoquinone was recrystallized from ether before use; N-phenyl-2-naphthylamine (Eastman), mp 108–109°, was used without further purification.

Cobalt Toluate Addition to N-Phenyl-2-naphthylamine and *t*-Butyl Hydroperoxide. I. 3 Mol of Hydroperoxide per Mol of 1.—A solution of the amine (2.82 g) and *t*-butyl hydroperoxide (3.48 g) in benzene (60 ml) was stirred during the addition of cobalt toluate (30 mg) in small portions during 30 min. After being stirred overnight, the mixture was made up to 100 ml and analyzed by thin layer chromatography. It contained **4** (8.4%), **5** (10%), **6** (28%), and **7** (27%).

The solution was reduced to 20 ml under reduced pressure, filtered to remove cobalt salts, and chromatographed on alumina (180 g). The materials eluted were (a) 7-phenyldibenzo[*c,g*]carbazole (**4**, 0.20 g, 8.8%), mp and mmp 142–143°, eluted with benzene–hexane (1:1); the infrared and ultraviolet spectra were identical with those of the authentic specimen prepared previously;[10] (b) 2-anilino-1,4-naphthoquinone-4-anil (**6**, 0.61 g, 29.4%), mp and mmp with an authentic[18] sample 185–186°, eluted with benzene; the identity was confirmed by comparison of infrared, nmr, and mass spectra; (c) 2-anilino-1,4-naphthoquinone (**5**, 0.36 g, 11.3%), mp 195–196°, eluted with benzene; this material also had physical properties identical with those of an authentic[17] sample; (d) 4-(N-phenyl-2-naphthylamino)-1,2-naphthoquinone (**7**, 0.70 g, 28.8%), purple needles, mp 203–207° dec, eluted with chloroform–benzene (1:1). This compound was too unstable for analysis. The infrared spectrum had ν_{max} 1690 and 1630 cm^{-1}, consistent with the 1,2-quinone structure. The ultraviolet spectrum in 95% alcohol had λ_{max} (log ϵ) 253 (4.57), 266 (shoulder, 4.44), 297 (shoulder, 4.09), 324 (3.82), 396 (3.53), and 518 mμ (3.81). With 1 mol of *o*-phenylenediamine in 95% alcohol, it gave **4-(N-phenyl-2-naphthylamino)-1,2-naphthophenazine** (**8**) as yellow needles, mp 204–205°, from benzene–hexane.

Anal. Calcd for $C_{32}H_{21}N_3$: C, 85.92; H, 4.72; N, 9.39; mol wt, 447. Found: C, 86.04; H, 4.66; N, 9.21; mol wt, 447 (vapor pressure osmometry, 453).

II. 2 Mol of Hydroperoxide per Mol of 1.—Cobalt toluate (20 mg) was added in small portions to a stirred solution of the

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[27] A reaction of this type, which probably involves hydrolysis of a quinone imine and the addition of the amine formed onto the remainder of the quinone imine, has been observed in the oxidation of 3-*t*-butyl-4-dimethylaminophenol.[28]

[28] D. F. Bowman and F. R. Hewgill, *J. Chem. Soc., C*, in press.

[29] This reflects the increased reactivity of nucleophiles toward the C=C—C=N system compared with the C=C—C=O system.[30]

[30] E. Schroeder, S. Preis, and K. P. Link, *Tetrahedron Lett.*, 23 (1960).

amine (2.19 g) and *t*-butyl hydroperoxide (1.80 g) in benzene at 20°, and the mixture was stirred overnight. It contained **1** (26%), **2** (1.9%), **3** (1.4%), **4** (6.3%), **5** (10%), **6** (21%), and **7** (24%).

Hydroperoxide Addition to N-Phenyl-2-naphthylamine and Cobalt Toluate. I. 2 Mol of Hydroperoxide per Mol of 1.—*t*-Butyl hydroperoxide (1.80 g) in benzene (10 ml) was added dropwise during 3 hr to N-phenyl-2-naphthylamine (2.19 g) and cobalt toluate (100 mg) in benzene (40 ml), and the mixture was stirred overnight. It contained **1** (24%), **2** (2.8%), **3** (1.3%), **4** (5.3%), **5** (8.1%), **6** (25%), and **7** (27%).

II. 1 Mol of Hydroperoxide per Mol of 1.—The above experiment was repeated with half the quantity of *t*-butyl hydroperoxide. The mixture contained **1** (57%), **2** (3.4%), **3** (1.8%), **4** (5.8%), **5** (4.0%), **6** (9.9%), and **7** (15%).

Oxidation of N-Phenyl-2-naphthylamine with AIBN in Decane. I. No Added Hydroperoxide.—The amine (1.10 g, 0.005 mol) and AIBN (1.64 g, 0.01 mol) were stirred in peroxide-free decane (240 ml) at 65.0 ±0.2° for 16 hr (2 half-lives) while a slow stream of oxygen was passed through the solution. The mixture was allowed to cool, the solvent was removed at 40° under reduced pressure, and the residue was made up to 50 ml with benzene. It contained **1** (18%), **2** (24%), **3** (13%), **4** (25%), **5** (1.2%), **6** (10%), and **7** (0%).

II. 1 Mol of Hydroperoxide per Mol of 1.—The above procedure was repeated in the presence of *t*-butyl hydroperoxide (0.45 g). The mixture contained **1** (22%), **2** (8.6%), **3** (3.9%), **4** (9.5%), **5** (23%), **6** (10%), and **7** (0%).

III. 3 Mol of Hydroperoxide per Mol of 1.—The above procedure was repeated in the presence of *t*-butyl hydroperoxide (1.35 g). The mixture was cooled to 0° and the precipitate was collected. Analysis showed this solid to be almost pure **5** (25% based on original **1**). The filtrate was evaporated at 40° under reduced pressure and the residue was dissolved in benzene (50 ml). The mixture contained **1** (28%), **2** (4.1%), **3** (2.5%), **4** (5.7%), **5** (16%), *i.e.*, total **5** = 41%, **6** (3.4%), and **7** (0%).

Reactions of Compounds 2-7 with Oxidizing Agents. I. *t*-Butyl Hydroperoxide.—The amines **2-7** were treated separately with *t*-butyl hydroperoxide (2 mol per mol of amine) and cobalt toluate in benzene for 16 hr, and the solutions were analyzed by tlc and uv absorption. **2** was recovered in 20% yield and no **4** was produced; **3** was completely consumed; **4**, **5**, and **7** were recovered in >80% yield; **6** was recovered in 60% yield; and no **5** was produced.

II. AIBN.—The amines **2-7** were stirred at 65° with AIBN (2 mol per mol of amine) for 16 hr in chlorobenzene under a slow stream of oxygen. The mixture contained **2** (10%) (no **4** produced), **3** (0%), **4** (90%), **5** (80%), **6** (40%) (no **5** produced), and **7** (0%).

Preparation of 2-Anilino-1-naphthol.—N-Phenyl-2-naphthylamine (17.6 g) in benzene (200 ml) was stirred in ice during the addition of recrystallized benzoyl peroxide (19.4 g) in small portions. The peroxide was added over a period of 20 min, so that the temperature did not rise above 10°. Benzene (50 ml) was then added, stirring was continued overnight, and the purple mixture was allowed to stand for 3 days. The precipitate was filtered off and washed with ether, and the residue was extracted with chloroform in a Soxhlet. The solution was reduced to 150 ml and set aside to crystallize. A specimen for analysis was recrystallized twice from acetic acid and twice from choroform to give **1-hydroxy-N-benzoyl-N-phenyl-2-naphthylamine** as needles, mp 248-250°.

Anal. Calcd for $C_{23}H_{17}NO_2$: C, 81.40; H, 5.05; N, 4.13. Found: C, 81.62; H, 5.27; N, 3.98.

The benzamide (4.0 g) was heated with potassium hydroxide (4.0 g) in water (70 ml) under reflux for 16 hr under nitrogen. The solution was neutralized with Dry Ice and extracted with ether under nitrogen. The organic layer was washed with aqueous sodium hydrogen carbonate and water and dried, and the solvent was removed under nitrogen. The 2-anilino-1-naphthol darkened immediately on exposure to air and could not be satisfactorily purified. With dimethyl sulfate and potassium hydroxide in refluxing acetone under nitrogen, it gave **1-methoxy-N-phenyl-2-naphthylamine** as prisms: mp 201-203° from benzene-hexane; nmr τ 6.02 (OCH_3), 4.00 (NH), and 1.8-3.3 (m, 11).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 82.07; H, 6.22; N, 5.64.

Reactions of 2-Anilino-1-naphthol (13). I. With Oxygen.—The aminophenol (0.3 g) and potassium hydroxide (0.4 g) in 50% aqueous alcohol (20 ml) and benzene (20 ml) were stirred while oxygen was passed through the solution for 1 hr. The mixture was acidified with 10% hydrochloric acid, the organic layer was separated and washed with water, and the solvent was removed. The residue was filtered through a short column of alumina to give 2-anilino-1,4-naphthoquinone (0.14 g), mp and mmp 195-196°.

II. With Silver Oxide.—The aminophenol (0.3 g) was shaken with silver oxide (1.3 g) in ether (50 ml) for 1 hr under nitrogen. The solution was filtered and evaporated to dryness. It contained **6** (8%). The experiment was repeated in the presence of aniline (0.14 g). The solution contained **6** (21%).

III. With *t*-Butyl Hydroperoxide.—The aminophenol (0.30 g), *t*-butyl hydroperoxide (0.14 g), and cobalt toluate (0.01 g) in benzene (20 ml) were stirred for 3 hr. None of the compounds **2-7** could be detected by thin layer chromatography.

The experiment was repeated in the presence of N-phenyl-2-naphthylamine (0.30 g). Only **1**, **2**, and the mixture **3-4** could be identified by thin layer chromatography.

Reactions of 1,2-Naphthoquinone and N-Phenyl-2-naphthylamine. I. In Alcohol.—The quinone (1.58 g, 0.01 mol) and N-phenyl-2-naphthylamine (2.19 g, 0.01 mol) were stirred in 95% alcohol (70 ml) for 18 hr in air. The purple solution was evaporated to dryness at 50° and the residue was chromatographed on alumina (90 g). Benzene-chloroform (1:1) eluted *4-(N-phenyl-2-naphthylamino)-1,2-naphthoquinone* (**7**, 2.01 g), mp and mmp 202-207°. With *o*-phenylenediamine in alcohol, it gave the phenazine **8**, mp and mmp 204-205°.

II. In Benzene.—The quinone (1.58 g), N-phenyl-2-naphthylamine (2.19 g), *t*-butyl alcohol (0.74 g, 0.01 mol), and *t*-butyl hydroperoxide (0.90 g, 0.01 mol) were stirred in benzene for 4 hr. No quinone **7** could be detected by thin layer chromatography.

III. With Silver Oxide.—The quinone (1.58 g) and N-phenyl-2-naphthylamine (2.19 g) were shaken with silver oxide (5.6 g) in ether (80 ml) for 3 hr. Thin layer chromatography showed the presence of **1**, **2**, and the mixture **3-4** and the absence of **7** in the solution.

Registry No.—**1**, 135-88-6; **2**, 17704-02-8; **3**, 17704-04-0; **4**, 21720-66-1; **5**, 6628-97-3; **6**, 21720-68-3; **7**, 21720-69-4; **8**, 21720-70-7; 1-hydroxy-N-benzoyl-N-phenyl-2-naphthylamine, 21720-71-8; 1-methoxy-N-phenyl-2-naphthylamine, 21720-72-9.

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