270. *The Oxidation of 2-Naphthylamine with Benzoyl Peroxide.*

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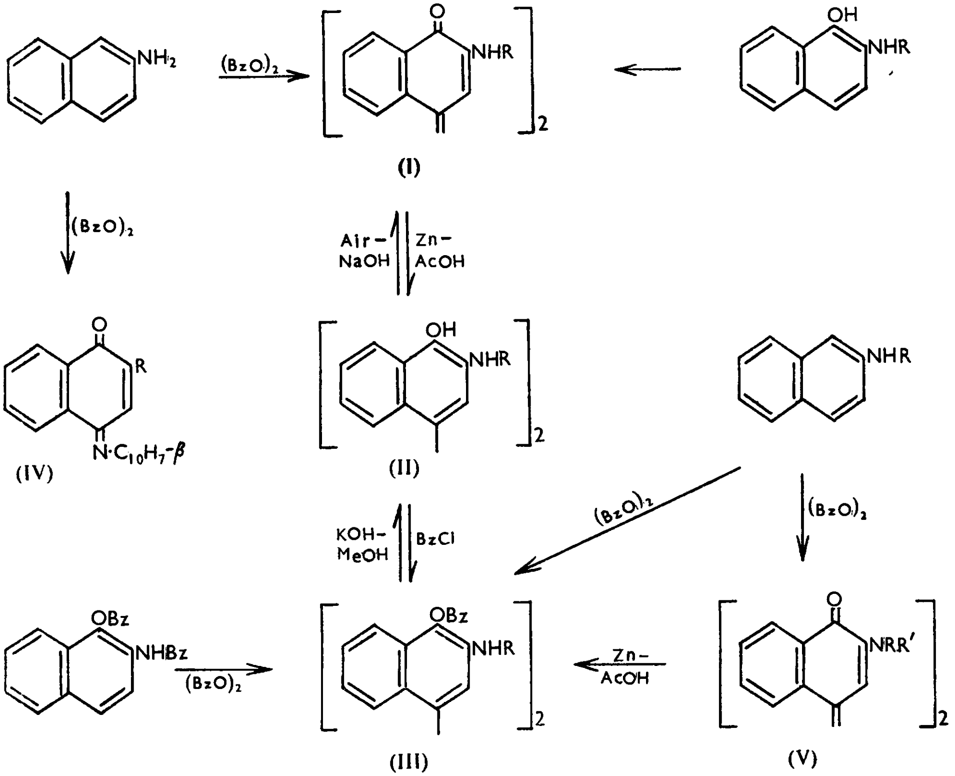
The action of benzoyl peroxide on 2-naphthylamine and some related compounds has been investigated, and a number of products identified. The infrared spectra of some of these products are described.

Benzoyl peroxide in chlorobenzene at 80° is known to give rise to free benzoate radicals, and the action of these radicals on polycyclic hydrocarbons has been examined by Roitt and Waters [1,2] in an attempt to understand the relation between the chemical and the biological properties of these compounds. For the same reason we have examined the action of these radicals on the carcinogenic agent, 2-naphthylamine.

The principal product of the oxidation was a high-melting, coloured compound, which, from a consideration of the evidence presented below, appears to be di-(3-benzamido-1 : 4-dihydro-4-oxonaphthylidene) (I; R = Bz). When reduced with zinc and acetic acid, it gave a phenol which was readily re-oxidised by air, particularly in the presence of alkali.



The structure (II; R = Bz) is assigned to it because on hydrolysis it yielded 3 : 3′-diamino-4 : 4′-dihydroxy-1 : 1′-dinaphthyl (II; R = H), and on benzoylation the corresponding tetrabenzoate (III; R = Bz).

The structure of the aminophenol (II; R = H) was proved by its synthesis by an independent route: 4 : 4′-dihydroxy-1 : 1′-dinaphthyl was treated with nitrous acid to yield a dinitroso-compound, which, because the positions *para* to the hydroxyl groups are

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[1] Roitt and Waters, *J.*, 1952, 2695.

[2] Cf. Perret and Perrot, *Helv. Chim. Acta*, 1945, **28**, 558.

blocked, should be 4 : 4′-dihydroxy-3 : 3′-dinitroso-1 : 1′-dinaphthyl. The dinitroso-compound was reduced with sodium dithionite to the diamine (II; R = H). The amino-groups must be *ortho* to the hydroxyl groups in this compound for its tetrabenzoate, identical with that given by the phenol (II; R = Bz) above, was also formed by reaction of 2-benzamido-1-naphthyl benzoate with benzoyl peroxide in chlorobenzene. The benzoate therefore has the structure (III; R = Bz) and this is confirmed by its infrared absorption which is almost identical with that of 2-benzamido-1-naphthyl benzoate itself in the NH and C=O stretching regions (Table). The subsidiary peaks at about 3420 and 3393 cm.$^{-1}$ on the low-frequency side of the main NH stretching band, absent in the simple derivatives, arise from forms showing weak intramolecular hydrogen bonding,[3,4] proving the benzoyloxy- and benzamido-groups to be *ortho* to one another in both compounds. For the same reason, the benzoyl-carbonyl band is broader in the mixed compounds than in 1-naphthyl benzoate.

The most likely structure for the coloured compound, therefore, is that formulated above (I; R = Bz), and this is supported from its infrared spectrum (Table), although the exceptionally low NH frequency of 3363 cm.$^{-1}$ and the position of the quinone band require some discussion. The latter, by comparison with that of diphenoquinone [5] at 1635 cm.$^{-1}$ and analogy with the benzoquinone series,[6] might be expected at about 1642 cm.$^{-1}$. The lower frequency observed can be explained by the interaction, through conjugation, of the quinone groups with the nucleophobic nitrogen atoms. As a result, the amide-carbonyl frequency should be correspondingly increased, which is not observed, or the nitrogen atoms must bear higher overall positive charges (cf. the analogous situation in unsaturated ester-nitriles [7]). The second possibility should give rise [8] to a lower NH frequency, which is actually observed and, in this way, explained. The NH and the CO stretching vibration of diacetamide confirm these assignments for they are respectively lowered and raised from the usual positions for a saturated secondary amide [9] of about 3437 and 1675 cm.$^{-1}$. In this case, the positive charge on the nitrogen atom is insufficiently increased to compensate for its effect's being shared between the two acetyl groups. One other feature of the spectrum of the quinone (I; R = Bz) is that the C=C band at 1596 cm.$^{-1}$ is as intense as the quinone C=O band, and both are exceptionally strong. This must be due to an interaction of the C=O and C=C vibrations, caused by their proximity in frequency, and resulting in modes which have a greatly increased dipole moment charge and hence absorption intensity.

Infrared characteristic frequencies (cm.$^{-1}$), with their assignments, in chloroform solution.

		Carbonyl bands				
	>NH	–O·CO·Ar	–NH·COMe	–NH·CO·Ar	Quinone	C=C
1-Naphthyl benzoate	—	1739	—	—	—	1601
Acetanilide	3437	—	1690	—	—	1601
2-Acetamidonaphthalene	3437	—	1689	—	—	1632, 1605, 1585
Benzanilide	3436	—	—	1676	—	1601, 1584
2-Benzamidonaphthalene	3437	—	—	1676	—	1635, 1603, 1584
2-Benzamido-1-naphthyl benzoate	3440, 3422, 3393	1740	—	1680	—	1638, 1607, 1583
Diacetamide	3400	—	1708	—	—	—
III; R = Ac	3439, 3423, 3384	1744	1697	—	—	1629, 1610, 1585
III; R = Bz	3440, 3420, 3393	1740	—	1681	—	1626, 1604, 1585
I; R = Ac	3363	—	1692	—	1619	1603
I; R = Bz	3361	—	—	1674	1620	1596
V; R = Ac, R′ = Bz	—	—	1715	1695	1634	1595
V; R = R′ = Bz	—	—	—	1694	1633	1594

The mode of formation of the quinone (I; R = Bz) seems reasonably certain. In the oxidation of *N*-alkylanilines with benzoyl peroxide, Edward [10] postulated that the action

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[3] Mizushima, Shimanouchi, Tsuboi, Sugita, Kato, and Kondo, *J. Amer. Chem. Soc.*, 1951, **73**, 1330.

[4] Mizushima, Tsuboi, Shimanouchi, and Asai, *ibid.*, 1954, **76**, 6003.

[5] Fuson, Josien, and Shelton, *ibid.*, p. 2526.

[6] Josien, Fuson, Lebas, and Gregory, *J. Chem. Phys.*, 1953, **21**, 331.

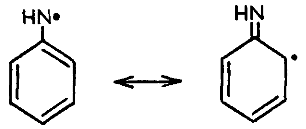
[7] Felton and Orr, *J.*, 1955, 2170.

[8] Fuson, Josien, Powell, and Utterbach, *J. Chem. Phys.*, 1952, **20**, 145.

[9] Richards and Thompson, *J.*, 1947, 1248.

[10] Edward, *J.*, 1954, 1464.

of the benzoate radicals leads first to the removal of hydrogen from the amino-groups to yield mesomeric radicals of the type :



These then react with benzoate radicals in the nucleus in positions *ortho* to the amino-groups. In the *o*-benzoyloxyamino-compounds thus formed, however, *ortho-O* $\longrightarrow$ *N* migrations of acyl groups readily take place (the reduction of *o*-nitrophenyl benzoate, for example, yields *o*-benzamidophenol [11]). A similar mechanism in the case of 2-naphthylamine would lead to the initial formation of 2-amino-1-naphthyl benzoate, followed by rearrangement to 2-benzamido-1-naphthol. Abstraction of hydrogen from this compound, followed by dimerisation in the 4-position, should then yield the product (I; R = Bz). When 2-benzamido-1-naphthol was treated with benzoyl peroxide in chlorobenzene, the quinone (I; R = Bz) was formed and, under similar conditions, 2-acetamido-1-naphthol yielded a coloured compound which probably has the structure (I; R = Ac). The infra-red spectrum of this compound was analogous to that of the benzamido-compound already discussed. The 1692 cm.$^{-1}$ band is due to the acetamido-carbonyl group, while the low quinone frequency of 1619 cm.$^{-1}$, intensified by interaction with the C=C frequency of 1603 cm.$^{-1}$, is again accompanied by a low NH frequency of 3363 cm.$^{-1}$.

Among the other products of the oxidation of 2-naphthylamine were 2 : 2′-azonaphthalene and 1 : 2-5 : 6-dibenzophenazine, the latter being a well-known product of the oxidation of 2-naphthylamine by other methods.[12, 13] Edward [14] has also obtained compounds of these types in the oxidation of aromatic amines with benzoyl peroxide. Another product was considered to be 2-benzamido-1 : 4-naphthaquinone 4-2′-naphthylimide (IV; R = NHBz). Hydrolysis with potassium hydroxide in methanol yielded the free base (IV; R = NH_2), whose infrared spectrum was identical with that of the 2-amino-1 : 4-naphthaquinone 2′-naphthylimide obtained by Teuber and Jellinek [15] in the oxidation of 2-naphthylamine with potassium nitrosodisulphonate. The free base was converted by acetic anhydride into the acetyl derivative (IV; R = NHAc) which had the same properties as those of a compound obtained by Pausacker and his co-workers [16] in the oxidation of 2-naphthylamine with phenyl iodosoacetate or lead tetra-acetate, and of 2-acetamidonaphthalene with phenyl iodosoacetate. These workers considered their compound to be 2-acetamido-1 : 4-naphthaquinone 1-2′-naphthylimide, but because 2-2′-naphthylamino-1 : 4-naphthaquinone 4-2′-naphthylimide (IV; R = $NH{\cdot}C_{10}H_7$-β) was obtained when the free base (IV; R = NH_2) was heated with 2-naphthylamine in acetic acid, it seemed to us more likely that our imide was 2-benzamido-1 : 4-naphthaquinone 4-2′-naphthylimide. The imide (IV; R = $NH{\cdot}C_{10}H_7$-β), which was also isolated in the oxidation of 2-naphthylamine with persulphate,[12] has been synthesised by Meldola [17] from 2 : 4-dibromo-1-naphthol and 2-naphthylamine. The further action of the mesomeric radicals already mentioned can account for the formation of the above oxidation products.

A number of other coloured products were formed in the oxidation of 2-naphthylamine, but these were not further examined.

The action of benzoyl peroxide on 2-acetamido- and 2-benzamido-naphthalene was also investigated. The reactions were much less vigorous than in the case of 2-naphthylamine itself, and some difficulty was experienced in separating the products. 2-Acetamido- and 2-benzamido-1-naphthyl benzoate were not isolated, but when the products from the

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[11] Böttcher, *Ber.*, 1883, **16**, 629.
[12] Boyland, Manson, and Sims, *J.*, 1953, 3623.
[13] Clemo and Dawson, *J.*, 1939, 1114.
[14] Edward, *J.*, 1956, 222.
[15] Teuber and Jellinek, *Chem. Ber.*, 1954, **87**, 1841.
[16] Barlin, Pausacker, and Riggs, *J.*, 1954, 3122; Barlin and Riggs, *ibid.*, p. 3125; Pausacker and Scroggie, *ibid.*, p. 4003.
[17] Meldola, *J.*, 1884, 156.

oxidation of 2-benzamidonaphthalene were chromatographed on alumina a little 2-phenylnaphth-2 : 1-oxazole was obtained. This oxidation also gave 2 : 2′-dibenzamido-1 : 1′-dinaphthyl in good yield, together with the tetrabenzoate (III; R = Bz) described above. The oxidation of 2-acetamidonaphthalene yielded a compound which, because it afforded 3 : 3′-diamino-4 : 4′-dihydroxy-1 : 1′-dinaphthyl (II; R = H) on hydrolysis, was presumed to be 3 : 3′-diacetamido-4 : 4′-dibenzoyloxy-1 : 1′-dinaphthyl (III; R = Ac). Its infrared spectrum was closely similar to that of the corresponding benzamido-compound (III; R = Bz); the bands at 1744 and 1697 cm.$^{-1}$ are assigned to the benzoate and the acetamido-carbonyl group respectively, and the NH absorption again showed the characteristics of an intramolecularly hydrogen-bonded system.

Oxidations of 2-acetamido- and 2-benzamido-naphthalene each yielded coloured compounds which, on evidence described below, have been formulated as di-(3-*N*-acetylbenzamido-1 : 4-dihydro-4-oxonaphthylidene) (V; R = Ac, R′ = Bz) and di-(3-dibenzoylamino-1 : 4-dihydro-4-oxonaphthylidene) (V; R = R′ = Bz), respectively. These compounds were both reduced by zinc and acetic acid to the derivatives (III; R = Ac and Bz respectively), but the reverse change could not be brought about, either with air or with benzoyl peroxide. Both compounds were unaffected by hot dilute hydrochloric acid but were readily decomposed by potassium hydroxide in methanol in the cold to ammonia and unidentified amorphous substances. When the hydrolyses were stopped after a few minutes by the addition of water, products were extracted into chloroform giving solutions which, on spectrographic analysis, showed maxima at 5750 Å. The compounds (I; R = Ac and Bz) both show maxima at this wavelength. The infrared spectrum of the dibenzoyl derivative (V; R = R′ = Bz) showed bands at 1694 and 1633 cm.$^{-1}$ in chloroform solution which were assigned to the dibenzoylamino- and the quinonoid-carbonyl group respectively. In this compound as formulated above, the nucleophobic nature of the nitrogen is shared with two benzoyl groups as well as with the quinonoid-carbonyl group. The frequency of the latter would therefore be expected to be reduced much less than in the monobenzoyl compound (I; R = Bz); at the same time the *N*-benzoyl-carbonyl frequency should be considerably higher than for a normal benzanilide type of compound. In the spectrum of the compound formulated as (V; R = Ac, R′ = Bz) analogous absorption bands were found and similar assignments made. In this case the upper band is split into two components as would be expected for a mixed acetyl-benzoyl compound, for the acetyl-carbonyl group should absorb at some 20 cm.$^{-1}$ higher than the benzoyl. In neither case was absorption due to NH observed.

It will be seen that the assignment of the frequencies in the four quinones is similar, in that the lower frequency is attributed to the quinonoid-carbonyl group in each case, and the upper frequencies to the *N*-benzoyl or *N*-acetyl group, being respectively lower and higher than the values in the respective simple compounds. Flett [18] has examined analogous benzamido- and acetamido-derivatives of anthraquinone, but was unable to make satisfactory assignments. This was due to his expecting " both the quinone and the other carbonyl bond to be weaker, with lowered characteristic frequencies," and his consequent attempt to assign the lowest frequency in each case to the benzamido- or acetamido-group. The amido-carbonyl bond, however, is only weaker compared to a ketone and, as has been shown above, the sharing of the nucleophobic nitrogen atom with the two carbonyl groups leads to opposite effects in the two cases, compared to the simple quinone or amide. Reassignment of Flett's bands with that of the highest frequency attributed to the benzamido- or acetamido-group gives results consistent among themselves and with the present figures.

A further consideration confirming the respective assignments of the two bands in the present case concerns some intensity measurements. The integrated absorption intensities in chloroform solution of the 1694 and 1633 cm.$^{-1}$ bands of the dibenzoyl compound (V; R = R′ = Bz) are 14·6 × 10^{4} and 8·9 × 10^{4} l. mole^{-1} cm.$^{-2}$ respectively, and of the 1715–1695 doublet and 1634 cm.$^{-1}$ band of the acetyl-benzoyl compound (V; R = Ac, R′ = Bz) 15·3 × 10^{4} and 9·8 × 10^{4} units respectively. Now the amide bands in 2-benzamido-1-naphthyl benzoate, benzanilide, and acetanilide have values of 3·3, 3·2, and 3·4 × 10^{4} units

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[18] Flett, *J.*, 1948, 1441.

respectively; the values for the benzamido- and the acetamido-groups in the two compounds above should each be quite close to these figures, so that it is the upper bands which are of about the right intensity for the four amido-carbonyl groups occurring in each case.

EXPERIMENTAL

Methods.—Chlorobenzene and benzoyl peroxide were purified as described by Roitt and Waters.[1] The first oxidations were carried out under a slow stream of purified nitrogen as described by these authors, carbon dioxide evolved being collected in weighed soda-lime tubes. In later experiments these precautions were omitted without affecting either the nature or the yield of the products.

Oxidation of 2-Naphthylamine.—2-Naphthylamine (5 g.), in chlorobenzene (250 ml.), was heated to 80°, and benzoyl peroxide (17 g.) (either as a solid or in chlorobenzene solution) was added at such a rate that the temperature remained at 78—82°. Carbon dioxide (0·09 g.) was evolved and a dark green solid (2·8 g.) separated. The solid, recrystallised from nitrobenzene, yielded *di-(3-benzamido-1 : 4-dihydro-4-oxonaphthylidene)* (I; R = Bz) in dark green needles with a metallic lustre, m. p. 332° (Found : C, 78·1, 78·1; H, 4·7, 4·35; N, 5·2. $C_{34}H_{22}O_4N_2$ requires C, 78·15; H, 4·2; N, 5·4%).

The chlorobenzene solution yielded benzoic acid (11·6 g., 68%) on extraction with aqueous sodium hydrogen carbonate. The solution was dried ($CaCl_2$), the chlorobenzene was removed under reduced pressure, and the red oil was extracted with boiling ether (10 × 150 ml.), to leave a brown amorphous solid (1·2 g.) which was not examined. The combined ether extracts were evaporated to dryness and the residue was chromatographed on alumina (200 g.) (Savory and Moore).

When the alumina column was eluted with light petroleum (b. p. 60—80°), two fractions were obtained which, on evaporation of the solvent, yielded a colourless gum (80 mg.) and a reddish, fluorescent gum (100 mg.) respectively. Elution of the column with benzene–light petroleum (b. p. 60—80°) (1 : 5) yielded a series of fractions, with colours ranging from orange to yellow, which slowly deposited a yellow solid. The combined fractions were evaporated to about 20 ml., more yellow solid separating. The solid, recrystallised from glacial acetic acid, yielded 1 : 2-5 : 6-dibenzophenazine (230 mg.) in pale yellow needles, m. p. and mixed m. p. 284—285° (Found : C, 85·5; H, 5·2; N, 10·1. Calc. for $C_{20}H_{12}N_2$: C, 85·7; H, 4·9; N, 9·9%). The filtrate was evaporated to dryness and the residue was recrystallised twice from ethanol, to yield 2 : 2′-azonaphthalene in red plates, m. p. and mixed m. p. 206—207° (Found : N, 10·0. Calc. for $C_{20}H_{14}N_2$: N, 9·9%).

Elution of the column with benzene–light petroleum (b. p. 60—80°) (1 : 1) yielded a red solution which, on evaporation, gave *2-benzamido-1 : 4-naphthaquinone 4-2′-naphthylimide* (IV; R = NHBz) (850 mg.), separating from ethyl acetate in red needles with a metallic lustre, m. p. 198—199° (Found : C, 80·3, 80·3; H, 4·7, 4·55; N, 7·0, 7·1. $C_{27}H_{18}O_2N_2$ requires C, 80·6; H, 4·5; N, 7·0%). Light absorption (in ethanol) : Max., 3020 and 4800 Å (ε 24,000 and 6000).

When the column was eluted with acetone, two fractions were obtained which afforded a blue and a brown powder respectively on evaporation of the solvent. These were not further examined.

(With D. MANSON) *Preparation of 3 : 3′-Diamino-4 : 4′-dihydroxy-1 : 1′-dinaphthyl* (II; R = H).—4 : 4′-Dihydroxy-1 : 1′-dinaphthyl (14·3 g.) in water (250 ml.) containing sodium hydroxide (4 g.) and sodium nitrite (7 g.) was cooled to 0° and 10% aqueous sulphuric acid (100 ml.) was added during 30 min., with stirring. After 90 min. the green precipitate (14·6 g.) was centrifuged off and washed with water. A small amount was crystallised from pyridine, to yield *4 : 4′-dihydroxy-3 : 3′-dinitroso-1 : 1′-dinaphthyl* as yellow needles, m. p. >400° (Found : N, 8·3. $C_{20}H_{12}O_4N_2$ requires N, 8·1%).

The crude nitroso-compound (4 g.), in an excess of 2N-sodium hydroxide, was heated to 50° with sodium dithionite (8 g.) until the colour of the nitroso-compound disappeared. The solution was cooled by the addition of ice and neutralised with 2N-hydrochloric acid, and the precipitate was collected, washed with water, and dissolved in hot aqueous 4% hydrochloric acid. The solution was treated with charcoal and an equal volume of concentrated hydrochloric acid was added. The product (3·3 g.) which separated was recrystallised by the addition of concentrated hydrochloric acid to a solution in 4% aqueous hydrochloric acid, to yield *3 : 3′-diamino-4 : 4′-dihydroxy-1 : 1′-dinaphthyl dihydrochloride* (2·6 g.) in silvery-grey plates, m. p. >400° (Found : N, 6·9. $C_{20}H_{18}O_2N_2Cl_2$ requires N, 7·2%). The hydrochloride gave with aqueous ammonia a green colour which could be extracted into benzene.

The *tetrabenzoate* (III; R = Bz) separated from ethyl acetate in needles, m. p. 263—264° (Found: C, 78·5; H, 4·2; N, 3·9. $C_{43}H_{32}O_6N_2$ requires C, 78·7; H, 4·4; N, 3·8%).

Oxidation of 2-*Benzamido*-1-*naphthyl Benzoate*.—This compound (1 g.), in chlorobenzene (10 ml.), was heated at 80° with benzoyl peroxide (1 g.) for 8 hr. The solution was washed with aqueous sodium hydrogen carbonate (3 × 20 ml.), dried ($CaCl_2$), and evaporated to dryness. The residue was chromatographed on alumina, and elution of the column with ether yielded a benzoate, separating from ethyl acetate in needles, m. p. and mixed m. p. 262—263° with the above tetrabenzoate (III; R = Bz). The infrared absorption spectra of the two benzoates were identical.

Reduction of Di-(3-*benzamido*-1 : 4-*dihydro*-4-*oxonaphthylidene*) (I; R = Bz).—The compound (I; R = Bz) (2 g.), zinc dust (2 g.), and acetic acid (780 ml.) were heated together under reflux until the mixture became colourless. The mixture was filtered and immediately diluted with water (1 l.), 3 : 3′-*dibenzamido*-4 : 4′-*dihydroxy*-1 : 1′-*dinaphthyl* (II; R = Bz) (1·9 g.) separating as a blue or pink powder. It was purified by dissolving it in boiling acetic acid containing a little zinc dust and diluting the filtered solution with water; it formed a white powder, m. p. 274—275° (darkening at 250°) (Found: C, 77·6; H, 5·0; N, 5·4. $C_{34}H_{24}O_4N_2$ requires C, 77·85; H, 4·6; N, 5·3%). The phenol yielded a tetrabenzoate, separating from ethyl acetate in needles, m. p. 261—263°, undepressed in admixture with (III; R = Bz), and with identical infrared absorption spectrum.

Hydrolysis of 3 : 3′-*Dibenzamido*-4 : 4′-*dihydroxy*-1 : 1′-*dinaphthyl* (II; R = Bz).—The phenol (2 g.), in methanolic 2N-potassium hydroxide (25 ml.), was heated under reflux for 2 hr., and the solution then diluted with water (100 ml.), acidified with 2N-hydrochloric acid, and filtered. Concentrated hydrochloric acid (100 ml.) was added to the filtrate, 3 : 3′-diamino-4 : 4′-dihydroxy-1 : 1′-dinaphthyl dihydrochloride (950 mg.) separating: it recrystallised, as previously described, in grey plates, m. p. >360° (Found: C, 61·9; H, 5·0; N, 6·8. Calc. for $C_{20}H_{18}O_2N_2Cl_2$: C, 61·7; H, 4·7; N, 7·2%). It formed a tetrabenzoate as needles (from ethyl acetate), m. p. 261—263°, undepressed in admixture with the benzoate (III; R = Bz).

Oxidation of 3 : 3′-*Dibenzamido*-4 : 4′-*dihydroxy*-1 : 1′-*dinaphthyl* (II; R = Bz).—A current of air was drawn through a solution of the phenol (1 g.) in 2N-sodium hydroxide (20 ml.) for 24 hr. The purple powder (800 mg.) which separated was crystallised from nitrobenzene, to yield di-(3-benzamido-1 : 4-dihydro-4-oxonaphthylidene) (I; R = Bz) in dark green needles, m. p. and mixed m. p. 332° (Found: N, 5·7%).

Oxidation of 2-*Benzamido*-1-*naphthol*.—2-Benzamido-1-naphthol (500 mg.), in chlorobenzene (5 ml.), was treated with benzoyl peroxide (1 g.) at 80° as before and the product which separated was recrystallised from nitrobenzene, to yield di-(3-benzamido-1 : 4-dihydro-4-oxonaphthylidene) (I; R = Bz) in dark green needles, m. p. and mixed m. p. 332° (Found: N, 5·3%). This product had an infrared absorption spectrum identical with that of the product from the oxidation of 2-naphthylamine.

Oxidation of 2-*Acetamido*-1-*naphthol*.—2-Acetamido-1-naphthol (500 mg.) was similarly oxidised, to yield *di*-(3-*acetamido*-1 : 4-*dihydro*-4-*oxonaphthylidene*) (I; R = Ac) (220 mg.), separating from nitrobenzene in green plates with a metallic lustre, m. p. 325° (Found: C, 72·5, 72·4; H, 4·7, 4·95; N, 6·8, 7·1. $C_{24}H_{12}O_4N_2$ requires C, 72·35; H, 4·55; N, 7·0%).

Hydrolysis of 2-*Benzamido*-1 : 4-*naphthaquinone* 4-2′-*Naphthylimide* (IV; R = NHBz).—The benzoate (2·5 g.) was heated under reflux with methanolic 2N-potassium hydroxide (50 ml.) for 1 hr. The solution was poured into water, and the red powder collected and crystallised from light petroleum (b. p. 80—100°). 2-Amino-1 : 4-naphthaquinone 4-2′-naphthylimide (IV; R = NH_2) (1·8 g.) formed a red powder, m. p. 136—138° (Found: C, 80·25; H, 4·9; N, 9·3. Calc. for $C_{20}H_{14}ON_2$: C, 80·5; H, 4·7; N, 9·4%). The infrared spectrum of this imide was identical with that of the product which melted at about 135° obtained by Teuber and Jellinek.[15]

When the imide (IV; R = NH_2) (100 mg.), in glacial acetic acid (5 ml.), was heated at 100° with 2-naphthylamine (100 mg.) for 30 min., 2-2′-naphthylamine-1 : 4-naphthaquinone 4-2′-naphthylimide (IV; R = $NH{\cdot}C_{10}H_7$-β) (120 mg.) separated; from benzene it formed red needles, m. p. 247—248° alone and in admixture with the product from the oxidation of 2-naphthylamine with persulphate [12] (Found: N, 6·5. Calc. for $C_{30}H_{20}ON_2$: N, 6·6%).

The imide (IV; R = NH_2) (50 mg.) was kept overnight with a few drops of acetic anhydride; 2-acetamido-1 : 4-naphthaquinone 4-2′-naphthylimide (IV; R = NHAc) separated: from ethanol it formed purple needles, m. p. 209—210° (Found: N, 8·5. Calc. for $C_{22}H_{16}O_2N_2$: N, 8·2%). Light absorption (in ethanol): Max. 3020 and 4800 Å (ε 25,000 and 6700). The product obtained by Pausacker *et al.*[16] formed purple needles (from ethanol), m. p. 210—212°.

Oxidation of 2-*Acetamidonaphthalene*.—2-Acetamidonaphthalene (10 g.) in chlorobenzene

(250 ml.) was heated at 80° with benzoyl peroxide (10 g.) for 24 hr. Carbon dioxide (0·11 g.) was evolved, and benzoic acid (5·8 g.; 58%) was separated by extraction with aqueous sodium hydrogen carbonate. During this extraction, 3 : 3′-*diacetamido*-4 : 4′-*dibenzoyloxy*-1 : 1′-*dinaphthyl* (IV; R = Ac) (3·1 g.) separated as a grey solid: from a large volume of ethyl acetate it formed a colourless powder, m. p. 259—260° (Found: C, 74·7; H, 4·8; N, 4·4, 4·6. $C_{38}H_{28}O_6N_2$ requires C, 75·0; H, 4·6; N, 4·6%). Hydrolysis of this product with hot methanolic 2N-potassium hydroxide and subsequent benzoylation yielded the tetrabenzoate (III; R = Bz), m. p. and mixed m. p. 258—259°.

The chlorobenzene solution was diluted with ether (750 ml.), a compound (320 mg.) separating in yellow needles, which recrystallised from chloroform on addition of ether to yield *di*-(3-N-*acetylbenzamido*-1 : 4-*dihydro*-4-*oxonaphthylidene*) (V; R = Ac, R′ = Bz) in bright yellow needles, m. p. 228—229° (decomp.) (Found: C, 75·0; H, 4·3; N, 4·5, 4·55. $C_{38}H_{26}O_6N_2$ requires C, 75·2; H, 4·3; N, 4·6%). When the yellow needles were ground a bright red powder was obtained, which gave, in chloroform, a magenta solution. The chlorobenzene solution was evaporated under reduced pressure to leave a gum which was not investigated further.

Oxidation of 2-*Benzamidonaphthalene*.—2-Benzamidonaphthalene (5 g.), in chlorobenzene (200 ml.), was heated at 80° with benzoyl peroxide (10 g.) for 36 hr. Carbon dioxide (0·19 g.) was evolved, and benzoic acid (7·3 g., 73%) was extracted from the chlorobenzene solution as before. The solution was then diluted with ether (500 ml.) and kept overnight at 0°. The red plates (210 mg.) which separated recrystallised from chloroform–ether, to yield *di*-(3-*dibenzoylamino*-1 : 4-*dihydro*-4-*oxonaphthylidene*) (V; R = R′ = Bz) as red needles with a golden lustre, m. p. 183—185° (Found: N, 3·9. $C_{48}H_{30}O_6N_2$ requires N, 3·8%), which formed a magenta solution in chloroform.

The chlorobenzene solution was evaporated to dryness under reduced pressure and the residual red oil was chromatographed on alumina. Elution of the column with light petroleum (b. p. 60—80°) and evaporation of the solvent yielded a yellowish oil (120 mg.), which had a bright blue fluorescence in ultraviolet light. The oil was kept for some weeks at 0°, and the crystals which separated were recrystallised from light petroleum (b. p. 60—80°), to yield 2-phenylnaphth-2 : 1-oxazole (15 mg.) in needles, m. p. 120—122°, undepressed on admixture with the product obtained by the method of Worms.[19]

The column was eluted with light petroleum (b. p. 60—80°)–benzene mixtures, with a gradually increasing proportion of benzene. The earlier fractions, on evaporation, yielded unchanged 2-benzamidonaphthalene, separating from benzene in flakes, m. p. and mixed m. p. 162°. The residues from the evaporation of the later fractions were combined and recrystallised three times from benzene, to yield 2 : 2′-dibenzamido-1 : 1′-dinaphthyl (780 mg.) in prismatic needles, m. p. 235—236° (lit.,[20] 235°) (Found: C, 82·95; H, 5·0; N, 5·7. Calc. for $C_{34}H_{22}O_2N_2$: C, 82·9; H, 4·9; N, 5·7%).

The mother-liquors from the recrystallisations of the above dibenzoate were combined and evaporated, and the residue was fractionally crystallised from benzene. From the more soluble fractions, small amounts of two substances were isolated. The first (20 mg.) crystallised from benzene–light petroleum (b. p. 60—80°) in needles, m. p. 145—146° (Found: C, 78·0; H, 5·7; N, 4·6%), whilst the second (25 mg.) (possibly 2 : 3′-dibenzamido-4′-benzoyloxy-1 : 1′-dinaphthyl) separated from benzene–light petroleum (b. p. 60—80°) in needles, m. p. 204—205° (Found: C, 80·0; H, 4·9; N, 4·2. Calc. for $C_{41}H_{28}O_4N_2$: C, 80·4; H, 4·6; N, 4·6%).

Elution of the column with ether–acetone (1 : 1) yielded 3 : 3′-dibenzamido-4 : 4′-dibenzoyloxy-1 : 1′-dinaphthyl (III; R = Bz) (520 mg.), separating from ethyl acetate in needles, m. p. and mixed m. p. 263—264° [Found: C, 78·5; H, 4·6; N, 4·0%; *M* (Rast), 697. Calc. for $C_{48}H_{32}O_6N_2$: C, 78·7; H, 4·4; N, 3·8%; *M*, 735]. The infrared absorption of this compound was identical with that of the tetrabenzoate derived from (II; R = Bz).

Elution of the column with acetone yielded an unidentified blue powder (400 mg.).

Reduction of the Compounds (V; R = Ac, R′ = Bz) *and* (V; R = R′ = Bz).—The compounds (100 mg.), in acetic acid (5 ml.), were each heated under reflux with zinc dust (100 mg.) until the colours disappeared. The mixtures were filtered and the filtrates diluted with water (20 ml.). The compound (V; R = Ac, R′ = Bz) yielded a benzoate (50 mg.) as a colourless powder (from ethyl acetate), m. p. and mixed m. p. 258—259° with (III; R = Ac) (Found: N, 4·5%). The infrared spectra of the two compounds were identical. The compound (V; R = R′ = Bz) yielded a tetrabenzoate (60 mg.), separating from ethyl acetate in needles, m. p.

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[19] Worms, *Ber.*, 1882, **15**, 1813.

[20] Cumming and Howie, *J.*, 1932, 528.

261—262° undepressed in admixture with (III; R = Bz). The infrared spectra of the two compounds were identical.

Infrared Spectra.—Spectra were measured on a Perkin-Elmer model 112 spectrometer, with a rock-salt prism from 5—15 μ, and one of lithium fluoride in the 3 μ region. Solutions in chloroform were measured in 1 or 3 mm. cells in the 6 μ region, and in 3 or 18 mm. cells at 3 μ. Frequencies quoted should be accurate within ±2 $cm.^{-1}$.

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