Nuclear Substitution by Anions and Self-union in 1 : 8-Naphthalimide and Its N-Methyl Derivative.

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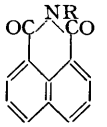
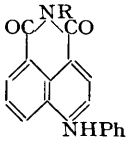
1 : 8-Naphthalimide is hydroxylated *para* to a carbonyl group with potassium hydroxide and manganese dioxide, and sodioaniline converts *N*-methyl-1 : 8-naphthalimide into the 4-anilino-derivative. Neither of the imides is as reactive as *meso*benzanthrone towards these reagents. The self-union of *N*-methyl-1 : 8-naphthalimide on treatment with alkalis involves the formation of a dinaphthyl derivative at the first stage, and the cyclisation of this to a perylene derivative. The second stage is facilitated by reducing agents.

IN most examples of nuclear substitution by hydroxyl ions and other bases which have been discussed recently (*e.g.*, Bradley and Bruce, *J.*, 1954, 1894) the reactivity of the nucleus has been due to the presence of at least one carbonyl group. For this reason Luttringhaus's observation (G.P. 492,320) that 1 : 8-naphthalimide (I; R = H) and sodioaniline afford 4-anilino-1 : 8-naphthalimide (II; R = H), amongst other products, is particularly interesting because of the low carbonyl-reactivity of imide groups. The present investigation is a more detailed study of related substitutions into (I; R = H and Me).



(I)



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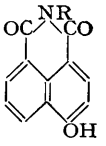

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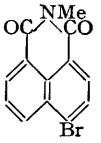

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Heating with ethanolic potassium hydroxide at 160—170° transforms (I; R = H) into perylene-3 : 4 : 9 : 10-tetracarbonyldi-imide (V; R = H), the constitution of which was established by its hydrolysis to the related tetracarboxylic acid and decarboxylation to perylene (G.P. 411,217, 486,491). There is no reaction with the same reagent at 130°,

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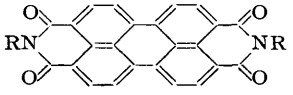

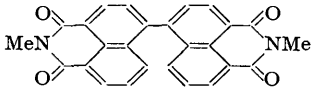

(VI)

showing that the nuclear reactivity of (I; R = H) is lower than that of *meso*benzanthrone which yields 4 : 4′-di*meso*benzanthronyl at 110° (Luttringhaus and Neresheimer, *Annalen*, 1929, **473**, 259).

Heating the imide (I; R = H) with potassium hydroxide and manganese dioxide at 220° gives the perylene derivative (V; R = H) together with 4-hydroxy-1 : 8-naphthalimide (III; R = H). The structure of this derivative was established by a synthesis from acenaphthene-3-sulphonic acid by way of 4-sulpho-1 : 8-naphthalic acid, and 4-hydroxy-1 : 8-naphthalic anhydride. The two samples of the hydroxy-compound showed the same absorption spectrum in alcohol, and gave the same red azo-derivative with diazotised *p*-nitroaniline.

The formation of a monohydroxy-derivative of 1 : 8-naphthalimide rather than a di-derivative may be regarded as due to the diminished reactivity of carbonyl groups in imides (cf. Bradley and Sutcliffe, *J.*, 1951, 2118; Bradley and Waller, *J.*, 1953, 3778).

N-Methyl-1 : 8-naphthalimide (I; R = Me) was similarly unaffected by ethanolic potassium hydroxide at 130°. With potassium hydroxide at 225—230° the main product was the perylene derivative (V; R = Me), with only an indication of the presence of phenolic compounds. With sodioaniline at 70—80° the product was 4-anilino-*N*-methyl-1 : 8-naphthalimide (II; R = Me), and this was also formed together with (V; R = Me) at 185°. The occurrence of substitution only at the lower temperature, and substitution accompanied by self-union at the higher temperature, illustrates the dual character of the action of sodioaniline. Like analogous reagents the anilide ion functions as a base which causes the ionisation of cyclic aromatic ketones, leading to their self-union, and as an active substitution agent which replaces nuclear hydrogen. The structure of the 4-anilino-derivative was proved by a synthesis from aniline and 4-bromo-*N*-methyl-1 : 8-naphthalimide (IV). The bromo-derivative (IV) showed an unexpected reaction with ethanolic potassium hydroxide at 130°, the bromine substituent being replaced by hydrogen. Heating the methylimide (IV) with copper bronze gave *NN'*-dimethyl-1 : 1'-dinaphthyl-4 : 5-4' : 5'-tetracarbonyldi-imide (VI). This was recovered unaltered after being heated with methanolic potassium hydroxide at 125°, but the perylene imide (V; R = Me) was formed with ethanolic potassium hydroxide at 130° and with potassium hydroxide at 220°. The cyclisation was facilitated by reducing agents, for example, glucose, but aluminium chloride was ineffective.

Experimental

Temperatures cited refer to the reactants, unless otherwise stated. Open vessels were used.

4-Hydroxy-1 : 8-naphthalimide.—(*a*) An intimate mixture of 1 : 8-naphthalimide (10 g.; m. p. 302°) and manganese dioxide (10 g.) was added during 10 min. at 220° to a stirred melt of potassium hydroxide (50 g.) and potassium acetate (5 g.). After being heated at 220—230° for 30 min. the pasty, deep violet product was added to water (500 c.c.), the resulting suspension was aerated for several hr., and then filtered. The residue (A) was extracted several times with cold and then with hot N-potassium hydroxide, and the filtered extracts were combined with the original filtrate. Acidification of the alkaline solutions gave an almost black solid (10·5 g.). This was extracted with cold 5% potassium hydrogen carbonate solution; acidification of the filtered extract gave a brown-black solid (4·9 g.). Repetition of the extraction with hot 5% potassium hydrogen carbonate gave a brownish-yellow solid (3·2 g.). The brown-black solid gave, after continuous extraction with acetone, a brownish-orange soluble fraction (2·5 g.), and this was sublimed at 300°/0·4 mm. A single bright yellow band formed, m. p. >350° (Found: C, 65·7, 66·3; H, 2·8, 3·2; N, 7·4, 6·2. $C_{12}H_7O_3N$ reuires C, 67·6; H, 3·3; N, 6·6%), which showed the following absorption in 95% EtOH: max. at 240 ($10^{-4}\varepsilon$ 2·61) and 389 mμ ($10^{-4}\varepsilon$ 1·08). *4-Hydroxy-1 : 8-naphthalimide* was sparingly soluble in alcohol with a green fluorescence. It gave a yellow, green-fluorescent solution in concentrated sulphuric acid. The brownish-yellow solid (3·2 g.) dissolved in hot water, and a portion (2·5 g.) separated on cooling. It was further purified by dissolution in 5% aqueous potassium hydroxide, reprecipitation by acidification, and sublimation at 325°/0·4 mm. A single bright yellow band of 4-hydroxy-1 : 8-naphthalimide resulted (Found: C, 67·4, 67·6; H, 3·2, 3·2; N, 6·2, 6·1%); light absorption in 95% EtOH, max. at 242 ($10^{-4}\varepsilon$ 2·78) and 377 mμ ($10^{-4}\varepsilon$ 1·11).

(*b*) 4-Sulpho-1 : 8-naphthalic acid (Dziewonski and Stalyhwo, *Ber.*, 1924, **57**, 1536) was converted into 4-hydroxy-1 : 8-naphthalic anhydride by Dziewonski and Kocwa's method (*Bull. intern. Acad. Polon.*, 1928, *A*, 405). After purification from aqueous alcohol the product had m. p. 249—251° (Found: C, 66·7; H, 2·7. Calc. for $C_{12}H_6O_4$: C, 67·2; H, 2·8%); light

absorption in 95% EtOH, max. at 256 ($10^{-4}\varepsilon$ 2·0), 322 ($10^{-4}\varepsilon$ 0·514), 374 mμ ($10^{-4}\varepsilon$ 0·827). Concentrated aqueous ammonia was added at intervals during 2 hr. to a refluxing solution of 4-hydroxy-1 : 8-naphthalic anhydride (0·3 g.) in ethanol (25 c.c.). The resulting orange solution was concentrated and then kept. A yellow solid (0·1 g.) separated and this was purified from aqueous alcohol (Found: C, 67·7; H, 3·2; N, 6·2%); light absorption in 95% alcohol, max. at 242 ($10^{-4}\varepsilon$ 2·75) and 377 mμ ($10^{-4}\varepsilon$ 1·08). In these as in other properties the product was identical with the 4-hydroxy-1 : 8-naphthalimide prepared by method (*a*).

Solutions of 4-hydroxy-1 : 8-naphthalic anhydride and 4-hydroxy-1 : 8-naphthalimide in 5% potassium hydroxide coupled with diazotised *p*-nitroaniline to give red azo-derivatives.

The portion (8·8 g.) of the product of the action of potassium hydroxide and manganese dioxide on 1 : 8-naphthalimide which was insoluble in potassium hydroxide was extracted with water, as described, and then with sulphuric acid and sodium metabisulphite to remove the excess of manganese dioxide. The insoluble portion was perylene-3 : 4 : 9 : 10-tetracarbonyldi-imide (3·15 g.).

1 : 8-Naphthalimide was recovered unchanged after 2 g. had been heated for 1 hr. at 130° with potassium hydroxide (15 g.) and ethanol (17·5 c.c.). With potassium hydroxide (20 g.) in ethanol (20 c.c.) at 160—170° for 1 hr. 1 : 8-naphthalimide (5 g.) gave crude perylene-3 : 4 : 9 : 10-tetracarbonyldi-imide (3·1 g.). This was extracted with acetone and then with aqueous potassium hydroxide, and a portion of the residue (2·5 g.) was sublimed at 500°/0·4 mm. The sublimate of the di-imide (Found: C, 74·4; H, 2·8; N, 7·0. Calc. for $C_{24}H_{10}O_4N_2$: C, 73·8; H, 2·6; N, 7·2%) showed the following absorption in "AnalaR" concentrated sulphuric acid, max. at 407 ($10^{-4}\varepsilon$ 0·78), 512 ($10^{-4}\varepsilon$ 1·405), 552 ($10^{-4}\varepsilon$ 4·06), and 598 mμ ($10^{-4}\varepsilon$ 7·8).

On being heated with potassium hydroxide (62 g.) and sodium acetate (6 g.) at 220° for 3 hr. according to the method of B.I.O.S. Final Report No. 1484, Item No. 22, 1 : 8-naphthalimide (20 g.) gave 18·2 g. of the crude di-imide. In addition there was an alkali-soluble product (0·3 g.), which, after purification from alcohol and sublimation at 300°/0·5 mm., gave a single bright yellow band of 4-hydroxy-1 : 8-naphthalimide, which was almost identical with the compound prepared as in (*a*) and (*b*); light absorption in 95% EtOH, max. at 240 ($10^{-4}\varepsilon$ 2·61) and 389 mμ ($10^{-4}\varepsilon$ 1·08).

4-*Anilino*-N-*methyl*-1 : 8-*naphthalimide*.—(*a*) *N*-Methyl-1 : 8-naphthalimide [2 g.; m. p. 205—206°; light absorption in "AnalaR" concentrated sulphuric acid, max. at 293 ($10^{-4}\varepsilon$ 0·548), 385 ($10^{-4}\varepsilon$ 1·56), and 407 mμ ($10^{-4}\varepsilon$ 1·48)] was refluxed and stirred for 3 hr. with sodioaniline prepared from freshly distilled aniline (30 c.c.), copper bronze (0·05 g.), nickel oxide (0·05 g.), and sodium (0·7 g.). A further addition of aniline (10 c.c.) was made after 1·5 hr. A violet colour developed. After being cooled the solution was added to an excess of dilute hydrochloric acid, and the yellow-brown powder (2·2 g.) which separated was extracted with acetone. The insoluble part (0·03 g.) was *NN'*-dimethylperylene-3 : 4 : 9 : 10-tetracarbonyldi-imide. The soluble fraction was recovered by evaporation of the solvent, dissolved in chlorobenzene, and chromatographed on alumina. On development two pale yellow bands passed rapidly through the column, but an orange band was more strongly retained. This was eluted with acetone, redissolved in chlorobenzene, and again chromatographed on alumina. The resulting deep orange band, eluted with acetone, afforded orange crystals of 4-*anilino*-N-*methyl*-1 : 8-*naphthalimide*, m. p. 256—258° (Found: C, 75·2; H, 4·5; N, 9·8. $C_{19}H_{14}O_2N_2$ requires C, 75·5; H, 4·6; N, 9·3%), not depressed by the compound prepared from 4-bromo-*N*-methyl-1 : 8-naphthalimide and aniline. It gave a strawberry-red solution in concentrated sulphuric acid. Addition of methanolic potassium hydroxide to the bright yellow solution in pyridine changed the colour to deep magenta. It was insoluble in 5% potassium hydroxide solution, alone or after the addition of sodium dithionite.

In a similar experiment carried out at 70—80° for 4 hr. *N*-methyl-1 : 8-naphthalimide (4 g.) and sodioaniline prepared from aniline (40 c.c.), copper bronze (0·05 g.), nickel oxide (0·05 g.), and sodium (1·1 g.), and with the further addition of aniline (20 c.c.) after 1 hr., gave an ochre-yellow product (3·8 g.). From this was obtained 4-anilino-*N*-methyl-1 : 8-naphthalimide, m. p. 258°, by extraction and chromatography, but there was no indication of the formation of *NN'*-dimethylperylene-3 : 4 : 9 : 10-tetracarbonyldi-imide.

(*b*) Aniline (11 g.) and 4-bromo-*N*-methyl-1 : 8-naphthalimide (0·7 g.) were refluxed for 11 hr., and then the resulting solution was added to dilute hydrochloric acid. The yellow precipitate which formed was collected, washed, and dried (0·65 g.), and then chromatographed from chlorobenzene on alumina. The main band, on elution with acetone and crystallisation from chlorobenzene, gave bright orange crystals (0·2 g.), m. p. 258°, identical with 4-anilino-*N*-methyl-1 : 8-naphthalimide prepared as in (*a*). The rate of replacement of the bromine

substituent was low; 4-bromo-*N*-methyl-1 : 8-naphthalimide (0·2 g.), refluxed with aniline (3 g.) for 2·5 hr., gave only 0·01 g. of the 4-anilino-derivative. A product, m. p. 178°, of unstated composition, has been described (G.P. 492,320) as the result of the action of sodioaniline on *N*-methyl-1 : 8-naphthalimide at 150°.

4-*Bromo*-N-*methyl*-1 : 8-*naphthalimide*.—4-Bromophthalic anhydride was prepared both by Rule and Thompson's method (*J.*, 1937, 1764) and according to *Org. Chem. Ind., U.S.S.R.*, 1937, **4**, 406. The products melted at 217—219° and 220—221°, respectively. 4-Bromo-1 : 8-naphthalic anhydride (8 g.), methylamine (10 c.c. of 33% w/v in water), and ethanol (2 l.) were refluxed for 30 min. On being cooled the solution gave pale yellow needles, m. p. 183—184° (6·6 g.), which were obtained colourless and of m. p. 185—186° (Found: C, 53·6; H, 2·8; N, 4·6; Br, 27·9. Calc. for $C_{13}H_8O_2NBr$: C, 53·8; H, 2·8; N, 4·8; Br, 27·6%) by crystallisation from glacial acetic acid; light absorption in " AnalaR " concentrated sulphuric acid, max. at 312 ($10^{-4}\varepsilon$ 0·58), 400 ($10^{-4}\varepsilon$ 1·74), and 420 mμ ($10^{-4}\varepsilon$ 1·74).

Action of Ethanolic Potassium Hydroxide at 130°.—4-Bromo-*N*-methyl-1 : 8-naphthalimide (1 g.) was heated at 130° and stirred for 1·5 hr. with potassium hydroxide (10 g.) and ethanol (9 c.c.). A purple colour developed. Addition to water gave a buff-coloured solid (0·75 g.). This separated from a solution in acetone as pale brown needles, m. p. 202—203°, and as pink needles (0·5 g.), m. p. 204—205°, not depressed by an authentic sample of *N*-methyl-1 : 8-naphthalimide, m. p. 205—206°.

NN′-*Dimethyl*-1 : 1′-*dinaphthyl*-4 : 5-4′ : 5′-*tetracarbonyldi-imide*.—The above 4-bromo-derivative (4 g.) was heated and frequently stirred with copper bronze (3 g.) at 240° for 4·5 hr. The cooled product was powdered, and extracted with alcohol which dissolved 2·1 g. of unchanged bromo-derivative. The insoluble part was stirred with concentrated aqueous ammonia and ammonium chloride, and the buff-coloured residue (1·2 g.) was extracted with acetone. The residue (0·6 g.), m. p. 399—402°, crystallised (m. p. 403—404°) from chlorobenzene, and a portion of the purified material gave pale yellow needles on sublimation (Found: N, 7·0, 6·6. $C_{26}H_{16}O_4N_2$ requires N, 6·7%). NN′-*Dimethyl*-1 : 1′-*dinaphthyl*-4 : 5-4′ : 5′-*tetracarbonyldi-imide* dissolved in " AnalaR " concentrated sulphuric acid, forming a bright yellow solution max. at 295 ($10^{-4}\varepsilon$ 0·84) and 412 mμ ($10^{-4}\varepsilon$ 3·7). It exhibited a blue fluorescence in glacial acetic acid and chlorobenzene. It was unaltered on being heated with 5% potassium hydroxide solution, alone or with the addition of sodium dithionite, with potassium hydroxide (5 g.) and methanol (5 c.c.) at 125° for 1 hr., with potassium hydroxide (0·5 g.) and *tert.*-butanol (7 c.c.) under reflux for 1 hr., or with aluminium chloride (1·5 g.) and sodium chloride (0·25 g.) at 170° for 0·5 hr.

Conversion into NN′-*Dimethylperylene*-3 : 4-9 : 10-*tetracarbonyldi-imide*.—(*a*) A purple colour developed almost immediately on the addition of the dinaphthyl derivative (0·05 g.) to potassium hydroxide (5 g.) and potassium acetate (0·4 g.) at 220°. After 40 min. the product was added to water and aerated, and the red precipitate (0·045 g.) was collected. Extraction with chlorobenzene afforded a residue (0·01 g.) which showed all the properties of *NN′*-dimethylperylene-3 : 4-9 : 10-tetracarbonyldi-imide. (*b*) The yield of the perylene derivative was increased to 0·02 g. when glucose (0·05 g.) was added to the reactants, and the heating was at 180° for 1 hr. and then at 200° for 10 min. (*c*) The dinaphthyl derivative (0·05 g.), potassium hydroxide (7 g.), and 95% ethyl alcohol (7 c.c.), stirred and heated at 130° for 1 hr., gave approx. 0·002 g. of the perylene derivative. (*d*) Under the same conditions as (*c*) but with the addition of glucose (0·05 g.), conversion into the perylene derivative (0·048 g.) was almost quantitative. (*e*) The perylene derivative (0·03 g.) was also obtained when the dinaphthyl derivative (0·05 g.) was refluxed for 10 hr. with potassium hydroxide (5 g.), water (5 c.c.), and sodium formaldehydesulphoxylate (0·5 g.).

4-*Bromo*-1 : 8-*naphthalimide* prepared from 4-bromonaphthalic anhydride and aqueous ammonia formed colourless needles, m. p. 298° (Found: C, 51·9; H, 2·0; N, 5·0; Br, 28·8. Calc. for $C_{12}H_6O_2NBr$: C, 52·2; H, 2·2; N, 5·1; Br, 29·0%).

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