111. Derivatives of Naphthalomethylimide.

By E. M. Francis and J. L. Simonsen.

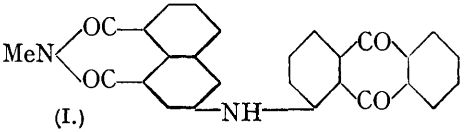
In view of the fact that naphthalimide and naphthalomethylimide yield perylene derivatives which have found application as dyes (Cain and Thorpe, " Synthetic Dyestuffs," p. 247), it appeared probable that derivatives of the latter might be of value as dye intermediates. We have found, however, that the methylimide is remarkably inert and that it cannot, for example, be condensed with acid chlorides or acid anhydrides by the Friedel–Crafts reaction. 4-*Benzoylnaphthalomethylimide* was prepared indirectly by the action of methylamine on 4-benzoylnaphthalic anhydride (Graebe, *Annalen*, 1903, **327**, 98), but attempts to cyclise it to the corresponding benzanthrone failed.

Nitration of the methylimide resulted in the formation of the 3-*nitro*- or the 3 : 6-*dinitro*-derivative, which were also prepared from 3-nitro- and 3 : 6-dinitro-naphthalic anhydride (Graebe, *loc. cit.*, p. 84; Leuck, Perkins, and Whitmore, *J. Amer. Chem. Soc.*, 1929, **51**, 1831; Rule and Brown, J., 1934, **171**) respectively. From 3-*aminonaphthalomethylimide*, the 3-*chloro*- and the 3-*hydroxy*-derivative were prepared. The latter was obtained also from naphthalic anhydride *via* the sulphonic acid (Anselm and Zuckmayer, *Ber.*, 1899, **32**, 3288), thus indirectly orienting the sulphonic acid and the related hydroxy-anhydride.

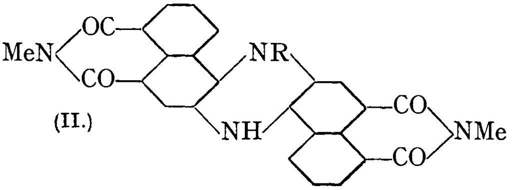
The condensation of 3-aminonaphthalomethylimide with 1-chloro-, 1-chloro-4-benzamido-, and 1-chloro-5-benzamido-anthraquinone gave 3-1′-*anthraquinonylaminonaphthalomethylimide* (I) and the 4′- and the 5′-*benzamido*-derivative respectively, but cyclisation of these to carbazoles could not be effected (contrast dianthraquinonylamine). In nitrobenzene the reaction proceeded abnormally; with 1-chloroanthraquinone a crystalline *substance*, $C_{26}H_{16}O_4N_4$, was obtained together with anthraquinone. We suggest that this substance is the dihydroazine (II; R = H), the chloroanthraquinone acting as a mild oxidising agent.

Substances of similar type were obtained also when 1-chloro-4-benzamido- and 1-

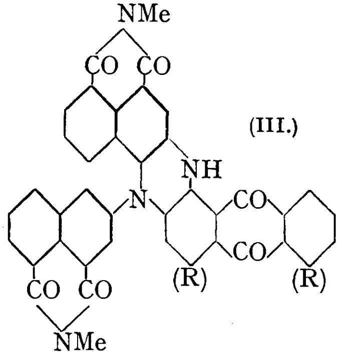
chloro-5-benzamido-anthraquinone were used as the second component. In addition to 4-benzamidoanthraquinone, crystalline *substances*, $C_{47}H_{27}O_7N_5$, were isolated, which



(I.)



(II.)



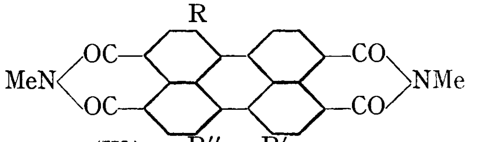
(III.)

from analogy with (II; R = H) may be represented by either (II; R = 4- or 5-benzamido-anthraquinonyl) or (III; R = H or benzamido-).

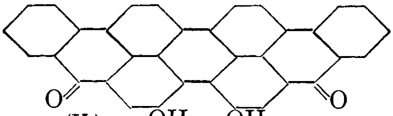
3-Chloronaphthalomethylimide did not react with 1-aminoanthraquinone under Ullmann conditions.

Condensation of 3 : 6-*diaminonaphthalomethylimide* with 1-chloro-4-benzamidoanthraquinone in amyl-alcoholic solution resulted in the formation of the *monoanthraquinonyl-*derivative, only one of the amino-groups reacting.

In earlier unpublished experiments by Dr. Fraser Thomson (private communication) it had been observed that the di-imide of perylene-3 : 4 : 9 : 10-tetracarboxylic acid gave on oxidation with manganese dioxide and sulphuric acid a phenol yielding on methylation a substance which was apparently a dimethoxydi-imide. In order to elucidate the structure of this substance, 3-hydroxynaphthalimide (Anselm and Zuckmayer, *loc. cit.*) was fused with potassium hydroxide and the phenol obtained was methylated with methyl sulphate. The dimethyl ether produced must be the perylene derivative (IV; R = R′ = OMe, R″ = H or R′ = R″ = OMe, R = H). This α-*di-imide* of 1 : 7 (or 1 : 12)-*dimethoxyperylene-*3 : 4 : 9 : 10-*tetracarboxylic acid* differed in colour reactions and dyeing properties from its isomeride, the β-*di-imide*, prepared by the methylation of the phenol produced by direct oxidation of the perylene. The positions of the methoxy-groups in the latter compound therefore remain undetermined but it seems not improbable that the two ethers are the isomerides (IV; R = R′ = OMe, R″ = H) and (IV; R′ = R″ = OMe, R = H), since in the somewhat analogous case of dibenzanthrone treatment with manganese dioxide and sulphuric acid results in the formation of the dihydroxydibenzanthrone (V).



(IV.)



(V.)

EXPERIMENTAL.

3-*Nitronaphthalomethylimide*.—To a gently boiling solution of naphthalomethylimide (20 g.) in acetic acid (300 c.c.) a mixture of acetic acid (100 c.c.) and nitric acid (*d* 1·5; 100 c.c.) was added during 20 minutes; after further boiling for 1 hour, water (100 c.c.) was added. When the combined products from five such operations were kept over-night, a crystalline solid (*A*) (50 g.; m. p. 213—217°) separated, repeated crystallisation of which from acetic acid gave 3-*nitronaphthalomethylimide* in fine needles, m. p. 226—228° (Found: C, 61·2; H, 3·4; N, 11·4. $C_{13}H_8O_4N_2$ requires C, 60·9; H, 3·1; N, 10·9%). Dilution with water of the filtrate from *A* deposited a mixture of the nitro-compound and unchanged imide. 3-*Nitronaphthalimide*, prepared by digestion of 3-nitronaphthalic anhydride with aqueous ammonia (*d* 0·88) for 1 hour, crystallised from nitrobenzene in small needles, m. p. 308° (sintering at 305°) (Found : N, 11·9. $C_{12}H_6O_4N_2$ requires N, 11·6%). Methylation of the imide in nitrobenzene solution with methyl sulphate and potassium carbonate gave 3-nitronaphthalomethylimide, m. p. 225—227° alone and in admixture with the above product.

3-*Aminonaphthalomethylimide.*—Sodium hydrosulphite (20 g. and after 1 hour a further 20 g.) was added to a stirred boiling solution of the 3-nitro-methylimide (10 g.) in alcohol (200 c.c.) and water (20 c.c.). Heating was continued an hour longer, the alcohol then evaporated, the residue mixed with an excess of dilute hydrochloric acid, and the filtered solution basified. The *amine* (9 g.) was crystallised from nitrobenzene and three times from xylene, forming fine yellow needles, m. p. 278—280° (Found: C, 68·9; H, 4·8. $C_{13}H_{10}O_2N_2$ requires C, 69·0; H, 4·4%). The diazonium sulphate of the base coupled with β-naphthol to yield the *azo*-derivative, crystallising from nitrobenzene in small red needles, m. p. 315—317° (Found : N, 11·4. $C_{23}H_{15}O_3N_3$ requires N, 11·3%). The *acetyl* derivative of the base separated from nitrobenzene in needles, m. p. 329—330° (Found : N, 11·0. $C_{15}H_{12}O_3N_2$ requires N, 10·4%).

3-*Hydroxynaphthalomethylimide.*—A mixture of sulphuric acid (*d* 1·84; 10 c.c.) and sodium nitrite (0·95 g.) was added to a cooled solution (salt–ice) of the preceding amine (3 g.) in sulphuric acid (*d* 1·84; 20 c.c.), and phosphoric acid (*d* 1·7; 45 c.c.) run into the stirred mixture. After 30 minutes the product was poured on ice and the diazo-solution was added during 1 hour to a vigorously stirred mixture of sulphuric acid (20 c.c.), water (80 c.c.), and tetrachloroethane (100 c.c.) in a bath at 110—120°. Heating was continued for a further 15 minutes, the tetrachloroethane separated from the hot aqueous layer, and the latter again extracted with hot tetrachloroethane. The combined extracts were distilled in steam and the solid (2 g.) remaining was sublimed in a low vacuum. The *hydroxy-methylimide* then crystallised from dichlorobenzene in yellow needles, m. p. 272—273° (Found : N, 6·2. $C_{13}H_9O_3N$ requires N, 6·2%). 3-*Chloronaphthalomethylimide*, purified by repeated crystallisation from alcohol (charcoal), separated in needles, m. p. 182—183° (Found : Cl, 14·2. $C_{13}H_8O_2NCl$ requires Cl, 14·5%).

Condensations of 3-*Aminonaphthalomethylimide.*—(a) *With* 1-*chloroanthraquinone.* (i) In amyl alcohol. A mixture of the base (6 g.), 1-chloroanthraquinone (7 g.), cupric chloride (1·5 g.), sodium acetate (7 g.), and amyl alcohol (50 c.c.) was heated at 160—170° for 16 hours. After removal of the amyl alcohol in steam, the solution was digested with dilute hydrochloric acid to dissolve unchanged base (5 g.), and the brown residue boiled with alcohol (160 c.c.); the undissolved portion (4·7 g.) crystallised from pyridine as a brown powder of microscopic needles of 3-1-*anthraquinonylaminonaphthalomethylimide* (I), m. p. 286—287° (Found : C, 74·0, 74·1; H, 4·1, 4·0; N, 6·6. $C_{27}H_{16}O_4N_2$ requires C, 75·2; H, 3·7; N, 6·5%).* This substance dyes cotton, for which it has little affinity, a weak brown colour from a pink vat.

(ii) In nitrobenzene. Similar quantities of the reactants were heated in nitrobenzene at 200—210° for 7 hours. After steam-distillation and extraction with dilute hydrochloric acid, the residue (8 g.) was crystallised twice from aniline, giving a mixture, m. p. 275—280°, of microscopic plates and needles. Recrystallisation from pyridine, which left undissolved a sparingly soluble *substance* (*A*), gave yellow needles, m. p. 275°, of anthraquinone. *A*, after digestion with nitrobenzene, crystallised from *o*-toluidine in purple-red plates, m. p. above 400° (Found : C, 69·5; H, 4·4; N, 12·1. $C_{26}H_{16}O_4N_4$ requires C, 69·6; H, 3·6; N, 12·3%). The possible structure of this substance is discussed on p. 496.

(b) *With* 1-*chloro*-5-*benzamidoanthraquinone.* (i) In amyl alcohol. A mixture of the amine (5 g.), 1-chloro-5-benzamidoanthraquinone (9 g.), sodium acetate (7 g.), cupric chloride (2 g.), and amyl alcohol (200 c.c.) was heated for 7 hours in an autoclave at 3 atms. After removal of the alcohol in steam and extraction with 10% hydrochloric acid to remove unchanged base (4 g.) and with acetic acid, the residue (0·6 g.) was repeatedly crystallised from pyridine, the 5′-*benzamido*-derivative of (I) separating in red needles, m. p. 338—339° (Found : C, 73·6; H, 4·4; N, 7·8. $C_{34}H_{21}O_5N_3$ requires C, 74·1; H, 3·8; N, 7·6%).

(ii) In nitrobenzene. A similar mixture of the reactants in nitrobenzene (100 c.c.) was heated at 210° for 7 hours. The neutral product, after extraction with chlorobenzene, left a red crystalline residue (*X*), and the solution deposited a solid, which had m. p. 244—246°, after crystallisation from chlorobenzene and was identified as 1-benzamidoanthraquinone by hydrolysis to 1-aminoanthraquinone, m. p. 243°. The solid (*X*) (II or III) crystallised from nitrobenzene in microscopic red needles, m. p. 331—333° (Found : C, 73·0; H, 4·0; H, 9·1. $C_{47}H_{27}O_7N_5$ requires C, 73·0; H, 3·5; N, 9·1%).

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* The majority of the substances described in this paper were very difficult to burn and good results were not obtained in microanalyses.

(c) *With* 1-*chloro*-4-*benzamidoanthraquinone.* (i) In amyl alcohol. Condensation of the base with the chloroanthraquinone was effected by heating at 170—180° for 7 hours, the quantities of reactants being as given above. The 4′-*benzamido*-derivative of (I) crystallised from pyridine in mauve needles, m. p. 330—331° (Found : C, 74·0; H, 4·2; N, 7·9%).

(ii) In nitrobenzene. The *substance* (II or III) was obtained in small yield and crystallised from nitrobenzene in purple needles, m. p. 320—323° (Found: N, 8·9%). Much 1-benzamidoanthraquinone was formed simultaneously.

3 : 6-*Dinitronaphthalomethylimide.*—To a solution of the *N*-methylimide (5 g.) in acetic anhydride (100 c.c.), nitric acid (*d* 1·5; 35 c.c.) was added at a rate sufficient to keep the solution gently boiling. The cooled solution deposited a solid (2·2 g.) m. p. 258—265°, from which after renitration under conditions similar to those described above, 3 : 6-*dinitronaphthalomethylimide* was obtained, which crystallised from acetic acid in pale yellow needles, m. p. 280° (Found : C, 52·3; H, 2·4. $C_{13}H_7O_6N_3$ requires C, 51·8; H, 2·3%). This substance was prepared also by the digestion of 3 : 6-dinitronaphthalic anhydride with dilute aqueous methylamine. The *diamine*, obtained by the reduction of the dinitro-methylimide with sodium hydrosulphite, crystallised from aniline in golden-yellow needles, m. p. above 400° (Found: N, 17·7. $C_{13}H_{11}O_2N_3$ requires N, 17·4%). The *diacetyl* derivative separated from acetic acid in yellow needles, decomp. 383—384° (Found : N, 12·9. $C_{17}H_{15}O_4N_3$ requires N, 12·9%). Condensation with 1-chloro-4-aminobenzoylanthraquinone in amyl-alcoholic solution gave the 4-*benzamidoanthraquinonyl*-derivative, crystallising from aniline in blue needles, m. p. 295—297° (sintering at 280°) (Found : N, 9·8. $C_{34}H_{22}O_5N_4$ requires N, 9·9%). It dyed cotton a weak grey shade from a port-wine coloured vat.

4-*Benzoylnaphthalomethylimide*, prepared by the digestion of 4-benzoylnaphthalic anhydride (Graebe, *loc. cit.*, p. 98) with dilute aqueous methylamine, crystallised from toluene in needles, m. p. 190—191°, and dissolved in sodium hydrosulphide to yield a red solution (Found : C, 76·4; H, 4·3. $C_{20}H_{13}O_3N$ requires C, 76·2; H, 4·1%).

α-*Di-imide of* 1 : 7 (or 1 : 12)-*Dimethoxyperylene*-3 : 4 : 9 : 10-*tetracarboxylic Acid* (IV).—A mixture of 3-hydroxynaphthalimide (12 g.), potassium hydroxide (100 g.), and ethyl alcohol (100 c.c.) was gradually heated to 230° in a nickel basin and with occasional stirring kept at this temperature for 2 hours. The cooled melt, after solution in water, was acidified and the purple solid (12 g.) which separated was collected. The phenol, which was insoluble in all the ordinary solvents, could not be purified. Its solution in sodium hydroxide was bright green and in sulphuric acid bluish-green. For the preparation of the dimethyl ether, the phenol (12 g.) with nitrobenzene (100 c.c.) and sodium carbonate (20 g.) was heated at 210°, and methyl sulphate (10 g.) added to the stirred mixture. At intervals of 1 hour three similar quantities of sodium carbonate and methyl sulphate were added and after one further hour the nitrobenzene was removed in steam and the residue digested with sodium hydroxide solution (10%) to dissolve unchanged phenol. The α-*di-imide* (5 g.) after four crystallisations from nitrobenzene separated in long slender black needles, m. p. above 400° [Found: C, 69·9; H, 4·0; OMe, 14·7. $C_{24}H_8O_4N_2(OMe)_2$ requires C, 69·4; H, 3·1; OMe, 14·2%]. The ether dissolved in sulphuric acid to yield a green solution; the alkaline hydrosulphite vat was blue and dyed cotton a bright purple to lilac colour.

β-*Di-imide of* 1 : 7 (or 1 : 12)-*Dimethoxyperylene*-3 : 4 : 9 : 10-*tetracarboxylic Acid*(?).—To a solution of the di-imide of perylene-3 : 4 : 9 : 10-tetracarboxylic acid (10 g.) in sulphuric acid (*d* 1·84; 400 g.) containing boric acid (10 g.), manganese dioxide (82%; 12·7 g.) was added; heat was evolved and the solution became blue. After 1 hour at 60° (stirring) the product was added to ice and sodium bisulphite (20 g.), and the solid collected. The phenol dissolved in sulphuric acid to give a blue solution. After methylation under conditions similar to those described for the α-di-imide, the product was recrystallised from nitrobenzene, the β-*di-imide* being obtained in black needles, m. p. above 400°. It dissolved in sulphuric acid to give a blue solution having a faintly green tinge; it dyed cotton a slightly redder shade than its isomeride (Found : C, 69·2; H, 4·4%).

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UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, February* 14*th*, 1935.]