64. *Reaction of Amino-derivatives of Anthraquinone, Fluorenone, and Fluorene with Nitrobenzene and α-Nitronaphthalene.*

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Nitrobenzene and α-nitronaphthalene undergo nuclear substitution by arylamino-groups *para* to the nitro-substituent on being heated with potassium hydroxide and one or other of the amines, 1-amino-, 2-amino-, and 2-amino-1-chloro-anthraquinone and 2-aminofluorenone. Under similar conditions nitrobenzene and 2-aminofluorene give 2-aminofluorenone and 2-*p*-nitroanilinofluorenone.

WHILST several examples are known in which an amine in the form of an alkali-metal derivative replaces hydrogen in an aromatic nitro-compound very few instances have been described in which the same kind of reaction occurs with free amines. Thus nitrobenzene forms *N*-*p*-nitrophenylcarbazole [1] with potassiocarbazole, and α-nitronaphthalene gives 1-nitro-4-piperidinonaphthalene with sodamide and piperidine.[2] With 2-aminoanthraquinone however, nitrobenzene forms 2-*p*-nitroanilinoanthraquinone [3] when only potassium hydroxide is present and experiments have been undertaken to explore this type of reaction further.

Like the 2-amino-derivative 1-aminoanthraquinone reacts with nitrobenzene in the presence of potassium hydroxide, the product being 1-*p*-nitroanilinoanthraquinone identical with the compound prepared either from 1-chloroanthraquinone and *p*-nitroaniline or from 1-aminoanthraquinone and *p*-chloronitrobenzene. With α-nitronaphthalene 1-aminoanthraquinone gives 1-(4-nitro-1-naphthylamino)anthraquinone identical with the derivative prepared from 1-chloroanthraquinone and 4-nitro-1-naphthylamine or from 1-aminoanthraquinone and 1-chloro-4-nitronaphthalene. The reaction with α-nitronaphthalene occurs more readily than with nitrobenzene. Indanthrone is formed in small amount in the nitrobenzene reaction but none is found with α-nitronaphthalene, probably because of the greater ease of substitution into the naphthalene derivative. 2-Aminoanthraquinone similarly reacts more rapidly with α-nitronaphthalene than with nitrobenzene, the product being 2-(4-nitro-1-naphthylamino)anthraquinone identical with the product from 2-aminoanthraquinone and 1-chloro-4-nitronaphthalene. The ease with which substitution occurs in these cases can be gauged from the occurrence of analogous reactions with 2-amino-1-chloroanthraquinone. This derivative readily yields indanthrone by self-condensation in the presence of alkalis, but in nitrobenzene and pyridine the main product is 1-chloro-2-*p*-nitroanilinoanthraquinone. With α-nitronaphthalene 2-amino-1-chloroanthraquinone forms 1-chloro-2-(4-nitro-1-naphthylamino)anthraquinone.

2-Aminofluorenone with nitrobenzene forms 2-*p*-nitroanilinofluorenone identical with the derivative prepared from 2-aminofluorenone and *p*-chloronitrobenzene.

No reaction occurs between nitrobenzene and carbazole or piperidine unless the amines are used in the form of their alkali-metal derivatives. For this reason it is probable that 1-amino-, 2-amino-, and 2-amino-1-chloro-anthraquinone, as well as 2-aminofluorenone, participate in their reactions with nitrobenzene and α-nitronaphthalene after they have reacted with potassium hydroxide to form the corresponding anions.[4, 5]

EXPERIMENTAL

Nitrobenzene and 1-Aminoanthraquinone.—1-Aminoanthraquinone (10 g.), powdered potassium hydroxide (6 g.), and dry nitrobenzene (80 c.c.) were stirred at 130—135° for 12 hr. The black suspension which was formed was mixed with alcohol (80 c.c.) and kept for a few hours,

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[1] G. and M. de Montmollin, *Helv. Chim. Acta*, 1923, **6**, 94.
[2] Bradley and Robinson, *J.*, 1932, 1254.
[3] F.I.A.T. Final Report 1313, III, 82.
[4] Bradley and Leete, *J.*, 1951, 2129.
[5] Bradley and Nursten, *J.*, 1951, 2170.

then filtered. The residue (12·5 g.) was extracted with four portions of glacial acetic acid and the purple insoluble part (3·3 g.) was further extracted (Soxhlet) with chlorobenzene until nothing more dissolved. On being cooled the extract gave a reddish-brown solid which on being crystallised twice from pyridine gave needles of 1-*p*-nitroanilinoanthraquinone (1·7 g.), m. p. 302—303° (Found: C, 69·7; H, 3·5; N, 8·1. Calc. for $C_{20}H_{12}O_4N_2$: C, 69·8; H, 3·5; N, 8·1%). The acetic acid extracts gave mainly unchanged 1-aminoanthraquinone. The residue from the chlorobenzene extraction was blue; dissolution in concentrated sulphuric acid and addition to water gave indanthrone (0·15 g.), characterised by comparison of its chemical reactions and absorption spectrum with those of authentic material.

The above 1-*p*-nitroanilinoanthraquinone was identical with the product (Found: C, 69·7; H, 3·7; N, 8·3%) prepared from 1-aminoanthraquinone and *p*-chloronitrobenzene as described by Ullmann and Fodor,[6] who record m. p. 311°, and with that prepared from 1-chloroanthraquinone (10 g.), *p*-nitroaniline (6·6 g.), potassium carbonate (5·5 g.), copper bronze (0·2 g.), cupric acetate (0·5 g.), and nitrobenzene (50 c.c.) refluxed for 3 hr. After crystallisation from pyridine the resulting reddish-brown needles (6·5 g.), m. p. 302—303° (Found: C, 69·5; H, 3·5; N, 8·2%), dissolved in pyridine to form an orange solution which changed to red-violet on the addition of a drop of concentrated methanolic potassium hydroxide. The same reagent[4] added to an orange-yellow solution of 1-*o*-nitroanilinoanthraquinone gave a deep blue colour.

1-*Nitronaphthalene and* 1-*Aminoanthraquinone*.—(*a*) 1-Aminoanthraquinone (10 g.), finely powdered potassium hydroxide (10 g.), and 1-nitronaphthalene (8 g.) were stirred and heated for 12 hr. at 75—80° in dry pyridine (100 c.c.). The product was cooled, mixed with sodium-dried benzene (150 c.c.), and then stirred for 3 hr. at 50—60°. The black insoluble part was filtered off, and extracted with benzene (Soxhlet) until no more dissolved. The brown solid which remained was extracted with hot, dilute acetic acid and then crystallised twice from pyridine. Dark reddish-brown needles of 1-(4-*nitro*-1-*naphthylamino*)*anthraquinone* (1·8 g.), m. p. 335—336° (Found: C, 73·2; H, 3·3; N, 7·3. $C_{24}H_{14}O_4N_2$ requires C, 73·1; H, 3·6; N, 7·1%), separated. This derivative is slightly soluble in glacial acetic acid, more readily soluble in nitrobenzene, trichlorobenzene, and pyridine. It dissolves in concentrated sulphuric acid with a yellow-brown colour. The orange-yellow solution in pyridine changes to dark brown on the addition of methanolic potassium hydroxide.

(*b*) 1-Aminoanthraquinone (5 g.), 1-chloro-4-nitronaphthalene (5·5 g.), potassium carbonate (2·75 g.), cupric acetate (0·25 g.) and copper bronze (0·1 g.) were refluxed for 45 min. in nitrobenzene (30 c.c.). The solid was collected from the hot suspension, then extracted continuously with hot alcohol, and washed with dilute hydrochloric acid. The residue (5·5 g.) was crystallised twice from pyridine. The dark red-brown needles (4·2 g.) had m. p. 335—336°, not depressed by 1-(4-nitro-1-naphthylamino)anthraquinone prepared by method (*a*) (Found: C, 73·0; H, 3·4; N, 7·1%).

The same product was formed when 1-chloroanthraquinone (5 g.), 1-amino-4-nitronaphthalene (4·7 g.), potassium carbonate (2·75 g.), cupric acetate (0·25 g.), and copper bronze (0·1 g.) were refluxed in nitrobenzene (30 c.c.) for 3 hr. The product was crystallised from pyridine, and further purified by chromatography on alumina from trichlorobenzene (Found: C, 72·8; H, 3·5; N, 7·0%).

2-p-*Nitroanilinoanthraquinone*.—2-Aminoanthraquinone (10 g.), *p*-chloronitrobenzene (8 g.), potassium carbonate (5·5 g.), cupric acetate (0·5 g.), and copper bronze (0·2 g.) were refluxed in nitrobenzene (50 c.c.) for 1 hr. Crystallisation of the product from pyridine gave yellow-brown crystals (0·8 g.), m. p. 350—351°, not depressed by 2-*p*-nitroanilinoanthraquinone prepared from 2-aminoanthraquinone and nitrobenzene.

2-p-*Aminoanilinoanthraquinone*.—The 4-nitro-derivative (1 g.) was prepared in a finely divided state by dissolution in concentrated sulphuric acid (25 c.c.), addition to ice-water, and collection of the flocculent orange precipitate. After being washed until neutral the nitro-compound was heated with crystalline sodium sulphide (1 g.) in alcohol (200 c.c.); a dark red colour developed. Most of the alcohol was then removed by distillation and the residue was added to water. The resulting precipitate on being crystallised twice from chlorobenzene gave maroon needles, m. p. 294—296°, which were further purified by chromatography on alumina from a solution in chlorobenzene and elution with 95% alcohol. 2-p-*Aminoanilinoanthraquinone* has m. p. 296—297° (Found: C, 76·3; H, 4·7; N, 9·3. $C_{20}H_{14}O_2N_2$ requires C, 76·4; H, 4·5; N, 8·9%). It forms a pale bluish-green solution in concentrated sulphuric acid.

[6] Ullmann and Fodor, *Annalen*, 1911, **380**, 324.

1-*Nitronaphthalene and* 2-*Aminoanthraquinone*.—(*a*) The 2-amino-quinone (8 g.) and potassium hydroxide (5 g.), both finely powdered, were shaken in a closed flask at the room temperature for 48 hr. with a solution of 1-nitronaphthalene (6·5 g.) in dry pyridine (125 c.c.). The dark green solid which was formed was mixed with chlorobenzene (250 c.c.) and stirred for 2 hr. at 50—60°. The undissolved black solid was collected (11·7 g.) and extracted, first with chlorobenzene and then with dilute acetic acid. Crystallisation from pyridine gave orange needles (3·6 g.) of 2-(4-*nitro*-1-*naphthylamino*)*anthraquinone*, m. p. 316—317° (Found: C, 73·0; H, 3·4; N, 7·1. $C_{24}H_{14}O_4N_2$ requires C, 73·1; H, 3·6; N, 7·1%). It dissolves sparingly in glacial acetic acid, more easily in trichlorobenzene, nitrobenzene, and pyridine. It gives a brown solution in concentrated sulphuric acid. Addition of methanolic potassium hydroxide to the orange solution in pyridine gives a deep purple colour. (*b*) The same compound, m. p. 316—317° (Found: C, 73·1; H, 3·5; N, 7·3%), resulted when 2-aminoanthraquinone (10 g.), potassium hydroxide (10 g.) and 1-nitronaphthalene (8 g.) were stirred and heated in pyridine (125 c.c.) for 8 hr. at 90—95° but the product prepared under these conditions was more difficult to purify. (*c*) It was also obtained (1·3 g.; m. p. 317—318°) (Found: C, 73·0; H, 3·6; N, 6·9%) when 2-aminoanthraquinone (10 g.) and potassium hydroxide (10 g.) were stirred for 4 hr. with molten 1-nitronaphthalene (75 g.) at 90°.

2-(4-Nitro-1-naphthylamino)anthraquinone was also prepared from 2-aminoanthraquinone (5 g.), 1-chloro-4-nitronaphthalene (5·5 g.), potassium carbonate (2·75 g.), copper acetate (0·25 g.), and copper (0·25 g.) refluxed in nitrobenzene (30 c.c.) for 1 hr. Crystallisation of the product from pyridine gave orange needles (0·9 g.) (Found: C, 73·4; H, 3·8; N, 7·3%), m. p. 316—317°, unchanged by admixture with the products obtained by methods (*a*), (*b*), and (*c*).

2-*Amino*-1-*chloroanthraquinone and Nitrobenzene*.—2-Amino-1-chloroanthraquinone (4 g.) and potassium hydroxide (4 g.) were stirred and heated with nitrobenzene (50 c.c.) at 50—60° for 12 hr. Chlorobenzene (100 c.c.) was then added and stirring was continued for 3 hr. The black suspension was cooled, kept overnight, and filtered, and the residue was washed with chlorobenzene and extracted exhaustively with benzene (Soxhlet). The undissolved portion was extracted with dilute acetic acid, and insoluble material (1·3 g.) was crystallised twice from pyridine. The resulting 1-*chloro*-2-p-*nitroanilinoanthraquinone* was obtained as orange needles, m. p. 343—345° (Found: C, 63·8; H, 2·8; N, 7·3; Cl, 9·4. $C_{20}H_{11}O_4N_2Cl$ requires C, 63·4; H, 2·9; N, 7·4; Cl, 9·4%). It dissolves in concentrated sulphuric acid with a deep blue colour (faint pink tinge); its orange-yellow solution in pyridine is changed to violet on the addition of methanolic potassium hydroxide.

Dehalogenation. On being heated with anhydrous potassium acetate (0·15 g.) and a small proportion of copper powder a solution of the above chloro-derivative (0·3 g.) in nitrobenzene (10 ml.) changed through dark green and reddish-brown to brown. The resulting solid was collected from the cooled suspension, washed with dilute hydrochloric acid, and crystallised from pyridine. The orange-brown needles, m. p. 352—354° (Found: C, 69·6; H, 3·4; N, 7·9. Calc. for $C_{20}H_{12}O_4N_2$: C, 69·8; H, 3·5; N, 8·1%), showed no depression of m. p. with authentic 2-*p*-nitroanilinoanthraquinone.

2-*Amino*-1-*chloroanthraquinone and* 1-*Nitronaphthalene*.—2-Amino-1-chloroanthraquinone (12 g.), potassium hydroxide (7·5 g.), and 1-nitronaphthalene (9 g.) were shaken in pyridine (100 c.c.) at the room temperature for 72 hr. The black product, treated as in the corresponding experiment with nitrobenzene and finally crystallised twice from pyridine, gave 1-*chloro*-2-(4-*nitro*-1-*naphthylamino*)*anthraquinone* (7·1 g.) as pale orange-yellow needles, m. p. 317—318° (Found: C, 67·5; H, 3·0; N, 6·4; Cl, 8·5. $C_{24}H_{13}O_4N_2Cl$ requires C, 67·2; H, 3·3; N, 6·5; Cl, 8·3%). It dissolves in concentrated sulphuric acid with a yellow-brown colour. The orange-yellow solution in pyridine is changed to violet on the addition of methanolic potassium hydroxide.

2-*Aminofluorenone and Nitrobenzene*.—2-Aminofluorenone [7] (10 g.) and potassium hydroxide (6 g.) were stirred for 5 hr. at 80—90° with nitrobenzene (100 c.c.). The black product which was formed was added to water, the resulting suspension was steam-distilled, and the residual dark brown solid was extracted with hot 3·5% hydrochloric acid. On being made alkaline the solution gave 2-aminofluorenone (3·2 g.). The acid-insoluble residue was extracted with toluene (Soxhlet). Crystals separated from the extract and these were recrystallised (2 g.) from toluene.

2-p-*Nitroanilinofluorenone* forms orange yellow prisms, m. p. 254—255° (Found: C, 72·3;

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[7] Diels, *Ber.*, 1901, **34**, 1758.

H, 3·9; N, 8·9. $C_{19}H_{12}O_3N_2$ requires C, 72·2; H, 3·8; N, 8·9%). It dissolves in concentrated sulphuric acid with a violet colour. A deep purple colour develops on addition of methanolic potassium hydroxide to the yellow solution in pyridine.

2-*p*-Nitroanilinofluorenone was also prepared by refluxing 2-aminofluorenone (5 g.), *p*-chloronitrobenzene (4·8 g.), potassium carbonate (2·5 g.), cupric acetate (0·2 g.), and copper bronze (0·1 g.) in nitrobenzene (25 ml.) for 45 min. The product, m. p. 254—255° (Found: C, 72·0; H, 4·2; N, 8·6%), did not depress the m. p. of 2-*p*-nitroanilinofluorenone prepared by the previous method.

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