Aromatic Nitro-compounds. Studies of the Amination of 9-Nitrophenanthrene and of the Mononitrobiphenylenes

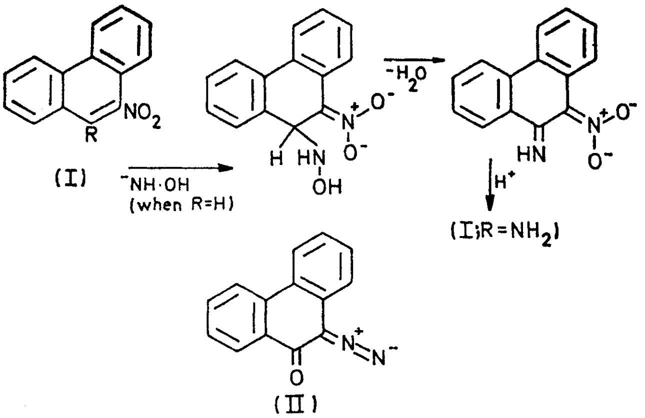
By **J. W. Barton,* A. R. Grinham,** and **K. E. Whitaker,** School of Chemistry, University of Bristol, Bristol BS8 1TS

Nucleophilic aminations of 9-nitrophenanthrene and of 2-nitrobiphenylene have given 9-amino-10-nitrophenanthrene (I; R = NH_2) and 2-amino-3-nitrobiphenylene (III; R = NH_2) respectively; under the same conditions 1-nitrobiphenylene is unreactive. Some reactions of amines (I; R = NH_2) and (III; R = NH_2) are described.

THE nucleophilic amination of nitro-compounds with hydroxylamine and alkali has not been extensively investigated.[1] Unlike most other direct amination reactions it does not involve the removal of hydride ion [2] (Scheme 1) and it proceeds under mild conditions, often giving high yields of *o*- or *p*-nitro-amines. In the benzene series two or more nitro-groups are required to provide activation of the nucleus but with bi- or poly-cyclic compounds one nitro-group is usually sufficient.

This investigation was conducted (*a*) in order to obtain *o*-nitro-amines to serve as starting materials for the synthesis of 1-amino-1*H*-triazoloarenes (aryne precursors), and (*b*) to determine the positions of nucleophilic attack in mononitrobiphenylenes.

9-*Nitrophenanthrene*.—The amination of 9-nitrophenanthrene (I; R = H) with hydroxylamine–potassium hydroxide in methanol at 60° gave moderate yields of 9-amino-10-nitrophenanthrene (I; R = NH_2). The orientation in compound (I; R = NH_2) was confirmed by the identity of its acetyl derivative (I; R = NHAc) with the compound previously obtained from the nitration of 9-acetamidophenanthrene.[3] This alternative route to the amine (I; R = NH_2) was also examined but it was found that the acetyl group in (I; R = NHAc) could not be removed without concomitant hydrolysis of the amino-group to give compound (I; R = OH) as the main product. While the formation of the phenanthrol (I; R = OH) under basic hydrolysis conditions is not unexpected, it is unusual for loss of an amino-group to occur under acidic conditions, where the amine formed is protected by salt formation. It was found that the weakly basic amine (I; R = NH_2) could be diazotised in strongly acidic solutions, and that treatment of the diazonium sulphate with potassium iodide gave a moderate yield of 9-iodo-10-nitrophenanthrene (I; R = I); however, when the diazonium solution was diluted, the nitro-group was hydrolysed with the formation of 9-diazo-10-phen-



SCHEME 1

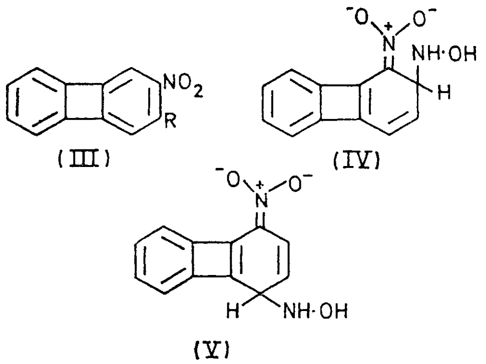
---

[1] F. Moller in 'Houben-Weyl, Methoden der Organischen Chemie,' ed. E. Muller, Stuttgart, 1957, vol. XI/1, p. 17.

[2] J. Sauer and R. Huisgen, *Angew. Chem.* 1960, **8**, 294.

[3] W. L. Mosby, *J. Org. Chem.*, 1959, **24**, 421.

anthrone (II).[4] These reactions underline the susceptibility to hydrolytic displacement of a group in the 9-position of a phenanthrene which bears an electron-withdrawing group at position 10.



SCHEME 2

Nitrobiphenylenes.—As expected from considerations of the bond structure of biphenylene,[5] the amination of 2-nitrobiphenylene (III; R = H) at 60° gave 2-amino-3-nitrobiphenylene (III; R = NH_2), identical with the product obtained in low yield from 2-acetamidobiphenylene by nitration and hydrolysis.[6] When the reaction time was extended only the hydroxy-compound (III; R = OH) was isolated. The *ortho*-orientation in (III; R = NH_2) was confirmed by reduction to the corresponding diamine, which gave a quinoxaline derivative with phenanthrene-9,10-quinone. The nitro-amine (III; R = NH_2) unlike 2-aminobiphenylene,[7] underwent diazotisation and conversion into the iodide (III; R = I) in the normal way.

The attempted amination of 1-nitrobiphenylene under the same conditions led to almost complete recovery of the starting material; even when reaction times were prolonged no nitro-amine or nitro-phenol was isolated. This result is not unexpected, as attack of hydroxamide ion at the 2- or 4-position would lead to Wheland-type intermediates to which the main contributors would be (IV) and (V), each having an unfavourable benzocyclobutadienoid structure. This situation parallels the behaviour of 1-acetamido- and 1-hydroxy-biphenylene towards electrophilic reagents;[5] these compounds are apparently much less reactive than the corresponding 2-substituted derivatives.

EXPERIMENTAL

9-*Acetamidophenanthrene.*—9-Phenanthrol was prepared from 9-bromophenanthrene *via* the methoxy-compound, by the method of Bacon and Rennison.[8] It was converted into 9-phenanthrylamine by the Bucherer reaction,[9] then acetylated.[10]

9-*Acetamido*-10-*nitrophenanthrene.*—A solution of 9-acetamidophenanthrene (7·5 g.) in acetic acid (75 ml.) and acetic anhydride (37·5 ml.) was stirred while nitric acid (*d* 1·5; 2·25 ml.) in acetic acid (19 ml.) was added dropwise; the temperature was maintained between 16 and 24° by external cooling. After 3 hr. the solution was poured into water (2 l.) and the product was filtered off. Crystallisation from acetic acid then ethyl acetate gave 9-acetamido-10-nitrophenanthrene (4·9 g., 55%) as pale yellow needles, m.p. 267—269° (lit.,[3] 267·5—269°), [*m*/*e* 280 (3% of base peak, *m*/*e* 234)].

Acidic Hydrolysis of 9-*Acetamido*-10-*nitrophenanthrene.*—The acetamido-compound (0·5 g.) was refluxed with hydrochloric acid (*d* 1·18; 13 ml.) and ethanol (25 ml.) until it dissolved (4 hr.). Rapid cooling and neutralisation with ammonia precipitated a solid (0·1 g.), the i.r. spectrum of which indicated it to be a mixture of the starting material with traces of 9-amino- and 9-hydroxy-10-nitrophenanthrenes. The filtrate later deposited a yellow solid which yielded 10-*nitro*-9-*phenanthrol* (0·28 g., 62%), m.p. 167·5—169° (from ethanol and then benzene) (Found: C, 70·1; H, 3·7; N, 5·3%; *m*/*e* 239·057. $C_{14}H_9NO_3$ requires C, 70·3; H, 3·8; N, 5·8%; *M*, 239·058.

Alkaline hydrolyses with aqueous 20% sodium hydroxide–ethanol mixtures gave similar results.

9-*Nitrophenanthrene.*— 9-Bromo-10-nitrophenanthrene was prepared by the nitration of 9-bromophenanthrene;[11] crystallisation from methyl ethyl ketone–ethanol, then from carbon tetrachloride, gave material, m.p. 207—212° (10% yield). It was debrominated to 9-nitrophenanthrene by heating with copper in moist *NN*-dimethylformamide[12] (69% yield).

9-*Amino*-10-*nitrophenanthrene.*—A solution of 9-nitrophenanthrene (10 g.) and hydroxylamine hydrochloride (25 g.) in methanol (600 ml.) at 50—60° was stirred rapidly and potassium hydroxide (50 g.) in methanol (320 ml.) was added in one portion. After 1 hr. at this temperature the methanol was removed rapidly *in vacuo*; the residue was triturated with water and filtered. The dried product was dissolved in benzene and chromatographed on an alumina column. After elution with benzene had removed starting material (1·9 g.), a more strongly adsorbed band was eluted with benzene–chloroform, giving 9-*amino*-10-*nitrophenanthrene* (3·0 g., 35%) as orange needles, m.p. 198—200° (from ethanol) (Found: C, 70·5; H, 4·3; N, 11·9. $C_{14}H_{10}N_2O$ requires C, 70·5; H, 4·2; N, 11·8%).

9-*Iodo*-10-*nitrophenanthrene.*— 9-Amino-10-nitrophenanthrene (0·45 g.) in hot acetic acid (15 ml.) was cooled and stirred to produce a fine suspension which was added in portions to a stirred solution of sodium nitrite (0·18 g.) in concentrated sulphuric acid (4·5 ml.) kept below 10°. After 20 min. crushed ice was added to give a total volume of *ca.* 30 ml. The resulting diazonium solution was allowed to come to 5°, filtered, and added to an excess of potassium iodide (3 g.) in 10% sulphuric acid, giving an orange-brown precipitate with evolution of nitrogen. After 2 hr. the mixture was heated to 90° on a water-bath,

---

[4] M. P. Cava, R. L. Little, and D. R. Napier, *J. Amer. Chem. Soc.*, 1958, **80**, 2257.

[5] J. W. Barton in 'Nonbenzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1970, vol. I, p. 53 *et seq.*

[6] J. M. Blatchly, D. V. Gardner, J. F. W. McOmie, and M. L. Watts, *J. Chem. Soc.* (*C*), 1968, 1545.

[7] W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 1958, 2666.

[8] R. G. R. Bacon and S. C. Rennison, *Chem. and Ind.*, 1966, 812.

[9] L. F. Fieser, R. P. Jacobsen, and C. C. Price, *J. Amer. Chem. Soc.*, 1936, **58**, 2163.

[10] G. H. Keyes and L. G. S. Brooke, *J. Amer. Chem. Soc.*, 1937, **59**, 74.

[11] R. K. Callow and J. M. Gulland, *J. Chem. Soc.*, 1929, 2424.

[12] R. S. W. Braithwaite and P. F. Holt, *J. Chem. Soc.*, 1959, 3025.

cooled, and treated with sodium disulphite. The solid collected, washed, dried, and recrystallised from methyl ethyl ketone–ethanol, then from carbon tetrachloride, giving the *iodo-compound* (0·29 g., 44%) as pale yellow needles, m.p. 198—200° (Found: C, 48·2; H, 2·55; N, 4·3. $C_{14}H_8INO_2$ requires C, 48·1; H, 2·3; N, 4·0%).

9-*Diazo*-10-*phenanthrone* (II).—When a solution of the diazonium sulphate, prepared as in the previous experiment, was further diluted or treated with sodium acetate, an orange-brown solid gradually separated. Recrystallisation from benzene–light petroleum gave 9-diazo-10-phenanthrone as orange needles (40—50%), m.p. 107—109° (decomp.), identical with a sample prepared by the reaction of toluene-*p*-sulphonohydrazide with phenanthrene-9,10-quinone.[4]

1-Nitro- and 2-nitro-biphenylenes were prepared by the pyrolysis of 3-nitro-[13] and 4-nitro-biphenylene-2,2′-iodonium[14] iodides with copper(I) oxide. 2-Nitrobiphenylene was also obtained by the direct nitration of biphenylene.[7]

2-*Amino*-3-*nitrobiphenylene*.—2-Nitrobiphenylene (3 g.) was aminated by the method already described for 9-nitrophenanthrene, but with a reaction time of 30 min. Chromatography on alumina gave first starting material (1·05 g.), then 2-amino-3-nitrobiphenylene (0·75 g., 36%) as red needles, m.p. 219—221° (lit.,[6] 217—218°) (from benzene–hexane) (Found: C, 67·8; H, 3·8; N, 13·0. Calc. for $C_{12}H_9N_2O_2$: C, 67·9; H, 3·8; N, 13·2%). Acidification of the alkaline solution from the amination reaction gave traces of a red-brown solid which on vacuum sublimation and chromatography on silica in chloroform solution gave orange-red needles, m.p. 148—150°, identical with a sample of 2-hydroxy-3-nitrobiphenylene (see later).

2-*Hydroxy*-3-*nitrobiphenylene* (with D. V. GARDNER).—To a refluxing solution of 2-amino-3-nitrobiphenylene (0·1 g.) in ethanol (7 ml.) was added sodium hydroxide (0·11 g.) in water (3 ml.). A red crystalline solid commenced to separate after 15 min. and after 3·5 hr. the solution had become almost colourless. The mixture was cooled, diluted, and acidified with hydrochloric acid, giving an orange solid which was collected in chloroform. Purification by preparative t.l.c. on Kieselgel G in chloroform and sublimation at 90°/0·1 mm. gave 2-*hydroxy*-3-*nitrobiphenylene* (0·086 g., 87%), m.p. 148—150° (Found: C, 67·5; H, 3·4. $C_{12}H_7NO_3$ requires C, 67·6; H, 3·3%), *m/e* 213. The compound gave a ruby-red colour with ethanolic iron(III) chloride.

2-*Iodo*-3-*nitrobiphenylene*.—Diazotisation of 2-amino-3-nitrobiphenylene (0·15 g.) and treatment with potassium iodide was carried out as described for 9-amino-10-nitrophenanthrene. The product was purified by chromatography on alumina in benzene solution, giving 2-*iodo*-3-*nitrobiphenylene* as yellow needles (0·105 g., 46%), m.p. 119—120° (from hexane) (Found: C, 44·5; H, 1·8; N, 4·6. $C_{12}H_6INO_2$ requires C, 44·6; H, 1·9; N, 4·3%).

2,3-*Diaminobiphenylene*.— 2-Amino-3-nitrobiphenylene (0·2 g.) was warmed on a water-bath with tin(II) chloride dihydrate (1 g.) in ethanol (3 ml.) and concentrated hydrochloric acid (2 ml.) until a clear yellow-brown solution was obtained (30 min.). The solution was basified with dilute sodium hydroxide and the diamine (0·14 g.) was extracted with ether. It crystallised as yellow-brown plates, m.p. 198—200° with sublimation, from benzene–hexane and darkened rapidly on exposure to air. The *diacetyl derivative* formed pale yellow needles, m.p. 285—287° (decomp.), from methanol (Found: C, 88·1; H, 4·1; N, 8·0. $C_{16}H_{14}N_2O_2$ requires C, 88·2; H, 3·95; N, 7·9%); the *quinoxaline derivative* formed with phenanthrene-9,10-quinone was obtained as yellow needles, m.p. 336—338° with sublimation (from *NN*-dimethylformamide) (Found: C, 88·1; H, 4·1; N, 8·0. $C_{26}H_{14}N_2$ requires C, 88·2; H, 3·95; N, 7·9%).

We thank the S.R.C. for studentships (to A. R. G. and K. E. W.).

[0/1863 *Received, November 2nd*, 1970]

---

[13] J. W. Barton and K. E. Whitaker, *J. Chem. Soc.* (*C*), 1967, 2097.

[14] W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 1958, 2658.