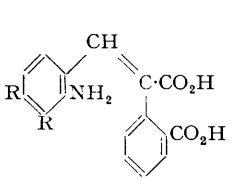
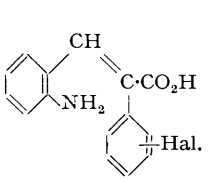
666. *Internuclear Cyclisation. Part II. The Application of the Pschorr Reaction to Some Substituted Derivatives of* o-*Amino-α-phenylcinnamic Acid.*

By D. H. Hey and John M. Osbond.

The Pschorr reaction has been carried out on a number of *o*-amino-α-phenylcinnamic acids with deactivating groups in the α-phenyl nucleus to afford the corresponding phenanthrene derivatives. These reactions, together with other examples already described in the literature, suggest that the facility of the internuclear cyclisation is *not* dependent to any appreciable extent on either the nature or the position of a substituent group in the α-phenyl nucleus. It is suggested that this behaviour, coupled with the results described in Part I, is characteristic of a free-radical mechanism.

It has been demonstrated (Part I, preceding paper) that it is possible to convert 2-2′-*o*-aminophenylethylpyridine in aqueous or in aqueous-dioxan solution by the Pschorr procedure using copper powder into 5 : 6-benzoquinoline and 7 : 8-dihydro-5 : 6-benzoquinoline, respectively. Since it is well known that the pyridine ring is normally highly resistant to cationoid attack under mild experimental conditions, it was considered to be of interest to review previous examples of the synthesis of phenanthrene derivatives by means of the Pschorr reaction in which the internuclear cyclisation had involved a benzene ring containing a deactivating group such as NO_2, CN, or CO_2H. From a recorded total of over 120 reactions carried out with derivatives of *o*-amino-α-phenylcinnamic acid, only two examples appear to have been recorded in which the α-phenyl nucleus contains a deactivating (*m*-directing) group. Thus, 2-amino-3 : 4-dimethoxy-α-*o*-carboxyphenylcinnamic acid (I; R = OMe) and 2-amino-α-*o*-carboxyphenylcinnamic acid (I; R = H) were each converted into the corresponding phenanthrenedicarboxylic acids in 75% and 40—45% yield, respectively (Pschorr and Tappen, *Ber.*, 1906, **39**, 3115). Cyclisation in good yields (60—80%) has also been achieved with *o*-amino-α-phenylcinnamic acids containing chlorine or bromine in the 2-, 3-, and 4-positions of the α-phenyl ring (II) (Pschorr, Schutz, and Popovici, *Ber.*, 1906, **39**, 3117; Barber and Stickings, *J.*, 1945, 167; Berger, *J. pr. Chem.*, 1932, **133**, 331; Nylen, *Ber.*, 1920, **53**, 158; Pschorr, *Annalen*, 1912, **391**, 40; May and Mosettig, *J. Org. Chem.*, 1946, **11**, 631; May, *J. Amer. Chem. Soc.*, 1947, **69**, 717).


(I.)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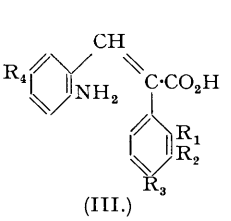
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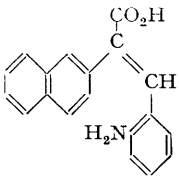
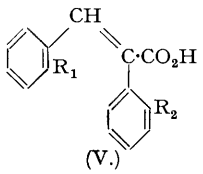

(IV.)

In these examples the internuclear cyclisation thus appears to proceed with equal ease irrespective of the nature and position of the substituent group in the α-phenyl nucleus (*i.e.*, *o*-, *m*-, or *p*- to the position at which ring closure takes place). In this respect it should be noted that in a similar manner *o*-aminobenzophenones have been converted into derivatives of fluorenone (Ullmann and Mallet, *Ber.*, 1898, **31**, 1694; Ullmann and Bleier, *Ber.*, 1902, **35**, 4273), which method has been of considerable preparative value (Miller and Bachman, *J. Amer. Chem. Soc.*, 1935, **57**, 2443; Huntress, Pfister, and Pfister, *ibid.*, 1942, **64**, 2845). The independence of the cyclisation reaction on the position of substituent groups in the phenyl nucleus is also evident in reactions involving an α-phenyl nucleus substituted with activating groups such as OMe, NH_2, CH_3, etc. For instance, the acids (III; R_1 = OMe, $R_2 = R_3 = R_4$ = H, and R_3 = OMe, $R_1 = R_2 = R_4$ = H) gave the corresponding phenanthrene-9-carboxylic acid in 55% and 50% yield, respectively (Pschorr, Wolfes, and Buckow, *Ber.*, 1900, **33**, 162), whilst the acid (III; $R_2 = R_4$ = OMe, $R_1 = R_3$ = H) gave a mixture of the two isomeric phenanthrene-9-carboxylic acids in a total yield of 63% (Rapson and Robinson, *J.*, 1935, 1533). Similarly, the lactam (3-*o*-aminobenzylideneoxindole) from the acid (III; $R_1 = NH_2$, $R_2 = R_3 = R_4$ = H) underwent ring-closure in 75% yield to give the lactam of 1-aminophenanthrene-10-carboxylic acid (Pschorr and Popovici, *Ber.*, 1906, **39**, 3120). Further examples could be given from the literature where the nature and position of the substituent atom or group would seem to have little influence on the course of the reaction, except, of course, where steric hindrance is encountered, as in the attempted synthesis by this method of 4 : 5-dialkylphenanthrenes

(Haworth and Sheldrick, *J.*, 1934, 1950; Lewis and Elderfield, *J. Org. Chem.*, 1940, **5**, 291). Mention may also be made of the formation of both 1 : 2-benz-4-anthroic acid and 3 : 4-benz-1-phenanthroic acid from (IV) (Weitzenbock and Lieb, *Monatsh.*, 1912, **33**, 564; Mayer and Oppenheimer, *Ber.*, 1918, **51**, 510; Cook, *J.*, 1931, 2524), in which internuclear cyclisation takes places at the β-position as well as at the more reactive α-position of the naphthalene ring. Further, in the recent application of the Pschorr procedure to the α- and β-naphthyl esters of aniline-*o*-sulphonic acid Schetty (*Helv. Chim. Acta*, 1949, **32**, 24) has indicated that ring closure appears to take place in both cases at two points in the naphthalene nucleus. More recently, Cook and Stephenson (this vol., p. 842) have shown that in the application of the Pschorr reaction to *o*-amino-α-2-fluorenylcinnamic acid cyclisation took place exclusively at the 1-position, which is known to be the less active position with regard to cationoid substitution (cf. Koelsch, *J. Amer. Chem. Soc.*, 1933, **55**, 3885).

Attempts have now been made to apply the normal Pschorr procedure to substituted *o*-amino-α-phenylcinnamic acids containing a nitro-, cyano-, or carboxyl group in various positions in the α-phenyl nucleus. It was considered that, if such reactions could be carried out successfully, further support would be given to the hypothesis that the decomposition of the diazonium salts with copper powder in these reactions involves the transient formation of a free aryl radical by a mechanism not dissimilar to that suggested for the Sandmeyer or the Gattermann reactions by Waters (*J.*, 1942, 266). In these reactions, however, the amino-group is normally replaced by a halogen atom with diaryls and polyaryls as by-products, especially when the phenyl ring contains nitro-groups (Ullmann *et al.*, *Ber.*, 1901, **34**, 3802; 1905, **38**, 725), whereas in the Pschorr reaction the union of two nuclei is the main reaction and the halogen replacement reaction results only when ring closure is not effected (cf. Part I).

2 : 2′-Dinitro-α-phenylcinnamic acid (V; $R_1 = R_2 = NO_2$), prepared by condensation of *o*-nitrobenzaldehyde with sodium *o*-nitrophenylacetate (Pschorr and Popovici, *Ber.*, 1906, **39**, 3120), was reduced with some difficulty with alcoholic ammonium sulphide to a *nitro-amine*, which was considered to be o-*amino*-α-(o-*nitrophenyl*)*cinnamic acid* (V; $R_1 = NH_2$, $R_2 = NO_2$)



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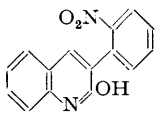

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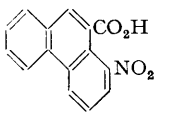

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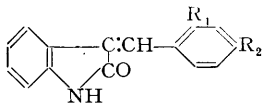
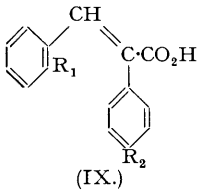


(VIII.)

rather than its isomer (V; $R_1 = NO_2$, $R_2 = NH_2$), because treatment with acetic anhydride and zinc chloride gave 3-(o-*nitrophenyl*)*carbostyril* (VI) (m. p. 301—301·5°) and not *o*-nitrobenzylidene-oxindole (VIII; $R_1 = NO_2$, $R_2 = H$) (m. p. 225°; Kirchner, *Nach. Ges. Wiss. Göttingen*, Math. Phys. Kl., 1921, 154). o-*Acetamido*-α-(o-*nitrophenyl*)*cinnamic acid* (V; $R_1 = NHAc$, $R_2 = NO_2$) was prepared by acetylation of the amino-acid at room temperature. *o*-Amino-α-(*o*-nitrophenyl)cinnamic acid (V; $R_1 = NH_2$, $R_2 = NO_2$) was diazotised in dilute acid solution and the diazonium solution was decomposed in 30 minutes by the addition of copper powder and warming. From the reaction mixture both 1-*nitrophenanthrene*-10-*carboxylic acid* (VII) in 24% yield and o-*hydroxy*-α-(o-*nitrophenyl*)*cinnamic acid* (V; $R_1 = OH$, $R_2 = NO_2$) were isolated. When, however, the diazonium chloride of *o*-amino-α-(*o*-nitrophenyl)cinnamic acid (V; $R_1 = N_2Cl$, $R_2 = NO_2$), prepared by addition of amyl nitrite to an alcoholic hydrogen chloride solution of the base (V; $R_1 = NH_2$, $R_2 = NO_2$), was decomposed under dry acetone by addition of copper powder, a smooth but vigorous reaction occurred at room temperature to give 1-nitrophenanthrene-10-carboxylic acid (VII) in 57% yield. This modification, previously described in Part I, was therefore superior in this instance to the normal Pschorr procedure in giving a cleaner product in better yield. 1-Nitrophenanthrene-10-carboxylic acid (VII) was decarboxylated smoothly by heating in quinoline solution in the presence of copper and copper chromite to give the hitherto unknown 1-*nitrophenanthrene*.

An attempt was made to prepare *o*-amino-α-(*p*-nitrophenyl)cinnamic acid (IX; $R_1 = NH_2$, $R_2 = NO_2$) by mono-reduction of *o*-nitro-α-(*p*-nitrophenyl)cinnamic acid (IX; $R_1 = R_2 = NO_2$) (Ruggli and Dinger, *Helv. Chim. Acta*, 1941, **24**, 173). Reduction of the dinitro-acid with sodium polysulphide or alcoholic ammonium sulphide, however, gave a *nitro-amine* which proved to be o-*nitro*-α-(p-*aminophenyl*)*cinnamic acid* (IX; $R_1 = NO_2$, $R_2 = NH_2$), because it gave a *mono-acetyl* derivative (IX; $R_1 = NO_2$, $R_2 = NHAc$) when acetylated both at room temperature and on boiling under reflux with acetic anhydride, whereas a compound with the alternative

formulation (IX; $R_1 = NH_2$, $R_2 = NO_2$) should give 3-(*p*-nitrophenyl)carbostyril when boiled with acetic anhydride. Further, the application of a Sandmeyer reaction to (IX; $R_1 = NO_2$, $R_2 = NH_2$), using cuprous chloride, gave a chloro-compound, m. p. 143—145°, which is regarded as *trans-o*-nitro-α-(*p*-chlorophenyl)cinnamic acid, m. p. 145° (IX; $R_1 = NO_2$, $R_2 = Cl$) (Nylen, *loc. cit.*). It would appear, therefore, that *cis-o*-nitro-α-(*p*-aminophenyl)cinnamic acid (cf. Ruggli and Dinger, *loc. cit.*) has been converted during the Sandmeyer reaction into *trans-o*-nitro-α-(*p*-chlorophenyl)cinnamic acid. If the nitro-amine were *o*-amino-α-(*p*-nitrophenyl)cinnamic acid (IX; $R_1 = NH_2$, $R_2 = NO_2$) replacement of the amino-group by chlorine would give o-*chloro*-α-(p-*nitrophenyl*)*cinnamic acid* (IX; $R_1 = Cl$, $R_2 = NO_2$), which compound was prepared for purposes of comparison by condensation of *o*-chlorobenzaldehyde with sodium *p*-nitrophenylacetate. *o*-Nitro-α-(*p*-chlorophenyl)cinnamic acid (IX; $R_1 = NO_2$, $R_2 = Cl$) was also isolated from the decomposition of the diazonium salt of the base (IX; $R_1 = NO_2$, $R_2 = NH_2$) under acetone in the presence of copper powder, indicating that the amine was (IX; $R_1 = NO_2$,



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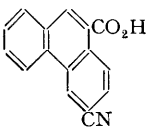

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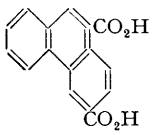

(XI.)

$R_2 = NH_2$) and not (IX; $R_1 = NH_2$, $R_2 = NO_2$), since the latter would have given under these conditions the corresponding nitrophenanthrene. The failure to obtain *o*-amino-α-(*p*-nitrophenyl)cinnamic acid (IX; $R_1 = NH_2$, $R_2 = NO_2$) led to an attempt to prepare *p*-nitro-α-(*o*-aminophenyl)cinnamic acid by ring fission of *p*-nitrobenzylideneoxindole (VIII; $R_1 = H$, $R_2 = NO_2$) with barium hydroxide solution (Windaus, Eickel, Jensen, and Schramme, *Ber.*, 1924, **57**, 1871, 1875) although it was realised that this nitro-amine, in which the *o*-aminophenyl group is attached to the α-carbon atom, would not lend itself to easy ring closure, since Mayer and Balle (*Annalen*, 1914, **403**, 167) obtained low yields of 3-methylphenanthrene-10-carboxylic acid from α-(2-amino-4-methylphenyl)cinnamic acid; a similar experience is reported by May and Mosettig (*J. Org. Chem.*, 1946, **11**, 435). *p*-Nitrobenzylideneoxindole (VIII; $R_1 = H$, $R_2 = NO_2$), first prepared by Neber and Rocker (*Ber.*, 1923, **56**, 1710), was obtained by heating *p*-nitrobenzaldehyde with oxindole at 125—130° (cf. Kliegl and Schmalenbach, *Ber.*, 1923, **56**, 1517), but was found to be resistant to hydrolysis and attempts to obtain the nitro-amine were unsuccessful. May and Mosettig (*loc. cit.*) report that *p*-chlorobenzylideneoxindole (VIII; $R_1 = H$, $R_2 = Cl$) is also very resistant to hydrolysis.

Since the attempts to prepare *o*-amino-α-*p*-nitrophenylcinnamic acid were unsuccessful attention was directed to the corresponding o-*amino*-α-p-*cyanophenylcinnamic acid*. The corresponding *nitro-acid* (IX; $R_1 = NO_2$, $R_2 = CN$) was obtained by the condensation of *o*-nitrobenzaldehyde with sodium *p*-cyanophenylacetate in acetic anhydride with zinc chloride at 70° for 15 hours. Heating for 45 hours at 110°, or on a boiling water-bath for 15 hours, gave a mixture of the cyano-acid and o-*nitro*-α-(p-*carboxyphenyl*)*cinnamic acid* (IX; $R_1 = NO_2$, $R_2 = CO_2H$). *o*-Amino-α-*p*-cyanophenylcinnamic acid (IX; $R_1 = NH_2$, $R_2 = CN$), obtained by reduction of the nitro-acid with ferrous sulphate and ammonia, was diazotised in dilute sulphuric acid solution and the warm diazonium salt was decomposed by the addition of copper to give 3-*cyanophenanthrene*-10-*carboxylic acid* (X) in 58% yield. *o*-Nitro-α-(*p*-carboxyphenyl)cinnamic acid (IX; $R_1 = NO_2$, $R_2 = CO_2H$), which was obtained as a by-product owing to the hydrolysis of *o*-nitro-α-(*p*-cyanophenyl)cinnamic acid (IX; $R_1 = NO_2$, $R_2 = CN$) at the higher temperature, was also reduced with ferrous sulphate and ammonia to o-*amino*-α-(p-*carboxyphenyl*)*cinnamic acid* (IX; $R_1 = NH_2$, $R_2 = CO_2H$). The amino-acid was diazotised in dilute sulphuric acid and the diazonium salt was decomposed with copper powder to yield *phenanthrene*-3 : 10-*dicarboxylic acid* (XI) in 48% yield. This acid proved to be insoluble in benzene, toluene, alcohol, ether, and acetone, and was only sparingly soluble in boiling acetic acid. It was finally crystallised from nitrobenzene or tetralin and melted at 318°. A phenanthrene-dicarboxylic acid of unknown constitution having these properties has been described by Scheidt (*Ber.*, 1938, **71**, 1248). The *diethyl* ester of (XI) was prepared in low yield by boiling the acid under reflux in ethyl alcohol containing sulphuric acid.

Experimental.

o-*Amino*-α-(o-*nitrophenyl*)*cinnamic Acid* (V; $R_1 = NH_2$, $R_2 = NO_2$).—Hydrogen sulphide was bubbled into a solution of the dinitro-acid (10·2 g.; Pschorr and Popovici, *Ber.*, 1906, **39**, 3120) in alcohol

(20 c.c.) and aqueous ammonia (15 c.c.; *d* 0·880) for 4 hours, the solution being alternately cooled to 0° and then heated to boiling point for a short time. Water was then added, and the excess of ammonia and hydrogen sulphide expelled by boiling. The solution was cooled, and the precipitated sulphur removed by filtration. The filtrate was made acid with acetic acid and the precipitated amino-acid was collected and dissolved in dilute aqueous ammonia. The filtered alkaline solution was made just acid with acetic acid, and crystallisation of the yellow solid from alcohol gave o-*amino*-α-(o-*nitrophenyl*)*cinnamic acid* (5·8 g.) in short yellow shining needles, m. p. 202—203° (Found: C, 63·2; H, 4·5. $C_{15}H_{12}O_4N_2$ requires C, 63·4; H, 4·2%). At temperatures above the m. p. some water is lost with formation of 3-*o*-nitrophenylcarbostyril (see below).

The acetyl derivative was obtained by addition of the amino-acid (3·8 g.) to acetic anhydride (10 c.c.) and concentrated sulphuric acid (2 drops). After this had been kept at room temperature for 2 days, water was added and the yellow solid was collected and crystallised from glacial acetic acid, in which it was sparingly soluble. o-*Acetamido*-α-(o-*nitrophenyl*)*cinnamic acid* separated in fine yellow needles, m. p. 254° (Found: C, 62·8; H, 4·7. $C_{17}H_{14}O_5N_2$ requires C, 62·6; H, 4·3%).

3-o-*Nitrophenylcarbostyril* (VI).—*o*-Amino-α-(*o*-nitrophenyl)cinnamic acid (0·15 g.), acetic anhydride (10 c.c.), and zinc chloride (1 g.) were heated on the water-bath for 12 hours. The small hard yellow crystals which separated were collected, and crystallisation from acetic acid gave 3-o-*nitrophenylcarbostyril* in yellow needles, m. p. 301—301·5° (Found: C, 67·1; H, 3·9. $C_{15}H_{10}O_3N_2$ requires C, 67·6; H, 3·8%).

1-*Nitrophenanthrene*-10-*carboxylic Acid* (VII).—(*a*) A solution of *o*-amino-α-(*o*-nitrophenyl)cinnamic acid (1·75 g.) in aqueous sodium carbonate [1 g. (hydrated) in 10 c.c.] was cooled to 0° and a solution of sodium nitrite (0·5 g.) in water (5 c.c.) was added. The yellow solution was then added dropwise to a mixture of concentrated sulphuric acid (7 c.c.) and water (20 c.c.) at 0°, and the whole was set aside for 15 minutes. Copper powder (1 g.) was added to the diazonium sulphate solution, and the mixture warmed on the water-bath. Nitrogen was slowly evolved and the reaction was complete after 30 minutes. The precipitate was collected and dissolved in dilute aqueous ammonia. The filtered alkaline solution afforded on acidification a gum, which was dissolved in ether, and washed with water and with aqueous sodium hydroxide. Reacidification of the alkaline extract gave a brown solid which on crystallisation from acetic acid gave 1-*nitrophenanthrene*-10-*carboxylic acid* (0·45 g.) in long buff shining needles, m. p. 231—232° (Found: C, 67·15; H, 3·5. $C_{15}H_9O_4N$ requires C, 67·4; H, 3·4%). From the mother-liquor a second solid (0·2 g.) was obtained, which after several recrystallisations from aqueous acetic acid afforded o-*hydroxy*-α-(o-*nitrophenyl*)*cinnamic acid* in small hard yellow crystals, m. p. 195—196° (Found: C, 63·8; H, 3·9. $C_{15}H_{11}O_5N$ requires C, 63·2; H, 4·0%). (*b*) Dry hydrogen chloride was passed through a solution of *o*-amino-α-(*o*-nitrophenyl)cinnamic acid (0·65 g.) in ethyl alcohol (20 c.c.). The solution was cooled to 0° and amyl nitrite (1 c.c.) was added in 2 portions. After this had been kept at 0° for 10 minutes, ether (200 c.c.) was added to precipitate the diazonium chloride, which was collected on a sintered-glass funnel and washed in turn with ether and AnalaR acetone. The diazonium chloride was covered with dry acetone at room temperature. Since no reaction appeared to take place, after 20 minutes copper powder (0·4 g.) was added. An immediate reaction set in with evolution of nitrogen, and the insoluble diazonium salt rapidly disappeared to give a clear red solution. After removal of the copper by filtration the acetone was distilled off and the dark solid residue was crystallised from glacial acetic acid (charcoal). 1-Nitrophenanthrene-10-carboxylic acid separated in fine long needles (0·35 g.), m. p. 230°, both alone and on admixture with the acid prepared by method (*a*) above.

1-*Nitrophenanthrene*.—1-Nitrophenanthrene-10-carboxylic acid (0·35 g.) was heated with quinoline (10 c.c.) under reflux in the presence of a small quantity of copper chromite and copper powder for 15 minutes. The mixture was poured on ice and concentrated hydrochloric acid, and the precipitate was collected and washed with aqueous sodium carbonate. Crystallisation from ethanol, after filtration from the copper, gave 1-*nitrophenanthrene* in slender yellow needles or plates (0·17 g.), m. p. 133° (Found: C, 74·9; H, 4·2. $C_{14}H_9O_2N$ requires C, 75·3; H, 4·1%).

o-*Nitro*-α-(p-*aminophenyl*)*cinnamic Acid* (IX; $R_1 = NO_2$, $R_2 = NH_2$).—(*a*) To a boiling solution of the dinitro-acid (4·4 g.; Ruggli and Dinger, *loc. cit.*) in water (250 c.c.) and aqueous ammonia (1 c.c.; *d* 0·880) a solution of sodium sulphide (6·5 g.) and sulphur (1·6 g.) in warm water (25 c.c.) was added dropwise during 20 minutes. After the addition the mixture was boiled for a further 20 minutes, during which it became deep red and sulphur was deposited. The solution was filtered whilst hot, and the filtrate acidified with dilute acetic acid. The crude red solid was collected and digested with a large volume of dilute hydrochloric acid and a small amount of sulphur was removed. The filtered solution was made just alkaline with dilute aqueous ammonia, concentrated to 750 c.c., and made acid with dilute acetic acid. Crystallisation of the orange-red precipitate from ethyl alcohol (400 c.c.) gave o-*nitro*-α-(p-*aminophenyl*)*cinnamic acid monohydrate* (2·4 g.) in yellowish-orange needles, m. p. 186—187° (Found: C, 59·5; H, 4·7. $C_{15}H_{12}O_4N_2,H_2O$ requires C, 59·6; H, 4·7%). (*b*) The dinitro-acid (4 g.), dissolved in alcohol (20 c.c.) and concentrated ammonia (10 c.c., *d* 0·880), was saturated at 0° with hydrogen sulphide. The solution was then heated until the excess of ammonia and hydrogen sulphide had been expelled. The sulphur was removed, and the filtrate acidified with glacial acetic acid. The precipitated solid was collected, dried, and crystallised from absolute ethyl alcohol to give hard red crystals (1·5 g.), m. p. 190—195°. Recrystallisation from absolute ethyl alcohol gave o-*nitro*-α-(p-*aminophenyl*)*cinnamic acid*, m. p. 194—195°, in orange-red crystals after drying at 120° (Found: C, 63·3; H, 4·4. $C_{15}H_{12}O_4N_2$ requires C, 63·4; H, 4·25%).

o-*Nitro*-α-(p-*acetamidophenyl*)*cinnamic Acid*.—The above nitro-amine (0·3 g.) (or the monohydrate) was warmed on the water-bath with a mixture of glacial acetic acid (10 c.c.), acetic anhydride (3 c.c.), and a drop of concentrated sulphuric acid until a clear solution was obtained, then set aside overnight; water was added and the precipitated whitish-yellow solid was crystallised from aqueous alcohol (charcoal). o-*Nitro*-α-(p-*acetamidophenyl*)*cinnamic acid* was obtained in short, stout, colourless needles, m. p. 201° (Found: C, 62·4; H, 4·4. $C_{17}H_{14}O_5N_2$ requires C, 62·6; H, 4·3%). The same acetyl derivative was obtained when the amino-acid (0·75 g.) was heated on the water-bath with acetic anhydride (10 c.c.) containing two drops of concentrated sulphuric acid.

o-*Nitro*-α-(p-*chlorophenyl*)*cinnamic Acid* (IX; $R_1 = NO_2$, $R_2 = Cl$).—(*a*) A solution of *o*-nitro-α-(*p*-aminophenyl)cinnamic acid (2·0 g.) in concentrated hydrochloric acid (3·5 g.) and water 5 c.c.) was diazotised at 0° by addition of a solution of sodium nitrite (0·7 g.) in water (5 c.c.). The diazonium salt separated as a yellow crystalline deposit. To this was added a solution of cuprous chloride, prepared by addition of sodium sulphite (1·35 g.) and sodium hydroxide (0·8 g.) in water (2 c.c.) to copper sulphate hydrate (6·25 g.) and sodium chloride (1·1 g.) in water (4 c.c.) with stirring, in concentrated hydrochloric acid. The reaction mixturewas heated on the water-bath; the cuprous chloride complex slowly decomposed to give a dark oil. The heating was continued until no more nitrogen was evolved. The oil was extracted with ether and shaken with aqueous sodium carbonate. When the alkaline layer was acidified an oily solid separated, from which two compounds were obtained by crystallisation from ether–light petroleum (b. p. 40—60°). The major product, which separated from aqueous alcohol in long colourless feathery needles, m. p. 143—145°, was considered to be *trans-o*-nitro-α-(*p*-chlorophenyl)-cinnamic acid (Nylen, *loc. cit.*, gives m. p. 146° for the *trans*-isomer and m. p. 186° for the *cis*-isomer) (Found: C, 59·7; H, 3·3. Calc. for $C_{15}H_{10}O_4NCl$: C, 59·3; H, 3·3%). The second product, obtained in only very small yield, separated from dilute acetic acid in brownish, short rods, m. p. 186—186·5°, and was not identified (Found: C, 62·1; H, 3·9%).

(*b*) Dry hydrogen chloride was passed through a warm solution of the nitro-amine (0·7 g.) in alcohol (20 c.c.) for 10 minutes, after which the solution was cooled to 0° and *iso*amyl nitrite (1 c.c.) was added. Then, after 15 minutes, dry ether was added and the precipitated diazonium salt was washed with ether and acetone and placed under dry acetone (20 c.c.). On addition of copper powder (1 g.), the insoluble diazonium salt passed into solution with the evolution of nitrogen. The solid obtained after evaporation of the acetone was crystallised from aqueous alcohol and then from benzene–light petroleum (b. p. 60—80°) to give *trans-o*-nitro-α-(*p*-chlorophenyl)cinnamic acid, which separated in colourless leaves, m. p. 138—140°.

o-*Chloro*-α-(p-*nitrophenyl*)*cinnamic Acid* (IX; $R_1 = Cl$, $R_2 = NO_2$).—Sodium *p*-nitrophenylacetate (6·1 g.) and *o*-chlorobenzaldehyde (4·2 g.) were heated with acetic anhydride (15 c.c.) in an oil-bath at 100—130° for 9 hours. The mixture was distilled with steam and the residual non-volatile oil was extracted with hot aqueous ammonia. Acidification of the filtered solution gave o-*chloro*-α-(p-*nitrophenyl*)-*cinnamic acid*, which separated from aqueous alcohol in short yellow needles, m. p. 213—215°, in rosette clusters (Found: C, 59·8; H, 3·3. $C_{15}H_{10}O_4NCl$ requires C, 59·3; H, 3·3%).

p-*Nitrobenzylideneoxindole* (VIII; $R_1 = H$; $R_2 = NO_2$).—Oxindole (1 g.) and *p*-nitrobenzaldehyde (1 g.) were heated together in an oil-bath at 125—130° for 15 minutes. The liquid melt, which soon began to eliminate water, became a hard red solid mass. The product was extracted with boiling glacial acetic acid, from which the *p*-nitrobenzylideneoxindole separated in red crystals (1·6 g.), m. p. 224—225° (Neber and Rocker, *loc. cit.*, give m. p. 229°). This oxindole (1·8 g.) and barium hydroxide (1·8 g.) in water (25 c.c.) were heated for 5 hours in a sealed tube at 135—140°. After the mixture had cooled, a solution of sodium carbonate (5 g.) in water (30 c.c.) was added, and the precipitated barium carbonate removed by filtration. Attempts to isolate the pure nitro-amine were unsuccessful.

o-*Nitro*-α-(p-*cyanophenyl*)*cinnamic Acid* (IX; $R_1 = NO_2$, $R_2 = CN$).—(*a*) *o*-Nitrobenzaldehyde (3·3 g.) and sodium *p*-cyanophenylacetate (4 g.; dried at 110°) (Jaeger and Robinson, *J.*, 1941, 744) were heated in acetic anhydride (35 c.c.) with freshly fused zinc chloride (0·5 g.) at 70° for 15 hours. The red mixture was poured into water (500 c.c.) and warmed to destroy excess of acetic anhydride. The crude acid was dissolved in warm aqueous sodium carbonate. Acidification of the filtered alkaline solution gave a yellow flocculent precipitate which was collected and crystallised from benzene. o-*Nitro*-α-(p-*cyano-phenyl*)*cinnamic acid* (1·7 g.) was obtained in colourless needles, m. p. 171—172° (Found: C, 65·7; H, 3·4. $C_{16}H_{10}O_4N_2$ requires C, 65·3; H, 3·7%). (*b*) *o*-Nitrobenzaldehyde (3·3 g.) and sodium *p*-cyano-phenylacetate (4·0 g.) were heated in acetic anhydride (35 c.c.) with freshly fused zinc chloride (0·5 g.) on a boiling water-bath for 24 hours. The reaction product was worked up as described above. A mixture of two acids was obtained. The more soluble acid was *o*-nitro-α-(*p*-cyanophenyl)cinnamic acid, m. p. and mixed m. p. 168—169°, and the less soluble acid, which separated from glacial acetic acid in pale yellow shining needles, m. p. 247—249°, proved to be o-*nitro*-α-(p-*carboxyphenyl*)*cinnamic acid* (Found: C, 61·2; H, 3·8. $C_{16}H_{11}O_6N$ requires C, 61·3; H, 3·5%). When the above reaction was carried out at 110° for 45 hours the dicarboxylic acid was the main product.

o-*Amino*-α-(p-*cyanophenyl*)*cinnamic Acid* (IX; $R_1 = NH_2$, $R_2 = CN$).—A solution of *o*-nitro-α-(*p*-cyano-phenyl)cinnamic acid (1·7 g.) in dilute aqueous ammonia was added dropwise, with mechanical stirring, to a boiling solution of ferrous sulphate hydrate (18 g.) in water (60 c.c.). The mixture was heated for a further 15 minutes with the addition of concentrated ammonia solution. Acidification of the hot filtered solution with glacial acetic acid gave a yellow precipitate which was collected and crystallised from ethyl alcohol. o-*Amino*-α-(p-*cyanophenyl*)*cinnamic acid* (0·9 g.) separated in yellow crystals, m. p. 215° (decomp.) (Found: C, 72·2; H, 4·7. $C_{16}H_{12}O_2N_2$ requires C, 72·7; H, 4·6%).

3-*Cyanophenanthrene*-10-*carboxylic Acid* (X).—To a solution of *o*-amino-α-(*p*-cyanophenyl)cinnamic acid (0·55 g.) in aqueous sodium carbonate (0·35 g., in 10 c.c.) was added a solution of sodium nitrite (0·2 g.) in water (10 c.c.). This solution was added dropwise to a mixture of concentrated sulphuric acid (2 c.c.) in water (15 c.c.) at 0°. The yellow diazonium solution was decomposed by addition of copper powder (0·5 g.) and the reaction was completed by warming on the water-bath for 30 minutes. The precipitated solid was collected and dissolved in dilute aqueous ammnoia, and acidification of the filtered solution gave a flocculent precipitate. Crystallisation from glacial acetic acid, in which it was only sparingly soluble, gave 3-*cyanophenanthrene*-10-*carboxylic acid* in colourless short needles (0·3 g.), m. p. 300° (Found: C, 77·6; H, 3·8. $C_{16}H_9O_2N$ requires C, 77·75; H, 3·7%).

o-*Amino*-α-(p-*carboxyphenyl*)*cinnamic Acid* (IX; $R_1 = NH_2$, $R_2 = CO_2H$).—A solution of *o*-nitro-α-(*p*-carboxylphenyl)cinnamic acid (5 g.) in dilute aqueous ammonia was added slowly to a boiling solution of ferrous sulphate hydrate (50 g.) in water (200 c.c.) with mechanical stirring. Concentrated aqueous ammonia was then added until the solution became strongly alkaline, and the mixture was heated for a further 30 minutes on the water-bath and filtered. Acidification of the filtrate with glacial acetic acid gave a yellow precipitate which on crystallisation from aqueous alcohol gave o-*amino*-α-(p-*carboxyphenyl*)-

cinnamic acid (3·5 g.) in bright yellow needles, m. p. 215° (Found : C, 67·7; H, 4·7. $C_{16}H_{13}O_4N$ requires C, 67·8; H, 4·6%).

Phenanthrene-3 : 10-*dicarboxylic Acid* (XI).—A solution of the foregoing acid (2·65 g.) in water (50 c.c.) containing sodium carbonate (1·6 g.) and sodium nitrite (0·75 g.) was added dropwise to a mixture of concentrated sulphuric acid (4 c.c.) in water (50 c.c.) at 0°. To the resulting clear yellow diazonium solution copper powder (1 g.) was added and the solution was warmed on the water-bath for 30 minutes; nitrogen was evolved and a white flocculent precipitate separated, which was collected and dissolved in aqueous sodium carbonate. Acidification of the filtered alkaline solution precipitated a colourless jelly-like mass which was boiled for 3 minutes, cooled, and filtered. The residue was insoluble in alcohol, benzene, toluene, acetone, and ether, but was sparingly soluble in boiling glacial acetic acid. Crystallisation from nitrobenzene gave *phenanthrene*-3 : 10-*dicarboxylic acid* (1·2 g.) in flat buff-coloured plates, m. p. 318° (Found : C, 72·4; H, 4·3. $C_{16}H_{10}O_4$ requires C, 72·2; H, 3·8%). The diethyl ester was prepared by boiling the dicarboxylic acid under reflux with ethyl alcohol in the presence of concentrated sulphuric acid for 6 hours. After filtration from unchanged dicarboxylic acid, the filtrate was diluted with water and the excess of alcohol removed by distillation. The resulting solid on crystallisation from methyl alcohol gave *ethyl phenanthrene*-3 : 10-*dicarboxylate* in colourless plates, m. p. 221° (Found : C, 74·2; H, 5·3. $C_{20}H_{18}O_4$ requires C, 74·2; H, 5·6%).

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