883. *A Novel Intramolecular Nucleophilic Displacement.*

By D. H. Hey, J. A. Leonard, and C. W. Rees.

When 2′-nitrobiphenyl-2-carboxylic acid is heated in quinoline or in an inert solvent containing piperidine, or when its potassium salt is heated alone, 3,4-benzocoumarin is formed by intramolecular nucleophilic displacement of the (unactivated) nitro-group by the carboxylate ion; the free acid does not decompose when heated. Some very similar reactions have previously been reported to yield fluorenones rather than benzocoumarins.

When 2′-nitrobiphenyl-2-carboxylic acid is boiled in tetralin or treated with zinc and ammonium chloride the strongly chelating *N*-hydroxyphenanthridone is formed. The corresponding reduction product of 6-nitrodiphenic acid, *N*-hydroxyphenanthridone-4-carboxylic acid, was previously thought to be phenanthridone-4-carboxylic acid.

Nitration of biphenyl-2-carboxylic acid provides a new example of intramolecular catalysis in electrophilic aromatic substitution. With concentrated nitric acid a high *ortho*/*para* ratio is observed, and with nitrogen pentoxide nitration occurs exclusively in the 2′-position. Mechanisms are proposed for these reactions.

4′-Nitrobiphenyl-2-carboxylic acid was required for another investigation, in amounts greater than could be conveniently prepared by decomposition of *p*-nitrobenzenediazonium hydroxide or of *p*-nitrobenzoyl peroxide in toluene, followed by separation and oxidation of 2-methyl-4′-nitrobiphenyl. Treatment of biphenyl-2-carboxylic acid, readily available from alkaline fusion of fluorenone, with fuming nitric acid at room temperature was reported [1] to give a mononitro-derivative, m. p. 221—222°; this was probably 4′-nitrobiphenyl-2-carboxylic acid, m. p. 231°, which is less soluble than the 2′-nitro-isomer, m. p. 170°, and hence more readily isolated. We were unable to repeat this mononitration with fuming nitric acid, and even at 0° dinitration occurred to give two new dinitro-acids, m. p. 183° and 246°. With concentrated nitric acid at room temperature, however, a mixture of 2′- (79%) and 4′-nitrobiphenyl-2-carboxylic acid (21%) was isolated in high yield.

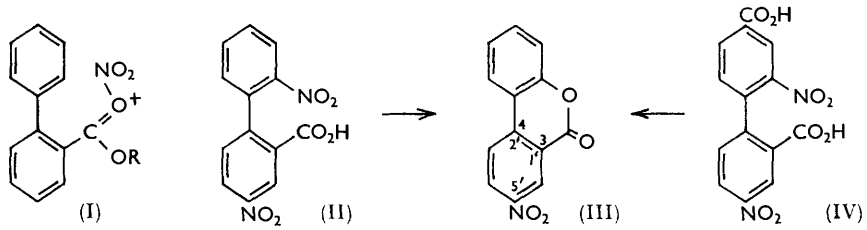
This *ortho*/*para* ratio of 3·8 for mononitration is high for biphenyls, values in the range 0·5—1 being more usual.[2] This suggests the possibility of intramolecular assistance by the carboxylic acid group, in the nitration, analogous to that proposed [3] many years ago to explain the high proportion of *ortho*-substitution in the nitration of acetophenone and recently by Norman and Radda [4] in the nitration of methyl phenethyl ether. A similarly high ratio (3 : 1) was found in the nitration of methyl biphenyl-2-carboxylate, and an intermediate complex (I; R = H or Me) may be responsible for this preferential formation of the 2′-nitro-isomers. Evidence for this is provided by the nitration of biphenyl-2-carboxylic acid with nitrogen pentoxide, the reagent considered to favour intermediate complex formation most strongly.[4] In this case 2′-nitrobiphenyl-2-carboxylic acid was the only product isolated and none of the much less soluble 4′-nitro-isomer could be detected. We believe this provides the first simple demonstration of the exclusive formation of one isomer in electrophilic aromatic substitution caused by prior interaction between a substituent group and the reagent.

A study of the infrared spectra of the dinitro-acids, m. p. 183° and 246°, suggested that these were 2′,4- (II) and 4,4′-dinitrobiphenyl-2-carboxylic acid, respectively. The structure

[1] Schmitz, *Annalen*, 1878, **193**, 123.
[2] de la Mare and Ridd, "Aromatic Substitution," Butterworths Scientific Publns., London, 1959, p. 157; Billing and Norman, *J.*, 1961, 3885.
[3] Lapworth and Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, 1928, **72**, 43; de la Mare and Ridd, ref. 2, p. 82.
[4] Norman and Radda, *J.*, 1961, 3030.

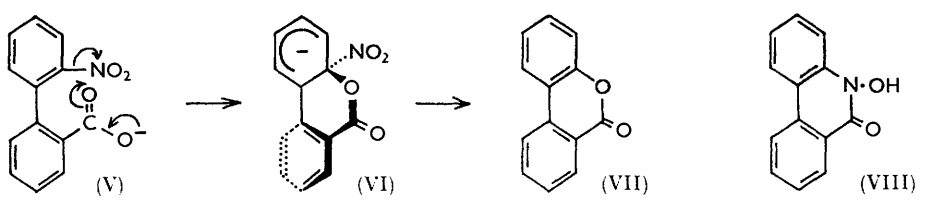
of the latter was confirmed by decarboxylation with copper chromite in quinoline to 4,4'-dinitrobiphenyl; similar treatment of the former acid (II), however, did not give the expected 2,4'-dinitrobiphenyl but gave 5'-nitro-3,4-benzocoumarin (III), m. p. 227—228°, $\nu_{max.}$ 1739 cm.$^{-1}$ (δ-lactone), which was soluble in hot aqueous sodium hydroxide. Similar decarboxylation of 2'-nitrobiphenyl-2-carboxylic acid was then attempted and gave 3,4-benzocoumarin (VII) in 80% yield.

Finzi and Bellavita [5] and, later, Angelini [6] have claimed that 2'-nitrobiphenyl-2-carboxylic acid and 2',4-dinitrobiphenyl-2,4'-dicarboxylic acid (IV) gave fluorenone and 2-nitrofluorenone, respectively, when heated with copper chromite in quinoline. They were presumably misled into proposing this mechanistically improbable reaction by the similarity in melting point of 3,4-benzocoumarin (92°) and fluorenone (84°) and their



mononitro-derivatives (227° and 223°, respectively), in spite of obtaining the supposed fluorenone as *cristalli bianchi*. The only analysis they report,[5] 6·0% of nitrogen for 2-nitrofluorenone (calc., 6·2%), is equally good for 5'-nitrobenzocoumarin (calc., 5·8%). The product we obtained from the decomposition of the acid (II) by copper chromite and quinoline was shown to depress the melting point of authentic 2-nitrofluorenone.

Since the conversion of 2'-nitrobiphenyl-2-carboxylic acid into 3,4-benzocoumarin (VII) does not involve decarboxylation the reaction was unaffected by omission of the copper chromite catalyst, and it was almost complete after 30 minutes' boiling in quinoline alone. The reaction also proceeded slowly in boiling xylene and rapidly in boiling tetralin, in the presence of piperidine (5% v/v) but not in its absence. It is thus base-catalysed, presumably involving the anionic form of the carboxylic acid. This was further demonstrated by pyrolysis of potassium 2'-nitrobiphenyl-2-carboxylate at 220°/2 mm.; pure benzocoumarin (89%) rapidly sublimed, leaving a residue of potassium nitrite (77%). Under the same conditions the free acid sublimed unchanged. Thus in this reaction the nitro-group is displaced by the carboxylate ion (see V) and the reaction belongs to the small group of intramolecular nucleophilic aromatic substitutions, the most notable of which, also reported from these laboratories, is the Smiles rearrangement.[7]



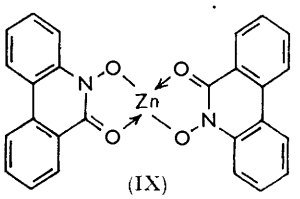
The extraordinary feature of our reaction is that an almost unactivated aromatic nitro-group is displaced by the very weakly nucleophilic carboxylate ion. Examples of normal nucleophilic displacement of such nitro-groups are virtually unknown, and examples where the carboxylate ion acts as a nucleophile in aromatic substitution are rare.[8] The very reactive chloro-2,4-dinitrobenzene, for example, does not react with potassium

[5] Finzi and Bellavita, *Gazzetta*, 1936, **66**, 421.
[6] Angelini, *Ann. Chim. (Rome)*, 1953, **43**, 247.
[7] Levy, Rains, and Smiles, *J.*, 1931, 3264.
[8] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.

benzoate in boiling ethanol, and the ester is formed only when the reactants are fused at 180°.[9] However, this intramolecular decomposition of 2′-nitrobiphenyl-2-carboxylic acid, though unfavourable energetically, is presumably greatly facilitated by the almost ideal disposition of the 2,2′-substituents for formation of the transition state (VI) at the extreme positions of rotation about the internuclear bond. An alternative mechanism can be visualised: nucleophilic attack by the carboxylate ion could occur at the 1′-carbon atom, which is *ortho* to the activating nitro-group, to give a spiro-lactone which could undergo a 1,2-shift and then aromatise to 3,4-benzocoumarin, with loss of a nitrite ion. This route is considered unlikely, however, since the isomeric potassium 4′-nitrobiphenyl-2-carboxylate, where the nitro-group is *para* to the 1′-position, was unchanged at 220°/2 mm.; on the basis of this mechanism this isomer would be expected to undergo some reaction, initially similar to that for the 2′-nitro-isomer. Presumably other leaving groups, such as halogen, in the 2′-position would be similarly displaced by the carboxylate ion and the apparent instability of 2′-bromobiphenyl-2-carboxylic acid [10] may be due to this reaction, the scope of which is under investigation.

The formation of 3,4-benzocoumarin when 2′-nitrobiphenyl-2-carboxylic acid was heated with piperidine in tetralin has been referred to above. In the absence of piperidine a different decomposition of the nitro-acid occurred yielding, as main product, the cyclic hydroxamic acid, *N*-hydroxyphenanthridone (VIII), which was soluble in aqueous sodium carbonate, gave an intense ferric chloride reaction, and had $\nu_{max.}$ 1626 cm.$^{-1}$ (hydrogen-bonded δ-lactam-carbonyl) and a broad shoulder at 3050 cm.$^{-1}$ (strongly hydrogen-bonded hydroxyl). It was also obtained, though in very small yield, from 2′-nitrobiphenyl-2-carboxylic acid by reduction with zinc and concentrated hydrochloric acid (cf. ref. 11 below); the main product of this reduction was phenanthridone. Reduction of the nitro-acid with zinc and ammonium chloride in ethanol, however, gave in very high yield a white insoluble zinc complex (IX), which was fairly stable to dilute mineral acids but was readily converted into *N*-hydroxyphenanthridone with concentrated sulphuric acid. Attempts to synthesise *N*-hydroxyphenanthridone (VIII) from 3,4-benzocoumarin (VII) by treatment with hydroxylamine failed, only starting material being recovered even under vigorous conditions, thus indicating increased stability of the heterocyclic ring in (VII) compared with that in the monocyclic α-pyrones. The conversion of 2′-nitrobiphenyl-2-carboxylic acid into *N*-hydroxyphenanthridone in boiling tetralin presumably resulted from reduction of the nitro-group to the hydroxyamino-group by the solvent in an uncatalysed, homogeneous hydrogen-transfer reaction, followed by cyclodehydration of the 2′-hydroxyaminobiphenyl-2-carboxylic acid.

The isolation of this *N*-hydroxy-compound suggested a reinterpretation of the reduction of 6-nitrodiphenic acid (X) with zinc and hydrochloric acid, which was considered by Bell [11]



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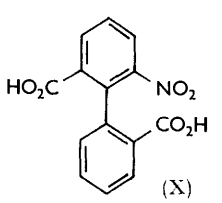

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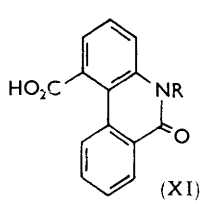

(XI)

to give the corresponding lactam (XI; R = H). The analytical figures obtained for this reduction product were consistently unsatisfactory, as was indeed recognised by Bell, but they are in excellent agreement, as are those of the monoacetyl derivative, with the presence of an extra oxygen atom. We suggest for it the cyclic hydroxamic acid structure (XI; R = OH). The puzzling observation [11] that this compound in an excess of aqueous alkali

[9] Kym, *Ber.*, 1899, **32**, 3539.
[10] Miller and Bachman, *J. Amer. Chem. Soc.*, 1935, **57**, 2446.
[11] Bell, *J.*, 1934, 835.

can act on titration as a dibasic acid (phenolphthalein) as well as a monobasic acid (Methyl Red) is thus explained.

Experimental

Infrared spectra are for Nujol mulls, and light petroleum refers to the fraction, b. p. 60—80°, unless otherwise stated. Solvent extracts were dried with anhydrous magnesium sulphate.

4'-Nitrobiphenyl-2-carboxylic Acid.—*p*-Nitrobenzoyl peroxide [12] and diazotised *p*-nitroaniline were separately allowed to decompose in toluene by the usual methods, to give mixtures of 2-, 3-, and 4-methyl-4'-nitrobiphenyl (b. p. 140—150°/0·1 mm.) consisting mainly of the 2-methyl isomer. This mixture (7 g.) and potassium permanganate (10 g.) in water (500 ml.) were boiled under reflux for 24 hr., more potassium permanganate (9 g.) being added during this time. The precipitated manganese dioxide was collected and this, and the mother-liquor, were extracted with ether from which starting material (3 g.) was recovered. On acidification the aqueous solution gave a white precipitate, which crystallised from ethanol to give 4'-nitrobiphenyl-4-carboxylic acid (0·15 g.), m. p. 344° (lit.,[13] m. p. 340°) and, on concentration of the mother-liquor, 4'-nitrobiphenyl-2-carboxylic acid (1·8 g.) in pale yellow prisms, m. p. 231° (lit.,[14] m. p. 226—227°).

Biphenyl-2-carboxylic Acid (cf. ref. 15).—Fluorenone (300 g.), distilled and crystallised from benzene–light petroleum (b. p. 40—60°), in diphenyl ether (800 ml.) was added to a vigorously stirred emulsion of potassium hydroxide (400 g.) in diphenyl ether (2 l.) at 180°. After being stirred for 30 min., during which a white solid separated, the mixture was allowed to cool. Extraction of the still molten mixture with water (3 l.) gave a clear aqueous extract, which on cooling slowly deposited a white solid. This was dissolved in hot water, the solution was acidified, and the precipitate formed was crystallised from benzene–light petroleum, to give colourless prisms (6 g.), m. p. 181—182°; the structure of this product will be described in a separate communication. Acidification of the original aqueous extract gave biphenyl-2-carboxylic acid (303 g.), m. p. 112—113°.

Nitration of Biphenyl-2-carboxylic Acid.—(*a*) *With fuming nitric acid* (cf. Schmitz [1]). Biphenyl-2-carboxylic acid (5 g.) was added in small portions to fuming nitric acid (15 ml.) at 0°. After 1 hour's stirring, the mixture was poured into water. Crystallisation of the precipitate from ethanol gave *4,4'-dinitrobiphenyl-2-carboxylic acid* (1·91 g.) in yellow prisms, m. p. 246° (Found: C, 54·3; H, 2·9; N, 9·8. $C_{13}H_8N_2O_6$ requires C, 54·2; H, 2·8; N, 9·7%). Concentration of the mother-liquor yielded *2',4-dinitrobiphenyl-2-carboxylic acid* (1·55 g.) in yellow needles or prisms, m. p. 182·5—183·5° (Found: C, 54·0; H, 2·8; N, 9·9%).

(*b*) *With concentrated nitric acid* (cf. Grieve and Hey [16]). Finely powdered biphenyl-2-carboxylic acid (300 g.) was added in one portion to concentrated nitric acid (5·5 l.) with stirring. After 2 hr. the mixture was poured into water (12 l.), and the precipitate formed was washed thoroughly with water. Crystallisation of the pale yellow powder (327 g.) from ethanol gave 4'-nitrobiphenyl-2-carboxylic acid (56 g.), which did not depress the m. p., and had an infrared spectrum identical with that of the sample prepared as described above. The mother-liquor gave impure 2'-nitrobiphenyl-2-carboxylic acid (208 g.), which after recrystallisation from chloroform had m. p. 170° (lit.,[11] m. p. 168°).

(*c*) *With nitrogen pentoxide.* Biphenyl-2-carboxylic acid (1 g.) in dry carbon tetrachloride (20 ml.) was stirred with nitrogen pentoxide (0·6 g.) in carbon tetrachloride (10 ml.) at 0° for 30 min. The solution was washed with water, dried, and evaporated to give a solid (1·05 g.), m. p. 130—150°. The absence of 4'-nitrobiphenyl-2-carboxylic acid was indicated by the high solubility of this solid in ethanol, from which it could not be crystallised. The solid was dissolved in benzene, adsorbed on silica gel (3·5 × 18 cm.), and eluted successively with light petroleum–benzene, benzene, benzene–ether, and ether to give 2'-nitrobiphenyl-2-carboxylic acid (0·84 g.) in several fractions, the first and last of which had identical infrared spectra. No evidence for the presence of 4'-nitrobiphenyl-2-carboxylic acid was obtained. After recrystallisation from chloroform the product did not depress the m. p. of, and was identical in infrared spectrum with, the 2'-nitro-acid prepared as described above.

[12] Hey and Walker, *J.*, 1948, 2216.
[13] Grieve and Hey, *J.*, 1932, 1891.
[14] Hey, Saunders, and Williams, *J.*, 1961, 554.
[15] Huntress and Seikel, *J. Amer. Chem. Soc.*, 1939, **61**, 816.
[16] Grieve and Hey, *J.*, 1933, 968.

Nitration of Methyl Biphenyl-2-carboxylate.—Methyl biphenyl-2-carboxylate [17] (2 g.) and concentrated nitric acid (75 ml.) were stirred at room temperature for 1·5 hr. The solution was poured into water, and the mixture was extracted with ether. The oil, obtained from the ether, and 20% aqueous sodium hydroxide (20 ml.) were boiled under reflux for 1 hr. Acidification and extraction with chloroform gave an oil, which on crystallisation from ethanol gave 4′-nitrobiphenyl-2-carboxylic acid (mixed m. p. and infrared comparison) (0·44 g.). Concentration of the mother-liquor gave 2′-nitrobiphenyl-2-carboxylic acid (mixed m. p. and infrared comparison) (1·2 g.).

Decarboxylation of 4,4′-Dinitrobiphenyl-2-carboxylic Acid.—The acid, m. p. 246° (0·5 g.), in quinoline (10 ml.) was boiled under reflux and copper chromite (0·05 g.) added in small portions. After 3 hr. the mixture was filtered into 5N-hydrochloric acid (50 ml.) and extracted with chloroform. Evaporation of the solvent and sublimation (250°/2 mm.) of the residue gave 4,4′-dinitrobiphenyl (0·24 g.) as a yellow powder, m. p. and mixed m. p. with an authentic sample [18] 245—246·5°.

Attempted Decarboxylation of 2′,4-Dinitrobiphenyl-2-carboxylic Acid (II).—The acid, m. p. 183° (0·4 g.), in quinoline (8 ml.) was treated with copper chromite (0·04 g.) as in the previous experiment. Crystallisation of the sublimate (0·17 g.) from ethanol gave *5′-nitro-3,4-benzocoumarin* (III) in pale yellow needles, m. p. 227—228° (Found: C, 64·3; H, 3·1; N, 5·7. $C_{13}H_7NO_4$ requires C, 64·7; H, 2·9; N, 5·8%), soluble in hot 5N-sodium hydroxide and was precipitated unchanged on acidification.

Attempted Decarboxylation of 2′-Nitrobiphenyl-2-carboxylic Acid.—The acid (0·5 g.) in quinoline (10 ml.) was treated with copper chromite (0·05 g.) as in the previous experiments, but the residue, after evaporation of the chloroform, was dissolved in benzene, adsorbed on alumina (1 × 15 cm.), and eluted with benzene–light petroleum and benzene to give a pale yellow solid (0·38 g.), which crystallised from light petroleum in colourless needles of 3,4-benzocoumarin (VII) (0·33 g.), m. p. 92·5°, $\nu_{max.}$ 1727 cm.$^{-1}$ (δ-lactone). The same yield of 3,4-benzocoumarin was obtained when the reaction time was reduced to 30 min. This product, and that from other experiments described below, had the same infrared spectrum as, and did not depress the m. p. of, authentic material prepared by the peracetic acid oxidation of fluorenone.[19]

Conversion of 2′-Nitrobiphenyl-2-carboxylic Acid into 3,4-Benzocoumarin.—(*a*) *In quinoline.* The acid (0·5 g.) in quinoline (10 ml.) was boiled under reflux for 30 min. The mixture was poured into 5N-hydrochloric acid (50 ml.) and extracted with chloroform. The extract was washed with saturated aqueous sodium hydrogen carbonate, from which starting material (0·08 g.) was recovered. The residue after removal of chloroform was dissolved in benzene, adsorbed on alumina (1 × 15 cm.), and eluted with benzene to give 3,4-benzocoumarin (0·28 g.).

(*b*) *In xylene.* The acid (0·5 g.) in xylene (10 ml.) was boiled under reflux and piperidine (0·5 ml.) added. After 24 hr. the mixture was cooled, diluted with ether, and extracted first with 2N-hydrochloric acid and then with saturated aqueous sodium hydrogen carbonate. Acidification of the alkaline extract gave starting material (0·4 g.). The residue obtained from the organic solution crystallised from light petroleum, to give 3,4-benzocoumarin (0·06 g.). 2′-Nitrobiphenyl-2-carboxylic acid was recovered (92%) after being boiled in xylene alone for 18 hr.

(*c*) *In tetralin.* The acid (0·5 g.) in tetralin (10 ml.) containing piperidine (0·5 ml.) was boiled under reflux for 3 hr. After filtration from a small amount of suspended material, the solution was diluted with ether and extracted, first with 2N-hydrochloric acid and then with saturated aqueous sodium hydrogen carbonate. No starting material was recovered on acidification of the alkaline extract. During evaporation of the organic solution a solid separated and was identified by mixed m. p. determination and infrared comparison as phenanthridone (0·015 g.). 3,4-Benzocoumarin (0·24 g.) was isolated by crystallisation (light petroleum) of the residue after complete evaporation of the mother-liquor.

(*d*) *Pyrolysis of the potassium salt.* 2′-Nitrobiphenyl-2-carboxylic acid (2 g.) in ethanol (20 ml.) was treated with potassium hydroxide (0·46 g.) in ethanol (20 ml.). The white precipitate was collected, washed with ethanol and ether, and dried to yield *potassium 2′-nitrobiphenyl-2-carboxylate* (1·5 g.) (Found: C, 55·5; H, 2·6. $C_{13}H_8KNO_4$ requires C, 55·5; H,

[17] Graebe and Rateanu, *Annalen*, 1894, **279**, 260.
[18] Gull and Turner, *J.*, 1929, 494.
[19] Doering and Speers, *J. Amer. Chem. Soc.*, 1950, **72**, 5515.

2·7%). When this salt (0·131 g.) was heated at 220° under reduced pressure (2 mm.) 3,4-benzocoumarin (0·081 g., 89%) rapidly sublimed, leaving a residue which was analysed for potassium nitrite (77%) by the method of Rider and Mellon.[20]

Potassium 4'-nitrobiphenyl-2-carboxylate was prepared (Found: C, 55·2; H, 3·1%) and treated in the same way. After 2 hr. no sublimate had been formed, the residue was unchanged in weight, and acidification of its aqueous solution gave 4'-nitrobiphenyl-2-carboxylic acid (93%).

Conversion of 2'-Nitrobiphenyl-2-carboxylic Acid into N-*Hydroxyphenanthridone* (VIII).—(*a*) *In tetralin.* The acid (2 g.) in tetralin (30 ml.) was boiled under reflux for 6 hr. On cooling, colourless needles (0·86 g.) separated and were recrystallised from chloroform, to give N-*hydroxyphenanthridone*, m. p. 258—259° (Found: C, 73·8; H, 4·5; N, 6·9. $C_{13}H_9NO_2$ requires C, 73·9; H, 4·3; N, 6·6%). This compound was soluble in saturated aqueous sodium hydrogen carbonate and was recovered unchanged upon acidification; it gave an intense purple colour with ferric chloride solution. Specimens of this compound obtained from the following experiments had identical infrared spectra and did not depress the m. p. of this product. The tetralin mother-liquor was adsorbed on alumina (1 × 40 cm.); elution with light petroleum (1·5 l.) gave tetralin; elution with benzene (1 l.) gave an oil (0·46 g.) which failed to crystallise and further elution with the same solvent (1 l.) gave a solid (0·43 g.), m. p. 120—135°, which crystallised from light petroleum as colourless prisms with unchanged m. p. (Found: C, 84·3; H, 6·1; N, 3·7%; *M*, 359. Calc. for $C_{23}H_{19}NO$: C, 84·9; H, 5·9; N, 4·3%; *M*, 325). This information and the infrared spectrum of the product is consistent with the structure *N*-(tetrahydro-1- and/or-2-naphthyl)-phenanthridone.

(*b*) *With zinc and ammonium chloride.* Treatment of 2'-nitrobiphenyl-2-carboxylic acid in ethanol with zinc at room temperature led only to the isolation of starting material. Then a mixture of the acid (2 g.), ammonium chloride (0·8 g.), ethanol (20 ml.), and water (2 ml.) was boiled under reflux. Zinc powder (2 g.) was added during 25 min. and boiling continued for a further 30 min. During this time a bulky white precipitate of the *zinc complex* of *N*-hydroxyphenanthridone separated, which was stirred with 2N-hydrochloric acid to remove the excess of zinc (Found: C, 64·3; H, 3·3. $C_{26}H_{16}N_2O_4Zn$ requires C, 64·0; H, 3·7%). The complex was dissolved in concentrated sulphuric acid and on dilution with water gave *N*-hydroxyphenanthridone (1·2 g.). The complex was only slowly affected by dilute mineral acid and gave the ferric chloride colour after several seconds' delay.

(*c*) *With zinc and hydrochloric acid* (cf. ref. 11). The acid (5 g.) in dioxan (50 ml.) and concentrated hydrochloric acid (50 ml.) was treated with zinc dust (3 g.) during 7 hr. and the mixture was stirred overnight. The white precipitate was collected and extracted with aqueous sodium hydrogen carbonate, to leave white phenanthridone (1·14 g.), which crystallised from ethanol as needles, m. p. and mixed m. p. 296° (this m. p. is very dependent upon the rate of heating). Acidification of the bicarbonate solution gave starting material (1·8 g.). The original filtrate was poured into water, and the precipitate (1·04 g.) was extracted first with hot ether, from which more starting material (0·9 g.) was recovered, and then with hot 10% sodium hydroxide solution, from which *N*-hydroxyphenanthridone (0·08 g.) separated upon acidification. The insoluble residue (0·06 g.) was phenanthridone. Very similar results were obtained when the dioxan was replaced by ethanol.

Treatment of 3,4-Benzocoumarin with Hydroxylamine.—3,4-Benzocoumarin was recovered after 15 hours' boiling under reflux with methanolic hydroxylamine. 3,4-Benzocoumarin (0·2 g.) and hydroxylamine hydrochloride (0·2 g.) in 2,6-lutidine (12 ml.) were boiled under reflux for 24 hr. 2,6-Lutidine hydrochloride, m. p. 230—231°, was filtered off, and the solution added to 2N-hydrochloric acid; starting material (0·14 g.) separated. No indication of the formation of *N*-hydroxyphenanthridone was obtained in either experiment by the very sensitive ferric chloride test.

Grateful acknowledgment is made to the Department of Scientific and Industrial Research for a Research Studentship to J. A. L. and to Dr. C. H. Rochester for help with the nitrite determination.

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[*Received, June 14th,* 1962.]

[20] Rider and Mellon, *Ind. Eng. Chem., Analyt.*, 1946, **18**, 96.