528. *Some Experiments on the Nitrofluorenones and Related Nitrophenanthridones, and Observations on the Ullmann Fluorenone Synthesis.*

By A. J. Nunn, K. Schofield, and R. S. Theobald.

(A) Beckmann rearrangement of 2-nitrofluorenone oxime gave a mixture of 2- and 7-nitrophenanthridone. The supposed 7-nitrophenanthridone and 4-nitro-2′-diphenamic acid of earlier workers were impure. The preparation of 9-methyl-7-nitrophenanthridine has been improved and it has been oxidised to 7-nitrophenanthridone. 1-, 3-, and 4-Nitrofluorenone have been prepared by Ullmann reactions, the first in very poor yield. Beckmann rearrangement of 3-nitrofluorenone oxime gave 3-nitrophenanthridone. The nitration products of phenanthridone are 1- and 3-nitrophenanthridone.

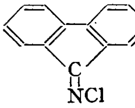
(B) 1-*o*-Benzoylphenyl-3 : 3- and 1-(*o*-*p*′-methoxybenzoylphenyl)-3 : 3-dimethyltriazen were decomposed by hydrogen chloride in benzene to give small yields of fluorenone and 3-methoxyfluorenone, together with larger amounts of 2-chloro- and 2-chloro-4′-methoxy-benzophenone. 1-(*o*-2′-Picolinoylphenyl)-3 : 3-dimethyltriazen is described.

(A) For reasons indicated in section (B) we were interested in the nitrofluorenones and their characterisation. Scrutiny of the literature showed that although 2-, 3-, and 4-nitrofluorenone, and their oximes, had been frequently described, the melting points of the latter were far from agreed. We therefore re-examined the nitrofluorenone oximes, and attempted to decide their geometrical configurations.

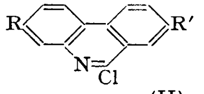
2-Nitrofluorenone oxime, prepared by Moore and Huntress (*J. Amer. Chem. Soc.*, 1927, **49**, 2618) from the ketone and hydroxylamine hydrochloride in ethanol, melted differently from the derivative obtained by Langecker (*J. pr. Chem.*, 1931, **132**, 145) from the same reagents but in the presence of barium carbonate and also by nitration and subsequent hydrolysis of fluorenone oxime acetate. Huntress and Cliff (*ibid.*, 1932, **54**, 826) suggested that the two products might be geometrical isomers. Moore and Huntress found purification of the oxime by crystallisation to be impossible, several solvents merely producing a widening of the melting range, supposedly because of Beckmann rearrangement. Such rearrangement by phosphorus pentachloride and oxychloride gave a chlorine-containing substance which, it was suggested, was an equilibrium mixture of (I) and (II; $R = H$, $R' = NO_2$), melting over a wide range and hydrolysable to a nitrophenanthridone, m. p. 282—284°. The last was said to be the 7-isomer (VII) because of its alleged identity with the supposed 7-nitrophenanthridone, m. p. 284—285°, obtained earlier by the same authors (*ibid.*, 1927, **49**, 1324). The earlier work consisted in treating 4-nitrodiphenic anhydride with ammonia, isolating two nitrodiphenamic acids by a difficult fractional crystallisation, and converting these into nitrophenanthridones by hypobromite (III $\longrightarrow$ V and VII). The higher-melting phenanthridone from the less-soluble diphenamic acid gave phthalic acid on oxidation, and was therefore 2-nitrophenanthridone (V), leaving the structure (VII) for the isomer. " *trans*-Migration " being assumed in the Beckmann rearrangement, these experiments pointed to the *syn*-configuration (VIII; $R = NO_2$, $R' = H$) for the oxime, m. p. 262·5—263° (decomp.). It might be mentioned at this point that the postulated equilibrium between (I) and (II; $R = H$, $R' = NO_2$) is rendered improbable by the work of Stieglitz and Peterson (*Ber.*, 1910, **43**, 782).

2-Nitrofluorenone is not normally prepared by Ullmann's application of the Gomberg synthesis (Graebe and Ullmann, *Ber.*, 1894, **27**, 3483; Ullmann and Mallet, *ibid.*, 1898, **31**, 1694), but because of our interest in this reaction we have re-examined its formation from 2-amino-5-nitrobenzophenone under various conditions, as described in the Experimental section. On re-examining 2-nitrofluorenone oxime prepared according to Moore and Huntress (*loc. cit.*, p. 2618) we observed m. p. 269—270° (decomp.), but this depended on the rate of heating and varied in the range 255—270° (decomp.). Oximation in presence of barium carbonate or sodium acetate gave products indistinguishable from that formed under acid conditions. The fact that melting is accompanied by decomposition may account for the variations previously recorded.* There was no difficulty in purifying the oxime by crystallisation. Its rearrangement by the method used by the earlier workers gave a chloro-derivative with a fairly wide melting range which was narrowed considerably by crystallisation, and the substance simulated the behaviour of a homogeneous chloronitrophenanthridine, particularly in giving on hydrolysis what seemed to be a nitrophenanthridine, melting sharply at 286—287°. The last observation coincided with Moore and Huntress's report (*loc. cit.*, p. 2618), but the material provided phthalic acid in about 30% yield on oxidation and therefore could not be 7-nitrophenanthridone (VII) as they claimed.

It was clearly necessary to repeat Moore and Huntress's experiments (*loc. cit.*, p. 1324) with 4-nitrodiphenic anhydride, and also to synthesise authentic 7-nitrophenanthridone.



(I)



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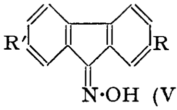
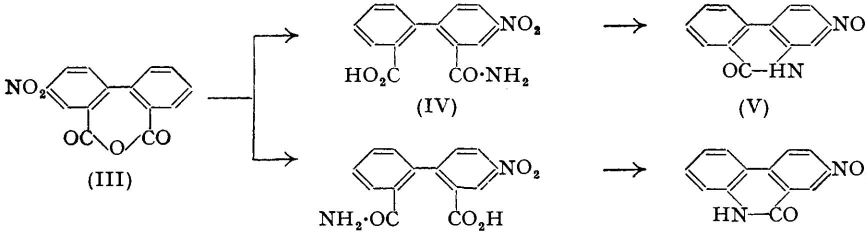


(VIII)



(III) (IV) (V) (VI) (VII)

Under the prescribed conditions for the reaction between 4-nitrodiphenic anhydride and ammonia, most of the anhydride was hydrolysed. Minor modifications enabled us to isolate workable amounts of 4-nitro-2-diphenamic acid (IV), but the isomer (VI) could not be obtained pure. We were able to prepare 2-nitrophenanthridone (V) and to confirm its orientation by oxidation. It was further characterised by conversion into 9-chloro-2-nitrophenanthridine.

Morgan and Walls (*J.*, 1932, 2225) prepared 9-methyl-7-nitrophenanthridine in low yield by cyclising 2-acetamido-4′-nitrodiphenyl with phosphorus oxychloride, and in our hands the recovery was impracticably small. Taking advantage of the work of Barber *et al.* (*J. Soc. Chem. Ind.*, 1950, **69**, 82), and of Petrow and Wragg (*J.*, 1950, 3516) we raised the yield to 25%, using stannic chloride as the cyclising agent. 7-Nitrophenanthridone, m. p. 326—327°, resulted on oxidation, and was characterised by conversion into 9-chloro-7-nitrophenanthridine.

These preparations of 2- and 7-nitrophenanthridone proved that the material, m. p. 286—287°, from the rearrangement of 2-nitrofluorenone oxime, was a mixture. It could not be resolved by crystallisation but the derived mixed chloronitrophenanthridines were separable to some extent by chromatographic methods. The ratio of 9-chloro-2- to 9-chloro-7-nitrophenanthridine in the mixture was very approximately 1 : 2, in rough agreement with the yield of phthalic acid obtained by oxidising the mixed phenanthridones. 9-Chloro-2-nitrophenanthridine isolated chromatographically from the mixture melted slightly higher than the specimen from 4-nitro-2-diphenamic acid, suggesting that the latter had not been completely purified. It follows from these experiments that Moore and Huntress's 4-nitro-2′-diphenamic acid was impure.

2-Nitrofluorenone oxime prepared for the present work was clearly either a mixture of both possible geometrical configurations or, if stereochemically pure, it suffered partial isomerisation during the Beckmann rearrangement. An attempt to resolve the oxime chromatographically failed. Dipole moment measurements might be useful here.

3-Nitrofluorenone has not previously been prepared by Ullmann's method. In

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* Bardout, *Anal. Asoc. Quim. Argentina*, 1934, **22**, 123, also found the m. p. to depend on the rate of heating.

attempting to clarify the confusion in the literature regarding this compound Ray and Barrick (*J. Amer. Chem. Soc.*, 1948, **70**, 1492) devised a new synthesis of it, and with a similar aim in mind we used 2-amino-4-nitrobenzophenone (Schofield and Theobald, *J.*, 1950, 1505) as a source of the compound. Despite considerable experimentation even the best conditions encountered gave only a mediocre yield of the pure fluorenone from the diazotised amine. The melting point of our product agreed fairly well with that recorded by Ray and Barrick (*loc. cit.*). The melting point of the oxime, prepared under acid conditions, coincided with that given by Bardout (*Anal. Asoc. Quim. Argentina*, 1931, **19**, 117; 1934, **22**, 123; we have not been able to consult these papers), but was lower than that recorded by Schmidt and Soll (*Ber.*, 1908, **41**, 3691) or Eckert and Langecker (*J. pr. Chem.*, 1928, **118**, 263) for material obtained in the same way, and also by Ray and Barrick (*loc. cit.*) who used neutral conditions. Beckmann rearrangement of our oxime gave 3-nitrophenanthridone, as was proved by oxidation of the latter to phthalic acid and by its identity with material prepared according to Walls (*J.*, 1935, 1405). The same 9-chloro-3-nitrophenanthridine was also obtained from both sources. It is noteworthy that our 3-nitrophenanthridone was colourless. Walls (*loc. cit.*) obtained it as red needles. Our evidence suggests that 3-nitrofluorenone oxime, m. p. 216—217°, possesses completely or largely (our experiments were on the small scale) the *anti*-configuration (VIII; $R = H$, $R' = NO_2$ at $C_{(3)}$).

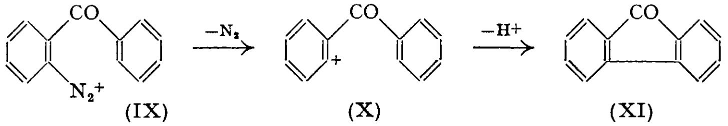
4-Nitrofluorenone has previously been obtained from 4-nitrophenanthraquinone by a benzilic acid change and air-oxidation of the resulting 4-nitrodiphenyleneglycollic acid (Schmidt and Bauer, *Ber.*, 1905, **38**, 3737). Later workers (Morgan and Thomason, *J.*, 1926, 2695; Bell, *J.*, 1928, 1990), including Courtot (*Ann. Chim.*, 1930, **14**, 5) who examined the method in some detail, seem to have found it satisfactory, but despite numerous attempts we failed to obtain suitably pure material from this route. It may be significant that Schmidt and Bauer (*loc. cit.*), who prepared the oxime from their ketone, described it as dark green needles, whereas it would be expected to be yellow. The ready availability of 2-amino-3-nitrobenzophenone (Schofield and Theobald, *loc. cit.*) suggested the application of Ullmann's method. Conditions have been devised which yield about 45% of 4-nitrofluorenone, and our experience suggests that this is the simplest route to the compound. The oxime prepared from our material under the conditions used by Schmidt and Bauer (*loc. cit.*) melted at a lower temperature than that reported by these workers, and was pale yellow. The Beckmann rearrangement of this oxime is being examined.

1-Nitrofluorenone was recently described for the first time by Chase and Hey (*J.*, 1952, 553). Diazotisation of 2-amino-6-nitrobenzophenone gave a very poor yield of a product which did not depress the melting point of a specimen kindly supplied by Professor Hey.

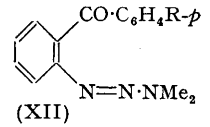
A feature of 2-amino-3- and 2-amino-6-nitrobenzophenone was the surprising persistence of their diazonium salts, which could be detected even after prolonged heating of their solutions. It is conceivable that reactions producing 1- or 4-substituted fluorenones therefrom might be retarded by steric factors. However, Chardonnens and Lienert (*Helv. Chim. Acta*, 1949, **32**, 2340) carried out several such reactions and evidently did not find them unusually slow.

The present experiments presented an opportunity for us to identify the two mono-nitration products of phenanthridone (Moore and Huntress, *loc. cit.*, p. 1324). These both gave phthalic acid on oxidation, and the major nitration product was identical with 3-nitro- and the minor with 1-nitro-phenanthridone (Stepan and Hamilton, *J. Amer. Chem. Soc.*, 1949, **71**, 2438). The nitration of phenanthridone is therefore qualitatively similar to the case of acylanilides (Holleman, "Die direkte Einfuhrung von Substituenten in den Benzolkern," Verlag von Veit, Leipzig, 1910), as would be expected.

(B) The above experiments were occasioned by interest in the mechanism of the Ullmann fluorenone synthesis (Saunders, "The Aromatic Diazo-compounds," Edward Arnold, London, 1949, p. 258, gives a useful summary of the reaction), a reaction normally effected by diazotising derivatives of 2-aminobenzophenone in acids of various concentrations. It seemed possible that in certain circumstances the cyclisation might be made to proceed by a free-radical mechanism, and in this form to find application to some synthetic problems in heterocyclic chemistry. Although the situation with regard to the formally similar Pschorr phenanthrene synthesis is not entirely clarified, it has been proved (Hey and Osbond, *J.*, 1949, 3164, 3172, who summarise the facts relating to the reaction) that in some circumstances it can proceed by intramolecular union of an aryl nucleus and an aryl free radical. However, DeTar and Sagmanli (*J. Amer. Chem. Soc.*, 1950, **72**, 965) have collected evidence which suggests that under normal conditions the Ullmann fluorenone synthesis involves ionic intermediates (IX ⟶ X ⟶ XI). The decomposition of diazotised 2-aminobenzophenone under alkaline conditions gave no fluorenone, and in the presence of benzene 2-benzoyldiphenyl was formed. They concluded that the failure of the diazonium salt to undergo an internal Gomberg–Bachmann reaction, whilst it underwent an ordinary Gomberg–Bachmann reaction with benzene, indicated that a free-radical mechanism could not account for the formation of fluorenone.



(IX) (X) (XI)



(XII)

We proposed to approach this problem through nitro-derivatives of 2-aminobenzophenone containing the nitro- and the amino-group in different rings, but, because of the need to carry out the experiments recorded in section (A), have so far examined only 2-amino- and 2-amino-4′-methoxy-benzophenone, both of which have been used previously in normal Ullmann–Gomberg reactions (Graebe and Ullmann, *loc. cit.*; Ullmann and Bleier, *Ber.*, 1902, **35**, 4273). It is now generally agreed that 1-aryl-3 : 3-dimethyltriazens decompose to give free radicals when treated with hydrogen chloride in benzene (Elks and Hey, *J.*, 1943, 441). Accordingly, we prepared the triazens (XII; R = H and OMe). These stable crystalline solids, on decomposition as mentioned, gave mainly 2-chlorobenzophenone and its 4′-methoxy-derivative, but also, though in small yield, fluorenone and 3-methoxyfluorenone. Decomposition of the triazen from 2-*o*-aminobenzoylpyridine (Nunn and Schofield, *J.*, 1952, 583) has so far failed to yield a recognisable product.

If it is accepted that the present decompositions produce free radicals we conclude that the Ullmann fluorenone synthesis *can* proceed by a free-radical mechanism, though it may not do so under the conditions normally used. We are attempting to apply the above findings to syntheses in the heterocyclic field.

EXPERIMENTAL

M. p.s are uncorrected.

Ullmann–Gomberg Reactions with 2-Amino-5-nitrobenzophenone.—Ullmann and Mallet (*loc. cit.*) mention the use of 25% sulphuric acid in this reaction. Unsatisfactory results which we obtained under these conditions prompted the following experiments : (*a*) The amine (3 g.) in concentrated sulphuric acid (30 c.c.) was treated with powdered sodium nitrite (1 g.) during ¼ hour at −5° to 0°. The solution was heated at 95° for 2 hours, then diluted with water (60 c.c.), and the product collected. Recrystallisation from alcohol gave 2-nitrofluorenone (1·7 g.; m. p. 220—221°) and 2-hydroxy-5-nitrobenzophenone (0·4 g.; m. p. 119—121°).

(*b*) The amine (3 g.) was treated in sulphuric acid (85%; 33 c.c.) with sodium nitrite (0·82 g.) in the concentrated acid (3 c.c.) at room temperature, and then heated for 2 hours at 95°, giving the fluorenone (1·58 g.) and the hydroxy-compound (0·48 g.).

(*c*) The amine (1 g.) in concentrated sulphuric acid (10 c.c.) was diazotised at 0° with powdered sodium nitrite. Addition of ice-water (10 c.c.) and copper powder (0·33 g.) gave a yellow precipitate and caused vigorous effervescence. After being heated for ¾ hour at 90° the mixture provided the fluorenone (0·42 g.) and the hydroxy-compound (0·17 g.).

2-Nitrofluorenone Oxime and its Rearrangement.—Prepared according to Moore and Huntress (*loc. cit.*, p. 2618) the oxime was a pale, matte yellow solid, m. p. 269—270° (decomp.) on rapid heating, or in the range 255—270° when heated at different rates. It could be crystallised from acetic acid or digested with boiling alcohol without deterioration. Langecker (*loc. cit.*) gave m. p. 249° (decomp.), and Moore and Huntress 262·5—263° [269—270° (corr.) (decomp.)]. Modification of the preparative conditions by the addition of 1 equivalent or excess of barium carbonate or sodium acetate gave products showing the characteristics mentioned above. A sample of the oxime collected in numerous fractions after passage in benzene–pyridine over alumina showed no sign of separation into components, the m. p.s of the fractions varying by a few degrees in an irregular manner.

The oxime (1 g.), phosphorus pentachloride (1·5 g.), and phosphorus oxychloride (8 c.c.) were refluxed for 6 hours. The mixture was poured on ice, neutralised with sodium acetate, and extracted with chloroform. Removal of the solvent after drying (Na_2CO_3) gave a pale yellow solid (0·87 g.), which after crystallisation from benzene gave small buff leaflets (0·53 g.), m. p. 171—173° (Found: C, 60·3; H, 2·7; Cl, 13·7%). More frequently the crystallised material melted over a range (169—174°). The crude product (1·45 g.; m. p. 131—176°) of such a rearrangement, in benzene (100 c.c.), was passed over alumina (40 × 2·5 cm.). The upper deep yellow, and the lower pale yellow band, when eluted with benzene and collected in 70-c.c. portions gave the following fractions [number, weight (g.), m. p.]: 1, 0·3, 175—176°; 2, 0·21, 176—177°; 3, 0·03, 157—170°; 4, 0·06, 200—202°; 5, 0·11, 205—206°; 6, 0·1, 200—201° (1—6 were colourless); 7, 0·12, 173—182° (cream-coloured); 8, 0·08, 172—182° (yellow); 9, 0·07, 194—203° (yellow); 10, 0·07, 195—204°; 11, 0·03, 202—210°; 12, 0·03, 211—214°; 13, 0·02, 211—214°; 14, 0·03, 212—214°; 15, 0·03, 211—214°; 16, 0·02, 202—211°; 17, 0·02, 214—215°; 18, 0·05, 213—215°; 19, 0·03, 214—215°; 20, 0·03, 210—214° (10—20 were yellow). Fraction 6 depressed the m. p. (204—205°, see below) of 9-chloro-2- but not of 9-chloro-7-nitrophenanthridine (m. p. 204—205°, see below). Fraction 17 behaved in the opposite way. Old specimens of the oxime gave similar results.

The reaction mixture from a further rearrangement of the oxime (3 g.) was concentrated under reduced pressure and the residual gum was boiled for 1½ hours with sulphuric acid (50%; 100 c.c.). After dilution the yellow product (2·86 g.) was collected and had m. p. 286—287° on crystallisation from acetic acid. Oxidation of this substance (1 g.) with permanganate according to Moore and Huntress (*loc. cit.*, p. 1324) gave crude phthalic acid (0·23 g.) melting, after crystallisation from water, at 195—196° alone or mixed with an authentic specimen.

4-*Nitro*-2-*diphenamic Acid*.—(*a*) 4-Nitrodiphenic acid was prepared by a modification of Moore and Huntress's method (*loc. cit.*, p. 1324): 2-nitrophenanthraquinone (see below) (20 g.) in concentrated sulphuric acid (60 c.c.) was added dropwise to vigorously stirred water (200 c.c.), more of the acid (30 c.c.) being used as a washing liquid. Potassium dichromate (80 g.) in hot water (800 c.c.) was added, and the mixture was stirred and refluxed for 5 hours. The hot solution was filtered from yellow material in suspension (8·35 g.) and on cooling deposited pure 4-nitrodiphenic acid (12·1 g.), m. p. 216—217°. The yellow solid was dissolved in sodium hydrogen carbonate solution, filtered from unchanged quinone, and precipitated by sulphuric acid, giving more of the product (7·7 g.; m. p. 216—217°). It was convenient to combine the impure crops from several such runs and purify them together.

(*b*) A suspension of 4-nitrodiphenic anhydride (13·2 g.; Moore and Huntress, *loc. cit.*, p. 2618), in dry benzene (100 c.c.) was treated dropwise at 0—5° with aqueous ammonia (*d* 0·88; 53 c.c.), whilst being vigorously shaken. After ½ hour at 0° the mixture was filtered, and the aqueous layer was separated and combined with the precipitate. The mixture was diluted with water (100 c.c.), stirred, and filtered. Addition of acetic acid (50 c.c.) to the filtrate, and then concentrated hydrochloric acid whilst cooling, gave a doughy solid which became granular and was dried at 110°. The solution of this product (9·8 g.) in hot alcohol (50 c.c.) was filtered, seeded with 4-nitro-2-diphenamic acid, and cooled in ice. The product was collected after 2 hours and a further 1½ hours, giving slightly impure 4-nitro-2-diphenamic acid (2·0 g.), m. p. 192—195°. Further crops were much less pure and could not be improved by crystallisation.

2-*Nitrophenanthridone*.—By Moore and Huntress's method (*loc. cit.*, p. 1324) the above acid (1·5 g.) gave crude 2-nitrophenanthridone (0·93 g.; m. p. 339—343°), which on crystallisation from acetic acid gave yellow needles, m. p. 357—358° (Found: C, 65·0; H, 3·4. Calc. for $C_{13}H_8O_3N_2$: C, 65·0; H, 3·4%). Moore and Huntress gave m. p. 348·5—349°. A mixture of 2- and 7-nitrophenanthridone (m. p. 326—327°, see below) melted at 283—284°.

9-*Chloro*-2-*nitrophenanthridine*.—Prepared in the same way as the 7-nitro-compound (see below), slightly impure 9-*chloro*-2-*nitrophenanthridine* separated from benzene as yellow needles, m. p. 204—205° (Found: C, 60·75; H, 3·0. $C_{13}H_7O_2N_2Cl$ requires C, 60·35; H, 2·7%), alone and with the pure material (m. p. 214—215°) isolated chromatographically from the rearrangement product of 2-nitrofluorenone oxime. A mixture of this impure 9-chloro-2- (m. p. 204—205°) with 9-chloro-7-nitrophenanthridine (m. p. 204—205°, see below) melted at 164—205°.

9-*Methyl*-7-*nitrophenanthridine*.—2-Acetamido-4′-nitrodiphenyl (5 g.; Scarborough and Waters, *J.*, 1927, 96), phosphorus oxychloride (12 c.c.), and stannic chloride (3 c.c.) were refluxed for 4 hours and the solution was concentrated under reduced pressure. The fawn-coloured solid was shaken with sodium hydroxide solution (2N; 300 c.c.) and extracted with chloroform. Concentration of the dried extract (K_2CO_3) afforded pale yellow needles (1·0 g.; m. p. 242—243°) (Found: C, 71·3; H, 4·2. Calc. for $C_{14}H_{10}O_2N_2$: C, 70·6; H, 4·2%) and a less pure second crop (0·2 g., m. p. 234—236°). Morgan and Walls (*loc. cit.*) gave m. p. 243—245°.

7-*Nitrophenanthridone*.—9-Methyl-7-nitrophenanthridine (1 g.), sodium dichromate (2·44 g.), and acetic acid (20 c.c.) were refluxed for 2 hours, and the product was precipitated by water. Crystallisation from acetic acid gave pale yellow needles (0·85 g.) of 7-*nitrophenanthridone*, m. p. 326—327° (Found: C, 65·3; H, 4·0%).

9-*Chloro*-7-*nitrophenanthridine*.—7-Nitrophenanthridone (0·3 g.), phosphorus pentachloride (0·2 g.), and phosphorus oxychloride (2 c.c.) were refluxed for 6 hours. The solution was poured on ice, neutralised with sodium acetate, and extracted with chloroform. The dried (Na_2CO_3) extract yielded 9-*chloro*-7-*nitrophenanthridine* (0·27 g.), which crystallised from benzene as colourless needles, m. p. 204—205° (Found: C, 60·7; H, 3·2%), alone or mixed with material obtained chromatographically from the rearrangement product of 2-nitrofluorenone oxime.

3-*Nitrofluorenone*.—2-Amino-4-nitrobenzophenone (1·5 g.; Schofield and Theobald, *loc. cit.*) in concentrated sulphuric acid (10 c.c.) was diazotised at 0° with powdered sodium nitrite (0·5 g.), and the solution was poured on a mixture of ice, excess of sodium acetate, and copper powder (0·5 g.). The temperature was slowly raised to 50° and kept there for ½ hour, and the collected product was then washed with water and extracted with acetone. The extract yielded crude 3-nitrofluorenone (1·3 g.), which gave small pale yellow needles, m. p. 232—233° (Found: C, 69·3; H, 3·1. Calc. for $C_{13}H_7O_3N$: C, 69·3; H, 3·1%), from acetic acid. Ray and Barrick (*loc. cit.*) gave m. p. 235—236°.

3-*Nitrofluorenone Oxime and its Rearrangement*.—3-Nitrofluorenone (0·1 g.) and hydroxylamine hydrochloride (0·06 g.) were heated under reflux for 2 hours in ethanol (20 c.c.). Concentration of the solution gave the oxime (0·08 g.), which formed very fine pale yellow needles, m. p. 216—217° (Found: C, 65·7; H, 3·6%), from dilute alcohol. Schmidt and Soll, and Eckert and Langecker (*locc. cit.*), gave m. p. 240°. Bardout (*locc. cit.*) records m. p. 217° [221° (corr.)], whilst Ray and Barrick (*loc. cit.*) claim m. p. 224—225°, and Scheer (Thesis, Univ. Cincinnati, 1942) m. p. 214°.

The oxime (0·08 g.), rearranged as described for the 2-isomer, gave crude 3-nitrophenanthridone (0·07 g.), which when crystallised from acetic acid gave small colourless needles, m. p. >340°. Walls (*loc. cit.*) obtained this compound as minute red needles, m. p. >350°. Oxidation of our product (0·05 g.) in the usual way gave phthalic acid (0·02 g.), m. p. 198—200°. The same 9-*chloro*-3-*nitrophenanthridine* was obtained by standard methods from material prepared in the present manner and also according to Walls. It formed almost colourless needles, m. p. 253—254° (Found: C, 60·4; H, 2·6%), from benzene–ligroin (b. p. 60—80°).

Diazotisation of 2-*Amino*-6-*nitrobenzophenone*.—The amine (0·5 g.; Schofield and Theobald, *loc. cit.*) in sulphuric acid (85%; 6 c.c.) was diazotised at room temperature with powdered sodium nitrite (0·2 g.), and the solution was then heated at 95° for 3 days. The precipitate (0·32 g.) formed on addition of water was dried and passed in benzene over alumina (23 × 1·4 cm.). The two yellow bands produced were both adsorbed very strongly. Elution with benzene–pyridine (1 : 1) gave a pale yellow solid (0·03 g.), m. p. 186—187°, alone or mixed with 1-nitrofluorenone (m. p. 188—189°; Chase and Hey, *loc. cit.*).

4-*Nitrofluorenone*.—(*a*) For experiments using the method of Schmidt and Bauer (*loc. cit.*) 2- (58%) and 4-nitrophenanthraquinone (26%) were obtained by nitrating phenanthraquinone according to Courtot (*loc. cit.*), who obtained yields of 61 and 20% respectively. The conversion of 4-nitrophenanthraquinone into 4-nitrofluorenone proceeded with good yields at each stage, but the m. p. of the ketone could not be raised above 167—168° and the compound was frequently discoloured green. Analyses were unsatisfactory. The by-product of the reaction described by Schmidt and Bauer was encountered, and the degree of concentration effected during the air-oxidation may be critical.

(*b*) 2-Amino-3-nitrobenzophenone (2·5 g.; Schofield and Theobald, *loc. cit.*) was diazotised and the solution was heated as described for 2-amino-6-nitrobenzophenone. Dilution with water (to 250 c.c.) gave a precipitate (2·1 g.) which was boiled with benzene (100 c.c.) and filtered from insoluble material (0·52 g.). Passage of the benzene solution over alumina (40 × 2 cm.) caused separation into a lower pale yellow and an upper dark yellow band. Elution with benzene provided first 4-nitrofluorenone (1·1 g.), m. p. 174—175°, which formed yellow needles (Found: C, 70·0; H, 3·7; N, 6·1. Calc. for $C_{13}H_7O_3N$: C, 69·3; H, 3·1; N, 6·2%).

Next came a solid (0·16 g.), m. p. 163—169°, then a product (0·05 g.), m. p. 195—197°, and finally a mixture (0·13 g.), m. p. 166—197°. The product, m. p. 195—197°, when crystallised from benzene–ligroin (b. p. 60—80°), formed small yellow needles, m. p. 218—219°, which, though not examined further, was presumably the hydroxy-nitrobenzophenone.

4-Nitrofluorenone (1·1 g.), hydroxylamine hydrochloride (0·6 g.), water (3 c.c.), and ethanol (40 c.c.) were refluxed for 5 hours. Concentration of the solution gave the oxime (1·6 g.), which formed pale yellow needles, m. p. 209—210° (Found : C, 65·2; H, 3·4%), from alcohol. Schmidt and Bauer (*loc. cit.*) described the compound as dark green needles, m. p. 255—256° (decomp.).

Nitration of Phenanthridone.—Under the conditions of Moore and Huntress (*loc. cit.*, p. 1324) phenanthridone (5 g.) provided 5·53 g. of mixed nitrophenanthridones. Soxhlet-extraction with alcohol left a residue of almost pure 3-nitrophenanthridone (3·8 g.; m. p. >330°), whilst the extract, once-crystallised (acetic acid), furnished 1-nitrophenanthridone (0·75 g.), m. p. 251—253°, alone or mixed with an authentic specimen (Stepan and Hamilton, *loc. cit.*). Each of the isomers provided phthalic acid when oxidised with permanganate. 9-Chloro-3-nitrophenanthridine, m. p. 253—254° (Found : C, 60·4; H, 2·6%), prepared from the high-melting nitration product was identical with specimens prepared from 3-nitrofluorenone oxime and 9-methyl-3-nitrophenanthridine as above. Similarly, 9-*chloro*-1-*nitrophenanthridine*, which crystallised from benzene–ligroin (b. p. 60—80°) in pale yellow leaflets, m. p. 178—179° (Found : C, 60·7; H, 2·9%), was obtained both from the minor nitration product, and also from Stepan and Hamilton's 1-nitrophenanthridone.

1-o-*Benzoylphenyl*-3 : 3-*dimethyltriazen.*—2-Aminobenzophenone (5 g.) in hydrochloric acid (5N; 80 c.c.) was diazotised at 0° with aqueous sodium nitrite (10%). The ice-cold filtered solution was added dropwise during ½ hour to a stirred mixture of sodium carbonate (75 g.), water (250 c.c.), and aqueous dimethylamine (25%; 5 c.c.) at 0°. After being stirred at this temperature for 1 hour the suspension was left overnight at room temperature, and the product (5·6 g.; m. p. 74—75°) crystallised from aqueous alcohol. The *triazen* formed small fawn-coloured prisms, m. p. 76—77° (Found : C, 71·1; H, 5·9; N, 16·4. $C_{15}H_{15}ON_3$ requires C, 71·1; H, 6·0; N, 16·6%).

A boiling solution of the triazen (10·8 g.) in dry benzene (200 c.c.) was treated with hydrogen chloride for ¾ hour. The benzene layer was decanted and the residual red gum was shaken with sodium hydroxide solution and extracted with benzene. The benzene solution was washed with aqueous sodium hydroxide, dried (Na_2SO_4), and passed over alumina (40 × 2 cm.), yielding 2-chlorobenzophenone (3·4 g.; b. p. 188—192°/13 mm.) and fluorenone (0·4 g.), m. p. 81—82° (yellow needles from alcohol), as well as impure fractions.

1-(o-p′-*Methoxybenzoylphenyl*)-3 : 3-*dimethyltriazen.*—By the above method 2-amino-4′-methoxybenzophenone (5 g.) gave the *triazen* (5·3 g.). Crystallisation from aqueous methanol provided cream-coloured needles, m. p. 73—74° (Found : C, 67·8; H, 6·1; N, 14·9. $C_{16}H_{17}O_2N_3$ requires C, 67·8; H, 6·05; N, 14·9%).

The triazen (13·5 g.) was decomposed as above. Removal of the benzene from the dried extract and distillation of the residue (7·5 g.) gave a yellow oil (6·4 g.), b. p. 220—230°/15 mm. A portion of this (3·2 g.) was chromatographed in benzene as before. Crystallisation from ligroin (b. p. 60—80°) of the first product obtained on elution gave white needles (1·3 g.) of 2-chloro-4′-methoxybenzophenone, m. p. 79—80° (Found : C, 67·8; H, 4·8. Calc. for $C_{14}H_{11}O_2Cl$: C, 68·2; H, 4·5%). Unger (*Annalen*, 1933, **504**, 285) gave m. p. 84·5°. Intermediate fractions formed yellow oils, but finally there was obtained 3-methoxyfluorenone (0·3 g.), which crystallised from benzene–ligroin as yellow needles, m. p. 98—99° (Found : C, 79·7; H, 4·9. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·8%). Ullmann and Bleier (*loc. cit.*) give m. p. 99°.

1-(o-2′-*Picolinoylphenyl*)-3 : 3-*dimethyltriazen.*—In the usual way 2-*o*-aminobenzoylpyridine (6 g.) gave the *triazen* (7·3 g.), which formed fawn-coloured needles, m. p. 116—117° (Found : C, 65·7; H, 6·0; N, 22·6. $C_{14}H_{14}ON_4$ requires C, 66·1; H, 5·55; N, 22·0%), from aqueous alcohol.

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