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STUDIES IN THE TRIAZINE SERIES INCLUDING A NEW SYNTHESIS OF 1:2:4-TRIAZINES

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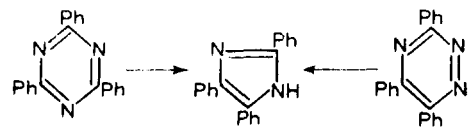
Abstract—The mono-aroylhydrazones of benzil are cyclised by ammonium acetate in hot acetic acid to tri-substituted-1:2:4-triazines. The yield is favourable and it is not necessary, or even advantageous, to isolate the presumed intermediates. The new synthesis has been applied to a sufficient range of examples to establish its status as a general method. In the case of phenanthraquinone the reaction took a more complex course and probably involved two molecules of the diketone.

A rational synthesis of kyaphenine (2:4:6-triphenyl-1:3:5-triazine) has been effected by reaction of 2-chloro-4:6-diphenyl-1:3:5-triazine with phenylmagnesium bromide and a similar method served to synthesise 5:6-diphenyl-3-*p*-tolyl-1:2:4-triazine also made from benzil and *p*-toluylhydrazide. Both kyaphenine and its isomeride in the *asymm*-triazine series afford lophine on reduction, and the mechanism of the long-known former reaction (Radziszewski) is discussed.

THE reduction of kyaphenine (I), by means of zinc and acetic acid, with formation of lophine[1] (II) appeared noteworthy from the point of view of reaction mechanism, and consideration of the problem prompted the present investigation. *Triphenyl-1:2:4-triazine* (III) was not known and, as the facile transformation of this substance to lophine could be predicted, independent step-wise syntheses of the isomeric triphenyl-triazines, I and III, were sought.



I II III

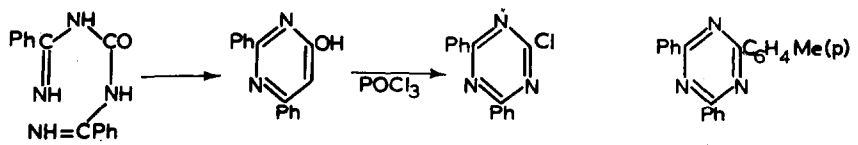
None of the known methods of synthesis of kyaphenine and analogous substances served to establish the structural formulae, e.g. both I and III could theoretically be obtained by trimerisation of benzonitrile. It transpired that the expression I for kyaphenine could be confirmed by unequivocal synthesis. The isomeride (III), obtained as described below, has very different properties, but, as anticipated, also gives a good yield of lophine on reduction with zinc and acetic acid. Most of the known kyaphenine syntheses can be assumed to proceed via benzonitrile, possibly in an activated form; examples are the reaction of benzene with cyanogen bromide in the presence of aluminium chloride[2] and the decomposition of benzimino methyl ether on keeping.[3]

The conversion of cyanuric chloride (trichloro-*symm*-triazine) to kyaphenine was

[1] B. Radziszewski *Ber.* **15**, 1493 (1882).
[2] R. Scholl and W. Nörr *Ber.* **33**, 1052 (1900).
[3] T. B. Johnson and L. W. Bass *J. Amer. Chem. Soc.* **54**, 1341 (1922).

claimed by Klason,[4] who treated the substance with bromobenzene and sodium in an ethereal medium. The main product was diphenylchloro-*symm*-triazine (IV). Kraft[5] repeated the experiment with some modifications and stated that kyaphenine, m.p. 233°, could be isolated. However, Cook and Jones[6] have further examined the reaction but did not obtain kyaphenine.

The present authors find that 6-chloro-2:4-diphenyl-1:3:5-triazine (IV), m.p. 141–142°, is converted into kyaphenine in good yield by reaction with phenylmagnesium bromide. Similarly diphenyl-*p*-tolyl-*symm*-triazine (V) was obtained by the use of *p*-tolylmagnesium bromide.

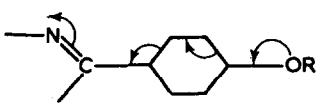


IV V

The method of preparation[7] of (IV) through the corresponding hydroxytriazine, itself made from benzamidine and phosgene,[8] appears to guarantee its *symm*-triazine structure.

A very convenient method for the trimerisation of benzonitrile and many of its derivatives is to treat them with chlorsulphonic acid in chloroform solution. This was first used[9] by Brown and Robinson in the case of piperononitrile, but, on account of its strong halochromic properties, the product was thought to be a dimeride, namely a dimethylenedioxyanthraquinonedi-imide. Unfortunately, this was fully confirmed by Keffler[10] by the determination of the M. W. (cryoscopic in thymol) of three substances. These all gave close to two-thirds of the correct figures, and a similar error was made later in the series of the condensation products of formaldehyde and veratrole. The only explanation of this appears to be a miscalculation of the constant for thymol. The trimeric character of the substances was established by Wilson.[11] During the present investigation it was noted that a moderately satisfactory result was obtained by the micro-Rast method (cryoscopic in camphor) of determination of the M. W. in the case of these sparingly soluble kyaphenines.

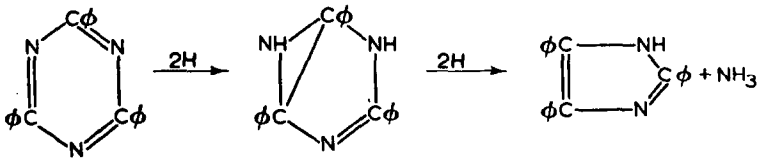
The halochromy of the *p*-alkyloxyphenyltriazines is characteristic and suggests an electron displacement of the annexed type.



There is, however, some contribution from each of the aryl groups, and how these are linked through the central nucleus can only be conjectured. The mechanism of the

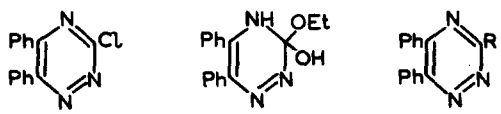
[4] P. Klason *J. Prakt. Chem.* (2), **36**, 82 (1887).
[5] F. Krafft *Ber.* **22**, 1759 (1889).
[6] A. H. Cook and D. G. Jones *J. Chem. Soc.* 279 (1941).
[7] J. Ephraim *Ber.* **26**, 2226 (1893); Cf. *Org. Synth. Coll.* **1**, 6 (1946).
[8] A. Pinner *Ber.* **23**, 163, 2920, (1890).
[9] J. G. McG. Brown and R. Robinson *J. Chem. Soc.* **111**, 952 (1917).
[10] L. P. G. Keffler *J. Chem. Soc.* **119**, 1476 (1921).
[11] C. V. Wilson *J. Amer. Chem. Soc.* **70**, 1901 (1948).

reduction of kyaphenine to lophine appears to the authors to be analogous to the formation of a pinacol from a ketone (cf. ref. 14):



It is very interesting that the process can be reversed[12] by reaction of lophine with iodine in gently boiling liquid ammonia with production of kyaphenine.

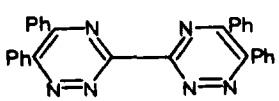
The 1:2:4-*triazine series.* It is curious how little attention has been paid to this group insofar as the analogues of alkyl or aryl *symm*-triazines are concerned. The hydroxy-, amino-, and thiol *asymm*-triazines have, however, been known for many years. Condensation of benzil and semicarbazide makes 3-hydroxy-5:6-diphenyl-1:2:4-triazine readily accessible.[13] We have examined the corresponding chloride (VI) which is obtained by the action of phosphoryl chloride on the hydroxy-compound. Unusually, it has a higher m.p. than its *symm*-analogue (IV). The halochromy of VI is more pronounced than that of IV; red and yellow solutions, respectively, in sulphuric acid. Furthermore, the halogen of VI is much more labile than that of IV. In boiling methanol or ethanol, hydrogen chloride is liberated and the products are found to be hydrates of the expected alkyloxydiphenyl-*asymm*-triazines. The product from ethanol has m.p. 220°, with decomposition to ethanol and 3-hydroxy-5:6-diphenyl-1:2:4-triazine. This substance can hardly be a hydrate or ethanolate, and may have the structure VII.



VI VII VIII

With hydrazine, VI affords a hydrazino-derivative (VIII, R = NH·NH_2) which is oxidised by cupric salts to 5:6-diphenyl-1:2:4-triazine (VIII, R = H). The halochromy is throughout stronger in the *asymm* than in the *symm* series. This diphenyl-*asymm*-triazine gives a crimson solution in sulphuric acid. With phenylhydrazine in pyridine solution, VI affords the phenylhydrazino-derivative (VIII, R = NH·NHPh), which was oxidised by ferric chloride to a dark-coloured material (presumably VIII, R = N=NPh).

The pyrolysis of this substance did not afford the expected triphenyl-*asymm*-triazine, but a compound which is probably di-(5:6-diphenyltriazinyl-3) (IX).



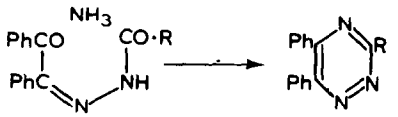
IX

The reaction between chloro-diphenyl-*asymm*-triazine (VI) and phenylmagnesium

[12] H. H. Strain *J. Amer. Chem. Soc.* **49**, 1564 (1927).
[13] H. Biltz *Annalen* **339**, 279 (1905).

bromide also gave an unanticipated result, and should be repeated. Using *p*-tolylmagnesium bromide, however, the diphenyl-*p*-tolyl-*asymm*-triazine (VIII, R = ·$C_6H_4Me(p)$) was isolated. This was identical with a specimen prepared by the method now to be described.

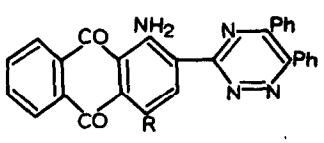
A new synthesis of triaryl-asymm-*triazines.* A preliminary account of this method has been given.[14] Benzil aroylhydrazones are cyclised by ammonium acetate in hot acetic acid solution.



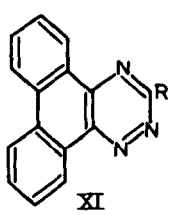
VIII

Since the mono-aroylhydrazones are not in general obtained in high yield from the condensation of benzil and an acid hydrazide, this intermediate stage was not usually isolated. It may be presumed that the *bis*-aroylhydrazone formed is not affected by the reagent in any important side-reaction, but may be a source of the mono-aroylhydrazone as the result of a hydrolytic equilibrium. Hence the generators, that is, α-diketone, acid hydrazide, and ammonium acetate, are mixed in acetic acid and the solution heated. In some cases the product separated from the hot liquid. There is every reason to suppose that the reaction is general for α-diketones, but it did not succeed with phenanthraquinone, at any rate under the usual conditions.

The aroylhydrazones used were those appropriate to introduce the groups, *phenyl* (III), p-*tolyl*, m-*nitrophenyl*, p-*nitrophenyl*, p-*chlorophenyl*, p-*hydroxyphenyl*, p-*aminophenyl*, m-*methoxyphenyl*, 2:4-*dimethoxyphenyl*, 3:4-*dimethoxyphenyl*, 3:4-*methylenedioxyphenyl*, 3:4:5-*trimethoxyphenyl*, α-*furyl*, 1-*amino*-2-*anthraquinonyl*, (X, R = H), and 1:4-*diamino*-2-*anthraquinonyl* (X, R = NH_2) as the group R in the structure VIII.



X



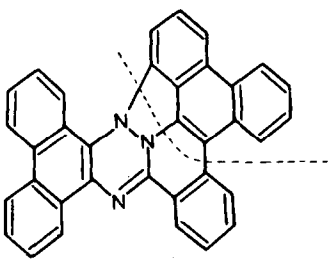
XI

Phenanthraquinone benzoylhydrazone is converted into 1-phenanthrol by boiling aqueous potassium hydroxide. The yield (50%) and convenience of this method constitute considerable improvements on known procedures. The reaction is evidently of Wolff-Kishner-Staudinger type, but when the monosemicarbazone (improved method) was substituted for the benzoylhydrazone cyclisation to 3-hydroxy-5:6-phenthratriazine, (XI, R = OH) occurred. This is a much more convenient process than those previously reported. In fact, we were unable to obtain the substance by De's method;[15] the semicarbazone was recovered unchanged. Our product was identical with a specimen made by the earlier method of Schmidt.[16] Some results incidental to the research are recorded.

[14] P. V. Laakso and R. Robinson *Festschrift Karrer* p. 38 Zürich (1948).
[15] S. C. De *J. Indian Chem. Soc.* 7, 361 (1930).
[16] J. Schmidt, O. Schairer, and E. Glatz *Ber.* 44, 276 (1911).

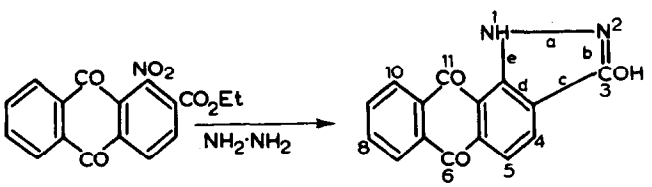
The crystalline, yellow substance obtained from phenanthraquinone benzoylhydrazone and ammonium acetate in boiling acetic acid is apparently $C_{23\text{ or }24}H_{12\text{ or }14}N_2$ on the N_2 basis. As $C_{14}H_8O_2 + C_7H_6O_2 + C_2H_4O_2 + 2NH_3 - 6H_2O = C_{23}H_{12}N_2$, the latter formula (Theory: C, 87·3; H, 3·8; H, 8·9%) may be preferred on analytical grounds. It is, however, hardly possible to construct a plausible formula with so few hydrogen atoms and $C_{23}H_{14}N_2$ (C, 86·8; H, 4·4; N, 8·8%) could be a phenylmethylphenanthrazine with an additional ring, or an isomeric phenanthriminazole derivative.

As this analysis leads to dubious conclusions, N_3 formulae may be considered. The best is $C_{35}H_{19}N_3$ (C, 87·3; H, 4·0; N, 8·7%), and this is $2C_{14}H_8O_2 + C_7H_8ON_2 + NH_3 + 2H - 5H_2O$. This, in our judgement, is the probably correct interpretation. A feasible structure is annexed:



Inspection of this suggestion shows that $C_{35}H_{17}N_3$ can be excluded on structural grounds; $C_{35}H_{21}N_3$ allows one of the rings to be broken (+ 2H) but the analytical results become unsatisfactory.

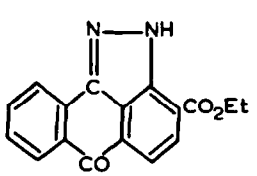
Ethyl 1-nitroanthraquinone-2-carboxylate was converted by hydrazine in hot pyridine into 3-hydroxy-6:11-diketo-1-anthra-(1:2-*d*)-pyrazole (XII) instead of the acid hydrazide.



XII

The enolic form is favoured on account of the ready solubility of the substance in cold aqueous sodium hydroxide.

A second product of the reaction was ethylpyrazole-anthrone-2-carboxylate (XIII), identified by hydrolysis to the corresponding acid which was already known.[17]



XIII

[17] D.R.P. 575,680; *Frdl.* 17, 1273 (1930).

These two substances (XII and XIII) were also obtained by the action of hydrazine on 1-nitro-anthraquinone-2-carboxylic acid chloride obtained by refluxing the acid with thionyl chloride. This is an improvement on methods previously described.[18]

In order to avoid the complication introduced by the lability of the 1-nitro group in the anthraquinone series, the requisite hydrazides were prepared from corresponding 1-amino-2-carboxylic acids and eventually some 1:2:4-triazines of this group were obtained.

EXPERIMENTAL

Kyaphenine (I). (A) Benzenylbenzamidine[19] (1·0 g, m.p. 77–78°) was heated during 12 hours in a closed vessel with benzaldehyde (0·6 g) on the steam-bath and then at 150° under reduced pressure. The kyaphenine produced (0·2 g) was crystallised from toluene, m.p. 232–33°, alone or mixed with an authentic specimen. (B) 2-Chloro-4:6-diphenyl-1:3:5-triazine was prepared according to the known procedures,[7,8] m.p. 141-42°.

A solution of phenylmagnesium bromide (from 1·1 c.c. of bromobenzene and 0·25 g of magnesium) in ether (10 c.c.) was added to one of the chlorotriphenyl-*symm*-triazine (1·0 g) in benzene (10 c.c.). After refluxing on a steam-bath for 12 hours, the product (0·7 g) was isolated and crystallised from toluene; m.p. 232–233°, alone or mixed with an authentic specimen.

A similar reaction using 2·0 g of *p*-bromotoluene instead of the bromobenzene afforded 2:4-*diphenyl*-6-*p-tolyl*-1:3:5-*triazine* (V) which crystallised from toluene in colourless needles, m.p. 199–200° (Found: C, 81·4; H, 5·3; N, 12·3. $C_{22}H_{17}N_3$ requires C, 81·9; H, 5·3; N, 13·0%). It dissolved in sulphuric acid to a yellow solution. It is doubtful whether the substance was previously obtained in a pure state by the co-polymerisation of benzonitrile and *p*-tolunitrile,[20] since the m.p. 176–178° was assigned to the product.

Tri-methylenedioxyphenyl-symm-*triazine.*[9,10,11] The M.W. by Rast's method in camphor was found to be 461, calc. 441. The halochromy of substituted kyaphenines is intensified by alkyloxy groups. In sulphuric acid the colorations are: triphenyl, yellow; tri-*p*-methoxy phenyl[21] and tri-*p*-ethoxyphenyl,[22] deeper yellow to orange-yellow; tri-methylenedioxyphenyl and tri-3:4-dimethoxyphenyl,[9,10,11] red. Curiously, diphenyl-*m*-nitrophenyl[6] gives an orange coloration in sulphuric acid.

3-*Chloro*-5:6-*diphenyl*-1:2:4-*triazine* (VI). A mixture of 3-hydroxy-5:6-diphenyl-1:2:4-triazine (140 g, m.p. 224–226°) and phosphoryl chloride (280 c.c.) was heated in an oil bath (150°) until evolution of hydrogen chloride ceased (*c.* 50 min). The cooled mass was added with stirring to about 3 kg of crushed ice and the yellow solid collected and washed with water. It was thrice triturated with excess of 2% aqueous sodium hydroxide at 50°, collected, and washed (148 g, m.p. 147–149°). The pure substance crystallised from benzene had m.p. 156–157° and gave a crimson solution in sulphuric acid (Found: C, 67·4; H, 3·9; N, 15·3; Cl, 12·9. $C_{15}H_{10}N_3Cl$ requires C, 67·3; H, 3·8, N, 15·6; Cl, 13·2%).

[18] P. P. T. Sah and T. S. Ma *Sci. Rep. Nat.* Tsing Hua Univ. **2**, 143 (1933).
[19] F. L. Pyman *J. Chem. Soc.* **123**, 3372 (1923).
[20] M. A. Kung and K. Koberle D. R. P. 549, 969 (1929).
[21] F. E. Francis and O. C. M. Davis *J. Chem. Soc.* **85**, 259 (1904).
[22] O. Diels and M. Lieberman *Ber.* **36**, 3193 (1903).

The reaction of this substance (0·5 g) with methanol, ethanol, and propanol (100 c.c.) at the boiling-point was followed by titration. In the cases of the two simpler alcohols, the reaction was completed in 4·5 hours. The formation of the ethoxy derivative was only a little slower than that of the methoxy compound. The reaction with propanol proceeded at about two-thirds of the rate, and 64% had reacted after 4·5 hours. The *methoxy diphenyl*-1:2:4-*triazine hydrate* had m.p. 221–222° (Found: C, 68·3; H, 5·1; N, 15·1. $C_{16}H_{15}O_2N_3$ requires C, 68·4; H, 5·4; N, 14·9%), whilst the *ethoxy-derivative* (VII) had m.p. 220–221° (Found: C, 69·3; H, 5·9; N, 14·1. $C_{17}H_{17}O_2H_3$ requires C, 69·3; H, 5·8; N, 14·2%). These substances crystallised on concentration of the respective solutions. They are slowly dissolved on boiling with dilute aqueous sodium hydroxide, and on acidification of the solution the 3-hydroxy-5:6-diphenyl-1:2-triazine was recovered.

3-*Hydrazino*-5:6-*diphenyl*-1:2:4-*triazine* (VIII, R = NH·NH_2). A mixture of chlorodiphenyl-1:2:4-triazine (5·4 g), hydrazine hydrate (3 c.c. of 90%) and pyridine (10 c.c.) was boiled for an hour. The precipitate after the addition of water was collected and crystallised from ethanol; yellow needles m.p. 171–173° (Found: C, 68·5; H, 5·0; N, 27·0. $C_{15}H_{13}N_5$ requires C, 68·0; H, 5·0; N, 26·4%). The solution in sulphuric acid had a crimson colour.

5:6-*Diphenyl*-1:2:4-*triazine* (VIII, R = H). The above hydrazine (0·5 g) in acetic acid (20 c.c. of 10%) was oxidised by the addition of cupric sulphate (1·0 g) dissolved along with sodium acetate (1·0 g) in water (10 c.c.). After 12 hours in the cold, the product (0·15 g) was isolated by means of ether and crystallised from aqueous ethanol; yellow plates, m.p. 112–115° (Found: C, 77·0; H, 4·6; N, 17·7. $C_{15}H_{11}N_3$ requires C, 77·3; H, 4·8; N, 18·0%). The solution in sulphuric acid had a crimson colour.

3-*Phenylhydrazino*-5:6-*diphenyl*-1:2:4-*triazine* (VIII, R = NH·NHPh). A mixture of chloro-diphenyl-1:2:4-triazine (20 g), phenylhydrazine (20 g), and pyridine (55 c.c.) was refluxed for an hour. The product was crystallised from toluene, m.p. 197–198°. (Found: C, 74·7; H, 5·2; N, 20·4. $C_{21}H_{17}N_5$ requires C, 74·4; H, 5·1; N, 20·6%). The yellow substance dissolves in sulphuric acid to a crimson solution. The corresponding azo-derivative was presumably formed in the process described below.

5:6:5′:6′-*Tetraphenyl*-3:3′-*di*-1:2:4-*triazinyl* (IX). The above phenylhydrazino-diphenyl-1:2:4-triazine (2·0 g) in acetic acid (10 c.c.) was added to a solution of ferric chloride (2·0 g) in acetic acid (10 c.c.). The resulting black precipitate was collected, washed, and dried; m.p. >280° (decomp.). This material (1·5 g) mixed with copper powder (1·5 g) was strongly heated under a good vacuum. The sublimate and distillate (0·8 g) was triturated with acetic acid and the yellow product crystallised from this solvent (85%), m.p. 219–222° (Found: C, 77·4; H, 3·9; N, 18·0. $C_{30}H_{20}N_6$ requires C, 77·7; H, 4·3; N, 18·1%). The usual crimson coloration in sulphuric acid was observed.

3-*Amino*-5:6-*diphenyl*-1:2:4-*triazine* (VIII, R = NH_2). Chlorodiphenyl-1:2:4-triazine (5·0 g) was heated with 10% ammonia (20 c.c.) for 6 hours at 140° in a sealed tube. The product was purified by solution in dilute hydrochloric acid and recovery on basification with ammonia; yellow needles, m.p. 175°, in agreement with Thiele and Bihan[23] (Found: C, 73·0; H, 4·7; N, 22·0. Calc. for $C_{15}H_{12}N_4$: C, 72·7; H, 4·9; N, 22·5%). The solution in sulphuric acid has a crimson colour.

[23] J. Thiele and R. Bihan *Annalen* **302**, 309 (1898).

Treatment with hydrochloric acid and sodium nitrite gave an immediate precipitate of 3-hydroxy-5:6-diphenyl-1:2:4-triazine, m.p. 220–1°, after crystallisation, and the same on admixture with an authentic specimen.

Reaction of 3-chloro-5:6-diphenyl-1:2:4-triazine with Grignard reagents. (a) An ethereal solution (200 c.c.) of phenylmagnesium bromide (10 g of magnesium and 41 c.c. of bromo-benzene) was gradually added to one of 3-chloro-5:6-diphenyl-1:2:4-triazine (20 g) in benzene (200 c.c.). The mixture was distilled until the boiling point rose to 70°; it was then refluxed for 12 hours. The cooled mixture was added to sulphuric acid (40 g), crushed ice (300 g), and water (200 c.c.), when the benzene layer became deep blue and later red. The benzene solution was separated, washed, dried, and evaporated. The residue (33 g) was distilled at 150°/0·2 mm and afforded 10 g of diphenyl, m.p. 69–71°. It was then dissolved in ether, and on slow evaporation of the solution afforded 1·6 g of kyaphenine (!); m.p. 231–232° after crystallisation from toluene, alone or mixed with a specimen made from benzonitrile.

Further distillation of the mother liquor gave only more diphenyl (5 g) and benzil (3·0 g).

(b) The reaction was carried out as under (a), except that the Grignard solution was made from *p*-bromotoluene (34 g) and magnesium (4·8 g). The cooled reaction product was heated with concentrated hydrochloric acid (30 g), water (30 g), and crushed ice (50 g). A small undissolved portion was collected and crystallised from acetic acid; long red needles with a metallic lustre, m.p. above 280° (Found: C, 62·1; H, 4·6; N, 13·7; Cl, 7·1 (or Br 11·9); residue after combustion, 0·89%). The nature of this by-product could not be ascertained. The benzene solution was washed, dried, and distilled. Ditolyl (11 g, m.p. 118–120°) passed over at 200°/0·2 mm, and the residue (17 g) was dissolved in ether.

Slow evaporation gave crystals (1·2 g), m.p. 130–135°. After recrystallisation from 90% acetic acid, it formed yellow prisms, m.p. 136–137° (Found: C, 81·7; H, 5·5, N, 12·4. $C_{22}H_{17}N_3$ requires C, 81·9; H, 5·3; N, 13·0%). The melting-point was not depressed on admixture with the specimen (see below) made from benzil and *p*-toluhydrazide.

3:5:6-*Triphenyl*-1:2:4:*triazine* (III). This was the first representative of the series to be made by the new method, and a better overall yield was obtained by following the direct process as used below for diphenyl-*p*-tolyl-1:2:4-triazine. However, in the earlier stages of the work (cf. also the *m*-nitrophenyl series below) an attempt was made to isolate the intermediate benzoylhydrazone of benzil.

Benzhydrazide (29·5 g) and benzil (50 g) were dissolved by gentle heating in ethanol (200 c.c.), and acetic acid (50 c.c.) added. After keeping for 7 days, the solution was filtered from a sparingly soluble precipitate (*bis*-benzoylhydrazone?), diluted with water, and the resulting solid collected and dried (36·6 g of m.p. 75–109°). After one crystallisation from methanol (sparingly soluble residue), m.p. 123–138°; two more crystallisations, pale yellow needles m.p. 126–128°, unchanged after three further crystallisations. The sparingly soluble residue crystallised from much methanol in colourless, prismatic needles, m.p. 142–143°.

The analyses of these substances were not quite satisfactory and will be re-examined. According to Struve, benzil *bis*-benzoylhydrazone[24] had m.p. 206°. The triphenyl-1:2:4-triazine was obtained by heating the crude mixture with ammonium acetate in

[24] G. Struve *J. Pr. Chem.* (2), **50**, 308 (1894).

acetic acid solution, as in later examples. The bright yellow base crystallised from benzene-light petroleum (b.p. 40–60°) as dense clusters of needles forming warty aggregates, m.p. 145–146° (Found: C, 81·5; H, 4·8; N, 13·4. $C_{21}H_{15}N_3$ requires C, 81·6; H, 4·8; N, 13·6%). The substance is only weakly basic and dissolves in sulphuric acid to a red solution. It was reduced in boiling acetic acid by means of an excess of zinc dust (5 min) to 2:4:5-triphenyliminazole (lophine). The product was crystallised twice from ethanol in needles, m.p. 273–274°, alone or mixed with an authentic specimen. The yield was quantitative (Found: N, 9·1. Calc. for $C_{21}H_{16}N_2$: N, 9·5%).

5:6-*Diphenyl*-1-3-p-*tolyl*-1:2:4-*triazine* (VIII, R = *p*-C_6H_4·Me). A mixture of benzil (0·5 g) *p*-tolhydrazide (0·8 g), ammonium acetate (3·0 g), acetic acid (5·0 c.c.), and water (0·5 c.c.) was refluxed for 6 hours. The oily product obtained on the addition of water was washed, dissolved in a little acetic acid, when crystals separated on keeping (1·1 g). After recrystallisation from 90% acetic acid, it formed yellow prisms, m.p. 136–137° (Found: C, 81·7; H, 5·5; N, 12·4. $C_{22}H_{17}N_3$ requires C, 81·9; H, 5·3; N, 13·0%). The solution in sulphuric acid had a deep red colour. Another method of preparation of this substance is reported above.

Benzil m-*nitrobenzoylhydrazone*. A mixture of benzil (21 g) and *m*-nitrobenzhydrazide (18 g) was dissolved in acetic acid (100 c.c.) by heating and the solution at once allowed to cool. The crude product (*c.* 30 g) had m.p. 105–115°.

On crystallisation of 4·0 g from alcohol, there was obtained a sparingly soluble residue and 1·8 g, m.p. 142–144°. On recrystallisation, 1·4 g, m.p. 144–145°, and again 1·2 g, m.p. 145–146°. Finally, a crystallisation from toluene raised the m.p. to 145–146° (Found: C, 67·4; H, 4·2; N, 11·2. $C_{21}H_{15}O_4N_3$ requires C, 67·7; H, 4·1; N, 11·2%). The less soluble product (100 c.c. boiling xylene dissolved 0·1 g) had m.p. 223–228°, raised by successive crystallisations from xylene and acetic acid to m.p. 231–233° (Found: C, 59·7; H, 4·3; N, 13·1%). These are far from the anticipated values for the *bis*-hydrazone (approx. correct for $+3H_2O$) and are in agreement with $C_{21}H_{18}O_6N_4$ (C, 59·8; H, 4·3; N, 13·2%) which could be tri-*m*-nitrobenzylamine, but the matter requires further investigation.

3-m-*Nitrophenyl*-5:6-*diphenyl*-1:2:4-*triazine* (VIII, R = *m*-C_6H_4·NO_2). A mixture of the above-described crude benzil *m* nitrobenzoylhydrazone (14·6 g) with ammonium acetate (20 g) and acetic acid (50 c.c.) was boiled for 10 min. The product crystallised from the hot liquid and after the addition of a little water and cooling was collected (12·0 g). It recrystallised from acetic acid-methanol in pale yellow needles, m.p. 197° (Found: C, 70·9; H, 4·0; N, 15·9. $C_{21}H_{14}O_2N_4$ requires C, 71·2; H, 4·0; N, 15·9%). The substance gives an orange-coloured solution in sulphuric acid.

3-(4′-*Chlorophenyl*)-5:6-*diphenyl*-1:2:4-*triazine*. Ammonium acetate (5 g) was added to a hot solution of benzil (0·6 g) and *p*-chlorobenzhydrazide (0·5 g) in acetic acid (10 c.c.), and the mixture refluxed for half an hour. On cooling, an oily mass separated which, after removal of the supernatant, was triturated with light petroleum (b.p. 80–100°). The solid so obtained was collected, and crystallised from alcohol, forming yellow, prismatic needles, m.p. 134–135° (Found: C, 73·7; H, 4·2; N, 12·3; Cl, 9·7. $C_{21}H_{14}N_3Cl$ requires C, 73·4; H, 4·1; N, 12·2; Cl, 10·3%).

The solution in concentrated sulphuric acid had a cherry-red colour.

3-(4′-*Hydroxyphenyl*)-5:6-*diphenyl*-1:2:4-*triazine*. A mixture of benzil (4 g)

p-hydroxybenzhydrazide (3 g),[25] acetic acid (50 c.c.), and ammonium acetate (40 g) was refluxed for half an hour, during which time the almost pure product began to separate. The solid was collected from the cooled mixture and dried at 100° (4·5 g); m.p. 250–253°. Crystallisation from ethyl acetate afforded light yellow, fluffy needles, m.p. 254–255·5° (Found: C, 77·8; H, 4·8; N, 12·3. $C_{21}H_{15}ON_3$ requires C, 77·5; H, 4·6; N, 12·9%).

The solution in concentrated sulphuric acid had a blood-red colour.

Acetyl derivative. A mixture of the triazine (0·5 g), acetic acid (25 c.c.), and acetic anhydride (5 c.c.) was refluxed for 4 hours. *The product* was collected and crystallised from acetic acid as yellow, irregular plates, m.p. 175–176° (Found: N, 11·6. $C_{23}H_{17}O_2N_3$ requires N, 11·4%).

Reduction of 3-(4′-*hydroxyphenyl*)-5:6-*diphenyl*-1:2:4-*triazine to* 2-p-*hydroxyphenyl*-4:5-*diphenyliminazole.* Zinc dust (2 g) was gradually added to a stirred suspension of the above triazine (0·5 g) in hot acetic acid (10 c.c.), when a clear solution was obtained. The mixture was heated on the steam-bath for about an hour. The solution was decanted from the excess of zinc, diluted with water, and made alkaline by addition of aqueous ammonia. The solid was collected, washed, and crystallised from aqueous alcohol, from which the product separated as pale yellow clusters of needles, m.p. 252–253°, alone or when mixed with an authentic specimen of 4:5-diphenyl-2-*p*-hydroxyphenylglyoxaline prepared by the method of Japp and Robinson,[26] as modified by Cook and Jones.[6]

3-(4′-*Aminophenyl*)-5:6-*diphenyl*-1:2:4-*triazine.* Ammonium acetate (20 g) was added to a hot solution of benzil (2 g) and *p*-aminobenzhydrazide (1·44 g)[27] in acetic acid (20 c.c.), and the mixture boiled under reflux for 15 min. *The product* was isolated in the usual manner. On crystallisation from acetic acid-alcohol, yellow, prismatic needles were obtained; m.p. 218–219° (yield, 2 g) (Found: C, 77·7; H, 5·4; N, 16·8. $C_{21}H_{16}N_4$ requires C, 77·8; H, 4·9; N, 17·3%).

The solution in concentrated sulphuric acid had a cherry-red colour.

Acetyl derivative. The triazine (0·8 g) was boiled with acetic acid (10 c.c.) and acetic anhydride (3 c.c.) for about an hour. After cooling, the solid was collected and crystallised from acetic acid, being so obtained in light yellow, fluffy needles, m.p. 264–265° (Found: C, 75·4; H, 4·9; N, 15·0. $C_{23}H_{18}ON_4$ requires C, 75·4; H, 4·9; N, 15·3%).

3-(4′-*Nitrophenyl*)-5:6-*diphenyl*-1:2:4-*triazine.* When a mixture of benzil (0·5 g) *p*-nitrobenzhydrazide (0·43 g), acetic acid (10 c.c.), and ammonium acetate (5 g) was refluxed for 20 min, the product separated as a crystalline precipitate. This was collected and recrystallised from acetic acid and so obtained in golden yellow needles, m.p. 200–201° (yield, 0·6 g) (Found: C, 71·4; H, 3·8; N, 15·6. $C_{21}H_{14}O_2N_4$ requires C, 71·2; H, 4·0; N, 15·8%).

In concentrated sulphuric acid the usual cherry-red coloration developed.

3-(3′-*Methoxyphenyl*)-5:6-*diphenyl*-1:2:4-*triazine.* Ammonium acetate (5 g) was added to a hot solution of benzil (0·5 g) and *m*-methoxybenzhydrazide (0·4 g) in acetic acid (10 c.c.), and the mixture refluxed for 20 min. After cooling, water was added and the pasty mass which separated was triturated with alcohol-light petroleum

[25] J. T. Hewitt and T. F. Winmill *J. Chem. Soc.* **91**, 446 (1907); G. Struve and R. Radenhausen *J. Pr. Chem.* (2) **52**, 236 (1895).
[26] F. R. Japp and V. Robinson *Ber.* **15**, 1268 (1882).
[27] D. Vorländer and F. Meyer *Annalen* **320**, 136 (1901); T. Curtius *J. Pr. Chem.* (2) **95**, 327 (1917).

(b.p. 60–80°). The solid which then separated was collected, and crystallised from alcohol-light petroleum (b.p. 60–80°), being so obtained in yellow needles, m.p. 129–130° (yield, 0·5 g) (Found: C, 78·2; H, 5·2; N, 11·9. $C_{22}H_{17}ON_3$ required C, 77·9; H, 5·0; N, 12·4%).

A blood-red coloration was obtained in concentrated sulphuric acid solution.

3-(3′:4′-*Dimethoxyphenyl*)-5:6-*diphenyl*-1:2:4-*triazine*. A solution of benzil (0·5 g), veratr-hydrazide (0·47 g), and ammonium acetate (5 g) in acetic acid (10 c.c.) was boiled for about 15 min under reflux. The solid that separated was collected and crystallised from acetic acid-alcohol, being obtained in yellow needles, m.p. 177–178° (yield, 0·66 g) (Found: C, 74·7; H, 5·3; N, 11·5. $C_{23}H_{19}O_2N_3$ requires C, 74·8; H, 5·2; N, 11·4%).

The concentrated sulphuric acid solution had a dark brown colour.

3-(2′:4′-*Dimethoxyphenyl*)-5:6-*diphenyl*-1:2:4-*triazine*. A mixture of benzil (0·5 g), 2:4-dimethoxybenzhydrazide (0·47 g), ammonium acetate (5 g), and acetic acid (15 c.c.) was refluxed for 20 min, when a solid separated and after cooling was collected. The base crystallised from acetic acid as yellow needles, m.p. 167–168° (yield, 0·65 g) (Found: C, 74·9; H, 4·9; N, 11·6. $C_{23}H_{19}O_2N_4$ requires C, 74·8; H, 5·2; N, 11·4%).

The solution in concentrated sulphuric acid had a dark brown colour.

3-(3′:4′:5′-*Trimethoxyphenyl*)-5:6-*diphenyl*-1:2:4-*triazine*. Benzil (0·5 g) and O-trimethylgallhydrazide (0·55 g) were dissolved in acetic acid (10 c.c.), ammonium acetate (5 g) added, and the solution was refluxed for 15 min. The solid which separated on cooling was collected and crystallised from acetic acid-alcohol, giving yellow needles, m.p. 158–159° (yield, 0·6 g) (Found: C, 72·3; H, 5·1; N, 10·0. $C_{24}H_{21}O_3N_3$ requires C, 72·2; H, 5·3; N, 10·5%).

A blood-red coloration was developed in concentrated sulphuric acid.

5:6-*Diphenyl*-3-(3′:4′-*methylenedioxyphenyl*)-1:2:4-*triazine*. Ammonium acetate (10 g) was added to a hot solution of benzil (1 g) and piperonhydrazide (0·9 g) in acetic acid (20 c.c.). The mixture was boiled under reflux for about 20 min during which time a solid separated. After crystallisation from acetic acid-alcohol it formed yellow needles, m.p. 159–160° (yield, 1·3 g) (Found: C, 74·9; H, 3·9; N, 12·1. $C_{22}H_{15}O_2N_3$ requires C, 74·8; H, 4·3; N, 11·9%).

The substance gave a dark brown solution in concentrated sulphuric acid.

3-α-*Furyl*-5:6-*diphenyl*-1:2:4-*triazine*. A solution of benzil (0·5 g), 2-furhydrazide (0·3 g), and ammonium acetate (5 g) in hot acetic acid (15 c.c.) was refluxed for 20 min, when a solid separated. The substance crystallised from acetic acid-alcohol in yellow needles, m.p. 181–183° (yield, 0·4 g) (Found: C, 76·3; H, 4·2; N, 13·7. $C_{19}H_{13}ON_3$ requires C, 76·3; H, 4·4; N, 14·1%).

The solution in concentrated sulphuric acid had a blood-red colour.

1-*Aminoanthraquinone*-2-*carboxylic acid hydrazide*. Methyl 1-aminoanthraquinone-2-carboxylate was prepared[28] by heating 1-aminoanthraquinone-2-carboxylic acid with methyl hydrogen sulphate at 140° for half an hour. After crystallisation from acetic acid it formed red needles, m.p. 224–226°.

This ester (4 g) was dissolved in hot pyridine (30 c.c.), hydrazine hydrate (16 c.c. of 90%) added, and the mixture was boiled under reflux in an oil-bath at 120–130° for 3 hours. The solid which separated on cooling was collected, washed, dried at 100° (2·4 g; m.p. 225°, decomp.), and crystallised from pyridine, forming brown needles,

[28] D.R.P. 609,401 *Frdl.* **21**, 1031 (1934).

m.p. 230° (decomp.) (Found: C, 64·1; H, 4·4; N, 15·0. $C_{15}H_{11}O_3N_3$ requires C, 64·1; H, 3·9; N, 15·0%).

3-(1′-*Amino*-2′-*anthraquinonyl*):5:6-*diphenyl*-1:2:4-*triazine* (X, R = H). A mixture of 1-aminoanthraquinone-2-carboxylic acid hydrazide (9 g), benzil (9 g), acetic acid (225 c.c.), and ammonium acetate (18 g) was heated under reflux for 2 hours. After cooling, the solid which separated was collected, washed, and dried at 110° (9 g, m.p. 232–234°). On crystallisation from pyridine, the substance formed brown needles, m.p. 236–237·5° (Found: C, 76·6; H, 4·2; N, 12·0. $C_{29}H_{18}O_2N_4$ requires C, 76·7; H, 4·0; N, 12·3%).

The substance dissolved in concentrated sulphuric acid to a yellow solution.

3-(1′-*Benzoylamido*-2′-*anthraquinonyl*)-5:6-*diphenyl*-1:2:4-*triazine*. The above triazine (0·6 g), pyridine (10 c.c.), and benzoyl chloride (0·5 c.c.) were heated together in an oil-bath at 124–135° for four hours. After cooling, water was added and the precipitate separated, collected, washed, and crystallised from acetic acid, being obtained in golden yellow, irregular plates, m.p. 275–277° (Found: N, 10·5. $C_{36}H_{22}O_3N_4$ requires N, 10·0%).

Its solution in concentrated sulphuric acid was red in colour.

3-(1′-*Amino*-4′-*bromo*-2′-*anthraquinonyl*)-5:6-*diphenyl*-1:2:4-*triazine*. The triazine (1 g) was dissolved in pyridine (10 c.c.), and bromine (1 c.c.) added very cautiously to the lukewarm solution and the mixture then heated on a steam-bath for about an hour.

The solid which separated was collected, washed with sodium hydrogen sulphite solution and again with water. Crystallisation from pyridine afforded violet needles (0·8 g), decomposing gradually at 250° (Found: Br, 15·0. $C_{29}H_{17}O_2N_4Br$ requires Br, 15·0%).

A yellowish-orange coloration developed in concentrated sulphuric acid.

When in another experiment the triazine (1 g) was suspended in hot acetic acid (75 c.c.) a solution of bromine (1 c.c.) in acetic acid (4 c.c.) added, and the mixture heated under reflux until the evolution of hydrobromic acid ceased (7 hours) the reaction took a different course. After cooling, the solid which separated was collected, washed with bisulphite solution and finally with water. On crystallisation from pyridine, yellow irregular crystals, decomposing above 340°, were obtained. (Found: C, 63·1; H, 2·9; N, 6·8; Br, 18·5%). The substance dissolved in concentrated sulphuric acid with an orange coloration. The structure of this compound is not yet known.

The authentic bromo-derivative could not be brought into reaction with *p*-toluidine at 200–210° (6 hours) in the presence of sodium and cupric chloride.

Ethyl 1:4-*Diaminoanthraquinone*-2-*carboxylate*. A slow stream of hydrogen sulphide was passed through a suspension of 1-amino-4-nitroanthraquinone-2-carboxylic acid (5 g)[29] in water (255 c.c.) and aqueous ammonia (120 c.c., *d* 0·88) for 40 min when the original reddish-brown solution had turned dark blue. The mixture was kept at room temperature for some time, and the excess of ammonia and hydrogen sulphide were then removed by boiling the solution. The clear solution was filtered hot from free sulphur and acidified with acetic acid. The diamino-acid which separated was collected, washed, and dried at 100° (4 g; m.p. 330°). The substance crystallised from nitrobenzene at 170–180° in blue needles with a copper-bronze lustre, m.p. 340°,

[29] D.R.P. 279,866 *Frdl.* **12**, 420 (1914).
[30] D.R.P. 293,100 *Frdl.* **12**, 445 (1914).

alone or when mixed with an authentic specimen. 1:4-Diaminoanthraquinone-2-carboxylic acid (4 g) was dissolved in concentrated sulphuric acid (16 c.c.), and ethanol (4 c.c.) added gradually with care. The mixture was heated on a steam-bath for 8 to 10 hours, cooled, and then poured on crushed ice and basified with potassium carbonate. The solid was collected, washed with hot water, and dried at 100° (2 g; m.p. *c.* 195°). The ester crystallised from acetic acid-alcohol in blue needles, m.p. *c.* 210°, when taken in a preheated bath (Found: C, 65·6; H, 4·5. $C_{17}H_{14}O_4N_2$ requires C, 65·8; H, 4·5%). The substance is soluble in benzene, and in sulphuric acid to a light yellow solution.

1:4-*Diaminoanthraquinone-2-carboxylic acid hydrazide.* Hydrazine hydrate (2·5 c.c. of 90%) was added to a solution of ethyl 1:4-diaminoanthraquinone-2-carboxylate (3·5 g) in hot pyridine (35 c.c.), and the mixture heated on the steam-bath for 4 hours. The almost-pure product, which separated on cooling, was collected, washed, and dried at 100° (2·5 g; m.p. about 265°). On recrystallisation from nitrobenzene at 170°, it formed blue, rectangular plates with copper-bronze lustre, m.p. 275°. (Found: C, 61·1; H, 4·0; N, 17·8. $C_{15}H_{12}O_3N_4$ requires C, 60·8; H, 4·1; N, 18·9%). The substance is insoluble in benzene.

3-(1′:4′-*Diamino*-2′-*anthraquinonyl*)-5:6-*diphenyl*-1:2:4-*triazine* (X, R = NH_2). 1:4-Diaminoanthraquinone-2-carboxylic acid hydrazide (6 g), benzil (4·8 g), acetic acid (420 c.c.), and ammonium acetate (60 g) were heated together under reflux for an hour. After cooling, water (200 c.c.) was added and the solid which separated was collected, washed, and crystallised from acetic acid, being obtained as a blue powder (3 g), m.p. 244–246° (Found: C, 73·3, 73·2; H, 4·2, 4·2; N, 14·8. $C_{29}H_{19}O_2N_5$ requires C, 74·2; H, 4·1; N, 14·9%).

A yellowish-brown coloration was obtained in concentrated sulphuric acid solution.

3-(1′-*Amino*-4′-*benzoylamido*-2′-*anthraquinonyl*)-5:6-*diphenyl*-1:2:4-*triazine.* A mixture of the last-mentioned triazine (1 g), pyridine (8·5 c.c.), and benzoyl chloride (0·33 c.c.) was heated in an oil-bath at 120–130° for 2 hours. The pasty mass obtained on treating the reaction mixture with water was triturated with alcohol, when a solid began to separate. This was collected, washed, and crystallised from acetic acid, giving blue, irregular crystals, m.p. 240–242° (Found: N, 12·3. $C_{36}H_{23}O_3N_5$ requires N, 12·3%). The substance dissolved in concentrated sulphuric acid to a yellowish green solution.

3-(1′:4′-*Dibenzoyldiamido*-2′-*anthraquinonyl*)-5:6-*diphenyl*-1:2:4-*triazine.* The triazine (1 g), pyridine (8·5 c.c.), and benzoyl chloride (1 c.c.) were heated in an oil-bath at 120–130° for 3 hours. On diluting the reaction mixture with water, a pasty mass was obtained which was triturated with alcohol, when a solid separated. The derivative separated from acetic acid in brown, irregular crystals, m.p. about 270° (decomp.). (Found: N, 9·7. $C_{43}H_{27}O_4H_5$ requires N, 10·3%). Its solution in concentrated sulphuric acid had a reddish brown colour.

Phenanthraquinone benzoylhydrazone. This substance was obtained by condensation of equimolecular amounts of phenanthraquinone and benzhydrazide in hot acetic acid, with or without the addition of ammonium acetate.

The derivative crystallised from acetic acid in yellow needles, m.p. 189–190°. (Found: C, 77·5; H, 3·8; N, 9·0. $C_{21}H_{14}O_2N_2$ requires C, 77·3; H, 4·3; N, 8·6%). When this substance (0·5 g) along with ammonium acetate (10 g) in acetic acid

(20 c.c.) was refluxed for 3 hours, a new substance separated on cooling. This crystallised from nitrobenzene as golden yellow, glistening plates that did not melt at 360° (Found: C, 87·6; H, 4·0; N, 8·6%). The possible nature of this oxygen-free compound is discussed in the Introduction. It dissolved in sulphuric acid to a deep-blue solution.

Phenanthraquinone p-*aminobenzoylhydrazone.* This derivative obtained in hot acetic acid solution, with or without ammonium acetate, crystallised from pyridine in brown needles exhibiting a green lustre (Found: C, 74·8; H, 4·7; N, 12·2. $C_{21}H_{15}O_2N_3$ requires C, 73·9; H, 4·4; N, 12·3%). On continued refluxing with acetic acid and ammonium acetate, *phenanthraquinone* p-*acetamidobenzoylhydrazone* was produced. This derivative crystallised from pyridine in pale-orange needles, m.p. 257–259°. A better yield was obtained on conventional acetylation by heating the aminobenzoylhydrazone with acetic acid and acetic anhydride; mixed m.p. 257–259° (Found: N, 10·5. $C_{23}H_{17}O_3N_3$ requires N, 10·0%).

Improved preparation of 9-*phenanthrol.* A mixture of phenanthraquinone benzoylhydrazone (1 g) and aqueous potassium hydroxide (250 c.c. of 5%) was refluxed for 5 hours. The hot solution was filtered, and acidified with dilute hydrochloric acid after cooling. The solid which separated was collected, washed with sodium hydrogen carbonate solution, and then with hot water. It crystallised from benzene-light petroleum (b.p. 80–100°) in light-brown needles (0·5 g), m.p. 152–153° (Found: C, 86·7; H, 5·1. Calc. for $C_{14}H_{10}O$: C, 86·6; H, 5·2%). On repeated crystallisation, almost colourless needles were obtained. It was soluble in aqueous sodium hydroxide and gave a blue coloration with chloroform and aqueous alcoholic caustic alkali.

Phenanthraquinone monosemicarbazone. A mixture of phenanthraquinone (10 g), acetic acid (120 c.c.), and semicarbazide hydrochloride (5 g in water, 15 c.c.) was refluxed for 3 hours. On concentrating and cooling the solution, yellow needles (9·5 g, m.p. 222°) were obtained. No rise in melting point occurred on recrystallisation from acetic acid (lit., m.p. 220°, decomp.).

3-*Hydroxyphenanthratriazine.* A mixture of phenanthraquinone monosemicarbazone (2 g) and aqueous potassium hydroxide (100 c.c. of 5%) was refluxed for 1½ hours, and the hot solution then filtered, cooled, and acidified with dilute hydrochloric acid. The solid which separated was collected, washed, and dried at 100° (1·5 g, m.p. 288°, decomp.). The substance crystallised from pyridine in yellow needles, m.p. 288°, (decomp.), alone or when mixed with an authentic specimen. It dissolved in concentrated sulphuric acid to a blood-red solution.

3-*Chlorophenanthratriazine.* 3-Hydroxyphenanthratriazine (2 g) and phosphoryl chloride (4 c.c.) were heated together at 140–150° for an hour. After cooling, the mixture was poured on crushed ice, and the resulting solid collected, washed with water until neutral, and then treated thrice with an excess of 2% potassium hydroxide at 50° in order to dissolve the unreacted hydroxytriazine. The residue was washed free from alkali, and crystallised from dioxane forming yellowish brown clusters of needles (1·5 g), m.p. 238–240° (Found: Cl, 13·4. $C_{15}H_8N_3Cl$ requires Cl, 13·4%). The substance dissolves in concentrated sulphuric acid to a blood-red solution.

An attempted condensation at 100–110° of 3-chlorophenanthratriazine with 1-aminoanthraquinone using phenol as the solvent and in presence of fused sodium acetate and cupric chloride afforded a product which crystallised from alcohol as a light yellow powder, m.p. 165–167° (Found: C, 78·2; H, 4·4; N, 13·3. $C_{21}H_{13}ON_3$

requires C, 78·0; H, 4·0; N, 13·0%). Because of its insolubility in hot or cold alkali, and the analysis, this material is considered to be 3-*phenoxyphenanthratriazine*. When nitrobenzene was used as the solvent, only the original chlorophenanthratriazine could be isolated.

Ethyl p-*acetamidobenzoate*. A mixture of ethyl *p*-aminobenzoate (2 g), acetic anhydride (4 c.c.), and acetic acid (2 c.c.) was refluxed for 2 hours. The solid which separated on addition of water crystallised from benzene as colourless plates, m.p. 101° (Found: C, 63·7; H, 6·2; N, 7·3. Calc. for $C_{11}H_{13}O_3N$: C, 63·8; H, 6·3; N, 6·8%). Reference to the literature showed that this substance has been prepared by two methods, and different melting-points have been reported, namely m.p. 110° [31] and m.p. 181°.[32] Nevertheless, this substance prepared according to the two earlier methods had m.p. 101°.

3-*Hydroxy*-6:11-*diketo*-6:11-*dihydro*-1-*anthra*-(1:2-*d*)-*pyrazole* (XII). Ethyl 1-nitroanthraquinone-2-carboxylate (2 g) was dissolved in pyridine (60 c.c.), hydrazine hydrate (2 c.c. of 90%) added, and the mixture heated on a steam-bath for 2 hours. The solid which separated on cooling was collected (M. L. below), washed, and dried at 100°. The substance crystallised from nitrobenzene in brown needles (0·6 g), decomp. above 300° (Found: C, 68·3; H, 3·1; N, 10·3. $C_{15}H_8O_3N_2$ requires C, 68·2; H, 3·0; N, 10·6%). Soluble in 10% sodium hydroxide to a violet solution.

The same substance was obtained by the action of hydrazine hydrate on 1-nitroanthraquinone-2-carboxyl chloride in nitrobenzene at the room temperature during 12 hours.

3-*Acetoxy*-6:11-*diketo*-6:11-*dihydro*-1-*anthra*-(1:2-d)-*pyrazole*. 3-Hydroxy-6:11-diketo-6:11-dihydro-1-anthra-(1:2-*d*)-pyrazole (0·2 g), acetic acid (10 c.c.), and acetic anhydride (5 c.c.) were heated together for 45 min. After cooling, the solid which separated was collected, washed, and crystallised from acetic acid-alcohol, giving yellow needles, m.p. 230–232°, with previous decomposition (Found: N, 9·2. $C_{17}H_{10}O_4N_2$ requires N, 9·2%).

Ethyl pyrazole-anthrone-2-*carboxylate* (XIII). The mother liquor indicated above was diluted with water. The yellow precipitate which separated was collected, washed, dried at 100° (0·6 g, m.p. 216–218°), and crystallised twice from acetic acid-alcohol, being so obtained in yellow needles, m.p. 221–222° (Found: C, 70·3; H, 3·9; N, 9·7. $C_{17}H_{12}O_3N_2$ requires C, 69·9; H, 4·1; N, 9·6%). It is sparingly soluble in alcohol, and the solution has a green fluorescence. On hydrolysis, the corresponding *acid*, already reported, was obtained, and this had the properties described in the literature.

1-*Aminoanthraquinone*-2-*carboxylic acid*. A slow stream of hydrogen sulphide was passed through a suspension of 1-nitroanthraquinone-2-carboxylic acid (10 g) in water (150 c.c.) and aqueous ammonia (30 c.c., *d* 0·88) for 30 to 40 min when the suspension had become dark brown. The mixture was kept at the room temperature for a few hours, the excess of ammonia and hydrogen sulphide removed by boiling and the hot solution was then acidified with acetic acid. The solid, which was contaminated with free sulphur, was collected, washed, and dried at 100°. As the sodium salt of the amino-acid is soluble only in very dilute alkali, the alkali extraction of the acid from the free sulphur was a tedious procedure. It was found more convenient to dissolve the acid containing free sulphur in concentrated sulphuric acid and to filter

[31] D.R.P. 151,795 *Frdl.* 7, 644 (1902).
[32] M. Covello *Chem. Zentr.* II, 76 (1939).

through sintered glass, whereby the sulphur remained undissolved. The acid-liquor was then poured on ice and diluted with water. The free amino-acid which separated was collected, washed, and dried at 100°. Crystallisation from nitrobenzene gave brown needles (8 g), m.p. 288–290° (lit., m.p. 286°).

Anhydride of 1-aminoanthraquinone-2-carboxylic acid. Thionyl chloride (1·1 c.c.) was added, with stirring, to a suspension of 1-aminoanthraquinone-2-carboxylic acid (3 g) in nitrobenzene (20 c.c.), and the mixture heated under reflux in a water-bath at 85–90° for 2 hours. The solid which separated on cooling was collected, washed with dry benzene, and crystallised from nitrobenzene, giving brown needles, which did not melt at 360° (Found: C, 72·2; H, 2·7; N, 6·7. $C_{30}H_{14}O_6N_2$ requires C, 72·3; H, 2·8; N, 5·6%). The substance was chlorine-free and was insoluble in aqueous alkali. Its solution in concentrated sulphuric acid exhibited a yellow coloration. On hydrolysis with aqueous potassium hydroxide, it afforded 1-aminoanthraquinone-2-carboxylic acid, m.p. 286–288°, alone or mixed with an authentic specimen.

Action of hydrazine hydrate on the above anhydride. A mixture of the anhydride of 1-aminoanthraquinone-2-carboxylic acid (0·5 g), nitrobenzene (55 c.c.), and hydrazine hydrate (1 c.c.) was heated at 130–140° for 6 hours. After cooling, the solid which separated was collected, washed with benzene, and crystallised from nitrobenzene, being obtained in brown, irregular crystals, which did not melt at 360° (Found: C, 68·9; H, 4·0; N, 9·5%). It dissolved in concentrated sulphuric acid to a yellow solution. The identity of this substance is not known.

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