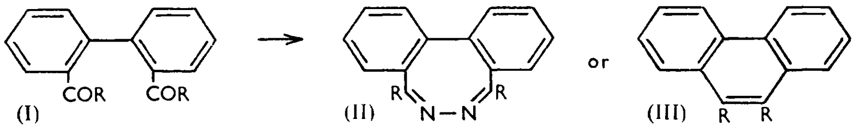
276. *Cyclisations with Hydrazine. Part I. The Preparation of Phenanthrene Compounds and of Pyrene from Aldehydes. A Variation in Reductions of the Wolff–Kishner Type.*

By R. G. R. Bacon and W. S. Lindsay.

Diphenyl-2 : 2′-dialdehyde reacts with hydrazine in polar solvents, at 0° to >100°, and under acidic or alkaline conditions, giving phenanthrene in yields of up to 100%. Phenanthrene may thus be synthesised in four steps from *o*-iodotoluene, and its derivatives may be obtained similarly, *e.g.*, 3 : 6-dinitrophenanthrene from 2-iodo-4-nitrotoluene, through 5 : 5′-dinitrodiphenyl-2 : 2′-dialdehyde. Reaction of hydrazine with 6 : 6′-dimethyldiphenyl-2 : 2′-dialdehyde fails to give 4 : 5-dimethylphenanthrene, but reaction with diphenyl-2 : 2′ : 6 : 6′-tetra-aldehyde gives pyrene. These reductive cyclisations with hydrazine are discussed in relation to known variations in the technique and products of the Wolff–Kishner reaction.

TRICYCLIC compounds are frequently formed by reactions involving 2- and 2′-substituents in a diphenyl derivative, producing a central ring of varying type and size. Recent research[1] on such compounds has been largely concerned with their stereochemistry, some aspects of which are discussed in Part II. An unexplored variation is the formation of cyclic azines (II), containing a central eight-membered (1 : 2-diazocine) ring, a reaction which should occur when 2 : 2′-diacyldiphenyls (I) are treated with hydrazine. As we show in Part II, the expected diazocines were thus obtained from diketones (I; R = alkyl or aryl). By contrast, the reaction with diphenyl-2 : 2′-dialdehyde (I; R = H) occurred with evolution of nitrogen, and the sole product was phenanthrene (III; R = H). Reductive cyclisation also occurred, though with more difficulty, as an accompaniment to the conversion of the diketones into cyclic azines, giving 9 : 10-disubstituted phenanthrenes (III; R = alkyl or aryl). An example of this dual process was simultaneously observed by Hall, Ladbury, Lesslie, and Turner[2] while studying the reduction of 2 : 2′-diacetyldiphenyl, which is one of the ketones we had examined.


(I) (II) (III)

The conversion of diphenyl-2 : 2′-dialdehyde into phenanthrene was studied in some detail, for polar solvents (*e.g.*, ethanol and acetic acid), in the presence of mineral acid or of alkali, and in their absence, at temperatures ranging from below 0° to above 100° (see Table, p. 1379). Approximately 1 mol. of nitrogen was evolved per mol. of phenanthrene produced. Gas evolution was complete in a few minutes at 60° and was faster at this temperature in the presence of alkali. In boiling acetic acid the conversion of the dialdehyde into phenanthrene was quantitative. An alternative method consisted in

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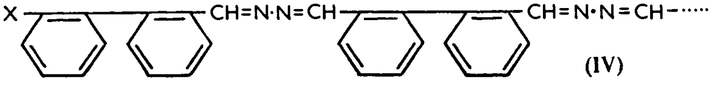
[1] See, *e.g.*, *Ann. Reports*, 1953, **50**, 154; Turner and his co-workers, *J.*, 1952, 854, and later papers.

[2] Hall, Ladbury, Lesslie, and Turner, *J.*, 1956, 3475; cf. Bacon and Lindsay, *Chem. and Ind.*, 1956, 1479.

prolonged boiling of an ethanolic solution of 2 : 2′-bisdibromomethyldiphenyl, alkali, and hydrazine, which gave a 60% yield of phenanthrene.



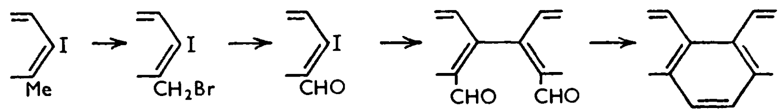
(IV)

When the yield of phenanthrene was not quantitative, the by-products were soluble resins and a yellow polyazine, presumably of type (IV; X = CHO or CH:N·NH$_2$), which was precipitated during the reaction. The formation of polyazines from dialdehydes or diketones has been reported.[3] In this case it was favoured by low temperature, absence of acid or alkali, and use of aqueous dioxan as the reaction medium. The polyazine can be hydrolysed; a sample obtained by reaction in ethanol at −10° gave phenanthrene in 80% yield when treated with boiling acetic acid.

Reductive cyclisations with hydrazine may prove to be widely applicable to the synthesis of polynuclear compounds through dialdehydes of suitable structure. We therefore examined some methods of obtaining the intermediates. Diphenyl-2 : 2′-dialdehyde was readily prepared in 65% yield from *o*-iodobenzaldehyde and copper at 160°, and reaction was particularly smooth in boiling dimethylformamide.[4] For *o*-iodobenzaldehyde we first used the procedure of Rapson and Shuttleworth,[5] and thus obtained phenanthrene in five steps from *o*-iodobenzoic acid, with an overall yield of 34%. An alternative starting point was *o*-iodotoluene, which with *N*-bromosuccinimide gave *o*-iodobenzyl bromide, convertible into the aldehyde by the Sommelet reaction [6] or through *o*-idobenzyl alcohol, which was oxidised by aqueous persulphate in the presence of silver ion.[7] By the Sommelet reaction, phenanthrene was obtained from *o*-iodotoluene in four steps, with an overall yield of 34%, while the route through the alcohol involved six steps and gave an overall yield of 31%.

Since the persulphate–silver reagent was known to oxidise toluene to benzaldehyde in good yield,[7] corresponding oxidation of *o*-iodotoluene was attempted, but the product was *o*-iodosobenzoic acid. The oxidation of the two adjacent ring substituents may be a co-operative process, since the iodine atom remained unoxidised when *o*-iodobenzoic acid was similarly treated. Another variation unsuccessfully tried was the conversion of 2 : 2′-dimethyldiphenyl into the dialdehyde by direct oxidation and through 2 : 2′-bisbromomethyldiphenyl.

One of the routes used for phenanthrene was tested in two cases for the synthesis of phenanthrene derivatives:



2-Amino-4-nitrotoluene was converted into 2-iodo-4-nitrotoluene and thence into the hitherto unreported 3 : 6-dinitrophenanthrene; the best overall yield was 13%, in four steps, from the iodide. In this synthesis the least efficient step was the Sommelet reaction; the final reductive cyclisation occurred almost quantitatively in boiling acetic acid and with good yield in boiling ethanol. In the second example, 2-iodo-1 : 3-dimethylbenzene was monobrominated in a methyl group, and then subjected to Sommelet and Ullmann reactions, giving 6 : 6′-dimethyldiphenyl-2 : 2′-dialdehyde in 15% overall yield. The final cyclisation, tried under various conditions, did not give 4 : 5-di-methylphenanthrene, but

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[3] Zimmerman and Lochte, *J. Amer. Chem. Soc.*, 1936, **58**, 948; 1938, **60**, 2456; Marvel and Hill, *bid.*, 1950, **72**, 4819; Naylor and Calico Printers' Association, B.P. 694,451/1953.

[4] Cf. Kornblum and Kendall, *J. Amer. Chem. Soc.*, 1952, **74**, 5782.

[5] Rapson and Shuttleworth, *J.*, 1941, 487.

[6] Angyal, Morris, Rassack, and Waterer, *J.*, 1949, 2704; Angyal, *Org. Reactions*, 1954, **8**, 197.

[7] Bacon, Bott, Doggart, Grime, and Munro, *Chem. and Ind.*, 1953, 897; Bacon and Doggart, unpublished work.

produced polyazine or resins. Treatment of the dialdehyde with excess of anhydrous hydrazine in boiling diethylene glycol, a procedure recommended for the Wolff–Kishner reduction of hindered oxo-steroids,[8] gave some crystalline material which appeared to be 2 : 2′ : 6 : 6′-tetramethyldiphenyl.

Difficulties attending the synthesis of 4 : 5-dimethylphenanthrene are well known [9] and failure to obtain it from the dialdehyde may be attributed to steric factors, associated with the methyl groups in the two other *ortho*-positions. It therefore seemed that if the cyclisation was to be successful with fully *ortho*-substituted diphenyls, the most favourable case should be the 2 : 2′ : 6 : 6′-tetra-aldehyde, which should give pyrene. This tetra-aldehyde has been prepared only by the ozonolysis of pyrene.[10] We repeated this preparation and found that reductive cyclisation with hydrazine in boiling acetic or propionic acid readily reconverted the aldehyde into pyrene, thus reversing the oxidative fission brought about by ozone.

The reductive cyclisations here described may be regarded as a variation in the Wolff–Kishner reaction. Traditional procedures for the normal reduction, $CORR' \longrightarrow CH_2RR'$, involve the use of alkali-metal hydroxide or alkoxide at 180—200°. We found that the disemicarbazone of diphenyl-2 : 2′-dialdehyde underwent normal reduction with potassium hydroxide above 200° to 2 : 2′-dimethyldiphenyl. Several variations on the original Wolff–Kishner methods have been reported. Thus, reductions without alkali, first carried out by Staudinger and Kupfer,[11] appear in about thirty examples in Todd's review.[12] Lock and Stach showed [13] that reduction occurs more readily (with alkali at 80—100°) when applied to the hydrazones of many aromatic aldehydes or ketones. Seibert found [14] a strongly activating effect with α-carbonyl and *o*-nitro-substituents, which permits reduction at about 100°, in the presence or absence of alkali. Various cases of abnormal reduction products are known. A relevant example is the reduction of fluorenone, which gives mainly fluorene or mainly di-9-fluorenyl, depending on conditions.[15] Since di-9-fluorenyl is readily formed by the reduction of difluorenylidene with hydrazine,[15] the "abnormal" course in this reaction may be: $2COR_2 \longrightarrow CR_2{:}CR_2 \longrightarrow CHR_2{\cdot}CHR_2$. Similar reductive couplings, occurring as side-reactions, are the formation of stilbene from benzaldehyde,[16] and of di-(2 : 3-6 : 7-dibenzo-9-fluorenyl) from 2 : 3-6 : 7-dibenzofluorenone.[17]

The reductions now reported are distinguished by their intramolecular and entirely "abnormal" course, by the low temperatures at which they may occur, and by their occurrence in acidic, as well as alkaline solutions. The course taken by the reactions may be due to the proximity of the aldehyde groups, to their conjugation through the diphenyl ring-system, and to the stability to be gained by formation of a new aromatic ring. The literature records a few similar intramolecular reductions, all involving aromatic rings and carbonyl groups in favourable spatial relationship. Thus, tetrabenzo*cyclo*decatetraene-1 : 6-dione gave tetrabenzonaphthalene with hydrazine in alcohol at 130—170°,[18] 5-formylphenanthrene-4-carboxylic acid gave 1-hydroxypyrene with hydrazine in hot acetic acid,[19] and trimethylbrazilone with phenylhydrazine, also in hot acetic acid,[20] gave deoxytrimethylbrazilone, which contains a new olefinic bridge conjugated with benzene rings.

[8] Barton, Ives, and Thomas, *J.*, 1955, 2056.

[9] Newman and Whitehouse, *J. Amer. Chem. Soc.*, 1949, **71**, 3664; Badger, Campbell, Cook, Raphael, and Scott, *J.*, 1950, 2326; Bergmann and Pelchowicz, *J. Amer. Chem. Soc.*, 1953, **75**, 2663; Wittig and Zimmermann, *Chem. Ber.*, 1953, **86**, 629.

[10] Fieser and Novello, *J. Amer. Chem. Soc.*, 1940, **62**, 1855.

[11] Staudinger and Kupfer, *Ber.*, 1911, **44**, 2197.

[12] Todd, *Org. Reactions*, 1948, **4**, 378.

[13] Lock and Stach, *Ber.*, 1943, **76**, 1252; 1944, **77**, 293.

[14] Seibert, *Chem. Ber.*, 1947, **80**, 494; 1948, **81**, 266.

[15] Weisberger and Grantham, *J. Org. Chem.*, 1956, **21**, 1160.

[16] Todd, *J. Amer. Chem. Soc.*, 1949, **71**, 1356.

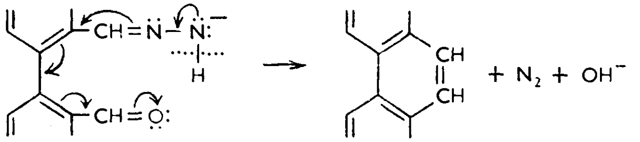
[17] Cook and Preston, *J.*, 1944, 553.

[18] Suszko and Schillak, *Roczn. Chem.*, 1934, **14**, 1216.

[19] Vollmann, Becker, Corell, and Streeck, *Annalen*, 1937, **531**, 1.

[20] Gilbody and Perkin, *J.*, 1902, 1040; Perkin and Robinson, *J.*, 1908, 489.

Both ionic and free-radical mechanisms have been proposed for Wolff–Kishner reductions. By adopting the mechanism which Seibert [14] and Szmant *et al.*[21] suggested for conventional Wolff–Kishner reductions, the intramolecular reaction in alkaline solution may be represented as a transformation of the anion of a monohydrazone:



Protonated molecules are presumably involved as intermediates under acidic reaction conditions.

EXPERIMENTAL

Synthesis of Phenanthrene.—o-*Iodobenzaldehyde.* (*a*) Anthranilic acid gave successively [22, 23] *o*-iodobenzoic acid (83%), *o*-iodobenzoyl chloride (90%), *o*-iodobenzanilide (89%), m. p. 144·5°, and *o*-iodobenzaldehyde (65%), m. p. 37°. The aldehyde was characterised as the *dimedone derivative*, m. p. 139° (decomp.) (Found: C, 55·8; H, 5·5; I, 25·6. $C_{23}H_{27}O_4I$ requires C, 55·8; H, 5·5; I, 25·7%), as the *dimedone anhydride derivative*, m. p. 229° (Found: C, 57·8; H, 5·3; I, 26·7. $C_{23}H_{25}O_3I$ requires C, 58·0; H, 5·3; I, 26·7%), and as the *azine*, which crystallised from ethanol in yellow needles, m. p. 182° (Found: C, 36·7; H, 2·2; I, 5·9. $C_{14}H_{10}N_2I_2$ requires C, 36·5; H, 2·2; I, 6·1%).

(*b*) *o*-Iodotoluene (0·5 mole) was heated for 3 hr. in boiling carbon tetrachloride with pure dry *N*-bromosuccinimide [23] (0·2—0·3 mole) and benzoyl peroxide (0·01 mole), giving *o*-iodobenzyl bromide, m. p. 55·5°, in a yield of 70—80% after allowance for *o*-iodotoluene recovered by distillation. *o*-Iodotoluene could not be converted into *o*-iodobenzyl chloride with sulphuryl chloride.[24] With excess of anhydrous sodium acetate in refluxing acetic acid, *o*-iodobenzyl bromide gave o-*iodobenzyl acetate* (80%), b. p. 92°/0·4 mm., n_D^{25} 1·5788 (Found: C, 39·2; H, 3·3. $C_9H_9O_2I$ requires C, 39·1; H, 3·3%). With boiling aqueous potassium hydroxide the acetate gave *o*-iodobenzyl alcohol (92%), which crystallised from benzene or light petroleum in needles, m. p. 91°; Olivier [25] records m. p. 89·5—90°. The alcohol was characterised as the *phenylurethane*, m. p. 103° (Found: C, 47·7; H, 3·6; N, 3·8. $C_{14}H_{12}O_2NI$ requires C, 47·6; H, 3·4; N, 4·0%), and as the α-*naphthylurethane*, m. p. 152° (Found: C, 53·8; H, 3·7; N, 3·2. $C_{18}H_{14}O_2NI$ requires C, 53·6; H, 3·5; N, 3·5%). The alcohol (0·02—0·2 mole) was oxidised to *o*-iodobenzaldehyde, in 60—80% yield, by 3 hours' stirring at 60° with aqueous 0·2M-sodium persulphate (1 mol.), containing silver nitrate (0·01—0·04 mol.).[7] The aldehyde was purified by steam-distillation.

(*c*) *o*-Iodobenzyl bromide was prepared, as in method (*b*), by using *N*-bromosuccinimide (0·3 mole), and the crude crystalline product was mixed with a slight excess of hexamethylenetetramine in chloroform at room temperature. Next day, the precipitated hexamethylenetetramine salt was collected in 76% yield (calc. on *N*-bromosuccinimide) and was converted into *o*-iodobenzaldehyde (68% yield) by the procedure of Angyal *et al.*[6]

(*d*) *o*-Iodotoluene failed to give *o*-iodobenzaldehyde when oxidised by aqueous sodium persulphate (2 mol.), containing silver nitrate, but gave some *o*-iodosobenzoic acid, which was obtained in 80% yield (after allowance for recovered *o*-iodotoluene) by using 4 mol. of persulphate; *o*-iodotoluene (22 g.) was stirred for 3 hr. at 60° with a solution of sodium persulphate (96 g.) in 0·007M-aqueous silver nitrate (300 ml.), giving unchanged *o*-iodotoluene (10 g.) and *o*-iodosobenzoic acid (12 g.), m. p. 222—222·5° (Found: C, 31·9; H, 2·0; I, 47·9. Calc. for $C_7H_5O_3I$: C, 31·8; H, 1·9; I, 48·1%). Fichter records decomposition at 223—225°.[26] *o*-Iodobenzoic acid gave no *o*-iodosobenzoic acid when similarly treated with sodium persulphate (1 mol.) in aqueous silver nitrate.

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[21] Szmant, Harnsberger, Butler, and Barie, *J. Amer. Chem. Soc.*, 1952, **74**, 2724.
[22] Cohen and Raper, *J.*, 1904, 1271.
[23] Chapman and Williams, *J.*, 1952, 5044.
[24] Kharasch and Brown, *J. Amer. Chem. Soc.*, 1939, **61**, 2142.
[25] Olivier, *Rec. Trav. chim.*, 1923, **42**, 516.
[26] Fichter, *Helv. Chim. Acta*, 1925, **8**, 438.

Diphenyl-2 : 2′-*dialdehyde*.—(*a*) *o*-Iodobenzaldehyde (23 g.) was stirred with copper bronze (20 g.) in refluxing dimethylformamide (30 ml.) for 3 hr. The product was extracted with chloroform and the extract distilled, to give diphenyl-2 : 2′-dialdehyde (65%), b. p. 169°/2·5 mm., pale yellow crystals, m. p. 62°. Similar yields of dialdehyde were obtained at 160° in the absence of dimethylformamide, but much more resin was then produced (cf. Rapson and Shuttleworth [5]). The derived *tetra-acetate* crystallised from ethanol in pale yellow needles, m. p. 133° (Found: C, 63·6; H, 5·15. $C_{22}H_{22}O_8$ requires C, 63·8; H, 5·35%). The *disemicarbazone* had m. p. 230° (Found: C, 59·3; H, 5·1; N, 25·8. $C_{16}H_{16}O_2N_6$ requires C, 59·3; H, 5·0; N, 25·9%). The oxime had m. p. 177°; Mayer [27] gives 175—176°.

(*b*) 2 : 2′-Bisbromomethyldiphenyl, m. p. 91°, was prepared in 65—95% yield from 2 : 2′-dimethyldiphenyl (1 mol.), *N*-bromosuccinimide (2·1 mol.), and benzoyl peroxide (0·1 mol.) in boiling carbon tetrachloride.[28] The dibromide and hexamethylenetetramine gave a salt of indefinite composition, from which no dialdehyde could be obtained. Treatment of the dibromide with sodium acetate in acetic acid gave 2 : 2′-bisacetoxymethyldiphenyl (69%), b. p. 207°/10 mm., converted by aqueous potassium hydroxide into 2 : 2′-bishydroxymethyldiphenyl (96%), m. p. 112°.[28, 29] Oxidation of this alcohol with aqueous sodium persulphate containing silver nitrate yielded only resin.

Phenanthrene.—A solution of diphenyl-2 : 2′-dialdehyde (2·00 g., 0·0095 mole) in acetic acid (100 ml.) was heated under reflux while a solution of 60% hydrazine hydrate (1·0 g., 0·012 mole) in acetic acid (20 ml.) was added dropwise during 1 hr. Refluxing was continued for 2 hr. more, the solvent then removed under reduced pressure, and the residue taken up in benzene. Chromatography of the solution on a column of alumina yielded pure phenanthrene (1·61 g., 95%) as colourless plates, m. p. and mixed m. p. 99·5° (Found: C, 94·4; H, 5·6. Calc. for $C_{14}H_{10}$: C, 94·4; H, 5·6%). It was characterised as the picrate, m. p. and mixed m. p. 143°.

Other preparations of phenanthrene, made from the dialdehyde and hydrazine under varied conditions, are summarised in the Table. Normally, 1·00 or 0·50 g. of dialdehyde was used, in 50 ml. of solvent. In some experiments the evolved nitrogen was measured in a gas burette. In ethanol at 60° gas evolution was complete in about 20 min. and if potassium hydroxide was also present it was too fast for measurement unless the hydrazine was added dropwise. Yellow polyazine was precipitated under some conditions. The only other by-products were soluble resins, which could be eluted only partially from an alumina column. In no case was unchanged dialdehyde recovered.

In the preparation summarised in the first line of the Table, the ethanol solution was kept for 2 days in a refrigerator, the hydrazine being added in two lots. Polyazine precipitation then appeared to be complete. Analyses of the polymer corresponded, *e.g.*, with a trimer or tetramer (*M*, 600—800) with one terminal hydrazone group and one terminal aldehyde group (Found: C, 79·0, 79·4; H, 5·4, 5·1; N, 13·6, 13·6. Calc. for trimer, $C_{42}H_{32}ON_6$: C, 79·2; H, 5·0; N, 13·2; for tetramer, $C_{56}H_{42}ON_8$: C, 79·8; H, 5·0; N, 13·3%). This polyazine gradually

Temp.	Reaction medium	N_2H_4 : dialdehyde (mol.)	N_2 (mol.) evolved per mol. of dialdehyde	Polyazine (wt. % of dialdehyde used)	Phenanthrene yield (%)	Notes
−10°	EtOH	2 : 1	—	30, 28	19, 15	*a*
60	EtOH	1 : 1	0·49	26	53	
60	EtOH	2·5 : 1	0·47	0	38	*c*
78	EtOH	2·5 : 1	—	0	90	
60	EtOH–H_2O (1 : 1 v/v)	1 : 1	0·52	15	48	
78	,, ,,	5 : 1	—	0	49	*b*
60	EtOH + KOH (~1 mol.)	1 : 1	— , 0·31	0	49, 44	
60	,, ,,	2·5 : 1	0·63, 0·63	0	66, 78	*c*
78	EtOH–10N-aq. H_2SO_4 (4 : 1 v/v)	1·1 : 1	—	0	94	*b*
60	Pr^{i}OH	1 : 1	0·43	16	40	
60	Dioxan–H_2O (1 : 1 v/v)	1 : 1	0·11	80	10	
80	EtOH–AcOH (3 : 1 v/v)	2·5 : 1	—	0	97	
117	AcOH	2·5 : 1	—	0	99	*c*

(*a*) Cf. text. (*b*) Hydrazine sulphate used. (*c*) Hydrazine added dropwise.

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[27] Mayer, *Ber.*, 1911, **44**, 2298.

[28] Wenner, *J. Org. Chem.*, 1952, **17**, 523; cf. ref. 29.

[29] Hall, Lesslie, and Turner, *J.*, 1950, 711.

dissolved in boiling acetic acid, with evolution of nitrogen, giving a red solution, from which phenanthrene was obtained (80% yield on polyazine) by evaporation and chromatography. When polyazine had been separated from the original reaction mixture, ethanol was removed from the filtrate at 20° in a vacuum and the residue chromatographed with benzene on alumina, phenanthrene (15—20%) and resin being obtained. If the ethanolic filtrate was refluxed for 2 hr. before evaporation and chromatography, the yield of phenanthrene was 60%.

Phenanthrene from 2 : 2′-bisdibromomethyldiphenyl. The tetrabromide[30] was recovered unchanged after 2 days in boiling ethanol containing excess of hydrazine. When the tetrabromide (1·00 g., 0·002 mole) was heated for 5 days with hydrazine hydrate (0·008—0·016 mole) and potassium hydroxide (0·008 mole) in boiling aqueous (1 : 1) ethanol (150 ml.), chromatography of the product on alumina yielded phenanthrene (60%) and unchanged tetrabromide (30%).

Wolff–Kishner Reduction of Diphenyl-2 : 2′-dialdehyde Disemicarbazone.—The semicarbazone (2·0 g.) was heated for 3 hr. at 230° with potassium hydroxide (0·5 g.) and the product diluted with water, ether-extracted, and chromatographed in benzene on alumina, to yield 2 : 2′-dimethyldiphenyl (0·70 g., 62%), m. p. and mixed m. p. 16—17°.

Synthesis of 3 : 6-*Dinitrophenanthrene.*—2-*Iodo*-4-*nitrobenzaldehyde.* 2-Amino-4-nitrotoluene, m. p. 100—102° (acetyl derivative, m. p. 152°), was converted through the diazonium salt into 2-iodo-4-nitrotoluene (63% on 0·4 mole scale), b. p. 114—116°/0·2 mm., yellow needles, m. p. 54° (from ethanol); Willgerodt and Kok[31] and Wheeler[32] give m. p. 58° (Found: C, 32·2; H, 2·0; N, 5·05. Calc. for $C_7H_6O_2NI$: C, 31·9; H, 2·3; N, 5·3%). This compound (0·2 mole) was treated in boiling carbon tetrachloride (50 ml.) for 7 hr. with *N*-bromosuccinimide (0·2 mole) and benzoyl peroxide (3 g.), yielding 2-*iodo*-4-*nitrobenzyl bromide* (42 g., 67%), as pale yellow needles, m. p. 84° after recrystallisation from light petroleum (Found: C, 24·8; H, 1·4; N, 3·9. $C_7H_5O_2NBrI$ requires C, 24·6; H, 1·5; N, 4·1%). Reaction of the bromide with hexamethylenetetramine in boiling chloroform resulted in 97% conversion into the *salt*, m. p. 184—185° (decomp.) (Found: C, 32·6; H, 3·7; N, 15·1. $C_{18}H_{17}O_2N_5BrI$ requires C, 32·4; H, 3·5; N, 14·6%). This salt (30 g.) was heated under reflux for 1·5 hr. with 60% aqueous acetic acid (180 ml.) and the product added to 3N-hydrochloric acid (250 ml.) to yield 2-*iodo*-4-*nitrobenzaldehyde* (5·6 g., 32%), which crystallised from *cyclo*hexane in pale yellow needles, m. p. 84·5° (Found: C, 30·3; H, 1·7; N, 4·9. $C_7H_4O_3NI$ requires C, 30·3; H, 1·5; N, 5·1%). It was characterised as the *oxime*, m. p. 134° (Found: C, 28·5; H, 1·8; N, 9·6. $C_7H_5O_3N_2I$ requires C, 28·8; H, 1·7; N, 9·6%), and as the *dimedone derivative*, m. p. 212° (decomp.) (Found: C, 51·2; H, 4·7; N, 2·5. $C_{23}H_{26}O_6NI$ requires C, 51·2; H, 4·8; N, 2·6%).

5 : 5′-*Dinitrodiphenyl*-2 : 2′-*dialdehyde.* 2-Iodo-4-nitrobenzaldehyde (6·0 g.) and copper bronze (4 g.) were heated for 2 hr. under nitrogen in refluxing dimethylformamide (30 ml.). Extraction with chloroform and removal of solvents left a solid product, from which *p*-nitrobenzaldehyde (0·4 g., 12%), m. p. 105—105·5°, was removed with *cyclo*hexane. Recrystallisation of the residue from aqueous acetic acid gave 5 : 5′-*dinitrodiphenyl*-2 : 2′-*dialdehyde* (2·1 g., 65%) in pale yellow plates, m. p. 203·5° (Found: C, 56·2; H, 2·6; N, 9·5. $C_{14}H_8O_6N_2$ requires C, 56·0; H, 2·7; N, 9·35%).

3 : 6-*Dinitrophenanthrene.* 100% Hydrazine hydrate (0·15 g., 0·003 mole) in glacial acetic acid (5 ml.) was added during 1 hr. to the aldehyde (0·50 g., 0·0017 mole) in refluxing glacial acetic acid and refluxing was continued for 4 hr. longer. 3 : 6-*Dinitrophenanthrene* was obtained in 80—96% yield as a precipitate, m. p. 278—279°. Recrystallisation from acetic acid gave yellow needles, m. p. 282—282·5° (Found: C, 62·7; H, 3·0; N, 10·8. $C_{14}H_8O_4N_2$ requires C, 62·6; H, 3·0; N, 10·5%). Reaction for 2 hr. in boiling ethanol gave a yield of 72%. The 3 : 6-dinitrophenanthrene was almost insoluble in benzene, did not fluoresce in ultraviolet light, and was unchanged when treated with peracetic acid under conditions[33] which resulted in a 57% yield of diphenyl-2 : 2′-dicarboxylic acid from phenanthrene.

Attempted Synthesis of 4 : 5-*Dimethylphenanthrene.*—2-*Iodo*-3-*methylbenzyl bromide.* 2-Iodo-1 : 3-dimethylbenzene was obtained in 62% yield from 2-amino-1 : 3-dimethylbenzene.[34] When 50 g. (0·21 mole) were heated for 5 hr. with *N*-bromosuccinimide (38 g., 0·21 mole) and benzoyl

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[30] Kenner and E. G. Turner, *J.*, 1911, 2101.

[31] Willgerodt and Kok, *Ber.*, 1908, **41**, 2077.

[32] Wheeler, *Amer. Chem. J.*, 1910, **44**, 139.

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[34] Jacobs, Reed, and Pacovska, *J. Amer. Chem. Soc.*, 1951, **73**, 4505.

peroxide (2 g.) in boiling carbon tetrachloride, 35 g. were recovered unchanged and the product was 2-iodo-3-methylbenzyl bromide (12·2 g., 61% after allowance for the recovered iodide), b. p. 144°/1·5 mm. The bromide was characterised as the yellow *thiuronium picrate* (92% yield in boiling ethanol), m. p. 223° (decomp.) (Found: C, 34·2; H, 2·7; N, 12·5. $C_{15}H_{14}O_7N_5SI$ requires C, 33·7; H, 2·6; N, 13·1%), and as the nearly colourless *hexamethylenetetramine salt* (92% yield in boiling chloroform), m. p. 180—183° (decomp.) (Found: C, 36·7; H, 4·5; N, 12·4. $C_{14}H_{20}N_4BrI$ requires C, 37·3; H, 4·5; N, 12·4%). With sodium acetate in boiling acetic acid the bromide gave 2-*iodo*-3-*methylbenzyl acetate* (77%), b. p. 108°/0·6 mm., n_D^{25} 1·5808 (Found: C, 41·6; H, 3·6. $C_{10}H_{11}O_2I$ requires C, 41·4; H, 3·8%). The acetate in boiling aqueous potassium hydroxide gave 2-*iodo*-3-*methylbenzyl alcohol* (92%), m. p. 70° on recrystallisation from light petroleum (Found: C, 39·0; H, 3·8; I, 51·3. C_8H_9OI requires C, 38·7; H, 3·6; I, 51·2%), characterised as the *phenylurethane*, m. p. 119° (Found: C, 48·9; H, 3·9; N, 4·0. $C_{15}H_{14}O_2NI$ requires C, 49·1; H, 3·8; N, 3·8%).

2-*Iodo*-3-*methylbenzaldehyde*. The above hexamethylenetetramine salt (90 g., 0·2 mole) was heated for 2 hr. in refluxing 50% aqueous acetic acid (180 ml.) and the product was treated with an equal volume of 3N-hydrochloric acid, the aldehyde separating (27 g., 55%) and being obtained in almost colourless needles, m. p. 53—54°, on recrystallisation from hexane; Mayer[35] gives m. p. 55—56°. It was characterised as the *semicarbazone*, m. p. 224° (Found: C, 35·8; H, 3·3; N, 13·9. $C_9H_{10}ON_3I$ requires C, 35·7; H, 3·3; N, 13·9%), as the *dimedone derivative*, m. p. 197° (decomp.) (Found: C, 56·8; H, 6·0. $C_{24}H_{29}O_4I$ requires C, 56·7; H, 5·7%), and as the *dimedone anhydride derivative*, m. p. 247° (Found: C, 58·7; H, 5·5. $C_{24}H_{27}O_3I$ requires C, 58·7; H, 5·5%).

6 : 6′-*Dimethyldiphenyl*-2 : 2′-*dialdehyde*. 2-Iodo-3-methylbenzaldehyde (20 g., 0·08 mole) was heated for 3 hr. at 190—220° with an equal weight of copper bronze. Ether-extraction and distillation of the residue at reduced pressure yielded a little *m*-tolualdehyde (semicarbazone, m. p. 217°) and 6 : 6′-dimethyldiphenyl-2 : 2′-dialdehyde (4·8 g., 50%), m. p. 114° (from aqueous methanol) (Found: C, 80·7; H, 6·1. Calc. for $C_{16}H_{14}O_2$: C, 80·7; H, 5·9%); Mayer[35] gives m. p. 118°. It formed a *disemicarbazone*, m. p. 254—256° (Found: C, 61·1; H, 6·2; N, 23·6. $C_{18}H_{20}O_2N_6$ requires C, 61·4; H, 5·7; N, 23·8%).

Treatment of the Dialdehyde with Hydrazine.—In boiling ethanol or boiling diethylene glycol the only product was a precipitate of polyazine (~85% of the weight of dialdehyde). In boiling ethanol containing potassium hydroxide, or in boiling acetic, propionic, or chloroacetic acid, no polyazine appeared, but chromatography of the products yielded only gums. After treatment with a large excess of anhydrous hydrazine in boiling dry diethylene glycol,[8] chromatography gave a crystalline fraction (~45%) which was not 4 : 5-dimethylphenanthrene. Recrystallisation from methanol gave colourless plates, m. p. 65—67·5°; Carlin[36] records m. p. 66—67° for 2 : 2′ : 6 : 6′-tetramethyldiphenyl. The ultraviolet absorption spectrum ($\lambda_{max.}$ 262 mμ, log ε 271) was similar to that reported for 2 : 2′ : 4 : 4′ : 6 : 6′-hexamethyldiphenyl.[37]

Opening and Re-formation of the Pyrene Ring System.—*Diphenyl*-2 : 2′ : 6 : 6′-*tetra-aldehyde*. Ozonolysis of pyrene, followed by hydrogenation, as described by Fieser and Novello[10] gave a product which was purified by chromatography in ethyl acetate on alumina, or by recrystallisation from water or benzene–hexane. The yield was similar (12% from 3 g. of pyrene), but the m. p. was 155·5°; Fieser and Novello give 162—162·8° (Found: C, 71·8; H, 4·0. Calc. for $C_{16}H_{10}O_4$: C, 72·2; H, 3·8%).

Pyrene. The tetra-aldehyde (250 mg.) in boiling acetic or propionic acid (45 ml.) was treated with excess of 100% hydrazine hydrate (500 mg.) in 5 ml. of the same solvent, added dropwise during 1—2 hr. A yellow precipitate, probably polyazine, was formed, but disappeared during 10 hours' further refluxing. Removal of solvent, followed by chromatography in benzene on alumina, yielded pure pyrene (63—66%), m. p. and mixed m. p. 149°. It was converted into the picrate, m. p. and mixed m. p. 226—227° (Found: C, 60·9; H, 2·6; N, 9·3. Calc. for $C_{22}H_{13}O_7N_3$: C, 61·3; H, 3·0; N, 9·7%).

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