## 63. *The Symmetrical Dianthryls. Part I.*

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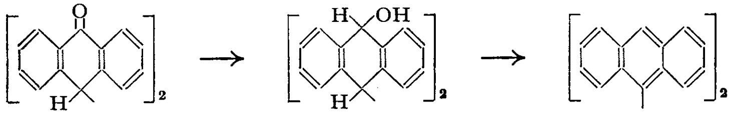
The preparation of 9 : 9′-dianthryl has been studied in detail and new methods devised. 1 : 1′-*Dianthryl* is described and compared with 2 : 2′- and 9 : 9′-dianthryls.

The literature on 9 : 9′-dianthryl is considerable but inconsistent. Schulze (*Ber.*, 1885, **18**, 3035) first prepared the hydrocarbon, m. p. 300°, by the dehydration of anthrapinacol by acetyl chloride in a sealed tube. Liebermann and Gimbel (*Ber.*, 1887, **20**, 1854) state that it can be obtained by the reduction of anthraquinone with tin and hydrochloric acid. This method was adopted by Eckert and Hofmann (*Monatsh.*, 1915, **36**, 497) who state, however, that a little platinic chloride should be added to the mixture. Some time later Barnett and Matthews (*J.*, 1923, **123**, 380) reported failure to produce 9 : 9′-dianthryl by reduction of anthraquinone, but, by reduction of anthrone in acetic acid with zinc and hydrochloric acid, obtained a hydrocarbon crystallising in colourless needles, m. p. above 360°, to which they ascribe this constitution. They attribute previous low melting points to impurities, as shown by the yellow colour recorded in the descriptions.

Schlenk and Bergmann (*Annalen*, 1928, **463**, 165), by the interaction of sodiodiphenylmethane and 9-bromoanthracene, obtained in small yield a 9 : 9′-dianthryl, m. p. 304°, depressed by admixture with Barnett and Matthews's compound. The isomerism of these hydrocarbons was attributed to a non-planar arrangement of the anthracene system (see also, *idem*, *Ber.*, 1929, **62**, 745). Subsequently, however, Bergmann and Schuchardt (*Annalen*, 1931, **487**, 244) state that Barnett and Matthews's method yields a product, m. p. 302°. The compound of high melting point is regarded by them as a dehydrogenation product produced by use of a high boiling solvent for the recrystallisation of the 9 : 9′-dianthryl—in our view a most improbable explanation. Clar (*Ber.*, 1932, **65**, 518), in agreement with Bergmann and Schuchardt, states that Barnett and Matthews's method yields a product, m. p. 308—310°, identical with that obtained by the reduction of anthraquinone with tin. Previous difficulties in the reduction of anthraquinone are attributed by him to the use of pure tin. Clar uses plumber's tin (löt Zinn). In spite of this Dufraisse, Vellus, and Vellus (*Bull. Soc. chim.*, 1938, **5**, 600) dispute the correctness of the tin reduction method and state that it is necessary first to prepare anthrone and then reduce this.


(I.) (II.) (III.)

In the meantime Minaev and Fedorow (*Ber.*, 1929, **62**, 2489) recorded the preparation of 9 : 9′-dianthryl, m. p. 300°, by the hydrolysis of the monosulphonic acid, obtained by the interaction of 9-nitroanthracene with sodium sulphite, and Barnett and Goodway (*J.*, 1929, 813) the preparation of a pale yellow " *iso*dianthryl ", m. p. 312°, by the interaction of anthrone with benzhydryl chloride and subsequent reduction of the benzhydrylanthrone.

Most of these previous experiments have been repeated, and 9 : 9′-dianthryl can now be obtained consistently by any of the following processes :

(i) Reduction of anthraquinone with ordinary tin and fuming hydrochloric acid. Use of plumber's tin or addition of platinic chloride secures no advantage ;

(ii) Reduction of anthrone in glacial acetic acid with either zinc or tin and hydrochloric acid ;

(iii) Conversion of 9-bromoanthracene into the Grignard reagent and decomposition of this with cupric chloride ;

(iv) Interaction of sodiodiphenylmethane with 9-bromoanthracene. The main product is anthracene ;

(v) Interaction of sodiotriphenylmethane with 9-bromoanthracene ;

(vi) Clemmensen reduction of 9 : 9′-dianthronyl (I) to 10 : 10′-*dihydroxy*-9 : 10 : 9′ : 10′-*tetrahydro*-9 : 9′-*dianthryl* (II) which is easily dehydrated to 9 : 9′-dianthryl (III) by boiling with phosphoric oxide in toluene. Dehydration could not be brought about by acetic anhydride which yielded anthracene and anthranyl acetate ;

(vii) Reduction of benzhydrylanthrone.

9 : 9′-Dianthryl, obtained by all of these processes, formed colourless plates, m. p. 308°, from

acetic anhydride and yielded additive *products* with toluene and pyridine. It did not combine with either maleic anhydride or benzoquinone but reacted readily with lead tetra-acetate to give dianthranol diacetate.

An attempt to extend method (vi) to the preparation of other dianthryls was unsuccessful. 1 : 4 : 1′ : 4′-Tetramethyl-9 : 9′-dianthronyl on Clemmensen reduction gave only 1 : 4-dimethylanthracene. Method (ii), which gives the highest yield of 9 : 9′-dianthryl, is also of limited application since 1 : 4-dimethylanthrone could not be reduced further by the process. The effect appears to be of a steric nature (cf. Barnett, *Ber.*, 1932, **65**, 1563).

The only reference to 2 : 2′-dianthryl is in a paper by Scholl (*Ber.*, 1919, **52**, 1834) who prepared it by the distillation of tetrahydroxy-2 : 2′-dianthraquinolyl with zinc dust. His results are confirmed and the slight possibility that the product might be 1 : 1′-dianthryl is now ruled out by the preparation of the latter hydrocarbon.

Previous attempts to prepare 1 : 1′-dianthryl proved unsuccessful owing to certain inherent difficulties. 1-Chloroanthracene is attacked by copper only at high temperature and then yields anthracene and, further, 1 : 1′-dianthraquinolyl on distillation with zinc dust or treatment with phosphorus and hydriodic acid yields only *meso*naphthodianthrone (Scholl, *loc. cit.*). However, Scholl and Turner (*Annalen*, 1923, **433**, 163) have described the preparation of 1 : 1′-dianthryl-2 : 2′-dicarboxylic acid by the reduction of 1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid and this has now been decarboxylated to yield 1 : 1′-dianthryl.

## EXPERIMENTAL.

(Analyses are by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.)

9 : 9′-*Dianthryl.*—(a) *Reduction of anthraquinone.* Anthraquinone (m. p. 277—280°; 10 g.), granulated tin (40 g.), and glacial acetic acid (120 c.c.) were boiled under reflux, and fuming hydrochloric acid (60 c.c.) added a little at a time over a period of 2 hours. The anthraquinone soon passed into solution and crystals of 9 : 9′-dianthryl began to separate after 1½ hours. The heating was continued until the solution on cooling did not deposit any needles of unchanged anthraquinone (total time about 4 hours). After cooling, the flaky solid (5 g.) was separated and crystallised first from toluene (50 c.c.) and then from pyridine or acetic anhydride. 9 : 9′-Dianthryl crystallises from pyridine or toluene with 1 molecule of solvent of crystallisation (Found, in material crystallised from pyridine : loss, 18·0. $C_{28}H_{18},C_5H_5N$ requires loss, 18·2%. Found, in material crystallised from toluene : loss, 20·75%. $C_{28}H_{18},C_7H_8$ requires loss, 20·7%). The solvent-free compound, obtained from acetic anhydride, forms colourless plates, m. p. 308°.

(b) *Reduction of anthrone with zinc.* Anthrone (20 g.), granulated zinc (20 g.), and acetic acid (100 c.c.) were heated under reflux for 8 hours, fuming hydrochloric acid (40 c.c.) being added slowly during the first 5 hours. Crystals of 9 : 9′-dianthryl began to separate after 1 hour. Yield, 8 g. (44%).

(c) *Reduction of anthrone with tin.* Anthrone (10 g.) was dissolved in a mixture of acetic acid (100 c.c.) and fuming hydrochloric acid (40 c.c.) and to the boiling solution granulated tin (40 g.) was cautiously added. Crystals began to separate after a few minutes and the refluxing was continued for 1½ hours. Yield, 4·6 g.

(d) *From* 9-*bromoanthracene.* The Grignard reagent from 9-bromoanthracene (11·25 g.), magnesium turnings (1·2 g.), and ether (200 c.c.) was decomposed with anhydrous cupric chloride (6·5 g.). The mixture was refluxed for 8 hours, the ether distilled off, and the residue decomposed with ice and acidified with hydrochloric acid. The solid material was filtered off, dried, extracted with alcohol and ether to remove soluble impurities, and the final residue recrystallised from toluene yielding 4·5 g. of 9 : 9′-dianthryl. The main by-product was anthracene.

(e) *Dehydration* of 10 : 10′-*dihydroxy*-9 : 10 : 9′ : 10′-*tetrahydro*-9 : 9′-*dianthryl.* This compound (see below) (0·5 g.) was heated under reflux for 3½ hours in toluene (15 c.c.) with phosphoric oxide (1 g.). The hot solution was filtered, and on cooling yielded pure 9 : 9′-dianthryl.

(f) *Interaction of* 9-*bromoanthracene with sodiodiphenylmethane.* Results are in accord with those of Schlenk and Bergmann (*loc. cit.*).

(g) *Interaction* of 9-*bromoanthracene with sodiotriphenylmethane.* 9-Bromoanthracene (8 g.) was shaken for 8 hours with sodiotriphenylmethane (*Org. Synth.*, Coll. Vol. II, 609) (100 c.c.; 17·8%). At the end of this time the red colour had been completely discharged. The mixture was decomposed by addition of water and the solid material filtered off. By crystallisation from xylene it was separated into 9 : 9′-dianthryl (2·38 g.) and anthracene (2·8 g.). The ether layer furnished 10·2 g. of triphenylcarbinol.

It is noteworthy that 9-bromoanthracene could be recovered unchanged when it (10 g.) was heated with sodium powder (10 g.) and anhydrous xylene (200 c.c.) under reflux for 7 hours. It therefore appears possible that changes (f) and (g) are initiated either (i) by the removal of bromine as a positive ion by the negative organic ion or (ii) by a free radical-mechanism involving aerial oxidation of the organic radical to the carbinol.

(h) *Reduction of benzhydrylanthrone* (Barnett and Goodway, *loc. cit.*). The product consists of dianthryl, anthrone, and diphenylmethane. It is probable that the reaction involves a preliminary scission of the compound into anthrone and diphenylmethane.

*Reactions of* 9 : 9′-*Dianthryl.*—(a) *With lead tetra-acetate.* 9 : 9-Dianthryl (10 g.) was suspended in a mixture of acetic acid (250 c.c.) and acetic anhydride (5 c.c.) and heated to the boiling point. Crystalline lead tetra-acetate (23 g.) was added over a period of 10 mins. and the heating continued for a further 30 mins. The solution was filtered from unchanged dianthryl (2·0 g.) and left overnight. The gelatinous red precipitate was filtered off and desiccated (3·3 g., m. p. 255° with darkening). Recrystallised from acetic acid it yielded 1·9 g. of dianthranol diacetate, m. p. 283—284° [hydrolysed to dianthranol, m. p. 230—235°; dibenzoate (yellow powder), m. p. >350°; Barnett, *J.*, 1923, **123**, 380].

(b) *With maleic anhydride.* Equimolecular quantities of maleic anhydride and 9 : 9′-dianthryl were refluxed for 8 hours in the following solvents: xylene, *o*-dichlorobenzene, and nitrobenzene. In all cases the dianthryl was recovered unchanged.

(c) *With benzoquinone.* As (b). No addition product was obtained.

10 : 10′-*Dihydroxy*-9 : 10 : 9′ : 10′-*tetrahydro*-9 : 9′-*dianthryl.*—Dianthronyl (10 g.) was dissolved in dioxan (300 c.c.) in a 1-l. round-bottom flask fitted with a mercury sealed stirrer and reflux condenser. To this solution were added hydrochloric acid (5 c.c.) and the well washed Zn–Hg couple prepared from zinc dust (24 g.) and mercuric chloride (6 g.). The solution was kept at the boiling point for 5 hours, hydrochloric acid (3 c.c.) being added at the end of each hour. The solution was filtered hot and the filtrate poured into 1 litre of water, acidified with hydrochloric acid. After being left overnight the pink precipitate was filtered off and extracted with ethyl alcohol which removed most of the colour, and the residue purified by repeated recrystallisation from acetic acid. 10 : 10′-*Dihydroxy*-9 : 10 : 9′ : 10′-*tetrahydro*-9 : 9′-*dianthryl* forms stout colourless prisms, m. p. 193°; yield, 3 g. (Found: C, 85·7; H, 5·66. $C_{28}H_{22}O_2$ requires C, 86·1; H, 5·64%). 0·5 G. was heated with acetic anhydride (5 c.c.) for 9 hours. On cooling, crystals of anthracene (m. p. 213—214°) separated. The acetic anhydride filtrate, on decomposition with water, deposited fine needles of anthranyl acetate, m. p. 127°. The dihydroxy-compound (0·5 g.) was maintained in the molten state for 1 hour. Some decomposition occurred as shown by slight effervescence and darkening but most of the material was recovered unchanged.

*Clemmensen Reduction* of 1 : 4 : 1′ : 4′-*Tetramethyldianthronyl.*—This compound, prepared by the method of Barnett (*Ber.*, 1932, **65**, 1563), was reduced by the method employed for dianthronyl. The only product was 1 : 4-dimethylanthracene, m. p. 73—74°, and no trace of less soluble material was obtained.

*Reduction of* 1 : 4-*Dimethylanthraquinone.*—1 : 4-Dimethylanthraquinone (m. p. 116°; 10 g.) was boiled with acetic acid (150 c.c.) and granulated tin (40 g.). Fuming hydrochloric acid (60 c.c.) was added during 2 hours and the heating continued for a further 3 hours. The yellow solution turned brown and then became colourless; it was filtered hot and left to cool. Pale yellow crystals of 1 : 4-dimethylanthrone separated. After recrystallisation from methanol this formed fine needles, m. p. 115° (4 g.).

2 : 2′-*Dimethyl*-1 : 1′-*dianthraquinonyl.*—1-Iodo-2-methylanthraquinone (20 g.) was throughly ground with copper powder (16 g.) and mixed with nitrobenzene (40 c.c.). The mixture was heated under reflux for 7 hours and the nitrobenzene then removed, as far as possible, by steam. The residual solid was filtered off, washed free from nitrobenzene by alcohol; dried, and extracted with sodium dithionite (hydrosulphite) according to the directions of Scholl (*Ber.*, 1907, **40**, 1691). Yield, 5·5 g. (50%). This was converted successively into 1 : 1′-dianthraquinonyl-2 : 2′-dicarboxylic acid (Scholl and Turner, *Annalen*, 1923, **433**, 163) and 1 : 1′-dianthryl-2 : 2′-dicarboxylic acid. The purified acid (Lauer, Oda, and Mijawaki, *J. pr. Chem.*, 1937, **148**, 310; 4·8 g.) was dissolved in dilute (0·5%) sodium hydroxide, and then concentrated (25%) sodium hydroxide added to the hot clear solution until precipitation of the sodium salt began. On cooling the salt (5·2 g.) separated as small white plates.

1 : 1′-*Dianthryl.*—Sodium 1 : 1′-dianthryl-2 : 2′-dicarboxylate (5·2 g.) was intimately mixed with dry lime and the mixture introduced into a long hard-glass test-tube which was closed with a loose plug of glass wool. The tube was heated to dull red for 10 minutes. The grey sublimate was purified by recrystallising three times from xylene. 1 : 1′-*Dianthryl* was obtained as colourless plates, m. p. 321—322°; yield 0·9 g. (Found: C, 95·1; H, 5·1. $C_{28}H_{18}$ requires C, 94·9; H, 5·1%).

2 : 2′-*Dianthryl.*—This was prepared from tetrahydroxy-2 : 2′-dianthraquinonyl by the method of Scholl (*Ber.*, 1919, **52**, 1834) except that the distillation with zinc was conducted under reduced pressure without introduction of hydrogen without any apparent disadvantage. A comparison of the three symmetrical dianthryls is given below:

| Dianthryl. | M. p. (uncorr.). | Crystalline form (solvent in parenthesis). | Fluorescence in solution, | | |
|---|---|---|---|---|---|
| | | | Benzene and toluene. | Pyridine. | Quinoline. |
| 9 : 9′- | 308° | Colourless plates (acetic anhydride) | Pale | Blue | None |
| 1 : 1′- | 321—322 | Microscopic colourless plates (toluene) | None | Very pale blue | None |
| 2 : 2′- | 355 | Thick needles (quinoline) | Blue green | Green | Green |

Mixed m. p.s (uncorr.): 9 : 9′- + 1 : 1′-Dianthryl 264—272°; 9 : 9′- + 2 : 2′-Dianthryl 290—294°; 1 : 1′- + 2 : 2′-Dianthryl 302—304°.

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