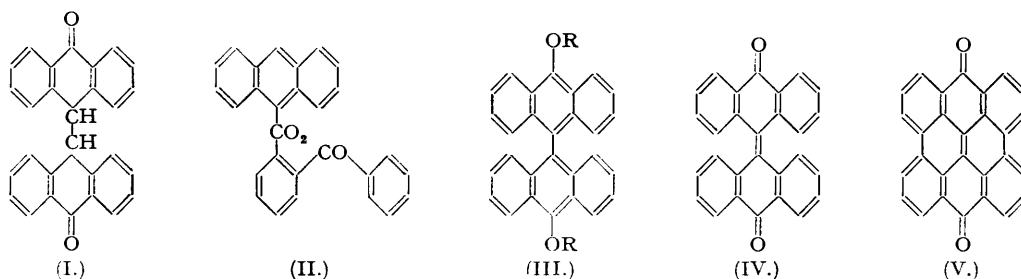


457. A Molecular Compound of Anthraquinone and Dianthron-9-yl.

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The preparation of a molecular compound, (anthraquinone)₂dianthron-9-yl, is described and its composition established.

DURING attempts to prepare derivatives of 10-diphenylmethylenanthrone by the condensation of anthrone with the keto-chlorides of aromatic ketones in boiling xylene solution (cf. Schönberg, *et. al.*, *J.*, 1946, 442) it was found that dichloro-*m*-nitrodiphenylmethane acted simply as an oxidising agent, the anthrone being converted into dianthron-9-yl (I) * (cf. Ingram, *J.*, 1950, 2246). When the keto-chlorides derived from *o*-benzoylbenzoic acid and its ethyl ester were employed, the product consisted of anthranyl *o*-benzoylbenzoate (II). Attempts to



condense *o*- and *m*-benzoylbenzoic acid with anthrone by prolonged heating in benzene solution in the presence of piperidine, ammonium acetate, and acetic acid according to Cope's method

* Previously known as 9 : 9'- or 10 : 10'-dianthronyl. The name now used is preferred as being less ambiguous.—ED.

(*J. Amer. Chem. Soc.*, 1941, **63**, 3452) resulted in the formation of a compound consisting of one molecule of dianthron-9-yl combined with two molecules of anthraquinone; the benzoylbenzoic acids take no part in this reaction.

This compound formed pale-yellow prisms, m. p. 241—243° (decomp.), dissolved unchanged in concentrated sulphuric acid, and showed delayed thermochromism in high-boiling solvents; when boiled vigorously for several minutes in methyl salicylate the initially yellow solution slowly became a deep emerald-green but faded to yellow again as the solution cooled. Curiously enough this change was only observed when heating was carried out in small soft-glass (not Pyrex) test-tubes. It appeared likely, therefore, that the thermochromism was not due to the original compound, but to another substance, produced during the heating by dehydration, aerial oxidation, or enolisation induced by the alkali of the glass, or by a combination of these reactions.

The first indications as to the constitution of the compound were obtained by an examination of its behaviour on acetylation and also on oxidation by bromine. When heated first with pyridine and then with acetic anhydride, it gave rise to anthraquinone and an acetyl derivative which could not be isolated in a pure condition, but showed in light-petroleum solution the characteristic mauve fluorescence of 10 : 10'-diacetoxydianthranyl (III; R = Ac).

Treatment of the compound with hot pyridine alone brought about a separation into two fractions, of which the less soluble was identified as anthraquinone, whilst the more soluble fraction gave orange solutions in aqueous alkalis and was oxidised by bromine in pyridine solution to dianthron-9-ylidene(9 : 9'-dianthraquinone) (IV).

From these results it would appear that the substance is a molecular compound of anthraquinone with 10 : 10'-dihydroxydianthranyl (III; R = H) or its keto-form, dianthron-9-yl. Since the original substance has only a very faint colour and does not dissolve in aqueous alkalis until it has been submitted to the enolising action of pyridine, the second component is undoubtedly present in the keto- or dianthranyl form. The relative proportions of the two components were determined by pouring a hot pyridine solution of the compound into an excess of aqueous sodium hydroxide. The weight of anthraquinone thus precipitated corresponded to 45% of that of the original compound. On acidification, the alkaline solution furnished the same amount of 10 : 10'-dihydroxydianthranyl, which was isolated as the diacetyl derivative. The compound therefore contains one molecule of dianthron-9-yl combined with two molecules of anthraquinone.

Confirmatory evidence of the composition was finally provided by the preparation of the compound in quantitative yield by cooling a hot concentrated solution of dianthron-9-yl (1 mol.) and anthraquinone (2 mols.) in a mixture of glacial acetic acid and methyl salicylate.

The peculiar behaviour of the molecular compound in exhibiting delayed thermochromism only when heated in small soft-glass tubes is now readily explicable. The alkali present in the soft glass induces enolisation of the dianthron-9-yl component, and this is followed by aerial oxidation of the resulting 10 : 10'-dihydroxydianthranyl to the thermochromic dianthron-9-ylidene, a process more likely to occur during the vigorous boiling of a small quantity of liquid.

EXPERIMENTAL.

M. p.s are uncorrected. The microanalyses are by Drs. Weiler and Strauss, Oxford.

Preparation of the Molecular Compound.—A mixture of anthrone (5.0 g.), ammonium acetate (4 g.), piperidine (1 c.c.), and glacial acetic acid (6 c.c.) was heated under reflux with benzene (75 c.c.), in an apparatus containing a Dean and Stark water separator, until the melting point of the crystals deposited from a sample of the solution rose to a temperature higher than 210°; this required 30 hours. The compound (3.0 g.) separated from glacial acetic acid in arborescent growths of pale greenish-yellow prismatic needles, m. p. 241—243° (decomp.) (Found: C, 83.7; H, 4.3; active H, 0.3. $C_{56}H_{34}O_6$ requires C, 83.8; H, 4.2; active H, 0.25%). It dissolved in concentrated sulphuric acid to form a fluorescent orange solution, from which, after 24 hours at room temperature, it was precipitated unchanged by the addition of ice-water.

Oxidation.—A solution of the compound (0.5 g.) in pyridine (4 c.c.) was boiled for 2 hours, cooled, and then treated dropwise with a solution of bromine in pyridine (16% w/v) until further addition no longer produced a transient green coloration. The yellow solid, which was deposited, separated from acetic acid-methyl salicylate (1 : 1) in magnificent golden-yellow rhomboids. The compound had too high a m. p. [335° (decomp.), copper block] to be used for identification purposes, but it showed the same thermochromic colour changes (emerald green, hot; yellow, cold) in solution as dianthron-9-ylidene (9 : 9'-dianthraquinone), and a microscopic comparison of the highly characteristic crystals with those of an authentic specimen of the quinone left no doubt as to its identity.

Separation of the Compound into its Components.—A pyridine solution (15 c.c.) of the compound (2.0 g.) was boiled for 2 hours and then poured into a well-stirred, aqueous solution of sodium hydroxide (100 c.c.; N.), containing a little sodium sulphite. The anthraquinone thus precipitated was again

heated for half an hour with pyridine (15 c.c.) and reprecipitated with aqueous sodium hydroxide (100 c.c.; N.). It then had m. p. and mixed m. p. 282—283°, and corresponded in amount (0.9 g.) to 90% of that present in the original molecular compound.

The aqueous solution from which the anthraquinone had been separated furnished, on acidification with 5N-hydrochloric acid, 10 : 10'-dihydroxydianthranyl as a pale-yellow precipitate, which after being dried was acetylated by being heated for one hour with pyridine (10 c.c.) and acetic anhydride (2 c.c.). Decomposition with water furnished 10 : 10'-diacetoxydianthranyl (1.1 g.; corresponding to 90% of the original dianthron-9-yl). The diacetyl derivative crystallised from glacial acetic acid (16 c.c.), containing a little acetic anhydride (0.5 c.c.), in needles which showed the characteristic mauve fluorescence in petroleum solution and had m. p. 279—282°, alone and also when mixed with an authentic specimen.

Dianthron-9-ylidene (9 : 9'-*Dianthraquinone*).—For purposes of comparison this compound was prepared according to Barnett and Matthews's method (*J.*, 1923, 380), but purification of the crude product was more rapidly effected by a single crystallisation from acetic acid-methyl salicylate (2 : 1) than by the method described by these authors. It melted with decomposition at 335° when introduced into a copper block at that temperature. Below this point, samples did not melt, but charred completely. Dianthron-9-ylidene exhibits the phenomenon of thermochromism; its solutions are yellow at ordinary temperatures, but become greenish-blue when heated, the colour fading again to yellow as the solution cools.

Solutions of the quinone in acetic acid-methyl salicylate remained unchanged when kept in the dark for a fortnight, but exposure to diffuse daylight at ordinary temperature produced, during the course of a few hours, extensive deposition of small orange needles, which were separated from unchanged dianthron-9-ylidene by being boiled with methyl salicylate. The product did not show thermochromism and was only very sparingly soluble in high-boiling organic solvents, but dissolved readily in sulphuric acid to form dark-red solutions having an intense greenish fluorescence. It does not melt, but chars completely when introduced into a copper block at temperatures above 300°. The constitution has not been determined, but from the results obtained by Schönberg (*loc. cit.*) on the action of sunlight on compounds similar to dianthron-9-ylidene, the substance probably represents a condensed polynuclear quinone of type (IV) (Found : C, 87.1; H, 3.25. $C_{28}H_{12}O_2$ requires C, 87.9; H, 3.2%).

Anthranyl o-Benzoylbenzoate (I).—A benzene solution of *o*-benzoylbenzoyl chloride, prepared from the acid (5 g.) and thionyl chloride (Martin, *J. Amer. Chem. Soc.*, 1916, 38, 1142), was gradually added to anthrone (4.5 g.) dissolved in the same solvent (20 c.c.), the anthrone having previously been enolised by heating for 20 minutes in the presence of pyridine (4 c.c.). The resulting yellow solid consisted of a mixture of anthraquinone, formed by the internal condensation of the acid chloride, and *anthranyl o-benzoylbenzoate*, which, after extraction from the quinone with hot xylene, crystallised from methyl salicylate in colourless hexagonal prisms, m. p. 237—238° (decomp.) (Found : C, 83.4; H, 4.6. $C_{28}H_{18}O_3$ requires C, 83.5; H, 4.5%). The ester was also produced in good yield (74%) in an attempt to prepare 10-(*o*-carbethoxydiphenylmethylene)anthrone by boiling a xylene solution (300 c.c.) of anthrone (17 g.) for 3 hours with the crude keto-chloride prepared from ethyl *o*-benzoylbenzoate (20 g.) and phosphorus pentachloride (20 g.).