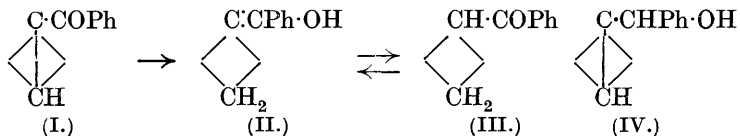


CCXIX.—*The Reactivity of meso-Substituted Anthracenes. Part II.*

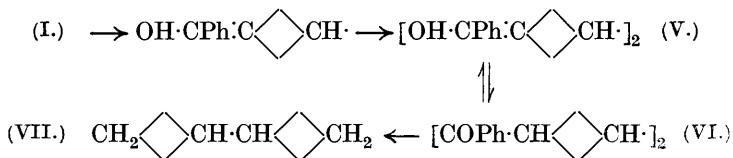
By JAMES WILFRED COOK.

By treating anthraphenone (I) with zinc dust and acetic acid Lippmann and Keppich (*Ber.*, 1900, **33**, 3090) obtained a dihydro-compound for which they preferred formula (III), since the substance was unaffected by acetic anhydride or benzoyl chloride.



Although it has now been shown to give an *acetate* on treatment with acetic anhydride and pyridine, it is certain that the dihydro-compound has the ketonic structure, since it forms an *oxime* and a *ketimine* and yields benzoic acid and 9 : 10-dihydroanthracene on hydrolysis with alcoholic potassium hydroxide. The acetate is therefore derived from the enolic form (II) of the ketone. It gives the ketone on hydrolysis with sulphuric acid in alcohol and 9 : 10-dihydroanthracene on hydrolysis with alcoholic potassium hydroxide; by no means was it possible to obtain the free enol (II). This failure is unfortunate, for the enol might give the carbinol (IV) by undergoing three-carbon tautomerism of a special type, evidence for which in the anthracene series has recently been obtained in these laboratories.

Another product of the reduction of anthraphenone, which appears to have been overlooked by Lippmann and Keppich, is 10 : 10'-*dibenzoyl*-9 : 9' : 10 : 10'-*tetrahydro*-9 : 9'-*dianthranyl* (VI). It is produced, in 20% yield, evidently in accordance with the scheme



and its constitution follows from its conversion into benzoic acid and 9 : 9' : 10 : 10'-*tetrahydrodianthranyl* (VII) by sodium amyloxide.

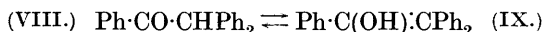
The reduction of anthraphenone is thus analogous to that of $\alpha\beta$ -unsaturated ketones (Meyer and Jacobson, "Lehrbuch der organischen Chemie," 2nd ed., 1907, Vol. I, Part I, p. 1015) such

as benzylideneacetone, which yields benzylacetone and also a saturated diketone by the union of two molecules (Harries and Eschenbach, *Ber.*, 1896, **29**, 380; Harries and Hübner, *Annalen*, 1897, **296**, 295). The seat of unsaturation of the anthracene ring system, whether it takes the form of a "bridge" bond or a conjugated system (compare Robinson, *Ann. Reports*, 1923, **20**, 121), therefore displays the properties of a single ethylenic bond, not only in its capacity to enter into additive reactions, but also in association with other unsaturated centres as part of a conjugated system.

Reduction of the central ring of the anthracene system does not usually take place so easily as in the case of anthraphenone. In the hope of obtaining definite proof that the reduction takes the form of "1:4-addition" of hydrogen with the primary formation of the enol (II or V), anthraphenone was reduced with zinc dust and acetic anhydride (compare Thiele, *Annalen*, 1899, **306**, 143). The acetate of the enol (II) was not obtained, however, the sole product isolated being dibenzoyltetrahydrodianthranyl. The formation of this compound in preference to the diacetate of the dienol (V) cannot be regarded as evidence of "9:10-addition," since ketonisation probably takes place more rapidly than acetylation. In one experiment, the diacetate seemed to be formed, but it was hydrolysed during purification.

The action of other reducing agents (zinc dust and ammonia, hydriodic acid and phosphorus in acetic acid, sodium and amyl alcohol) on anthraphenone leads to the formation of 9:10-dihydroanthraphenone as the sole product. The carbonyl group in the latter compound is very resistant to further reduction, being attacked only by hydriodic acid and phosphorus at high temperatures, when 9-benzyl-9:10-dihydroanthracene is produced. In no case has a carbinol or a pinacol been obtained by reduction of anthraphenone.

It seemed of interest to compare the properties of dihydroanthraphenone with those of the closely-related phenyldeoxybenzoin (VIII) or triphenylvinyl alcohol (IX).



Biltz showed (*Ber.*, 1893, **26**, 1957; 1899, **32**, 650; *Annalen*, 1897, **296**, 242) that this tautomeric compound readily yields acyl derivatives corresponding to the enol (IX), but does not give ketonic derivatives, and this evidence in favour of the enolic structure is supplemented by the observation that the compound absorbs electric waves (but see McKenzie and Boyle, *J.*, 1921, **119**, 1131; Meyer and Gottlieb-Billroth, *Ber.*, 1921, **54**, 575; Ley and Manecke,

Ber., 1923, 56, 777). Union of the two *gem*-phenyl groups through a methylene radical has considerable influence on the tautomeric equilibrium, for dihydroanthraphenone readily yields an oxime, but does not give acyl derivatives except in the presence of an enolising solvent. The ease with which dihydroanthraphenone-oxime is obtained is in striking contrast with the failure of anthraphenone to form such a derivative (Lippmann and Keppich, *loc. cit.*, and confirmed by the author). This inactivity of the latter substance can scarcely be attributed entirely to steric influences and must be due to the lack of a tautomeric hydrogen atom (compare Gane and Ingold, this vol., p. 13).

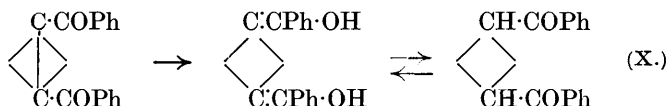
Dihydroanthraphenone resembles phenyldeoxybenzoin in losing its benzoyl group under the influence of alcoholic sodium hydroxide or alkyloxide—another reaction which seems to require the presence of potentially mobile hydrogen, since anthraphenone is unaffected by this treatment.

The formation of a ketimine from dihydroanthraphenone and semicarbazide in alcoholic solution is probably due to decomposition of the semicarbazone and not to primary decomposition of semicarbazide, since ammonia has no action on dihydroanthraphenone under the experimental conditions employed.

Dihydroanthraphenone reacts readily with bromine in cold carbon disulphide solution. The reaction probably involves primary addition of the halogen to the ethylenic bond of the enol, since dihydroanthracene is attacked but slowly under these conditions. The additive compound could not be isolated, as it lost hydrogen bromide in two directions and underwent further bromination with the production of 10-bromoanthraphenone. The acetate of dihydroanthraphenone reacted similarly, but more slowly. With a view to obtain definite evidence of addition to the enol, dihydroanthraphenone was treated with bromine in pyridine solution, but no quaternary salt was formed, the ketone being recovered unchanged.

The "tribenzoylanthracene" obtained by Lippmann and Keppich (*loc. cit.*) as a by-product in the preparation of anthraphenone was probably impure 9 : 10-dibenzoylanthracene (see this vol., p. 1285). They stated that on reduction with zinc and acetic acid it yielded a tetrahydro-compound, m. p. 187—188°. Dibenzoylanthracene gives 9 : 10-dibenzoyl-9 : 10-dihydroanthracene (X), m. p. 194—195°, under similar conditions, and the tetrahydro-compound of Lippmann and Keppich was doubtless an impure specimen of this substance, the properties of which agree with their description. The structure assigned to dibenzoyldihydroanthracene is based on analysis and on its conversion into benzoic acid and 9 : 10-dihydroanthracene by treatment with sodium amyloxide. Evidence has

been obtained that dibenzoyldihydroanthracene also displays tautomerism, and its production is probably due to addition of hydrogen to the extreme ends of an extended conjugated system with subsequent rearrangement into the ketone :



The action of bromine on (X) consists in removal of hydrogen with re-formation of dibenzoylanthracene. By reduction with hydriodic acid and phosphorus at a high temperature, dibenzoyldihydroanthracene loses a benzoyl group and passes into benzyldihydroanthracene.

EXPERIMENTAL.

Reduction of Anthraphenone.—(a) A solution of anthraphenone (25 g.) in acetic acid (250 c.c.) was boiled with zinc dust (50 g.) for 5 hours. After cooling, the solid was collected, freed from zinc by treatment with hydrochloric acid, and recrystallised (5.2 g.) in turn from pyridine-alcohol, xylene, and benzene-light petroleum (Found : C, 88.9; H, 5.6. $\text{C}_{42}\text{H}_{30}\text{O}_2$ requires C, 89.0; H, 5.3%). 10 : 10'-Dibenzoyl-9 : 9' : 10 : 10'-tetrahydro-9 : 9'-dianthranyl (VI) forms colourless, glistening needles, m. p. 269°. It is sparingly soluble in most media.

The acetic acid liquor was poured into water, and the resinous substance which separated was fractionally crystallised from alcohol, 5.4 g. of pure 9 : 10-dihydroanthraphenone (III), m. p. 103°, being obtained (Lippmann and Keppich, *loc. cit.*, give m. p. 101°).

If hydrochloric acid was added during the reduction, the same products were obtained, but the proportion of the bimolecular compound was larger.

(b) To a solution of anthraphenone (25 g.) in acetic acid (200 c.c.) were added 50% hydriodic acid (12.5 c.c.) and red phosphorus (6.5 g.), and the whole was boiled for 4 hours. The product, after recrystallisation from alcohol, consisted of 19 g. of pure dihydroanthraphenone. This is the most convenient method for the preparation of this substance.

(c) Anthraphenone (5 g.) was heated on the water-bath for 5 hours with zinc dust and ammonia, and 3 g. of pure dihydroanthraphenone were obtained.

(d) Anthraphenone (5 g.), zinc dust (10 g.), and acetic anhydride (50 c.c.) were boiled together for 2 hours and the hot solution was filtered. The filtrate, after cooling, was treated with water, and the viscid residue extracted with boiling alcohol (which removed unchanged anthraphenone and unidentified products). The in-

soluble, white powder was recrystallised from xylene and then melted at 267°, alone or when mixed with dibenzoyltetrahydrodianthranlyl.

In another experiment, the crude product, after extraction with alcohol, melted indefinitely at about 296°, but recrystallisation lowered the melting point to 267°. [The diacetate of the dienol (V) melts at 315°.]

(e) Sodium (0.5 g.) was added to a boiling solution of anthraphenone (2.8 g.) in amyl alcohol (10 c.c.). After the sodium had dissolved, the solution was poured into water and yielded 9 : 10 dihydroanthracene (identified by comparison with an authentic sample) and benzoic acid. That fission of the molecule had not preceded reduction to dihydroanthraphenone was shown by the fact that anthraphenone was decomposed to the extent of less than 1% by boiling for $\frac{1}{2}$ hour with a sodium amyloxide solution of the same concentration.

(f) When anthraphenone (1 g.) was reduced with 50% hydriodic acid (14 c.c.) and red phosphorus (0.6 g.) by heating at 180° for 6 hours, a product was obtained which melted at 95—105°. It probably consisted largely of dihydroanthracene, formed by fission of the anthraphenone molecule under the influence of the acid.

Reactions of 9 : 10-Dihydroanthraphenone (III).—(a) *Fission.* Although dihydroanthraphenone is stable towards acids (this vol., p. 1284), it is readily converted by boiling ethyl-alcoholic potassium hydroxide or sodium ethoxide or boiling amyl-alcoholic sodium amyloxide into 9 : 10-dihydroanthracene and a benzoate: Anthraphenone (1 g.) was boiled for 15 minutes with sodium (1 g.) dissolved in alcohol (25 c.c.); on dilution, the solution yielded 0.5 g. of 9 : 10-dihydroanthracene, m. p. 108—110° after recrystallisation from alcohol (Found: C, 93.4; H, 6.9. Calc.: C, 93.3; H, 6.7%). Benzoic acid was precipitated when the alkaline liquor was acidified.

The colour of the solution indicated that dihydroanthraphenone, when treated with sodium in anhydrous alcohol, first yielded a sodio-derivative. This, however, could not be condensed with alkyl iodides on account of the ease with which it underwent fission.

(b) *Reduction.* Dihydroanthraphenone was not reduced by prolonged treatment with zinc and hydrochloric acid in acetic acid solution. With sodium and alcohol or with zinc dust and 50% aqueous potassium hydroxide, it yielded dihydroanthracene. By heating dihydroanthraphenone (1 g.) for 7 hours at 180° in a sealed tube with 50% hydriodic acid (14 c.c.) and red phosphorus (0.6 g.), 9-benzyl-9 : 10-dihydroanthracene was obtained, which, alone or when mixed with a sample prepared by the reduction of 9-benzylanthracene, melted at 119—120° (Bach, *Ber.*, 1890, **23**, 2530, gives

m. p. 110—111°). The compound gave no colour with sulphuric acid in the cold, but on heating gave the dark green solution with a red fluorescence characteristic of benzylanthracene (Found : C, 93.0; H, 6.85. Calc. : C, 93.3; H, 6.7%).

(c) *Acetylation*. A solution of dihydroanthraphenone (2.5 g.) in pyridine (7.5 c.c.) and acetic anhydride (2.5 c.c.) was heated on the water-bath for 4½ hours. Water was added cautiously to the cooled solution, and the resulting solid extracted with a little boiling alcohol to remove unchanged dihydroanthraphenone. The residue was recrystallised from much alcohol and from benzene and light petroleum and then formed colourless, microscopic needles, m. p. 202° (Found : C, 84.4; H, 5.6. C₂₃H₁₈O₂ requires C, 84.7; H, 5.5%).

This *acetate* yielded ethyl acetate and dihydroanthraphenone on hydrolysis with sulphuric acid in alcohol and dissolved in sulphuric acid with a brilliant green colour.

(d) *Ketonic derivatives*. i. A solution of dihydroanthraphenone (2.5 g.) in alcohol (30 c.c.) was heated with a concentrated aqueous solution of hydroxylamine hydrochloride (2 g.) and sodium acetate (3 g.) on the water-bath for 5 hours. The *oxime* obtained on cooling was recrystallised from alcohol and then from benzene and light petroleum, separating in colourless needles, m. p. 162—163° (Found : C, 84.3; H, 5.65. C₂₁H₁₇ON requires C, 84.3; H, 5.7%).

Triphenylvinyl alcohol (IX) is oxidised to phenylethoxydeoxybenzoin by hydroxylamine hydrochloride in alcoholic solution (Biltz, *Ber.*, 1896, **29**, 2080; *Annalen*, 1897, **296**, 249). Dihydroanthraphenone, under these conditions, yields a colourless, crystalline compound, m. p. 187—190°, which contains nitrogen but no chlorine. The substance, which may possibly be a stereoisomeric oxime, has not been further investigated.

ii. A solution of dihydroanthraphenone (2.5 g.) in alcohol (30 c.c.) was heated with semicarbazide hydrochloride (2.5 g.) and sodium acetate (5 g.) in a little water on the water-bath for 8 hours. The orange needles which separated were recrystallised from benzene and light petroleum, the *ketimine* being thus obtained as a yellow, crystalline powder, m. p. 185—186° (Found : C, 89.4; H, 6.2. C₂₁H₁₇N requires C, 89.1; H, 6.0%).

The *ketimine* was not affected by prolonged boiling with alcoholic sodium hydroxide and was but slightly decomposed by hydrochloric acid in acetic acid, but it was completely hydrolysed by boiling for ½ hour with sulphuric acid (1 part) in acetic acid (10 parts); the resulting dihydroanthraphenone was identified by the method of mixed melting points.

(e) *Action of bromine*. To a solution of dihydroanthraphenone

(1.4 g.) in carbon disulphide (10 c.c.), bromine (0.25 c.c.; 1 mol.) was added. Hydrogen bromide was liberated and decoloration was complete after a few minutes. After evaporation of the solvent, the viscid residue was washed with alcohol, recrystallised from acetic acid and then from ethyl acetate, and identified as 10-bromoanthraphenone by the method of mixed melting points.

10 : 10'-Dibenzoyl-9 : 9' : 10 : 10'-tetrahydro-9 : 9'-dianthranyl (VI).—This substance (1 g.) was added to a solution of sodium (0.25 g.) in amyl alcohol (10 c.c.), and the resulting solution was boiled for $\frac{1}{2}$ hour, poured into water, and cooled. The solid product was washed with boiling alcohol and recrystallised from benzene and light petroleum. The resulting colourless, crystalline powder melted at 256—257°, alone or when mixed with 9 : 9' : 10 : 10'-tetrahydro-9 : 9'-dianthranyl (VII) prepared by another method (Found: C, 93.6; H, 6.3. Calc.: C, 93.8; H, 6.1%). The aqueous liquor from the above preparation yielded benzoic acid when acidified.

Tetrahydrodianthranyl (VII) was obtained by Sachse (*Ber.*, 1888, **21**, 2512) by the reduction of dianthranyl with sodium amalgam and alcohol, but it is more conveniently prepared by reduction with sodium (1 part) and boiling amyl alcohol (15 parts). The dihydrodianthranyl obtained by Matthews (this vol., p. 236) also gives the same tetrahydrodianthranyl by this treatment.

Dibenzoyltetrahydrodianthranyl (1 g.) was acetylated by 4 hours' heating on the water-bath with acetic anhydride (1 c.c.) and pyridine (5 c.c.), and the product well washed with alcohol. The *diacetate*, which was almost insoluble in all the usual media, separated from nitrobenzene-alcohol as a colourless, crystalline powder, m. p. 315° (Found: C, 84.5; H, 5.4. $C_{46}H_{34}O_4$ requires C, 84.9; H, 5.2%).

Reduction of 9 : 10-Dibenzoylanthracene.—A suspension of dibenzoylanthracene (2 g.) in acetic acid (50 c.c.) was boiled with zinc dust (5 g.) for 6 hours, the excess of zinc filtered off, and the solution cooled. The substance thus obtained was recrystallised from benzene and light petroleum, 9 : 10-dibenzoyl-9 : 10-dihydroanthracene (X) separating as a colourless, crystalline powder, m. p. 194—195° (Found: C, 86.3; H, 5.2. $C_{28}H_{20}O_2$ requires C, 86.6; H, 5.15%).

When boiled with a solution of sodium amyloxide in amyl alcohol, it developed a fugitive, deep orange-red colour and decomposition into benzoic acid and 9 : 10-dihydroanthracene was complete in $\frac{1}{2}$ hour.

A pure sample of an acetyl derivative of the enol corresponding to dibenzoyldihydroanthracene could not be prepared, since the latter compound was so readily oxidised that the product was

always contaminated with dibenzoylanthracene. By crystallising the acetylated product, a fraction, m. p. 145—150°, was obtained which gave ethyl acetate when warmed with alcohol and sulphuric acid.

Dibenzoyldihydroanthracene (0.9 g.), suspended in carbon disulphide (15 c.c.), was treated with bromine (0.5 c.c.) in excess. After 12 hours, the solid in suspension was collected and identified as dibenzoylanthracene.

When heated at 200° for 6 hours with 50% hydriodic acid (14 c.c.) and red phosphorus (0.6 g.), dibenzoyldihydroanthracene (1 g.) was converted into 9-benzyl-9 : 10-dihydroanthracene.

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