

115. *The Constitution of the Chlorination Products of Benzanthrone.*

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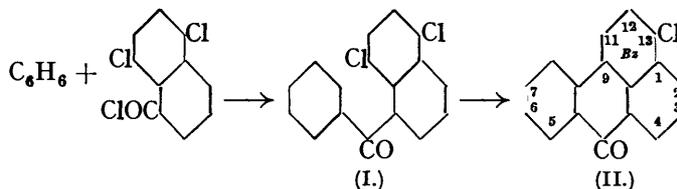
MUCH uncertainty exists regarding the constitution of the chlorination products of benzanthrone (cf. Martinet and Drobatshev, *Chim. et Ind.*, 1929, **21**, 227). Although constitutions have been assigned to them from time to time in the patent claims (*e.g.*, G.P. 193959, 436533; E.P. 20837), no direct proof has, so far as we are aware, yet appeared in the scientific literature.

Treatment of benzanthrone with a variety of chlorinating agents leads first to a monochlorobenzanthrone, m. p. 176°, and further chlorination of either benzanthrone or this chloro-derivative yields a mixture of two dichlorobenzantrones, m. p. 267—268° and 218° (*loc. cit.*). The directions given in the patent literature for the preparation of the monochloro-compound by the potassium chlorate method led (on a laboratory scale) to a mixture containing mostly the two dichloro-derivatives. The monochloro-compound was, however, readily prepared by means of dichloramine-*T*, and, when pure, melted at 182—183° (cf. Lüttringhaus and Neresheimer, *Annalen*, 1929, **473**, 259). The dichlorination of benzanthrone appeared to be very sensitive to small changes in the experimental conditions, with the result that the proportions in which the isomerides were formed varied considerably. We believe that the two isomerides isolated are not the sole products formed in the reaction, although we were not successful in isolating any other derivative in a pure state.

It was readily established that chlorination occurs in the first place in the *Bz*-nucleus, since oxidation of chlorobenzanthrone, m. p. 182—183°, yielded anthraquinone-1-carboxylic acid identical with that obtained from benzanthrone itself. We consider that position 13 is the most probable site for this chlorine atom, and shall name the compound, m. p.

182—183°, 13-chlorobenzanthrone (II), although there is, in our opinion, no conclusive proof of this orientation. Arguments which can be devised involving the formation of dibenzanthrones, isodibenzanthrones or dibenzanthranoyls from halogenobenzanthrones by the use of alkali or of copper powder at a high temperature appear to us invalid owing to (a) the great mobility of halogen atoms attached to the Bz-nucleus of benzanthrone and (b) the peculiar tautomerism of the benzoyldinaphthyls reported by Lüttringhaus and Neresheimer (*loc. cit.*).

In an attempt to synthesise 13-chlorobenzanthrone according to the scheme



the chloro-ketone (I) was prepared, but the benzanthrone ring closure could not be effected.

Dichlorobenzanthrone, m. p. 218°, yielded on oxidation 8-chloroanthraquinone-1-carboxylic acid, identical with that obtained from 8-chloro-1-aminoanthraquinone by the Sandmeyer reaction. The position 8 for the second chlorine atom in this dichlorobenzanthrone is thus assured.

Dichlorobenzanthrone, m. p. 267—268°, yielded on oxidation 6-chloroanthraquinone-1-carboxylic acid, identical with that obtained from 6-chlorobenzanthrone, the constitution of which was determined by its synthesis (see below). The position 6 of the second chlorine atom in dichlorobenzanthrone, m. p. 267—268°, is thus proved, and it has been confirmed by the preparation of this compound by chlorination of 6-chlorobenzanthrone.

We are thus able to assign the following constitutions: m. p. 182—183°, 13-chlorobenzanthrone; m. p. 218°, 8 : 13-dichlorobenzanthrone; m. p. 267—268°, 6 : 13-dichlorobenzanthrone.

During the above work it was necessary to identify 6- and 8-chloroanthraquinone-1-carboxylic acids. A review of the literature showed that the series of chloroanthraquinone-1-carboxylic acids was incomplete, and the melting point of the acid was not in every case characteristic. We therefore completed the series:

Chloroanthraquinone-1-carboxylic acids.

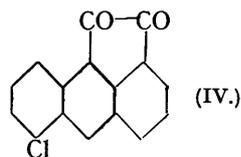
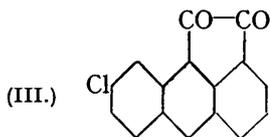
Position of Cl.	M. p. of acid.	M. p. of methyl ester.	References.
2-	176—177°	—	I.G., F.P. 659962.
3-	{ 297—299 286—287 (decomp.)	—	Scholl and Seer, <i>Ber.</i> , 1922, 55 , 116. Keimatsu, Hirano, and Tanabe, <i>J. Pharm. Soc. Japan</i> , 1929, 49 , 85.
4-	229 (decomp.)	188—189°	Stanley and Adams, <i>J. Amer. Chem. Soc.</i> , 1931, 53 , 2364.
5-	about 306	181	
6-	306	190—191	Scholl and Seer, <i>loc. cit.</i>
7-	262—264	193—194	
8-	228—231	124—125	

(If the substance is new, the m. p. is in italics. All the m. p.'s are our own determinations except those of the 2- and the 3-chloro-acid.)

We are indebted to Professor Adams for a specimen of the ester of the 4-chloro-acid. The 5-chloro-acid was prepared by the Sandmeyer reaction from 5-chloro-1-aminoanthraquinone, the 7-chloro-acid by oxidation of 7-chlorobenzanthrone. The 6- and the 8-chloro-acid have been referred to previously.

By condensation of oxalyl chloride with β -chloroanthracene in the presence of aluminium chloride Butescu (*Ber.*, 1912, **45**, 1213; 1913, **46**, 212) prepared a chloroacanthrenequinone, which gave on oxidation an acid, m. p. 260°. He did not attempt to orient this acid, but

called it β -chloroanthraquinone-1-carboxylic acid. It is obviously the 7-chloro-acid, and the chloroaceanthrenequinone has the formula (III).

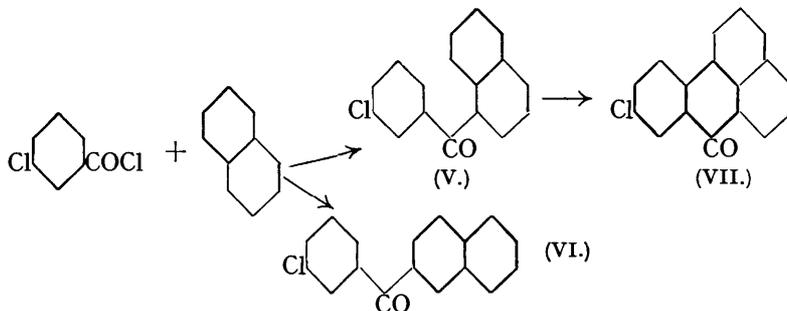


By a similar reaction Butescu prepared from α -chloroanthracene an α -chloroaceanthrenequinone. He states that this yields on oxidation an α -chloroanthraquinone-1-carboxylic acid, m. p. 205°. No such melting point is given in the above table. We repeated Butescu's experiment and obtained 5-chloroanthraquinone-1-carboxylic acid, m. p. about 306° (methyl ester, m. p. 181°). Butescu's melting point is probably a clerical error. The chloroaceanthrenequinone is therefore (IV).

Stelzner ("Literatur-Register," 1912—1913, p. 1157) lists Butescu's α - and β -chloroacids as the 8- and the 7(or 2)-chloro-acid, respectively, but, as stated, this orientation was not given by Butescu.

It may be noted that oxalyl chloride has condensed in both cases with the unsubstituted ring.

Our work necessitated the preparation of 6-chlorobenzanthrone (cf. Scholl and Seer, *Ber.*, 1922, 55, 109). These authors report that condensation of *m*-nitrobenzoyl chloride with naphthalene gives *m*-chlorophenyl α -naphthyl ketone, m. p. 77—79°, which is stated to be yellow: we obtained, however, both the α - and the β -naphthyl ketone, m. p. 86° and 143°, respectively, which are colourless. The constitution of these ketones is determined by the fact that the former (V) gives a 2 : 4-dinitrophenylhydrazone only slowly, and readily gives a benzanthrone (VII), whereas the latter (VI) rapidly forms the 2 : 4-dinitro-



phenylhydrazone and does not give a benzanthrone. The dinitrophenylhydrazone of (V) was isolated in two forms, which are probably *cis-trans* isomerides (cf. Brederick, *Ber.*, 1932, 65, 1833), but only one form of the derivative of (VI) was obtained. The low reactivity of the α -naphthyl ketone is due to the contiguity of the second ring of the naphthalene nucleus. It is not due to the diaryl nature of the ketone, since benzophenone (as well as the β -naphthyl ketone) very readily reacts with 2 : 4-dinitrophenylhydrazine. It is not necessary to separate the isomeric ketones if it is desired to prepare the benzanthrone; this can readily be isolated if the crude mixture is subjected to ring closure.

Condensation of *p*-chlorobenzoyl chloride with naphthalene in the presence of aluminium chloride gave similarly a semi-solid material which was obviously a mixture of α - and β -naphthyl derivatives, as in the *m*-chlorophenyl series. In this case, however, only the α -naphthyl ketone was isolated in a pure state. The semi-solid mixture and the pure α -naphthyl ketone both yielded 7-chlorobenzanthrone, but in both cases the yield was poor, as noted by Scholl and Seer (*loc. cit.*).

We have also prepared for comparison 7 : 13-dichlorobenzanthrone, m. p. 251—252°, by chlorination of 7-chlorobenzanthrone. The position of the entering chlorine atom is assumed by analogy.

EXPERIMENTAL.

13-Chlorobenzanthrone.—Benzanthrone (9.25 g.), dichloramine-*T* (4.95 g.; 1 mol.), and conc. HCl (1 c.c.) in AcOH (180 c.c.) were heated on the water-bath until no reactive Cl remained (10 hr.). When cold, needles (4.95 g.; m. p. 154—168°) separated, and a further 4 g. of the same material were obtained by dilution. The products were united and the 13-chlorobenzanthrone was crystallised (6 times) to const. m. p. (182—183°) from AcOH (Found: Cl, 13.7. Calc. for $C_{17}H_9OCl$: Cl, 13.4%).

Chlorination of 6-Chlorobenzanthrone.—6-Chlorobenzanthrone (2 g.), chloramine-*T* (85%, 2.2 g.; 1 mol.), and conc. HCl (0.6 c.c.) in AcOH (80 c.c.) were heated on the water-bath for 77 hr.; 96% of the available Cl had then disappeared. The cooled solution deposited impure 6:13-dichlorobenzanthrone, m. p. 240—245°, raised to 263—265° by crystn. from AcOH and Ac_2O , followed by sublimation in vac. Mixed with the product, m. p. 267—268°, obtained by direct chlorination of benzanthrene, this material had m. p. 264—267°. Dilution of the original AcOH mother-liquor gave an impure product containing much 6-chlorobenzanthrone.

Preparation of 7-Chlorobenzanthrone.— $AlCl_3$ (49 g.) was added during 45 min. to a mixture of *p*-chlorobenzoyl chloride (49 g.) and $C_{10}H_8$ (40.5 g.) in dry CCl_4 (135 g.) at 0°. Reaction was sluggish, but commenced when the mixture was allowed to warm slightly; further cooling then kept it under control. The mixture was kept at 0° for 4 hr. and then at room temp. for 135 hr. The separated solid was added to conc. HCl (370 c.c.) and H_2O (1250 c.c.), and the $C_{10}H_8$ removed by distillation in steam. The insol. tar remaining in the distillation vessel was boiled with 4% NaOH aq. (400 c.c.) and then repeatedly with EtOH, which did not dissolve a quantity of a dark solid. The EtOH deposited about 3.8 g. of the α -naphthyl ketone, which when pure had m. p. 127—128°. The oil from the mother-liquors was extracted with Et_2O , which gave on evaporation an oily mixture of the α - and the β -naphthyl ketone (31.2 g.). This partly solidified on keeping in vac. The α -ketone gave (in 2 hr.) a bright red 2:4-dinitrophenylhydrazone, m. p. 233—235°. The pure α -ketone (2 g.), when heated with $AlCl_3-NaCl$ (10 g.: 2 g.) at 160° for 2.5 hr., gave 0.05 g. of 7-chlorobenzanthrone, whereas the semi-solid mixture of ketones (23 g.), heated with $AlCl_3-NaCl$ (115 g.: 23 g.) at 130—150° for 11 hr., gave 0.65 g. of 7-chlorobenzanthrone, m. p. 188—190°.

7:13-Dichlorobenzanthrone.—7-Chlorobenzanthrone (0.3 g.) was heated on the water-bath for 8 hr. with an approx. *N*-solution of Cl in AcOH (20 c.c.). The solution was filtered at about 40°; the insol. matter, mostly dichlorobenzanthrone, had m. p. 230—240°. The substance obtained from the mother-liquor was rechlorinated and then yielded a further amount of dichloro-derivative. Recryst. twice from AcOH (sol. in boiling AcOH, ca. 0.5 g. in 100 c.c.), 7:13-dichlorobenzanthrone was obtained in rosettes of pale yellow needles, m. p. 251—252° (Found: C, 67.9; H, 3.2. $C_{17}H_8OCl_2$ requires C, 68.2; H, 2.7%).

α - and β -Naphthyl *m*-Chlorophenyl Ketones.—Condensation of *m*-chlorobenzoyl chloride (41.5 g.; b. p. 111—112°/21 mm.) with $C_{10}H_8$ (34.2 g.) according to the directions of Scholl and Seer (*loc. cit.*) gave a gum; crystals were obtained by grinding a portion with Et_2O , and the whole, when seeded, readily crystallised. It formed yellow prisms from EtOH (47.5 g.; 73% theo.), which melted from 78—105°, although only a little solid remained above 79°. Purification could not be effected by means of EtOH, MeOH, or C_6H_6 , but when a large amount of EtOAc was used a first fraction, m. p. 141—142°, was obtained. Crystn. of this substance from MeOH, in which it was sparingly sol. (ca. 1 g. in 100 c.c.), gave pure *m*-chlorophenyl β -naphthyl ketone, m. p. 143° (Found: C, 76.4; H, 4.5; Cl, 13.2. $C_{17}H_{11}OCl$ requires C, 76.5; H, 4.2; Cl, 13.3%). Subsequent fractions obtained from the EtOAc liquor consisted mainly of the α -naphthyl ketone, which after further treatment with EtOAc and repeated crystn. from MeOH formed colourless needles, m. p. 86° (Found: Cl, 13.2%).

When the β -naphthyl ketone (0.5 g. in hot EtOH, 60 c.c.) was added to a cold solution of 2:4-dinitrophenylhydrazine (0.4 g.) and H_2SO_4 (0.8 c.c.) in EtOH (6 c.c.), an orange-red dinitrophenylhydrazone was immediately pptd.; it was kept over-night, collected, extracted with hot EtOH, and recrystallised first from C_6H_6 -ligroin and then from C_5H_5N ; m. p. 264—265° (decomp.) after sintering (Found: N, 13.0. $C_{22}H_{15}O_4N_4Cl$ requires N, 12.9%). The α -naphthyl ketone gave no immediate ppt. under similar conditions and the hydrazone formation was incomplete after a week at room temp.; the 2:4-dinitrophenylhydrazone (m. p. 188—221°), when recryst. from C_5H_5N , gave a less sol. scarlet form, m. p. 247° (Found: N, 12.9%), and an orange form, m. p. 198—200° (Found: N, 12.7%); the latter was obtained on dilution of the C_5H_5N liquors with H_2O and recrystn. of the ppt. from C_5H_5N or acetone. That

the low reactivity of the α -naphthyl ketone is due to the proximity of the second ring of the $C_{10}H_8$ nucleus is shown by the immediate formation under similar conditions of benzophenone-2 : 4-dinitrophenylhydrazone; this forms reddish-orange plates, m. p. 232°, from EtOAc containing a little EtOH (Found : N, 15.6. Calc. for $C_{19}H_{14}O_4N_4$: N, 15.5%).

When treated with a little $AlCl_3$ as described by Scholl and Seer, the pure α -naphthyl ketone (2 g.) gave pure 6-chlorobenzanthrone (0.9 g.), m. p. 187°. The crude ketone (15 g.) gave 4.5 g. The β -naphthyl ketone gave only indefinite materials, which in conc. H_2SO_4 gave pale brown colours similar to that given by the ketone.

Preparation of 5 : 8-Dichloro- α -naphthyl Phenyl Ketone.—A mixture of 5 : 8-dichloro- α -naphthoic acid (6.5 g., m. p. 181—185°), freshly distilled PCl_5 (2.72 g.; 1.1 mols.), and dry C_6H_6 (73 c.c.) was heated under reflux until evolution of HCl ceased (45 min.). The acid almost completely dissolved, but, after about 20 min., a yellow cryst. material was deposited. The mixture was cooled to 0°, and freshly prepared $AlCl_3$ (7.95 g.) added. The whole was heated gradually until reaction commenced (at about 70°) and then under reflux for 8.5 hr. The C_6H_6 solution was decanted and treated at 0° with conc. HCl (40 c.c.) in H_2O (90 c.c.). After removal of the C_6H_6 in steam, the insol. semi-solid residue was boiled with 4% NaOH aq. (100 c.c.), washed twice by decantation with H_2O , and extracted with hot EtOH. A small quantity of inorg. material was thus eliminated. Removal of the EtOH left a dark gum, which was taken up in Et_2O , washed with H_2O until the aq. layer was colourless (5 times), dried, and recovered as an oil which slowly and partly solidified. When dissolved in hot EtOH and allowed to cool, this deposited at first an oil; the solution decanted from this oil then deposited the required ketone in needles (2 g.), which after crystn. from EtOH had m. p. 93° after previous sintering (Found : C, 67.0; H, 3.0. $C_{17}H_{10}OCl_2$ requires C, 67.8; H, 3.3%).

When this ketone was heated with $AlCl_3$ -NaCl at 155—165° for 6 hr., evolution of HCl took place: the product was worked up in the usual manner. It was almost entirely sol. in Et_2O and the sparingly sol. portion had an indefinite m. p. (160—250°) and gave in H_2SO_4 a non-fluorescent, pale brownish-red solution. Since the pure ketone behaved similarly, it was concluded that no benzanthrone formation had taken place.

5-Chloroanthraquinone-1-carboxylic Acid.—5-Chloro-1-aminoanthraquinone forms scarlet needles, m. p. 215—217°, from AcOH; the acetyl derivative crystallises from AcOH in orange needles, m. p. 218—220° (Found : N, 4.9. $C_{16}H_{10}O_3NCl$ requires N, 4.7%). A solution of $NaNO_2$ (3.5 g.) in conc. H_2SO_4 (20 c.c.) was added slowly to a solution of 5-chloro-1-aminoanthraquinone (10 g.) in H_2SO_4 (50 c.c.). Diazotisation was complete in 5—10 min. and addition to ice (250 g.) pptd. the diazonium sulphate, which was collected, drained, and gradually added to a hot $KCu(CN)_2$ solution (prepared from $CuSO_4 \cdot 5H_2O$, 10.5 g.). After heating on the water-bath for 2 hr., the yellow product was collected, extracted twice with hot 3% NaOH aq., and dried. The nitrile could not be purified. The alkali extracted an acidic product which was not further investigated. The crude nitrile (5.5 g.) was gently boiled with H_2SO_4 (75 c.c. in H_2O , 20 c.c.) for 20 min.; a yellow sublimate (not α -chloroanthraquinone) then formed in small quantity. The dark solution was poured on ice, the product collected, and the acid extracted therefrom with hot Na_2CO_3 aq. The acid was best purified by way of the methyl ester, which formed pale yellow needles, m. p. 181°, from MeOH (Found : C, 64.1; H, 3.3. $C_{16}H_9O_4Cl$ requires C, 63.9; H, 3.0%). The m. p. of the ester was unchanged by admixture with the ester prepared from Butescu's α -chloroanthraquinone-1-carboxylic acid. It was hydrolysed by boiling for 20 hr. with HCl-AcOH (1 : 1). 5-Chloroanthraquinone-1-carboxylic acid formed yellow needles, m. p. 306° (decomp.), from AcOH (Found : C, 63.0; H, 3.0. $C_{15}H_7O_4Cl$ requires C, 62.8; H, 2.5%). The m. p. of the acid varies greatly with the rate of heating and is unreliable for identification, for which purpose, however, the methyl ester is suitable.

8-Chloroanthraquinone-1-carboxylic Acid.—8-Chloro-1-aminoanthraquinone forms red needles from AcOH, m. p. 225—227° (Found : N, 5.75. $C_{14}H_8O_3NCl$ requires N, 5.4%). The acetyl derivative crystallises from AcOH in rosettes of pale yellow needles, m. p. 223—225° (Found : Cl, 11.8. $C_{16}H_{10}O_3NCl$ requires Cl, 11.8%). This base (3.5 g.) in H_2SO_4 (18 c.c.) was rapidly diazotised by $NaNO_2$ (1.0 g.) in H_2SO_4 (17 c.c.) at room temp. The solution was poured on ice, and separation of the diazonium sulphate increased by addition of Na_2SO_4 . The diazonium salt in suspension in H_2O was converted into the nitrile by $KCu(CN)_2$ solution in the usual way and the crude nitrile (1 g.) was hydrolysed by gentle boiling with conc. H_2SO_4 (9 c.c.) and H_2O (3 c.c.) for 15 min. Dilution and extraction of the ppt. with alkali gave crude 8-chloroanthraquinone-1-carboxylic acid (0.4 g.) as a brown powder, m. p. 228—232°, alone or mixed with the acid obtained from 8 : 13-dichlorobenzanthrone. The methyl ester formed pale yellow needles

from MeOH, m. p. 124—125°, not depressed by admixture with the ester obtained from 8 : 13-dichlorobenzanthrone.

Oxidation of Benzanthrones.—This was best carried out by A. G. Perkin's method (J., 1920, 117, 706), which gave good yields in all cases. The acids were crystallised from AcOH, and the esters from MeOH. The following substituted anthraquinone acids were thus prepared, identity being confirmed in each case by mixed m. p. determinations: (a) 6-chloro-, m. p. 306° [*methyl* ester, m. p. 190—191° (Found: C, 64.1; H, 3.3. $C_{16}H_9O_4Cl$ requires C, 63.9; H, 3.0%); *acid chloride*, pale yellow prisms from C_6H_6 , m. p. 234—236° (decomp.) after previous sintering (Found: Cl, 22.9. $C_{15}H_8O_3Cl_2$ requires Cl, 23.3%)], from 6-chloro- and 6 : 13-dichloro-benzanthrones: (b) 8-chloro-, m. p. 228—232° [*methyl* ester, m. p. 124—125° (Found: C, 64.1; H, 3.3%)], from 8 : 13-dichlorobenzanthrone; (c) 7-chloro-, m. p. 262—264° (Found: C, 62.9; H, 3.0. $C_{15}H_7O_4Cl$ requires C, 62.8; H, 2.5%) [*methyl* ester, m. p. 193—194° (Found: C, 63.5; H, 3.0%)], from 7-chlorobenzanthrone (Scholl and Seer, *loc. cit.*). Anthraquinone-1-carboxylic acid itself, m. p. 289° (decomp.), was obtained from benzanthrone and 13-chlorobenzanthrone.

The authors gratefully acknowledge a grant from Imperial Chemical Industries, Ltd.

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[Received, March 11th, 1933.]