CCLIII.—*Anthracene*-1-*carboxylic and* -1 : 5-*dicarboxylic Acids and their Derivatives.*

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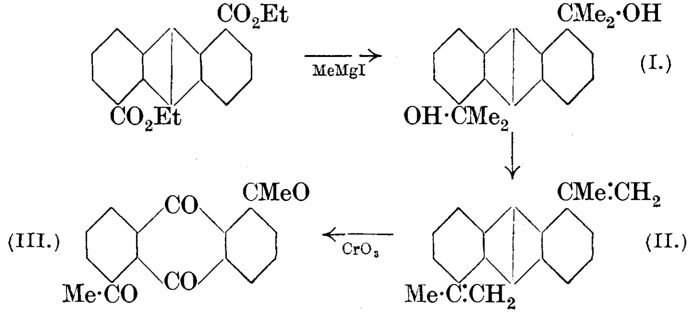
THE discovery of methylanthracenes in certain low-temperature tar distillates (Morgan and Coulson, J., 1929, 2203, 2551), together with the possibility that other alkylanthracenes might also be present, rendered it desirable to review the methods available for the preparation of such compounds. Some of these substances should be obtainable by a process depending primarily upon the action of a Grignard solution on the ester of an anthracenecarboxylic acid, and as a number of such acids are easily available it was decided to examine this method. Since Barnett and his co-workers have shown that substituents in α-positions may profoundly influence the properties of an anthracene derivative, it was decided in the first place to confine the investigation to the esters of the two acids mentioned in the title.

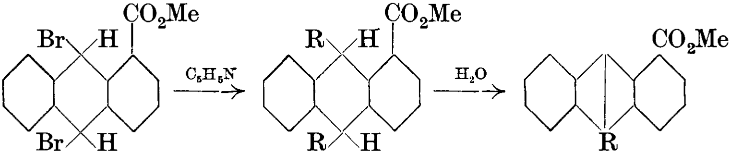
The results were disappointing, for the methyl monocarboxylate gave only resinous products both with methyl magnesium iodide and with benzyl magnesium chloride; and it was only with methyl magnesium iodide that any crystalline product was obtained from the ethyl dicarboxylic ester. This *diol* (I) lost water very easily, giving 1 : 5-*diï*so*propenylanthracene* (II), and this in turn yielded 1 : 5-*diacetylanthraquinone* (III) on oxidation.



This diacetylanthraquinone is probably identical with that, m. p.

318—319°, described (B.P. 289,585; U.S.P. 1,730,081) as being obtained by oxidising one of the diacetylanthracenes formed to a slight extent when anthracene is condensed with acetyl chloride.

Methyl anthracene-1-*carboxylate* when treated with bromine gives an additive compound which is undoubtedly (IV) although too unstable to be analysed. It readily passes into *methyl* 10(or 9)-*bromo-anthracene*-1-*carboxylate* by loss of hydrogen bromide, and with pyridine gives an unstable compound (undoubtedly V) which very easily loses a molecule of pyridine hydrobromide and passes into the stable *monopyridinium* salt (VI; or analogous 9-compound) (compare Barnett and Matthews, *Rec. trav. chim.*, 1924, **43**, 538).



(IV.) (V.) (VI.)

(R = $C_5H_5NBr\cdot$).

Of the possible formulæ for the bromoanthracene-1-carboxylic ester and the monopyridinium bromide, the two first-mentioned are the more probable, since Barnett and his co-workers (*Ber.*, 1929, **62**, 3064; 1930, **63**, 472, 1114, etc.) have brought forward considerable evidence in support of the suggestion that a group with lone electrons in an α-position tends to immobilise a hydrogen atom in the *peri*-position to it through co-ordination.

Ethyl anthracene-1 : 5-*dicarboxylate* is very inert towards halogens but a 9-*monobromo*-derivative was obtained in poor yield by bromination in boiling acetic acid solution. The prolonged action of chlorine resulted in the production of a substance which was not purified but was probably the 9 : 10-dichloro-compound. It reverted to the original ester when warmed or treated with pyridine.

EXPERIMENTAL.

Anthraquinone-1-*carboxylic Acid*.—In the preparation of this acid (Barnett, Cook, and Grainger, *Ber.*, 1924, **57**, 1777), oxidation proceeds more rapidly if 50 g. of benzanthrone, dissolved in 3 litres of water and 600 c.c. of concentrated sulphuric acid, are treated with 200 g. of chromium trioxide.

1 : 5-*Dicyanoanthraquinone*.—The method of Scholl, Haas, and Meyer (*Ber.*, 1927, **62**, 107), who prepared the compound from 1 : 5-diaminoanthraquinone, is less convenient than the following which is based on a method outlined in E.P. 261,422. 1 : 5-Dichloroanthraquinone (100 g.), benzyl cyanide (300 g.), and cuprous cyanide (80 g.)

were heated in an oil-bath beneath a wide air-condenser. At *ca.* 230° (bath temp.) a vigorous reaction set in, the cuprous cyanide and dichloroanthraquinone dissolved, and 1 : 5-dicyanoanthraquinone began to crystallise from the boiling solution. After ½ hour the solution was cooled, and the nitrile filtered off and repeatedly boiled with dilute nitric acid and water to free it from copper salts; yield 78 g. (83%). Although very sparingly soluble in the common solvents, it can be crystallised from benzyl cyanide and forms yellowish-brown needles, m. p. >360° (Scholl and co-workers give m. p. >390°, decomp.).

Anthraquinone-1 : 5-*dicarboxylic Acid.*—The nitrile (78 g.) was readily hydrolysed by a few minutes' boiling with 265 g. of concentrated sulphuric acid and 47 g. of water. Most of the dicarboxylic acid crystallised out at once; the mixture was cooled and diluted, and the acid filtered off and purified by extraction with dilute caustic soda and precipitation with acid. It formed colourless or white needles; yield 81 g., m. p. >360° (Scholl and co-workers obtained yellowish needles, m. p. >390°). No trace of the ethyl ester was obtained after boiling the acid (5·0 g.) for 6 hours with 20 g. of absolute alcohol containing 2·0 g. of concentrated sulphuric acid.

Anthracene-1-*carboxylic and* -1 : 5-*dicarboxylic Acids.*—The anthraquinone-mono- and -di-carboxylic acids were reduced in boiling, moderately concentrated, ammoniacal solution with zinc dust. In each case the reaction was complete in 4 hours, the initial carmine-red coloration being completely discharged. After filtration, the solutions were acidified. Anthracene-1-carboxylic acid was precipitated in yellow needles, m. p. 245° (compare Graebe and Blumenfeld, *Ber.*, 1897, **30**, 1118). *Anthracene*-1 : 5-*dicarboxylic acid*, also precipitated in yellow needles, was well washed with water. It is sparingly soluble in acetic acid and boiling water, and melts above 360° (Found : C, 71·9; H, 3·9. $C_{16}H_{10}O_4$ requires C, 72·2; H, 3·8%). In each case the yield was practically quantitative.

Methyl Anthracene-1-*carboxylate.*—5·0 G. of the dry acid and 7·0 g. of phosphorus pentachloride were ground together and then heated gently until the mixture reacted with liquefaction. The product was cooled, treated with methyl alcohol in slight excess in portions, and kept over-night. The *ester* which had separated was crystallised from acetic acid and formed irregular yellow plates, m. p. 108° (Found : C, 81·2; H, 4·96. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%).

Ethyl Anthracene-1 : 5-*dicarboxylate.*—A solution of the acid in dilute caustic soda was well shaken for 2 hours with excess of methyl *p*-toluenesulphonate but no crystalline ester separated. The acid (13 g.) was boiled with a solution of phosphorus pentachloride (21 g.) in phosphorus trichloride (50 g.), but it did not dissolve. Finally the ester was prepared by grinding the acid (33 g.) with phosphorus pentachloride (50 g.), heating the mixture to 150° for 2 hours, and treating it with alcohol after cooling. The crude ester was washed with cold caustic soda solution and water, and crystallised from acetic acid; yield 18·3 g., and 7·2 g. of acid were recovered from the soda extract. *Ethyl anthracene*-1 : 5-*dicarboxylate* separates from alcohol (in which it is slightly soluble), acetic acid, or benzene in pale yellow rhombic plates, m. p. 185° (Found: C, 74·3; H, 5·7. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%).

The two esters show brilliant purple fluorescence when illuminated by the carbon arc, but not noticeably in daylight.

Ethyl Anthraquinone-1 : 5-*dicarboxylate*.—The anthracenedicarboxylic ester, 3·2 g., was dissolved in sufficient boiling acetic acid, and 2·0 g. of chromium trioxide were added in portions. After a few minutes the solution was poured into water, and the viscous solid which separated on standing was recrystallised from acetic acid, forming tufts of very pale yellow, stout needles or prisms of the anthraquinone *ester*, m. p. 155°; yield 2·3 g. (Found: C, 67·9; H, 4·6. $C_{20}H_{16}O_6$ requires C, 67·9; H, 4·5%).

Action of Grignard Reagents upon Anthracene-1 : 5-*dicarboxylic Ethyl and* -1-*carboxylic Methyl Esters.* 1 : 5-*Di*iso*propylolanthracene* (I).—To the Grignard reagent prepared from 11·4 g. of methyl iodide and 2·0 g. of magnesium (8 mols.) in a little ether were added 3·2 g. of ethyl anthracene-1 : 5-dicarboxylate (1 mol.). The ester dissolved readily on boiling to give a deep yellow solution. After a further 2 hours' boiling, this was poured upon a mixture of crushed ice and ammonium chloride. A yellow gum separated and soon solidified. It was washed with dilute ammonium chloride solution and water, and crystallised from alcohol. The 1 : 5-*di*iso*propylolanthracene* (yield almost quantitative) formed pale yellow prisms containing 1 mol. of alcohol of crystallisation, which is lost at 100° (Found: C, 77·8; H, 7·9. $C_{20}H_{22}O_2,C_2H_5OH$ requires C, 77·6; H, 8·2%); the unsolvated *diol* crystallises from benzene in yellow flakes, m. p. 182·5°, showing a brilliant purple fluorescence when illuminated by the carbon arc (Found: C, 81·3; H, 7·5. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%); it dissolves in cold concentrated sulphuric acid with a deep green coloration.

The product from the interaction of methyl magnesium iodide (8 mols.) and methyl anthracene-1-carboxylate (1 mol.), carried out as above, was resinous and could not be obtained crystalline.

Benzyl magnesium chloride (8 mols.) and ethyl anthracene-1 : 5-dicarboxylate (1 mol.) did not interact in boiling ether: the ester did not dissolve and was recovered unchanged (m. p. and mixed m. p.). Methyl anthracene-1-carboxylate when treated with this Grignard reagent yielded an uncrystallisable gum. When ethyl magnesium bromide and the ethyl dicarboxylic ester reacted in boiling ether, and the product was worked up as before, there resulted a resinous mass from which nothing crystalline could be isolated.

1 : 5-*Di*iso*propenylanthracene* (II).—When the above diol was dissolved in boiling acetic acid it lost 2 mols. of water and the unsaturated *hydrocarbon* crystallised from the solution on cooling in large irregular yellow flakes, m. p. 121° (Found : C, 93·1 ; H, 6·7. $C_{20}H_{18}$ requires C, 93·0 ; H, 7·0%).

1 : 5-*Diacetylanthraquinone* (III).—To the hydrocarbon (1·50 g.), dissolved in sufficient boiling acetic acid, 3·67 g. of chromium trioxide were added in portions. The latter was rapidly reduced and the pale yellow oxidation product began to crystallise from the boiling solution. After ¼ hours' boiling, the whole was poured into water, which precipitated the crude *quinone.* This was washed with cold dilute caustic soda solution and water, and then crystallised from acetic acid in short pale yellow needles, m. p. 317° (darkening above 280°) (Found : C, 73·6 ; H, 4·3. $C_{18}H_{12}O_4$ requires C, 73·95 ; H, 4·1%).

Action of Bromine upon Methyl Anthracene-1-*carboxylate.*—A solution of 2·8 c.c. of bromine in 10 c.c. of carbon disulphide was gradually added with stirring to 12·0 g. of the ester suspended in 20 c.c. of carbon disulphide and cooled in ice and salt. The ester dissolved but no hydrogen bromide was evolved and a mass of colourless or white crystals began to separate. After 20 minutes the methyl 9 : 10-dibromo-9 : 10-dihydroanthracene-1-carboxylate (IV) was filtered off. In view of its instability no attempt was made to crystallise it.

Methyl 10(or 9)-*Bromoanthracene*-1-*carboxylate.*—The crystalline residue obtained by allowing carbon disulphide to evaporate from the mother-liquor was recrystallised from acetic acid (in which it is very soluble) and alcohol until it melted constantly at 130° and formed yellow needles (Found : Br, 25·4. $C_{16}H_{11}O_2Br$ requires Br, 25·4%).

1-*Carbomethoxyanthranyl*-10(or 9)-*pyridinium Bromide* (VI or similar).—When the dibromide (IV) was added to excess of cold pyridine it rapidly dissolved and a resin separated. After 2 days this was collected and crystallised from alcohol and ether. The colourless or white crystals of 1-carbomethoxy-9 : 10-dihydroanthraquinyl-9 : 10-dipyridinium dibromide (V), m. p. 180°, so obtained was exceedingly unstable and began at once to lose pyridine hydrobromide. The compound was boiled for ¼ hour with water, in which it is very soluble even in the cold. The aqueous solution rapidly became bright yellow, and on cooling, yellow needles of 1-*carbomethoxyanthranyl*-10(or 9)-*pyridinium bromide* separated, which when recrystallised from water melted at 271° (decomp.) (Found: Br, 25·2. $C_{21}H_{16}O_2NBr$ requires Br, 25·5%). It is insoluble in ether but moderately easily soluble in water or alcohol.

1-*Carbomethoxyanthranyl*-10(or 9)-*pyridinium dichromate*. This *salt* was precipitated when potassium dichromate solution was added to a boiling aqueous solution of the pyridinium bromide. It was recrystallised from boiling water, in which it is sparingly soluble, and formed orange needles, m. p. 192° [Found: Cr, 12·0. $(C_{21}H_{16}O_2N)_2Cr_2O_7$ requires Cr, 12·3%].

Action of Bromine upon Ethyl Anthracene-1 : 5-*dicarboxylate*.—The ester (3·0 g.), suspended in carbon disulphide (20 c.c.), was cooled in a freezing mixture, and a solution of bromine (1·6 g.) in carbon disulphide (10 c.c.) slowly added. There was no reaction even when the whole had acquired room temperature, and the ester was recovered after the bromine and carbon disulphide had been allowed to evaporate. It was also recovered unchanged after treatment with a solution of bromine in pyridine at the ordinary temperature for 3 days. When 3·0 g. of the ester and 1·6 g. of bromine were dissolved in 50 c.c. of acetic acid and boiled under reflux, hydrogen bromide was freely evolved. The mixture was cooled, crystals of unchanged ester (0·5 g.) were removed, and the solution was treated with water. The precipitated gummy product crystallised from acetic acid (in which it is very soluble) and alcohol, forming pale yellow rhombs, m. p. 117°, of *ethyl* 9-*bromoanthracene*-1 : 5-*dicarboxylate* (Found: Br, 19·8. $C_{20}H_{17}O_4Br$ requires Br, 19·95%).

Action of Chlorine upon Ethyl Anthracene-1 : 5-*dicarboxylate*.—The ester, when kept for several days with a solution of chlorine in carbon tetrachloride partly dissolved, and from the solution, by evaporation at the ordinary temperature and extraction of the residue with chloroform, a solution of the very unstable 9 : 10-dichloride was obtained which crystallised, as the chloroform evaporated, in very pale yellow rhombic plates, m. p. 125°; it could not be purified, however, as it so readily lost chlorine, re-forming the unchlorinated ester.

Bromine and 1 : 5-*Di*iso*propylolanthracene*.—No reaction occurred between equimolecular proportions dissolved in carbon disulphide at room temperature, and the diol was recovered unchanged after evaporation of the bromine and carbon disulphide.

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