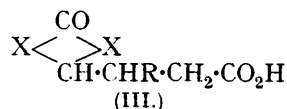
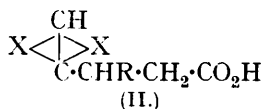
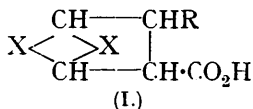


256. *Studies in the Anthracene Series. Part X.*

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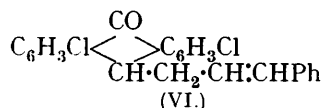
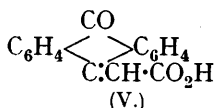
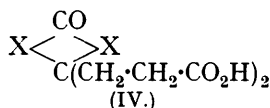
THE statements (E.P. 303,389) that the adjects of anthracene derivatives with certain $\alpha\beta$ -unsaturated acids are characterised by a strong fluorescence suggested that they might be tautomeric mixtures of (I) and (II), although no evidence of this was detected with the maleic acid adjects (Barnett, Goodway, and Higgins, J., 1934, 1224). It has now been found



that the pure adjects show no visible fluorescence, and that those of anthracene and cinnamic acid (I; X = C₆H₄, R = Ph) and of 1:4-dimethylantracene and acrylic acid (I; X = C₆H₃Me, R = H) are quite different from the corresponding anthranlypropionic acids (II), obtained by condensing the anthrone with the unsaturated acid and then reducing the resulting anthronylpropionic acid (III). No indication of the interconvertibility of the isomerides could be detected.

The formation, under the influence of hydrogen chloride, of the endocyclic adjects (I; R = H) from anthracene derivatives and acrylic acid (most conveniently used in the form of β -chloropropionic acid) is very general, and the adjects formed from 9:10-dichloro- and 9:10-dibromo-anthracene, like the corresponding adjects from maleic anhydride (Barnett, Goodway, and Higgins, *loc. cit.*), are stable towards alcoholic alkali. With cinnamic acid, adject formation takes place less readily, and no addition compound was formed with 9:10-dichloroanthracene.

The condensation of an anthrone with acrylic acid is also a general reaction, and when a substituent is present in the *peri*-position to the carbonyl group, the product is the anthronylpropionic acid (III). In the absence of such a substituent, the product is the anthronylidenedipropionic acid (IV), a type of compound not formed from maleic acid



(Barnett, Goodway, and Higgins, *loc. cit.*). Condensation of an anthrone with cinnamic acid takes place very much less readily, and even anthrone itself gives only β -phenyl- β -anthronylpropionic acid (III; X = C₆H₄, R = Ph).

The presence of a chlorine atom in the *peri*-position to the propionic acid residue does not lead to the loss of this residue on reduction, the anthronylpropionic acids differing in this way from the corresponding anthronylsuccinic acids (Barnett, Goodway, and Higgins, *loc. cit.*).

In the above patent specification, it is stated that an $\alpha\beta$ -unsaturated acid will condense with any polycyclic aromatic hydrocarbon containing more than two condensed benzene nuclei, and an acid, m. p. 132°, is specifically mentioned as being obtained from phenanthrene and β -chloropropionic acid. We have been unable to obtain any indication of the formation of such a compound under any conditions. Further, in an attempt to condense commercial pyrene with β -chloropropionic acid, the former was merely decolorised, the recovered hydrocarbon being completely colourless (compare Clar, *Ber.*, 1932, 65, 1425).

Chloroacetic acid could not be condensed with either anthracene or anthrone (alone or in the presence of alkali). Dichloroacetic acid, however, condensed with anthrone in the presence of caustic soda to give *anthronylideneacetic acid* (V), but the yield was extremely poor and the reaction unreliable. An attempt to condense anthrone with cinnamyl chloride gave only resinous products, but 1:5-dichloroanthrone gave the *cinnamylanthrone* (VI) in poor yield, and from this 1:5-dichloroanthronylacetic acid was obtained by oxidation.

EXPERIMENTAL.

$\alpha\beta$ -endo-9 : 10-Dihydroanthraquinyl-9 : 10-propionic Acids (I; R = H).—The anthracene (0.1 mol.) and β -chloropropionic acid (0.15 mol.) were boiled in *o*-dichlorobenzene (50 c.c.) for 8 hrs., the solvent removed with steam, and the acid precipitated from its filtered alkaline solution with hydrochloric acid. The following four compounds were prepared in this way and, after repeated recrystallisation from the solvent shown in parentheses, were colourless and showed no visible fluorescence when their neutral or alkaline solutions were inspected in the light of the arc lamp.

Condensation product from anthracene (methanol), m. p. 186°; from 1 : 4-dimethylanthracene (toluene), m. p. 250° (Found: C, 82.1; H, 6.5. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%); from 9 : 10-dichloroanthracene (anisole), m. p. 245° (Found: C, 63.8; H, 3.9. $C_{17}H_{12}O_2Cl_2$ requires C, 63.9; H, 3.8%); from 9 : 10-dibromoanthracene (anisole), m. p. 252° (Found: C, 50.2; H, 3.1. $C_{17}H_{12}O_2Br_2$ requires C, 50.0; H, 2.9%). No ionised halogen could be detected after the last two had been boiled for 40 mins. with 10% alcoholic caustic potash.

$\alpha\beta$ -endo-9 : 10-Dihydroanthraquinyl-9 : 10- β -phenylpropionic Acid (I; X = C_6H_4 , R = Ph).—A current of hydrogen chloride was passed for 12 hours through a boiling solution of 17 g. of anthracene and 20 g. of cinnamic acid in 50 c.c. of *o*-dichlorobenzene. After distillation with steam, the residue was extracted with caustic soda, and the precipitate obtained by adding hydrochloric acid to the filtered alkaline solution was extracted with boiling 50% acetic acid to remove cinnamic acid. After recrystallisation from anisole, the product was colourless and non-fluorescent both in neutral and in alkaline solution. It melted at 248° (bath preheated to 225°) and depressed the m. p. of the phenylanthranlypropionic acid mentioned below (Found: C, 84.5; H, 5.7. $C_{23}H_{18}O_2$ requires C, 84.6; H, 5.5%).

Anthronylidenedipropionic Acids (IV) and Anthronylpropionic Acids (III).—The anthrone (1 part) and β -chloropropionic acid (1 part) were boiled with *o*-dichlorobenzene (3—4 parts) for 8 hrs., the solvent removed with steam, and the product precipitated from its filtered solution in sodium carbonate by hydrochloric acid. After recrystallisation from the solvent given in parentheses, the products were all colourless. The acids of type (IV) gave colourless solutions in caustic soda, and those of type (III) gave orange solutions, except the 4 : 5-dichloro- and the 1 : 4-dimethyl-compound, which gave colourless solutions (compare the corresponding anthronylsuccinic acids, Barnett, Goodway, and Higgins, *loc. cit.*).

Anthronylidenedipropionic acid (ethyl acetate), m. p. 248—250° (decomp.) (Found: C, 70.8; H, 5.5. $C_{20}H_{18}O_5$ requires C, 71.0; H, 5.3%). 2 : 3-Dimethylanthronylidenedipropionic acid, (anisole), m. p. 298° (Found: C, 72.0; H, 6.1. $C_{22}H_{22}O_5$ requires C, 72.1; H, 6.0%). 1 : 5-Dichloroanthronylpropionic acid (anisole), m. p. 163° (after drying at 110°) (Found: C, 61.2; H, 3.8. $C_{17}H_{12}O_3Cl_2$ requires C, 60.9; H, 3.6%). 1 : 8-Dichloroanthronylpropionic acid (ethyl acetate), m. p. 204° (Found: C, 60.9; H, 3.8). 4 : 5-Dichloroanthronylpropionic acid (benzene), m. p. 174° (Found: C, 60.7; H, 3.8%). 1 : 4-Dimethylanthronylpropionic acid (ethyl acetate), m. p. 168° (Found: C, 77.5; H, 6.2. $C_{19}H_{18}O_3$ requires C, 77.5; H, 6.1%).

1 : 4-Dimethylanthronylpropionic Acid (II; X = C_6H_3Me , R = H).—1 : 4-Dimethylanthronylpropionic acid (3.5 g.) was boiled for 4 hrs. with 10 g. of zinc dust (activated with copper sulphate) and 100 c.c. of 2*N*-caustic soda. The product obtained by adding hydrochloric acid to the filtered solution was recrystallised from methanol and from toluene, and was then yellow and had m. p. 205°. Its neutral and alkaline solutions were strongly fluorescent (Found: C, 81.8; H, 6.5. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%).

The reduction of the other anthronylpropionic acids gave products which were completely soluble in alkali but could not be crystallised.

β -Phenyl- β -anthronylpropionic Acid (III; X = C_6H_4 , R = Ph).—Hydrogen chloride was passed for 15 hrs. through a boiling solution of 30 g. of anthrone and 30 g. of cinnamic acid in 100 c.c. of *o*-dichlorobenzene. The sodium carbonate extract, obtained as for (IV), was cooled, saturated with carbon dioxide, and the filtered solution made strongly acid with hydrochloric acid. Unchanged cinnamic acid was removed from the precipitate by boiling water, and the residue recrystallised from xylene. The colourless product (14 g.) was recrystallised from anisole and then had m. p. 197° as stated by Meerwein (*J. pr. Chem.*, 1918, **97**, 284), who obtained it by a different method (Found: C, 80.4; H, 5.4%).

β -Phenyl- β -anthranlypropionic Acid (II; X = C_6H_4 , R = Ph).—The foregoing acid (5 g.) was reduced as above (1½ hrs.; 20 g. of zinc dust), and the product obtained by adding hydrochloric acid to the filtrate was recrystallised from glacial acetic acid containing a little hydro-

chloric acid and then from xylene. The resulting colourless crystals, m. p. 225° , were strongly fluorescent in neutral and in alkaline solution. They showed reversible deepening in colour, and were yellow at 130° (Found: C, 84.5; H, 5.8. $C_{23}H_{18}O_2$ requires C, 84.6; H, 5.5%).

Anthronylideneacetic Acid (V).—Dichloroacetic acid (100 g.) was slowly added to 50 g. of anthrone and 150 g. of caustic potash in 1 l. of boiling water, the mixture cooled and acidified with hydrochloric acid, the washed solid extracted with sodium carbonate, the cold extract saturated with carbon dioxide, and the filtrate acidified with hydrochloric acid. After recrystallisation from methanol and from anisole, the product (1 g.) was colourless and non-fluorescent, and melted at 205° (Found: C, 76.6; H, 4.2. $C_{16}H_{10}O_3$ requires C, 76.8; H, 4.0%).

1:5-Dichloro-10-cinnamylanthrone (VI).—1:5-Dichloroanthrone (5 g.) was boiled for 1 hr. with 5 c.c. of cinnamyl chloride and 3.5 g. of caustic potash in 12.5 c.c. of water. The viscous product was dried (potassium carbonate) in ethereal solution, and the solution concentrated and cooled in a freezing mixture. The resulting crystals after recrystallisation from ethyl acetate were colourless and melted at 148° (yield < 20%) (Found: C, 72.9; H, 4.4. $C_{23}H_{16}OCl_2$ requires C, 72.8; H, 4.2%).

1:5-Dichloroanthronylacetic Acid.—A solution of 1 g. of chromium trioxide in aqueous acetic acid was added during 1 hr. to 1 g. of the above anthrone in 15 c.c. of boiling glacial acetic acid, and the whole boiled for another hour. The product obtained by pouring the cooled solution into water was extracted with cold sodium carbonate, and the solid which separated from the filtered extract on the addition of hydrochloric acid was extracted with boiling water to remove benzoic acid. The residue after recrystallisation from methanol (charcoal), toluene, and anisole was colourless; m. p. 218° after slight sintering (Found: C, 59.8; H, 3.3. $C_{16}H_{10}O_3Cl_2$ requires C, 59.8; H, 3.1%).

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