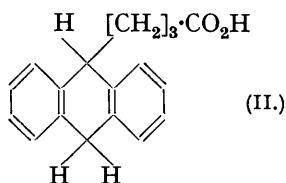
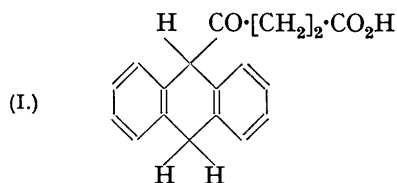


57. Polycyclic Aromatic Hydrocarbons. Part XIX.

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The Friedel-Crafts reaction between 9:10-dihydroanthracene and succinic anhydride leads, in nitrobenzene solution, to β -9-(9:10-dihydro)anthroylpropionic acid (I). Thus, substitution occurs at a saturated carbon atom, in a molecule in which aromatic rings with free positions are present.

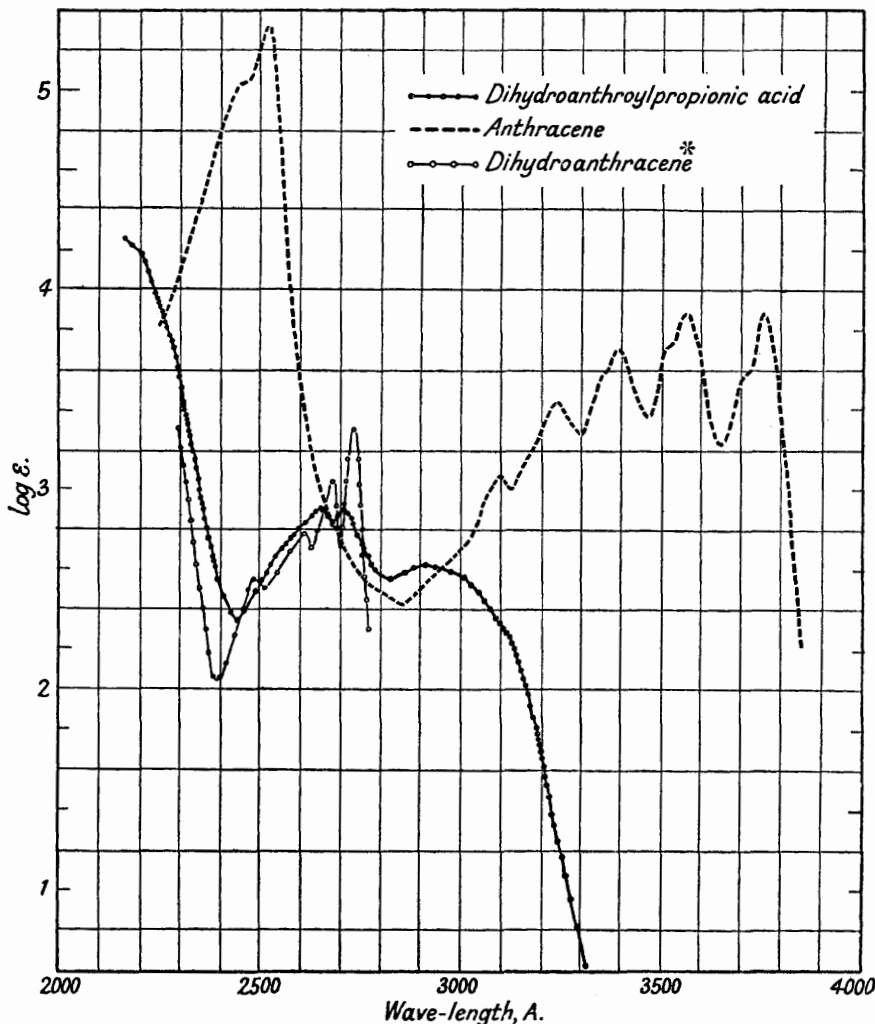
In the synthesis of 1'-methyl-1:2-benzanthracene (Cook and Robinson, J., 1938, 505) use was made of the ready isolation of β -2-anthroylpropionic acid from the products of interaction of anthracene and succinic anhydride (compare Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, 54, 4355). Isomerides were also formed, so that the yield of this keto-acid was less than 20%, and in the expectation that 9:10-dihydroanthracene would undergo substitution almost exclusively in position 2 we have studied the condensation of this hydrocarbon with succinic anhydride, in an attempt to improve the synthesis of 1'-methyl-1:2-benzanthracene. A homogeneous keto-acid was obtained, but this could be oxidised with great facility to 9:10-anthraquinone and hence was β -9-(9:10-dihydro)anthroylpropionic acid (I). On account of the known tendency for dihydroanthracene derivatives to undergo



dehydrogenation under the influence of aluminium chloride, it was necessary to exclude the possibility that our product was β -9-anthroylpropionic acid. This was done by

spectroscopic comparison, which shows clearly that the keto-acid conforms to the dihydroanthracene type rather than to the more complex anthracene type of absorption (see Figure), and also by reduction (Wolff-Kishner method) to γ -9-(9:10-dihydro)-anthranilylbutyric acid (II), the dihydro-character of which was established by its dehydrogenation to γ -9-anthranilylbutyric acid.

This unusual type of substitution, replacement of aliphatically-bound hydrogen during



* From Barnett, Cook, and Ellison (J., 1928, 886).

a Friedel-Crafts reaction in a molecule in which aromatic rings with free positions are also present, illustrates the exceptional reactivity of the methylene groups of 9:10-dihydroanthracene. Under the same conditions diphenylmethane underwent normal nuclear substitution with the production of β -p-benzylbenzoylpropionic acid. There are numerous examples of substitution (halogenation, oxidation, nitration) in a methylene group attached to an aromatic nucleus, but such substitution is very exceptional in the Friedel-Crafts reaction. The closest analogy to the example now recorded is the facile conversion of ϵ -phenyl-*n*-amyl chloride into phenylcyclopentane rather than benzsuberane by cyclisation with aluminium chloride (v. Braun and Deutsch, *Ber.*, 1912, 45, 1267).

The Friedel-Crafts reaction with saturated hydrocarbons is commonly regarded as

proceeding through an intermediate unsaturated hydrocarbon formed by the dehydrogenating action of aluminium chloride (see, for example, Zelinsky and Tarassowa, *Annalen*, 1934, 508, 115; Nenitzescu and Cantuniari, *ibid.*, 1934, 510, 269; Nenitzescu and Curcăneanu, *Ber.*, 1938, 71, 2063). In the case of 9 : 10-dihydroanthracene such a mechanism seems excluded, for the intermediate compound would be anthracene, which is known to undergo considerable substitution in the lateral rings under the conditions used. Hence we conclude that direct replacement of hydrogen is the most probable course of the reaction.

EXPERIMENTAL.

β -9-(9 : 10-Dihydro)anthroylpropionic Acid (I) (compare Meister Lucius and Brüning, D.R.P. 376,635).—Succinic anhydride (2.8 g.), aluminium chloride (3.7 g.), and 9 : 10-dihydroanthracene (5 g.) were added consecutively, with stirring, to nitrobenzene (28 g.), and the ice-cooled suspension was subsequently stirred for 5 hours. The product was decomposed with ice and hydrochloric acid, the solvent removed in steam, and the residue extracted with dilute sodium carbonate solution; the solution was filtered from unreacted dihydroanthracene (2.4 g.), and the acidic product precipitated (3 g.). A single crystallisation from alcohol gave pure β -9-(9 : 10-dihydro)anthroylpropionic acid (I), which after recrystallisation from benzene formed colourless needles, m. p. 160—161° (Found : C, 77.0; H, 5.8. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.75%). Its semicarbazone formed colourless needles (from methyl alcohol), m. p. 203—204° (decomp.) (Found : C, 67.4; H, 5.7. $C_{19}H_{19}O_3N_3$ requires C, 67.6; H, 5.7%).

Oxidation of the keto-acid with chromic acid in boiling acetic acid or with ice-cold dilute alkaline permanganate gave anthraquinone, m. p. 279—280°, identified by comparison with an authentic sample.

γ -9-(9 : 10 Dihydro)anthranylbutyric Acid (II).—The aforesaid semicarbazone (2 g.) was heated in a sealed tube at 180° for 18 hours with sodium ethoxide (2 g. of sodium in 30 c.c. of absolute alcohol). The resulting γ -9-(9 : 10-dihydro)anthranylbutyric acid (II) (5 g. from 10 g. of semicarbazone) formed colourless plates (from ligroin), m. p. 132—133° (Found : C, 81.1; H, 6.8. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%). A by-product of the reduction was an unidentified neutral compound which crystallised from benzene in yellowish prismatic needles, decomposing above 220°.

γ -9-Anthranylbutyric Acid.—The dihydro-acid (1 g.) was heated with sulphur (0.12 g.) at 220—230° for 1½ hours. The dehydrogenated acid was recrystallised from benzene (yield, 0.75 g.; m. p. 184—186°) and purified by crystallisation of its sodium salt from a little dilute sodium carbonate solution. γ -9-Anthranylbutyric acid formed pale yellow prisms (from benzene), m. p. 187.5—188.5°, and was oxidised to anthraquinone by sodium dichromate in boiling acetic acid (Found : C, 81.9; H, 6.1. $C_{18}H_{16}O_2$ requires C, 81.8; H, 6.1%).

β -p-Benzylbenzoylpropionic Acid.—The condensation of diphenylmethane and succinic anhydride was carried out as described above and gave β -p-benzylbenzoylpropionic acid, m. p. 125—126° (from alcohol) (Found : C, 76.0; H, 5.8. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%). Oxidation with hot dilute alkaline permanganate solution gave p-benzoylbenzoic acid, m. p. 195—196° (lit., 194°).

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