

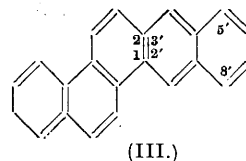
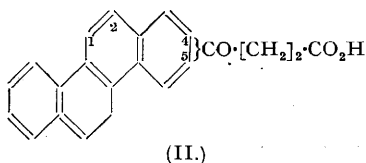
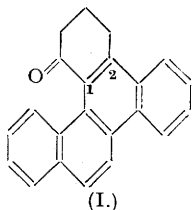
88. The Condensation of Chrysene with Succinic Anhydride.

By J. W. COOK and WALTER GRAHAM.

The product obtained by condensation of chrysene with succinic anhydride by means of aluminium chloride in nitrobenzene solution has been shown to be β -(4- or 5-chrysenoyl)propionic acid (II). Through the stages leading to a new fused benzene ring it has been converted into 1 : 2-(2' : 3'-naphtha)phenanthrene (III).

By the Friedel-Crafts reaction between chrysene and succinic anhydride in benzene solution, Beyer (*Ber.*, 1938, **71**, 915) obtained a keto-acid, m. p. 197—198°, to which he attributed the structure of β -(2-chrysenoyl)propionic acid. Reduction to the butyric acid followed by cyclisation gave 1'-keto-1' : 2' : 3' : 4'-tetrahydro-1 : 2-benzchrysene (I), and the anomalous behaviour of the carbonyl group in this pentacyclic ketone is in accord with the hindered structure assigned to it. Beyer found that Clemmensen reduction of the ketone gave the corresponding hydroxy-compound, and we have obtained this as the only crystalline product when the reduction was carried out with hydrazine hydrate in alcoholic sodium ethoxide at 200° (compare Kon and Soper, *J.*, 1940, 1335). We were unable to convert this carbinol into 1 : 2 : 3 : 4-dibenzphenanthrene.

When the Friedel-Crafts reaction between chrysene and succinic anhydride was carried out in nitrobenzene solution, Beyer obtained an isomeric keto-acid, m. p. 221—223°, which he regarded provisionally as β -(1-chrysenoyl)propionic acid. Funke and Müller (*J. pr. Chem.*, 1936, **144**, 242) had obtained, from chrysene, acetyl chloride, and aluminium chloride in carbon disulphide solution, two acetylchrysenes, one of which has been shown to be 2-acetylchrysene (see Newman and Cathcart, *J. Org. Chem.*, 1940, **5**, 618). The other is not 1-acetylchrysene, as Funke and Müller supposed, for the ethylchrysene which it gave on reduction is different from synthetic 1-ethylchrysene (Newman, *J. Amer. Chem. Soc.*, 1940, **62**, 873). Moreover, it is well known that in Friedel-Crafts reactions with phenanthrene in nitrobenzene solution the substituent enters a β -position of a side ring. Hence we considered it more likely that Beyer's chrysenoylpropionic acid, m. p. 221°, was the 4- or the 5-compound (II). We have confirmed this by converting it into the 1 : 2-(2' : 3'-naphtha)phenanthrene (III) of Clar (*Ber.*, 1929, **62**, 350, 1574; compare Cook, Hieger, Kennaway, and Mayneord, *Proc. Roy. Soc.*, 1932, *B*, **111**, 465). The non-formation of picene (3 : 4-benzchrysene) in this synthesis makes position 5 more probable for the substituent in the chrysenoylpropionic acid.



EXPERIMENTAL.

β -(4- or 5-Chrysenoyl)propionic Acid (II).—A solution of anhydrous aluminium chloride (13.3 g.) in nitrobenzene (75 c.c.) was added to a stirred suspension of chrysene (11.4 g.) and succinic anhydride (5 g.), both finely powdered, in nitrobenzene (100 c.c.). Stirring was continued for 6 hours at 20°. After being kept overnight the dark red solution was poured on ice and hydrochloric acid, and the nitrobenzene removed in steam. The residue, washed with a little ether, was extracted with hot sodium carbonate solution and filtered from unreacted chrysene (6.5 g.). Acidification of the filtrate gave a grey precipitate which was dried, washed with boiling ether, and then extracted with boiling benzene. The solid which separated from the cold benzene extract was twice recrystallised from acetic acid (charcoal) and gave β -(4- or 5-chrysenoyl)propionic acid (0.9 g.) as pale yellow plates, m. p. 218—221°. When the amounts of succinic

anhydride and aluminium chloride were increased by 25% and 12.5%, respectively, and the reaction carried out at 30°, the yield was increased to 1.5 g. A lower yield was obtained at 45°, and an inseparable mixture of acids at 0°.

By concentration of the benzene liquors, followed by fractional crystallisation of the residue from acetic acid, there was obtained a small amount of β -(2-chrysenoyl)propionic acid, m. p. 192—194°.

Reduction of β -(4- or 5-chrysenoyl)propionic acid (2 g.) by Martin's modification (*J. Amer. Chem. Soc.*, 1936, 58, 1438) of Clemmensen's method gave γ -(4- or 5-chrysenyl)butyric acid (1.5 g.), m. p. 210.5—212.5° (Beyer, *loc. cit.*, gives m. p. 213—214°).

5'- or 8'-Keto-5': 6': 7': 8'-tetrahydro-1: 2-(2': 3'-naphtha)phenanthrene.—Phosphorus pentachloride (0.75 g.) was added gradually, with shaking, to a suspension of the aforesaid butyric acid (1 g.) in dry benzene (10 c.c.). After an hour a clear solution of the acid chloride was formed, and a solution of stannic chloride (0.5 c.c.) in benzene (2 c.c.) was then added. After being kept for 20 hours at room temperature, with occasional shaking, the tin complex was decomposed with ice and hydrochloric acid, the benzene was removed in steam, and the suspended solid was extracted with sodium carbonate solution and then crystallised from acetic acid (charcoal). The pentacyclic ketone (0.75 g.) formed pale yellow plates which decomposed above 275° (Found: C, 89.1; H, 5.4. $C_{22}H_{16}O$ requires C, 89.2; H, 5.4%).

5': 6': 7': 8'-Tetrahydro-1: 2-(2': 3'-naphtha)phenanthrene.—The foregoing ketone (0.25 g.) was heated in a sealed tube at 200° for 18 hours with alcoholic sodium ethoxide (from 0.5 g. of sodium and 11 c.c. of alcohol) and 99% hydrazine hydrate (1 c.c.). The pale yellow solid was collected and extracted 4 times with boiling alcohol (portions of 40 c.c.). The yellow insoluble residue, probably an azine, could not be crystallised. Concentration of the alcoholic extract gave the hydrocarbon (0.45 g. from 0.8 g. of ketone), which formed colourless plates (from alcohol), m. p. 217—218° (Found: C, 93.5; H, 6.3. $C_{22}H_{18}$ requires C, 93.6; H, 6.4%). Dehydrogenation of this hydrocarbon (0.2 g.) was effected by heating at 300° for 3 hours with palladium black (20 mg.) in an evacuated sealed tube. Unchanged material was extracted with boiling alcohol, and the residual solid was recrystallised several times from xylene. The resulting yellowish leaflets had m. p. 292—294°, alone or mixed with a specimen of 1: 2-(2': 3'-naphtha)phenanthrene prepared from phenanthrene (Cook *et al.*, *loc. cit.*). To complete the identification the 2: 7-dinitroanthraquinone complex was prepared from each specimen. It formed maroon-coloured microscopic needles, m. p. 278—279° (Found: N, 4.9. $C_{28}H_{20}O_6N_2$ requires N, 4.9%).

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UNIVERSITY OF GLASGOW.

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