

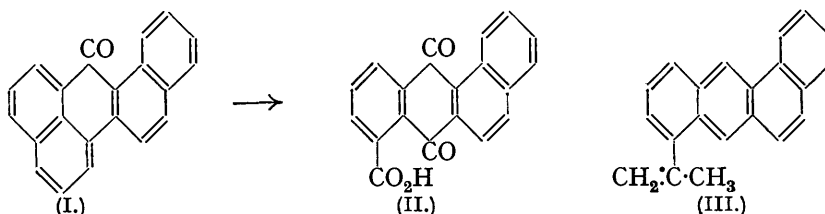
### 58. *Polycyclic Aromatic Hydrocarbons. Part XX.*

By J. W. COOK and C. G. M. DE WORMS.

5-isoPropyl-1:2-benzanthracene, which could not be obtained from 5-keto-5:6:7:8-tetrahydro-1:2-benzanthracene and isopropylmagnesium bromide, has been synthesised from ethyl 1:2-benz-5-anthroate and methylmagnesium iodide. The requisite 1:2-benz-5-anthroic acid was obtained by degradation of 1:2:5:10-dibenz-9-anthrone.

INTRODUCTION of a methyl group into position 10 of the 1 : 2-benzanthracene molecule gives a potent carcinogenic hydrocarbon, whereas an *isopropyl* group in this position is ineffective. On the other hand, 6-*isopropyl*-1 : 2-benzanthracene is much more active than the 6-methyl compound. These curious relationships led us to synthesise 5-*isopropyl*-1 : 2-benzanthracene for comparison with the 5-methyl compound. A series of 5-alkyl-1 : 2-benzanthracenes has been prepared by the action of Grignard reagents on 5-keto-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene, but this method failed in the case of the *isopropyl* compound (J., 1933, 1592; 1937, 393; and unpublished experiments), so that in this case an alternative route was necessary. A satisfactory method is now recorded.

The *peri* ring-closure of 1 : 1'-dinaphthyl ketone to 1 : 2 : 5 : 10-dibenz-9-anthrone (I) has been mentioned in the patent literature (Scholl, D.R.-P. 239,761) and also the synthesis of a dibenzanthrone of undetermined constitution from 1 : 2-benzanthraquinone by the glycerol method (Badische Anilin und Soda Fabrik, D.R.-P. 181,176). Repetition of the latter synthesis has shown that the product is likewise 1 : 2 : 5 : 10-dibenz-9-anthrone, although for preparative purposes the former method is to be preferred.



Oxidation of the dibenzanthrone with chromic acid in boiling acetic acid led to 1 : 2-benzanthraquinone-5-carboxylic acid (II), which was reduced to 1 : 2-benz-5-anthraic acid, the ethyl ester of which reacted with methylmagnesium iodide to give a carbinol, dehydrated by picric acid to 5-*isopropenyl*-1 : 2-benzanthracene (III). 5-*iso*Propyl-1 : 2-benzanthracene was obtained from (III) by catalytic hydrogenation.

#### EXPERIMENTAL.

1 : 2 : 5 : 10-Dibenz-9-anthrone (I).—The 1 : 1'-dinaphthyl ketone required for this was most suitably obtained by hydrolysis of the ketimine resulting from 1-naphthylmagnesium bromide and 1-naphthonitrile (Tschitschibabin and Korjagin, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1828), the procedure of Newman (*J. Amer. Chem. Soc.*, 1937, **59**, 2472) for the preparation of 1-naphthonitrile being simplified as follows :

A mixture of 1-bromonaphthalene (150 g.) and cuprous cyanide (75 g.) was slowly heated to 270° and the temperature maintained at this point for  $\frac{1}{2}$  hour, during which a violent reaction sometimes set in. The temperature was then raised so that the nitrile distilled (b. p. ca. 290°; yield, 96 g. = 86%); purification was completed by redistillation under reduced pressure.

For cyclisation, 1 : 1'-dinaphthyl ketone (80 g.) was intimately mixed with anhydrous aluminium chloride (320 g.) and sodium chloride (80 g.), and the mechanically stirred mixture was slowly heated to 100°, at which temperature the mass fused and hydrogen chloride was liberated. After continued stirring at 100° for an hour, the black viscous liquid was poured on much ice. After the aluminium chloride complex was fully decomposed, the solid was collected and extracted five times with glacial acetic acid. Much tarry material remained undissolved. The crystalline product obtained from the extract was recrystallised from acetic acid (charcoal); it then had m. p. 182—185° (yield, 21 g. = 27%). For analysis, a sample was sublimed in a vacuum and then recrystallised from glacial acetic acid. 1 : 2 : 5 : 10-Dibenz-9-anthrone (I) formed orange needles, m. p. 184—185° (Found : C, 89.8; H, 4.8. Calc. for  $C_{21}H_{12}O$  : C, 89.95; H, 4.3%).

1 : 2-Benzanthraquinone-5-carboxylic Acid (II).—A solution of chromic acid (90 g.) in 80% acetic acid (200 c.c.) was added during  $1\frac{1}{2}$  hours to a boiling suspension of finely powdered 1 : 2 : 5 : 10-dibenz-9-anthrone (21 g.) in acetic acid (400 c.c.). After a further hour's boiling, the solution was evaporated under reduced pressure, the residue dissolved in water and treated with excess of dilute sodium carbonate solution, and the chromium hydroxide repeatedly extracted with boiling dilute sodium carbonate solution. The orange filtrate was acidified, and the precipitated acid dissolved in a small volume of boiling 2*N*-sodium carbonate. On cooling,

the sodium salt of 1 : 2-benzanthraquinone-5-carboxylic acid (II) separated in gold spangles (10.1 g.). The free acid, not obtained analytically pure, crystallised from a large volume of acetic acid in yellow needles, m. p. 295—296° (Found : C, 74.7; H, 3.3.  $C_{19}H_{10}O_4$  requires C, 75.4; H, 3.3%). The methyl ester, obtained with methyl alcohol and hydrogen chloride, formed golden needles (from methyl alcohol), m. p. 163—165° (Found : C, 75.8; H, 4.0.  $C_{20}H_{12}O_4$  requires C, 75.9; H, 3.8%).

The structure of the acid (II) was confirmed by oxidation with permanganic acid to anthraquinone-1 : 2 : 5-tricarboxylic acid, identified by comparison of its trimethyl ester with an authentic specimen (Cook, J., 1933, 1592).

1 : 2-Benz-5-anthroic Acid.—A solution of stannous chloride (37 g.) in hydrochloric acid (120 c.c.) was added to a boiling suspension of the sodium salt of the quinone-acid (10 g.) in acetic acid (900 c.c.) and the whole was boiled for an hour and then poured into water. The red precipitate was collected as rapidly as possible and reduced with zinc dust (70 g.) and boiling *N*-sodium hydroxide (800 c.c.) (9 hours). The resulting acid was purified through its somewhat sparingly soluble sodium salt and was then recrystallised from acetic acid. 1 : 2-Benz-5-anthroic acid (3.8 g.) formed yellow leaflets, m. p. 286—287° (Found : C, 82.9; H, 4.4.  $C_{19}H_{12}O_2$  requires C, 83.8; H, 4.4%).

The amide, formed by the action of dry ammonia on a benzene solution of the acid chloride, formed colourless leaflets (from dioxan), m. p. 309—310° (Found : C, 83.9; H, 5.0.  $C_{19}H_{13}ON$  requires C, 84.1; H, 4.8%), and was dehydrated to the nitrile, orange needles, m. p. 190—191° (from benzene-alcohol) (Found : C, 89.9; H, 4.6.  $C_{19}H_{11}N$  requires C, 90.1; H, 4.4%), by boiling phthalic anhydride (compare Waldmann and Oblath, *Ber.*, 1938, 71, 366). Ethyl 1 : 2-benz-5-anthroate, prepared by esterification with alcoholic hydrogen chloride, formed fluffy yellowish needles (from hexane), m. p. 89—90° (Found : C, 84.1; H, 5.3.  $C_{21}H_{16}O_2$  requires C, 84.0; H, 5.4%).

5-isoPropenyl-1 : 2-benzanthracene (III).—The foregoing ester (2.8 g.) was added to an ice-cold filtered Grignard solution prepared from methyl iodide (3.3 c.c.), magnesium turnings (1.3 g.), and anhydrous ether (40 c.c.). The solution was allowed to warm to room temperature and was then boiled for 2 hours, and decomposed with ice and hydrochloric acid. The crude tertiary carbinol isolated from the ethereal solution was boiled in alcoholic solution for 2 hours with picric acid (3 g.). On cooling, the dark red picrate of 5-isopropenylbenzanthracene (3.75 g.; m. p. 137—139°) crystallised. The hydrocarbon obtained from this picrate formed a gum which slowly crystallised; recrystallisation was not attempted.

The *s*-trinitrobenzene complex of 5-isopropenyl-1 : 2-benzanthracene formed light red needles (from benzene-alcohol), m. p. 155° (Found : C, 67.5; H, 3.95.  $C_{21}H_{16}, C_6H_3O_6N_3$  requires C, 67.3; H, 4.0%). It underwent fission when its dilute solution in benzene was passed through a column of alumina (compare Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1937, 59, 2502; 1938, 60, 945, 1664). The picrate, prepared from the regenerated hydrocarbon, crystallised from benzene in ruby-red needles, m. p. 141—142° (Found : C, 65.5; H, 3.85.  $C_{21}H_{16}, C_6H_3O_7N_3$  requires C, 65.2; H, 3.85%).

5-isoPropyl-1 : 2-benzanthracene.—The crude unsaturated hydrocarbon (III), from 3.75 g. of picrate, was shaken in alcoholic solution (100 c.c.) for 12 hours with hydrogen and palladium-black (0.25 g.). The product was purified through its picrate, sublimed at 120°/0.001 mm., and recrystallised from alcohol. 5-isoPropyl-1 : 2-benzanthracene formed colourless needles, m. p. 111—112° (Found : C, 93.1; H, 6.8.  $C_{21}H_{18}$  requires C, 93.3; H, 6.7%), and gave a picrate which crystallised from benzene in dark red needles, m. p. 166.5—167.5° (Found : C, 64.6; H, 4.3.  $C_{21}H_{18}, C_6H_3O_7N_3$  requires C, 64.9; H, 4.2%), and a *s*-trinitrobenzene complex which formed bright red needles, m. p. 168.5—169.5° (Found : C, 67.1; H, 4.5.  $C_{21}H_{18}, C_6H_3O_6N_3$  requires C, 67.05; H, 4.4%). Oxidation of the hydrocarbon with sodium dichromate (2 parts) in boiling acetic acid (25 parts) gave 5-isopropyl-1 : 2-benzanthraquinone, canary-yellow needles (from alcohol), m. p. 80—82° (Found : C, 83.8; H, 5.5.  $C_{21}H_{16}O_2$  requires C, 84.0; H, 5.4%).

Note on 8-Methyl-1 : 2-benzanthracene (By J. W. COOK and J. IBALL).—In Part XVII (J., 1938, 505) was recorded the synthesis of 8-methyl-1 : 2-benzanthracene, m. p. 107°, unaltered after regeneration of the hydrocarbon from its picrate, m. p. 161—162°, or its *s*-trinitrobenzene complex, m. p. 164—165°. A further quantity of hydrocarbon of the same m. p. has now been prepared, but it was found that the m. p. was raised by recrystallisation from benzene, and after further purification through the *s*-trinitrobenzene complex the hydrocarbon crystallised from alcohol in well-formed, thick, hexagonal plates, m. p. 117—118°. The picrate prepared from this material had m. p. 158—159°, and the *s*-trinitrobenzene complex had m. p. 167—168°. These values should be substituted for those previously recorded.

The crystals of pure 8-methyl-1 : 2-benzanthracene were orthorhombic. The main face was {001} and the crystals also showed small {100} faces. The remaining faces were {111}. The unit cell dimensions were :  $a$ , 14.28 Å;  $b$ , 12.26 Å;  $c$ , 14.44 Å. The space group was  $D_{2h}^{15} - Pcab$ , and there were 8 molecules per unit cell.

It was possible that the lower-melting substance represented a different crystalline modification, but the crystals were too small and irregular for  $X$ -ray examination. When recrystallised by slow evaporation of a dilute alcoholic solution, they gave crystals, m. p. 114—116°, the  $X$ -ray analysis of which gave results identical with those cited above. Hence there is little doubt that the product, m. p. 107°, was impure.

RESEARCH INSTITUTE OF THE ROYAL CANCER HOSPITAL (FREE),  
LONDON, S.W. 3.

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