328. *Polycyclic Aromatic Hydrocarbons. Part XI. The Acetylation of* 1 : 2-*Benzanthracene.*

By J. W Cook and C. L. Hewett.

The condensation of acetic anhydride and 1 : 2-benzanthracene in presence of anhydrous aluminium chloride gave five of the twelve possible monoacetyl compounds. At low temperatures the chief product was 9- or 10-*acetyl*-1 : 2-*benzanthracene*, which was hydrolysed by acids to 1 : 2-benzanthracene, and oxidised by chromic acid to 1 : 2-benzanthraquinone. At 40° this *meso*-ketone was isomerised by aluminium chloride to 7-*acetyl*-1 : 2-*benzanthracene*, which, moreover, was always isolated as a product of the Friedel–Crafts reaction. 6-*Acetyl*-1 : 2-*benzanthracene* was also obtained in small yield, together with two other *monoketones* of undetermined orientation. The orientation of the 6- and the 7-acetyl compound was shown by oxidation of their quinones to anthraquinone-1 : 2 : 6- and -1 : 2 : 7-tricarboxylic acid, respectively.

7-Acetyl-1 : 2-benzanthracene reacted with methylmagnesium iodide to give a *carbinol*, which was readily dehydrated by hydrochloric acid in boiling acetic acid. The resulting 7-*iso*propenyl-1 : 2-benzanthracene could not be isolated, however, for it was converted under these conditions into a *dimeride*, the constitution of which has not been determined. No pure olefinic hydrocarbon could be isolated by using milder conditions for dehydration.

The poor yields of the pure acetylbenzanthracenes have precluded their utilisation in the synthesis of higher homologues of 1 : 2-benzanthracene, which was the purpose of this investigation.

The Friedel–Crafts condensations were effected by adding first the acetic anhydride (1·1 mols.; usually diluted with nitrobenzene), and then the finely powdered 1 : 2-benzanthracene (1 mol.), to a well-stirred solution of anhydrous aluminium chloride (1 mol.) in nitrobenzene (15 mols.). After **3—4** hours the product was decomposed with ice and hydrochloric acid, the nitrobenzene removed in steam, and the residual resin dissolved in acetic acid and treated with excess of picric acid. The resulting mixture of picrates was dried and repeatedly crystallised from benzene. In this way a constant-melting picrate was usually obtained, from which the pure ketone was regenerated by shaking the benzene solution with sodium carbonate solution. The benzene mother-liquors were likewise freed from picric acid; in many cases solid mixtures of ketones were then obtained. These were subjected to fractional crystallisation from alcohol or ethyl acetate, and the fractions again submitted to treatment with picric acid. No fraction was regarded as a pure substance unless it was recovered with the m. p. unaltered after conversion into the picrate, crystallisation from benzene to constant m. p., followed by decomposition with sodium carbonate. The following experiments were made :

(*a*) The solution was cooled in ice during addition of the 1 : 2-benzanthracene (11·4 g.) and then kept at 0° for 4 hours. The less soluble picrates yielded 0·5 g. of ?-*acetyl*-1 : 2-*benzanthracene*, which separated from *cyclo*hexane in pale yellow, prismatic needles, m. p. 147° (Found : C, 88·9; H, 5·2. $C_{20}H_{14}O$ requires C, 88·8; H, 5·2%); its *picrate* formed light orange-red needles, m. p. 192° (from benzene) (Found : N, 8·3. $C_{20}H_{14}O,C_6H_3O_7N_3$ requires N, 8·4%), and the corresponding *quinone*, obtained by oxidation with 3 parts of sodium dichromate in boiling acetic acid for 20 minutes, crystallised from alcohol in orange needles, m. p. 196—197° (Found : C, 80·0; H, 3·9. $C_{20}H_{12}O_3$ requires C, 80·0; H, 4·0%). The liquors from which the above picrate was isolated yielded 0·3 g. of 7-*acetyl*-1 : 2-*benzanthracene*, pale straw-coloured leaflets (from benzene–alcohol), m. p. 151—152° (Found : C, 89·2; H, 5·3%); its *picrate* (from benzene) formed an orange crystalline powder, m. p. 147—148° (Found : N, 8·25%). 7-*Acetyl*-1 : 2-*benzanthraquinone* formed an orange crystalline powder (from benzene), m. p. 219° (Found : C, 80·2; H, 4·1%).

(*b*) The 1 : 2-benzanthracene (70 g.) was added at such a rate that the temperature did not rise above 0°, the whole being cooled in a freezing mixture. The less soluble picrates yielded 12·5 g. of the *picrate* of 9- or 10-*acetyl*-1 : 2-*benzanthracene*, brick-red needles, m. p. 153·5—154·5° (Found : C, 62·5; H, 3·5. $C_{20}H_{14}O,C_6H_3O_7N_3$ requires C, 62·5; H, 3·4%). The *ketone*, regenerated from this picrate, crystallised from alcohol in small colourless plates, m. p. 104—105° (Found : C, 89·0; H, 5·5%). In contrast with the other ketones this *meso*-compound was non-fluorescent. When boiled for ½ hour with a solution of sulphuric acid (1 c.c.) in acetic acid (10 c.c.), it (0·5 g.) was hydrolysed to 1 : 2-benzanthracene, m. p. and mixed m. p. 159—160°. Oxidation of the ketone with sodium dichromate in acetic acid yielded 1 : 2-benzanthraquinone, m. p. and mixed m. p. 168·5—169·5°.

From the more soluble picrates obtained in this experiment there were isolated 7 g. of 7-acetyl-1 : 2-benzanthracene, whereas the final benzene liquors of the mixed picrates deposited, on standing, a small amount of a *picrate* which crystallised from benzene in reddish-brown needles, m. p. 187·5—188°, depressed by the picrate, m. p. 192°, mentioned above (Found : N, 8·1%).

(*c*) The mixture was cooled in ice during addition of the benzanthracene (14 g.) and subsequently kept at room temperature for 4 hours. The chief product was 7-acetyl-1 : 2-benzanthracene. The mother-liquors from the crystallisation of the picrate of this ketone were freed from picric acid, and the resulting ketones crystallised from acetic acid and then from benzene, yielding 6-*acetyl*-1 : 2-*benzanthracene*, pale yellow needles, m. p. 192·5—193·5° (Found : C, 88·8; H, 5·2%); the *quinone* formed golden-yellow needles (from benzene), m. p. 197—199° (Found : C, 80·0; H, 4·1%). 6-Acetyl-1 : 2-benzanthracene crystallised unchanged from a benzene solution of picric acid, although the deep red colour of the solution suggested picrate formation.

(*d*) Repetition of the conditions described under (*a*) furnished a mixture of ketones from which 6-, 7-, and the *meso*-acetyl compounds were isolated.

Isomerisation of meso-*Acetyl*-1 : 2-*benzanthracene*.—Addition of a solution of aluminium chloride (1·4 g.) in nitrobenzene (5 c.c.) to a solution of the *meso*-ketone (2·7 g.) in nitrobenzene (10 c.c.) resulted in separation of a thick meal of dark red crystals. After 4½ hours at room temperature the *meso*-ketone was recovered entirely unchanged, but when this mixture was heated at 40° for 4 hours isomerisation occurred. The product was decomposed with ice and hydrochloric acid, the nitrobenzene removed in steam, and the residue treated with picric acid. Two crystallisations from benzene gave the picrate of 7-acetyl-1 : 2-benzanthracene, the identification being completed by conversion of the picrate into the ketone.

Orientation of 6- *and* 7-*Acetylbenzanthracenes.*—A solution of the appropriate acetyl-1 : 2-benzanthraquinone (0·5 g.) in concentrated sulphuric acid (5 c.c.) was poured into water (25 c.c.), and the boiling suspension treated gradually with finely powdered potassium permanganate (2·3 g.). The manganese dioxide was then destroyed by addition of oxalic acid, the whole cooled, and the solid in suspension collected, extracted with dilute sodium carbonate solution, and the reprecipitated acid boiled for 3 hours with an aqueous solution of chromic acid (1 g.). The acid so purified was methylated by heating its silver salt with excess of methyl iodide in benzene for 24 hours, and the product crystallised from xylene (in the case of the 1 : 2 : 6-compound) or chloroform–alcohol (in the case of the 1 : 2 : 7-compound). The ester obtained from 6-acetyl-1 : 2-benzanthraquinone had m. p. 232·5—233·5°, not depressed by methyl anthraquinone-1 : 2 : 6-tricarboxylate (m. p. 233·5—234·5°), and the ester obtained from 7-acetyl-1 : 2-benzanthraquinone had m. p. 197—198°, not depressed by methyl anthraquinone-1 : 2 : 7-tricarboxylate (m. p. 204—204·5°), but strongly depressed by methyl anthraquinone-1 : 2-dicarboxylate (m. p. 208°). The preparation of the authentic esters will be described in a future communication.

7-(1 : 2-*Benz*)*anthranyldimethylcarbinol.*—An ice-cold Grignard solution prepared from methyl iodide (2·8 c.c.), magnesium turnings (1·1 g.), and anhydrous ether (25 c.c.) was slowly treated with finely powdered 7-acetyl-1 : 2-benzanthracene (4 g.). The product was allowed to warm to room temperature, boiled for 2 hours, and decomposed with ice and ammonium chloride, more ether being necessary to dissolve the *carbinol.* The washed ethereal extract was dried (sodium sulphate), and the ether removed on the water bath. The solid residue, twice recrystallised from alcohol, formed colourless plates which dried to a powder, m. p. 135° (Found : C, 88·1; H, 6·4. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%).

Dimeride of 7-iso*Propenyl*-1 : 2-*benzanthracene.*—When concentrated hydrochloric acid (1·5 c.c.) was added to a solution of the aforesaid carbinol (1·5 g.) in glacial acetic acid (50 c.c.), an oil separated which became converted into a crystalline solid during an hour's boiling. The product (0·9 g.) was washed with acetic acid and recrystallised from benzene–alcohol, forming small colourless needles, m. p. 248—251° (Found : C, 94·0; H, 6·0; *M*, Rast method, 497, 513. $C_{42}H_{32}$ requires C, 94·0; H, 6·0%; *M*, 536). Solutions of this *hydrocarbon* had an intense violet fluorescence.

All the analyses are microanalyses by Dr. A. Schoeller. The 1 : 2-benzanthracene was prepared by reduction of 1 : 2-benzanthraquinone (Sirius Yellow G), for supplies of which we are indebted to I.G. Dyestuffs Ltd.

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

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