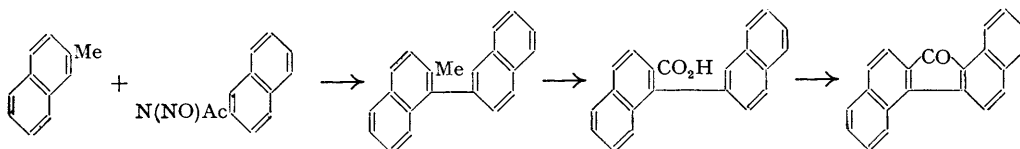


8. Some Synthetic Experiments leading to Formation of Methyl-1 : 2-benzanthraquinones.

By D. E. A. RIVETT, G. SWAIN, and A. R. TODD.

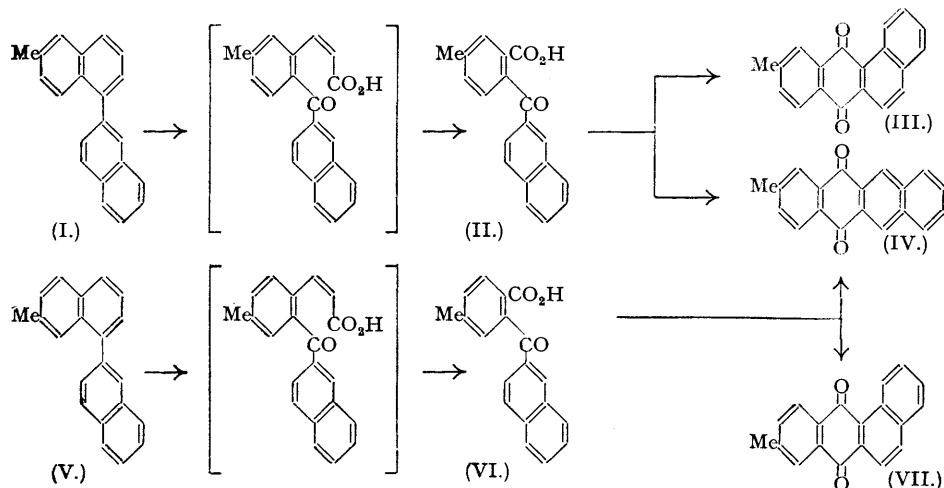
N-Nitrosoaceto-2-naphthalide reacts with 2-methylnaphthalene to yield a mixture of 2-methylidinaphthyls. The mixture on oxidation gives, in addition to neutral products, an acid, $C_{19}H_{14}O_3$, cyclised by sulphuric acid to 7-methyl-1 : 2-benzanthraquinone and an apparently isomeric quinone, m. p. 151—152°, differing substantially in m. p. from any of the recorded methyl-1 : 2-benzanthraquinones. In an attempt to clarify the position by an alternative synthesis, 4-methylphthalic anhydride was brought into reaction with naphthalene under Friedel-Crafts conditions; two isomeric naphthoyltoluic acids were obtained, of which one, obtained in very small amount, could be cyclised to 7-methyl-1 : 2-benzanthraquinone. The other, which formed the main product, yielded on similar treatment an isomeric quinone, m. p. 139—140°. It is suggested on available evidence that the quinones, m. p. 151—152° and m. p. 139—140°, represent mixed crystals of 6-methyl- and 7-methyl-1 : 2-benzanthraquinones, and are formed by molecular rearrangement of naphthoyltoluic acids during cyclisation.

THE investigations here recorded had their origin in an attempt to synthesise 1 : 2 : 5 : 6-dibenzfluorenone (cf. Swain and Todd, *J.*, 1941, 674) by the following hypothetical route :



N-Nitrosoaceto-2-naphthalide was allowed to react with molten 2-methylnaphthalene. The product, a brown resin, could be distilled in superheated steam, but even after further purification by high vacuum distillation only a small fraction of it could be crystallised, and this proved to be a mixture. By fractional crystallisation of this solid material one component could be obtained as colourless plates, m. p. 121—122°, and this was shown by analysis and molecular-weight determination to be a 2-methylidinaphthyl. The crude resinous condensation product treated with picric acid gave a crystalline *picrate*, m. p. 152—154°, from which a second hydrocarbon, or hydrocarbon mixture, with an indefinite m. p. 135—145°, could be regenerated; this too gave analytical values agreeing for a 2-methylidinaphthyl. Since individual 2-methyl-

dinaphthyls could evidently be isolated from the initial reaction product only with difficulty and in poor yields, the crude resin was directly oxidised with chromic acid in the hope that the dinaphthylcarboxylic acid, or acids, produced would be more easily separated. Most of the oxidation product was an intractable neutral orange resin with quinonoid properties which could not be crystallised. The smaller acidic fraction yielded on sublimation under reduced pressure 2-naphthoic acid and a second acid, m. p. 160—162°. Analysis showed that, contrary to

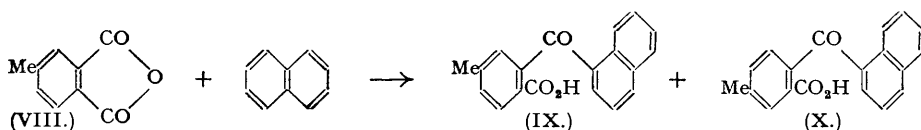


expectation, the latter was not a dinaphthylcarboxylic acid but a *keto-acid* of empirical formula $C_{19}H_{14}O_3$ which gave on acetylation an *acetoxy-lactone*, $C_{21}H_{16}O_4$. Treatment of the crude acid fraction from the oxidation as a whole, or of the isolated acid, m. p. 160—162°, with sulphuric acid, gave two products separated by fractional crystallisation—yellow plates, m. p. 151—152° and yellow needles, m. p. 159—160°. Analysis and molecular-weight determinations indicated that these were isomers of formula $C_{19}H_{12}O_2$, and that they were quinones was demonstrated by reductive acetylation to colourless diacetates.

The production of a keto-acid, $C_{19}H_{14}O_3$, from a 2-methyldinaphthyl can only be explained by fission of a ring in one of the naphthalene nuclei during oxidation to give an acid in which the 2-methyl group is still intact; moreover, there are only two possible 2-methyldinaphthyls (I and V) from which such an acid (II or VI) could be produced.

Ring closure of each of the keto-acids (II) or (VI) could theoretically give rise to two methylbenzanthraquinones, as shown in the above scheme, the linear compound (IV) being a common product in both cases. The yellow quinone, m. p. 159—160°, proved to be slightly impure 7-methyl-1 : 2-benzanthraquinone (III) (m. p. 167°). The obvious conclusion would be that the acid, m. p. 160—162°, has structure (II), but in that case one would expect that the isomeric quinone, m. p. 151—152°, would be the linear 2-methyl-6 : 7-benzanthraquinone (IV). (IV), however, has m. p. 240—242° (Waldmann and Mathiowetz, *Ber.*, 1931, **64**, 1717), whilst 6-methyl-1 : 2-benzanthraquinone (VII), which might conceivably have been formed from (II) by rearrangement during ring-closure, has m. p. 174° (Cook, *J.*, 1932, 470). The common origin of the isomeric yellow quinones and their close similarity in properties made it difficult to believe that they were not both methylbenzanthraquinones. All the possible methyl-1 : 2-benzanthraquinones have, however, been described (Cook, *J.*, 1938, 505), and all of them melt above 152°. The amount of the product, m. p. 151—152°, at our disposal was rather small for structural determination by degradation, and, although it seemed rather unlikely that any of the recorded methyl-1 : 2-benzanthraquinones had constitutions other than those assigned to them, it was decided to seek some clarification of the situation by an alternative synthesis.

4-Methylphthalic anhydride (VIII) was condensed with naphthalene in presence of aluminium chloride with the object of preparing one or more naphthoyltoluic acids according to the scheme :



The reaction between 4-methylphthalic anhydride and naphthalene might conceivably yield (II) and (VI) as well as (IX) and (X). That (II) and (VI) would be produced in any quantity is extremely improbable, however, for, although it has been claimed that the reaction between phthalic anhydride and naphthalene gives some 2-naphthoylbenzoic acid (Willstätter and Waldschmidt-Leitz, *Ber.*, 1921, 54, 1423; Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1937, 59, 1029), contrary to the findings of Graebe (*Annalen*, 1905, 340, 249), in neither paper where the claim is made is there any record of the properties of the acid. Ring-closure of (IX) and (X) should yield respectively 7-methyl-1 : 2-benzanthraquinone (III) and 6-methyl-1 : 2-benzanthraquinone (VII) unaccompanied by isomers, provided no rearrangements occur.

In practice, the chief product of the reaction between 4-methylphthalic anhydride and naphthalene was a 1-naphthoyltoluic acid, m. p. 211—213°, accompanied in one experiment by a small amount of a second isomeric acid, m. p. 214—216°. Ring-closure of the acid, m. p. 214—216°, with sulphuric acid yielded 7-methyl-1 : 2-benzanthraquinone (III). The acid, m. p. 211—213°, gave 1-naphthoic acid on fusion with alkali, and cyclisation with sulphuric acid or phosphoric oxide furnished a yellow quinone, $C_{19}H_{12}O_2$, m. p. 139—140°, unchanged by recrystallisation, chromatography, or vacuum sublimation. On reduction, this quinone yielded a mixture of methyl-1 : 2-benzanthracenes, from which only 7-methyl-1 : 2-benzanthracene could be isolated in pure condition. As it was suspected that the mixture also contained 6-methyl-1 : 2-benzanthracene, a mixture of equal parts of the 6- and 7-methyl-1 : 2-benzanthraquinone (VII) and (III) was recrystallised from ethyl acetate-methanol. The yellow needles obtained had m. p. 139—140°, undepressed in admixture with the material formed by cyclisation of the acid, m. p. 211—213°, and we were unable to separate it again into its components. It is therefore concluded that the acid, m. p. 211—213°, yields a mixture of 6- and 7-methyl-1 : 2-benzanthraquinone. It will be observed that whatever be the orientation of the 1-naphthoyltoluic acid, m. p. 211—213°, [(X) might be regarded as the more likely since the acid, m. p. 214—216°, yielding only (III) is probably (IX)], rearrangement by migration of the 1-naphthoyl residue must have occurred during ring-closure. Migrations of this type are well known and have been discussed by Cook (*J.*, 1932, 1472), who found, for example, that cyclisation of 2-carboxy-1 : 2'-dinaphthyl ketone yielded a mixture of 1 : 2 : 5 : 6-, 1 : 2 : 6 : 7-, and 1 : 2 : 7 : 8-dibenzanthraquinone.

In view of these results, attention was again turned to the quinone, m. p. 151—152°. Reduction by the procedure of Cook (*loc. cit.*) gave a product which appeared to be a mixture of methylbenzanthracenes. With the quantities available no pure hydrocarbon could be isolated, but by fractional recrystallisation a product was obtained which we regard as impure 6-methyl-1 : 2-benzanthracene, since re-oxidation gave a quinone, m. p. 158°, undepressed in admixture with a small proportion of 6-methyl-1 : 2-benzanthraquinone. Again, reductive acetylation of the quinone, m. p. 151—152°, gave a diacetate, m. p. 231—233°; the mixed m. p. of this product with 9 : 10-diacetoxy-6-methyl-1 : 2-benzanthracene (m. p. 248—250°) was 236—238°, whereas a mixture with 9 : 10-diacetoxy-7-methyl-1 : 2-benzanthracene (m. p. 212—213°) softened at 193° and melted indefinitely at 195—202°. It is tentatively concluded that the material, m. p. 151—152°, is a mixture of 6- and 7-methyl-1 : 2-benzanthraquinone. An additional point in favour of this view is that the coloration with sulphuric acid, given both by the quinone m. p. 139—140° and that of m. p. 151—152°, is intermediate between the olive-green of 6-methyl-1 : 2-benzanthraquinone and the orange-brown of 7-methyl-1 : 2-benzanthraquinone, and corresponds with those given by artificially prepared mixtures of these compounds. It is impossible on present evidence to decide whether the keto-acid $C_{19}H_{14}O_3$, m. p. 160—162°, has structure (II) or (VI), since either could yield the same two products if rearrangement occurs during the cyclisation process with sulphuric acid.

EXPERIMENTAL.

Reaction between N-Nitrosoaceto-2-naphthalide and 2-Methylnaphthalene.—(a) *N-Nitrosoaceto-2-naphthalide* (28 g. dry powder; Hey and Lawton, *J.*, 1940, 374) was added in small amounts during 5½ hours to 2-methylnaphthalene (500 g.) kept at 35° and well stirred. Stirring was continued for 1 hour, the red solution allowed to cool overnight, and excess of 2-methylnaphthalene (470 g.) removed by distillation in steam. The residual dark red tar was distilled in superheated steam at 190—200°. The first small fraction of red oil (mainly 2-methylnaphthalene) was rejected, and the remainder of the distillate collected as a viscous light brown oil which set to a resin (22 g.) on cooling. Its solution in ether was dried (Na_2SO_4) and the solvent removed. Slow crystallisation from acetone-light petroleum (b. p. 40—60°) gave some slightly oily solid (2.2 g., m. p. 82—85°). Recrystallisation from the same solvent yielded an obvious mixture (1.1 g.) (A), but concentration of the mother liquor gave a crystalline product (0.4 g.) which after 7 recrystallisations from methanol formed colourless prismatic plates of 2-methyldinaphthyl, m. p. 121—122° (Found: C, 93.4; H, 6.5; M, 247. $C_{21}H_{16}$ requires C, 94.0; H, 6.0%; M, 268). No picrate was formed in alcoholic solution.

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The mixture (A) (1.1 g.) was treated with picric acid in ethanol solution, and the *picrate* which separated as a mass of fine orange-yellow needles (0.5 g., m. p. 149—153° sintering at 135°) was recrystallised thrice from ethanol. It separated in orange plates, m. p. 152—154° (decomp.) (Found: N, 11.3. $C_{21}H_{16}, 2C_6H_3O, N_3$ requires N, 11.5%).

(b) A preparation in which *N*-nitrosoaceto-2-naphthalide (prepared from 30 g. of 2-acetonaphthalide) was added whilst moist (wt. of filter cake, 60 g.) to 2-methylnaphthalene (450 g.), kept at 35° with stirring, yielded the same crude resin (20 g.) after distillation in superheated steam as described under (a).

Formation of Picrate from Crude Resin and Regeneration of Hydrocarbon.—The crude methylindinaphthyl resin (30 g.) obtained after distillation in superheated steam was dissolved in hot ethanol (450 c.c.), and picric acid (20 g.) in ethanol (150 c.c.) added. After several days the dark brown crystalline solid (7.7 g.) which separated was collected and recrystallised from ethanol. 2-Methylindinaphthyl picrate (4.5 g.) separated in golden orange plates, m. p. 152—154°, undepressed in admixture with the specimen previously obtained.

The picrate (4.5 g.) was warmed with aqueous sodium hydroxide (2.5 g. in 150 c.c. water), cooled, and extracted with ether. The ethereal extract was washed with aqueous sodium hydroxide (1%) then water, and dried (Na_2SO_4). Removal of the solvent left a colourless crystalline solid (1.8 g.) which was twice recrystallised from ethyl acetate-methanol (1:1) and finally from ethyl acetate. The 2-methylindinaphthyl separated in small colourless plates, m. p. 135—145°. No sharp m. p. could be obtained by further recrystallisation (Found: C, 93.9; H, 6.1. Calc. for $C_{21}H_{16}$: C, 94.0; H, 6.0%).

Oxidation of Reaction Product from 2-Methylnaphthalene and N-Nitrosoaceto-2-naphthalide.—The crude methylindinaphthyl mixture (29 g.) was dissolved in glacial acetic acid (300 c.c.) and the temperature adjusted to 50°. Chromic acid (33 g.) dissolved in water (22 c.c.) and acetic acid (110 c.c.) was added with vigorous stirring during 3 hours, the temperature of the mixture being kept at 50°. After a further 30 minutes' stirring, water (300 c.c.) and methanol (15 c.c.) were added, and the mixture left overnight. The product was extracted with ether and the acid fraction separated by washing it with sodium carbonate solution, acidifying, and re-extracting. Evaporation of the dried ethereal extract gave a brown resin (6.0 g.). A portion of this resin (2.4 g.) was sublimed at 10^{-4} mm. Two distinct sublimates were obtained: (I) m. p. 145—148° (0.25 g.); (II) m. p. 152—155° (0.5 g.). (I), recrystallised from benzene-light petroleum, yielded colourless plates, m. p. 180°, showing no depression in admixture with authentic 2-naphthoic acid (m. p. 181°). (II), recrystallised from benzene-light petroleum (3:1), gave colourless needles of the *keto-acid*, m. p. 160—162° (sintering at 155°), readily soluble in cold sodium carbonate solution and giving an intense olive-green colour with concentrated sulphuric acid (Found: C, 79.2; H, 4.1. $C_{19}H_{14}O_3$ requires C, 78.6; H, 4.8%).

Acetoxy-lactone of Acid, m. p. 160—162°.—The acid (0.1 g., m. p. 160—162°) was heated on the steam-bath for 3 hours with pyridine (0.7 c.c.) and acetic anhydride (0.35 c.c.), and the mixture poured into water. An oil separated which solidified slowly. Recrystallised from methanol, the *acetoxy-lactone* separated in colourless prismatic needles, m. p. 129—130° (Found: C, 75.9; H, 4.4. $C_{21}H_{16}O_4$ requires C, 75.9; H, 4.8%).

Ring-closure of Acid Fraction of above Oxidation Product.—(a) The crude resinous acid fraction (6.0 g.) was heated on the steam-bath for 2½ hours with sulphuric acid (40 c.c. of conc. diluted with 20 c.c. of water). The black tarry mass which resulted was poured into water, made alkaline by addition of solid sodium carbonate, and extracted with benzene. The benzene extract was washed, dried, and evaporated. The orange-brown solid residue (1.9 g.) was dissolved in warm benzene (20 c.c.), and light petroleum (10 c.c., b. p. 40—60°) added. A small amount of dark resin (0.1 g.) separated on cooling and was removed by filtration. The clear filtrate was passed through a column of activated aluminium oxide (1 cm. × 35 cm.) prepared by using benzene-light petroleum (b. p. 40—60°) (1:1). A band of brown impurity remained at the top of the column with a large yellow band below. The yellow band was eluted with benzene-light petroleum (100 c.c.) (1:1). Removal of the solvent left a yellow crystalline residue (1.4 g., m. p. 123—133°) which was dissolved in boiling methanol. On cooling, two distinct types of crystal separated—yellow plates and yellow needles. By re-warming, the latter were dissolved more rapidly than the former, and a separation was effected by decantation from the undissolved solid, which was then recrystallised from fresh methanol giving yellow plates, m. p. 151—152° (0.6 g.) (Found: C, 83.6; H, 4.2; *M*, 269. Calc. for $C_{19}H_{12}O_2$: C, 83.8; H, 4.4%; *M*, 272). The product gave a dirty olive-green colour with concentrated sulphuric acid, and an anthraquinol colour reaction with zinc and aqueous sodium hydroxide. It was soluble in ether, acetic acid, benzene, and chloroform, and sparingly so in ethanol.

A portion of the yellow substance, m. p. 151—152° (50 mg.), was reductively acetylated by heating it under reflux for 1½ hours with acetic anhydride (5 c.c.), fused sodium acetate (30 mg.), and zinc dust (100 mg.). Two further additions of zinc dust (100 mg.) were made at hourly intervals. The still yellow solution was decomposed with water and extracted with ether. The diacetate obtained from the ethereal solution was repeatedly recrystallised from methanol. It separated in colourless prisms, m. p. 231—233°, showing a bluish fluorescence in alcoholic solution (Found: C, 76.5; H, 4.8. Calc. for $C_{23}H_{18}O_4$: C, 77.1; H, 5.0%).

The decanted methanolic solution left after separating the quinone, m. p. 151—152°, deposited on cooling long felted yellow needles (m. p. 139—143°) which were more difficult to purify. After several recrystallisations from methanol, yellow needles (0.2 g.), m. p. 159—160°, were obtained (Found: C, 83.7; H, 4.5; *M*, 287. Calc. for $C_{19}H_{12}O_2$: C, 83.8; H, 4.4%; *M*, 272). With concentrated sulphuric acid the compound gave an orange-brown colour, and with zinc and aqueous sodium hydroxide an anthraquinol colour reaction. 7-Methyl-1:2-benzanthraquinone (m. p. 167°) gave the same colour with sulphuric acid, and the mixed m. p. with this compound was 163—165°.

The diacetate, prepared by reductive acetylation in the manner already described for the isomeric product, separated from methanol in colourless needles, m. p. 201—202° (Found: C, 77.2; H, 5.0. Calc. for $C_{23}H_{18}O_4$: C, 77.1; H, 5.0%). A mixture of this product with 9:10-diacetoxy-7-methyl-1:2-benzanthracene (m. p. 212—213°) had m. p. 208—210°.

(b) The pure acid, m. p. 160—162° (0.1 g. isolated as above), was heated on the steam-bath for

2½ hours with sulphuric acid (0.66 c.c. of conc., diluted with 0.33 c.c. of water). The cooled product was made alkaline with sodium carbonate and extracted with benzene. The neutral fraction (40 mg.) left as a yellow solid after removal of the solvent was dissolved in a little benzene and filtered through a column of activated aluminium oxide (0.6 cm. × 8 cm.). The yellow band was washed through with a little benzene and the benzene solution evaporated. Fractional crystallisation of the yellow residue from methanol yielded yellow plates, m. p. 151—152°, and yellow needles, m. p. 159—160°, identical with the products obtained by ring-closure of the crude acid fraction [see (a) above].

Condensation of 4-Methylphthalic Anhydride with Naphthalene.—4-Methylphthalic acid, prepared by the method of Alder and Rickert (*Annalen*, 1936, 524, 180), was converted into its anhydride by sublimation under reduced pressure at 200°; the overall yield calculated on acetylenedicarboxylic ester was 21%. 4-Methylphthalic anhydride (8.1 g.) and naphthalene (9.6 g.) were dissolved in warm carbon disulphide (80 c.c.), and the solution cooled to 0° in ice-salt with stirring. Some solid separated. Powdered anhydrous aluminium chloride (13.3 g.) was added during 10 minutes, and the mixture stirred at 0° for 1 hour. The temperature was allowed to rise to room temperature during 30 minutes, and the mixture then heated under reflux on the steam-bath for 4 hours. After standing overnight, the dark brown product was decomposed with ice (50 g.) and hydrochloric acid (50 c.c., *d*, 1.16). Carbon disulphide and excess of naphthalene were removed by steam distillation. Water was decanted from the solid residue which was washed and dissolved in hot sodium carbonate solution (150 c.c. of 10%), cooled, and filtered. Acidification yielded a sticky precipitate which was separated, dissolved in ether, and dried (Na₂SO₄). Removal of the ether gave an orange-brown resin (14 g.) which on crystallisation from benzene (30 c.c.) yielded almost colourless prisms (6.3 g.), m. p. 185—195° (sintering at 155—165°). By fractional crystallisation from ethyl acetate and then from benzene, two isomeric naphthoyltoluic acids were isolated. The first (1-naphthoyltoluic acid) separated from ethyl acetate in colourless prisms (1.8 g.), m. p. 211—213° (Found : C, 78.8; H, 4.8. C₁₉H₁₄O₃ requires C, 78.6; H, 4.8%). The second acid crystallised from benzene in colourless needles (0.6 g.), m. p. 214—216° (Found : C, 78.7; H, 4.9. C₁₉H₁₄O₃ requires C, 78.6; H, 4.8%). Mixed with the acid, m. p. 211—213°, it melted indefinitely at 183—195°.

In other experiments only the acid, m. p. 211—213°, was obtained. Heated on the steam-bath for 3 hours with acetic anhydride and pyridine it gave an *acetoxy-lactone* crystallising from acetic acid-methanol in colourless needles, m. p. 173—174° (Found : C, 75.5; H, 5.1. C₂₁H₁₆O₄ requires C, 75.9; H, 4.8%). The pure acid regenerated from the acetoxy-lactone by hydrolysis with ethanolic potassium hydroxide had m. p. 211—213°.

Alkali Fusion of Naphthoyltoluic Acid, m. p. 211—213°.—The acid (0.4 g.) was gradually stirred into molten potassium hydroxide (3 g.) at 260°, and the melt kept at 260—280° for 15 minutes, cooled, and extracted with water. The solution was acidified, and the precipitate collected, dried, and recrystallised first from benzene and then from aqueous acetic acid. The product formed colourless needles, m. p. 159—160°, alone or in admixture with an authentic specimen of 1-naphthoic acid.

Ring-closure of Naphthoyltoluic Acid, m. p. 211—213°.—The acid (0.85 g.) was heated to boiling point with sulphuric acid (12 c.c. concentrated acid, *d*, 1.84, diluted with 6 c.c. of water) and allowed to cool. The product was poured into water, and the yellow solid collected and washed thoroughly with water. Recrystallisation from methanol and then from ethyl acetate-methanol gave a yellow solid (0.45 g.) in clusters of very small needles, m. p. 139—140° (Found : C, 83.3; H, 4.6; *M*, 274. Calc. for C₁₉H₁₂O₂ : C, 83.8; H, 4.4%; *M*, 272). With concentrated sulphuric acid it gave a dirty olive-green colour. A depression of m. p. to 125° was observed in admixture with the quinone, m. p. 151—152°, obtained from the acid, m. p. 160—162° (see above).

The same product, m. p. 139—140°, was obtained when cyclisation was effected in nitrobenzene solution with phosphoric oxide.

Ring-closure of Naphthoyltoluic Acid, m. p. 214—216°.—The acid, m. p. 214—216° (0.3 g.), was heated on the steam-bath for 2 hours with sulphuric acid (4 c.c., *d*, 1.84, diluted with 2 c.c. of water). The product was poured into water, and the flocculent yellow solid collected and thoroughly washed. Recrystallisation from methanol gave 7-methyl-1 : 2-benzanthraquinone in felted yellow needles, m. p. 164—165°, undepressed in admixture with an authentic specimen, m. p. 167°. It gave an orange-brown colour with sulphuric acid (Found : C, 83.9; H, 5.2. Calc. for C₁₉H₁₂O₂ : C, 83.8; H, 4.4%).

Reduction of Quinone, m. p. 139—140°.—Aluminium powder (0.1 g.) was added gradually with constant stirring to a solution of the quinone (0.4 g.) in concentrated sulphuric acid (10 c.c.). After 3 hours the solution was poured into ice-water, and the precipitate collected and refluxed with zinc dust (2 g.) and aqueous sodium hydroxide (25 c.c. of *N*) for a further 3 hours. The mixture was cooled, extracted with benzene, and the extract thoroughly washed with alkaline dithionite to remove any traces of quinone, and dried (Na₂SO₄). The benzene was removed, and the residue dissolved in light petroleum (b. p. 60—80°) and poured on a column of activated aluminium oxide (1 cm. × 20 cm.). An orange band of impurity formed at the top of the column with a broad lower band showing a strong blue fluorescence in ultra-violet light. The lower band was eluted by passing through the column light petroleum (b. p. 60—80°) to which increasing amounts of benzene were added, the column being finally washed with pure benzene. Three arbitrary fractions of eluate (each 50 c.c.) were collected and evaporated separately, and the solid residues fractionally recrystallised from benzene-light petroleum (1 : 4). In each case material which separated first formed colourless needles, m. p. 181—182° (Found : C, 93.8; H, 5.9. Calc. for C₁₉H₁₄ : C, 94.2; H, 5.8%). That this product was 7-methyl-1 : 2-benzanthracene (m. p. 182°) was confirmed by oxidation with chromic acid to 7-methyl-1 : 2-benzanthraquinone, m. p. 165—167°, showing no depression in m. p. when mixed with an authentic specimen. No other homogeneous hydrocarbon could be isolated from the crystallisation mother liquors.

Reduction of Quinone, m. p. 151—152°.—The quinone (0.6 g.) was reduced first with aluminium in sulphuric acid and then with zinc dust and sodium hydroxide as described above for the product, m. p. 139—140°. The colourless product obtained on evaporating the eluate from the chromatogram behaved like a mixture of methylbenzanthracenes, giving with concentrated sulphuric acid a carmine-red solution, which turned purple and finally blue on standing (cf. Cook, *J.*, 1932, 464). Recrystallisation of this

product first from benzene–light petroleum (b. p. 60–80°) and then from glacial acetic acid gave a small amount of a substance forming colourless plates, m. p. 150–151°. Oxidation of the substance (10 mg.) with chromic acid in acetic acid and recrystallisation from ethyl acetate–methanol gave a quinone, m. p. 158°; admixture with a small amount of 6-methyl-1 : 2-benzanthraquinone (m. p. 174°) caused no depression in m. p. It is therefore suggested that the reduction product, m. p. 150–155°, is impure 6-methyl-1 : 2-benzanthracene.

9 : 10-Diacetoxy-6-methyl-1 : 2-benzanthracene.—This *compound*, prepared by reductive acetylation of 6-methyl-1 : 2-benzanthraquinone (20 mg.) with acetic anhydride, fused sodium acetate, and zinc dust, and recrystallised from acetic acid, formed colourless needles, m. p. 248–250° (Found : C, 76.6; H, 5.2. $C_{23}H_{18}O_4$ requires C, 77.1; H, 5.0%).

9 : 10-Diacetoxy-7-methyl-1 : 2-benzanthracene.—Prepared in the same way from 7-methyl-1 : 2-benzanthraquinone and recrystallised from acetic acid, this *compound* formed colourless needles, m. p. 212–213° (Found : C, 77.3; H, 5.1. $C_{23}H_{18}O_4$ requires C, 77.1; H, 5.0%).

We are indebted to Prof. J. W. Cook for samples of 6- and 7-methyl-1 : 2-benzanthraquinones and for helpful discussions of the problems encountered. The work described was initiated in the University of Manchester, and we record our thanks to Messrs. I.C.I. Ltd. (Dyestuffs Division) for a grant held by one of us (G. S.). We also thank the University of South Africa for the award of a Scholarship (to D. E. A. R.).

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