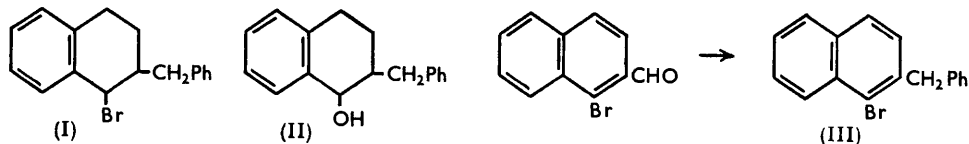


538. ^{14}C -Labelled Polycyclic Aromatic Hydrocarbons. Part II.¹ The Synthesis of 1 : 2-Benzanthracene and Some Methyl-substituted [^{14}C]-Benzanthracenes.

By E. A. EVANS.

Syntheses from $^{14}\text{CO}_2$ of 1 : 2-benzanthracene and 5-methyl- and 9 : 10-dimethyl-1 : 2-benzanthracene labelled with ^{14}C in the 9- or 10-position are described. Alternatively 1 : 2-[^{14}C]benzanthracene may be prepared from 1-naphth[^{14}C]aldehyde.

PREVIOUS syntheses of [^{14}C]benzanthracenes have employed Wagner–Meerwein rearrangement of 5-(hydroxy[^{14}C]methyl)-2 : 3-benzofluorene, which has given 1 : 2-benzanthracene labelled in the 5- and 6-positions,² in 76% overall yield from $^{14}\text{CO}_2$, or neutron irradiation of benzacridine,³ which gave only poor yields. To prepare the bromo-compound (I) was first tried. 2-Benzylidenetetralone was reduced with lithium aluminium hydride to 2-benzyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol (II), both the carbonyl group and the exo-ethylenic bond being reduced under the conditions employed, as has been observed in other cases.⁴ This same hydroxy-compound was obtained by lithium aluminium hydride reduction of 2-benzyltetralone. In an attempt to replace the hydroxyl group in (II) by a bromine atom, with phosphorus tribromide in toluene, there was ready loss of hydrogen bromide and on distillation only 2-benzyl-3 : 4-dihydronaphthalene was obtained, which was identified by its ultraviolet absorption spectrum and dehydrogenation with 5% palladium-charcoal to 2-benzyl-naphthalene. It was thus necessary to aromatise the ring system completely in the bromide (I) and so prevent dehydrobromination. 2-Benzyl-1-bromonaphthalene was prepared from phenylmagnesium bromide and 1-bromo-2-naphthaldehyde,



the resulting secondary alcohol being reduced to (III) with iodine and red phosphorus in glacial acetic acid. In a Grignard reaction the bromo-compound (III) gave an 84–86% yield of 2-benzyl-1-naphthoic acid, which was cyclised with anhydrous hydrogen fluoride and on reduction with zinc in sodium hydroxide gave 1 : 2-[9- ^{14}C]benzanthracene (83% radiochemical yield, from $^{14}\text{CO}_2$).

In an alternative synthesis the aldehyde (IV) was prepared by carboxylation of 1-naphthylmagnesium bromide with $^{14}\text{CO}_2$, reduction of the labelled acid with lithium aluminium hydride, and oxidation of the resulting 1-naphthylmethyl alcohol with tetrachloro-1 : 2-benzoquinone⁵ to the aldehyde which was isolated as semicarbazone in 62% yield. Oxidation of the alcohol with chromium trioxide in pyridine⁶ gave an 86% yield of 1-naphthaldehyde, the overall yield from $^{14}\text{CO}_2$ being 65–70%. The labelled 1-naphthaldehyde with *o*-tolylmagnesium bromide gave the alcohol (V), which was pyrolysed directly with zinc dust at 410°, or converted into the ketone (VI) by chromic acid in sulphuric acid⁷ and then pyrolysed. In both methods the pyrolysis yielded only 30% of 1 : 2-benzanthracene. The overall radiochemical yield from $^{14}\text{CO}_2$ in the five stages was however only 6–8%.

¹ Part I, preceding paper.

² Collins, Burr, and Hess, *J. Amer. Chem. Soc.*, 1951, **73**, 5176.

³ Muxart, *Compt. rend.*, 1956, **242**, 2457.

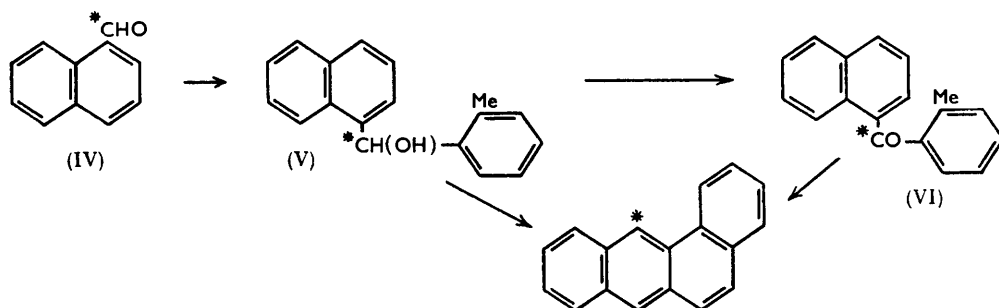
⁴ Hochstein and Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3484; Phillips and Mentha, *ibid.*, 1956, **78**, 140; cf. following paper.

⁵ Cf. Braude, Linstead, and Wooldridge, *J.*, 1956, 3070.

⁶ Cf. Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422; Braude, Forbes, and Evans, *J.*, 1953, 2202.

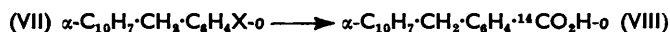
⁷ Cf. Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548.

For the synthesis of 1:2-[10-¹⁴C]benzanthracene, 1-2'-bromobenzyl-naphthalene (VII; X = Br) was prepared from *o*-bromobenzaldehyde and 1-naphthylmagnesium bromide, followed by reduction with red phosphorus and iodine. Carboxylation of the Grignard reagent from the bromo-compound (VII) with ¹⁴CO₂ gave the [¹⁴C]acid (VIII) in 80% yield. This was cyclised with anhydrous hydrogen fluoride and then reduced to 1:2-[10-¹⁴C]benzanthracene with zinc in sodium hydroxide. The overall radiochemical yield from ¹⁴CO₂ was 24%, which is considerably lower than that in the corresponding synthesis of 1:2-[9-¹⁴C]benzanthracene owing to the relatively poor yield in the cyclisation stage, which had previously been extensively investigated by Fieser and Hershberg.⁸ An attempt to cyclise the acid (VIII) with boron trifluoride in ether gave only unchanged

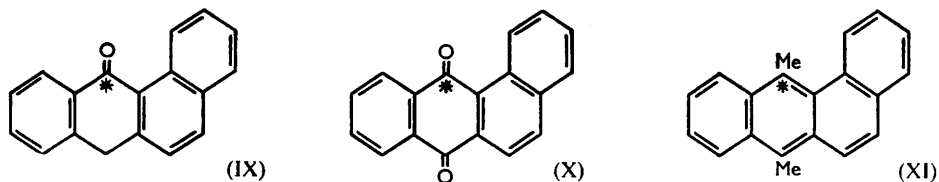


acid. The chloro-compound⁹ (VII; X = Cl) did not react with magnesium and could not be cross-metallated with *n*-butyl-lithium, but reacted with lithium and on carboxylation gave <30% of impure acid (VIII).

An attempt to convert 1:2-benzanthracene into 9:10-dimethyl-1:2-benzanthracene (XI) by treating its dilithio-derivative with methyl bromide and dehydrogenating the product¹⁰ failed on the semimicro-scale employed, giving only mixtures.



9:10-Dimethyl-1:2-[9-¹⁴C] benzanthracene was best prepared¹¹ by oxidising 1:2-benzanthracene or the benzanthrone (IX) to 1:2-benzanthraquinone (X) and converting this by methylmagnesium iodide followed by hydriodic acid into 10-iodomethyl-9-methyl-1:2-benzanthracene, which on treatment with stannous chloride in dioxan gave 9:10-dimethyl-1:2-[9-¹⁴C]benzanthracene. The overall radiochemical yield from the ketone (IX) or benzanthracene was 18%. Reaction of the ketone (IX) with methylmagnesium iodide failed to give 9-methyl-1:2-benzanthracene.



5-Methyl-1:2-[9-¹⁴C]benzanthracene was prepared from 1-bromo-2-2'-methylbenzyl-naphthalene, by carboxylation of the Grignard reagent, cyclisation of the resulting acid with anhydrous hydrogen fluoride, and reduction of the keto-group, as in the above cases. The overall radiochemical yield from ¹⁴CO₂ was 59%.

In the syntheses described above, cyclisations of the acids are only likely to take place

⁸ Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1937, **59**, 1028.

⁹ Bradsher, *ibid.*, 1940, **62**, 1077; Vingiello, Borkovec, and Shulman, *ibid.*, 1955, **77**, 2320.

¹⁰ Mikhailov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1946, 619.

¹¹ Cf. Sandin and Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 3100.

in one position. In no case was any cyclisation to the *peri*-naphthalene position observed. In the formation of most of the Grignard reagents it was necessary to add 1–2 drops of methyl iodide to initiate the reaction. Although the minimum quantity of methyl iodide was used, on a small scale this reduces the yield of required acid owing to the formation of a little acetic acid from the methylmagnesium iodide. This effect could be reduced by making the Grignard reagent on a larger scale and taking an aliquot portion for the carboxylation.

EXPERIMENTAL

For general methods see Part I.

1-Bromo-2-methylnaphthalene.—2-Methylnaphthalene (75 g.) was brominated in carbon tetrachloride as described by Hall and Mitchell,¹² giving 1-bromo-2-methylnaphthalene (97.5 g.), b. p. 114–116°/10⁻² mm. (Hall and Mitchell¹² give b. p. 112–117°/1 mm.).

1-Bromo-2-bromomethylnaphthalene.—1-Bromo-2-methylnaphthalene (50 g.), *N*-bromo-succinimide (40 g.), and benzoyl peroxide (0.5 g.) in carbon tetrachloride (100 g.) were refluxed in nitrogen for 2 hr. The solution was diluted with carbon tetrachloride (50 ml.), then filtered hot and the succinimide washed several times with hot carbon tetrachloride (total 100 ml.). The solvent was allowed to evaporate overnight in air, giving 1-bromo-2-bromomethylnaphthalene (53 g.), m. p. 107–108° (lit.,¹³ m. p. 103–105°, 106–108°).

1-Bromo-2-naphthaldehyde.—1-Bromo-2-bromomethylnaphthalene (40 g.) in boiling glacial acetic acid (100 ml.) was treated with hexamine (20 g.) and heated for about 30 sec., until the solution was clear. Water (75 ml.) was added and the solution allowed to cool. 1-Bromo-2-naphthaldehyde recrystallised from acetic acid as yellow prisms (15.5 g.), m. p. 117–118° (Hewett¹⁴ gives m. p. 117–118°).

1-Bromo-2-2'-methylbenzyl-naphthalene.—1-Bromo-2-naphthaldehyde (5 g.), in benzene (30 ml.) and ether (20 ml.), was added to *o*-tolylmagnesium bromide (from magnesium, 0.6 g., and *o*-bromotoluene, 4 g.) in ether (20 ml.). The solution was heated under reflux for 3 hr., then cooled, and excess of saturated aqueous ammonium chloride added. The organic layer was separated and most of the solvent distilled off under reduced pressure. The residue was dissolved in acetic acid (100 ml.), and iodine (3 g.), red phosphorus (3 g.), and water (20 ml.) were added. After 24 hr. under reflux and cooling, excess of phosphorus was filtered off and most of the acetic acid neutralised with 10% sodium hydroxide solution. The solution was extracted with ether (3 × 100 ml.), and the combined extracts were washed with 10% aqueous sodium hydroxide, dried (Na₂SO₄-K₂CO₃), and distilled, giving 1-bromo-2-2'-methylbenzyl-naphthalene (5.8 g., 57%), m. p. 54°, b. p. 163–164°/10⁻⁴ mm. (Found: Br, 24.8. C₁₈H₁₅Br requires Br, 25.7%).

2-Benzyl-1-bromonaphthalene.—1-Bromo-2-naphthaldehyde (7 g.) in benzene (30 ml.) and ether (20 ml.) was added to phenylmagnesium bromide (from magnesium, 0.8 g., and bromobenzene, 5 g.) in ether (25 ml.), then treated as above, giving 2-benzyl-1-bromonaphthalene, m. p. 39–40°, b. p. 136–138°/10⁻⁴ mm., *n*_D²⁰ 1.6690 (Found: C, 68.6; H, 4.6; Br, 26.5. C₁₇H₁₃Br requires C, 68.7; H, 4.4; Br, 26.9%).

2-Benzyl-1-naphth[¹⁴C]oic Acid.—A Grignard reagent was prepared by heating under reflux 2-benzyl-1-bromonaphthalene (1.3 g.), magnesium (0.13 g.), iodine (1 crystal), and methyl iodide (2–3 drops) in ether (20 ml.) for 2 hr. ¹⁴CO₂, generated with concentrated sulphuric acid from barium [¹⁴C]carbonate (591 mg., 3 mc) in a closed vacuum-system, was condensed into the Grignard solution by cooling it in liquid nitrogen. Isolation of the acid as for *o*-benzylbenzoic acid (see preceding paper) gave after one crystallisation from cyclohexane plates of 2-benzyl-1-naphth[¹⁴C]oic acid (0.66 g., 84%), m. p. 132–133°. A yield of 86% was obtained from a similar experiment. A sample recrystallised to constant m. p. from cyclohexane had m. p. and mixed m. p. 135–137° (Found: C, 82.1; H, 5.4. C₁₈H₁₄O₂ requires C, 82.5; H, 5.3%).

1 : 2-[9-¹⁴C]Benzanthracene.—The above acid (0.66 g.) was dissolved in anhydrous hydrogen fluoride (ca. 15 ml.) in a platinum crucible and kept at room temperature for 15 min. with occasional shaking. The orange liquid was poured on ice-water and the 1 : 2-benzanthr-10-one

¹² Hall and Mitchell, *J.*, 1951, 1375; cf. Adams and Binder, *J. Amer. Chem. Soc.*, 1941, **63**, 2773.

¹³ Newman and Kosak, *J. Org. Chem.*, 1949, **14**, 375; Hebbelynck and Martin, *Bull. Soc. chim. belges*, 1952, **61**, 635.

¹⁴ Hewett, *J.*, 1940, 293.

(or mixed isomers¹⁵) (0.61 g.), m. p. 140—141°, filtered off, dried *in vacuo*, and used without purification. This product (170 mg.) was heated with activated zinc dust (1 g.) in 2*N*-sodium hydroxide (8 ml.) and toluene (5 ml.) for 5 hr., then allowed to cool. The aqueous layer was extracted with benzene (2 × 5 ml.), and the excess of zinc washed with hot benzene (2 × 5 ml.). The combined solvents and washings were dried (Na₂SO₄) and distilled. The residual solid 1 : 2-[9-¹⁴C]benzanthracene crystallised from methanol in plates (140 mg.), m. p. 157—158°, 0.96 mc/mmole; to the mother-liquors was added carrier 1 : 2-benzanthracene (220 mg.), giving on concentration and crystallisation 1 : 2-[9-¹⁴C]benzanthracene (250 mg.), m. p. 156—157°, 71.7 μc/mmole (overall radiochemical yield from ¹⁴CO₂ 83%).

2-2'-Methylbenzyl-1-naphth[¹⁴C]oic Acid.—Carboxylation of a Grignard reagent from 1-bromo-2-2'-methylbenzyl-naphthalene (1.9 g.), magnesium (0.15 g.), iodine (1 crystal), and methyl iodide (2 drops) in ether (20 ml.) with ¹⁴CO₂ (from barium [¹⁴C]carbonate, 0.591 g., 3 mc) with stirring at room temperature for 1 hr., gave 2-2'-methylbenzyl-1-naphth[¹⁴C]oic acid (0.69 g., 83%), plates (from cyclohexane), m. p. and mixed m. p. 145—146° (Found : C, 82.4; H, 5.5. Calc. for C₁₅H₁₆O₂ : C, 82.6; H, 5.8%) (Fieser and Newman¹⁶ give m. p. 144—145°).

5-Methyl-1 : 2-[9-¹⁴C]benzanthracene.—The above acid (0.40 g.) was kept in anhydrous hydrogen fluoride (*ca.* 8 ml.) at room temperature for 15 min., then poured on ice-water, and the 5-methyl-1 : 2-benzanthr-10-one (0.39 g.), m. p. 162—163°, filtered off, dried *in vacuo*, and used without purification. It (150 mg.) was heated with activated zinc dust (1 g.) in 2*N*-sodium hydroxide (8 ml.) and toluene (5 ml.) for 6 hr. Crystallisation of the product from methanol gave 5-methyl-1 : 2-[9-¹⁴C]benzanthracene (120 mg.), m. p. 150—152°. This was chromatographed on alumina in benzene, then crystallised from methanol as plates (95 mg.), m. p. 152—153°, 1.1 mc/mmole. The m. p. was undepressed on admixture with an inactive sample of m. p. 151—152° (Fieser and Newman¹⁶ give m. p. 158.5—159.1°) (Found : C, 93.7; H, 5.8. Calc. for C₁₆H₁₄ : C, 94.2; H, 5.8%).

2-Benzyltetralone.—Tetral-1-one (5 g.) and benzyl bromide (6 g.) were added in one lot to a boiling solution of potassium (2.8 g.) in *tert.*-butyl alcohol (30 ml.), heated under reflux for 35 min., allowed to cool, and treated with ice-cold concentrated hydrochloric acid (50 ml.). The solution was ether-extracted, dried (Na₂SO₄), and evaporated under reduced pressure. Distillation of the residue gave tetralone (2 g.) and 2-benzyltetralone (1.8 g.), b. p. 155—159°/10⁻² mm., m. p. 53—54° [from light petroleum (b. p. 60—80°)] (Borsche *et al.*¹⁷ give m. p. 53—54°).

2-Benzyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol.—2-Benzyltetralone (1.5 g.) in ether (25 ml.) was added to a stirred suspension of lithium aluminium hydride (0.5 g.) in ether (75 ml.), and stirred at room temperature for 1 hr., and excess of hydride decomposed with 2*N*-sulphuric acid. Isolation with ether gave 2-benzyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol (1.2 g.), plates [from light petroleum (b. p. 60—80°)], m. p. 119—120° (Found : C, 85.6; H, 7.6. C₁₇H₁₈O requires C, 85.7; H, 7.6%).

2-Benzylidenetetralone.—Benzaldehyde (7 g.) and tetral-1-one (10 g.) were added in one lot to 5% methanolic potassium hydroxide (80 ml.) at 50°. The solution was allowed to cool overnight, the alkaline solution was neutralised with acetic acid, and the crystals were filtered off. Crystallisation from methanol gave pale yellow needles of 2-benzylidenetetralone (13.5 g.), m. p. 105° (Rapson and Shuttleworth¹⁸ give m. p. 105°).

Reduction of 2-benzylidenetetralone (4 g.) in ether (150 ml.) with lithium aluminium hydride (1.5 g.) under reflux for 60 min. gave a quantitative yield of 2-benzyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol, m. p. and mixed m. p. 119—120°.

2-Benzyl-3 : 4-dihydronaphthalene.—2-Benzyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol (15 g.) was dissolved in benzene (150 ml.), and phosphorus tribromide (25 g.) and 2—3 drops of pyridine were added. The mixture was heated for 3 hr. at 55°. Next morning the solution was poured on crushed ice, and the organic layer separated, washed with water, and dried (Na₂SO₄). Removal of the solvent under reduced pressure gave an oil. On distillation hydrogen bromide was evolved, giving only 2-benzyl-3 : 4-dihydronaphthalene (11.5 g.), b. p. 126°/0.1 mm., n_D^{25} 1.6162 (Found : C, 92.1; H, 7.2. C₁₇H₁₄ requires C, 92.7; H, 7.3%), λ_{max} 2660 Å (ϵ 13,600 in EtOH).

¹⁵ Cf. Thomson, *Quart. Rev.*, 1956, **10**, 27.

¹⁶ Fieser and Newman, *J. Amer. Chem. Soc.*, 1936, **58**, 2376.

¹⁷ Borsche, Hofmann, and Kuhn, *Annalen*, 1943, **554**, 23.

¹⁸ Rapson and Shuttleworth, *J.*, 1940, 636.

2-Benzyl-naphthalene.—2-Benzyl-3:4-dihydronaphthalene (0.9 g.) and 5% palladium-charcoal (0.3 g.) were heated at 200° for 1 hr., then at 290–300° for 15 min. The products were isolated with hot ethanol and on cooling in carbon dioxide-methanol 2-benzyl-naphthalene (0.8 g.) crystallised in plates, m. p. 54–55° (Nenitzescu *et al.*¹⁹ give m. p. 55–5°).

1-2'-Chlorobenzyl-naphthalene.—*o*-Chlorobenzaldehyde (42 g.) in ether (150 ml.) and 1-naphthylmagnesium bromide (from magnesium, 8.4 g., and 1-bromonaphthalene, 67.5 g.) in ether (450 ml.) gave a crude alcohol which was heated in glacial acetic acid (750 ml.) with iodine (15 g.), red phosphorus (15 g.), and water (75 ml.) for 27 hr., filtered, treated with ice, and extracted with ether (3 × 100 ml.). The combined extracts were washed several times with 10% aqueous sodium hydroxide, dried (Na₂SO₄-K₂CO₃), and distilled, giving the chloro-compound (47 g.), b. p. 139–140°/0.05 mm. (Bradsher⁹ gives b. p. 189–192°/2 mm.).

o-Bromobenzaldehyde similarly gave *1-2'-bromobenzyl-naphthalene* (62%), b. p. 150°/10⁻³ mm., *n*_D²⁰ 1.6645 (Found: C, 69.5; H, 4.4; Br, 27.0. C₁₇H₁₃Br requires, C, 68.7; H, 4.4; Br, 26.9%).

1-2'-[¹⁴C]Carboxybenzyl-naphthalene.—A Grignard reagent, prepared by heating the preceding bromide (3.2 g.) for *ca.* 1 hr., with magnesium (0.35 g.), iodine (1 crystal), and methyl iodide (1–2 drops), in ether (15 ml.), was treated with ¹⁴CO₂ (from barium [¹⁴C]carbonate, 1.97 g. 1 mc) and stirred for 30 min. at room temperature, giving the desired acid (80%), which after several crystallisations from cyclohexane had m. p. 144–145° (Bergmann and Loewenthal²⁰ give m. p. 147°).

An attempt to form a Grignard reagent from the chloro-compound failed even after refluxing in ether or tetrahydrofuran for up to 24 hr.

1:2-[10-¹⁴C]Benzanthracene.—The foregoing acid (0.5 g.) was kept in anhydrous hydrogen fluoride (*ca.* 5 ml.) at room temperature for 10 min. Isolation of the product as before gave a solid which was heated in acetone (40 ml.) with charcoal, filtered, and cooled slowly to –10°. A product (250 mg.), m. p. 157–158°, was obtained, and on recrystallisation from acetone a product (160 mg.) (*a*), m. p. 157–158°. The solid did not dissolve in cold 10% potassium hydroxide solution but on warming exhibited a strong green fluorescence in ultraviolet light. From the mother-liquors of the crystallisation was obtained a solid (125 mg.) (*b*), m. p. 230–232°, which was not investigated.

The product (*a*) above (135 mg.) was reduced with zinc dust (1 g.) as previously described, giving *1:2-[10-¹⁴C]benzanthracene* (105 mg.), m. p. 153–154°, 104 μc/mmole.

1-Naphth[¹⁴C]oic Acid.—¹⁴CO₂ (from barium [¹⁴C]carbonate, 1.97 g., 1 mc) was condensed into 1-naphthylmagnesium bromide (from magnesium, 0.3 g., and 1-bromonaphthalene, 3.2 g.) in ether (30 ml.) in a closed vacuum-system. The solution was stirred at room temperature for 1 hr. Isolation as described above gave 1-naphth[¹⁴C]oic acid (1.62 g., 94%), m. p. 158–159° (lit.,²¹ m. p. 160–161°). The acid was used without purification.

1-Naphthyl[¹⁴C]methyl Alcohol.—Labelled 1-naphthoic acid (1.62 g.) was reduced with lithium aluminium hydride (2 g.) in ether (75 ml.). Isolation of the product with ether and crystallisation from cyclohexane gave 1-naphthyl[¹⁴C]methyl alcohol (1.2 g., 81%), m. p. 63–64° (Manske and Ledingham²² gave m. p. 64°).

1-Naphth[¹⁴C]aldehyde.—(*a*) 1-Naphthyl[¹⁴C]methyl alcohol (1.2 g.) and tetrachloro-1:2-benzoquinone (2 g.) in chloroform (50 ml.) were left for 3 days at room temperature. The solution was then chromatographed on alumina in chloroform, and the chloroform eluate distilled under reduced pressure. The residual oil of 1-naphth[¹⁴C]aldehyde was used for the next stage. The 2:4-dinitrophenylhydrazone, crystallised from ethyl acetate, had m. p. and mixed m. p. 257–258° (decomp.) (lit.,²³ m. p. 254°). The semicarbazone, crystallised from aqueous methanol, had m. p. 215–218° (lit.,²³ 219°). Derivatives were prepared from aldehyde isolated during an inactive run. Yields of derivatives indicated a 62% yield of 1-naphthaldehyde.

(*b*) The alcohol (0.5 g.), in pyridine (5 ml.), was added to chromium trioxide (0.5 g.) in pyridine (5 ml.). Next morning the mixture was poured into water (200 ml.) and ether-extracted. The extract was washed with 2*N*-hydrochloric acid (2 × 50 ml.), dried (Na₂SO₄), and evaporated

¹⁹ Nenitzescu, Isacescu, and Ionescu, *Annalen*, 1931, **491**, 217.

²⁰ Bergmann and Loewenthal, *Bull. Soc. chim. France*, 1952, 66.

²¹ King, *J. Amer. Chem. Soc.*, 1944, **66**, 894.

²² Manske and Ledingham, *Canad. J. Res.*, 1939, **17**, 14.

²³ Coles and Dodds, *J. Amer. Chem. Soc.*, 1938, **60**, 853.

under reduced pressure. The residue was converted into the semicarbazone (0.58 g., 86%), m. p. 215—218°.

1-(α -Hydroxy-2-methylbenzyl)naphthalene.—To 1-naphth[^{14}C]aldehyde (method *a*) was added carrier aldehyde (1 g.) dissolved in ether (25 ml.); the mixture was added dropwise to *o*-tolylmagnesium bromide (from magnesium, 0.4 g., and *o*-bromotoluene, 2.5 g.) in ether (50 ml.). The whole was stirred at room temperature for 30 min. and then treated with excess of saturated aqueous ammonium chloride. Isolation with ether gave the alcohol (1.8 g.) which crystallised in plates [from light petroleum (b. p. 60—80°)], m. p. 115°, undepressed on admixture with a non-radioactive sample of m. p. 118—118.5° (Found: C, 87.5; H, 6.4. $\text{C}_{18}\text{H}_{16}\text{O}$ requires C, 87.1; H, 6.4%).

1 : 2-[9- ^{14}C]Benzanthracene.—The above alcohol (0.5 g.) and zinc dust (0.3 g.) were heated at 400—410° for 3 hr. and, after cooling, extracted with hot light petroleum (b. p. 60—80°) and chromatographed on alumina. Removal of solvent gave 1 : 2-[9- ^{14}C]benzanthracene (140 mg.), m. p. 152—154°, which crystallised from methanol in plates (100 mg.), m. p. 156—157°, 35 $\mu\text{C}/\text{mmole}$. The overall radiochemical yield from $^{14}\text{CO}_2$ was 6%.

1-Naphthyl *o*-Tolyl Ketone.—The preceding alcohol (2 g.) was treated in acetone (50 ml.) with excess of chromic acid in aqueous sulphuric acid.⁷ After 5 min. the mixture was diluted with water (300 ml.) and ether-extracted. The ether layer was dried ($\text{Na}_2\text{SO}_4\text{-K}_2\text{CO}_3$) and solvent removed under reduced pressure. The residual crude ketone was heated with zinc dust (0.5 g.) for 2 hr. at 410°. Isolation with light petroleum (b. p. 60—80°) as in the above pyrolysis gave after chromatography 1 : 2-benzanthracene (0.6 g., 33%), m. p. 156—157°.

Metallation of 1-2'-Chlorobenzyl-naphthalene.—The chloro-compound (3.5 g.) in ether (10 ml.) was added to lithium (0.3 g.) in ether (50 ml.) at -10° to -20° . The solution became green after 3—4 minutes' stirring, and deep crimson after *ca.* 30 min. The solution was stirred for 2 hr., then poured on excess of powdered carbon dioxide and allowed to attain room temperature. Isolation of acidic products as above gave a gum which was dissolved in benzene and precipitated with light petroleum (b. p. 40—60°). Crystallisation from light petroleum gave pale yellow plates (1.8 g.), m. p. 133—134° (Found: C, 81.6; H, 5.6. Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_2$: C, 82.5; H, 5.3%). From the neutral fraction was obtained 1-benzyl-naphthalene (0.9 g.) which, crystallised from light petroleum (b. p. 40—60°), had m. p. 54—55°, undepressed on admixture with a sample of m. p. 56—58°.

1 : 2-Benz[9- ^{14}C]anthraquinone.—The crude 1 : 2-benzanthrone (above) (240 mg., *ca.* 1 mc) was dissolved in glacial acetic acid (10 ml.) and heated to boiling. Excess of 30% hydrogen peroxide (6 ml.) was added and the solution heated under reflux for 5 min. The solution was diluted with water (15 ml.). The crude orange quinone (200 mg.), m. p. 157—167°, crystallised. Inactive quinone (500 mg.) was added to the active product and the whole recrystallised from acetic acid, giving the [9- ^{14}C]quinone (550 mg.), m. p. 165—166° (*a*). To the mother liquors was added carrier inactive quinone (500 mg.); crystallisation gave a further yield of active quinone (460 mg.), m. p. 165—167° (*b*). A further crop (170 mg.) crystallised overnight [m. p. 165—167° (*c*)] (Badger and Cook²⁴ give m. p. 163—168°).

9 : 10-Dimethyl-1 : 2-[9- ^{14}C]benzanthracene.—The quinone (720 mg., *a + c*) in benzene (5 ml.) was added to methylmagnesium iodide (from magnesium, 1.2 g., and methyl iodide, 8 g.) in ether (15 ml.). After 30 minutes' heating the solution was left for 18 hr. at 2° in nitrogen, then poured at 0° into hydriodic acid (12 ml.; *d* 1.7) in methanol (35 ml.), and glacial acetic acid (35 ml.) was added. The iodomethyl compound slowly separated, was filtered off, dissolved in dioxan (40 ml.) containing concentrated hydrochloric acid (2 ml.), and was added to stannous chloride (8 g.) in dioxan (30 ml.) containing concentrated hydrochloric acid (20 ml.). After 5 min. under reflux, the solution was set aside for 30 min., water (*ca.* 250 ml.) added, and the solution left at 0° for 2—3 hr., giving 9 : 10-dimethyl-1 : 2-[9- ^{14}C]benzanthracene (330 mg.), m. p. and mixed m. p. 122—123° (Sandin and Fieser¹¹ give m. p. 122—123°), 124 $\mu\text{C}/\text{mmole}$. The quinone (460 mg., *b*) gave a hydrocarbon (210 mg.), m. p. 122—123°, 23.5 $\mu\text{C}/\text{mmole}$. The radiochemical yield from crude 1 : 2-benzanthrone was thus 18%.

1 : 2-[9- ^{14}C]Benzanthracene of High Activity.—1 : 2-[9- ^{14}C]Benzanthracene (270 mg., 59%), m. p. 155—156°, 22.2 mc/mmole, was prepared as described above from barium [^{14}C]carbonate (0.394 g., 46 mc). Dilution analysis indicated a radiochemical purity > 98%.

Oxidation of 1 : 2-[9- ^{14}C]Benzanthracene.—The hydrocarbon (120 mg., 11.6 mc) was treated in boiling glacial acetic acid (20 ml.) with 30% hydrogen peroxide (4 ml.) and heated under

²⁴ Badger and Cook, *J.*, 1939, 804.

reflux for 5 min., rapidly becoming orange. 1 : 2-Benzanthraquinone (250 mg.) was dissolved in the solution, water (15 ml.) was added, and the solution allowed to cool. 1 : 2-[^{14}C]Benzanthraquinone (276 mg.), m. p. 163—165° (*a*), crystallised. To the mother-liquors was added carrier quinone (450 mg.); crystallisation yielded radioactive quinone (427 mg.), m. p. 164—166° (*b*).

9 : 10-Dimethyl-1 : 2-[^{14}C]benzanthracene.—Conversion of the quinone (*a*) into the hydrocarbon as described above gave 9 : 10-dimethyl-1 : 2-[^{14}C]benzanthracene (126 mg.), m. p. 122—123°, 2.6 mc/mmole (radiochemical purity by dilution analysis >98%). From quinone (*b*) was obtained hydrocarbon (237 mg.), m. p. 122—123°, 0.71 mc/mmole. The overall radiochemical yield from benzanthracene was thus 18%.

The Reaction of 1 : 2-Benzanthr-9-one with Methylmagnesium Iodide.—The crude ketone (150 mg.) in benzene (5 ml.) was added to methylmagnesium iodide (from magnesium, 72 mg., and methyl iodide, 430 mg.) in ether (10 ml.) and the mixture heated under reflux for 3 hr. The solution was cooled and excess of hydrochloric acid (50% v/v) added. The aqueous layer was extracted with benzene (2×10 ml.). The combined organic layers were dried (Na_2SO_4), and the solvent was removed under reduced pressure. Crystallisation of the residue from acetone-methanol gave a product (60 mg.), m. p. 237—239° (Found : C, 87.9; H, 4.5. Calc. for $\text{C}_{18}\text{H}_{12}\text{O}$: C, 88.5; H, 4.9%), which is probably the starting ketone or its tautomer. No fluorescent hydrocarbons were obtained.

THE RADIOCHEMICAL CENTRE, AMERSHAM, BUCKS.

[Received, January 31st, 1957.]