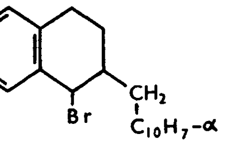
539. *^{14}C-Labelled Polycyclic Aromatic Hydrocarbons. Part III.*[1] *The Synthesis of* 1 : 2-5 : 6-[9-^{14}C]*Dibenzanthracene.*

By J. R. Catch and E. A. Evans.

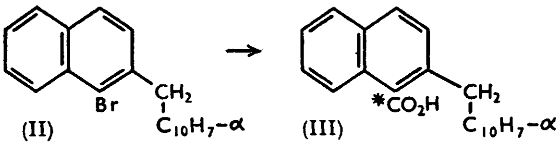
1 : 2-5 : 6-[9-^{14}C]Dibenzanthracene has been synthesised in three radioactive stages from $^{14}CO_2$, the overall yield being 30%.

This paper records a synthesis of 1 : 2-5 : 6-dibenzanthracene in three radioactive stages from $^{14}CO_2$, in about 30% overall yield, which, although lower than in the tri- and tetracyclic series, is better than was obtained by Heidelberger and his collaborators.[2]

The bromo-compound (I) was prepared by condensing 1-naphthaldehyde with tetral-1-one, reducing the naphthylidene compound with lithium aluminium hydride, and treating the resulting saturated alcohol with phosphorus tribromide. 1-Bromo-1 : 2 : 3 : 4-tetrahydro-2-1′-naphthylmethylnaphthalene (I) however did not react with magnesium, and could not be cross-metallated with *n*-butyl-lithium, perhaps owing to dehydrobromination (cf. Part II). 1-Bromo-2-1′-naphthylmethylnaphthalene (II) was prepared by treating 1-bromo-2-naphthaldehyde with 1-naphthylmagnesium bromide and reducing the secondary alcohol with red phosphorus and iodine. This bromide had to be purified by chromatography before it would form a Grignard reagent, but impure bromide could be cross-metallated with *n*-butyl-lithium and on carboxylation gave 2-1′-naphthylmethyl-1-naphthoic acid (III) in 67% yield based on $^{14}CO_2$: carboxylation of the Grignard reagent gave 83—98% yields. The acid was cyclised with anhydrous hydrogen fluoride and the product reduced to 1 : 2-5 : 6-dibenzanthracene with zinc dust in sodium hydroxide. The overall radiochemical yield was 31%.



(I)



(II) (III)

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[1] Part II, preceding paper.

[2] Heidelberger, Brewer, and Dauben, *J. Amer. Chem. Soc.*, 1947, 69, 1390.

Cyclisation of the acid was less complete than in the previous cases (Parts I and II); use of concentrated sulphuric acid followed by reduction failed to yield dibenzanthracene.

(IV) $2:1\text{-}C_{10}H_6Me{\cdot}CO{\cdot}C_{10}H_7\text{-}\alpha$ $\quad$ $2:1\text{-}C_{10}H_6Me{\cdot}CO{\cdot}C_{10}H_7\text{-}\beta$ (V)

In another attempted route the ketones (IV and V) were prepared from 1- and 2-naphthaldehyde respectively with 2-methyl-1-naphthylmagnesium bromide, the secondary alcohol being oxidised with chromic acid in aqueous sulphuric acid.[3] Pyrolysis of either ketone at *ca.* 500° gave only traces of fluorescent gums on a small scale (*viz.*, *ca.* 200 mg.) although up to 33% yield of dibenzanthracene has been obtained in larger-scale experiments.[4] 2-Naphth[^{14}C]aldehyde was prepared in 81% yield by oxidation of 2-naphthyl-[^{14}C]methyl alcohol with tetrachloro-1 : 2-benzoquinone.[1, 5]

The radiochemical purities of the hydrocarbons described in this and the preceding papers were determined by dilution analysis, *viz.*, by dilution of the active material with pure carrier inactive material, homogenising the whole in a suitable solvent, and evaporating the solution to dryness. The residue is assayed (result *A*) in the usual manner, then crystallised and assayed again (result *B*). *B*/*A* gives a measure of the radiochemical purity.

The 1 : 2-5 : 6-[9-^{14}C]dibenzanthracene prepared from the acid (III) had the same ultraviolet absorption spectrum as the carrier hydrocarbon, but although the melting point (261—262°) was also the same it contained *ca.* 10% of a radioactive impurity which was removed only by crystallisation from benzene; chromatography on alumina in benzene and sublimation were only partially successful. After crystallisation the radiochemical purity was >95%.

The method of assay of the radioactive dibenzanthracene adopted by Heidelberger *et al.*[2] would not indicate the radiochemical purity of the product.

EXPERIMENTAL

For general methods see Part I. Ultraviolet absorptions refer to ethanol solutions and were measured with a Unicam S.P. 500 instrument.

1-*Naphthylmethyl Alcohol.*—1-Naphthaldehyde (25 g.) in anhydrous ether (25 ml.) was added dropwise to a stirred suspension of lithium aluminium hydride (5 g.) in ether (300 ml.) at room temperature. Excess of lithium aluminium hydride was decomposed with water, and excess of sulphuric acid (25% v/v) added. The ether layer was dried (Na_2SO_4–K_2CO_3) and the solvent removed under reduced pressure, giving 1-naphthylmethyl alcohol (22 g.) which crystallised in plates (from benzene–*cyclo*hexane), m. p. 63—64° (Manske and Ledingham [6] gave m. p. 64°). Similar reduction of 1-naphthoic acid gave a quantitative yield of 1-naphthylmethyl alcohol, m. p. 64°.

1-*Bromomethylnaphthalene.*—The alcohol (18 g.) was heated in benzene (150 ml.) with phosphorus tribromide (9·5 ml.) and pyridine (2—3 drops) at 55° for 2 hr., then treated with ice. The organic layer was washed with water, 2N-sodium hydrogen carbonate and saturated salt solution. After drying (Na_2SO_4) the solvent was removed under reduced pressure and the residual oil crystallised from light petroleum (b. p. 40—60°), giving 1-bromomethylnaphthalene (18 g.), m. p. 54—55° (Szmuszkovicz and Bergmann [7] give m. p. 54—55·5°). A lower yield was obtained by the action of *N*-bromosuccinimide on 1-methylnaphthalene as described by Buu-Hoï.[8]

1-*Bromo*-2-1′-*naphthylmethylnaphthalene.*—1-Bromo-2-naphthaldehyde (14 g.) in benzene (100 ml.) was added to 1-naphthylmagnesium bromide (from magnesium, 1·6 g., and 1-bromonaphthalene, 13 g.) in ether (100 ml.), and the mixture heated under reflux for 5 hr. The solution was treated with excess of saturated ammonium chloride, and the organic layer

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[3] Cf. Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548.

[4] Fieser, " Organic Reactions," John Wiley & Sons, New York, 1942, Vol. I, p. 151.

[5] Braude, Linstead, and Wooldridge, *J.*, 1956, 3070.

[6] Manske and Ledingham, *Canad. J. Res.*, 1939, **17**, 14.

[7] Szmuszkovicz and Bergmann, *J. Amer. Chem. Soc.*, 1953, **75**, 353.

[8] Buu-Hoï, *J.*, 1946, 830.

separated. Most of the solvent was distilled off under reduced pressure and the residue heated in glacial acetic acid (150 ml.) with phosphorus (3 g.), iodine (3 g.), and water (25 ml.) for 24 hr. After cooling, excess of red 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 extracts were washed with 10% aqueous sodium hydroxide and dried (Na_2SO_4–K_2CO_3). The ether was distilled under reduced pressure and the residual dark red oil repeatedly extracted with hot light petroleum (b. p. 40—60°) (total 500 ml.) and chromatographed on alumina in the same solvent. Removal of the solvent gave prisms (10 g.), m. p. 96—97°. Crystallisation from light petroleum (b. p. 40—60°) gave 1-*bromo*-2-1′-*naphthylmethylnaphthalene*, m. p. 96—97° (Found: C, 72·6; H, 4·4; Br, 22·6. $C_{21}H_{15}Br$ requires C, 72·7; H, 4·3; Br, 23·0%).

2-1′-*Naphthylmethyl*-1-*naphth*[^{14}C]*oic Acid*.—(a) *Grignard method.* A Grignard reagent was prepared from 1-bromo-2-1′-naphthylmethylnaphthalene (1·5 g.), magnesium (0·13 g.), iodine (1 crystal), and methyl iodide (1—2 drops) in ether (20 ml.) under reflux in 2—3 hr. $^{14}CO_2$ (generated from barium [^{14}C]carbonate, 0·394 g., 46 mc, with concentrated sulphuric acid) was condensed into the above Grignard reagent in a closed vacuum-system by freezing in liquid nitrogen. Working up the product as before (see Part I) gave the *acid* which crystallised from benzene–*cyclo*hexane (yield 0·613 g., 98%) and had m. p. 191—192°, undepressed on admixture with a non-radioactive sample (Found: C, 84·2; H, 5·2. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·3%). In other experiments yields of 83% and 92% were obtained.

(b) *Cross-metallation.* 1-Bromo-2-1′-naphthylmethylnaphthalene (1·7 g.) in ether (5 ml.) was added to *n*-butyl-lithium (from lithium, 0·07 g., and *n*-butyl bromide, 1 g.) in ether (20 ml.) at −20°. The solution was stirred for 1½ hr. at room temperature. $^{14}CO_2$ (from barium carbonate, 0·591 g., 1 mc) was condensed into the solution. After 30 minutes' stirring at room temperature the solution was left overnight and worked up as before. Crystallised from *cyclo*hexane–benzene, the acid (0·6 g., 67%) had m. p. 190—192°.

1 : 2-5 : 6-[9-^{14}C]*Dibenzanthracene*.—(*a*) The acid (0·5 g., from method *b*; *ca.* 0·3 mc/mmole) was left in anhydrous hydrogen fluoride (10—15 ml.) for 30 min. at room temp., then poured on ice. The product was filtered off and heated under reflux for *ca.* 7 hr. with zinc dust (3 g.), 2N-sodium hydroxide (20 ml.), and toluene (15 ml.). Working up as described for 1 : 2-benzanthracene (Part II) gave 1 : 2 : 5 : 6-dibenzanthracene which, crystallised from benzene, had m. p. and mixed m. p. 258—260° (230 mg., 55% based on acid). This material was slightly brown but on chromatography on alumina in benzene, and then crystallisation from benzene formed colourless plates (110 mg.), m. p. 261—262°, 0·3 mc/mmole. To the mother-liquors of the crystallisation was added carrier dibenzanthracene (50 mg.) and the solution was concentrated, yielding 1 : 2 : 5 : 6-dibenzanthracene (62 mg.), m. p. 259—261°, 176 μc/mmole. This represents a total radiochemical yield of 32% (158 μc) based on acid (the acid recovered was taken into account in determining yields).

A small quantity (50 mg.) of unchanged acid, m. p. and mixed m. p. 191—192°, was isolated from the alkaline layer of the reduction by acidification and ether-extraction.

(*b*) The acid (0·575 g., 46 mc) was converted into dibenzanthracene as described above. The crude product (150 mg.), m. p. 230—250°, was chromatographed on alumina in benzene and then crystallised from benzene–methanol, yielding almost colourless plates of [9-^{14}C]dibenzanthracene (120 mg., 35% from acid), m. p. 259—261° (radiochemical purity at this stage by dilution of a rechromatographed sample, m. p. 261—262°, was 90%). Carrier dibenzanthracene (*ca.* 150 mg.) was added to the above, and the whole crystallised from benzene, yielding [9-^{14}C]dibenzanthracene (168 mg.), m. p. 261—262°, 10·5 mc/mmole (dilution analysis indicated a radiochemical purity >95%). To the mother-liquors of the crystallisation was added carrier dibenzanthracene and a further 3 mc of active hydrocarbon were isolated (m. p. 261—262°). The product had absorption max. at 2220 (ε 54,000), 2310 (ε 27,300), 2780 (ε 40,700), 2860 and 2880 (ε 82,400), 2970 (ε 143,000), 3200 (ε 16,400), 3320 (ε 13,900), 3490 (ε 12,600), 3750 (ε 200) and 3930 Å (ε 700). The same maxima and intensity were found with the dibenzanthracene of 90% radiochemical purity. From the aqueous alkaline layer of the reduction was recovered starting acid (190 mg.), m. p. and mixed m. p. 189—192°.

2-1′-*Naphthylmethyltetralone*.—Tetral-1-one (12 g.) in toluene (15 ml.) was added under nitrogen to a suspension of sodamide (3·3 g.) in toluene (80 ml.) and the mixture heated under reflux for 6 hr. After cooling, 1-bromomethylnaphthalene (16·5 g.) in toluene (25 ml.) was added and the mixture cautiously heated. When the vigorous reaction had subsided the mass was refluxed for 6 hr. and then treated with water and excess of 25% sulphuric acid. The aqueous layer was extracted with ether (2 × 50 ml.). The combined extracts were washed with water (100 ml.) and saturated salt solution (50 ml.) and dried (Na_2SO_4). The solvents were distilled under reduced pressure and the residue distilled, giving unchanged tetralone (4 g.), b. p. 74°/5 mm., and the product (10·5 g.), b. p. 188—192°/10^{-2} mm., which crystallised from methanol in prisms, m. p. 92—93° (7·5 g.) (Szmuszkovicz and Bergmann [7] give m. p. 92—93°).

1 : 2 : 3 : 4-*Tetrahydro*-2-1′-*naphthylmethyl*-1-*naphthol*.—The foregoing ketone (6 g.) in anhydrous ether (100 ml.) was heated with lithium aluminium hydride (2 g.) in ether (200 ml.) for 15 min., then stirred for 1 hr. at room temperature. Isolation with ether gave the alcohol (6 g.) which, crystallised from aqueous methanol, had m. p. 112—114°, $\lambda_{\text{max.}}$ 2740 (ε 6900), 2830 (ε 8000), 2950 (ε 5500), 3140 Å (ε 500).

Condensation of Tetral-1-*one and* 1-*Naphthaldehyde*.—Tetral-1-one (19 g.) and 1-naphthaldehyde (21·5 g.) were added in one lot to 10% methanolic potassium hydroxide (250 ml.) at 60—65° and left for 1 day at room temperature. The solution was neutralised with glacial acetic acid and the solid filtered off and crystallised from methanol, giving pale yellow needles of 2-1′-naphthylidenetetralone (35 g., 95%), m. p. 131—132° (Buu-Hoï and Cagniant [9] give m. p. 131°), $\lambda_{\text{max.}}$ 2680 Å (ε 23,000). The m. p. was not raised by chromatography on alumina in benzene.

1 : 2 : 3 : 4-*Tetrahydro*-2-1′-*naphthylmethyl*-1-*naphthol*.—The preceding tetralone (15 g.) was stirred in anhydrous ether (500 ml.) with lithium aluminium hydride (3 g.) under reflux for 2 hr. Next morning water and excess of 25% sulphuric acid were added, the products isolated with ether and dried (Na_2SO_4–K_2CO_3), and the solvents distilled off. The residual solid crystallised from aqueous ethanol, giving a quantitative yield of the *tetrahydronaphthol*, m. p. and mixed m. p. 114° (Found : C, 87·3; H, 7·2. $C_{21}H_{20}O$ requires C, 87·3; H, 6·9%), $\lambda_{\text{max.}}$ 2740 (ε 6400), 2830 (ε 7200), 2950 Å (ε 5000). The alcohol was recovered unchanged after being shaken for 6 hr. with hydrogen and platinic oxide in ethanol or acetic acid.

1-*Bromo*-1 : 2 : 3 : 4-*tetrahydro*-2-1′-*naphthylmethylnaphthalene*.—The tetrahydronaphthol (3 g.) was heated in benzene (25 ml.) with phosphorus tribromide (1·5 ml.) and pyridine (1 drop) at 55° for 2 hr., then poured on ice. The organic layer was separated, washed with water and 2N-sodium hydrogen carbonate, dried (Na_2SO_4), and evaporated under reduced pressure, giving the *bromide* (2·1 g.), m. p. 108—109° (decomp.) [from light petroleum (b. p. 60—80°)] (Found : Br, 23·0. $C_{21}H_{19}Br$ requires Br, 22·8%).

The alcohol (1·02 g.) in acetone (25 ml.) was treated with a slight excess of chromic acid in aqueous sulphuric acid [3] at room temperature. Water (50 ml.) was added and the products were isolated with ether giving the ketone (1 g.), m. p. and mixed m. p. 90—92°.

2-*Methyl*-1-*naphthyl* 1-*Naphthyl Ketone* (IV).—1-Naphthaldehyde (7 g.) in ether (25 ml.) was added dropwise to 2-methyl-1-naphthylmagnesium bromide (from magnesium, 1·5 g., and 1-bromo-2-methylnaphthalene, 11 g.), in ether (100 ml.). The solution was stirred for 1 hr., then treated with excess of saturated aqueous ammonium chloride. The ether layer was dried (Na_2SO_4) and the residue, after removal of solvent, was dissolved in acetone (500 ml.) and treated with a slight excess of chromic acid in aqueous sulphuric acid.[3] Water (*ca.* 50 ml.) was added and most of the acetone distilled off under reduced pressure. The residue was poured into water (300 ml.), and the red solid which separated crystallised from ethanol (pale yellow plates, 10 g., 75%). A sample crystallised to constant m. p. had m. p. 169—170° (Found : C, 89·1; H, 5·3. Calc. for $C_{22}H_{16}O$: C, 89·2; H, 5·4%) (Fieser and Dietz [10] give m. p. 171°).

Pyrolysis. The ketone (0·4 g.) was heated for 3 hr. at *ca.* 500°. The products were extracted with hot benzene and chromatographed on alumina in benzene. Removal of the solvent gave 1 : 2 : 5 : 6-dibenzanthracene (25 mg.) which crystallised from benzene in plates, m. p. and mixed m. p. 261—262°. Heating for 5 hr. gave 30 mg. of the hydrocarbon.

2-*Naphth*[^{14}C]*aldehyde*.—2-Naphthyl[^{14}C]methyl alcohol (350 mg.) (tracer level activity, *ca.* 30 μc/mmole), prepared from 2-naphth[^{14}C]oic acid by reduction with lithium aluminium hydride, was dissolved in chloroform (10 ml.), and tetrachloro-1 : 2-benzoquinone (500 mg.) added. The mixture was left for 3 days at room temperature and then chromatographed on alumina in chloroform. Distillation of the eluate gave a solid (320 mg.) which crystallised from light petroleum (b. p. 40—60°) giving 2-naphth[^{14}C]aldehyde (280 mg., 81%), m. p. 62—63° (lit.,[11] m. p. 57—58°).

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[9] Buu-Hoï and Cagniant, *Rev. Sci.*, 1942, **80**, 384.
[10] Fieser and Dietz, *Ber.*, 1929, **62**, 1829.
[11] Williams, *Org. Synth.*, 1943, **23**, 63.

2-*Methyl*-1-*naphthyl* 2-*Naphthyl Ketone* (V).—2-Naphthaldehyde (3·5 g.) in ether (25 ml.) was added to 2-methyl-1-naphthylmagnesium bromide (from magnesium, 0·8 g.) in ether (100 ml.). Working up as for ketone (IV) gave ketone (V) (4·3 g., 65%; m. p. 133—136°), which crystallised from ethanol in pale yellow needles (3·5 g.), m. p. 138—139° (Fieser and Dietz [10] give m. p. 142—143°).

The ketone (160 mg.), m. p. 134—136°, 28 μc/mmole, was obtained from 2-naphth-[^{14}C]aldehyde (240 mg.).

Pyrolysis. Pyrolysis of the ketone (200 mg.) at *ca*. 430° for 3·5 hr. gave only traces of fluorescent gums after chromatography on alumina in benzene.

THE RADIOCHEMICAL CENTRE, AMERSHAM, BUCKS.

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