# 84. *The Preparation of* 9 : 10-*Di*-(4-*carboxybutyl*)*anthracene and Related Reactions.*

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Hydrobromination of 9 : 10-diallylanthracene and its homologues does not yield terminally-brominated 9 : 10-dialkylanthracenes, but only secondary dibromides, probably because of the interference of the 9- and the 10-position of the relevant anthracene with any homolytic mechanism. The synthesis of 9 : 10-di-(4-carboxybutyl)anthracene has therefore been completed from 9 : 10-di-(3-ethoxypropyl)-9 : 10-dihydro-9 : 10-dihydroxyanthracene.

PREVIOUSLY [1] it was reported that 9 : 10-diallylanthracene, on treatment with hydrobromic acid in the presence of peroxide, gave a 90% yield of a dihydrobromide, designated as 9 : 10-di-($x$-bromopropyl)anthracene, in which it was hoped that the two bromine atoms were situated on the terminal carbon atoms of the two propyl chains (*i.e.*, $x = 3$). Such a dibromide could then be used for the preparation of 9 : 10-di-(4-carboxybutyl)anthracene, by the malonic ester synthesis. This dibromide, prepared in either acetic acid or benzene solution in the presence of perphthalic acid or benzoyl peroxide, does not, however, react with sodiomalonic ester or potassium cyanide, and similarly the dihydriodide of 9 : 10-diallylanthracene (83%) does not react with these substances.

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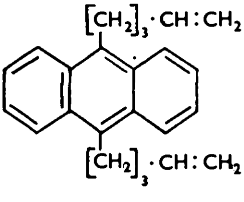
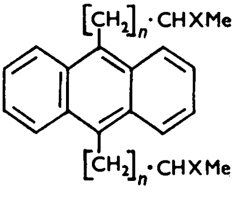
[1] Clark, *J.*, 1956, 1511.

In analogous reactions, 9 : 10-dihydro-9 : 10-dihydroxy-9 : 10-dipent-4′-enylanthracene was obtained from 5-bromopent-1-ene, magnesium, and anthraquinone under standard Grignard conditions in 31% yield. Reduction with phenylhydrazine gave an 84% yield of 9 : 10-dipent-4′-enylanthracene (I), whose dihydrobromide, obtained in 92% yield under peroxide-catalysed conditions, showed a lack of reactivity similar to that displayed by 9 : 10-di-(*x*-bromopropyl)anthracene.

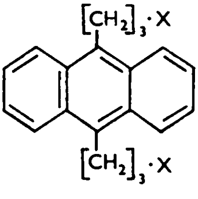


(I)



(IIa) ; $n = 1$, X = Br or I

(IIb) ; $n = 3$, X = Br

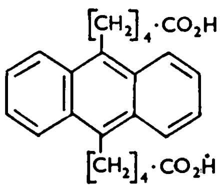


(IIIa) ; X = OEt

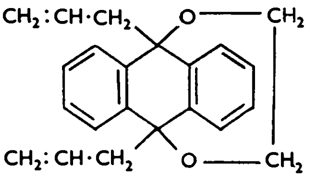
(IIIb) ; X = Br

(IIIc) ; X = I

(IIId) ; X = CN



(IV)



(V)

It was therefore suspected that the dihydrobromide and the dihydriodide from 9 : 10-diallylanthracene were, in fact, 9 : 10-di-(2-halogenopropyl)anthracenes (IIa), which would be less reactive than the isomeric 9 : 10-di-(3-halogenopropyl)anthracenes (IIIb and IIIc). Similarly, the dihydrobromide derived from 9 : 10-dipent-4′-enylanthracene must be 9 : 10-di-(4-bromopentyl)anthracene (IIb). Such a situation could arise only by failure of the peroxide-catalysed addition of hydrobromic acid to olefinic bonds, in this particular instance because of the affinity of the 9- and the 10-carbon atom of the anthracene nucleus for free radicals.[2]

Reduction by phenylhydrazine of 9 : 10-di-(3-ethoxypropyl)-9 : 10-dihydro-9 : 10-dihydroxyanthracene gave a 96% yield of 9 : 10-di-(3-ethoxypropyl)anthracene (IIIa), which was treated with hydrobromic acid in glacial acetic acid and with aqueous hydriodic acid. Both 9 : 10-di-(3-bromopropyl)anthracene (IIIb) and 9 : 10-di-(3-iodopropyl)-anthracene (IIIc), isolated in 83% and 82% yields respectively, exhibited properties and spectra quite different from the substances produced by the hydrohalogenation of 9 : 10-diallylanthracene, and, unlike the latter, were active. Thus the iodo-compound, treated with alcoholic potassium cyanide, gave an 82% yield of 9 : 10-di-(3-cyanopropyl)anthracene (IIId), and sodiomalonic ester and the iodide gave the expected dimalonic ester. Hydrolysis of the latter with alcoholic potassium hydroxide, followed by acidification and decarboxylation as described by Miller, Amidon, and Tawney,[3] gave a 72% yield of 9 : 10-di-(4-carboxybutyl)anthracene (IV).

An attempt to prepare a bridged dihydroanthracene (V) from ethylene glycol and 9 : 10-diallyl-9 : 10-dihydro-9 : 10-dihydroxyanthracene gave only 9 : 10-diallyl-9 : 10-dihydro-9 : 10-di-(2-hydroxyethoxy)anthracene.

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[2] Beckwith and Waters, *J.*, 1956, 1108.

[3] Miller, Amidon, and Tawney, *J. Amer. Chem. Soc.*, 1955, **77**, 2845.

## EXPERIMENTAL

9 : 10-*Di*-(2-*iodopropyl*)*anthracene*.—9 : 10-Diallylanthracene (5 g.) in benzene (50 ml.) was saturated at room temperature with hydrogen iodide (prepared by dropping an aqueous solution of the acid on phosphoric oxide, and passing the gas through red phosphorus supported upon glass wool). The solution was kept for 1 hr.; dilution with alcohol then yielded a yellow solid (8·2 g., 83%). Crystallisation from acetic acid and finally from alcohol gave pale yellow needles of the *di-iodide*, m. p. 135° (decomp.) (Found: C, 46·9; H, 4·3; I, 49·6. $C_{20}H_{20}I_2$ requires C, 46·7; H, 3·9; I, 49·4%).

5-*Hydroxypent*-1-*ene*.—This alcohol was prepared by the method of Linstead *et al.*[4] from tetrahydrofurfuryl chloride in 80% yield. A more convenient procedure was as follows. At 0°, ethylene oxide was passed into a molar solution of allylmagnesium bromide [1] for 6 hr., and the mixture then kept at room temperature overnight. Decomposition was effected with ammonium chloride solution, the aqueous layer being washed with ether (2 × 150 ml.), and the ethereal extracts combined and dried ($Na_2SO_4$). Distillation gave 5-hydroxypent-1-ene, b. p. 136° (69 g., 80%).

9 : 10-*Dihydro*-9 : 10-*dihydroxy*-9 : 10-*dipent*-4′-*enylanthracene*.—5-Bromopent-1-ene (320 g.), prepared from the alcohol by the method of Linstead *et al.*,[4] in ether (1900 ml.) was added dropwise to magnesium (51·3 g.) in ether (250 ml.) under Grignard conditions. To the Grignard solution at 0° was added anthraquinone (109 g.) in small portions, with vigorous stirring (4 hr.). Next day the mixture was refluxed (6 hr.), and decomposed with ammonium chloride solution. The ethereal extract was evaporated, the residual oil dissolved in hot benzene, and the solution shaken with boiling alkaline sodium hydrosulphite (dithionite) solution. The dried ($Na_2SO_4$) benzene solution was evaporated to leave the *diol* which was crystallised from benzene; it then had m. p. 163° (60·9 g., 31%) (Found: C, 82·4; H, 8·3. $C_{24}H_{28}O_2$ requires C, 82·75; H, 8·0%).

The yield of *dipentenyl-diol*, obtained by the use of 5-chloropent-1-ene [5] in the above preparation, was only 5%.

9 : 10-*Diethoxy*-9 : 10-*dihydro*-9 : 10-*dipent*-4′-*enylanthracene*.—The foregoing diol (4 g.) and ethanol (40 ml.) containing concentrated sulphuric acid (5 drops), immediately gave the *diethyl ether*. This was washed with water, ammonium hydroxide solution and ethanol, and crystallised from ethanol; it had m. p. 154·5° (Found: C, 83·2; H, 8·9. $C_{28}H_{36}O_2$ requires C, 83·1; H, 8·9%).

9 : 10-*Dipent*-4′-*enylanthracene*.—9 : 10-Dihydro-9 : 10-dihydroxy-9 : 10-dipent-4′-enylanthracene (7·5 g.), phenylhydrazine (15 ml.), and glacial acetic acid (50 ml.) were heated on the water bath (¼ hr.), and then refluxed for ¼ hr. Yellow plates separated on cooling, and were washed with a little cold methanol. Crystallisation from ethanol (Norite) gave pale yellow plates of 9 : 10-*dipent*-4′-*enylanthracene* (5·7 g., 84%), m. p. 82° (Found: C, 91·8; H, 8·5. $C_{24}H_{26}$ requires C, 91·7; H, 8·3%). Light absorption occurred at 5·45, 10·08, and 10·93 μ (allyl).

9 : 10-*Di*-(4-*bromopentyl*)*anthracene*.—A solution of 9 : 10-dipent-4′-enylanthracene (2 g.) in glacial acetic acid (25 ml.) containing perphthalic acid (0·1 g.) was saturated with hydrogen bromide (tetralin) at 10° then refluxed for ½ hr., cooled, and diluted with water; of the solid obtained (2·8 g., 92%), a small portion was recrystallised from ethanol to give pale yellow spangles of the *dibromide*, m. p. 140° (Found: C, 60·6; H, 6·1; Br, 33·3. $C_{24}H_{28}Br_2$ requires C, 60·5; H, 5·9; Br, 33·6%).

9 : 10-*Di*-(3-*ethoxypropyl*)*anthracene*.—9 : 10-Di-(3-ethoxypropyl)-9 : 10-dihydro-9 : 10-dihydroxyanthracene [1] (33·6 g.) was treated with phenylhydrazine (65 ml.) and glacial acetic acid (250 ml.). The mixture was diluted with water (500 ml.) and extracted with ether (3 × 150 ml.), and the ethereal extracts were washed with dilute hydrochloric acid, sodium carbonate solution (10%), and water, and dried ($Na_2SO_4$). On evaporation of the solvent an oil (29·5 g., 96%) remained, which slowly solidified to yellow needles, m. p. 59°. This could be distilled with little decomposition at 230—240°/0·15 mm., but could not be recrystallised. A small portion of the *compound* was distilled at 230°/0·05 mm. (oil bath) (Found: C, 82·3; H, 8·5. $C_{24}H_{30}O_2$ requires C, 82·3; H, 8·6%). Light absorption occurred at 9 μ (ethoxy).

9 : 10-*Di*-(3-*bromopropyl*)*anthracene*.—9 : 10-Di-(3-ethoxypropyl)anthracene (2 g.) in glacial acetic acid (35 ml.) was saturated with hydrogen bromide at room temperature, and the solution

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[4] *Org. Synth.*, Coll. Vol. III, p. 698. Gaubert, Linstead, and Rydon, *J.*, 1937, 1971.

[5] Paul, *Ann. Chim.*, 1932, **18**, 303.

kept overnight. After being refluxed for 2 hr. the solution was cooled and diluted with water. The pale green solid (2 g., 83%) was crystallised repeatedly from alcohol (Norite) for analysis; it formed pale leaf-green needles of the *dibromide*, m. p. 150° (Found: C, 56·9; H, 5·1; Br, 37·8. $C_{20}H_{20}Br_2$ requires C, 57·1; H, 4·8; Br, 38·1%).

9 : 10-*Di*-(3-*iodopropyl*)*anthracene*.—9 : 10-Di-(3-ethoxypropyl)anthracene (28 g.) was refluxed (6 hr.) with hydriodic acid (300 ml.). The green product was washed with water and ethanol, and dissolved in hot benzene. The *di-iodide* (34 g., 82%) was precipitated from cold benzene by addition of a large volume of alcohol. Crystallisation from acetic acid, and finally benzene, gave lime-green needles, m. p. 199° (Found: C, 46·9; H, 4·0; I, 49·1. $C_{20}H_{20}I_2$ requires C, 46·7; H, 3·9; I, 49·4%).

9 : 10-*Di*-(3-*cyanopropyl*)*anthracene*.—9 : 10-Di-(3-iodopropyl)anthracene (3 g.) was refluxed in suspension with a solution of potassium cyanide (1 g.) in ethanol (100 ml.) for 24 hr. On dilution of the clear solution with water, a yellow solid (1·5 g., 82%) was deposited. Crystallisation from ethanol gave the *dinitrile* as a pale yellow powder, m. p. 185° (Found: C, 84·4; H, 6·7; N, 8·7. $C_{22}H_{20}N_2$ requires C, 84·6; H, 6·4; N, 9·0%). Light absorption occurred at 4·41 μ (nitrile).

9 : 10-*Di*-(4-*carboxybutyl*)*anthracene*.—9 : 10-Di-(3-iodopropyl)anthracene (5·95 g.) was treated with the solution from sodium (0·5 g.) and diethyl malonate (6·4 g.) in benzene (50 ml.). On warming, reaction took place immediately and was completed by refluxing for 6 hr. The mixture was washed with dilute sulphuric acid, sodium carbonate solution (10%), and water, and dried ($Na_2SO_4$). The benzene and excess of malonic ester were distilled *in vacuo*, leaving a viscous oil which would not distil at 0·05 mm. This was refluxed for 2 hr. with a solution of potassium hydroxide (3 g.) in alcohol (50 ml.). The yellow potassium salt was filtered off, washed with hot alcohol, and precipitated as the dimalonic acid by dilute hydrochloric acid (4·55 g.). The tetracarboxylic acid was refluxed in diphenyl ether (20 g.) until the evolution of carbon dioxide ceased (½ hr.). The solution was cooled, diluted with ether (100 ml.), and extracted with sodium hydroxide solution (10%; 2 × 100 ml.). Acidification of the basic extracts gave 9 : 10-*di*-(4-*carboxybutyl*)*anthracene* (3·15 g., 72% overall). A small portion was crystallised from dioxan–water giving yellow needles, m. p. 216° (Found: C, 76·0; H, 6·8. $C_{24}H_{26}O_4$ requires C, 76·2; H, 6·9%). Light absorption occurred at 5·89 μ (carboxyl) and 3·5 μ (associated hydroxyl).

The *dimethyl ester* was prepared by use of sulphuric acid–methanol. The solid had m. p. 89°, b. p. 243—245°/0·07 mm. (oil bath) (Found: C, 76·6; H, 7·5. $C_{26}H_{30}O_4$ requires C, 76·8; H, 7·4%).

9 : 10-*Diallyl*-9 : 10-*dihydro*-9 : 10-*di*-(2-*hydroxyethoxy*)*anthracene*.—9 : 10-Diallyl-9 : 10-dihydro-9 : 10-dihydroxyanthracene [1] (3·5 g.) was dissolved in warm ethylene glycol (25 ml.). Ethylene glycol (5 ml.) containing concentrated sulphuric acid (5 drops) was added, and the solution was shaken, cooled, and set aside for 2 hr. The solution was then diluted with water, and the white solid washed with ammonium hydroxide solution and water. Crystallisation from benzene and ethanol gave fine needles, m. p. 128° (Found: C, 75·8; H, 7·3. $C_{24}H_{28}O_4$ requires C, 75·8; H, 7·4%).

In the ultraviolet, all the anthracenes described had $\lambda_{max.}$ (approx.) 2600, 3400, 3600, 3800, and 4000. In some cases an additional peak was observed at 2520—2540.

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