727. *Bi(anthracene-9,10-dimethylene) (Tetrabenzo-[2,2]-paracyclophane).*

By J. H. Golden.

Reaction of 9,10-di(chloromethyl)anthracene with sodium iodide in acetone yields bi(anthracene-9,10-dimethylene) (I), the structure, properties, and reactions of which are discussed. Exposure to light converts the hydrocarbon into an isomer related to " para-anthracene " in structure. When heated the hydrocarbon is rapidly polymerised ($\Delta H = 47{\cdot}1 \pm 5$ kcal./mole). Unsuccessful attempts to prepare a similar dimer from 2,6-di(bromomethyl)naphthalene and the formation of an analogous naphthalene polymer are described.

Tardieu [1] recently obtained an infusible orange solid on refluxing the dimethanesulphonates of *cis*- and *trans*-9,10-dihydro-9,10-di(hydroxymethyl)anthracene with alcoholic alkali and formulated it as $(C_{16}H_{12})_n$. Treatment of the same diesters with Triton B reagent at $-25°$ gave a colourless solution ($\lambda_{max.}$ 283 mμ in ether) of the hitherto unknown 9,10-dihydro-9,10-dimethyleneanthracene which fixed iodine immediately to give 9,10-di(iodomethyl)anthracene although the solution could not be concentrated without formation of a yellow polymer.

Reaction of sodium iodide with 9,10-di(chloromethyl)anthracene in acetone has been stated [2] to yield a yellow, amorphous, iodine-free compound similar to that obtained by

[1] Tardieu, *Compt. rend.*, 1959, **248**, 2885.
[2] Rio, *Ann. Chim.* (*France*), 1954, **12**, 229.

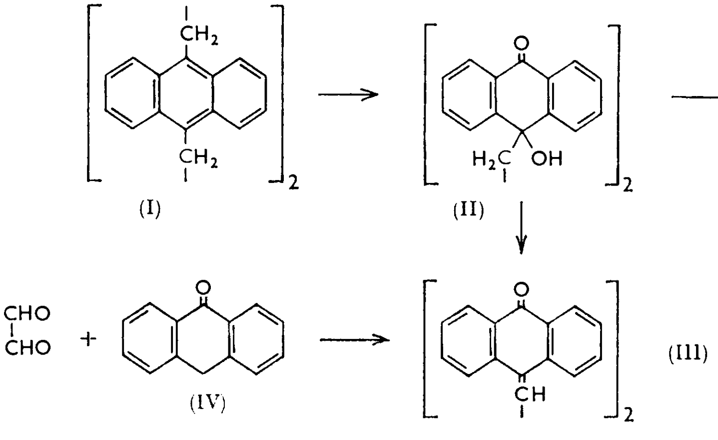
the action of zinc powder in methanol, and both products were tentatively described as polymers of 9,10-dihydro-9,10-dimethyleneanthracene. The former of these reactions has now been re-investigated and in the present work a sparingly soluble, infusible, orange crystalline compound was isolated which recrystallised from chloroform (63% yield after purification) and gave analytical figures for $(C_{16}H_{12})_n$. An identical product was obtained similarly from 9,10-di(bromomethyl)anthracene.

The ultraviolet light absorption of the present hydrocarbon in chloroform is similar to that of the compound described as a polymer by Tardieu.[1] Attempts to measure the molecular weight by ebullioscopic or isopiestic methods failed because of the low solubility of the compound in organic solvents and its ready decomposition in solution at elevated temperatures. However, the properties are consistent with those of a cyclic dimer $C_{32}H_{24}$ and lead us to postulate structure (I), bi(anthracene-9,10-dimethylene) (tetrabenzo-[2,2]-paracyclophane) (cf. Fig. 1) for the hydrocarbon. The formation of this dimer instead of the expected di-iodo-compound is analogous to the preparation of benzocyclobutanes from ωω′-dibromo-*o*-xylenes by the action of sodium iodide [3] and of bifluoren-9-yl from 9-iodofluorene in the presence of iodide ion.[4]

Evidence for structure (I) is as follows.

Although vigorous oxidation yielded anthraquinone (90%) milder oxidation led to a compound $C_{30}H_{22}O_4$, the molecular weight of which was established by cryoscopy. This contained two active hydrogen atoms and infrared analysis revealed hydroxyl (3432 cm.$^{-1}$) and carbonyl (1603, 1650 cm.$^{-1}$) groups. Dehydration with sulphuric acid in acetic acid readily eliminated the hydroxyl groups and gave 1,2-di-(9,10-dihydro-10-oxo-9-anthrylidene)ethane (III), whose structure was established by a mixed melting point and identity of infrared spectrum with that of a specimen prepared by condensing anthrone (IV) with glyoxal.[5] The compound $C_{30}H_{22}O_4$ thus has structure (II).

The hydrocarbon (I) formed a monopicrate analogous to that from bi(naphthalene-2,7-dimethylene).[6] The picrate readily decomposed into its constituents when treated with ethanol.



The crystalline hydrocarbon (I) did not melt when heated above 200° but the cooled material was insoluble in organic solvents. Similarly when it was heated above 100° in, *e.g.*, xylene, aniline, or nitrobenzene under air or in a vacuum, a lemon-yellow, insoluble,

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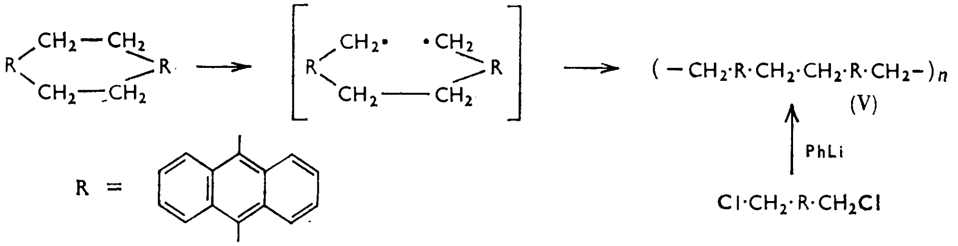
[3] Finkelstein, *Ber.*, 1910, **43**, 1528; Finkelstein, *Chem. Ber.*, 1959, **92**, 5; Jensen and Coleman, *J. Amer. Chem. Soc.*, 1958, **80**, 6149.

[4] Sampey and King, *Bull. Furman Univ., Furman Studies*, 1949, **31**, No. 5, 22; Dickinson and Eaborn, *J.*, 1959, 3574.

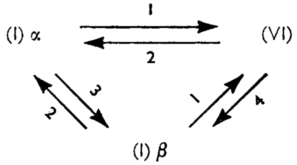
[5] I.G. Farbenind., D.R.P. 453,768/1927.

[6] Baker, Glockling, and McOmie, *J.*, 1951, 1118.

amorphous powder, $(C_{16}H_{12})_n$, was deposited. This melted with decomposition above 360° and was similar in properties and infrared spectrum to a specimen of the polymer (V) prepared by reaction of 9,10-di(chloromethyl)anthracene with phenyl-lithium.[7] The formation of this polymer from the hydrocarbon (I) can be explained by homolysis of one of the dimethylene bridges and subsequent intermolecular coupling of the diradicals thus formed. This ready polymerisation is unexpected in view of previous unsuccessful attempts to obtain the polymer (V), *e.g.*, by pyrolysis of 9,10-dimethylanthracene.[8] As the solid-state reaction was very rapid it was studied by differential thermal analysis in a nitrogen atmosphere. Polymerisation caused a very sharp exothermal peak with a maximum differential temperature of 25—30° from which the heat of polymerisation of the dimer was calculated to be $\Delta H = 47{\cdot}1 \pm 5$ kcal./mole, a value considerably higher than the heats of polymerisation recorded for ethylenic monomers.[9]



Exposure of the orange crystalline compound (I) to sunlight rapidly transformed it into a colourless, crystalline isomer. Similarly, exposure of the orange chloroform solution caused loss of colour and replacement of the characteristic anthracene ultraviolet spectrum by a typical dihydroanthracene spectrum [10] with a single band at 299·5 mμ. The mode of formation of this photo-isomer and its properties suggest a close relation with the dimers formed by intermolecular reaction from anthracene and its 9-substituted derivatives in the presence of light [11,12] although in the present case intramolecular reaction to give a structure (VI) (Fig. 1) is more likely. This transformation is supported by the close similarity in infrared spectra between compound (I) and anthracene and between the photo-isomer and " para-anthracene " in the 5—6·5 μ region (Fig. 2) which is very sensitive to slight changes in the substitution patterns of aromatic compounds. The replacement of the two aliphatic C–H stretching bands at 2928 and 2965 cm.$^{-1}$ for (I) by bands at 2962 and 3002 cm.$^{-1}$ for the photo-isomer is evidence of the further strain placed upon the methylene groups in the cyclobutane portions of structure (VI).



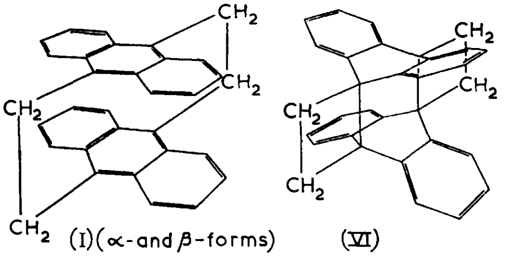
1, Light. 2, Recrystn. from $CHCl_3$. 3, Storage under $CHCl_3$. 4, Dark.

The formation of dimers from 9,10-disubstituted anthracenes is not common, and the photo-products are generally less stable than those from monosubstituted anthracenes and are readily depolymerised by heat.[12,13] The ready formation of the photo-isomer in

[7] Golden, *J.*, 1961, 1604.
[8] Errede and Szwarc, *Quart. Rev.*, 1958, **12**, 301.
[9] Roberts, *J. Res. Nat. Bur. Stand.*, 1950, **44**, 221.
[10] Roitt and Waters, *J.*, 1952, 2695.
[11] Greene, Misrock, and Wolfe, *J. Amer. Chem. Soc.*, 1955, **77**, 3852.
[12] Calas and Lalande, *Bull. Soc. chim. France*, 1959, 763.
[13] Calas and Lalande, *Bull. Soc. chim. France*, 1959, 770; 1960, 144; Dufraisse and Mathieu, *ibid.*, 1947, 307.

the present case can be attributed to the constraint of the two anthracene nuclei in a position favourable for interaction, but reversion to compound (I) occurs when the photo-isomer is kept in the dark at room temperature or when heated, the rate of the transformation increasing with temperature. The chemical identity of the regenerated compound with the initial hydrocarbon was established by analysis and infrared spectroscopy although *X*-ray powder analysis showed it to be a polymorph of the original with a distinctive *X*-ray pattern; the initial and regenerated forms have been designated α and β. Interconversions of the α- and the β-form and the photo-isomer were followed by *X*-ray powder photography and the following relationships established, as in the chart. A preliminary *X*-ray analysis of single crystals was carried out (by Mr. J. R. C. Duke) and data obtained from Weissenberg films are given in the Table.*

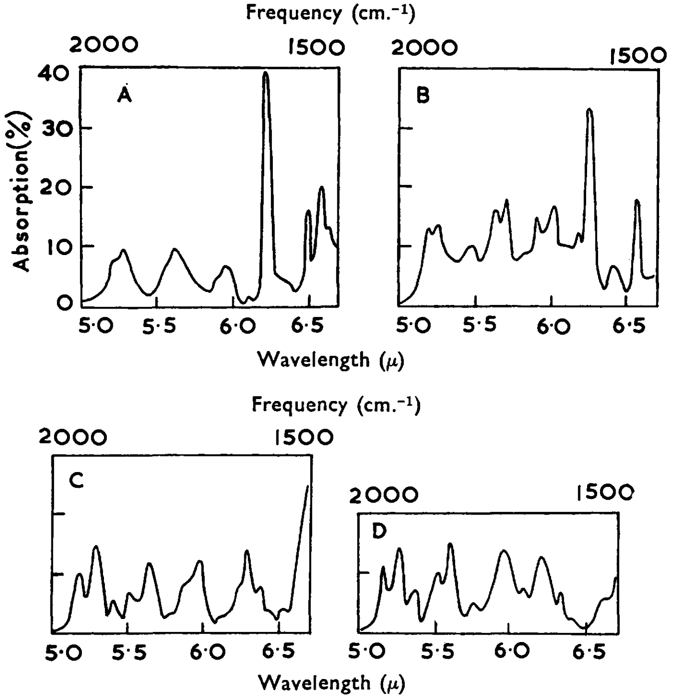
Fig. 1.



(I)(α-and β-forms)

(VI)

Fig. 2. *Infrared absorption (in Nujol) of* (A) *bi(anthracene-9,10-dimethylene)* (I) (α-form), (B) *anthracene,* (C) *photo-isomer* (VI), *and* (D) "*para-anthracene.*"



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* More detailed *X*-ray analyses of bi(anthracene-9,10-dimethylene) and its photo-isomer are being carried out by Dame Kathleen Lonsdale, F.R.S., and her co-workers at University College, London.

X-*Ray single-crystal data for bi*(*anthracene*-9,10-*dimethylene*): α- *and* β- *forms and photo-isomer.*

		Form	
	(I) α	(I) β	(VI) (photo-isomer)
Crystal system	Monoclinic	Monoclinic	Monoclinic
a (Å)	8·28	8·50	8·54
b (Å)	13·26	12·85	13·06
c (Å)	21·55	10·36	9·98
β	116°	112·9°	111·9°
Density	1·314	1·325	1·338
Space-group	$P2_1/c$	$P2_1/a$	$P2_1/a$
Mol. wt.	840 (Z = 2)	414 (Z = 2)	416 (Z = 2)
	420 (Z = 4)	207 (Z = 4)	208 (Z = 4)

Z = no. of molecules per unit cell.

The results are consistent with the view that the hydrocarbon has a molecular weight of 417 in all three forms (theory, 408); in this case no molecular symmetry is necessarily entailed for the α-form, but the molecules of the β-form and the photo-isomer must possess centres of symmetry.

The hydrocarbon (I) with iodine and iodine monochloride did not yield identifiable products and with maleic anhydride in benzene it gave a crystalline compound, m. p. 365°, containing anhydride groupings (infrared absorption at 1751, 1821 cm.$^{-1}$), whose formula, $(C_{24}H_{16}O_6)_n$, corresponded to two maleic anhydride residues per anthracene nucleus.

Several dimers related to bi(anthracene-9,10-dimethylene) have been described, *e.g.*, di-*p*-xylylene,[14] bi(naphthalene-2,7-dimethylene),[6] and bi(pyridine-2,6-dimethylene),[15] but the yields were lower than in the present case. In an attempted preparation of bi(naphthalene-2,6-dimethylene) by the present method 2,6-di(bromomethyl)naphthalene with sodium iodide in acetone gave the corresponding iodo-compound in good yield. The dibromo-compound with phenyl-lithium gave a polymer; this was not formed by the pyrolysis of the corresponding dimethyl compound; [16] again no dimer was isolated despite variation of the conditions.

EXPERIMENTAL

M. p.s were determined on a Kofler hot-stage.

9,10-Di(chloromethyl)anthracene was obtained by Miller's method,[17] as yellow needles (44%), m. p. 255—260° (decomp.) (from toluene). More vigorous preparative conditions led to the rapid formation of polymers.

9,10-*Di*(*bromomethyl*)*anthracene*.—9,10-Di(chloromethyl)anthracene (10 g.) was extracted (Soxhlet) into a refluxing solution of sodium bromide (20 g.) in acetone (700 ml.). The precipitate was filtered off, washed with acetone, and re-extracted as before into sodium bromide solution. The resultant precipitate (12·3 g.) was extracted (Soxhlet) with toluene to give 9,10-di(bromomethyl)anthracene (10·9 g., 82%), yellow needles (Found: C, 53·2; H, 3·4; Br, 43·4. Calc. for $C_{16}H_{12}Br_2$: C, 52·8; H, 3·3; Br, 43·9%), decomp. >300° (Barnett and Matthews [18] mention blackening at 315°).

Bi(*anthracene*-9,10-*dimethylene*) (*Tetrabenzo*-[2,2]-*paracyclophane*).—(a) *From* 9,10-*di*(*chloromethyl*)*anthracene*. The chloro-compound (5·12 g.) was extracted (Soxhlet) into a refluxing solution of sodium iodide (15 g.) in acetone (250 ml.). The red-brown solution was filtered hot and the residue was washed thoroughly with acetone and water and dried. No identifiable product was isolated from the liquors, which contained much free iodine. The orange precipitate (2·85 g., 75%) was extracted (Soxhlet) with chloroform (250 ml.) until the extract was colourless; hot filtration then yielded orange crystals (2·2 g., 63%). Recrystallisation from chloroform gave monoclinic plates of *bi*(*anthracene*-9,10-*dimethylene*) (*α-form*) (Found: C, 93·9; H, 5·8. $C_{32}H_{24}$ requires C, 94·1; H, 5·9%), $\nu_{max.}$ 2928, 2965 (aliphatic CH stretch), 3038, 3056, 3072

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[14] Brown and Farthing, *Nature*, 1949, **164**, 915; Farthing, *J.*, 1953, 3261; Brown, *J.*, 1953, 3265.

[15] Baker, Buggle, McOmie, and Watkins, *J.*, 1958, 3594.

[16] Szwarc, *J. Polymer Sci.*, 1951, **6**, 319.

[17] Miller, *J. Amer. Chem. Soc.*, 1955, **77**, 2845.

[18] Barnett and Matthews, *Ber.*, 1926, **59**, 1429.

(aromatic CH stretch), and 1500—2000 cm.$^{-1}$ (Fig. 2), (in chloroform) $\lambda_{max.}$ 257, 302, 381, 418, 449, and 459 mμ (log ε 3·02, 3·60, 3·82, 3·50, 2·71, and 2·68). The hydrocarbon, when heated in nitrobenzene to 130° and then cooled, gave a yellow solution $\lambda_{max.}$ 431 mμ (log ε 2·50). When heated on a Kofler hot-stage the transparent crystals developed spots above 200° and gradually became opaque and brown but did not melt. The hydrocarbon was sparingly soluble in chloroform, benzene, dioxan, and pyridine but insoluble in other low-boiling solvents. Attempts to obtain the molecular weight by ebullioscopic and isopiestic methods failed owing to the low solubility and ready polymerisation.

(b) *From* 9,10-*di(bromomethyl)anthracene.* The bromo-compound, by the above procedure, yielded bi(anthracene-9,10-dimethylene) (α-form) (40% after purification).

The hydrocarbon (α-form) (0·5 g.) was extracted (Soxhlet) into a refluxing solution of picric acid (2·5 g.) in benzene (300 ml.). The solution was rapidly cooled and the microcrystalline olive-black precipitate was filtered off, washed sparingly with benzene–light petroleum (b. p. 40—60°) (1 : 4) and light petroleum (b. p. 40—60°), and dried. This *picrate* (Found: C, 72·1; H, 4·0; N, 6·4. $C_{38}H_{27}N_3O_7$ requires C, 71·6; H, 4·3; N, 6·6%) did not melt below 360° and gave an *X*-ray powder pattern free from those of the components. Treatment of the picrate with ethanol at room temperature removed picric acid and left the hydrocarbon (β-form and trace of α-form) as an orange powder identified by its *X*-ray powder pattern.

*Polymerisation of Bi(anthracene-*9,10-*dimethylene).*—(a) *In solution.* The hydrocarbon (156 mg.) and naphthalene (700 mg.) were mixed in a tube, and degassed at 10^{-6} mm. and the tube was then sealed and heated at 150° for 3 hr. The mixture produced was refluxed with benzene (100 ml.) and filtered. The insoluble portion was exhaustively extracted (Soxhlet) with benzene, leaving a lemon-yellow, amorphous *polymer* (VI) (153 mg.) [Found: C, 94·4; H, 5·9. $(C_{16}H_{12})_n$ requires C, 94·1; H, 5·9%], insoluble in organic solvents, darkening above 300°, and melting with decomposition above 360°. Similarly, when bi(anthracene-9,10-dimethylene) (5 mg.) in nitrobenzene (50 ml.) was heated slowly with rapid stirring, the orange solution changed to deep yellow sharply at 122° and deposited flocculent yellow polymer at 180—185°; this behaviour was also observed in other solvents (*e.g.*, aniline, xylene) with b. p. above 100°. (b) *In the solid state.* Heating the solid hydrocarbon yielded polymer identical (infrared) with that formed as in (a).

Differential thermal analysis of the polymer (by DR. C. P. CONDUIT).—The analyses were performed in a conventional apparatus at a heating rate of 5°/min. and with 0·1—0·2 g. of the specimen. The specimen and reference containers were of fused silica with pockets for the chromel–alumel thermocouple junctions. Sand was used as the inert reference material. When the hydrocarbon was heated in air no thermal effects occurred below 280°; at this temperature a very sharp exotherm with a maximum differential temperature of 25—30° occurred. Beyond this peak the ΔT trace exhibited a second exothermal process which continued irregularly; examination of the specimen at this stage showed that this was due to extensive oxidative degradation. Repetition of the analysis in a nitrogen atmosphere gave a ΔT trace containing only the single, very sharp peak, due to polymerisation, from which the heat of polymerisation was calculated by Vold's method,[19] the constants used being: mol. wt. of monomer, 408·5; spec. heat of monomer, 0·30 cal./per g. per degree (c); heat capacity of specimen holder, 0·393 cal./per degree (c). The mean of five determinations gave $\Delta H_p =$ 47·1 ± 5 kcal./mole.

Reaction of 9,10-*Di(chloromethyl)anthracene with Phenyl-lithium.*—Phenyl-lithium (16·8 g.) in ether (400 ml.) was added dropwise during 2 hr. to a stirred, refluxing solution of 9,10-di(chloromethyl)anthracene (27·5 g.) in toluene (1500 ml.) under nitrogen. A yellow solid was precipitated; ether was removed continuously throughout. The green mixture was decomposed with water (100 ml.), acidified, and filtered. The precipitate was washed with water and solvents, dried (11·5 g.), refluxed with dioxan–concentrated hydrochloric acid (3 : 1) for 8 hr., washed, dried, and extracted (Soxhlet) with chloroform until the extract was colourless. The insoluble, yellow polymer (6·4 g.) [Found: C, 92·1; H, 5·9; Cl, 1·1. Calc. for $(C_{16}H_{12})_{31}Cl_2$: C, 93·0; H, 5·9; Cl, 1·1. Calc. for $(C_{16}H_{12})_n$: C, 94·1; H, 5·9%] darkened above 300° and decomposed above 360°. Infrared analysis showed the polymer to be substantially identical with that obtained from bi(anthracene-9,10-dimethylene).

The Photo-isomer (VI).—Orange bi(anthracene-9,10-dimethylene) (I), α- or β-form, when exposed to sunlight in air or in a vacuum, rapidly gave colourless monoclinic plates of the

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[19] Vold, *Analyt. Chem.*, 1949, **21**, 683.

photo-isomer (VI) (Found: C, 94·0; H, 5·95. $C_{32}H_{16}$ requires C, 94·1; H, 5·9%). This reverted to orange monoclinic plates of the β-*form* of bi(anthracene-9,10-dimethylene) (Found: C, 94·3; H, 5·8%) slowly at room temperature or rapidly at 100°. A solution of compound (I) in chloroform, exposed to sunlight for 5 min., gave a colourless solution ($\lambda_{max.}$ 299·5 mμ; log ε 3·29). The hydrocarbon (I) (α-form) was unaffected (*X*-ray powder pattern and infrared spectrum) by electron-irradiation to a dose of one gigarad.

Oxidation of Bi(*anthracene*-9,10-*dimethylene*) (α-*form*).—(a) *Mild conditions.* Chromic oxide (5 g.) in 75% acetic acid (20 ml.) was added to a suspension of the hydrocarbon (1 g.) in refluxing acetic acid (35 ml.). The mixture was refluxed for 5 min. and poured into water (1 l.), and the precipitate was filtered off, washed with water and aqueous ammonia, and dried. The white solid (1·1 g.) was sublimed at 200°/10^{-6} mm. to remove anthraquinone (0·2 g.), m. p. and mixed m. p. 282° (identity confirmed by infrared analysis). The buff residue (0·9 g., 82%), m. p. 288°, was purified by extractive crystallisation (Soxhlet) from benzene (3 times), to give colourless rods of 1,2-*di*-(9,10-*dihydro*-9-*hydroxy*-10-*oxoanthryl*)*ethane* (II) [Found: C, 80·7; H, 5·0; active H, 0·54%; *M* (Rast), 444. $C_{30}H_{22}O_4$ requires C, 80·7; H, 5·0; active H, 0·45%; *M*, 446·5], m. p. 287—288°, $\nu_{max.}$ 1603, 1650 (C=O), 3432 (OH, frequency shift by intramolecular association; O–O distance 2·80 Å) cm.$^{-1}$. The compound was sparingly soluble in organic solvents but in concentrated sulphuric acid gave an intensely sea-green solution and when melted in alcoholic potassium hydroxide gave an intense Bordeaux-red colour.

(b) *Vigorous conditions.* The hydrocarbon (1 g.) was treated as in (a) but the mixture was refluxed for 12 hr. and then worked up as before, to give a white solid (1 g.). Sublimation at 200°/10^{-6} mm. gave anthraquinone (Found: C, 81·0; H, 3·9. Calc. for $C_{14}H_8O_2$: C, 80·8; H, 3·9%) (0·92 g., 90%), m. p. and mixed m. p. 284° (identity confirmed by infrared analysis).

The hydroxy-compound (139 mg.) was suspended in acetic acid (6 ml.), treated with sulphuric acid (0·3 ml.), and refluxed for 10 min. The orange crystals were filtered off, washed with acetic acid and ether, and dried (90 mg., 70%; m. p. 287—288°). Extractive crystallisation (Soxhlet) from acetic acid gave orange rhombs of 1,2-di-(9,10-dihydro-10-oxo-9-anthrylidene)ethane (III) (Found: C, 87·8; H, 4·3. Calc. for $C_{30}H_{18}O_2$: C, 87·8; H, 4·4%), m. p. 288°. The infrared spectrum [$\nu_{max.}$ 1590, 1642 cm.$^{-1}$ (C=O)] was identical with that of a specimen prepared by condensation of anthrone and glyoxal [5] and purified by chromatography in nitrobenzene on aluminium oxide; a mixed m. p. was undepressed.

Reaction of Bi(*anthracene*-9,10-*dimethylene*) *with Maleic Anhydride.*—The hydrocarbon (α-form) (1 g.) was extracted (Soxhlet) into a refluxing solution of maleic anhydride (2 g.) in benzene (250 ml.), and the solution was then refluxed for 16 hr. Filtration of the cold solution gave a pale yellow solid (1·15 g.), m. p. 360° (decomp.), which on extractive crystallisation (Soxhlet) from benzene gave pale cream needles of the *adduct* (Found: C, 71·8; H, 4·3. $C_{16}H_{12},2C_4H_2O_3$ requires C, 72·0; H, 4·0%), m. p. 365° (decomp.), $\nu_{max.}$ (in Nujol) 1751, 1821 (anhydride) cm.$^{-1}$.

Halogenation of Bi(*anthracene*-9,10-*dimethylene*).—(a) *With iodine.* A chloroform solution (50 ml.) of the hydrocarbon (0·2695 g. in 500 ml.) was treated with water (100 ml.) and a chloroform solution (25 ml.) of iodine (2·6806 g. in 500 ml.). After a known time the residual iodine was titrated against aqueous 0·025N-sodium thiosulphate. Reaction was complete after 48 hr. when 1·90 iodine atoms had been consumed per hydrocarbon molecule (*M*, 408). A preparative experiment on an increased scale yielded an intractable yellow oil. (b) *With iodine monochloride.* With iodine monochloride reaction was complete after 48 hr. with the consumption of 7·4 iodine atoms per hydrocarbon molecule.

2,6-*Di*(*bromomethyl*)*naphthalene.*—A refluxing solution of 2,6-dimethylnaphthalene (172 g.) and benzoyl peroxide (1 g.) in benzene (2 l.) was treated with a mixture of *N*-bromosuccinimide (431 g.) and benzoyl peroxide (5 g.) during 40 min. After a further 20 min. the hot solution was filtered to remove succinimide (168 g.), washed with alkali, concentrated, and cooled. The precipitate (194·5 g.) recrystallised from toluene as colourless rods of 2,6-di(bromomethyl)-naphthalene (170 g., 49%), m. p. 182—183° (Ried and Bodem [20] give m. p. 182°).

2,6-*Di*(*iodomethyl*)*naphthalene.*—2,6-Di(bromomethyl)naphthalene (5 g.) was extracted (Soxhlet) into sodium iodide (12·5 g.) in acetone (250 ml.) during 3 hr. and the solution then poured into water (1 l.). The solid (6·2 g.) was washed with water and dried in a vacuum-desiccator. The product readily lost iodine during recrystallisation from benzene or carbon tetrachloride and was purified by addition of a chloroform solution (200 ml.) to light petroleum

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[20] Ried and Bodem, *Chem. Ber.*, 1958, **91**, 1981.

(b. p. 40—60°; 1 l.). The pale yellow needles (5·5 g., 85%) of 2,6-*di*(*iodomethyl*)*naphthalene* (Found: C, 35·4; H, 2·8; I, 61·9. $C_{12}H_{10}I_2$ requires C, 35·3; H, 2·5; I, 62·2%) began to decompose with loss of iodine at 109°. Crystals (1·2176 g.) of the pure iodo-compound, heated at $200°/10^{-6}$ mm. for 3 hr., evolved iodine (59·2% of original weight, calculated iodine content 62·3%), leaving a black residue.

Naphthalene: Polymer [*as* (V)].—An ether solution of phenyl-lithium (11·0 g. in 300 ml.) was added dropwise to a stirred, refluxing solution of 2,6-di(bromomethyl)naphthalene (20 g.) in benzene (400 ml.) during 45 min., the ether being removed continuously by distillation. The solution was refluxed for a further 15 min., decomposed with methanol (25 ml.), and poured into 10% hydrochloric acid (2 l.). The greenish-yellow solid was filtered off, dried, refluxed with ethanol–concentrated hydrochloric acid (1 : 1) for 5 hr., washed, and dried. The *polymer* [Found: C, 92·5; H, 6·3; Br, 1·6. $(C_{12}H_{10})_{81}Br_2$ requires C, 92·3; H, 6·45; Br, 1·3%] (8·4 g., 85%) softened above 300° and was not appreciably soluble in organic solvents. Modifications of this procedure and the use of dilution techniques gave lower yields of polymer and some starting material was recovered; no dimer was isolated.

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