101. *Diaryls. Part III.*[1, 2] *Reactions of Some Dihalogenonaphthalenes with Lithium Amalgam, and Simple Syntheses of* 2,3:6,7-*Dibenzobiphenylene.*

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The reactions of some *o*-dihalogenonaphthalenes with lithium amalgam in ether or tetrahydrofuran have been studied. 2,3-Dibromonaphthalene yields 2,3:6,7-dibenzobiphenylene, which thus becomes readily accessible. The dibenzobiphenylene is also simply obtained by refluxing 2-bromo-3-iodonaphthalene with copper bronze in dimethylformamide, this being a completely new type of synthesis for aromatic derivatives of cyclobutadiene.

2,3:6,7-DIBENZOBIPHENYLENE was synthesised by Ward and Pearson[1] and by Curtis and Viswanath,[3] by methods involving at least ten stages from 1,2,3,4-tetrahydronaphthalene. We have now obtained it, in low yield, in two stages from the commercially available 2,3-diaminonaphthalene.[4] The latter is converted into 2,3-dibromonaphthalene by a

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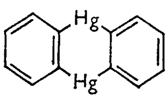
[1] Part I, Ward and Pearson, *J.*, 1959, 1676.
[2] Part II, Ward and Pearson, *J.*, 1959, 3378.
[3] Curtis and Viswanath, *J.*, 1959, 1670.
[4] Pearson, *Chem. and Ind.*, 1960, 899.

Sandmeyer reaction and then treated with lithium amalgam in ether. 2,3:6,7-Dibenzobiphenylene is presumably formed by way of a β-naphthalyne intermediate.

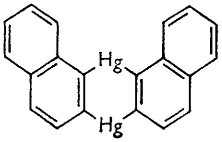
Wittig and Pohmer [5] found that *o*-bromofluorobenzene reacted with lithium amalgam in ether to give 24% of biphenylene, 3% of triphenylene, and 2% of the 9,10-dimercura-anthracene (I), whereas *o*-dibromobenzene gave 9% of biphenylene and 42% of the mercurial; formation of biphenylene was ascribed to the dimerisation of a benzyne intermediate. Following their procedure we have now treated lithium amalgam (prepared in a Schlenk tube) with solutions of *o*-dihalogenonaphthalenes in ether (E) or tetrahydrofuran (T) for 24 hr. The products were separated, as far as possible, by fractional crystallisation, vacuum-sublimation, or vacuum-distillation, with results as tabulated.

Compound	Products
1,2-Dibromonaphthalene (E)	Mercury compound, (II)
,, ,, (T)	2,2′-Binaphthyl
1-Bromo-2-fluoronaphthalene (E)	(II) and a polymer (?)
,, ,, (T)	2-Fluoronaphthalene
2,3-Dibromonaphthalene	2,3:6,7-Dibenzobiphenylene
6-Bromo-7-fluoro-1,2,3,4-tetrahydronaphthalene failed to react.	

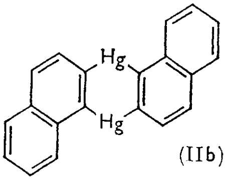
The mercury compound (II), by analogy with (I), may be formulated as (IIa or b). Since 1,2-dibromonaphthalene gives 2,2′-binaphthyl when the reaction is carried out in tetrahydrofuran it seems possible that 1,2:7,8-dibenzobiphenylene could have been formed initially, decomposing to the binaphthyl, a known reduction product.[6] The molecular weight (590) suggests that the supposed polymer is $(C_{10}H_6F)_4$ (M, 580).



(I)



(IIa)



(IIb)

A new method of synthesising aromatic derivatives of cyclobutadiene was discovered when we found that refluxing 2-bromo-3-iodonaphthalene with copper bronze in dimethylformamide gave 2,3:6,7-dibenzobiphenylene in low yield. This reaction also probably proceeds through a β-naphthalyne intermediate; the latter may be stabilised in this case by solvation with the highly polar solvent. Since a similar reaction with *o*-bromoiodobenzene yielded only biphenyl, the success recorded above may be due to the exceptional stability of 2,3:6,7-dibenzobiphenylene.[4]

In the preparation of 1,2-dibromonaphthalene it was found that rapid addition of diazotised 1-bromo-2-naphthylamine to the Sandmeyer reagent gave 1,1′-dibromo-2,2′-azonaphthalene as a by-product, confirming the work of Bogoslovskii and Kozakova.[7]

EXPERIMENTAL

1,2-*Dibromonaphthalene*.—1-Bromo-2-naphthylamine (10 g.) was diazotised as previously described [1] and the filtered solution added rapidly to the stirred solution of cuprous bromide (20 g.) in 48% w/w hydrobromic acid (200 ml.). After 4 hr. the mixture was poured into ice-water (2 l.) and the brown solid collected (12 g.; 90%, m. p. 58°). Crystallisation of this from benzene gave 1,1′-dibromo-2,2′-azonaphthalene (0·5 g.), m. p. 266° (Bogoslovskii and Kozakova [7] give 252°) (Found: C, 55·4; H, 2·9; N, 6·3; Br, 35·4. Calc. for $C_{20}H_{12}Br_2N_2$: C, 54·5; H, 2·7; N, 6·4; Br, 36·4%). Further concentration of the benzene gave pure 1,2-dibromonaphthalene, m. p. 68° (lit.,[8] 68°), whose *complex* with 2,4,7-trinitrofluorenone had m. p. 163° (from benzene) (Found: C, 46·6; H, 1·9; N, 7·4; Br, 26·5. $C_{23}H_{11}Br_2N_3O_7$ requires C, 45·8; H, 1·8; N, 7·0; Br, 26·6%).

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[5] Wittig and Pohmer, *Ber.*, 1956, **89**, 1334.
[6] Cava and Stucker, *J. Amer. Chem. Soc.*, 1955, **77**, 6022.
[7] Bogoslovskii and Kozakova, *J. Gen. Chem.* (*U.S.S.R.*), 1952, **22**, 1183.
[8] Meldola and Streatfield, *J.*, 1893, **63**, 1054.

1-*Bromo*-2-*fluoronaphthalene*.—1-Bromo-2-naphthylamine (30 g.) was dissolved in hydrochloric acid (*d* 1·2; 34 ml.) and water (34 ml.) and diazotised by sodium nitrite (12 g.) in water (30 ml.) at 0°, and the filtered diazo-solution added to 40% fluoroboric acid (50 ml.). After 3 hr. the diazonium fluoroborate was collected, washed with ice-water (50 ml.), and air-dried (34 g., 78%). It was then heated at 145° for 1 hr. The resultant tar was extracted with boiling benzene (2 × 100 ml.), and the extract filtered through alumina (2 × 20 cm.) and evaporated, giving a yellow solid (17 g.; m. p. 62°). Vacuum-distillation gave 1-bromo-2-fluoronaphthalene (15 g., 63%), b. p. 90—92°/2 mm., m. p. 68° (from methanol–water, 5 : 1 v/v) (Nakata [9] gives 49°) (Found: C, 54·0; H, 3·1; Br, 34·4. Calc. for $C_{10}H_6BrF$: C, 53·3; H, 2·7; Br, 35·4%).

2-*Bromo*-1-*fluoronaphthalene*, obtained similarly (75%) from 2-bromo-1-naphthylamine, had b. p. 164°/2 mm., n_D^{25} 1·648 (Found: C, 53·9; H, 2·8%).

6-*Amino*-7-*bromo*-1,2,3,4-*tetrahydronaphthalene*.—6-Bromo-1,2,3,4-tetrahydro-7-nitronaphthalene (12 g.) was refluxed with iron powder (300-mesh; 120 g.), ferrous ammonium sulphate (6 g.), and water (600 ml.) for 4 hr. Steam-distillation gave 6-amino-7-bromo-1,2,3,4-tetrahydronaphthalene (6·6 g., 62%), m. p. 46—47° [from light petroleum (b. p. 80—100°)] (Found: C, 54·0; H, 5·5; Br, 34·5. Calc. for $C_{10}H_{12}BrN$: C, 53·1; H, 5·3; Br, 35·4%).

6-*Bromo*-7-*fluoro*-1,2,3,4-*tetrahydronaphthalene*.—Proceeding as for 1-bromo-2-fluoronaphthalene gave a 65% yield of diazonium fluoroborate, decomposition of which followed by vacuum-distillation gave 6-bromo-7-fluoro-1,2,3,4-tetrahydronaphthalene (2·6 g., 60%), b. p. 126°/4 mm., n_D^{25} 1·70 (Found: C, 53·7; H, 4·6. Calc. for $C_{10}H_{10}BrF$: C, 52·4; H, 4·4%).

Reaction of Lithium Amalgam with o-*Dihalogenonaphthalenes*.—(a) *General procedure*. Lithium (0·3 g.) was weighed in an atmosphere of oxygen-free hydrogen (all operations being carried out under this gas) and added portionwise to mercury (100 g.; previously heated to 180°) in a Schlenk tube. Then the temperature was raised to 210° for 30 min.; when cool, the apparatus was transferred to a dry box, and the solution (15 ml.; but for 2,3-dibromonaphthalene 75 ml.) of the halogeno-compound (15 millimoles) was added. The Schlenk tube was shaken, horizontally, for 24 hr., then washed out with solvent, the mercury was separated from solvent and other solids, and the solids (A) were collected, washed with water to remove lithium salts, and dried. From the residual solvent a tar (B) was obtained by evaporation.

(b) 1,2-*Dibromonaphthalene in ether*. Extraction of the solids (A) with boiling dimethylformamide (50 ml.) left a grey residue (0·8 g.), m. p. 360° (Found: C, 11·8; H, 0·84%). Concentration of the extract gave the *dimercura-anthracene* as a white amorphous powder (2·35 g.), m. p. 323—325° (Found: C, 36·8; H, 1·8. $C_{20}H_{12}Hg_2$ requires C, 36·7; H, 1·5%). Attempts to obtain products from the tar (B) failed.

(c) 1,2-*Dibromonaphthalene in tetrahydrofuran*. The buff-grey material (A) (0·7 g.), m. p. 360° (Found: C, 22·7; H, 3·5%), was insoluble in boiling dimethylformamide. Chromatography of the tar (B) in benzene on alumina gave two bands; the first was eluted with benzene giving an orange tar (0·6 g.), which, from ethanol, gave pure 2,2′-binaphthyl (identified by mixed m. p.).

(d) 1-*Bromo*-2-*fluoronaphthalene in ether*. Boiling dimethylformamide (50 ml.) was used to extract the solid (A), leaving a grey mercury-contaminated residue. Concentration of the extract gave a product, supposedly (II) (0·9 g.), m. p. 323°. The tar (B) was dissolved in dimethylformamide (15 ml.); adding this solution to water gave a buff solid *polymer* (1·6 g.), m. p. 256—258° [Found: C, 83·0; H, 4·2%; *M*, 590. $(C_{10}H_6F)_4$ requires C, 82·8; H, 4·2%; *M*, 580]. This sublimed at 4 mm.; it did not form a complex with 2,4,7-trinitrofluorenone.

(e) 1-*Bromo*-2-*fluoronaphthalene in tetrahydrofuran*. The grey solids (A) (0·15 g.), m. p. 360°, were insoluble in dimethylformamide. Chromatography of the tar (B) on alumina in benzene gave two bands; the first, eluted with benzene, gave 2-fluoronaphthalene (1·0 g., 45%), m. p. 58° [from light petroleum (b. p. 80—100°)] (picrate, m. p. 100°) (Schiemann *et al.*[10] give m. p. 60° and 100° respectively); the second band afforded only a tar (0·2 g.).

(f) 2,3-*Dibromonaphthalene in ether*. Extraction of material (A) by boiling dimethylformamide (50 ml.) gave a mercury-contaminated residue but concentration of the extract afforded a buff solid (1·4 g.), m. p. 263° (Found: C, 60·8; H, 4·0; Br, 6·5%). Chromatography of the tar (B) on alumina in benzene gave two bands; the first, by elution with benzene, gave 2,3:6,7-dibenzobiphenylene (7 mg. identified by its ultraviolet spectrum, m. p., and trinitrofluorenone complex) and a brown tar (0·1 g.). The second, eluted by benzene–ethyl acetate (4 : 1 v/v) gave a tar (0·2 g.), which on extraction with warm ethanol (10 ml.) left an amorphous

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[9] Nakata, *Ber.*, 1931, **64**, 2059.

[10] Schiemann, Gueffroy, and Winkelmuller, *Annalen*, 1931, **487**, 270.

brown powder (0·2 g.), m. p. 238° (Found: C, 72·6; H, 4·7; Br, 10·0%; *M*, 692), which did not crystallise or sublime.

Reaction of 2-*Bromo*-3-*iodonaphthalene with Copper Bronze in Dimethylformamide*.—2-Bromo-3-iodonaphthalene (2·5 g.) was refluxed with copper bronze (4 g.) in dimethylformamide (25 ml.) for 3 hr. The solids were then removed and the hot filtrate was poured into water (250 ml.). The next day the sticky solids that separated were collected, dissolved in benzene, and filtered through alumina (2 × 20 cm.). Concentration gave 2,3:6,7-dibenzobiphenylene (identified as above) (8 mg., 0·9%), and further concentration a tar (1·3 g.). Steam-distillation of the tar gave 2-bromonaphthalene (0·3 g., 19%) and left an uncrystallisable residue.

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