243. *Eight- and Higher-membered Ring Compounds. Part V. Di(naphthalene-2 : 7-dimethylene) and its Conversion into Coronene.*

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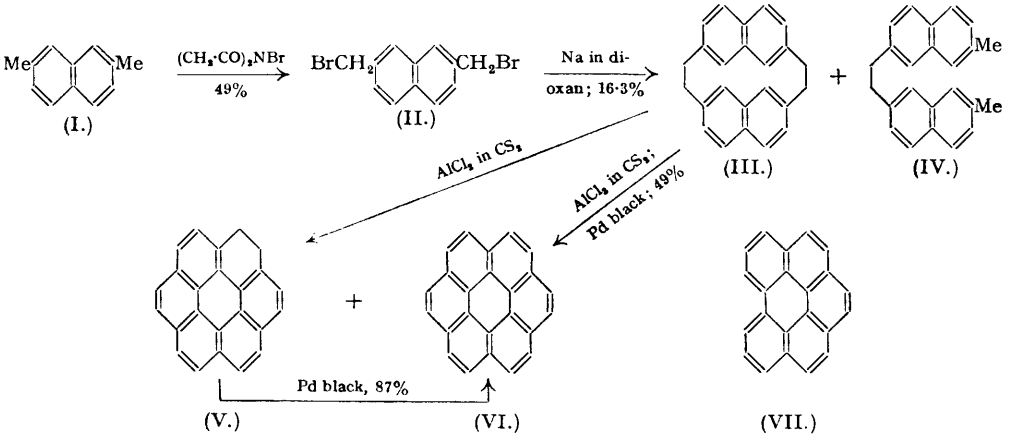
2 : 7-Bisbromomethylnaphthalene (II), prepared by bromination of 2 : 7-dimethylnaphthalene (I) with *N*-bromosuccinimide, reacts with sodium to give the fourteen-membered cyclic compound di(naphthalene-2 : 7-dimethylene) (III). Catalytic dehydrogenation of (III) gives a trace of coronene (VI), but with aluminium chloride in carbon disulphide at the boiling point it gives in good yield a mixture of 1 : 2-dihydrocoronene (V) and coronene. The 1 : 2-dihydrocoronene is dehydrogenated by palladium, giving coronene in 87% yield. The yield of pure coronene obtainable from (III) is 49%, or 4% from 2 : 7-dimethylnaphthalene.

The preceding paper described the reaction of *m*-xylylene dibromide with sodium to give di-*m*-xylylene, and the catalytic dehydrogenation of this ten-membered *meta*-bridged benzene derivative to the tetra-cyclic aromatic hydrocarbon pyrene. In a preliminary note (Baker, McOmie, and Norman, *Chem. and Ind.*, 1950, 77) it was suggested that a similar series of reactions starting from 2 : 7-dimethylnaphthalene (I) should lead to coronene (VI), and the present communication records a successful and practicable synthesis of coronene along these lines. Our work was facilitated by a generous gift, from L. Light and Company, Limited, of 75 g. of 2 : 7-dimethylnaphthalene. This compound has been isolated from coal-tar, and is preparable by a nine-stage synthesis starting from *p*-toluidine (Bailey, Bryant, Hancock, Morell, and Smith, *J. Inst. Petroleum*, 1947, **33**, 523), the overall yield from that compound being about 20% (calculated on the maximum yields given in the literature).



2 : 7-Dimethylnaphthalene (I) was converted by pure *N*-bromosuccinimide in carbon tetrachloride in presence of benzoyl peroxide into 2 : 7-bisbromomethylnaphthalene (II), the yield being 49%. The possibility of nuclear bromination having occurred was excluded by the formation of a bisthiuronium bromide. In addition to (II) was isolated 2-bromomethyl-7-

methylnaphthalene, a compound previously prepared in a similar manner by Buu-Hoï and Lecocq (*J.*, 1946, 830), who, however, did not isolate the bisbromomethyl derivative. The action of sodium on 2 : 7-bisbromomethylnaphthalene in dioxan in the presence of sodium iodide gave dioxan-insoluble polymeric material and a mixture consisting mainly of two colourless, saturated compounds, the separation of which was effected by fractional sublimation at low pressures, crystallisation from benzene, and hand-sorting. One of the compounds, the desired di(naphthalene-2 : 7-dimethylene) (III), was obtained in a yield of 16·3%. The other, 1 : 2-di-(7-methyl-2-naphthyl)ethane (IV), isolated in 4·3% yield, has been formed as the result of both a Würtz–Fittig synthesis and reduction; such reduction is a general feature of this type of reaction, and was encountered in the similar cases described in Part IV.

Di(naphthalene-2 : 7-dimethylene) (III) is a fourteen-membered ring compound with two rigid groups of seven atoms, in which considerable strain must be present owing to the close proximity of the two pairs of interior α-CH groups. The necessary separation of these groups to a carbon–carbon distance of something over 3 A. is probably achieved by distortion of the normal bond angles; the problem is precisely similar to that presented by di-*m*-xylylene discussed in the previous paper.

Direct dehydrogenation of (III) was unsuccessfully attempted in an inert atmosphere with sulphur, selenium, palladium–charcoal, and palladium black; the last two were also employed in inert solvents. After treatment with palladium black in an evacuated sealed tube at 300° for twenty-four hours a trace of the yellow coronene was isolated by hand-sorting, and identified spectroscopically by the presence of strong absorption bands at 3025 and 3400 A. When the reaction was continued for seven days and the product was fractionally sublimed and then crystallised from benzene, a fraction of a milligram of pure coronene was isolated and characterised by the identity of its *X*-ray powder photograph with that of an authentic specimen.

In view of the unsatisfactory nature of these direct dehydrogenations we investigated the action of aluminium chloride on (III) in boiling carbon disulphide, and found that it gave in high yield a mixture of 1 : 2-dihydrocoronene and a much smaller quantity of coronene. When the crude, mixed product was treated with palladium black at 260°, the dehydrogenated material isolated by sublimation in a vacuum and purified by passing its solution in benzene through a short column of alumina it gave finally pure coronene (VI) in 49% yield, calculated on the amount of (III) used. The coronene was identified by elementary analysis, *X*-ray powder photography, ultra-violet absorption spectroscopy, melting point, and formation of its picrate. In another experiment an attempt was made to separate the constituents of the mixture obtained from the aluminium chloride reaction, by processes involving sublimation, picrate formation, crystallisation, and hand-sorting. Two distinct crystalline materials were isolated in 40% and 0·34% yield respectively. The first, crystallising in compact, cubic crystals, formed a deep purple picrate (coronene picrate is bright red), and gave analytical figures corresponding to a dihydrocoronene. It was thought that this compound would be most probably 1 : 2-dihydrocoronene because of its method of preparation and because, of the five possible dihydrocoronenes (1 : 2-, 1 : 3-, 1 : 6-, 1 : 7-, 2 : 5-), the 1 : 2-compound has the greatest degree of aromatic character. This was confirmed by comparison of the ultra-violet absorption spectrum of the supposed 1 : 2-dihydrocoronene with that of 1 : 12-benzperylene (VII) (Clar, *Ber.*, 1932, **65**, 849) which differs from 1 : 2-dihydrocoronene only in the absence of the ethylene bridge. However, although the curves were almost identical for wave-lengths between 225 and 310 mμ., they differed appreciably between 310 and 400 mμ., and comparison with the absorption curve for coronene made it evident that there was not less than 15% of coronene present in the dihydro-compound, probably as a mixed crystal. Insufficient material was available to allow further separation of the constituents. The minor constituent of the reaction product of (III) with aluminium chloride crystallised in needles, and gave analytical figures close to those of coronene, and the ultra-violet absorption spectrum showed that it was probably mainly coronene with a certain amount of 1 : 2-dihydrocoronene, doubtless again in the form of a mixed crystal. We are greatly indebted to Mr. R. C. Seymour of the Department of Inorganic and Physical Chemistry of this University, and to Dr. E. Clar of the Department of Chemistry, The University, Glasgow, for advice in connection with the interpretation of the ultra-violet absorption curves. This minor constituent gave an *X*-ray powder photograph scarcely distinguishable from that of coronene, and it yielded coronene, isolated as its picrate, when dehydrogenated in presence of palladium black. Under these conditions the major product of the aluminium chloride reaction gave pure coronene (identified by an *X*-ray powder photograph) in 87% yield.

The use of aluminium chloride for bringing about cyclodehydrogenation to polycyclic aromatic hydrocarbons is well known. The process employed in this paper was suggested

mainly by the work of Ruzicka and Hösli (*Helv. Chim. Acta*, 1934, **17**, 471) and of Buu-Hoï (*J. Org. Chem.*, 1949, **14**, 1031).

The present method gives coronene in a four-step (virtually a three-step) synthesis from 2 : 7-dimethylnaphthalene in a yield of 4%; the overall yield from *p*-toluidine, the starting point for the synthesis of 2 : 7-dimethylnaphthalene, is about 0·8%. This synthesis has advantages over those previously described, and the yield could doubtless be improved by closer study. The first preparation of coronene, due to Scholl and Meyer (*Ber.*, 1932, **65**, 902), proceeded in ten steps from the chloride of anthraquinone-1 : 5-dicarboxylic acid; the yield from this intermediate was not recorded but was undoubtedly extremely small. The second, due to Newman (*J. Amer. Chem. Soc.*, 1940, **62**, 1683), required six steps from 7-methyltetralone and gave a 1·7% yield from this ketone; the latter was itself prepared in a four (virtually three)-step synthesis from toluene in probably about 50—60% yield, making the overall yield of coronene of the order of 1%. A disadvantage of the Newman synthesis is that the final step proceeds in only 5·5% yield.

When this work was nearly complete it was found that Wood and Stansfield (*J. Amer. Chem. Soc.*, 1942, **64**, 2343) had proposed to prepare coronene from 2 : 7-dithioformylnaphthalene by reaction with copper to give the diolefinic analogue of (III), and then to convert this into coronene by cyclodehydrogenation. They were, however, unable to prepare 2 : 7-dithioformylnaphthalene, and for steric reasons it seems most unlikely that the diolefin corresponding to (III) could exist.

Experimental.

M. p.s, except those over 350°, are uncorrected. Microanalyses are by Mr. W. M. Eno, Bristol, and Drs. Weiler and Strauss, Oxford.

2 : 7-*Bisbromomethylnaphthalene* (II).—A mixture of 2 : 7-dimethylnaphthalene (I) (20·0 g., 1 mol.), *N*-bromosuccinimide (52·0 g., *ca.* 2·2 mols.; freshly prepared by the method of Lecocq, *Ann. Chim.*, 1948, **3**, 62), and benzoyl peroxide (0·3 g.) in dry carbon tetrachloride (150 c.c.), was boiled under reflux for 4½ hours, then cooled, and the solid containing the 2 : 7-*bisbromomethylnaphthalene* which is almost insoluble in cold carbon tetrachloride was collected and washed with cold carbon tetrachloride. The product was next ground with carbon tetrachloride, collected again, and washed with the same solvent. This material (40 g.) was extracted with boiling benzene (200 c.c.), the mixture filtered hot from undissolved succinimide (m. p. and mixed m. p. 123—124°), and the filtrate diluted with more benzene, extracted with 5% aqueous sodium hydroxide to remove the remaining succinimide, and finally washed, dried, and concentrated to a small bulk. The 2 : 7-bisbromomethylnaphthalene (19·8 g., 49%) separated slowly as elongated, hexagonal plates, m. p. 146—147° (Found, in material twice crystallised from benzene: C, 45·8; H, 3·3; Br, 50·9. $C_{12}H_{10}Br_2$ requires C, 45·9; H, 3·2; Br, 50·9%). The carbon tetrachloride-soluble product (30·5 g.) had m. p. 70—112°, and consisted of a difficultly separable mixture containing 2-bromomethyl-7-methylnaphthalene [m. p. 100° (decomp.); Buu-Hoï and Lecocq, *J.*, 1946, 830] and a tribromo-2 : 7-dimethylnaphthalene of unproved structure, probably 1-*bromo*-2 : 7-*bisbromomethylnaphthalene*. In another experiment in which less pure *N*-bromosuccinimide was used the latter compound was isolated by repeated crystallisation from benzene–light petroleum as needles (2·5 g.), m. p. 113—114° (Found: C, 37·3; H, 2·2; Br, 60·0. $C_{12}H_9Br_3$ requires C, 36·7; H, 2·4; Br, 61·0%).

The 2 : 7-bisbromomethylnaphthalene (1·0 g.) was converted into the related *bisthiuronium bromide* by boiling it with ethanol (100 c.c.) and thiourea (0·49 g.) for 2·5 hours, concentration (to *ca.* 50 c.c.), and addition of benzene. The solid was collected, washed (yield, 1·3 g.), and crystallised from ethanol, giving colourless prisms, m. p. 241° (decomp.), which may not be quite pure {Found, in material dried for 2 hours at 65°: C, 36·5; H, 4·0; N, 11·2; S, 14·3; Br, 31·5. $C_{10}H_6[CH_2{\cdot}S{\cdot}C(:NH){\cdot}NH_2,HBr]_2$ requires C, 36·0; H, 3·9; N, 12·0; S, 13·7; Br, 34·4%}.

Reaction of 2 : 7-*Bisbromomethylnaphthalene with Sodium. Formation of* 1 : 2-*Di*-(7-*methyl*-2-*naphthyl*)-*ethane* (IV) *and Di*(*naphthalene*-2 : 7-*dimethylene*) (III).—2 : 7-Bisbromomethylnaphthalene (II) (6·5 g.) in purified dioxan (125 c.c.) was heated under reflux with sodium (2·0 g.) and sodium iodide (0·05 g.) for 24 hours, the mixture being shaken vigorously during the initial stages of the reaction in order to disperse the sodium. The cooled mixture was filtered, and the solid washed with warm dioxan (100 c.c.) (the solid insoluble in dioxan was freed from excess of sodium and inorganic salts by cautious addition to aqueous ethanol, collected, and dried, leaving polymeric material, 1·26 g.). The united dioxan filtrate and washings were evaporated under diminished pressure and the resulting pale pink solid was sublimed (*ca.* 0·1 mm.) at a temperature slowly rising to 220° (metal-bath). The colourless sublimate (1·60 g.) was again sublimed, and the following fractions were separately collected at the temperatures and during the times recorded: (1) 0·19 g., m. p. 80—88°; 100°, 3 hours; (2) 0·12 g., m. p. 122—123°; 135°, 1½ hours; (3) 0·16 g., m. p. 130—160°; 150°, ½ hour; (4) 0·31 g., m. p. >180°; 160°, 2 hours; (5) 0·63 g., m. p. up to 230°; 200°, 4 hours; (6) 0·04 g., m. p. 200—250°; 220°, 2 hours. The sublimate fractions (4) and (5) were united and dissolved in benzene, and the solution was allowed to cool very slowly so that large well-developed crystals were formed. The crystals were of two distinct types which, after being collected and dried, were separated by hand-sorting. The compound present in smaller quantity crystallised in thin, flat, nacreous plates, which after recrystallisation from benzene had m. p. 214—215° [Found: C, 92·6; H, 7·1%; *M* (Rast), 329. $C_{24}H_{22}$ requires C, 92·85; H, 7·15%; *M*, 310]; this substance is 1 : 2-*di*-(7-*methyl*-2-*naphthyl*)*ethane* (IV). The other component of the mixture, present in larger quantity, formed thick, clear, hexagonal plates (3—5-mm. sides), which after crystallisation from benzene had m. p. 237—238° [Found: C, 93·5; H, 6·8%; *M* (Rast), 288. $C_{24}H_{20}$ requires C,

93·5; H, 6·5%; *M*, 308]; this substance is *di(naphthalene-2 : 7-dimethylene)* (III). Repeated concentration of the benzene mother-liquors yielded further quantities of both compounds which were hand-separated, and each was then crystallised individually from benzene, giving finally as the total yields 1 : 2-di-(7-methyl-2-naphthyl)ethane, 0·14 g., and di(naphthalene-2 : 7-dimethylene), 0·53 g. Of the remaining fractions of the second sublimation process (1) was mainly 2 : 7-dimethylnaphthalene, (2) and (3) contained considerable amounts of bromine-containing material, and (6) was neglected.

The *picrate* of (III) was prepared from the hydrocarbon (14 mg.) and picric acid (20 mg.) in benzene (2 c.c.); it separated in ruby-red prisms, m. p. 180—181° (Found : N, 8·0. $C_{24}H_{20},C_6H_3O_7N_3$ requires N, 7·8%).

Preparation of Coronene (VI) *by Cyclodehydrogenation of Di(naphthalene-2 : 7-dimethylene)* (III) *with Aluminium Chloride followed by Dehydrogenation with Palladium.*—Di(naphthalene-2 : 7-dimethylene) (III) (0·16 g.) was boiled under reflux for 23 hours with carbon disulphide (25 c.c.) and finely powdered aluminium chloride (0·75 g.). The solution became green and deposited a deep green solid, which was finally treated with ice and dilute hydrochloric acid and extracted with chloroform, and the organic layer was washed with water, dried ($MgSO_4$), and evaporated, leaving a yellow-brown solid which was intimately mixed with palladium black (0·4 g.) and heated at 260° for 4·5 hours in an atmosphere of carbon dioxide in a sublimation apparatus with a cold finger. The organic material was finally sublimed on to the cold finger by careful heating with a free flame at *ca.* 0·1 mm. pressure. The yellow sublimate was dissolved in boiling benzene, the solution filtered from a small amount of palladium, and by next morning the crude coronene had separated as rather dark, yellow-brown needles (0·102 g.). This product was passed in benzene (200 c.c.) through a short alumina column which did not retain the coronene but removed a strongly adsorbed dark impurity; evaporation of the solvent and final recrystallisation from benzene gave pure coronene as amber-yellow needles (5—15 mm. long) (0·077 g., 49%) (Found : C, 95·6; H, 4·1. Calc. for $C_{24}H_{12}$: C, 96·0; H, 4·0%). This coronene gave m. p. 442°, determined in a sealed tube in an electrically heated apparatus, the temperature being recorded by means of a calibrated thermocouple. It was finally identified by the complete correspondence of all the lines in its *X*-ray powder photograph with those given by an authentic specimen of coronene.

The picrate was prepared in benzene solution, and separated as bright red needles which decomposed between 310° and 325° (Found : C, 67·8; H, 2·9; N, 7·8. Calc. for $C_{24}H_{12},C_6H_3O_7N_3$: C, 68·1; H, 2·9; N, 7·9%).

Reaction of Di(naphthalene-2 : 7-dimethylene) (III) *with Aluminium Chloride.* 1 : 2-*Dihydrocoronene.*—Di(naphthalene-2 : 7-dimethylene) (0·30 g.) was treated with aluminium chloride (1·4 g.) in carbon disulphide (40 c.c.), and the product isolated by extraction with chloroform as previously described. This product was passed in benzene through a column of alumina which retained dark material, and the eluate was distilled, leaving a yellow-brown powder (0·23 g.) which showed a yellow-green fluorescence in ultra-violet light but could not be satisfactorily crystallised. It was therefore sublimed at 0·1 mm. at the temperatures given below, the following fractions being collected : (1) yellow, partly crystalline material, 35 mg., 150°, 2 hours; (2) yellow crystalline material, 185 mg., 190—250° during 4 hours. The second fraction (185 mg.) was treated in benzene solution with a solution of picric acid in benzene and a little light petroleum added; after several hours the purple needles were collected and dissolved in benzene, and the picrates decomposed by passage through a short column of alumina which was finally eluted with hot benzene. The yellow eluate was evaporated, and the residue crystallised from benzene, giving, first, long yellow needles, and then compact yellow, almost cubic crystals. This mixture was collected, dried, and separated as far as possible by hand-picking, and each product separately recrystallised from benzene, a few more of the almost cubic crystals being obtained from the recrystallisation of the needle form.

The 1 : 2-*dihydrocoronene* (V) (now known to be contaminated with coronene; see Introduction) which forms the yellow, cubic crystals was obtained in a total yield of 114 mg. It is more soluble in benzene than the needles, and the solution shows a strong blue fluorescence even in daylight, being thereby distinguished from that of coronene. The m.p., determined as for coronene (above), was 365—367° (Found : C, 95·3; H, 4·8. $C_{24}H_{14}$ requires C, 95·3; H, 4·7%). The *picrate* prepared in benzene solution formed deep purple needles which decomposed between 330° and 370° (Found : C, 67·8; H, 3·4; N, 7·6. $C_{24}H_{14},C_6H_3O_7N_3$ requires C, 67·8; H, 3·2; N, 7·9%).

The material which formed the needle-shaped crystals was obtained in a yield of 10 mg. only. After further crystallisation from benzene–light petroleum (b. p. 60—80°) it had m. p. 418° (Found : C, 95·6; H, 4·6%). It showed a blue fluorescence in ultra-violet light, and the picrate formed short, reddish-purple needles from benzene.

Dehydrogenation of these two products was effected with palladium. The cubic 1 : 2-dihydrocoronene (30 mg.) was mixed with palladium black (200 mg.) and heated in an atmosphere of carbon dioxide for 5 hours at 200—255° in a sublimation apparatus. The volatile material was now transferred to the cold finger by careful heating with a free flame at 0·1 mm., collected, and crystallised from benzene. Coronene separated as long yellow needles, m. p. 442° (26 mg., 87%), and was identified by an *X*-ray powder photograph. The derived picrate was indistinguishable from coronene picrate.

A similar experiment starting from the needles (2 mg.) yielded red needles of a picrate which were indistinguishable from those of coronene picrate.

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