242. *Eight- and Higher-membered Ring Compounds. Part IV. Di-*m-*xylylene, Tri-*p-*xylylene, and New Syntheses of Pyrene and of Coronene.*

By WILSON BAKER, J. F. W. MCOMIE, and MISS J. M. NORMAN.

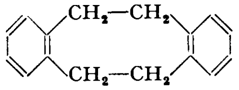
m-Xylylene dibromide reacts with sodium to give di-*m*-xylylene (II) containing a ten-membered ring, thus confirming earlier work of Pellegrin. Di-*m*-xylylene is dehydrogenated to pyrene (IV) in 60% yield when heated with palladium–charcoal, and is isomerised to 1 : 2 : 2*a* : 3 : 4 : 5-hexahydropyrene (V) when treated with aluminium chloride. *p*-Xylylene dihalides react with sodium to give a mixture containing tri-*p*-xylylene (VII) and *p*-di-(2-*p*-tolylethyl)benzene (VIII). The former, containing an eighteen-membered ring, is a novel type of molecule with three linear sides, and is converted into coronene (IX) in 1·9% yield when heated with palladium oxide. The stereochemistry of di-*m*- and of tri-*p*-xylylene is discussed.

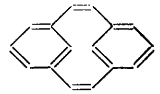
THE main idea underlying this series of papers, set out in Part I (Baker, McOmie, and Ollis, *J.*, 1951, 200), was briefly a general investigation of the formation of eight- and higher-membered ring systems, in which a number of atoms forming part of the chain undergoing cyclisation are combined in a rigid group or groups, thereby diminishing the rotational possibilities and increasing the chance of cyclisation. This " rigid-group principle " has been applied in the formation of *s*-dibenzo*cyclo*octadiene (I) (Baker, Banks, Lyon, and Mann, *J.*, 1945, 27) from *o*-xylylene dibromide by reaction with sodium, and was illustrated more strikingly in Parts II and III (Baker, Ollis, and Zealley, *J.*, 1951, 201; Baker, Gilbert, Ollis, and Zealley, *J.*, 1951, 209) by the formation of large-ring anhydro-compounds derived from salicylic and cresotic acids. Thus, salicylic acid gives the eight-membered *cis*-disalicylide, the twelve-membered trisalicylide, the sixteen-membered tetrasalicylide, and the twenty-four-membered hexasalicylide.

The application of the " rigid-group principle " to *m*- and *p*-disubstituted benzenes, referred to in Part I, forms the subject of this communication; the results in the *meta*-series have been briefly reported elsewhere (*Chem. and Ind.*, 1950, 77). It was decided to work in the hydrocarbon series and to employ the Würtz–Fittig synthesis because (1) this reaction had proved successful in the preparation of *s*-dibenzo*cyclo*octadiene (I); (2) the compounds would be stable, thus allowing a variety of techniques for their isolation; and (3) the ethylene bridges would allow less steric interference between interior, benzenoid CH groups (*e.g.*, those marked with asterisks in formula II) than would occur in the shorter –CO–O– or –CO–NH– bridges in the corresponding cyclic anhydro-derivatives of phenolic acids or aromatic amino-acids. The reaction between *m*-xylylene dibromide and sodium had been previously investigated by Pellegrin (*Rec. Trav. chim.*, 1899, **18**, 458), but no work had been carried out in the *para*-series.

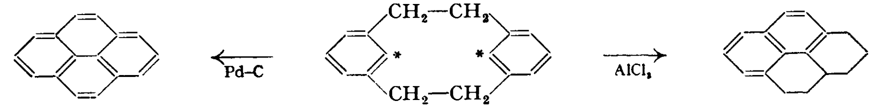
*Di-*m-*Xylylene and its Conversion into Pyrene.*—Pellegrin heated a mixture of *m*-xylylene dibromide (1 mol.) and bromobenzene (2 mols.) with sodium in ether and isolated diphenyl, a very variable yield (0—18% of crude product) of a hydrocarbon, m. p. 131·5°, of which the analysis and molecular weight established the formula $C_{16}H_{16}$, and a smaller quantity of a third hydrocarbon, $C_{16}H_{12}$, m. p. 191°. The compound $C_{16}H_{16}$, which yielded a dibromo-derivative $C_{16}H_{14}Br_2$, was regarded as di-*m*-xylylene (II), and to the compound $C_{16}H_{12}$, which showed unsaturated properties, was assigned the related diolefinic structure (III). Attempts to effect oxidative degradation of the hydrocarbon $C_{16}H_{16}$ were unsuccessful. Reinvestigation of this reaction has shown that the hydrocarbon $C_{16}H_{16}$, for which we find m. p. 132—133°, may be isolated in the pure state in 12% yield after heating *m*-xylylene dibromide in anhydrous ether with powdered sodium and a small quantity only of bromobenzene and sodium iodide. The last two substances act catalytically; the sodium iodide brings about an increased yield of the hydrocarbon but is not essential. In dioxan the yield fell to 6%; in ether the reaction was unsuccessful when the sodium was replaced by potassium, a liquid sodium–potassium alloy, lithium, or phenyl-lithium. An Ullmann-type reaction with copper bronze in the absence of a solvent was also ineffective. In no case did we find the hydrocarbon $C_{16}H_{12}$, m. p. 191°.

(I.)





(III.)



(IV.) (II.) (V.)

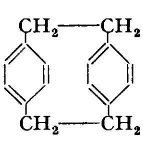
The formula (II) assigned by Pellegrin to the hydrocarbon $C_{16}H_{16}$ has, in spite of its stereochemically unfavourable structure, proved to be correct. This has been established by the fact that, when heated with palladium–charcoal, best in an open tube at 270—310°, it undergoes cyclodehydrogenation with loss of six atoms of hydrogen and bridging of the ten-membered ring to give the fully aromatic hydrocarbon pyrene (IV) in 60% yield. The pyrene was isolated as its picrate, from which it was regenerated. This very simple production of pyrene in a three-stage synthesis from *m*-xylene proceeds in an overall yield of 2·4%, but no attempt has been made to improve the yield of pure *m*-xylylene dibromide normally obtained (*ca.* 35%, not allowing for recovered *m*-xylene) by bromination of *m*-xylene.

Dehydrogenation and ring-closure to polycyclic aromatic hydrocarbons have been effected in a number of cases by means of aluminium chloride (see, *e.g.*, Scholl and Seer, *Ber.*, 1910, **43**, 2202; Ruzicka and Hösli, *Helv. Chim. Acta*, 1934, **17**, 470; Buu-Hoï, *J. Org. Chem.*, 1949, **14**, 1031), but the reaction took an unexpected course with di-*m*-xylylene (II), giving the isomeric 1 : 2 : 2*a* : 3 : 4 : 5-hexahydropyrene (V) which was characterised as its picrate.

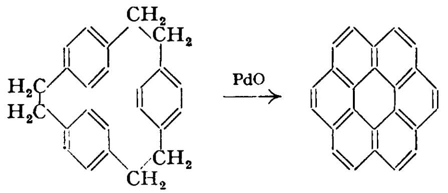
Models of di-*m*-xylylene show that this mobile molecule may take up three main forms, (1) a step-like *trans*-form in which the benzene rings are arranged in parallel planes separated by about 1·7 A., (2) two identical *cis*-forms with benzene rings inclined at an angle of about 60°, and (3) a twisted form through which the *cis*-forms pass during interconversion. These correspond closely with the forms of *s*-dibenzo*cyclo*octadiene illustrated in the paper by Baker, Banks, Lyon, and Mann (*J.*, 1945, 27) by Figs. 1, 1*B*, and 1*A*. If the molecule (II) possessed the normal bond angles and bond lengths, then the marked carbon atoms would be separated by a maximum distance of about 1·8 A. in the *trans*- and *cis*-forms. Since the minimum distance between non-bonded aromatic CH groups would normally be expected to be of the order of 4 A., it is clear that considerable strain must be present in (II), and the most probable form of the molecule appears to be a somewhat distorted *trans*-form. It is interesting to note that Brown and Farthing (*Nature*, 1949, **164**, 915) have shown that di-*p*-xylylene (VI) is produced in very small quantity from *p*-xylene at high temperatures. In this remarkable compound four pairs of non-bonded benzenoid CH groups would be expected to be separated by only 1·55 A., but *X*-ray examination has shown that, owing to distortion of the benzene rings, this distance is, in fact, increased to 3·09 A., which may be taken as possibly the minimum for non-bonded aromatic CH groups. It is evident that the total strain involved in increasing the distance between the carbon atoms marked * in (II) from 1·8 to 3·09 A. is not prohibitive, but we consider it unlikely that the hydrocarbon, m. p. 191°, obtained by Pellegrin has the formula (III), which represents a considerably more strained molecule. Di-*m*-xylylene contains benzene rings bridged in the *meta*-positions by chains of seven carbon atoms; the smallest *m*-bridges appear to be those containing six methylene groups which have been prepared by Prelog from nitromalondialdeyde and *cyclo*nonanone (see *J.*, 1950, 420).

In our original note (*Chem. and Ind.*, 1950, 77) we suggested that pyrene in coal tar may arise, in part at least, by synthesis from *m*-xylene, and this could occur either *via* di-*m*-xylylene, or *via* 2 : 6 : 2′ : 6′-tetramethyldiphenyl. We now find that traces of pyrene have been obtained from mixed xylenes at about 700° (Bradley and Parr, *Chem. Met. Eng.*, 1922, **27**, 737), though there is no indication of the intermediate steps, and the synthesis of pyrene described in this paper is the simplest though not the most convenient, that has been achieved (see Elsevier "Encyclopædia of Organic Chemistry," Vol. XIV, p. 376).

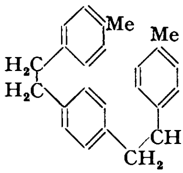
*Tri-*p*-xylylene and its Conversion into Coronene.*—In investigating the action of sodium on *p*-xylylene dihalides, it was not thought probable that di-*p*-xylylene (VI) would be produced, and the simplest cyclic compound expected was tri-*p*-xylylene (VII), containing a triangular arrangement of three linear groups. The action of sodium on either *p*-xylylene dibromide or dichloride gave much material of high molecular weight, 1 : 2-di-*p*-tolylethane, and a difficultly separable mixture of *p*-di-(2-*p*-tolylethyl)benzene, $C_{24}H_{26}$ (VIII), m. p. 140—141°, and tri-*p*-xylylene, $C_{24}H_{24}$ (VII), m. p. 166—167°, which were finally isolated in a state of purity, though with considerable loss, in just under 5% and 4% yield respectively. The presence of di-*p*-xylylene (VI) in the reaction mixture could not be detected, and Brown and Farthing (*loc. cit.*) were also unable to isolate di-*p*-xylylene (or other crystalline products) from the material of high molecular weight which they obtained in a similar reaction. Substances (VII) and (VIII) were separated by fractional distillation under diminished pressure followed by fractional crystallisation from ethanol; chromatographic methods, fractional sublimation under diminished pressure, and co-distillation with ethylene glycol were not effective.



(VI.)



(VII.) (IX.)



(VIII.)

The structures (VII) and (VIII) assigned to the hydrocarbons of m. p. 166—167° and 140—141°, which show no properties due to unsaturation, are based on analysis and molecular-weight determinations, and on the fact that the first, like dibenzyl, showed no infra-red absorption band at 1380 cm.$^{-1}$ characteristic of the methyl group, whilst the second, like 1 : 2-di-*p*-tolylethane, did exhibit absorption at this wave-length. Neither (VII) nor (VIII) was attacked under the Kuhn–Roth conditions for estimation of *C*-methyl groups. Further evidence in support of the cyclic structure (VII) for the hydrocarbon of m. p. 166—167° has been obtained by dehydrogenation and oxidation with palladium monoxide at 360°; this brings about triple bridging of the eighteen-membered ring and dehydrogenation of the three dimethylene groups with production of coronene (IX) in 1·9% yield. This experiment was carried out with pure tri-*p*-xylylene, and the coronene was isolated as its picrate, regenerated therefrom on an alumina column, and identified by an *X*-ray powder photograph. A similar experiment with *p*-di-(2-*p*-tolylethyl)benzene (VIII) gave no trace of coronene. The dehydrogenation of (VII) to coronene is difficult and was attempted without success by treatment with palladium–charcoal, palladium–strontium carbonate, and selenium. The action of aluminium chloride on (VII) in carbon disulphide gave a trace of a picrate-forming, coronene-like compound. This synthesis of coronene from *p*-xylene by a three-stage process is by far the simplest which has been achieved, but it is scarcely of a practicable nature. The separate yields, *ca.* 60%, 4%, and 1·9%, give an overall of only about 0·05%, and the last two stages are not adaptable to large-scale work (cf. the coronene synthesis described in the succeeding paper).

Unlike di-*m*-xylylene (II), the molecule of tri-*p*-xylylene (VII) should be strainless because the three benzene rings can take up positions inclined to the general plane of the eighteen-membered ring, thus avoiding interference between non-bonded aromatic CH groups.

Tri-*p*-xylylene is a *para*-bridged benzene derivative, and contains fourteen carbon atoms in the bridge. Other *para*-bridged structures are known, recent examples being di-*p*-xylylene (VI) with an eight-membered bridge, and a compound containing a ten-membered hydroxy-ketone bridge prepared by the acyloin reaction (Kelley, MacDonald, and Weisner, *Nature*, 1950, **166**, 225).

EXPERIMENTAL.

M. p.s are uncorrected. Analyses are by Drs. Weiler and Strauss, Oxford, and Mr. W. M. Eno, Bristol.

Reaction of m*-Xylylene Dibromide with Sodium. Di-*m*-xylylene* (II).—A solution of *m*-xylylene dibromide (26 g.; m. p. 78—79°; prepared by the method of Ruggli, Bussemaker, and Müller, *Helv. Chim. Acta*, 1935, **18**, 616, and recrystallised from light petroleum, b. p. 60—80°) in anhydrous ether

(200 c.c.) was added to powdered sodium (10 g.) and, after the addition of sodium iodide (0·5 g.) and bromobenzene (1 c.c.), the mixture was boiled under reflux and continuously stirred (mercury-sealed stirrer). After the first hour a blue colour appeared and deposition of solid began; the reaction appeared to be complete after 18 hours. The cooled solution was then filtered, and distillation of the ether left a viscous oil which partly crystallised on storage; after crystallising four times from ethanol di-*m*-xylylene (1·2 g., 11·7%) was obtained in rhombic prisms, m. p. 132—133° [Found : C, 91·9; H, 7·8%; *M* (Rast), 200. Calc. for $C_{16}H_{16}$: C, 92·25; H, 7·75%; *M*, 208]. This compound did not decolorise a solution of potassium permanganate in acetone, nor did it combine with bromine.

Dehydrogenation of Di-m-*xylylene* (II) *to Pyrene* (IV).—A 30% palladium–charcoal catalyst was prepared from norite charcoal previously heated with 10% nitric acid for 6 hours. To palladium chloride (2 g.) dissolved in water (12 c.c.) and concentrated hydrochloric acid (1·2 c.c.), 40% aqueous formaldehyde (12 g.) and charcoal (2·7 g.) were added at 0°, followed by potassium hydroxide (12 g.) in water (12 c.c.). After ¼ hour's heating at 60° the catalyst was collected, washed thoroughly with hot water, and dried at 100°.

Di-*m*-xylylene (II) (200 mg.) intimately mixed with the catalyst (300 mg.) was placed in an open tube (20 × 0·9 cm.), covered with a layer of catalyst (200 mg.), and heated for 6 hours in a metal-bath, the temperature of which was gradually raised from 270° to 310°. Repeated extraction of the contents of the tube with benzene yielded a colourless crystalline solid (162 mg.) which, when treated in alcoholic solution with picric acid, gave long, thin, orange-red prisms of a picrate (202 mg.) having m. p. 222° after crystallisation from alcohol (Found : N, 9·6. Calc. for $C_{16}H_{10},C_6H_3O_7N_3$: N, 9·75%). This was indistinguishable from authentic pyrene picrate (m. p. 223°) and the mixed m. p. was 223°. The filtrate from the picrate formation yielded unchanged di-*m*-xylylene, m. p. 132—133° (40 mg.). The yield of pyrene as picrate, after allowing for recovered di-*m*-xylylene, is 60%.

Pyrene was regenerated by shaking the picrate with ether and aqueous sodium carbonate, the ethereal layer yielding colourless, stout, rhombic prisms, m. p. 149°; when mixed with pure pyrene (m. p. 150°) it gave m. p. 149—150° (Found : C, 95·3; H, 5·2. Calc. for $C_{16}H_{10}$: C, 95·0; H, 5·0%).

Cycloisomerisation of Di-m-*xylylene to* 1 : 2 : 2*a* : 3 : 4 : 5-*Hexahydropyrene* (V).—Di-*m*-xylylene (100 mg.) was heated under reflux for 3 hours with carbon disulphide (5 c.c.) and anhydrous aluminium chloride (500 mg.), water was added, and the whole was extracted with chloroform. The residue left after removal of the solvents was sublimed at about 130°/17 mm., giving a pale yellow solid (52·5 mg.), which, after recrystallisation from alcohol, was converted into an orange picrate, m. p. 147—148°, by treatment with alcoholic picric acid. Decomposition of the picrate on an alumina column and elution with alcohol gave the hexahydropyrene (V) as colourless plates, m. p. 103—105°, from dilute alcohol (Found : C, 92·0; H, 7·7. Calc. for $C_{16}H_{16}$: C, 92·25; H, 7·75%). Cook and Hewett (*J.*, 1933, 404) give m. p. 147·5—148° for the picrate of this hexahydropyrene, and 105—105·5° for the hydrocarbon itself; *s*-hexahydropyrene has m. p. 132—133° (see also E. A. Coulson, *J.*, 1937, 1298).

Reaction of p-*Xylylene Dibromide and* p-*Xylylene Dichloride with Sodium. Isolation of* 1 : 2-*Di*-p-*tolylethane*, p-*Di*-(2-p-*tolylethyl*)*benzene* (VIII), *and Tri*-p-*xylylene* (VII).—(*a*) *p*-Xylylene dibromide [26 g.; m. p. 141—143°; prepared according to Atkinson and Thorpe, *J.*, 1907, **91**, 1698, Titley, *J.*, 1926, 514, and recrystallised from light petroleum (b. p. 60—80°)] in dioxan (200 c.c.; purified and freshly distilled over sodium) was added to powdered sodium (10 g.) and heated under reflux with the addition of sodium iodide (0·5 g.) and efficient mechanical stirring (mercury-sealed stirrer). As the b. p. was reached, a blue colour developed and a very vigorous reaction set in, necessitating the removal of the source of heat for a short time; the mixture was then boiled and stirred for a further 8 hours, then filtered, and the filtrate evaporated, leaving a product (6·2 g.) which crystallised on storage. (*b*) A similar product was obtained when parallel experiments were performed using (1) *p*-xylylene dichloride [17 g. (equiv. to 26 g. of *p*-xylylene dibromide), m. p. 97—99°; Kulka, *Canad. J. Res.*, 1945, **23**, *B*, 106], dioxan (300 c.c.), sodium (10 g.), and sodium iodide (0·5 g.) (yield of dioxan-soluble product, 5·3 g.), and (2) *p*-xylylene dichloride (17 g.), dioxan (900 c.c.; less vigorous reaction), sodium (10 g.), and sodium iodide (0·5 g.) (yield of dioxan-soluble product, 5·6 g.).

Mixed crude material (9 g.) from these experiments was distilled through a 4-cm. column at 0·2 mm. pressure, and the following fractions were collected : (1) b. p. <120°, m. p. 76—82°, 1·8 g.; (2) b. p. 170—185°, m. p. 100—123°, 1·2 g.; (3) b. p. 185—200°, m. p. 110—145°, 1·3 g.; (4) b. p. 195—215°, 0·6 g. Fraction (1) was recrystallised from ethanol, giving thin, irregular flakes, m. p. 78—81°; a mixed m. p. with an authentic specimen of 1 : 2-di-*p*-tolylethane, m. p. 81—82°, was 79—81°. Crystallisation from ethanol of fraction (2) gave a mixture of long, prismatic needles (*A*) and fine, white crystals; fraction (3) similarly gave some needles and irregular, stellate, crystalline aggregates (*B*); and fraction (4) gave mainly the stellate aggregates (*B*). By repeated crystallisation from ethanol, and by taking advantage of the fact that the prismatic needles formed rapidly on cooling, thus permitting the decantation of the mother-liquor before deposition of the other more slowly-separating product, there were finally obtained in the pure state 0·61 g. of (*A*) and 0·76 g. of (*B*).

Tri-p-*xylylene* (VII) (*A*) has m. p. 166—167° (Found : C, 92·1; H, 7·8%; *M*, ebullioscopic in benzene, 317. $C_{24}H_{24}$ requires C, 92·3; H, 7·8%; *M*, 312). The prisms frequently show feather-like, parallel growth. They do not reduce potassium permanganate.

p-*Di*-(2-p-*tolylethyl*)*benzene* (VIII) (*B*) has m. p. 140—141° (Found : C, 91·2; H, 8·8%; *M*, ebullioscopic in benzene, 318. $C_{24}H_{26}$ requires C, 91·7; H, 8·3%; *M*, 314).

Conversion of Tri-p-*xylylene* (VII) *into Coronene* (IX).—Pure tri-*p*-xylylene (VII) (50 mg.) mixed with palladium oxide (120 mg.) was heated in a sealed tube for 84 hours, the temperature being slowly raised from 280° to 380°, and the opened tube was dried in an evacuated desiccator and extracted six times with boiling toluene. The filtered toluene solution gave a residue which was sublimed at 200° rising to 300°/20 mm.; the sublimate (2·5 mg.) was dissolved in benzene and treated with alcoholic picric acid, the red needles of a picrate which separated were dissolved in benzene, and the solution was passed through an alumina column, which was finally eluted with benzene. When concentrated to a small bulk the benzene solution gave bright yellow needles which were recrystallised from benzene (final yield, 0·9 mg.). This material and its picrate were indistinguishable from coronene and coronene picrate, and complete identity of the hydrocarbons was established by an *X*-ray powder photograph which showed complete coincidence of all lines, which were also of the same relative intensities.

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