LXII.—*The Diphenylbenzenes.* I. *Metadiphenylbenzene.*

By FREDERICK D. CHATAWAY, M.A., and R. C. T. EVANS.

ACCORDING to theory, three isomeric diphenylbenzenes, $C_6H_4(C_6H_5)_2$, are possible, in which the phenyl groups occupy the ortho-, meta-, and para-positions respectively, but of these, up to the present, only two are known, namely, paradiphenylbenzene and the so-called isodiphenylbenzene. The constitution of the former is established as it has been obtained from paradibromobenzene and yields, on oxidation, paradiphenylcarboxylic acid and terephthalic acid; the constitution of the latter is still doubtful. The authors have undertaken

the synthesis of the ortho- and meta-diphenylbenzenes, and the present paper, containing an account of the synthesis of metadi-phenylbenzene, which proves to be identical with "isodiphenylbenzene," is the first part of this investigation.

When benzene is passed through a red-hot tube, besides diphenyl, a complicated mixture of other hydrocarbons is obtained. From this mixture Berthelot (*Compt. rend.*, 1866, **63**, 788), who first examined it, thought that he had isolated three substances which he named chrysene, benzerythrene, and bitumen. Berthelot's three products are undoubtedly mixtures, although the first two have been assumed to be identical with the hydrocarbons chrysene and picene which have been shown (Bamberger and Chattaway, *Annalen*, 1895, **284**, 52) to belong to the phenanthrene series. On distilling the product obtained on passing benzene vapour through a red-hot iron tube, unchanged benzene and diphenyl first come over, then the thermometer rises rapidly above 360° , and the yellow substance which Berthelot termed "chrysene" distils. From this, Schultz (*Annalen*, 1874, **174**, 201) isolated two hydrocarbons, one an easily soluble, well-crystallised substance melting at 85° and boiling at about 360° , the other a less soluble compound melting at 205° . The hydrocarbon of high melting point was shown by him to be the paradiphenylbenzene previously obtained by Riese (*Annalen*, 1872, **164**, 161) and to yield paradiphenylcarboxylic and terephthalic acids on oxidation. The compound melting at 85° was found to have a composition and molecular weight agreeing with the formula $C_{18}H_{14}$, and was termed isodiphenylbenzene.

A diphenylbenzene identical with this has also been obtained, together with paradiphenylbenzene and chlorobenzene, by Mohlau and Berger (*Ber.*, 1893, **26**, 1999), by acting on diphenyl with diazobenzene chloride in presence of aluminium chloride.

The determination of the constitution of this isodiphenylbenzene, however, is not a simple process. By oxidising a large quantity of the hydrocarbon, dissolved in glacial acetic acid, with chromic acid, Schmidt and Schultz (*Annalen*, 1880, **203**, 131) obtained as chief product benzoic acid, considerable quantities of paradiphenylcarboxylic acid and terephthalic acid, however, were formed, and also a very small quantity of another acid; the latter was converted into a barium salt, and the barium in it determined. From the results thus obtained, they regarded the acid as a diphenylcarboxylic acid.

Oligiati has more recently (*Ber.*, 1894, **27**, 3385) investigated the oxidation of the monobromo-derivative of this hydrocarbon. He considered that Schmidt and Schultz's results were due to admixed paradiphenylbenzene, but this is impossible as their product melts at exactly the same temperature as the product Oligiati obtained by

reducing the monobromo-derivative with sodium amalgam, and even if some slight impurity were present it would scarcely explain the occurrence of terephthalic acid as one of the chief products of oxidation. The probable explanation is that such oxidation processes resulting in the formation of carboxylic acids are not always to be relied on as methods for determining the constitution of hydrocarbons; the first result of such oxidation being the linking together of molecules into more complicated systems by the removal of hydrogen and the subsequent breaking down of these added rings, carboxyl groups remaining attached. Many well-known facts support such an explanation, for example, the formation of α -dinaphthyl by the oxidation of naphthalene (Lossen, *Annalen*, 1867, **144**, 77) and the formation of benzoic acid and phthalic acid in the oxidation of benzene (Carius, *Annalen*, 1868, **148**, 50). The fact that metadiphenylcarboxylic acid is produced by the reduction of the monobromodiphenylcarboxylic acid obtained by the oxidation of monobromodiphenylbenzene, however, renders it probable that in isodiphenylbenzene the phenyl groups occupy the meta-positions.

The authors considered that the constitution of isodiphenylbenzene could best be settled by the synthesis of both ortho- and meta-diphenylbenzene from substances of known constitution, and this synthesis they have undertaken.

The most direct methods for these syntheses are the action of sodium on a mixture of the particular dichlorobenzene and chlorobenzene, and the action of the chlorobenzenes on benzene in presence of aluminium chloride.

Ortho- and meta-dichlorobenzene, however, have hitherto only been obtained in quantity with great difficulty, and this is probably the reason why previous investigators have neglected this method of testing their conclusions. The authors, having succeeded in obtaining metadichlorobenzene easily in any amount (this vol., p. 848), have been able to carry out the synthesis of metadiphenylbenzene, which proves to be identical with Schultz's product. Only the first method has proved practicable, metadichlorobenzene scarcely reacting with benzene in presence of aluminium chloride.

When melted sodium is allowed to act on a mixture of metadichlorobenzene and chlorobenzene dissolved in boiling xylene, metadiphenylbenzene is produced in addition to diphenyl, a liquid substance probably metachlorodiphenyl, and resinous products of high boiling point. The metadiphenylbenzene can be separated easily in a pure condition by fractionating the product. On distillation, after the xylene and unchanged halogen derivatives of benzene have passed over, diphenyl distils, then metachlorodiphenyl, and next metadiphenylbenzene; the appearance of the metachlorodiphenyl, which does not solidify on

long standing, marking the point of complete separation between the diphenyl and the metadiphenylbenzene. One crystallisation from alcohol of the solid substances distilling below and above this liquid gives pure diphenyl and pure metadiphenylbenzene respectively.

Synthesis of Metadiphenylbenzene, $C_6H_4(C_6H_5)_2$ [1 : 3].

Perfectly dry xylene, boiling at about 145° , was placed in a capacious flask and heated to gentle ebullition in an oil bath, and to this was added somewhat more than the amount of sodium required, cut into thin slices, keeping it well covered by the boiling xylene. A mixture of 1 part of metadichlorobenzene, 2 parts of chlorobenzene, and 1/20th part of ethylic acetate was then run in in quantities of about 5 c.c. at a time, allowing, each time, the action to cease before more was added. It is best to keep an excess of sodium present, and a few grams may be added with advantage from time to time. The action is very violent at the high temperature, and so much heat is developed that, unless the mixture be added very cautiously, it becomes uncontrollable, and the whole contents may boil out of the flask. It is dangerous to use water in the condenser if a glass inner tube be used. We have found it convenient to keep the condenser about one-quarter filled with alcohol which quietly boils in the outer tube, and is sufficient to condense the xylene. If the action becomes so vigorous that xylene escapes from the condenser, this can be prevented by blowing a rapid stream of air through the alcohol from the lower tube of the condenser. As the action progresses the flask becomes filled with a pasty, brown mass which is partly sodium chloride, but chiefly a very insoluble, organic compound similar to that formed at high temperatures by the action of sodium on nearly all aromatic halogen derivatives. When the mixture had all been added, another half part of chlorobenzene was run in in small quantities. After boiling for a few hours the product was mixed with a large excess of hot benzene, the brown liquid filtered off, and the residue finally extracted several times with hot benzene. The benzene and xylene were then distilled from the filtrate and the product fractionated.

At first, between about 150° and 230° , a small quantity of metadichlorobenzene, which had not been acted on, came over, then, between about 230° and 305° , diphenyl distilled, the last portions being mixed with a liquid, probably metachlorodiphenyl; this liquid product was then obtained apparently nearly pure between 320° and 340° . Between 340° and 450° a thick oil distilled which on long standing solidified to a pasty, crystalline mass of metadiphenylbenzene. Above 450° , small quantities of metadiphenylbenzene still came over, mixed,

however, with an increasing quantity of a thick, light brown, resinous substance, easily soluble in benzene. The hydrocarbon is most easily obtained pure by stirring up the portion of the distillate coming over between 340° and 460° with a very little light petroleum, and leaving the mixture for some days, when metadiphenylbenzene crystallises out. This, when separated by means of a filter-pump and dried on a porous tile, is nearly pure, and, after one crystallisation from alcohol, melts constantly at $84-85^{\circ}$. Further quantities of metadiphenylbenzene may be obtained by re-fractionating the mother liquors and high boiling portions of the original distillate. The yield of metadiphenylbenzene was about 12 per cent. of the theoretical calculated on the metadichlorobenzene used, which is quite as large as could be expected, considering the complexity of the action and the number of atoms and molecules that must meet in an ordered manner for the action to take place at all. The amount of diphenyl obtained is about twice the weight of the metadiphenylbenzene.

Metadiphenylbenzene is a colourless, well crystallised substance, separating from an alcoholic solution in star-shaped groups of fine needles which, when collected by filtration, appear to be small, elongated, rhombic plates, aggregated into pearly masses. The hydrocarbon has, at first, like most hydrocarbons prepared in this manner, a faint yellow colour, which is very difficult to get rid of by crystallisation, although this trace of impurity does not in the slightest degree affect the melting point. It is easily soluble in ether, alcohol, benzene and its homologues, and in glacial acetic acid. When dissolved in glacial acetic acid, it is readily oxidised by chromic acid, but its synthesis is too tedious to allow of enough being prepared thus to investigate its oxidation products; the preparation of even a few grams entails several weeks' work. It melts at 84° (uncorr.) and boils at 369° under a pressure of 766 mm. with about half the mercury column immersed in the vapour. This boiling point can only be taken as approximate, for, unfortunately, we had not at our disposal a thermometer reading sufficiently high with a column of mercury short enough to be immersed completely in the vapour. The number given was taken with a mercury thermometer filled with nitrogen, and reading to 460° .

A combustion of the hydrocarbon was made with the following result.

0.2066 gave 0.7113 CO_2 and 0.1133 H_2O . C = 93.90; H = 6.11.

$\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2$ requires C = 93.91; H = 6.08 per cent.

The molecular weight was also taken by Raoult's method, using benzene as a solvent.

1.2994 gram of hydrocarbon dissolved in 40.8 grams of benzene

lowered the freezing point by 0.67° . This gives 233 as the molecular weight, whilst 230 is required by the formula $C_6H_4(C_6H_5)_2$.

Action of Metadichlorobenzene on Benzene in presence of Aluminium Chloride.

Metadichlorobenzene was dissolved in about four times its weight of dry benzene and an excess of aluminium chloride added. Very little action took place. After a few days, small quantities of hydrogen chloride were evolved, but even at the expiration of four weeks the total amount disengaged was small. As so little action took place at the ordinary temperature, the mixture was heated for several days on a water bath; a slight evolution of hydrogen chloride ensued, but soon ceased, and the total action appeared inconsiderable. The product was finally poured into an excess of water and the brown benzene solution separated, dried, and fractionated. Almost the whole of the benzene and the metadichlorobenzene used were recovered unchanged, only a very small quantity of a reddish-brown product of high boiling point having been formed. This probably contained a little metadiphenylbenzene, but, as the amount produced was too small to admit of fractionation, it was very difficult to isolate the hydrocarbon crystallising from such distillation products until nearly pure. However, by extracting the residue with alcohol, distilling off the solvent, and re-extracting the residue, a product was finally obtained which, on long standing, deposited crystals of metadiphenylbenzene in the characteristic, star-shaped aggregates.

*Chemical Laboratory,
St. Bartholomew's Hospital.*