THE MECHANISM OF THE WURTZ-FITTIG REACTION[1]

BY W. E. BACHMANN AND H. T. CLARKE

In a search for a convenient laboratory method for the preparation of relatively large quantities of biphenyl, one of us with T. F. Murray, some three years ago, investigated the action of sodium on chlorobenzene at the boiling temperature. It was found that while biphenyl was produced in about 20% of the calculated yield, it was accompanied not only by a high proportion of benzene, but the residue, on distillation with steam, yielded a hydrocarbon of higher boiling point, which melted at 57° and was apparently identical with the hydrocarbon melting at 57–58° isolated by Weiler[2] from the products of the action of sodium upon bromobenzene. Analysis and molecular-weight determination of this compound show it to be a diphenylbenzene; since the *meta* and *para* isomers are well known, the new compound must be the *ortho* derivative. This has been confirmed by synthesis.

We have also been able to isolate two other hydrocarbons of high molecular weight, which are not volatile with steam; these are triphenylene, which was isolated (although not identified) by Schultz[3] from the products of the action of sodium upon bromobenzene according to the directions of Fittig,[4] and a hydrocarbon, $C_{24}H_{18}$, which we have proved by synthesis to be *o,o'*-diphenylbiphenyl. All three of these hydrocarbons were isolated by Weiler who, however, made no attempt to characterize them beyond determining their molecular weight.

Two other products, melting at 167–168° and 151–152°, respectively, were described by Weiler, but we have been unable to detect either of them among the products of the action of sodium upon chlorobenzene. On the other hand, like Weiler, we have isolated very small amounts of *p*-diphenylbenzene from among the products of our reaction.

A considerable quantity of a sirupy hydrocarbon is also formed; analysis shows it to consist of hydrocarbons of approximately the same empirical composition and molecular weight as the above products, but we have no clue as to their constitution.

The mechanism of the Wurtz-Fittig reaction has received ample discussion, particularly in the recent papers of Schlubach and Goes[5] and Goldschmidt and Schön.[6] The alternative theories advanced in

[1] Reported before the Organic Division, American Chemical Society, at Richmond, Virginia, April, 1927.

[2] Weiler, *Ber.*, **29**, 115 (1896).

[3] Schultz, *Ann.*, **174**, 228 (1874). Dreher and Otto, *Ann.*, **154**, 99, footnote (1870). Carstanjen, *J. prakt. Chem.*, [1] **110**, 80 (1870).

[4] Fittig, *Ann.*, **132**, 202 (1864).
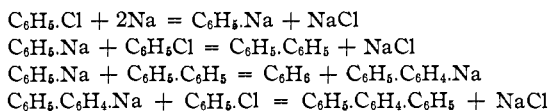
[5] Schlubach and Goes, *Ber.*, **55**, 2889 (1922).

[6] Goldschmidt and Schön, *Ber.*, **59**, 948 (1926).

these papers, involving on the one hand the formation of free radicals, and on the other the reaction between sodium aryls[7] and halogen compounds, are equally capable of interpreting the formation of benzene[8] and biphenyl.

Now Schorigin[9] has demonstrated that metallic alkyls can exchange their metal for hydrogen when treated with aromatic hydrocarbons, and we have been able to show that an analogous migration of sodium takes place in the sodium aryls.

A suspension of mercury di-p-tolyl was converted into the corresponding sodium derivative by the action of metallic sodium in the presence of benzene; by the action of carbon dioxide there were formed not only p-toluic acid but also benzoic and phenylacetic acids, indicating the partial migration of sodium (either simultaneously with the replacement of the mercury or subsequently thereto) from the $para$ carbon atom of the toluene to the side chain and to the benzene in which the mixture was suspended.

By assuming the transference of sodium from sodium phenyl to biphenyl, an explanation of the formation of diphenylbenzene is readily forthcoming.

$$C_6H_5.Cl + 2Na = C_6H_5.Na + NaCl$$
$$C_6H_5.Na + C_6H_5Cl = C_6H_5.C_6H_5 + NaCl$$
$$C_6H_5.Na + C_6H_5.C_6H_5 = C_6H_6 + C_6H_5.C_6H_4.Na$$
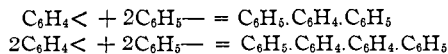$$C_6H_5.C_6H_4.Na + C_6H_5.Cl = C_6H_5.C_6H_4.C_6H_5 + NaCl$$

The diphenylbiphenyl may be regarded as being formed in an analogous manner from diphenylbenzene.

On the other hand, this type of mechanism cannot be made to account for the formation of triphenylene, and we regard the presence of this compound among the reaction products as decisive in favor of the free radical explanation. This involves the interaction of two free phenyl radicals to form benzene and free phenylene, $2 C_6H_5— = C_6H_6 + C_6H_4<$, which condenses either with itself, to form triphenylene

$$3C_6H_4< = C_6H_4 \Big\langle \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}$$
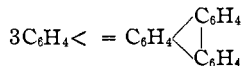
or with phenyl, to form diphenylbenzene and diphenylbiphenyl.

$$C_6H_4< + 2C_6H_5— = C_6H_5.C_6H_4.C_6H_5$$
$$2C_6H_4< + 2C_6H_5— = C_6H_5.C_6H_4.C_6H_4.C_6H_5$$

We are, however, far from suggesting that sodium aryls play no part in the Fittig reaction, for it has been shown by Schlenk[10] that free aryls and alkali metals can unite to form metallic aryls.

$$C_6H_5— + Na = C_6H_5.Na$$
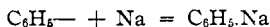
[7] Krafft and Göttig, $Ber.$, 21, 3180 (1888). Nef, $Ann.$, 308, 291 (1899). Acree, $Am. Chem. J.$, 29, 588 (1903). Hilpert and Grüttner, $Ber.$, 46, 1679 (1913). Schlenk and Holtz, $Ber.$, 50, 262 (1917).

[8] Wieland, Popper and Seefried, $Ber.$, 55, 1816 (1922).

[9] Schorigin, $Ber.$, 43, 1938 (1910).

[10] Schlenk, $Ber.$, 49, 608 (1916).

In the hope of throwing more light on the problem, the reaction between sodium and chlorobenzene was carried out in the presence of an excess of toluene, with the idea that this latter hydrocarbon might act as a hydrogen donor and thus appear among the products of reaction.

$$C_6H_5— + C_7H_8 = C_6H_6 + C_7H_7—$$
or
$$C_6H_5.Na + C_7H_8 = C_6H_6 + C_7H_7.Na$$
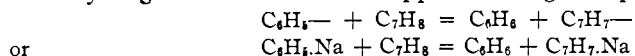
This was found to be the case; the formation of biphenyl was apparently entirely suppressed, and the fraction which should have contained it consisted of a mixture or p-methylbiphenyl and diphenylmethane. The yield of benzene rose to 34% in the case when the sodium was added to the mixture of chlorobenzene and toluene and to 46.5% when the chlorobenzene was added to the sodium suspended in the toluene.

This participation of the toluene in the reaction recalls the observation of Schorigin[11] on the action of sodium upon mixtures of mercury diethyl and benzene, toluene, etc., in the presence of carbon dioxide, whereby benzoic acid, phenylacetic acid, etc., are formed. It also finds an analogy in the experiment above quoted in which we have obtained benzoic and phenylacetic acids by treating mercury di-p-tolyl successively with sodium and carbon dioxide in the presence of benzene.

Similarly, when chlorobenzene is added to a suspension of sodium in hot dimethylaniline, the latter compound acts as a donor of hydrogen; 49% of the chlorobenzene is recovered as benzene, biphenyl is formed in only minute amounts, and the pitch-like residue contains nitrogen. This pitch, the nature of which was not closely investigated, is insoluble in dil. hydrochloric acid, and appears to contain compounds related to diphenylamine, since its solution in acetic acid readily develops a blue color on exposure to air. Basic compounds are also formed in small (about 2%) amounts; no systematic attempt was made to separate them but derivatives of benzylaniline appear to be present, as is indicated by the formation of benzaldehyde on oxidation in acid solution.

The fact that the yield of benzene appears never to exceed 50% of that theoretically obtainable from the chlorobenzene in the presence of a hydrogen donor, leads us to advance the tentative hypothesis that the free phenyl radical can exist in two electromeric forms, of which only one is capable of accepting hydrogen under the given conditions. The formation of these types of opposite polarity could be explained by postulating their formation by the interaction of chlorobenzene and sodium phenyl.
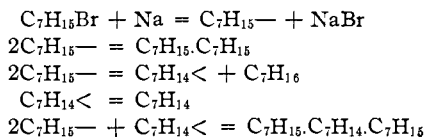
$$C_6H_5.\overset{+}{C}l + C_6H_5.\overset{+}{Na} = C_6H_5— + C_6H_5— + NaCl$$
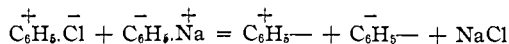
It is noteworthy that no o-diphenylbenzene could be detected in the residues from about 5 kg. of pyrogenic biphenyl, which yields relatively large quantities of m- and p-diphenylbenzene and a small amount of triphenylene.[12] The hypothesis that this last compound is formed by the dehydrogenation of any o-diphenylbenzene initially produced was disproved by passing the latter substance through a red-hot tube, in an atmosphere of carbon dioxide, when only biphenyl and a little carbon were found together with unchanged o-diphenylbenzene.

[11] Schorigin, *Ber.*, **41**, 2723 (1908); Ref. 9.

[12] Compare Schmidt and Schultz, *Ann.*, **203**, 135 (1880). Mannich, *Ber.*, **40**, 164 (1907).

The Wurtz synthesis of aliphatic hydrocarbons appears to proceed along analogous lines. When n-heptyl bromide is treated at the boiling temperature with sodium, the following products are formed: heptane, 9%; heptylene, 3%; tetradecane, 67%; heneicosane, 3%, as well as hydrocarbons of higher molecular weight. A qualitative experiment with *iso*-amyl bromide and sodium yielded a pentadecane analogous to the above heneicosane.

Michael,[13] who noted the formation of alkylene and the paraffin corresponding to it, considered that hydriodic acid was first eliminated and that the nascent hydrogen, resulting from the action of sodium upon it, converted a part of the alkylene into paraffin. This explanation takes no account of the formation of products of high molecular weight, and we believe that the facts can be more satisfactorily explained by the assumption of free radicals.

$$C_7H_{15}Br + Na = C_7H_{15}- + NaBr$$
$$2C_7H_{15}- = C_7H_{15}.C_7H_{15}$$
$$2C_7H_{15}- = C_7H_{14}< + C_7H_{16}$$
$$C_7H_{14}< = C_7H_{14}$$
$$2C_7H_{15}- + C_7H_{14}< = C_7H_{15}.C_7H_{14}.C_7H_{15}$$

The formation of alkylene[14] is represented as being preceded by that of free alkylidene, part of which reacts with free alkyl to form the triple compound. The chain of reasoning in this instance is incomplete, owing to the difficulty in determining the constitution of the heneicosane, which should, according to the above hypothesis, possess the structure

$$C_6H_{13}.CH \Big\langle {}^{CH_2.C_6H_{13}}_{CH_2.C_6H_{13}}$$
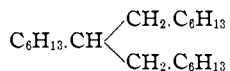
Analogous reactions have been observed among the alkyl magnesium halides. Späth[15] showed that when the alkyl group contains two or more carbon atoms, the action of alkyl halides on alkyl-magnesium halides consists not only in the direct union of the participating alkyl groups but also in the formation of alkylene and the corresponding paraffin, while Fuson,[16] in a recent study of the action of benzyl chloride upon methylmagnesium iodide, noted as the principal reaction the formation of equivalent quantities of dibenzyl and ethane, with the formation of ethylbenzene as a side reaction. Both of the above cases can be readily explained by assuming the intermediate formation of free radicals.

[13] Michael, *Am. Chem. J.,* **25,** 429 (1901).

[14] It is noteworthy that the action of sodium upon bromocyclopentane leads to very poor yields of dicyclopentyl and much cyclopentene [Zelinsky, Titz and Fatejew, *Ber.,* **59,** 2580 (1926)]. The formation of cyclopentane is not recorded.

[15] Späth, *Monatsh.,* **34,** 1965 (1913).

[16] Fuson, THIS JOURNAL, **48,** 2681 (1926).

Experimental Part

Action of Sodium on Chlorobenzene.—Five kg. (44.4 moles) of chlorobenzene was heated in a 12-liter Pyrex flask, provided with an efficient stirrer and a reflux condenser, the inner tube of which was constructed of brass tubing of 15–20 mm. internal diameter. When boiling began the flame was extinguished and 460 g. (20 g. atoms) of sodium was added, piece by piece, through the condenser, at such a rate that the mixture boiled as rapidly as possible without loss of vapor. Vigorous stirring was maintained throughout the addition, which required four to five hours. When all had been added, the rather pasty mixture was allowed to cool somewhat and subjected to steam distillation until all of the unchanged chlorobenzene had been driven over. The distillate was separated and the oil carefully fractionated through a bubbler column[17] when the following fractions were obtained: up to 83°, 407 cc.; 83–95°, 14 cc.; 95–110°, 8 cc.; 110–125°, 26 cc.; 125–130°, 28 cc.; from which the total amount of benzene was estimated at 427 cc. or 375 g., corresponding to 4.8 moles or 24%. The balance of the chlorobenzene was distilled through the column, and the small amount of residue containing biphenyl was joined to the dark, tarry residue from the steam distillation.

This was separated from the solution of sodium chloride and distilled under 15 mm. pressure through a short fractionating column. The following fractions were collected: up to 126°, 14 g.; 126–130°, 330 g.; 130–150°, 20 g.; 150–175°, 25 g.; 175–190°, 14 g.; 190–200°, 176 g.; 220–225°, 33 g.; 225–250°, 62 g.; residue, 350 g. Fraction 126–130° (15 mm.) consisted of almost pure biphenyl. Chlorine could not be detected in any of the fractions distilling above 130° (15 mm.).

o-Diphenylbenzene.—The fraction 190–200° (15 mm.), on cooling, solidified to a mass of long, heavy needles, the setting-point being 50–51°. On recrystallizing from methyl alcohol, large, colorless monoclinic prisms were obtained which melted at 57°; the mother liquor, on evaporation at ordinary temperature, yielded a further crop of the same crystals contaminated with a little oily impurity. Further recrystallization did not raise the melting point above 57°. The compound boils under atmospheric pressure at 332° (corr.). It is somewhat soluble in cold methyl alcohol, and extremely readily in acetone and in chloroform.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Subs. 0.2079, 0.2317: CO_2, 0.7148, 0.7960: H_2O, 0.1154, 0.1275. Found: C, 93.80, 93.72; H, 6.21, 6.16.

Mol. Wt. Ebullioscopic method of Menzies and Wright;[18] solvent, benzene. Solvent, 25.296. Subs., 0.2473, 0.5807, 0.9191; Δt, 0.1084°, 0.2546°, 0.4021°. Calcd.: 230. Found: 235, 235, 236.

By oxidation of 5 g. of o-diphenylbenzene with chromic acid in acetic acid, according to the method employed by Kuhn and Winterstein[19] for the oxidation of p-diphenylbenzene, there was obtained 0.2 g. of an acid which after recrystallization from petroleum ether melted at 108–110° and showed no change in melting point on mixing with o-phenylbenzoic acid prepared from fluorenone. When heated with phosphorus pentachloride it yielded yellow crystals of fluorenone. The corrected melting points and boiling points of the isomeric diphenylbenzenes were determined under the same conditions.

Diphenylbenzene	M. p., °C.	B. p., °C.
o	57	332
m	87	365
p	213	376

[17] Clarke and Rahrs, *Ind. Eng. Chem.*, **18**, 1092 (1926). A column having less than one-half the linear dimensions of that originally described was found to be entirely satisfactory

[18] Menzies and Wright, THIS JOURNAL, **43**, 2314 (1921).

[19] Kuhn and Winterstein, *Ber.*, **60**, 434 (1927).

p-Diphenylbenzene.—The fraction boiling at 200–225° (15 mm.) partially solidified on long standing. The solids were separated by moistening the mass with acetone and filtering. On recrystallization from acetone there was obtained a small quantity of leaflets which on recrystallization from a mixture of chloroform and acetone melted at 210° (corr.) and were identical with *p*-diphenylbenzene obtained by the action of a hot wire on benzene. The total amount obtained was 0.15 g.

The mother liquor from the *p*-diphenylbenzene yielded about 3 g. of *o*-diphenyl-benzene, but the greater part of this fraction consisted of an uncrystallizable sirup.

Triphenylene.—The fraction boiling at 225–250° (15 mm.), the bulk of which passed over at about 240°, was recrystallized from a mixture of chloroform and methyl alcohol, which removed some pale yellow, sirupy material. The product, which melted at 110–115° and was evidently a mixture, was twice recrystallized from chloroform, when colorless needles melting at 199° (corr.) were obtained. The melting point was not changed on recrystallization from acetone. The boiling point was found to be 425° (corr.).

Mol. Wt. Ebullioscopic method; solvent, benzene, Solvent, 24.546. Subs., 0.2498, 0.4898, 0.6475, 0.7871; Δt, 0.1169°, 0.2264°, 0.2965°, 0.3691°. Calcd. for $C_{18}H_{12}$: 228. Found: 227, 230, 232, 227.

On mixing a cold saturated solution in acetone with a saturated solution of picric acid in the same solvent, the picrate separated as a yellow crystalline precipitate. On recrystallization from acetone it formed long, yellow needles which melted at 223° (corr.). This picrate was identified with the triphenylene picrate obtained from the residues of biphenyl produced by the action of a red-hot wire on benzene.

o,o'-Diphenylbiphenyl.—The chloroform mother liquor from the triphenylene was evaporated to dryness and the residue recrystallized from acetone. Two types of crystal were obtained, the long, fine needles of triphenylene and some more massive pyramids. After decanting the mother liquor, the mixture was gently stirred for a few seconds with cold acetone; the solubilities of the two compounds appeared to be about the same, but the fine needles dissolved more rapidly. By repeating this procedure three or four times, all the triphenylene was removed and the residual crystals were finally recrystallized from acetone. The product forms large tetragonal or rhombic pyramids which melt at 118° and boil at 420° (corr.). It is readily soluble in acetone and chloroform and almost insoluble in cold methyl alcohol. It appears to form no compound with picric acid.

Anal. Subs., 0.1980, 0.1957: CO_2, 0.6845, 0.6767; H_2O, 0.1056, 0.1023. Calcd. for $C_{24}H_{18}$: C, 94.12, H, 5.88. Found: C, 94.31, 94.29: H, 5.95, 5.85.

Mol. Wt. Ebullioscopic method; solvent, benzene. Solvent, 23.905. Subs., 0.2047, 0.4396, 0.5900, 0.7895; Δt, 0.0799°, 0.1619°, 0.2180°, 0.3455°. Calcd.: 306. Found: 298, 296, 295, 292.

The mother liquor from the triphenylene and diphenylbiphenyl on concentration yielded a pale yellow sirup, which was freed of solvent by warming under reduced pressure. It was readily soluble in acetone and chloroform, but only slightly in methyl alcohol; it was indistinguishable from the principal constituent of the fraction collected at 220–225° (15 mm.).

Anal. Subs., 0.2224: CO_2, 0.7635; H_2O, 0.1173. Found: C, 93.70; H, 5.90.

Mol. Wt. Ebullioscopic method; solvent, benzene. Solvent, 24.465. Subs., 0.3352, 0.5850, 0.9583; Δt, 0.1392°, 0.2417°, 0.3656°. Found: 257, 257, 265.

Synthesis of *o,o'*-Diphenylbiphenyl.—An intimate mixture of 4 g. of *o*-iodobiphenyl, prepared from fluorenone by the method of Graebe and Rateanu,[20] and 5 g. of copper

---

[20] Graebe and Rateanu, *Ann.*, **279**, 257 (1894).

bronze (Naturkupfer C) was heated at 260° for 20 minutes. The product was cooled and extracted with acetone in a Soxhlet apparatus. The extract was boiled with charcoal, filtered and concentrated; large, colorless pyramids separated on cooling. The yield was 1.5 g. (72% of the calculated amount) of a product melting at 115–116°. On recrystallization from a mixture of alcohol and benzene it melted at 116–117°, and a mixture of it with the o,o′-diphenylbiphenyl obtained from chlorobenzene showed no change in melting point.

Synthesis of o-Diphenylbenzene.—A mixture of 5 g. of o-iodobiphenyl, 10 g. of o-iodobenzene and 15 g. of copper bronze (Naturkupfer C) was heated in a sealed tube at 240° for three hours. The product solidified on cooling. It was extracted with benzene in a Soxhlet apparatus and the extract boiled with charcoal, filtered and freed from solvent by distillation. The residue was distilled under 2 mm. pressure and the following fractions were collected: 110–130°, 2 g.; 160–170°, 2 g.; above 200°, 1 g. The fraction boiling at 110–130° (2 mm.) was recrystallized from alcohol and found to consist of biphenyl. The fraction boiling at 160–170° was dissolved in warm methyl alcohol; on cooling, laige prisms were obtained which melted at 55° and boiled at 320–325° (uncorr.). A mixture of this material with the o-diphenylbenzene obtained from chlotobenzene melted at 55–56°; a sample became oily at room temperature on mixing with biphenyl. The fraction boiling above 200° was washed with methyl alcohol, and the undissolved crystals, amounting to 0.5 g., were found to be identical with the o,o′-diphenylbiphenyl obtained by heating copper bronze and o-iodobiphenyl alone.

Action of Sodium on Chlorobenzene in the Presence of Toluene.—A. To a mixture of 2500 g. (22.2 moles) of chlorobenzene and 4600 g. (50 moles) of toluene was added 460 g. of sodium, exactly as in the previous experiment. The mixture was steam distilled and the distillate separated and fractionated. The resulting benzene was estimated as 603 g. (7.74 moles). The residual tar, on long standing, partially crystallized but it was not further examined.

B. To a suspension of 460 g. (20 g.-atoms) of sodium in 4600 g. (50 moles) of boiling toluene was added, with stirring, 2500 g. (22.2 moles) of chlorobenzene at such a rate that the mixture boiled vigorously but without loss of vapor. This required about five hours. The products were worked up exactly as in the experiment in which chlorobenzene alone was employed. Estimation of the benzene in the steam distillate showed the presence of 725 g. (9.3 moles). Distillation of the high-boiling portions under 20 mm. pressure yielded the following fractions: up to 135°, 14 g. of oil; 135–150°, 120 g. of oil; 150–170°, 19 g. of oil; 170–200°, 7 g. of solid; 200–230°, 84 g. of solid; 230–270°, 82 g. of semi-solid; 270–300°, 53 g. of solid; residue, 122 g.

Oxidation Experiments.—The only fraction which was closely investigated was that boiling at 135–150° (20 mm.) which should correspond to the biphenyl fraction in the first experiment. A 10g. sample of this material was stirred for eight hours with a boiling solution of 18 g. of potassium permanganate in 1500 cc. of water. After decolorizing the unchanged permanganate by the addition of alcohol, the precipitate was filtered off and washed with ether; the filtrate was shaken with ether, separated, concentrated to 100 cc. and acidified with hydrochloric acid. In this way, 2.0 g. of a mixture of acids melting at 115–180° was obtained. This was recrystallized from carbon tetrachloride, when p-phenylbenzoic acid (m. p., 223–224°) was obtained. The ethereal solution was evaporated to dryness, and the residue treated with hydroxylamine hydrochloride and alkali, when 2.0 g. of crude benzophenone-oxime (m. p., 138–140°) was obtained. On recrystallization from alcohol this appeared as long needles melting at 141–142°. Steam distillation of the alkaline mother liquor yielded no biphenyl.

In another experiment, 10 g. of the same fraction was oxidized by means of 30 g. of chromic acid in 75 cc. of glacial acetic acid. The reaction mixture was cooled and poured into 2 liters of water. After standing overnight the crystals were separated and extracted

with 15 cc. of warm petroleum ether (35–60°). The extract deposited 2.3 g. of almost pure benzophenone; m. p., 49°.

Migration of Sodium in Sodium *p*-Tolyl

To 7.7 g. of mercury di-*p*-tolyl in 200 cc. of dry benzene was added 10 g. of metallic sodium in clean shavings. After standing for a month, the brown suspension was decanted from the sodium amalgam and unchanged sodium, and a stream of dry carbon dioxide was passed through the mixture. Reaction began immediately with evolution of heat. After an hour the mixture was warmed on a steam-bath and carbon dioxide passed through the gently boiling solution for four hours, when cold water was added and the upper layer shaken with dilute alkali. The combined aqueous solutions were acidified. The resulting precipitate was found to consist almost entirely of *p*-toluic acid. The weight was 1.64 g. On recrystallization from benzene it melted at 176–177°.

The aqueous filtrate was extracted with benzene; on evaporation to dryness a slightly oily solid remained which on recrystallization from water yielded 1.65 g. of benzoic acid. After sublimation and recrystallization from petroleum ether, and finally from water, it melted at 116–118°. This melting point was unchanged on mixing with authentic benzoic acid. A sample also yielded benzanilide possessing the correct melting point which was unchanged on mixing with benzanilide of known purity.

The first mother liquor from the benzoic acid, which possessed a strong odor of phenylacetic acid, was neutralized and concentrated to a small bulk. Addition of hydrochloric acid yielded an oil which solidified on cooling in ice. After repeated crystallization from water, there was obtained 0.20 g. of phenylacetic acid. This was identified by comparison with authentic phenylacetic acid.

Action of Sodium on Chlorobenzene in the Presence of Dimethylaniline

To a suspension of 520 g. (22.6 g.-atoms) of sodium in 4600 g. of hot dimethylaniline was gradually added, with stirring, 2500 g. (22.2 moles) of chlorobenzene at such a rate that the mixture boiled continually. When the addition was complete, the mixture was allowed to cool, and the slight excess of sodium brought into reaction by adding methyl alcohol, after which 3 l. of water was added. The aqueous solution was separated by siphon, and 1.5 liters more water added to the oily portion. This mixture was then distilled through a column until the temperature of the vapor rose to 99°. The distillate was acidified with hydrochloric acid, and the undissolved oil washed with water and finally with 50% sulfuric acid. The benzene so obtained weighed 845 g. (10.8 moles) and distilled entirely at 79–80°. The residue from which the benzene had been distilled was treated with excess of dil. hydrochloric acid and the insoluble portion warmed with a dil. solution of hydrochloric acid in 30% methyl alcohol. The united acid solutions were neutralized with sodium hydroxide and the resulting oil fractionally distilled under reduced pressure with the use of a column, when the bulk of the unchanged dimethyl-aniline was recovered in pure condition. The residue from this distillation, amounting to about 85 g., was distilled from a small flask, when it gave the following fractions: 235–271°, 5 g.; 271–282°, 9 g.; 282–292°, 7 g.; 292–296°, 7 g.; 296–304°, 7 g.; 304–308°, 11 g.; 308–315°, 10 g.; 160–190° (16 mm.), 15 g.; 190–280° (16 mm.), 5 g.; residue, 5 g. The last two fractions partially crystallized on cooling; the bulk of the crystallizable material appeared to pass over between 185 and 195° under 16 mm. pressure. The fraction boiling at 304–308° was examined independently; it was soluble in fairly strong acids but was partially precipitated on dilution. A solution in dil. sulfuric acid developed an intense fuchsin color on the addition of dichromate solution; the color was destroyed on warming and an odor of benzaldehyde developed. Benzyl-methylaniline was found to behave somewhat similarly, although its solution in dil.

sulfuric acid was considerably less hydrolyzed on further dilution, while on the addition of dichromate a yellow-red color was formed; this, when the mixture was warmed, turned green, and an odor of benzaldehyde developed.

The tar which remained after extraction with dil. hydrochloric acid weighed 960 g. and was found to contain 2.54% of nitrogen, corresponding to 1.75 g. equivalents. On steam distillation it yielded a very small quantity of biphenyl. It was found to be soluble in glacial acetic acid; the solution on exposure to air developed a blue color reminiscent of that obtained by the oxidation of certain derivatives of diphenylamine.

Action of Sodium on *n*-Heptyl Bromide

To 1074 g. of *n*-heptyl bromide (6 moles) heated to about 150° was added sodium in small quantities, with vigorous stirring, at such a rate that the mixture boiled briskly but under control. When about 100 g. of sodium had been added, the mixture became too thick to stir satisfactorily; it was allowed to cool, water was added and the oil separated, dried, and again treated with sodium until no further reaction took place. The unreacted sodium was removed by the addition of alcohol, the salts were dissolved with water and the oil distilled through a small bubbler column; the material distilling up to 101° (after which the temperature rose very rapidly) was collected. The distillate was well washed with water to remove methyl alcohol and treated with a solution of bromine in hydrobromic acid until a permanent excess of bromine was present. After it had been washed with sodium sulfite solution, the resulting liquid was distilled, in the presence of water, through a bubbler column and the distillate collected until only a small proportion of oil passed over with the water. The distillate was separated and the oil shaken repeatedly with concd. sulfuric acid and distilled under atmospheric pressure. It boiled entirely at 96–99° and was practically pure heptane; wt., 50 g. The brominated oil, which was only slightly volatile with steam, was distilled under reduced pressure when it passed over entirely at 103–104° (10 mm.); wt. 79 g. Its properties corresponded to those given in the literature for heptylene bromide.

The residue from which the heptane and heptylene had been distilled was fractionated under reduced pressure, when 395 g. of tetradecane boiling at 115–117° (10 mm.) was obtained. This solidified in a freezing mixture and melted at 4–4.5°. The high-boiling residue on further fractionating yielded a main fraction boiling at 185–195° (10 mm.) and a small quantity of a yellowish oil of still higher boiling range. Analysis of the fraction boiling at 185–195° (10 mm.) showed the presence of 84.3–84.4% of carbon and 14.4–14.6% of hydrogen. It was suspected that the deficiency was due to the presence of oxygenated impurities; the fraction was accordingly repeatedly shaken with concd. sulfuric acid until color was no longer imparted to the acid; it then distilled entirely at 340–345° (corr.). The loss on this purification was very slight.

Anal. Subs., 0.1959, 0.1891: CO_2, 0.6144, 0.5896; H_2O, 0.2630, 0.2538. Calcd. for $C_{21}H_{44}$: C, 85.04; H, 14.96. Found: C, 85.55, 85.06; H, 15.02, 15.02.

Mol. Wt. Ebullioscopic method; solvent, benzene. Solvent, 26.275. Subs., 0.6672, 0.7806, 0.8898; Δt, 0.2290°, 0.2652°, 0.3405°. Calcd.: 296. Found: 289, 292, 290.

Pentadecane from *Iso*-Amyl Bromide.—The high-boiling residue from the preparation of *iso*-decane (by dropping *iso*-amyl bromide slowly onto an excess of sodium on the steam-bath) was distilled under atmospheric pressure and the principal fraction, boiling at 235–245°, repeatedly shaken with concd. sulfuric acid and again distilled, when it passed over almost entirely at 239–242° (corr.).

Anal. Subs., 0.1834. CO_2, 0.5690; H_2O, 0.2503. Calcd. for $C_{16}H_{32}$: C, 84.81; H, 15.19. Found: C, 84.64; H, 15.27.

Mol. wt. Ebullioscopic method; solvent, benzene. Solvent, 25.949. Subs.,

0.2521, 0.4098, 0.5616; Δt, 0.1175°, 0.1861°, 0.2485°. Calcd.: 212. Found: 215, 221, 232.

The authors desire to express their gratitude to Professor Gomberg at the University of Michigan for permitting some of the experiments and analyses to be carried out in his Laboratory.

Summary

1.   The action of sodium upon boiling chlorobenzene leads to the formation of benzene, biphenyl, o-diphenylbenzene, p-diphenylbenzene (minute amount), triphenylene, o,o'-diphenylbiphenyl, together with unidentified resinous and tarry hydrocarbons.

2.   The reaction is conveniently interpreted by assuming the intermediate formation of free phenyl and o-phenylene radicals.

3.   The action of sodium upon n-heptyl bromide leads to the formation of heptane, heptylene, tetradecane, a heneicosane of undetermined structure, and hydrocarbons of higher molecular weight. This type of reaction appears to be general for the bromides of primary alcohols.

4.   The action of sodium upon chlorobenzene in the presence of an excess of toluene leads to the formation of nearly 50% of benzene; biphenyl is not produced, diphenylmethane, p-methylbiphenyl being formed in its stead. The reaction takes an analogous course in the presence of an excess of dimethylaniline, the condensation products containing nitrogen.

5.   The constitution of o-diphenylbenzene and o,o'-diphenylbiphenyl has been confirmed by synthesis.

ROCHESTER, NEW YORK

SOME CYCLOHEXYL-PHENOLS AND PHENOL ETHERS

BY J. F. BARTLETT[1] WITH C. E. GARLAND

RECEIVED JUNE 4, 1927   PUBLISHED AUGUST 5, 1927

Considering the many recent developments in the preparation of alkyl and aryl phenols[2] and the studies made of their germicidal properties, it was decided to prepare some of the cyclohexyl derivatives in order that they might be compared with those already known.

Previous to this time, cyclohexyl-phenol[3] is the only derivative of this particular type recorded in the literature. Wuyts prepared this compound

[1] This communication is an abstract of a thesis submitted by J. F. Bartlett, in partial fulfilment of the requirements for the degree of Master of Arts in Chemistry, at West Virginia University.

[2] The chief contributions have been made by the following investigators. (a) Johnson and Hodge, THIS JOURNAL, 35, 1014 (1913). (b) Johnson and Lane, ibid., 43, 348 (1921). Leonard, J. Am. Med. Assoc., 83, 2005 (1924). (c) Dohme, Cox and Miller, THIS JOURNAL, 48, 1688 (1926). (d) Klarmann, ibid., 48, 791, 2358 (1926).

[3] Wuyts, Bull. soc. chim. Belg., 26, 304 (1912).