T = absolute temperature in degrees Centigrade
d = diameter of particles in centimeters
v = fractional voids in the bed

Expressing the equations in English units,

$$h_v = \frac{0.00014u^{0.75}\ T}{d^{0.9}} \times 10^{1.68v\ -\ 3.56v2} \qquad (13)$$

$$h_a = 0.0000028u^{0.75}\,T \times 10^{1.68v\ -\ 3.56v2} \qquad (14)$$

h_v = coefficient of heat transfer in B. t. u. per second per cubic foot of volume of bed per degree Fahrenheit difference between gas and solid
h_a = coefficient of heat transfer in B. t. u. per second per square foot of surface per degree Fahrenheit difference between gas and solid
u = rate of flow in standard cubic feet of gas per second per square foot of cross-sectional area of bed
T = temperature in degrees Fahrenheit absolute
d = diameter of particle in inches

Temperature History of a System

A coefficient of heat transfer is a differential quantity. A system that is changing its heat content continuously has a temperature history that can be determined only by integration of equations involving the coefficients of heat transfer. The integration of these equations for a fluid flowing through a bed of solid particles has been very cleverly accomplished by Schumann (*10*).

Acknowledgment

The author wishes to express thanks to S. P. Burke and T. E. W. Schumann, of the Combustion Utilities Corporation, to W. H. McAdams of the Massachusetts Institute of Technology, and to W. L. Badger, of the University of Michigan, for numerous helpful suggestions at the beginning of this work.

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Syntheses in the Diphenyl Series[1,2]

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Simple methods which give excellent yields are described for the preparation of the following monosubstituted derivatives of diphenyl: ortho and para, chloro-, nitro-, and amino-diphenyls. The melting points and boiling points of these materials are given. The methods for four of these derivatives have been applied on a semi-plant scale. The commercial production of any of them awaits only the development of a sufficient demand.

The very high cost of diphenyl has heretofore permitted relatively little research on this material with the idea of developing practical uses for its derivatives. Recently a commercial process has been developed which makes possible the sale of diphenyl at 40 to 50 cents a pound, or approximately 1 per cent of its former price. This development has made diphenyl easily available to investigators and has stimulated research to find uses for this hydrocarbon.

An extensive program of research in the field of chemicals derivable from diphenyl was begun by this laboratory during the past year. In the course of this program it was necessary to prepare considerable quantities of the simpler derivatives as starting points for more complex syntheses.

The literature reveals the comparative ease by which diphenyl undergoes substitution, but though many of. the simpler derivatives have been described there is lacking any general procedure that gave promise of commercial adaptation. It was therefore necessary for the writers to develop practical methods of nitration, reduction, and chlorination as applied to diphenyl. The purpose of this paper is to present the best methods for the preparation of the ortho and para isomers of the chloro-, nitro-, and amino-diphenyls. Methods have also been developed for the preparation of several disubstituted and mixed derivatives, such as the nitrochlorodiphenyls, although they are not described in this paper.

Raw Material

The technical diphenyl which is now available in large quantities is a light yellow, crystalline solid. Its freezing point is 68° C. This material is approximately 97 per cent diphenyl, the remainder consisting of higher boiling hydrocarbons, boiling mostly above 380° C.

For the preparation of most derivatives the technical diphenyl is sufficiently pure as a starting material. If higher purity is desired, the technical material may be recrystallized from alcohol or distilled at atmospheric pressure. For recrystallization 4 cc. of alcohol are recommended for each gram of material. The product is pure white and in the form of plates. For distillation an efficient fractionating column is recommended, by the use of which it has been possible to obtain, in one distillation, diphenyl boiling within a range of 0.3° C. in over 95 per cent yield. The technical diphenyl contains a small amount of volatile coloring matter which is difficult to separate by distillation, and the distilled product is therefore slightly yellow. Repeated distillation at atmospheric pressure, however, removes the color.

Monochlorination

Monochlorination has been carried out by previous workers in the presence of catalysts, notably antimony pentachloride (*10*, *21*). The use of iron as a catalyst for this reaction appears to have been overlooked.

Monochlorination leads to the production mainly of 2-

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[1] Received September 27, 1929. Presented before the Division of Organic Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

[2] Contribution No. 1 from the Organic Research Laboratory of the Federal Phosphorus Company.

chlorodiphenyl and 4-chlorodiphenyl. In this reaction some dichlorodiphenyl is always produced, the amount depending on the temperature of chlorination and on the quantity of chlorine added. The higher the temperature of the reaction mixture during the chlorination the higher is the percentage of dichlorodiphenyl formed. When the theoretical amount of chlorine for monochlorodiphenyl is added, considerable dichlorodiphenyl is formed. The conditions recommended are, therefore, low temperature during chlorination and the introduction of less chlorine than that theoretically required for complete monochlorination.

A simple and practical laboratory method which has been found suitable for preparing 4 to 5 pounds (1.8 to 2.3 kg.) of each of the monochlorodiphenyls consists essentially of three steps—chlorination, filtering and washing, and distillation.

APPARATUS—The apparatus consisted of a 2-gallon (7.6-liter) enameled bucket equipped with a mechanical stirrer and a chlorine inlet. The chlorine inlet was made of $^{1}/_{8}$-inch standard iron pipe, bent to conform to the sides of the chlorinating vessel at the bottom, and connected to the chlorine supply. Holes $^{1}/_{32}$ inch (0.8 mm.) in diameter were drilled in the circular pipe at 1-inch (2.5-cm.) intervals to permit uniform introduction of chlorine. It is advisable to drill at least one hole through the under side of the circular pipe near the closed end to aid drainage of reaction mixture from the pipe during the chlorination.

In order to maintain an approximately uniform temperature, the chlorinating bucket was placed in a galvanized tub partly filled with water and resting on a hot plate.

CHLORINATION—Twelve pounds (5443 grams) of melted diphenyl and 120 grams of iron filings, through 100 mesh, were put in the bucket and the agitator was started. The flow of chlorine was then started and was controlled with a flowmeter at 12 cubic feet (0.34 cubic meter) per hour.

The temperature of the reaction mixture during the chlorination decreased from 79° C. at the start to 66° C. at the end of the reaction. With the rate of chlorine addition employed (0.1 pound or kilogram of chlorine per pound or kilogram of diphenyl per hour), the temperature was easily controlled by the occasional addition of cold water to the water jacket surrounding the chlorinator.

The total time required was 2 hours, during which time the reaction mixture increased 1078 grams in weight. This gain in weight corresponded to 88.4 per cent monochlorination.

At the end of the reaction the product was a black oil which partially solidified to a blue-black, soft paste on cooling.

FILTERING AND WASHING—The iron filings were easily removed by filtering the hot, crude reaction product.

The filtered oil was washed with 1 per cent hydrochloric acid until the wash water was free from iron. The oil was then washed with water to remove the acid. Throughout the washing the mixture was maintained at a temperature above 30° C. to avoid freezing. After the washing the product was yellow to light brown in color.

The filtering and washing losses were 2.84 per cent.

DISTILLATION—The crude product was then fractionally distilled. The fractionating column consisted of an electrically lagged Vigreux-type column 76 cm. long by 16 mm. inside diameter. The column was provided with a controlled reflux. The fractions in Table I were obtained.

The separation by fractional distillation in the laboratory column was not so complete as was possible in the plant column employed for the larger scale runs.

The net yield of the crude 2-chlorodiphenyl, based on the diphenyl not recovered, was 36.8 per cent, boiling point 273–280° C., freezing point 22° C.; and of the crude 4-chlorodiphenyl was 29.9 per cent, boiling point 287–294° C., freezing point 71° C. The yield figures do not include the amount of monochlorodiphenyls contained in the intermediate fractions which actually contain appreciable quantities of the monochlorodiphenyls. In larger scale operations the intermediate fractions are returned to the still with the next charge.

Table I

FRACTION	MAIN COMPONENT	RANGE[a] ° C.	WEIGHT *Grams*	PER CENT OF TOTAL
1	Diphenyl	254–263 (mainly 254–256)	996	15.69
2	Intermediate	263–273	691	10.90
3	2-Chlorodiphenyl	273–280	2003	31.61
4	Intermediate	280–287	287	4.53
5	4-Chlorodiphenyl	287–294	1627	25.69
6	Intermediate	294–300	40	0.64
7	Dichlorodiphenyls	300–350	119	1.88
Residue			453	7.16
Losses			120	1.90
Total			6336	100.00

[a] The temperatures given are corrected temperatures.

The crude 2-chlorodiphenyl may be purified by redistillation followed by crystallization from alcohol. The crude 4-chlorodiphenyl may be conveniently crystallized from alcohol.

In order to determine the melting points and boiling points, the chlorodiphenyls were repeatedly recrystallized from alcohol until the cooling curve showed no further change and finally distilled at atmospheric pressure. For recrystallizing the 2-chlorodiphenyl, 1.0 cc. of alcohol for each gram of material (yield, 64.4 per cent), and for the 4-chlorodiphenyl, 0.81 cc. of alcohol for each gram of material (yield, 94 per cent) is recommended. The constants obtained on the pure materials are tabulated below.

ANALYSES—Analyses for chlorine made by the Parr peroxide bomb method consistently gave results 0.42 to 0.35 per cent too low. Analyses made by the Carius method[3] indicated that the chlorodiphenyls were slow and difficult to decompose and confirmed the same conclusion from the peroxide bomb analyses. When sufficient time was given for complete decomposition, the results were entirely satisfactory.

Calculated for $C_{12}H_9Cl$: chlorine, 18.81 per cent. 2-Chlorodiphenyl, found: 18.81, 18.79 per cent. 4-Chlorodiphenyl, found: 18.86, 18.90, 18.79 per cent.

Mononitration of Diphenyl

Previous workers (*2, 3, 5, 6, 7, 9, 15, 16, 17, 18, 22, 23, 24, 25, 26*) mononitrating diphenyl have employed solvents or long contact with strong nitric acid. The use of mixed acid for the reaction has apparently not been developed previous to this work. In the method about to be described a mixture of nitric and sulfuric acids nitrates diphenyl to form a mixture of 2- and 4-nitrodiphenyls in yields of over 90 per cent. The process consists essentially of four steps: nitration, washing, preliminary separation, and distillation.

APPARATUS—The nitration was carried out in a 2000-cc. beaker equipped with a Cenco stirrer and immersed in a water bath. The nitrating acid was contained in a graduated separatory funnel. For the separation a Cyclone bronze basket, 5000-r. p. m. centrifuge was used. The distillations were made in the Vigreux-type column previously described.

NITRATION—Four mols (616 grams) of powdered diphenyl were suspended in a mixture of 356 cc. sulfuric acid (d. 1.84), 316 cc. nitric acid (d. 1.42), and 228 cc. water. The suspension was vigorously stirred and nitrating acid, consisting

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[3] These analyses were kindly made by E. H. Huntress, of Massachusetts Institute of Technology.

of a mixture of 284 cc. sulfuric acid (d. 1.84) and 512 cc. nitric acid (d. 1.42) was added slowly. The reaction was maintained at 35–40° C. The addition of acid required 2 hours. The reaction mixture was then stirred for 4 hours more to insure completion of the reaction. The spent acid was removed from the product and was used as the acid for suspending the diphenyl in subsequent batches.

Washing—The pasty mass was washed once with water, once with dilute sodium carbonate solution, and twice with water. The product was dried by heating in an open vessel to slightly over 100° C. The crude yield was 98 to 100 per cent of the theory.

Separation—The washed and dried nitration product was heated until completely melted and permitted to crystallize without stirring. When the temperature reached 50° C., the pasty mass was thoroughly mixed and centrifuged. A good yield of well-formed crystals of 4-nitrodiphenyl was obtained. The crystals were freed from adhering mother liquor by blowing live steam on them while the centrifuge was running and spinning to dryness.

The oil from the centrifuging was heated until completely melted and crystallized without agitation at 25° C. A further yield of 4-nitrodiphenyl was obtained which was centrifuged and steamed as before. The total yield of 4-nitrodiphenyl was 52 per cent of the crude; melting point 108–110° C.

Distillation—The oil from the centrifuging was vacuum-distilled at 30 mm. pressure. The following table shows a typical distillation:

Fraction	Range[a]	Weight	Per Cent of Total
	° C.	Grams	
Intermediate	142–199	15.3	4
2-Nitrodiphenyl	199–201	271.0	71
Intermediate	201–221	30.6	8
4-Nitrodiphenyl	221–223	42.0	11
Loss		23.0	6
Total		381.9	100

[a] The temperatures given are corrected temperatures.

The freezing points of the 2-nitro- and the 4-nitrodiphenyls were 31–32° C. and 112–113° C., respectively.

For the determination of the freezing points and boiling points of the pure materials, they were repeatedly recrystallized from alcohol and finally carefully distilled at 30 mm. For recrystallizing 2-nitrodiphenyl 4 cc. of alcohol for each gram of material, and for 4-nitrodiphenyl 10 cc. for each gram of material, are recommended.

The constants obtained on the pure materials are tabulated below.

Analyses—A modified Kjeldahl method was employed (*4, 8, 11*).

Calculated for $C_{12}H_9O_2N$: nitrogen, 7.04 per cent. 2-Nitrodiphenyl, found: 6.67, 6.61 per cent. 4-Nitrodiphenyl, found: 6.96, 6.92 per cent.

The analyses of 2-nitrodiphenyl were repeated by the Dumas[3] method.

2-Nitrodiphenyl, found: 7.33, 7.35 per cent.

Preparation of Monoaminodiphenyls

Previous workers (*1, 2, 9, 12, 14, 15, 16, 19, 20, 22*) have reduced the mononitrodiphenyls to the corresponding amines by the use of tin and hydrochloric acid, tin and acetic acid, and stannous chloride and hydrochloric acid. Under certain conditions some of these methods give chlorinated amines as well as the desired amino compounds. The aminodiphenyls have also been produced by reduction of the corresponding nitro compounds by aluminum amalgam (*12*) and by electrolysis (*8*). There is no record of the use of iron and water alone for this reduction. This method avoids the formation of chlorinated products and employs cheap materials.

Complete reduction was obtained by the use of 1 part of the nitro compound, 10 parts of iron borings, a little water, and a few drops of hydrochloric acid. The use of one-fifth of this quantity of iron gave poor yields. Yields of 90 to 92 per cent of the amines were obtained, however, with a ratio of iron to nitro compound of 2 to 1—provided the nitro compound was dissolved in benzene, this solution poured over "treated" iron, the mixture heated to boiling, and water added in small quantities during the reaction. The amine was separated as the hydrochloride from the unreduced nitrodiphenyls and tars by agitation of the benzene solution of the amine with dilute hydrochloric acid.

Reduction of 4-Nitrodiphenyl

One hundred grams of 4-nitrodiphenyl were dissolved in 100 cc. of commercial benzene. This solution was poured over the "treated" iron, prepared as follows: 200 grams of dry cast-iron borings, −28 + 65 mesh, which had been washed free from grease and dirt, were moistened with 35 cc. of concentrated hydrochloric acid, dried at room temperature, and either promptly used or kept in air-tight containers. The reaction mixture, contained in a vessel equipped with a reflux condenser, was heated to the boiling point of benzene and 1 cc. of water was added. When the refluxed benzene became clear, another cubic centimeter of water was added; this was repeated until 26 cc. of water had been added. The reaction required about 4 hours. Occasional stirring and reheating of the reaction mixture were necessary during the course of the reaction.

The mixture was centrifuged and steam was passed through the iron filings in the centrifuge. The iron filings were extracted with about 100 cc. of benzene and rejected. The benzene extract was separated from the water layer and filtered. The water layer was rejected.

The filtered benzene solution was vigorously agitated with 220 cc. of 3 *N* hydrochloric acid. The amine was precipitated as the hydrochloride in the form of a white, finely divided solid, which was filtered, washed with benzene, and dried. If the amine was desired, the hydrochloride was treated with a base.

Reduction of 2-Nitrodiphenyl

The procedure was the same as for the 4-nitrodiphenyl, except that 100 grams of the nitro compound were dissolved in only 50 cc. of commercial benzene. The water solutions from the centrifuging step must be worked up, since this amine and amine hydrochloride are appreciably soluble in water. The yields for both 2- and 4-aminodiphenyls are 90 to 93 per cent of the theory.

For the determination of freezing and boiling points the amines were repeatedly recrystallized from alcohol until their freezing curves showed no change on further recrystallization, and finally vacuum-distilled at 30 mm.

For the recrystallization of the 2-aminodiphenyl, 0.4 cc. of alcohol for each gram of material, and for the 4-aminodiphenyl, 0.61 cc. of alcohol for each gram of material is recommended.

Analyses—A Kjeldahl method was employed (*18*).

Calculated for $C_{12}H_{11}N$: nitrogen, 8.29 per cent. 2-Aminodiphenyl, found: 8.29, 8.32 per cent. 4-Aminodiphenyl, found: 8.33, 8.23 per cent.

Physical Constants

Since the authors believed that this was the first time that considerable quantities of these various diphenyl derivatives had been prepared from diphenyl of good purity, it was thought desirable to determine their melting, freezing, and boiling points. The accuracy attempted was that which can be reproduced in the organic laboratory without recourse to special apparatus and methods.

In each case, except that of 2-chlorodiphenyl, the material was repeatedly recrystallized until freezing points checking to 0.1° C. were obtained. The products were distilled and freezing points checking to 0.1° C. were obtained on successive fractions and residue. In the case of the 2-chlorodiphenyl, the products from successive crystallizations varied 0.5° C. in freezing point after five crystallizations. The material was carefully distilled. Two successive fractions and the residue then checked exactly in their freezing points.

The number of crystallizations used in the purifications was as follows:

4-Nitrodiphenyl—Three crystallizations from specially denatured alcohol.[4]

2-Nitrodiphenyl—One crystallization from melt and three crystallizations from specially denatured alcohol.

4-Aminodiphenyl—Crystallization as the hydrochloride from water, conversion to the free base with ammonia, and two crystallizations from specially denatured alcohol.

2-Aminodiphenyl—Two crystallizations from water as the hydrochloride, conversion to the free base with ammonia, and two crystallizations from specially denatured alcohol.

4-Chlorodiphenyl—Three crystallizations from specially denatured alcohol.

2-Chlorodiphenyl—Three crystallizations from specially denatured alcohol, crystallization from melt, and crystallization from carbon tetrachloride.

The recrystallized products were distilled and in every case the boiling and freezing points of successive fractions checked to 0.1° C.

Melting point determinations were made on the purified samples. These determinations were made in a bath of Nujol which was agitated during the tests.

The constants in Table II were found for the derivatives. The temperatures are corrected values. The thermometers used were checked against primary standard thermometers certified by the National Physical Laboratory (British), and corrections were applied accordingly. All boiling points were taken with total stem immersion. Stem corrections were applied where necessary to the melting and freezing points.

Table II

DIPHENYL DERIVATIVE	BOILING POINT		FREEZING POINT	MELTING POINT
	° C.	*Mm. Hg*	*° C.*	*° C.*
4-Nitrodiphenyl	224.1–223.7	30	113.8	113.7
2-Nitrodiphenyl	201.0–201.3	30	36.9	37.2
4-Aminodiphenyl	211.0–211.2	30	52.6	54.1
2-Aminodiphenyl	182.0	30	48.7	49.3
4-Chlorodiphenyl	291.2	745	76.8	77.2
2-Chlorodiphenyl	273.7–273.8	738	31.2	32.2

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[4] Specially denatured alcohol formula No. 3A was used in each purification.

Methylation of Phenol by Dimethyl Sulfate[1]

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MANY experiments on the methylation of phenol by dimethyl sulfate have been carried out under the direction of the senior author during the past eight years.[2] A preliminary report of the work was presented in abstract form to the Iowa Academy of Science in 1924, but the experimental data were not included. Since a similar study on sodium methyl sulfate has been completed, it seems desirable to publish at this time the accumulated data on the use of dimethyl sulfate.

Previous Work

The use of dimethyl sulfate as a methylating agent dates from the work of Dumas and Peligot (*3*) in 1835. They found dimethyl sulfate useful in methylating hydroxyl and amino groups as well as lactones. Many other papers have appeared since then, the most important being those of Ullmann and Wenner (*13*), Graebe (*5*), Werner and Seybold (*15*), Meyer (*11*), Wegscheider (*14*), Perkin and Robinson (*12*), Decker and Koch (*2*), Liebig (*10*), Kostanecki and Lampe (*7*), and Klemenc (*6*).

Theoretical Considerations

Dimethyl sulfate may be used as a methylating agent in an alkaline solution of sodium phenolate, in an alcoholic solution of sodium ethylate and sodium phenolate, by heating dimethyl sulfate and phenyl alone, and by dissolving the dimethyl sulfate and phenol in ether and heating the mixture.

In the first case two reactions are possible. One takes place rapidly (unless the solutions are too dilute) and results in the formation of sodium methyl sulfate and anisole.

$$(CH_3)_2SO_4 + C_6H_5ONa \longrightarrow CH_3NaSO_4 + C_6H_5OCH_3 \quad (1)$$

Under the conditions described for the preparation of anisole with dimethyl sulfate as found in laboratory manuals (*4*), this will be the chief reaction.

A second reaction takes place as well, when the concentration of water is cut down, and sodium sulfate and anisole are end products.

$$CH_3NaSO_4 + C_6H_5ONa \longrightarrow Na_2SO_4 + C_6H_5OCH_3 \quad (2)$$

Under some conditions as much as 90 per cent of the available methyl groups has been converted into anisole. This is contrary to common experience with dimethyl sulfate and checks more nearly with the action of diethyl sulfate (*1*).

When sodium is dissolved in alcohol and phenol and di-

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[1] Received April 3, 1929. Revised manuscript received October 24, 1929.

[2] Destruction of the Cornell College Science Hall by fire made necessary the repetition of the earlier portion of the work.