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

4-Nitrodiphenyl-Three crystallizations from specially denatured alcohol.

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 ther-

mometers certified by the National Physical Laboratory Specially denatured alcohol formula No. 3A was used in each puri-

fication.

(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.

	т	able II		
Diphenyl Derivative	BOILING POINT		Freezing Point	Melting Point
	° C.	Mm. Hg	° C.	° C.
4-Nitrodiphenyl 2-Nitrodiphenyl 4-Aminodiphenyl 2-Aminodiphenyl 4-Chlorodiphenyl 2-Chlorodiphenyl	$\begin{array}{c} 224.1{-}223.7\\ 201.0{-}201.3\\ 211.0{-}211.2\\ 182.0\\ 291.2\\ 273.7{-}273.8\end{array}$	30 30 30 745 738	113.8 36.9 52.6 48.7 76.8 31.2	$113.7 \\ 37.2 \\ 54.1 \\ 49.3 \\ 77.2 \\ 32.2$

Literature Cited

- (1) Bamberger, Ber., 28, 404 (1895).
- (2) Bell, Kenyon, and Robinson, J. Chem. Soc., 1926, 1239.
- (3) Fichter and Sulzberger, Ber., 37, 878 (1904).
- (4) Flamand and Prager, Ibid., 38, 559 (1905).
- (5) Fortinski, J. Russ. Phys. Chem. Soc., 44, 781 (1912); C. A., 6, 2914 (1912).
- (6) Friebel and Rassow, J. prakt. Chem., [2], 63, 448 (1901).
- (7) Hove, van, Bull. soc. chim. Belg., 32, 53 (1923).
- (8) Houben-Weyl, "Die Methoden der Organischen Chemie," Vol. I, p. 52.
- (9) Hübner, Ber., 8, 871 (1875); Ann., 209, 341 (1881).
 (10) Kramers, Ibid., 189, 142 (1877).
- (11) Krüger, Ber., 27, 1633 (1894).
- (12) LeFevre and Turner, J. Chem. Soc., 1928, 253.
- (13) Mulliken, "Identification of Pure Organic Compounds," Vol. I, p. 218.
- (14) Osten, Ber., 7, 171 (1874).
- (15) Piccard and de Montmollin, Helv. Chim. Acta., 6, 1011 (1923). (16) Raiford and Colbert, J. Am. Chem. Soc., 47, 1456 (1925).
- (17) Rassow, Ann., 282, 141 (1894).
- (18) Scarborough and Waters, J. Chem. Soc., 1926, 559.
- (19) Scarborough and Waters, Ibid., 1927, 89.
- (20) Schlenk, Ann., 368, 303 (1909).
- (21) Schmidt and Schultz, Ibid., 207, 339 (1881).
- (22) Schultz, Ibid., 174, 210 (1874); Ber., 7, 52 (1874).
- (23) Schultz, Schmidt, and Strasser, Ann., 207, 352 (1881).
- (24) Schultz and Strasser, Ber., 14, 613 (1881).
- (25) Willstätter and Kalb, Ibid., 39, 3474 (1906).
- (26) Zimmerman, Ibid., 13, 1960 (1880).

Methylation of Phenol by Dimethyl Sulfate

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Theoretical Considerations

ANY 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).

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.

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.

$(CH_3)_2SO_4 + C_6H_5ONa \longrightarrow CH_3NaSO_4 + C_6H_6OCH_3$

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.

$CH_3NaSO_4 + C_6H_5ONa \longrightarrow Na_2SO_4 + C_6H_5OCH_3$ (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-

methyl sulfate is added, a reaction similar to (1) takes place. At the same time dimethyl sulfate reacts rather rapidly with the sodium alcoholate to form sodium methyl sulfate and methyl ethyl ether.

$(CH_3)_2SO_4 + C_2H_5ONa \longrightarrow CH_3NaSO_4 + CH_3OC_2H_5 \quad (3)$

When dimethyl sulfate and phenol alone are mixed and heated to 100° C., methyl hydrogen sulfate and anisole are slowly formed.

$$(CH_3)_2SO_4 + C_6H_5OH \longrightarrow CH_3HSO_4 + C_6H_5OCH_3 \qquad (4)$$

When the same reagents are dissolved in water, methylation of the phenolic hydroxyl is replaced by methylation of the hydroxyl of water; methyl hydrogen sulfate and free sulfuric acid are formed as the result of the hydrolysis (\mathcal{G}) . Under these conditions anisole is not formed.

$$(CH_3)_2SO_4 + H_2O \longrightarrow CH_3HSO_4 + CH_3OH$$
(5)
$$CH_3HSO_4 + H_2O \longrightarrow H_2SO_4 + CH_3OH$$
(6)

The addition of such salts as sodium chloride, sodium sulfate, and magnesium chloride to the aqueous mixture of phenol and dimethyl sulfate has little effect on the reaction producing anisole although in these cases traces of anisole are noted. Similarly, the presence of acids such as hydrochloric, sulfuric, or acetic in the aqueous mixture of dimethyl sulfate and phenol has no effect on the reactions involved in producing anisole (4), for not even traces of anisole are to be obtained from such reactions. The principal reactions are those of hydrolysis (5, 6).

Only small quantities of anisole are formed from the action of dimethyl sulfate on phenol in solution in absolute alcohol. This is due, no doubt, to the fact that dimethyl sulfate reacts rapidly with alcohol at the reflux temperature to form methyl hydrogen sulfate and methyl ethyl ether. Titration of the reaction mixture above at the end of a 2hour period indicates not only that the dimethyl sulfate is converted completely to methyl hydrogen sulfate, but also that a small amount of the methyl hydrogen sulfate is in turn hydrolyzed to free sulfuric acid.

$$\begin{array}{l} (\mathrm{CH}_3)_2\mathrm{SO}_4 + \mathrm{C}_2\mathrm{H}_6\mathrm{OH} \longrightarrow (\mathrm{CH}_3)\mathrm{HSO}_4 + \mathrm{C}_2\mathrm{H}_6\mathrm{OCH}_3 & (7) \\ (\mathrm{CH}_3)\mathrm{HSO}_4 + \mathrm{C}_2\mathrm{H}_6\mathrm{OH} \longrightarrow \mathrm{C}_2\mathrm{H}_6\mathrm{OCH}_3 + \mathrm{H}_2\mathrm{SO}_4 & (8) \end{array}$$

Reaction 7 takes place rapidly, Reaction 8 much more slowly, and Reaction 4 very slowly under the conditions of the experiment.

On the other hand, when phenol is dissolved in diethyl ether and dimethyl sulfate is added, Reaction 4 is the chief reaction and anisole is formed up to the limit of the first methyl group.

Experimental

In order to establish the most effective conditions for methylating with dimethyl sulfate, a standard method has been developed and modified so as to determine the influence of such factors as time, relative concentrations of sodium hydroxide and water, solvents other than water, and other variables.

STANDARD PROCEDURE—A 500-cc. round-bottom flask equipped with a reflux condenser and a dropping funnel is set up on a water bath and a solution of 0.2 mol (18.8 grams) of phenol, 0.3 mol (12 grams) of sodium hydroxide, and 1.6 mols (28.8 grams) of water is added. Dimethyl sulfate to the amount of 0.1 mol (12.6 grams) is then run in slowly through the dropping funnel after the solution in the flask has reached the temperature of boiling water.

The mixture is heated in this manner for an hour, 300 cc. of 1 per cent sodium hydroxide solution are added, and the cooled solution is extracted several times with ether. The ether extract is dried with a small amount of calcium chloride and carefully fractionated; that portion distilling between 150° and 155° C. is collected as anisole. The yield of anisole

calculated on the basis of the phenol employed is about 55 per cent.

The amount of anisole in the ether solution may also be estimated by determining the refractive index of the dried ether solution. A large number of determinations have shown that this solution contains practically nothing but anisole and ether. Duplicate experiments carried out using the standard procedure will give anisole yields checking within 5 per cent.

Results

Variations from the foregoing procedure and the results obtained are shown in Table I.

	1	able I—E	perimental	Dataa				
Тімв	DIMETHYL SULFATE	PHENOL	SODIUM Hydroxide	WATER	ANISOLE			
Hours	M	M	M	М	Per cent			
1100/3 214 214 214 214 10/00/00 17 A DT A DT I - 11/A TUD								
1 01 02 03 00 545								
î	0 1	0.2	0.3	0.2	70.0			
ī	0.1	0.2	0.3	0.4	64.5			
1	0,1	0.2	0.3	0.8	61.8			
1	0.1	0.2	0.3	1.0	04.0 30.3			
5	0 1	0.2	0.3	0.2	90.1			
ð	0.1	$\tilde{0}, \bar{2}$	0.3	0.4	81.2			
VARIABLE-SODIUM HYDROXIDE								
1	0.1	0.2	0.2	1.6	6.9			
ī	0,1	0.2	0.1	1.6	35.2			
1	0.1	0.2	0.3	1.6	55.0			
1	0,1	0.2	0.6	1.6	48.1			
1/	0.1	VARIABLES	-IIME AND W	1 6	54 0			
1/0	0.1	$0.2 \\ 0.2$	0.3	1.6	54.4			
´1	0.1	0.2	0.3	1.6	55.0			
3	0.1	0.2	0.3	1.6	54.6			
1	0.1	0.2	0.3	0.4	64.5 79.7			
2 5	0.1	0.2	0.3	0.4	10.1			
8	0.1	0.2	0.3	0.4	82.6			
ĩ	0.1	0.2	0.3	0.2	71.0			
2	0.1	0.2	0.3	0.2	75.6			
5	0.1	0.2	0.3	0.2	90.1			
DIMETHYL SODIUM ACID, SALT,								
TIME SU	LFATE PHENO	L HYDROXI	DE WATER	OR SOLVENT	ANISOLE			
Hours	M M	M	M	Per cent	Per cent			
		ACID REA	CTION MIXTUI	RES				
$\frac{1}{2}$	0.2 0.2		1.6	1 Acetic	Trace			
$\frac{1}{2}$	0.2 0.2 0.2 0.2	• • •	1.0	25 Acetic	Trace			
$\frac{1}{2}$	0.2 0.2 0.2		1.6	25 HCl	Trace			
1/2	0.2 0.2		1.6	$1 H_2SO_4$	Trace			
1/2	0.2 0.2		1.6	$25 H_2SO_4$	Trace			
AQUEOUS SALT SOLUTIONS								
1/2	0.2 0.2		1.6	$10 \text{ Na}_2\text{SO}_4$	Trace			
$\frac{1}{2}$	0.2 0.2		1.6	10 NaCl	Trace			
1/2	0.2 0.2	•••	1.0	10 Mg504	Trace			
	MISCELLAS	NEOUS REAC	TIONS IN ORG	Cc.				
1	0.1 0.2	• • •		50 Ether	47.0			
1	0.1 0.2	• · •		50 Toluene	47.8			
1	0.1 0.2	0 3 codie		ou Alconol	Trace			
. +	0.1 0.2	alcoho	late	50 Alcohol	43.0			
a Te	emperature wa	s 100° C. i	n all cases ex	cept where org	anic solvents			
were use	d, when reflux	temperatur	e for each sol	vent was emplo	oyed.			

Conclusions

1—Under suitable operating conditions, the first methyl group of dimethyl sulfate reacts rapidly with sodium phenolate to form anisole.

2—The second group of the dimethyl sulfate reacts slowly in the presence of a relatively large amount of water; when the water concentration is reduced, the second methyl group may be largely used in the formation of anisole.

3—In acid or neutral aqueous solution or in alcoholic solution, the phenolic hydroxyl is not methylated to an appreciable extent; in these cases either the aqueous or alcoholic hydroxyl group enters into the methylation reaction.

4—A proportion corresponding to 90 per cent of the methyl in dimethyl sulfate is used in the methylation of phenol when 0.2 mol of phenol reacts with 0.1 mol dimethyl sulfate in the presence of 0.3 mol sodium hydroxide and 0.2 mol water for 5 hours at 100° C.

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Literature Cited

- (1) Cade, Chem. Met. Eng., 29, 319 (1923).
- (2) Decker and Koch, Ber., 40, 4794 (1907).
- (3) Dumas and Peligot, Centralblatt, 1835, 279.
- (4) Fisher, "Laboratory Manual of Organic Chemistry," p. 180, Wiley, 1924.
- (5) Graebe, Ber., 38, 152 (1905).
 (6) Klemenc, Monatsh., 38, 555 (1917).
- (7) Kostanecki and Lampe, Ber., 37, 774 (1904); 41, 1330 (1908).
- (8) Lewis, Mason, and Morgan, IND. ENG. CHEM., 16, 811 (1924).
- (9) Lewis and Trieschmann, Proc. Iowa. Acad. Sci., 31, 282 (1924); C. A., 20, 2319 (1926).
- (10) Liebig, Ber., 37, 4036 (1904).
- (11) Meyer, Ibid., 37, 4144 (1904); 40, 2432 (1907).
- (12) Perkin and Robinson, J. Chem. Soc., 91, 1079 (1907).
- (13) Ulimann and Wenner, Ber., 33, 2476 (1900).
- (14) Wegscheider, Monatsh., 23, 383 (1902).
- (15) Werner and Seybold, Ber., 37, 3658 (1904).

Boiler Reactions at High Temperatures¹ Boiler Corrosion at 10.54 and 14.06 kg. per sq. cm. Pressure

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G ENERATION of steam within boilers results in a concentration in the feed water of material consisting of suspended solids and soluble salts. This material, together with the several gases commonly found dissolved in water, causes boiler troubles which may include scale formation, foaming and priming, embrittlement, and corrosion. Of these, corrosion is by far the most serious.

Various theories, including the carbonic acid theory, the peroxide theory, and the colloidal theory, have been used to explain the mechanism of corrosion, but noneissological as Whitney's electrolytic hypothesis (6). He showed that iron, by virtue of its solution pressure, will displace hydrogen from solution in water with the formation of ferrous Boiler corrosion has been studied under approximately actual operating conditions by means of a small laboratory boiler. A modified form of apparatus for cleaning the test plates by reduction with hydrogen liberated from the plates, as they served as the cathodes in an electrolytic cell, gave very good results.

It has been found that corrosion is directly proportional to the amount of dissolved oxygen; that caustic alkalinity, dichromates, and arsenites inhibit corrosion when present in sufficient quantity; and that the removal of dissolved oxygen by means of reducing agents such as red-oak extract or sulfur dioxide results in greatly reduced corrosion. Removal of dissolved oxygen is accomplished with the minimum of corrosion by the use of oak extract. If an inhibitor such as potassium dichromate is used in the presence of a high chloride concentration, extreme care must be taken to insure the addition of sufficient inhibitor. If too little is added, the resulting corrosion is highly localized and more severe than when no inhibitor is present.

Determination of the concentration of boiler water may be accomplished by means of analysis of alkali metals or chlorides. The use of chloride is by far the most convenient.

ions. Equilibrium is determined by the rate of diffusion of oxygen to the surface, the rate of reaction of the liberated hydrogen with oxygen, and the rate of formation of molecular hydrogen.

Considerable work on boiler corrosion has been published, but little of it was done with laboratory equipment. Bosshard and Pfenniger (1) investigated the behavior of iron in a number of salt solutions using a small laboratory boiler. They found that magnesium chloride was the most corrosive and that sodium hydroxide was the least.

General Experimental Procedure

The writers have investigated corrosion problems under conditions which approximate, as closely as possible, those encountered in actual operation of steam boilers. To this end, a small boiler 12 inches (30 cm.) in diameter by 24 inches (60 cm.) long was constructed. (Figures 1 and 2) It operated at a maximum pressure of 16.04 kg. per sq. cm. The electric heating unit gave three heats—1250, 2500, and 5000

¹ Received August 27, 1929.

² Abstract of thesis submitted by W. L. Denman in partial fulfilment of the requirements for the degree of doctor of philosophy in the Graduate College of the State University of Iowa, January 29, 1929. watts. Water was added by means of an injector and the amount of water present in the boiler was determined with a platform scale on which the boiler was placed.

In the corrosion tests, charcoal-iron plates, $9.9 \times 5.0 \times$ 0.25 cm., were suspended by means of small wire as shown in Figure 1. Three or 4 plates were used in each test. At the end of the test the oxide laver must be removed. Probably the best method for this is that of Jacob and Kaesbohrer (4). They placed the test plates in an electrolytic cell as cathodes with platinum or carbon anodes. The hydrogen liberated on the cathode disintegrates and reduces the oxide film to a finely divided mass, which may be removed quantitatively with a stiff brush. In this work a modification of their method was used. Sodium sulfate served as electrolyte.

In the tables the extent of corrosion is tabulated in two columns. The first column is merely the average loss in weight of the test plates in milligrams, while in the second column the values are calculated from the following formula of Bosshard and Pfenniger (1):

$$C = \frac{\text{Loss in wt. (mg.)} \times 10}{\text{Area (sq. dm.)} \times (30 + \text{liters feed water)}}$$

Examination will show that C merely expresses the loss in milligrams per square decimeter per 10 liters of feed water.

The pressure is maintained within narrow limits for a period of 24 hours. The initial rate of corrosion is the most rapid, and after the oxygen present is exhausted corrosion practically ceases. Although the oxygen is used up in less than 24 hours, pressure is maintained for that time in order to insure equilibrium conditions and hence comparable results. In this respect these tests, with the possible exception of those in which circulation takes place, are not directly comparable to conditions in an actual boiler, where the rate of reaction is of tremendous importance and final equilibrium is rarely approached. For example, a boiler fed with water