Bromine reacts with triphenylgermanyltriethylsilicon with the formation of triphenylgermanium bromide and triethylsilicon bromide. Lithium reacts with the same compound in ethylamine solution with the formation of an equimolar mixture of lithium triethylsilicide and lithium triphenylgermanide. The mixture of these two salts reacts with ammonium bromide to yield triethylsilane and triphenylgermane and with ethyl bromide to yield tetraethylsilicon and ethyltriphenylgermanium.

Benzyltriethylsilicon has been prepared and characterized. An improved method for the preparation of hexaethyldisilane is described.

Providence, R. I. Received September 6, 1933

[Contribution from the Chemistry Department of the University of Oklahoma]

Chlorine Derivatives of 4-Hydroxydiphenyl

By J. C. Colbert, Wyman Meigs and Brown Mackin

While the bromination of 4-hydroxydiphenyl[1] has been exhaustively investigated, the action of chlorine upon this phenol appears to have been neglected. Raiford and Colbert[2] found that in carbon disulfide solution bromine entered the two ortho positions of 4-hydroxydiphenyl. In chloroform solution, according to Bell and Robinson, bromination followed the so-called normal course *i. e.*, the first bromine atom entered one ortho position, the second entered the remaining ortho position while the third took the 4′-position.

The present investigation was carried out for the purpose of comparing the action of chlorine upon this phenol with that of bromine and to study the influence, if any, of various solvents upon the entry of chlorine into the molecule.

Influence of Time and Solvent upon the Number of Entering Chlorine Atoms.—When chlorine was bubbled through a suspension of 4-hydroxydiphenyl in a large volume of chloroform, in carbon disulfide and in carbon tetrachloride, respectively, until all starting material had dissolved, the same monochloro derivative was obtained in fairly good yield and in quite pure condition. When chlorination was continued for one to three hours after starting material had dissolved, a dichloro compound was formed in each case, but the yield was diminished after two hours. In no case, thus far, have a mono- and a dichloro compound been isolated from the same reaction mixture.

Chlorination in glacial acetic acid solution resulted in but one recognizable product, a trichlorophenol melting at 137°. While the yield was, in this case, 55% on the basis of entry of three chlorine atoms, recrystallization to obtain a constant melting point reduced the yield to 10%. Clearly a mixture was obtained which we have not yet been able to separate. Analogy with the bromination of 4-hydroxydiphenyl indicates the monochloro derivative to be 3-chloro-4-hydroxydiphenyl, the dichloro to be 3,5-dichloro-4-hydroxydiphenyl and the trichloroderivative to be 3,5,4′-trichloro-4-hydroxydiphenyl. Thus the chlorination of this phenol follows the normal course. An investigation into the chlorination and nitration of *m*-hydroxydiphenyl is now under way in this Laboratory.

Action of Bromine upon 3-Chloro-4-hydroxydiphenyl.—Bromination of this compound in carbon tetrachloride yields a monobromo derivative while substitution of acetic acid or carbon disulfide as the solvent leads to the introduction of two bromine atoms. The dibromo derivative is almost certainly 3-chloro-5,4′-dibromo-4-hydroxydiphenyl while the monobromo derivative is very probably 3-chloro-5-bromo-4-hydroxydiphenyl. The possibility of bromine entering the 4′-position rather than the 5 is not to be lost sight of since Hübner[3] reported the formation of 4′-bromo-4-acetylaminodiphenyl by direct bromination of 4-acetylaminodiphenyl. Investigation of this reaction is being continued.

Experimental Part

3-Chloro-4-hydroxydiphenyl.—Twenty grams of 4-hydroxydiphenyl was suspended in 200 cc. of chloroform contained in a 500-cc. round-bottomed flask and chlorine bubbled through for one hour, *i. e.*, to complete solution. The total volume was reduced, under diminished pressure, to 50 cc., 30 cc. of petroleum ether added, the mixture cooled in an ice-bath, filtered, and the crystals washed with petroleum ether; yield 65% of small white prisms, m. p.

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(1) Bell and Robinson, *J. Chem. Soc.*, **130**, 1128 (1927).

(2) Raiford and Colbert, This Journal, **47**, 1127 (1925).

(3) Hübner, *Ann.*, **209**, 339 (1881).

76–77.5° corr. Repetition of the chlorination with substitution of carbon tetrachloride as the solvent raised the yield to 73%, while use of carbon disulfide followed by recrystallization from glacial acetic acid lowered the yield to 46%. The melting point was the same in all preparations and was not affected by mixing samples.

Anal. Calcd. for $C_{12}H_9OCl$: C, 70.40; H, 4.44; Cl, 17.34. Found: C, 70.57; H, 4.46; Cl, 17.27.

3-Chloro-5-bromo-4-hydroxydiphenyl.—To a solution of 3.0 g. of 3-chloro-4-hydroxydiphenyl in 20 cc. of carbon tetrachloride there was added 0.7 cc. (one molar proportion) of bromine. After standing for five days at room temperature the solvent was removed by distillation and the solid residue twice recrystallized from chloroform; yield 44% of white prisms, m. p. 84–86° corr.

Anal. Calcd. for $C_{12}H_8OClBr$: hal., 40.71. Found: hal., 41.20.

3-Chloro-5,4'-dibromo-4-hydroxydiphenyl.—A solution made by dissolving 3.0 g. of 3-chloro-4-hydroxydiphenyl in 20 cc. of glacial acetic acid stood for two days at room temperature with two molar proportions of bromine. Precipitation began immediately, 25% yield being obtained. Repetition substituting carbon disulfide raised the yield to 56.4% of coarse white needles melting at 143–146° corr.

Anal. Calcd. for $C_{12}H_7OClBr_2$: hal., 53.90. Found: hal., 54.08.

3,5-Dichloro-4-hydroxydiphenyl.—A solution of 20 g. of 4-hydroxydiphenyl in 200 cc. of chloroform was chlorinated for two hours, *i. e.*, for one hour following solution. The volume was reduced to 50 cc., diluted by addition of 30 cc. of petroleum ether, allowed to stand, filtered, and the crystalline mass recrystallized from glacial acetic acid as white needles, m. p. 80.5–82° corr., in 50% yield. In a similar experiment chlorination was continued for two and one-half hours following solution. While the reaction mixture became red and a 39% yield was obtained, analysis and mixed melting points indicated the identity of the products obtained in the two preparations. Repetition using carbon tetrachloride gave a yield of 58% based upon the recrystallized material. Again an increase in the period of chlorination reduced the yield to 38%. Substitution of carbon disulfide, removal of solvent at room temperature and recrystallization from 15 cc. of chloroform with addition of two volumes of petroleum ether gave a 35% yield. While decrease in the yield on prolonged chlorination is probably due to the oxidizing action of the chlorine, secondary products were not isolated.

Anal. Calcd. for $C_{12}H_8OCl_2$: C, 60.25; H, 3.37; Cl, 29.67. Found: C, 59.85; H, 3.26; Cl, 29.94.

4'-Phenyl-2',6'-dichloro-2,4-dinitrodiphenyl Ether.—Attempts to obtain this ether by the method of Raiford and Colbert[5] failed due to hydrolysis of 2,4-dinitrochlorobenzene to the corresponding phenol. This difficulty was obviated by refluxing with 30 cc. of pyridine and 10 cc. of water instead of with water alone as in the method previously referred to. Light yellow prisms were obtained from glacial acetic acid, m. p. 112–113.5° corr., yield 80%.

Anal. Calcd. for $C_{18}H_{10}O_5N_2Cl_2$: C, 53.33; H, 2.50; N, 6.91; Cl, 17.51. Found: C, 53.41; H, 2.67; N, 7.10; Cl, 17.69.

3,5,4'-Trichloro-4-hydroxydiphenyl.—A solution of 20 g. 4-hydroxydiphenyl in 300 cc. of glacial acetic acid was chlorinated for four hours. The volume was reduced under diminished pressure to 50 cc., cooled, precipitated and filtered. The crude material represented a yield of 55% on the basis of the trichloro compound. Two recrystallizations from chloroform to obtain a constant melting sample reduced the yield to 10%; white prisms, m. p. 133.5–137° corr.

Anal. Calcd. for $C_{12}H_7OCl_3$: Cl, 38.90. Found: Cl, 38.92.

Derivatives of the Halogenated Phenols already Described.—Benzoates and 2,4-dinitrophenyl ethers were prepared for all of the chlorophenols previously described. Results are summarized in the tables.

DERIVATIVES OF THE CHLOROHYDROXYDIPHENYLS

	Name	Reaction medium	Solvent	Color
1	4'-Phenyl-2'-chloro-2,4-dinitrodiphenyl ether	Water	HAc	Yellow
2	Benzoate of 3-chloro-4-hydroxydiphenyl[a]	Water	HAc	White
3	Benzoate of 3,5-dichloro-4-hydroxydiphenyl	Pyridine	HAc	White
4	4'-(*p*-Chlorophenyl)-2',6'-dichloro-2,4-dinitrodiphenyl ether	Pyridine	HAc	Yellow
5	Benzoate of 3,5,4'-trichloro-4-hydroxydiphenyl	Pyridine	HAc	White

				Analytical data, %							
				C		H		Cl		N	
	Formula	Yield, %	M. p., °C.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	$C_6H_5C_6H_3ClOC_6H_3(NO_2)_2$	70.0	109–111	58.29	57.86	2.99	3.03	9.58	10.0	7.56	7.55
2	$C_6H_5C_6H_3ClOCOC_6H_5$	80.0	95–97	73.89	73.35	4.25	4.56	11.49	11.94	..	..
3	$C_6H_5C_6H_2Cl_2OCOC_6H_5$	80.0	144–146	66.47	66.41	3.53	3.63	20.73	21.27	..	..
4	$C_6H_4ClC_6H_2Cl_2OC_6H_3(NO_2)_2$	85.0	174–176	...	...	..	..	24.21	23.96	..	..
5	$C_6H_4ClC_6H_2Cl_2OCOC_6H_5$	80.0	161	...	...	..	..	28.18	27.86	..	.

[a] This benzoate was obtained by the Schotten–Baumann reaction while the benzoates of the dichloro and trichlorophenols were prepared by the method of Einhorn.[4]

The 2,4-dinitrophenyl ether of monochlorohydroxydiphenyl was readily obtained using Raiford and Colbert's method, while the same derivative of the trichlorophenol was prepared by the modification already described.

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[4] Einhorn, *Ann.*, **301**, 99 (1898).

[5] Raiford and Colbert, THIS JOURNAL, **48**, 2652 (1926).

The senior author takes this opportunity of expressing his appreciation to Professor L. Charles Raiford of the University of Iowa under whose direction he first became interested in diphenyl. The present work has been continued with the kind permission of Professor Raiford.

Summary

1. The chlorination of 4-hydroxydiphenyl using a number of solvents is described. The investigation of the trichloro derivative is continuing.

2. 3-Chloro-4-hydroxydiphenyl forms monobromo or dibromo derivatives depending somewhat upon the choice of solvents.

3. The chlorohydroxydiphenyls have been further characterized by the preparation of their 2,4-dinitrophenyl ethers and of the benzoates. 2,4-Dinitrochlorobenzene serves as a useful reagent in the preparation of phenolic derivatives.

NORMAN, OKLA. RECEIVED SEPTEMBER 7, 1933

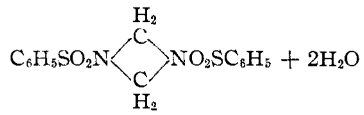
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Condensations of Some Toluenesulfonamides with Trioxymethylene and with Formaldehyde Solution

BY L. McMASTER

In 1893 Magnus-Levy[1] prepared, by the action of formaldehyde on benzenesulfonamide, a condensation product consisting of two isomeric substances, $(C_7H_7SO_2N)_2$ and $(C_7H_7SO_2N)_3$. There was no evidence of the formation of a lower molecular weight compound. He concluded that the following reaction took place, forming di-benzenesulfon-di-methylene-di-imide

$2C_6H_5SO_2NH_2 + 2CH_2O \longrightarrow$

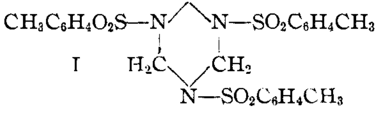


Tri-benzenesulfon-tri-methylene-tri-imide was formed at the same time.

In 1922–23 Meister Lucius and Brüning[2] obtained patents on resinous substances resulting from the condensation of aromatic sulfonamides with 40% formaldehyde solution. In the first patent are described the results for *p*-toluenesulfonamide. Under various conditions several resinous substances were obtained having different properties with respect to solubility and hardness. A mixture of *o*- and *p*-toluenesulfonamide was condensed with formaldehyde, resulting in the formation of still different products. No statement is made of the composition or structure of the products formed. In one of the above patents, only mention is made of the possibility of using trioxymethylene in place of formaldehyde solution.

Since the product formed by the condensation of trioxymethylene and *p*-toluenesulfonamide is now manufactured for use as a plasticizer, it was suggested to us by the Monsanto Chemical Works to determine its composition and properties. I wish to thank this company for proposing this part of the work. I also wish to express my appreciation for the suggestions of Dr. Jules Bebie. The problem was then extended to include the *o*-compound and several alkyl derivatives of the para in order to study the course of the condensations and the properties of the compounds formed, not only when trioxymethylene but also when a 40% formaldehyde solution was used. I was assisted in portions of this work by Messrs. M. J. and C. W. Wiegand, R. S. Wobus and S. S. Cooper, to whom I extend my thanks.

Whereas Magnus-Levy obtained both the di- and tri-imides when benzenesulfonamide was condensed with 40% formaldehyde solution, we obtained by our methods only tri-*p*-toluenesulfon-tri-methylene-tri-imide or 1,3,5-tri-*p*-toluenesulfon-hexahydro-*sym*-triazine (Formula I) when trioxymethylene or 40% formaldehyde was used with *p*-toluenesulfonamide.



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It was then decided to try the possibility of preparing a condensation product by the action of an

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(1) Magnus-Levy, *Ber.*, **26**, 2148 (1893).

(2) Farbwerke vorm. Meister Lucius and Brüning in Hoechst a. M., German Patents 359,676 and 369,644.