the data for those obtained from N-monophenylpiperazine.

All of the condensation products are readily decomposed by acids. In contrast to the products from piperazine those from N-monophenylpiperazine were readily crystallized from appropriate solvents.

All of the condensation products were prepared by reacting the amine with the aldehyde either in the absence or presence of a solvent. The method recommended by Cummings, Hopper and Wheeler[4] was used in all reactions which involved alkyl halides.

Summary

It has been shown that when aldehydes react with piperazine or N-mono-substituted piperazines, one molecule of the aldehyde reacts with two amino groups and a molecule of water is eliminated.

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[4] Cummings, Hopper and Wheeler, "Synthetic Organic Chemistry," p. 294.

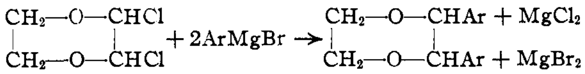
GAINESVILLE, FLORIDA RECEIVED AUGUST 22, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Studies in the Dioxane Series. II. Aryl Substituted Dioxanes Synthesis of *p*-Dioxene[1]

BY R. K. SUMMERBELL AND L. N. BAUER

The preparation of 2,3-diphenyl-1,4-dioxane by the reaction of 2,3-dichloro-1,4-dioxane with phenylmagnesium bromide was described by Christ and Summerbell.[2]



$$\begin{array}{l} CH_2\text{—}O\text{—}CHCl \\ | \qquad\quad | \\ CH_2\text{—}O\text{—}CHCl \end{array} + 2ArMgBr \rightarrow \begin{array}{l} CH_2\text{—}O\text{—}CHAr + MgCl_2 \\ | \qquad\quad | \\ CH_2\text{—}O\text{—}CHAr + MgBr_2 \end{array}$$

The same method of synthesis has been satisfactorily applied to a number of aryl substituted dioxanes.

Although two 2,3-disubstituted dioxanes may be predicted from theory, only one was obtained in each case. In a repetition of the 2,3-diphenyl-1,4-dioxane synthesis, a yield of 80% of the previously described material was obtained, and attempts to isolate a second disubstituted dioxane were unsuccessful. The high yield of a single product in this case, and the failure to obtain two isomers in any of the experiments described in this paper, may be taken to indicate that the 2,3-dichloro-1,4-dioxane used was a pure compound, rather than a mixture of *cis* and *trans* isomers.

The reaction of benzylmagnesium chloride with dichlorodioxane might give an *o*-tolyl derivative.[3] As only a small amount of phthalic acid was obtained on permanganate oxidation of the reaction product, there is very little, if any, of this type of rearrangement. Further work on high molecular weight residues must be carried out to explain all that takes place in this reaction.

In an attempt to extend this method of synthesis to alkyl substituted dioxanes, only small yields of dimethyl, diethyl and dibutyl-1,4-dioxanes were obtained. The yields were so small that a discussion of their properties will be withheld, pending the outcome of experiments now under way on modifications of procedure designed to increase the yield and hence the material available for investigation.

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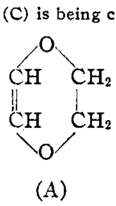
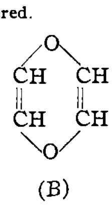
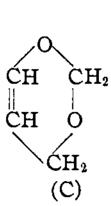
[1] The name 1,4-(or *p*-)dioxene for a new compound (A) described in this paper requires explanation. It follows logically from 1,4-dioxane, the preferred name [Patterson, THIS JOURNAL, **55**, 3911 (1933)] of the fully hydrogenated analog. It might be called 2,3-dihydro-1,4-dioxin since dioxin has been proposed [Widman, *Ber.*, **42**, 3269 (1909)] to represent the least hydrogenated member. Unfortunately for the logic involved, dioxin turns out to be either $C_4H_4O_2$ or $C_4H_6O_2$ depending on whether 1,4-dioxin (B) or 1,3-dioxin (C) is being considered.



(A)



(B)



(C)

(See *Chem. Abs.*, **28**, 8219 (1934) for both structures.) It is incredible that two related non-isomeric substances of known structures should needlessly be assigned the same name.

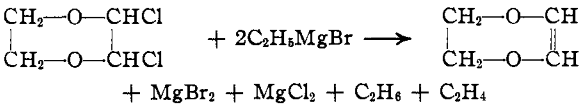
The logical name for (C) is 1,3-dioxene. Instead of 1,4-dioxin, the name dioxadiene is proposed for (B). The name is simple, informative, and free from an ambiguous past.

This plan applies equally well for the sulfur analogs: dithiane, dithiene, oxathiane and oxathiene. The last two names are preferable to thioxane and thioxene since, according to the rules of numbering ring systems, the oxygen should be numbered one; thus 1,4-oxathiane, etc. We acknowledge assistance in this formulation from E. J. Crane and A. M. Patterson, members of the A. C. S. committee on nomenclature.—C. D. HURD, C. M. SUTER AND R. K. SUMMERBELL.

[2] Christ and Summerbell, THIS JOURNAL, **55**, 4547 (1933).

[3] Gilman and Kirby, *ibid.*, **54**, 345 (1932); John R. Johnson, *ibid.*, **55**, 3029 (1933); and earlier work to which these articles contain references.

The chief product in the reaction of methyl, ethyl, and butylmagnesium bromides with 2,3-dichlorodioxane was *p*-dioxene.

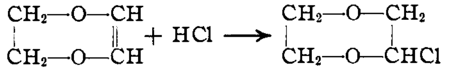


The identity of this compound was proved by: (a) analysis and molecular weight determinations; (b) ozonization and identification of the expected products, formic acid and ethylene glycol; and (c) addition of chlorine to form the known 2,3-dichloro-1,4-dioxane.

The chief hydrocarbon products of the reaction are as represented in the equation above, although there was produced also a small amount of a saturated hydrocarbon of higher molecular weight, probably butane.

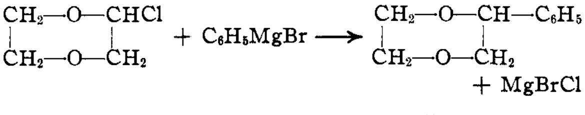
Dioxene adds bromine very readily to form 2,3-dibromo-1,4-dioxane. This compound had previously been described in a very impure liquid state by Tellegen.[4] As we obtained it, it is an unstable solid, constantly evolving hydrogen bromide. It reacts with phenylmagnesium bromide to yield 2,3-diphenyl-1,4-dioxane, thus indicating its structure.

Hydrogen chloride also adds to the double bond of *p*-dioxene to give monochloro-*p*-dioxane. The chlorine atom of the latter compound, being alpha to an oxygen atom, should be reactive, and



thus the compound should be a valuable intermediate for the sythesis of monosubstituted *p*-dioxanes.

Monochloro-*p*-dioxane does react with phenylmagnesium bromide to give phenyl-*p*-dioxane.



The isolation of monochloro-*p*-dioxane is of peculiar interest, in that it has never been isolated in the direct chlorination[5] of *p*-dioxane. The failure to isolate monochloro-*p*-dioxane is easy to understand from its properties, for it is unstable at room temperature, and would be much less stable at the usual temperature of chlorination. If one assumes that the addition of hydrogen chloride to *p*-dioxene is reversible, one has a satisfactory picture of a mechanism for the chlorination of 1,4-dioxane to give 2,3-dichloro-1,4-dioxane. Probably monochloro-*p*-dioxane is first formed. It readily loses hydrogen chloride to give *p*-dioxene, which, in turn, adds a molecule of chlorine to give 2,3-dichloro-1,4-dioxane. The addition of chlorine to a double bond would probably give chiefly one isomer, whereas chlorination of the two carbon atoms independently would give a mixture of isomers. The 2,3-dichloro-1,4-dioxane obtained by us seems to be a pure compound and not a mixture of isomers.

Further work on the role of this compound in the chlorination of dioxane and its use in synthesis is contemplated and under way at the present time.

Experimental

A. **General.**—As the procedure was in all cases similar to that previously described,[6] only notes on important details, analysis, etc., will be given here. Grignard reagents were prepared with at least five moles of ether for each mole of freshly distilled halide. They were titrated[7] by the method of Gilman.

The 2,3-dichloro-1,4-dioxane was prepared by chlorinating[8] 632 g. of purified 1,4-dioxane which melted at 11–12.5° for sixteen hours at 90° with mechanical stirring. The product was obtained in 61% yield, m. p. 28–30°; b. p. 85° (15 mm.).

Molecular weights were determined by the lowering of the melting point of camphor.[9,10]

B. **2,3-Diphenyl-1,4-dioxane.**[11]—The synthesis of this compound was repeated in order to determine accurately the yield on a run of moderate scale, and to furnish material for a more intensive search for an isomeric 2,3-diphenyldioxane.

Phenylmagnesium bromide was prepared in the usual manner, using the following quantities of materials: 701 g. of bromobenzene, 108 g. of magnesium, and 2300 cc. of anhydrous ether; yield of Grignard reagent, 4.27 moles or 95.7%. The entire preparation, a large excess, was treated with 167.6 g. (1.067 mole) of 2,3-dichloro-1,4-dioxane. Hydrolysis of the reaction product was carried out with dilute sulfuric acid. The ether layer was fractionally distilled, the major part of high boiling material distilling at 185–187° (13 mm.). After recrystallizing seven times from ligroin in an effort to separate any foreign

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[4] Tellegen, Dissertation, "Dioxaan en derivaten," Delft, Holland, Oct., 1934, Chap. II.

[5] Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931); THIS JOURNAL, **55**, 1284 (1933); Butler and Cretcher, *ibid.*, **54**, 2987 (1932); Summerbell and Christ, *ibid.*, **54**, 3777 (1932); **55**, 4547 (1933); Baker, *J. Chem. Soc.*, 2666 (1932); Baker and Shannon, *ibid.*, 1598 (1933); Kucera and Carpenter, Organic Chem. Division, American Chemical Society, New York, April, 1935.

[6] Christ and Summerbell, THIS JOURNAL, **55**, 4547 (1933).

[7] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923); Gilman, Zoellner and Dickey, *ibid.*, **51**, 1576 (1929).

[8] Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931).

[9] Rast, *Ber.*, **55**, 1051 (1922).

[10] Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927).

[11] This experiment and several of the analyses were performed by Mr. Maxwell Pollack.

material, 205 g. of 2,3-diphenyl-1,4-dioxane melting at 49–50° was obtained. The yield is 80%. No isomeric substance was found in the mother liquors.

C. New Symmetrical 2,3-Diaryl-1,4-dioxanes.—Other new symmetrical 2,3-diaryl-1,4-dioxanes were prepared and analyzed as shown in Tables I and II.

The smaller yields are due partially to smaller scale experiments.

Table I

Symmetrical 2,3-Diaryl-1,4-dioxanes

Substituents	Yields, in % RMgX	Yields, in % Dioxane	M. p., °C. (corr.)	Mol. wt. Found	Mol. wt. Calcd.
o-Tolyl	95	61	105.7–106.2	268	268
m-Tolyl	85	51	84.2	270	268
p-Tolyl	89	72	56–57.2	259	268
p-ClC_6H_4	93	49	152–153	304	309
p-Anisyl	85	67	79–80.2	299	300
α-Naphthyl	98	53	vitreous[a]	351	340
Xenyl[b]	59	..	144.5–146	394	392
Benzyl[c]	91	22	62.2	266	268

[a] Observed b. p. 255–258° (3–4 mm. (uncorr.)).

[b] Part of product lost in purification.

[c] A viscous, sirup-like mass remaining in the distilling flask which would not distil below a bath temperature of 300° at a pressure less than 1 mm. has not been investigated. Permanganate oxidation [Gilman and Kirby, This Journal, **54**, 345 (1932)] of the 2,3-dibenzyldioxane gave a large quantity of benzoic acid and only traces of phthalic acid, indicating very little rearrangement to the *o*-tolyl derivative. The small yield is doubtless connected with the low yields of aliphatic dioxanes prepared by this method. They are being investigated.

Table II

Substituents	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
o-Tolyl	$C_{18}H_{20}O_2$	80.60	7.46	80.55	7.49
m-Tolyl	$C_{18}H_{20}O_2$	80.60	7.46	80.76	7.44
p-Tolyl	$C_{18}H_{20}O_2$	80.60	7.46	80.39	7.30
p-ClC_6H_4	$C_{16}H_{14}O_2Cl_2$	Cl, 22.98		23.04	
p-Anisyl	$C_{18}H_{20}O_4$	72.00	6.67	72.20	6.69
α-Naphthyl	$C_{24}H_{20}O_2$	84.71	5.58	84.19	5.68
Xenyl	$C_{28}H_{24}O_2$	85.71	6.12	85.35	6.18
Benzyl	$C_{18}H_{20}O_2$	80.60	7.46	80.46	7.58

Several of the aryl disubstituted dioxanes form picrates. Use was made of this fact in obtaining solid 2,3-*p*-ditolyl-1,4-dioxane. The reaction product was a very viscous liquid which, however, formed a solid picrate. On treatment of this picrate with alkali, a solid was obtained which was used to seed the main mass of material, which then solidified; m. p. of picrates: *m*-ditolyldioxane, 91–92°; *p*-ditolydioxane 96.5°; *p*-dianisyldioxane, 107–108°; α-dinaphthyldioxane, 166–167°.

D. Preparation of *p*-Dioxene.—2,3-Dichloro-1,4-dioxane (2.43 moles) dissolved in 500 cc. of anhydrous ethyl ether was added over a period of four hours to 4.85 moles of ethylmagnesium bromide. The heat evolved resulted in gentle refluxing. After standing for twenty hours, the reaction product was hydrolyzed with an excess of water at 0°. The ether layer was separated, dried over anhydrous sodium sulfate, and fractionated by distillation in a 50-cm. vacuum-jacketed column containing a nichrome wire coil. Two chief products were obtained: (a) 140.5 g. of a liquid which was light greenish-yellow in color immediately after distillation, but which turned colorless on standing, b. p. 94.5° (754.3 mm.); (b) 22.3 g. of a colorless liquid having the odor of green willow bark, b. p. 164–175° (747.9 mm.). This compound is evidently an impure sample of 2,3-diethyldioxane. It is being investigated.

During the addition of 2,3-dichloro-1,4-dioxane to ethylmagnesium bromide, copious quantities of gas were evolved. The small yield of the expected product made the identification of this gas of interest. A similar run was made, and a sample of the evolving gas collected. This gas was analyzed by absorption and combustion.[12,13] Of 91.8 cc. of gas, 44.5 cc. was absorbed by 96% sulfuric acid. Combustion of the saturated remainder showed *n*, the number of carbon atoms, to be 2.13, 2.14. The analysis then corresponds to 48.5% unsaturated hydrocarbon, probably ethylene, 48.2% ethane, and 3.4% butane. The butane may have been the result of a side reaction of the original Grignard reagent synthesis. The principal course of the reaction must have followed the equation given in the theoretical part.

E. Properties and Structure of *p*-Dioxene

(a) **Properties.**—Fraction (a) of the above was again distilled; b. p. 94.2° (749.9 mm.); d^{20}_4 1.083; $n^{22.5}_D$ 1.4375; n^{25}_D 1.4362.

Anal. Calcd. for $C_4H_6O_2$: R_L[14] 21.38; mol. wt., 86; C, 55.81; H, 6.98. Found: R_L, 20.99; mol. wt., 89.9[15] 90.6;[16] C, 55.94; H, 7.11.

(b) **Ozonization.**—Pure dioxene (4.55 g.) was dissolved in 80 cc. of carbon tetrachloride and placed in a flask surrounded by ice. Over a period of eight and one-half hours, 0.03 cu. meter of pure dry oxygen was run through an ozonizer and bubbled through the solution. The ozonide thus formed was hydrolyzed with water at the temperature of a steam-bath for two hours. Titration with 0.4554 *N* potassium hydroxide required 194.6 cc., indicating a yield of 83.7% of formic acid. The solution of the potassium salt was evaporated, and the presence of the formate ion proved by reaction of a portion of the neutral potassium salt with 0.005 mole of *p*-bromophenacyl bromide.[17] The *p*-bromophenacyl ester of formic acid, m. p. 140°, mixed m. p. 140°, was obtained.

To prove that ethylene glycol was also a product of ozonization and hydrolysis, the solution obtained by neutralization was treated with benzoyl chloride in the presence of an excess of potassium hydroxide. An excellent yield of the dibenzoate of ethylene glycol resulted, m. p. 70°, mixed m. p. 70°.

F. Reaction of 2,3-Dichlorodioxane with other Alkylmagnesium Halides

(a) **Methylmagnesium Bromide.**—The reaction of 2,3-dichlorodioxane with methylmagnesium bromide was

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[12] Gas analyses in this paper by Mr. E. Field.

[13] Lunge and Ambler, "Technical Gas Analysis," Gurney and Jackson, London, 1934.

[14] R_L, the molecular refractivity. The formula of Lorentz and Lorenz was used.

[15] Method of Dumas.

[16] Method of Victor Meyer.

[17] Hurd and Christ, This Journal, **57**, 2007 (1935).

carried out as described for the reaction with ethylmagnesium bromide. The chief product isolated was *p*-dioxene.

(b) **Butylmagnesium Bromide.**—The reaction of 0.573 mole of 2,3-dichlorodioxane with 1.146 mole of *n*-butylmagnesium bromide was carried out as described for ethylmagnesium bromide. A yield of 38.8 g. (78.7%) of crude *p*-dioxene was obtained. A small fraction, 2.5 cc. boiling at 122.5–125° (746.7 mm.), $n^{20}{}_D$ 1.3985, was probably *n*-octane. Another fraction, 2.5 g., b. p. 120–122° (16–17 mm.), is probably 2,3-dibutyl-1,4-dioxane and will be investigated when more material is available.

The gases evolved during the reaction were condensed in a solid carbon dioxide trap. A portion was allowed to distil and analyzed. The sample analyzed 46.3% saturated, butane, and 53.7% soluble in 82% sulfuric acid, butylene.

G. **Addition of Chlorine to *p*-Dioxene.**—*p*-Dioxene (23.27 g. or 0.271 mole) was dissolved in pure carbon tetrachloride. Fifteen and three-tenth grams of chlorine gas mixed with dry nitrogen was dried over anhydrous magnesium perchlorate, and passed into the vigorously stirred solution at 0° during a period of four hours. The reaction product was fractionated, and 22.7 g. of a liquid boiling at 85° (15 mm.) (2,3-dichloro-1,4-dioxane) was obtained; yield, 53.4%. The product was positively identified by reaction of a portion with *o*-tolylmagnesium bromide to form 2,3-*o*-ditolyl-1,4-dioxane, m. p. 106–107°.

H. **The Addition of Bromine to *p*-Dioxene.**—To 4.29 g. (0.05 mole) of *p*-dioxene dissolved in 15 cc. of dry carbon tetrachloride was added 7.97 g. (0.05 mole) of bromine dissolved in 25 cc. of dry carbon tetrachloride. During the dropwise addition of the latter, which took one hour, the reaction mixture was stirred vigorously and the temperature maintained at 0°. The carbon tetrachloride was evaporated by decreasing the pressure (26–15 mm.) and white crystals formed. Recrystallization from dry ether gave 11.3 g. of a product that softened at 64° and melted at 69–70°; yield 92.2%. The crystals were soluble in ether, carbon tetrachloride, dioxane, and water, but not readily so in petroleum ether. They may be kept in an evacuated (approx. 15 mm.) desiccator for several days, but on exposure to the atmosphere, hydrogen bromide is continuously evolved and a dark brown oil eventually results.

Anal. Calcd. for $C_4H_6O_2Br_2$: Br, 65.00. Found: Br, 63.60, 63.22.

A sample which had stood for two days in a vacuum desiccator showed a slight lowering of melting point and gave 63.06% of bromine. The continually decreasing bromine content serves to explain why all of the analyses are below theoretical.

Since these analyses were only moderately satisfactory, it seemed desirable to prepare a derivative that would prove whether or not the above crystals were 2,3-dibromodioxane; 22.6 g. of the compound was prepared as described above, dissolved in 50 cc. of anhydrous ether, and added over a period of an hour to an ether solution of phenylmagnesium bromide (0.20 mole). The reaction mixture was cooled to 0°, hydrolyzed with water and dilute sulfuric acid, and the ether layer separated. On distillation, 13 g. of a colorless oil, b. p. 185–189° (11–12 mm.), resulted. On crystallization of this oil from petroleum ether, 12.4 g. of 2,3-diphenyldioxane, m. p. 49°, mixed m. p. 49°, was obtained; yield, 56.2%.

I. **Addition of Hydrogen Chloride to *p*-Dioxene. (Monochloro-*p*-dioxane.)**—It was observed that much heat is evolved when dry hydrogen chloride is passed into *p*-dioxene. As one of the reactions that may be postulated would indicate the unknown monochloro-*p*-dioxane, the following experiment was carried out in an attempt to isolate this compound.

p-Dioxene (6.5 g. or 0.076 mole) was cooled to 0°. Hydrogen chloride was slowly bubbled through the *p*-dioxene with stirring at 0°. Immediate fractionation yielded 6.6 g. of a product, b. p. 59° (17 mm.). Approximately 1 g. of a tarry residue remained. Redistillation gave a b. p. of 62–63° (14 mm.); $d^{20}{}_{20}$ 1.276.

Anal. Calcd. for $C_4H_7O_2Cl$: Cl, 28.94. Found: Cl, 26.84.

An experiment using ether as a solvent failed to give as good a yield as the above procedure.

In yet another experiment, bismuth trichloride was used as a catalyst, with rather surprising results. To 12.04 g. (0.14 mole) of *p*-dioxene was added 0.0135 g. (0.0001 mole) of bismuth trichloride. Dry hydrogen chloride was passed in for thirty minutes as the liquid was agitated, the temperature being maintained at 0°. The reaction product became light brown to orange in color. Less than 1 cc. distilled at 12–13 mm. when the temperature of the bath surrounding the distilling flask was raised to 275°. The material remaining in the distilling flask became a dark colored tarry residue. It is probably a polymer of *p*-dioxene, and is being further investigated.

Monochloro-1,4-dioxane is a colorless liquid. It constantly loses hydrogen chloride, and on standing for a few minutes becomes yellow. Within a week it changes to a black, viscous tar. Analyses other than those given above on freshly distilled material gave 25.66% Cl and 27.62% Cl compared with the calculated value of 28.94% Cl. Evidently the compound decomposes to such an extent that a satisfactory analysis is impossible; however, the identity of the compound was proved by the following experiment.

J. **Monophenyl-*p*-dioxane.**—A Grignard reagent was prepared by reaction of 19.28 g. (0.126 mole) of bromobenzene with 3.064 g. (0.126 mole) of magnesium, using 75 cc. of dry ether.

Freshly prepared monochloro-*p*-dioxane (7.31 g. or 0.06 mole) was dissolved in 10 cc. of dry ether and added to the agitated Grignard reagent at such a rate that the vigorous reaction resulted in a gentle refluxing of the solvent. Hydrolysis was carried out with water and dilute sulfuric acid at 0°. The ether layer upon evaporation yielded 4.8 g. of crystals, m. p. 45–46°. Recrystallization of the product from either alcohol or petroleum ether gave a melting point of 46°; yield, 49%.

Alkaline permanganate oxidation of the monophenyl-*p*-dioxane prepared above gave benzoic acid, proving a phenyl radical attached to carbon. The identity of the benzoic acid was ascertained by the formation of the *p*-toluidide, m. p. 156.5–157°.

Anal. Calcd. for $C_{10}H_{12}O_2$: mol. wt., 164.1; C, 73.13; H, 7.37. Found: mol. wt., 175;[18] C, 73.43; H, 7.36.

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(18) Mol. wt. by Rast camphor method.

Conclusions

1. A number of 2,3-diaryl-1,4-dioxanes have been synthesized for the first time.
2. The reaction of alkylmagnesium halides with 2,3-dichloro-1,4-dioxane produces *p*-dioxene, a new compound, of which the structure has been proved.
3. The reactions of *p*-dioxene have been studied.
4. Monochloro-*p*-dioxane has been obtained for the first time, and a mechanism for the chlorination of dioxane proposed.
5. Monophenyl-*p*-dioxane has been prepared.
6. The work is being continued.

EVANSTON, ILLINOIS RECEIVED JULY 29, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Identification of Phenols with 2,4-Dinitrochlorobenzene

BY R. W. BOST AND FRANK NICHOLSON

Although numerous reagents have been proposed for the identification of phenols,[1-5] nevertheless serious objections may be raised against most of them. The method of Koelsch[5] is perhaps the best but many of his derivatives melt so close together that identification is difficult, whereas the *o*- and *p*-nitrophenols were not obtained.

The value of 2,4-dinitrochlorobenzene as a reagent for the identification of mercaptans has been shown in previous communications.[6,7] Since the reactions of mercaptans and phenols are similar in many respects, it seemed desirable to study the usefulness of 2,4-dinitrochlorobenzene as a reagent for phenols. In a few cases 2,4-dinitrophenyl ethers occur in the literature and in such cases the melting points and literature references are given in the table. In cases where discrepancies occur between the melting points of those reported in the literature and of those obtained in our study, analyses were made and herein recorded.

Procedure

0.01 Mole of the phenol is added to 0.01 mole of sodium hydroxide dissolved in 5 cc. of water. The resulting solution of sodium phenolate is added to 0.01 mole of 2,4-dinitrochlorobenzene dissolved in 30 cc. of ethyl alcohol (95%). In some cases with difficultly soluble compounds more alcohol must be added to keep the substance in solution. The solution at this point is always highly colored. In most cases it turns dark red in color; however in some cases it is almost black. The solution is then heated under reflux on a steam-bath until the red color is discharged and a copious precipitate of salt appears. (Usually one-half hour is sufficient.) The reaction mixture is diluted with an equal part of water whereupon the 2,4-dinitrophenyl ether is precipitated, then filtered, washed with water and finally recrystallized from alcohol. As a rule one recrystallization is sufficient.

Discussion of Results

There are times when a precipitate occurs at the point when the aqueous solution of the phenolate is added to the alcoholic solution of the reagent. This precipitate is not to be confused with the precipitate of salt which appears after heating for some time. It has been shown[8] that 2,4-dinitrochlorobenzene forms addition products with certain phenols, and apparently the precipitate first formed in our work is of such a nature, since it contains both nitrogen and chlorine. Upon heating, it loses chlorine as well as its color, and sodium chloride is precipitated.

The 2,4-dinitrophenyl ethers which were obtained are easily purified, highly crystalline, and possess sharp melting points widely enough separated to ensure identification. An exception is noted only in the case of derivatives of 2,4-dibromophenol and 2,4,6-tribromophenol, which have the same melting point. However, in this case, the original phenols melt 56° apart. With the exception of the derivatives of thymol, carvacrol and hexylresorcinol, all are precipitated from the reaction mixture as solids. The reagent is superior to the isocyanates in that the presence of water in the phenol does not interfere with the formation of the derivative. The melting points are high enough so that very few are obtained as oils, again indicating the superiority of the reagent. 2,4-Dinitrochlorobenzene is more stable than both

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(1) Herzog, *Ber.*, **40**, 1831 (1907).

(2) Reid, THIS JOURNAL, **39**, 304 (1917); Lyman and Reid, *ibid.*, **42**, 615 (1920).

(3) Brown and Kramers, *J. Am. Pharm. Assoc.*, **11**, 607 (1922).

(4) French and Wertel, THIS JOURNAL, **48**, 1736 (1926).

(5) Koelsch, *ibid.*, **53**. 304 (1931).

(6) Bost, Turner and Norton, *ibid.*, **54**, 1985 (1932).

(7) Bost, Turner and Conn, *ibid.*, **55**, 4456 (1933).

(8) Buehler, Hisey and Wood, *ibid.*, **52**, 1939 (1930).