takes place at first, slowing up to about 1° to 4° per minute through the melting-point range. The temperature of the mercury bath does not fall the instant the substance melts, but a few seconds later. The temperature lag is usually less than 0.3° and can be allowed for.

When the substance melts, the operator is warned, and he then may open the switches A and F at his leisure. He then reads the thermometer, removes it and shakes down the mercury thread. Thermometer and Contact J are cleaned, and the surface of the mercury is skimmed, after which the apparatus is ready to be used again. The great majority of compounds melt below 250°, but when the substance in question melts above this temperature, a 360° thermometer may be substituted for the maximum thermometer. Contact K is cut out of the circuit and the heating is continued up to 360° if necessary, the melting point being read when the bell rings, as in Dubosc's apparatus.

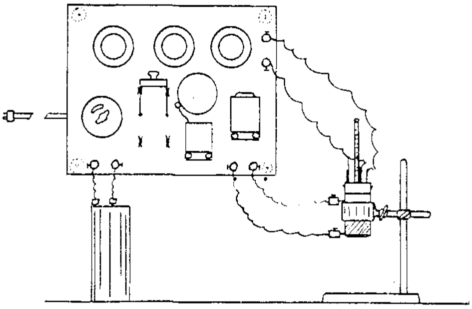

Fig. 4.—Apparatus mounted.

The apparatus is really simple and the parts (with the exception of the thermometer) can generally be found in any laboratory or obtained at little cost. The electrical appliances are best mounted on an asbestos board panel, 20 × 30 cm. and fastened to the wall just above the desks as shown in Fig. 4. The time and patience saved in taking melting points in the organic laboratory with this apparatus can hardly be overestimated.

Niagara Falls, New York

[Contribution from the School of Chemistry of the University of Minnesota]

THE CONSTITUTION OF TRIBROMOPHENOL BROMIDE AND ITS CONGENERS[1]

By Walter M. Lauer

Received August 21, 1925 Published February 5, 1926

Two structures have been proposed for tribromophenol bromide. Benedikt,[2] who first prepared this substance, concluded that the fourth atom of bromine was not in the ring since it formed tribromophenol very readily by reduction. Accordingly, he assigned to it Formula I. A number of

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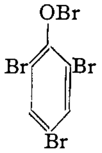
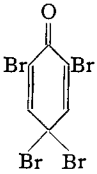
[1] This article is based upon part of a thesis presented by Walter M. Lauer, in June, 1924, to the Faculty of the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.—W. H. Hunter.

[2] Benedikt, *Ann.*, **199**, 127 (1879).

years later Thiele and Eichwede[3] introduced a second structure (II) in view of the strong oxidizing properties of this substance.



I



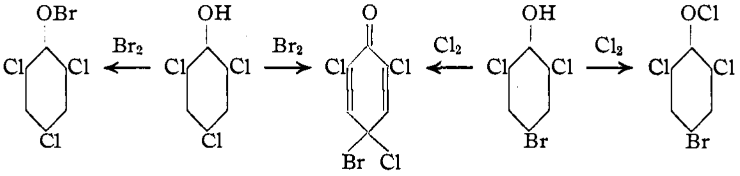
II

Somewhat later, Kastle and Speyer[4] attempted to decide between the "phenol bromide" structure (I) and the "cyclohexadienone" structure (II) in the following way. If Structure I is correct, they argued, Reactions a and b should give the same product.

(a) $C_6H_5SO_2Cl + C_6H_2Br_3ONa \longrightarrow C_6H_5SO_2OC_6H_2Br_3 + NaCl$
(b) $C_6H_5SO_2Na + C_6H_2Br_3OBr \longrightarrow C_6H_5SO_2OC_6H_2Br_3 + NaBr$

They found, however, that Reaction a yielded the expected compound, but they obtained an amorphous product from Reaction b. From these data they concluded that Structure I was incorrect. That tribromophenol bromide loses bromine very readily to form amorphous products was first noted by Benedikt. In view of this fact, these experiments do not necessarily eliminate I, for Reaction a went in the normal fashion, but in the case of Reaction b the tribromophenol bromide was decomposed to form an amorphous substance.

The facts heretofore available, therefore, do not enable us to choose between these two structures. Consequently, the following method of attack was devised. If the "cyclohexadienone" structure II is the correct one the same compound III should result whether we introduce a bromine atom into the molecule of trichlorophenol or a chlorine atom into the 4-bromo-2,6-dichlorophenol molecule. However, if the "hypobromite" structure I represents the correct structure, two different products IV and V should be obtained. In one case trichlorophenol bromide IV should result, whereas the second would lead to *p*-bromo-dichlorophenol chloride V.



IV III V

When the products of these reactions were finally obtained, it was found that all of them decomposed when heated instead of giving a true melting point. Furthermore, the decomposition temperature varied with the

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[3] Thiele and Eichwede, *Ber.*, **33**, 673 (1900).

[4] Kastle and Speyer, *Am. Chem. J.*, **27**, 40 (1902).

manner of heating and also with the age of the sample. As a result, no distinction could be made between them in this manner. Their colors and crystal habits were also similar. If two pairs had not been selected, it might have been concluded that the compounds, formed in the two different manners, were identical, thus confirming Structure II and eliminating Structure I. Since the compound obtained by brominating trichlorophenol also resembled in physical properties the one of different composition, obtained by brominating *p*-chloro-dibromophenol, it became evident that it was necessary to find some other method to use as a criterion for identity.

It has long been known that when tribromophenol bromide is heated with alcohol, tribromophenol is formed together with acetaldehyde and hydrobromic acid.[2]

If Structure I is correct, the "hypobromite bromine" atom should be the one which is removed. If Structure II is correct either of the two halogen atoms, which are *para* to the quinoid oxygen atom should be removed. In this case we have no means of deciding which of these two represents the correct reaction mechanism.

If we consider the compounds obtained by the bromination of trichlorophenol and chlorination of *p*-bromo-dichlorophenol we reach the following conclusions. The "phenol bromide" formulation will obviously give two different structures, IV and V, and on treatment with alcohol, trichlorophenol and *p*-bromo-dichlorophenol, respectively, should result. On the other hand, the "cyclohexadienone" structure will give one and the same compound (III) in the two reactions mentioned and, therefore, the same molecular ratio of bromine to chlorine should be removed from the products of the two reactions. For these reasons it was decided to study the behavior of these substances with alcohol.

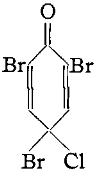
Owing to the ease of decomposition all experiments were carried out with samples freshly prepared and dried in the absence of direct sunlight for several hours. Analyses were run at the same time as the reactions with alcohol were started and the latter continued to completion only if the analyses gave good results. The phenol or mixture of phenols, which resulted from the action of alcohol, was then heated in a sealed tube with fuming nitric acid and silver nitrate. The *relative* amounts of silver bromide and silver chloride were then determined and the results expressed as the molar ratio of silver bromide to silver chloride. For example, when the compound $C_6H_2ClBr_3O$, obtained by brominating *p*-chloro-dibromophenol, was studied in this way the molar ratio of silver bromide to silver chloride was found to be 2.13. The final product, after treatment with alcohol, however, contained only three halogen atoms per benzene ring. Therefore, in this case, the average molecule, which originally contained three atoms of bromine and one of chlorine, now contained 2.04

atoms of bromine and 0.96 atoms of chlorine. Consequently, treatment with alcohol removed on the average 3 minus 2.04, or 0.96, of a bromine atom and 1 minus 0.96, or 0.04, of a chlorine atom. That is, out of every hundred molecules of $C_6H_2ClBr_3O$, ninety-six lost a bromine atom and four lost a chlorine atom. This information is indicated in the table below under the heading Composition of "Halogen Atom" Lost. The method of study was the same in the case of the other compounds.

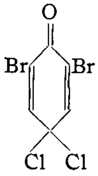
			Composition of product obtained	Composition of "halogen atom" lost	
				Br. %	Cl. %
I.	*p*-Chloro-dibromophenol	$\xrightarrow{Br_2}$	$C_6H_2ClBr_3O$ (A)	96	4
II.	Tribromophenol	$\xrightarrow{Cl_2}$	$C_6H_2ClBr_3O$ (B)	43.5	56.5
III.	Trichlorophenol	$\xrightarrow{Br_2}$	$C_6H_2Cl_3BrO$ (C)	96	4
IV.	*p*-Bromo-dichlorophenol	$\xrightarrow{Cl_2}$	$C_6H_2Cl_3BrO$ (D)	40	60

Discussion

A consideration of these results leads to the conclusion that A and B are not identical. The same is true for C and D. This eliminates the simple "cyclohexadienone" structure, for according to this formulation A and B must be identical. The same holds true for C and D. This proof, however, assumes that in the case of the compounds B and D, no substitution of chlorine for bromine has taken place. That there is some justification for this assumption is shown by the following line of reasoning. If the quinoid structure is the correct one, and if partial replacement has taken place, the compounds resulting when tribromophenol is treated with chlorine would probably be represented by the two structures BI and BIV.



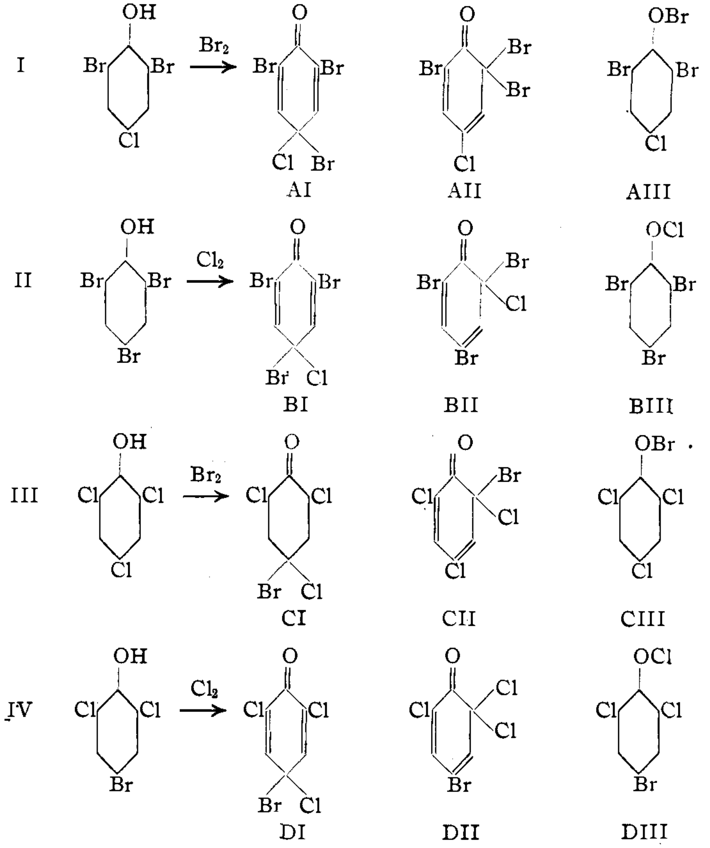
BI



BIV

According to this view, B I should also result when *p*-chloro-dibromophenol is brominated. The product, which results from *p*-chloro-dibromophenol loses bromine almost exclusively when treated with alcohol, since the ratio of AgBr/AgCl obtained in this case was about 2.1:1; that is, it was converted almost exclusively to *p*-chlorodibromophenol. BIV can only lose chlorine and, therefore, must be converted to *p*-chloro-dibromophenol, which will give a ratio AgBr/AgCl of 2.0:1. Therefore, the ratio of the mixture postulated cannot be greater than 2.1:1. However, the value actually obtained in this case was 5.9:1.

Thiele and Eichwede[3] have eliminated the possibility of simple *ortho*-quinoidation. However, another view, which assumes both *ortho*- and *para*-quinoidation, should perhaps be considered.



When the product obtained in I is treated with alcohol it loses 96% of bromine and 4% of chlorine. If this product is a mixture of AI and AII, in order to explain these results it must be assumed that AI loses bromine almost exclusively, since AII can lose only bromine. The only alternative is that AI is present in small amounts.

In III a product is also obtained which upon treatment with alcohol loses 96% of bromine and 4% of chlorine. In this case the product according to this hypothesis is a mixture of CI and CII. Therefore, both CI and CII must lose bromine almost exclusively. Thus it might be said that when both a bromine and chlorine atom are tied to the *ortho* or *para* carbon atom of a quinoid ring (at least in the case of these compounds), bromine will be removed almost to the exclusion of chlorine when treated with alcohol.

When IV is considered, DI and DII result according to this hypothesis. Now, DI is identical with CI; therefore, since it has been assumed that the bromine is removed almost to the exclusion of chlorine in order to account for the results in III, in order to be consistent, our hypothesis requires that DI should also lose bromine almost exclusively upon treatment with alcohol. There is only one choice in the case of DII and only chlorine may be removed. The results show that 40% of bromine and 60% of chlorine are lost. Since we have supposed the two forms DI and DII to exist, and that DI must lose bromine and DII must lose chlorine, we may temporarily account for the results obtained in this case by supposing that there is a mixture of about 40% of DI and 60% of DII. It will be shown a little further on that this is highly improbable.

In II, a mixture of BI and BII should result. BI is identical with AI. It has been assumed that AI loses bromine so that BI must lose bromine almost to the exclusion of chlorine. BII is analogous to CII. In the case of CII, in order to explain the results obtained, it was necessary to assume that this compound lost bromine almost to the exclusion of chlorine. Therefore, if this analogy is allowed, BII would lose bromine and practically no chlorine. The results, however, show that 43.5% of bromine and 56.5% of chlorine are lost in the case of the product resulting in II. This hypothesis, therefore, leads to an inconsistency, since only bromine should be lost.

The validity of this argument depends principally upon the analogy between BII and CII. This hypothesis, however, demands that AI and CI lose bromine and practically no chlorine. Evidently, then, the corresponding *para*-quinoid forms behave in an analogous manner. It therefore seems probable that a similar relationship should exist between the corresponding *ortho*-quinoid forms, BII and CII. If this analogy is allowed, this view becomes untenable.

If these results are examined on the basis of Benedikt's "phenol bromide" structure, the structures AIII, BIII, CIII and DIII are obtained.

CIII is the hypobromite of trichlorophenol. When treated with alcohol only bromine should be lost. The small amount of chlorine lost may be accounted for on the basis of analytical errors. For example, one sample of the "mixed silver halides," obtained from the "mixed phenols" resulting from the $C_6H_2BrCl_3O$ which, in turn, was formed by the action of bromine on trichlorophenol, lost 0.0004 g. when treated with chlorine. The second sample lost 0.0014 g.

BIII and DIII are both hypochlorites. Only chlorine should be removed here, but this is not the case. Chlorine and bromine are removed in almost equal amounts.

Hantzsch[5] has shown that brominated diazonium chlorides rearrange to form chlorinated diazonium bromides. For example, when an alco-

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[5] Hantzsch, *Ber.*, **30**, 2334 (1897).

holic solution of 2,4-dibromo-diazonium chloride was allowed to stand for an hour, the ionizable halogen consisted of both chlorine and bromine. The rearrangement was not complete in two days, but fortunately Hantzsch was able to separate the rearrangement product from the parent substance.

Chattaway and Orton[6] have studied the replacement of bromine by chlorine in the anilines. They state, "We have every reason to believe that in the reaction between acyl chloro-amino derivatives and anilines there is first formed a chloro-amino derivative of the aniline, which then undergoes the usual isomeric change, producing a *para* or *ortho* substituted aniline; the chlorine in this case exchanges positions with the hydrogen. In the case under consideration (the replacement of bromine by chlorine), there is a replaceable bromine atom, which is, however, much less mobile than the hydrogen." They further state, "Whatever the intermediate configurations (if any) through which a chloro- or bromoamino derivative passes during the isomeric change, it is certain that those which lead to the formation of *para* compounds are assumed more readily than those which lead to the formation of *ortho* compounds."

If the "phenol halides" are viewed in similar fashion, the hypochlorites would rearrange to form hypobromites. All of the "phenol halides" that are described exhibit practically the same behavior, so that any attempt to separate the hypochlorite from its rearrangement product, the hypobromite, if rearrangement actually takes place, would be met with very great difficulties. However, in spite of the fact that no such separation was accomplished, a rearrangement of this type seems to be the most plausible explanation. If a rearrangement of this kind is postulated, then the results obtained in II and IV may be explained, by assuming that partial rearrangement has taken place.

Experimental Part

I. The so-called trichlorophenol bromide was prepared as follows, by a slight modification of the method of Benedikt.

Ten g. of pure trichlorophenol was dissolved in about 150 cc. of water containing about 3 g. of potassium hydroxide. A solution of 3 cc. of bromine in about 400 cc. of water containing potassium bromide was then prepared. The potassium trichlorophenolate was treated with about 9 cc. of glacial acetic acid diluted with about 150 cc. of water. The solution was stirred vigorously during this operation, to yield the trichlorophenol in a very finely divided state. The bromine solution was then added and the mixture was stirred mechanically for about one hour. The color of the precipitate changed from a pure white to a lemon-yellow. This precipitate was filtered off, and washed with water. The wet material was then dissolved in a small amount of boiling chloroform. The chloroform layer was separated from the water layer by means of a separatory funnel, and the chloroform solution was placed in a vacuum desiccator and concentrated. Lemon-yellow crystals were thus obtained. The properties of this

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[6] Chattaway and Orton, *J. Chem. Soc.*, **79**, 822 (1901).

substance corresponded with the description of the compound previously obtained by Benedikt.

II. The Action of Chlorine on *p*-Bromo-dichlorophenol.

(a) **The Preparation of *p*-Bromo-dichlorophenol.**—This compound was prepared in the manner described by Hunter and Joyce[7] from *p*-bromophenol, which had been prepared according to the directions of Adams, Kamm and Marvel.[8]

(b) **The Preparation of $C_6H_2BrCl_3O$.**—Ten g. of 4-bromo-2,6-dichlorophenol was dissolved in water containing potassium hydroxide, and the solution was made up to about 1.5 liters with water. One hundred cc. of concd. hydrochloric acid was then added during stirring so as to obtain a finely divided precipitate of the halogenated phenol. Chlorine was passed into the solution. Vigorous mechanical stirring was continued during this entire process. The solution was then filtered. The material obtained in this way was dissolved in a small amount of boiling chloroform. The water layer was removed by means of a separatory funnel. The hot chloroform solution was immediately concentrated in a vacuum desiccator. Lemon-yellow crystalline material separated. The crystals were washed with a small amount of petroleum ether (b. p., less than 65°). The material was then allowed to dry in the air for about four hours and analyzed for total halogens.

Anal. Subs., 0.1726: AgX, 0.3827. Calcd. for $C_6H_2BrCl_3O$: 0.3856.

This material decomposed at about 114° with the evolution of bromine. The decomposition temperature varied with the rate of heating, however.

III. The Action of Bromine on *p*-Chloro-dibromophenol.

(a) **The Preparation of *p*-Chloro-dibromophenol.**—This compound was prepared according to the directions of Hunter and Joyce.[7]

(b) **The Preparation of $C_6H_2ClBr_3O$.**—About 10 g. of the trihalogenated phenol was dissolved in water containing sufficient potassium hydroxide to bring about complete solution of the phenol. About 150 cc. of water containing 15 cc. of glacial acetic acid was then added, so as to obtain a finely divided precipitate of the *p*-chloro-dibromophenol. An aqueous solution of potassium bromide containing 4 cc. of bromine was next added. During the entire process the reaction mixture was stirred vigorously by means of a mechanical stirrer. Stirring was continued for about one and one-half hours, at the end of which time the reaction mixture was filtered. The yellow material which collected upon the filter was washed with cold water to remove any free bromine. It was then dissolved in a small amount of boiling chloroform, and any water which separated was removed by means of a separatory funnel. The hot chloroform solution was then concentrated in a vacuum desiccator. Lemon-yellow crystals separated. These were filtered off, and washed with low-boiling petroleum ether. They were then allowed to dry in the air for 4 to 5 hours and analyzed.

Anal. Subs., 0.1726, 0.1657: AgX, 0.3358, 0.3224. Calcd. for $C_6H_2ClBr_3O$: 0.3338, 0.3204.

This material decomposed with the evolution of bromine at about 115°, but as with the other phenol derivatives of this type, the temperature of decomposition was dependent on the rate of heating.

IV. The Action of Chlorine on Tribromophenol.—Ten g. of pure tribromophenol was dissolved in water containing sufficient potassium hydroxide to react with all of the tribromophenol.

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[7] Hunter and Joyce, THIS JOURNAL, **39,** 2644 (1917).

[8] Adams, Kamm and Marvel, "Organic Chemical Reagents," *Univ. Illinois Bull.,* **16,** No. 43, p. 61 (1919).

The volume was made up to about 1.5 liters with cold water and the solution was stirred vigorously. Common salt and about 40 cc. of concd. hydrochloric acid were added to precipitate the phenol in a finely divided state. A stream of chlorine was then passed into this suspension. Stirring was continued throughout this process. After 30–45 minutes the suspension was filtered and washed with cold water. A cream-colored material was obtained in this manner. This material was dissolved in hot chloroform and the solution was separated from water by means of a separatory funnel. The chloroform solution, while still hot, was concentrated in a vacuum desiccator. A lemon-yellow crystalline material resulted. The crystals were filtered off and washed with a small amount of petroleum ether. After being dried in the air for several hours, the substance was analyzed for halogens.

Anal. Subs., 0.1808: AgX, 0.3484. Calcd. for $C_6H_2ClBr_3O$: 0.3496.

This material, when slowly heated, decomposed at about 131° with the evolution of bromine, but the temperature depended upon the rate of heating.

V. The Behavior of the Products Described Above when Treated with Alcohol.—Each one of the four samples was treated in the following manner.

About 1 g. of the freshly prepared material was placed in a small Erlenmeyer flask and 100 cc. of ethyl alcohol was added. No perceptible reaction took place until the temperature was raised. The samples were therefore placed on a hot plate and heated to boiling. The odor of acetaldehyde became very pronounced in every case. Boiling was continued for a few minutes. The pale yellow solution was then allowed to stand for at least one day. At the end of this time the solution was poured with stirring into 400 cc. of distilled water, which precipitated the trihalogenated phenols formed by the treatment with alcohol. The trihalogenated phenols were then separated on a Gooch crucible and washed free from soluble halides by means of distilled water. The Gooch crucible with its contents was then placed in a desiccator over sulfuric acid and allowed to dry for several days.

ANALYSIS OF PHENOLS OBTAINED.—About 0.2 g. of this material was then sealed in a Carius tube with solid silver nitrate and 2 cc. of halogen-free fuming nitric acid. The tube was heated for at least 12 hours at a temperature not less than 250°. The contents of the tube were then washed into a beaker, heated for about 20 minutes and separated on a Gooch crucible; the silver halides thus obtained were washed and dried.

A weighed portion of the sample was dried to constant weight in a porcelain boat. This sample was then placed in a tube containing a thermometer and a slow stream of dry chlorine was passed through the tube, which was surrounded with a small electrical heating unit. The temperature was raised gradually until the sample just began to fuse. Dry air was then substituted for chlorine, and the temperature again raised until fusion just began. After the boat had been cooled in a desiccator, the sample was weighed. The treatment with chlorine and then with air was repeated until the weight of the sample became constant. The results follow.

	Wt. AgX taken, g.	AgCl, g. (wt. after treatment with chlorine)
$C_6H_2ClBr_3O$ from $C_6H_2Br_3OH$	0.2908	0.2298
$C_6H_2ClBr_3O$ from $C_6H_2ClBr_2OH$	.1638, 0.1673, 0.2842	.1355, 0.1383, 0.2344
$C_6H_2BrCl_3O$ from $C_6H_2Cl_3OH$	.3151, .2651	.3147, .2637
$C_6H_2BrCl_3O$ from $C_6H_2BrCl_2OH$	.1465	.1380

The writer wishes to take this opportunity to express his indebtedness to Professor W. H. Hunter for constant assistance and invaluable criticism during the course of the work.

Summary

1. The tetrabromo-cyclohexadienone formula, which was proposed for the compound resulting from the action of bromine on tribromophenol, is improbable.

2. Facts are brought forward which render very remote the possibility of tribromophenol bromide being a mixture of *ortho*- and *para*-quinoid forms.

3. Benedikt's original structure for tribromophenol bromide accounts for the facts introduced if a partial rearrangement of trihalogenated phenol chlorides, which contain bromine in the *para* position, to the isomeric trihalogenated phenol bromides, is postulated.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE FELLOWSHIP OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE INFLUENCE OF TEMPERATURE ON THE RECIPROCAL SOLUBILITY OF THE MONO-ALKYL ETHERS OF ETHYLENE GLYCOL AND WATER

BY HENRY L. COX AND LEONARD H. CRETCHER

RECEIVED SEPTEMBER 14, 1925 PUBLISHED FEBRUARY 5, 1926

A considerable number of binary-liquid systems are known, the solubility curves of which approach one another with increasing temperature and meet at an upper consolute point. In relatively fewer cases the curves approach one another with diminishing temperature and meet at a lower consolute point. Only a limited number of systems have been discovered which possess both upper and lower consolute temperatures. The first example, that of nicotine and water, was discovered by Hudson.[1] The other known systems are methylethyl ketone and water,[2] *sec.*-butyl alcohol and water,[3] β-picoline and water, α,α-lutidine and water, 3-methylpiperidine and water, 4-methylpiperidine and water[4] and 2-methylpiperidine and water.[5]

With the exception of the liquid mixtures, methylethyl ketone and water and *sec.*-butyl alcohol and water, which possess completely closed solubility curves only at high pressures, all of the systems previously described have as one component a cyclic nitrogen base.

In an earlier paper from this Laboratory[6] it was stated that the members

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[1] Hudson, *Z. physik. Chem.*, **47**, 113 (1903).

[2] Kohnstamm and Timmermans, *Verslag Akad. Wetenschappen Amsterdam*, **21**, 783 (1913).

[3] Timmermans, *Arch. Néerland. sci.*, **6**, 147 (1922).

[4] Flaschner, *J. Chem. Soc.*, **95**, 668 (1909).

[5] Flaschner and MacEwen, *ibid.*, **93**, 1000 (1908).

[6] Cretcher and Pittenger, THIS JOURNAL, **47**, 164 (1925).