

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WEST VIRGINIA UNIVERSITY]

MERCURY DERIVATIVES OF CYCLOHEXYL- AND BENZYL-PHENOLS¹BY JOHN W. HAUGHT,² C. E. GARLAND AND H. A. H. PRAY

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Only a few references to the mercuration of compounds similar to the cyclohexyl- and benzylphenols have been found.

Dimroth³ prepared mercury derivatives of *p*-cresol by heating with alcoholic mercuric acetate at 90° for half an hour. About equal quantities of the mono- and di-mercurated products were formed but the latter, being less soluble, separated out almost pure. The mono-acetoxymercuri-*p*-cresol was rather difficult to crystallize on account of its solubility, so it was precipitated from solution in the form of chloromercuri-*p*-cresol by the addition of sodium chloride solution. He dissolved chloromercuri-*p*-cresol in sodium hydroxide and precipitated the anhydride by passing carbon dioxide into the solution. The di-acetoxymercuri-*p*-cresol as crystallized from the reaction mixture contained one molecule of water of crystallization. When the compound was heated to drive off this water it was converted into hydroxymercuriacetoxymercuri-*p*-cresol.

Henry and Sharp⁴ have mercurated several alkyl phenols and alkyl-phenol aldehydes and studied their bactericidal properties. They found that the bactericidal action of organo-mercury compounds was not entirely dependent on the number of mercury groups present, but was largely influenced by the configuration of the organic part of the molecule. They prepared both mono- and di-mercurated derivatives of *p*-tertiary butyl phenol by refluxing the alcoholic solution of the phenol with mercuric acetate dissolved in alcohol containing a small quantity of acetic acid. When this solution was diluted with water the acetoxymercuri compounds were precipitated. The mono- and di-acetoxymercuri compounds were also prepared from *p*-isoamylphenol, carvacrol and thymol. The acetoxymercury groups assumed the ortho position to the hydroxyl group in the mono derivatives and the ortho, ortho prime positions in the di-substituted compounds. These positions were determined by converting the mercury groups to nitro groups by treatment with cold nitric acid.

Mameli⁵ found that *o*-cresol could be mercurated in either hot or cold

¹ This communication is an abstract of part of a thesis submitted by John W. Haught in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at West Virginia University.

² D. A. Burt Fellow in Chemistry, 1929-1930.

³ Dimroth, *Ber.*, **35**, 2856 (1902); Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921, pp. 275-277.

⁴ Henry and Sharp, *J. Chem. Soc.*, 2432 (1926).

⁵ Mameli, *Gazz. chim. ital.*, **56**, 948 (1926); *Chem. Abstracts*, **21**, 1252 (1927).

alcohol or acetic acid solution. The best results were obtained for mono-acetoxymercuri-*o*-cresol in cold dilute acetic acid and for di-acetoxymercuri-*o*-cresol in hot dilute acetic acid. Both the mono- and di-acetoxymercuri-*o*-cresols dissolved in sodium hydroxide, from which mono- and di-chloromercuri-*o*-cresols were precipitated by the addition of sodium chloride solution.

Either 95% alcohol slightly acidified with acetic acid or glacial acetic acid may be used as a solvent for the mercuration of ortho and para cyclohexyl and benzyl phenols. The acidified alcohol was found to be more satisfactory because there was less coloration of the product in this solvent. If the mercuration was carried out in dilute acetic acid, the product separated on cooling as a sticky mass which could not be crystallized.

The di-acetoxymercuri compounds of both ortho and para cyclohexyl phenol and ortho and para benzylphenol were so soluble in the acidified alcohol that they could not be crystallized from solution even by evaporation to a small volume. They were precipitated by slowly diluting the alcoholic solution with water.

Much difficulty was encountered in freeing these compounds of water. They slowly decomposed at 100° so they were heated for twenty-four hours in an oven at 50° but without effect. They were further heated in a vacuum oven at 60° for twenty-four hours. This treatment removed the water from the mercurated para cyclohexyl and benzyl phenols but not entirely from the similar ortho compounds. This was especially true of the chloromercuri and hydroxymercuri derivatives of ortho benzylphenol.

An effort was made to prepare the anhydromercuri or hydroxymercuri derivatives by treatment of the chloromercuri compounds with hot concentrated sodium carbonate solution but the conversion was not complete. Sodium hydroxide solution was substituted for the sodium carbonate solution and complete conversion resulted.

The hydrogen in the hydroxyl group of the phenols used seems to have only very slight acid properties, because the mercury derivatives of the para cyclohexyl and benzyl phenols were not soluble in sodium hydroxide and the similar derivatives of ortho cyclohexyl and benzyl phenols only slightly soluble. This is in marked contrast to the action of the mercury derivatives of phenol and the cresols.

The acetic acid in the acetoxymercuri derivatives was determined by the method of Brieger and Schulemann, as described by White,⁶ which is based on the decomposition of the compound with phosphoric acid in water solution, followed by distillation and titration of the acetic acid. The acetoxy compounds analyzed in this work were so insoluble that it was found necessary to use a larger quantity of phosphoric acid and to collect more of the distillate than indicated by White.

⁶ White, THIS JOURNAL, 42, 2355 (1920).

All of the preparations were dissolved for mercury determination by the method described by Hart and Hirschfelder.⁷ The mercury was then determined by the method of Jamieson.⁸

The ortho cyclohexylphenol and para cyclohexylphenol used in preparing these mercuration products were supplied through the courtesy of Dr. R. R. Read, of Sharp and Dohme, Baltimore, to whom the thanks of the authors are due.

Experimental Part

Di-acetoxymercuri derivatives of cyclohexyl and benzyl phenols were prepared by reacting 0.025 mole of the phenol dissolved in 15 cc. of ethyl alcohol with 0.05 mole of mercuric acetate dissolved in 100 cc. of ethyl alcohol acidified with 5 cc. of glacial acetic acid. The two solutions were mixed and heated on a steam-bath for two hours, after which time the reaction mixture did not give a test for inorganic mercury with sodium hydroxide. The resulting solution was evaporated to a volume of 50 cc. and the mercury derivative either crystallized from this solution or precipitated by dilution with a large volume of water. The precipitate was filtered, washed, dried at 50° and then in a vacuum oven at 60°. The numerical data appear in Table I.

TABLE I
PREPARATION, DATA AND ANALYSES

| Compound, -phenol | Yield, % | Dec. at | Formula | Analyses | | | | | |
|--------------------------------|-------------|---------|--|------------|-------|--------|-------|-------|-------|
| | | | | Mercury, % | | OAc, % | | | |
| | | | | Calcd. | Found | Calcd. | Found | | |
| Diacetoxymercuri- | | | | | | | | | |
| - <i>p</i> -Benzyl- | 95 | 110-115 | C ₁₇ H ₁₆ O ₃ Hg ₂ | 57.22 | 56.81 | 57.02 | 16.83 | 16.31 | 16.70 |
| - <i>o</i> -Benzyl- | 92 | 115-125 | C ₁₇ H ₁₆ O ₃ Hg ₂ ·H ₂ O | 55.78 | 55.35 | 55.67 | 16.40 | 16.02 | 16.16 |
| - <i>p</i> -Cyclohexyl- | 95 | 105-110 | C ₁₅ H ₂₀ O ₃ Hg ₂ | 57.86 | 57.15 | 57.59 | 17.02 | 16.52 | 16.25 |
| - <i>o</i> -Cyclohexyl- | 95 | 135-140 | C ₁₅ H ₂₀ O ₃ Hg ₂ ·H ₂ O | 56.4 | 56.07 | 55.92 | 16.41 | 16.02 | 15.95 |
| Dichloromercuri- | | | | | | | | | |
| - <i>p</i> -Benzyl- | 97 | 128-134 | C ₁₂ H ₁₀ OHg ₂ Cl ₂ | 61.34 | 61.56 | 61.57 | | | |
| - <i>p</i> -Cyclohexyl- | 93 | 225-230 | C ₁₂ H ₁₄ OHg ₂ Cl ₂ | 62.10 | 61.93 | 61.76 | | | |
| - <i>o</i> -Cyclohexyl- | 92 | 155-160 | C ₁₂ H ₁₄ OHg ₂ Cl ₂ ·H ₂ O | 60.41 | 59.96 | 60.00 | | | |
| Anhydromercuri-hydroxymercuri- | | | | | | | | | |
| - <i>p</i> -Benzyl- | 90 | 245-250 | C ₁₃ H ₁₀ O ₂ Hg ₂ | 66.95 | 66.96 | 66.27 | | | |
| Dihydroxymercuri- | | | | | | | | | |
| - <i>p</i> -Cyclohexyl- | 90 | 255-260 | C ₁₂ H ₁₆ O ₃ Hg ₂ | 65.88 | 65.85 | 65.37 | | | |
| - <i>o</i> -Cyclohexyl- | 85 | 230-235 | C ₁₂ H ₁₆ O ₃ Hg ₂ ·H ₂ O | 63.16 | 62.94 | 63.16 | | | |

Di-chloromercuri derivatives were prepared from the corresponding acetoxymercuri compounds by dissolving them in glacial acetic acid and adding the solution so obtained to a saturated sodium chloride solution. The insoluble di-chloromercuri compounds were precipitated as white powders. These were washed free of sodium chloride and dried in the same way as the acetoxymercuri derivatives. It was not found possible to free the di-chloromercuri-*o*-benzylphenol of water without decomposi-

⁷ Hart and Hirschfelder, *THIS JOURNAL*, **42**, 2678 (1920).

⁸ Jamieson, *J. Ind. Eng. Chem.*, **11**, 296 (1919).

tion, so a satisfactory analysis of this material was not obtained and therefore it does not appear in the above table.

Anhydromercuri-hydroxymercuri and di-hydroxymercuri derivatives were obtained by moistening the di-chloromercuri compounds with ethyl alcohol and treating with hot (10%) sodium hydroxide solution. The mixture was filtered and the sodium hydroxide washed from the residue which was dried in a vacuum oven. In the case of the di-hydroxymercuri-*o*-benzylphenol and the di-hydroxymercuri-*o*-cyclohexylphenol, it was found necessary to neutralize with dilute hydrochloric acid in order to cause precipitation. Due to the difficulty of drying the former, a satisfactory analysis of this material was not obtained.

Summary

The following ten mercury derivatives of ortho and para cyclohexylphenol and ortho and para benzylphenol have been prepared and analyzed: di-acetoxymercuri-*p*-benzylphenol, di-acetoxymercuri-*o*-benzylphenol, di-acetoxymercuri-*p*-cyclohexylphenol, di-acetoxymercuri-*o*-cyclohexylphenol, di-chloromercuri-*p*-benzylphenol, di-chloromercuri-*p*-cyclohexylphenol, di-chloromercuri-*o*-cyclohexylphenol, anhydromercuri-hydroxymercuri-*p*-benzylphenol, di-hydroxymercuri-*p*-cyclohexylphenol, and di-hydroxymercuri-*o*-cyclohexylphenol.

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FORMIC ACID FROM HYDROLYSIS OF CELLULOSE OXALATE¹

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One of the usual laboratory methods for making formic acid is to prepare glyceryl mono oxalate, convert it to glyceryl mono formate by heating, and hydrolyze by adding more crystallized oxalic acid, the water of the crystallized acid serving as that required for the hydrolysis. Finally, steam distillation completes the hydrolysis and delivers all the formic acid produced.²

It has been found that cellulose in the form of absorbent cotton can be substituted for glycerine with some changes in the technique of the process.

Procedure.—Eighty grams of crystallized oxalic acid, 100 g. of absorbent cotton and 100 cc. of concentrated hydrochloric acid are required. The oxalic acid is melted in its water of crystallization in a 1000-cc. round-bottomed flask over the water-bath and the cotton, torn into small bits, thoroughly shaken with it. The hydrochloric acid is added and the flask

¹ Presented before the Division of Cellulose Chemistry of the American Chemical Society at the Indianapolis Meeting, March 30–April 3, 1931.

² Cohen, "Practical Organic Chemistry," 3rd ed., The Macmillan Co., Preparation 47, p. 130.