[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY]

# SOME MERCURY DERIVATIVES OF PHENOL ETHERS[1]

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In an earlier paper[3] it was shown that mercurated phenols react with iodides of alkali metals to give the original phenols, inorganic mercury compounds and 1 equivalent of alkali for each carbon-mercury linkage broken. When, however, the hydroxyl group is protected by acylation iodides react in quite a different way giving mercuri-bis compounds and inorganic mercury compounds but not alkali. The two processes may be illustrated as follows.

$$\mathrm{HO{-}C_6H_4{-}HgI + 3\,KI + H_2O \longrightarrow C_6H_6OH + K_2HgI_4 + KOH}$$
$$\mathrm{2\,AcO{-}C_6H_4{-}HgI + 2\,KI \longrightarrow (AcO{-}C_6H_4)_2Hg + K_2HgI_4}$$

The present work was undertaken to determine the effect of replacing the phenolic hydrogen by an alkyl group instead of an acyl group. An observation made by Dimroth[4] indicated that the effect of the 2 groups might be similar. In determining the structure of *o*-chloromercuri-phenol, he treated it with ethyl iodide in alkaline alcoholic solution to prepare the known *o*-phenetylmercuric iodide. Besides the desired product he obtained a good yield of *o*-mercury-diphenetyl. Since sodium iodide is formed in the reaction it seemed reasonable that it might change the mercurated phenetole first formed to the mercuri-bis compound. Dimroth's results may then be formulated as follows.

$$\mathrm{NaO{-}C_6H_4{-}HgCl + RI \longrightarrow RO{-}C_6H_4{-}HgCl + NaI}$$
$$\mathrm{2\,RO{-}C_6H_4{-}HgCl + 4\,NaI \longrightarrow (RO{-}C_6H_4)_2Hg + Na_2HgI_4 + 2\,NaCl}$$

In order to test this theory and to study further the effect of protecting a phenolic hydroxyl group upon the stability of the carbon-mercury linkage, the action of potassium iodide on mercurated phenol ethers was studied.

Iodomercuri-anisoles and -phenetoles were prepared by the method of Dimroth.[4] As the *ortho* mercurated compounds are much more soluble than the *para* compounds, the study was limited to the former. When an alcoholic solution of *o*-iodomercuri-anisole or of *o*-iodomercuri-phenetole is refluxed with potassium iodide, no splitting of the carbon-mercury linkage takes place as no alkali is formed. *o*-Mercury-dianisyl or *o*-mercury-diphenetyl is obtained in good yield. The mother liquors contain large amounts of inorganic mercury compounds. Potassium thiocyanate acts

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[2] Research Fellow under a grant from the U. S. Interdepartmental Social Hygiene Board, General M. W. Ireland, Chairman. Some of the organic mercury compounds related to those studied are being investigated pharmacologically under the direction of Dr. A. S. Loevenhart of the Department of Pharmacology of the University of Wisconsin.

[3] THIS JOURNAL, **43**, 622 (1921).

[4] Dimroth, *Ber.*, **32**, 763 (1899).

like potassium iodide but gives poorer yields of the mercuri-bis compounds.

The *para* mercurated phenol ethers react to some extent with potassium iodide or with potassium thiocyanate; some inorganic mercury is formed. No alkali is found. The corresponding mercuri-bis compounds are not obtainable in a pure state by these reactions.

Sodium thiosulfate is the most convenient reagent for making the mercuri-bis compounds of the phenol ethers. The *o*-iodomercuri compounds dissolve readily in it giving solutions from which the mercuri-bis compounds separate on standing.

*o*-Mercury-dianisyl and *o*-mercury-diphenetyl react normally with mercuric chloride; quantitative yields of the chloromercuri compounds are obtained.

## Experimental Part

**Preparation of *o*- and *p*-Iodomercuri-phenetoles.**—A mixture of 5 g. of *o*-chloromercuri-phenol[3] in 50 cc. of 50% ethyl alcohol, 0.7 g. of sodium hydroxide, and 3.5 g. of ethyl iodide is heated gently for 1 hour. A small amount of *o*-mercury-diphenetyl separates as the solution cools. This is removed and the filtrate is diluted with water to precipitate the *o*-iodomercuri-phenetole which is recrystallized from alcohol; yield, 7 g. The *para* compound is prepared in a similar way. Five g. of *p*-chloromercuri-phenol gives 5 g. of a mixture of the corresponding iodomercuri and mercuri-bis-compounds which is difficult to separate. Because the *ortho* compounds are obtained more easily, the experiments with potassium iodide, with thiocyanate, and with thiosulfate were carried out with *o*-iodomercuri-phenetole and *o*-iodomercuri-anisole.

**Preparation of *o*-Iodomercuri-anisole.**—Eight g. of *o*-chloromercuri-phenol, 1 g. of sodium hydroxide, 50 cc. of alcohol, and 3 g. of methyl iodide are heated for half an hour. About 1 g. of *o*-mercury-dianisyl separates as the solution cools. Dilution of the mother liquor with water gives 7 g. of the iodomercuri compound.

**Reaction of Potassium Iodide with *o*-Iodomercuri-anisole and with *o*-Iodomercuri-phenetole.**—Four g. of *o*-iodomercuri-anisole, recrystallized from alcohol, is heated under a reflux condenser for 6 hours with 3 g. of potassium iodide and 50 cc. of alcohol. When the product is cooled and diluted somewhat the *o*-mercury-dianisyl is precipitated. It is recrystallized from alcohol; yield, 1.5 g.; m. p., 108°. The filtrate from the reaction mixture is neutral and gives an immediate precipitate with hydrogen sulfide.

A solution of 2 g. of *o*-iodomercuri-phenetole in 50 cc. of alcohol together with 2 g. of potassium iodide is refluxed for 1 hour. When this product is cooled and diluted with water, 1.5 g. of *o*-mercury-diphenetyl separates. After crystallization from alcohol it melts at 81°. The filtrate is not alkaline. It contains inorganic mercury compounds.

**Reaction of Potassium Thiocyanate with the *o*-Iodomercuri-phenol Ethers.**—A mixture of 2 g. of *o*-iodomercuri-anisole, 2 g. of potassium thiocyanate and 50 cc. of alcohol was heated under a reflux condenser for 3 hours. The product, cooled and diluted, gave 1.5 g. of the mercuri-bis compound. Recrystallization from alcohol raised the melting point only to 75–80°. The filtrate contains inorganic mercury compounds but is neutral.

A mixture of 1.6 g. of *o*-iodomercuri-phenetole, 2 g. of potassium iodide and 50 cc. of alcohol, heated under a reflux condenser for 3 hours gives 0.8 g. of the mercuri-bis compound melting at 80° after several crystallizations from alcohol.

**Reaction of Sodium Thiosulfate with the *o*-Iodomercuri-phenol** ethers.—Two g. of *o*-iodomercuri-phenetole dissolved in a solution of 4 g. of sodium thiosulfate in 50 cc. of water deposits 1.2 g. of the mercuri-bis compound on standing; m. p., 81–83°.

Similarly, *o*-iodomercuri-anisole gives the mercuri-bis compound melting at 108°.

**Reaction of the *p*-Iodomercuri-phenol Ethers with Potassium Iodide and with Potassium Thiocyanate.**—The reactions between these substances apparently lead to the formation of mercuri-bis compounds, as the filtrates contain inorganic mercury and are not alkaline. However, the products are very difficult to purify.

**Reaction of Mercuric Chloride with the Mercuri-bis-phenol Ethers.**—One g. of *o*-mercury-dianisyl is heated with 0.7 g. of mercuric chloride in 25 cc. of alcohol for 15 minutes. The chloride deposits on cooling, and is recrystallized from alcohol; m. p., 177–178°. Dimroth obtained the same compound in small amount by direct mercuration of anisole. He gives the melting point as 173–174°.

Similarly, *o*-mercury-diphenetyl reacts with mercuric chloride to give pure *o*-chloromercuri-phenetole.

## Summary

1. Protection of the hydroxyl groups in mercurated phenols by alkylation has the same effect as protection by acylation, that is, the stability of the carbon-mercury linkage to iodides, thiocyanates, and to thiosulfates is increased.

2. Mercurated phenol ethers react with iodides, with thiocyanates, and with thiosulfates to form the corresponding mercuri-bis compounds giving solutions which contain inorganic mercury but no alkali, showing that the protection of the phenolic hydroxyl has prevented the splitting of the carbon-mercury linkage with the accompanying formation of alkali which occurs with the mercurated phenols.

3. The formation of the mercuri-bis compounds takes place much more readily in the case of the *ortho* compounds than with the *para* compounds.

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# THE PREPARATION OF ALKYLGUANIDINES

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In a recent paper, Arndt[1] describes a new and convenient reagent, methyl iso-thio-urea sulfate, from which methyl mercaptan may be obtained in a pure condition by warming it with dil. alkalies; dicyanodiamide is formed as a by-product. This reagent, produced by the addition of dimethyl sulfate to thio-urea, bears a close relation to the alkyl iodide addition products of thio-urea,[2] which react with primary and secondary aliphatic amines to form alkyl guanidines and alkyl mercaptans.

We have found that methyl iso-thio-urea sulfate undergoes an exactly analogous reaction with methylamine and dimethylamine, methyl mercap-

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[1] Arndt, *Ber.*, **54B**, 2236 (1921).

[2] Wheeler and Jamieson, *J. Biol. Chem.*, **4**, 111 (1907). Schenck, *Z. Physiol. Chem.*, **77**, 328 (1912).