The change in rotation shown by the pure crystalline methyl-2-desoxypentoside treated in the same manner was only very slight for the first four hours so that the quick rise and fall in rotation must have been essentially due to the dimethylacetal of 4-formylerythrose.

***l*-Erythrose from Acetone Methyl Erythroside.**—One gram of acetone methyl erythroside was dissolved in 25 cc. of 0.1 *N* sulfuric acid. After standing for three days at room temperature 1.5 cc. of glacial acetic acid[17] was added and the sulfate removed quantitatively with the calculated amount of barium hydroxide. After filtration through charcoal, the water was removed by distillation *in vacuo*. The residue was completely soluble in absolute alcohol. For the determination of the mutarotation we dried at 78° in vacuum over phosphorus pentoxide to constant weight (sample 0.3064 g.; *V*, 9.98 cc.; *l*, 1 dcm.; *t*, 24°).

TABLE IV

MUTAROTATION OF *l*-ERYTHROSE

Time after dissolving, min.	8	15	120	720	1440	2880
α	+0.38	0.41	0.51	0.85	0.95	1.03
$[\alpha]^{24}\text{D}$	+11.5	12.3	15.2	25.2	28.2	30.5

Summary

It has been demonstrated that ozonization products of *l*-arabinal include *l*-erythrose and 4-formylaldehydoerythrose. Both substances could be characterized, the former as a monoacetone-methylerythroside, the latter as 4-formylaldehydoerythrosedimethylacetal.

Acid hydrolysis of acetone-methylerythroside resulted in a preparation of *l*-erythrose, which has an equilibrium rotation of +30.5°.

Yeast does not ferment aqueous solutions of *l*-erythrose.

The synthesis of *l*-hydroarabinal is described.

AMES, IOWA
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RECEIVED MAY 27, 1935

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[17] Witzemann, THIS JOURNAL, **36**, 1914 (1914).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

The Mercuration of Para-Cymene

BY JOHN E. NEWSTROM AND KENNETH A. KOBE

There have been many suggested methods of converting *p*-cymene, the "spruce turpentine" by-product of the sulfite pulp industry, into more useful products. These include sulfonation,[1,2] nitration,[3,4] chlorination,[4] and bromination.[4] No work has been reported on the direct mercuration of *p*-cymene so this method of attack has been used in this work.

Mercury derivatives of *p*-cymene have been described in which the mercury is adjacent to the methyl group. These are prepared by treating 2-bromo-*p*-cymene (1-methyl-2-bromo-4-isopropylbenzene) with sodium amalgam to form 2-di-*p*-cymylmercury, from which the chloride, bromide, and iodide have been prepared.[5] Whitmore and Sobatzki[6] prepared the 2-*p*-cymylmercuric chloride from the 2-sulfinate and then prepared the 2-di-*p*-cymylmercury by treating with sodium iodide in alcoholic solution.

In the direct mercuration of *p*-cymene, two mono-mercurated derivatives are possible; the 2-*p*-cymylmercuric salts previously described and the 3-*p*-cymylmercuric salts which have not been prepared previously. A number of polymercurated compounds can be formed.

Experimental

Cymene was purified by shaking commercial spruce turpentine with five small portions of concentrated sulfuric acid, washing with dilute sodium carbonate solution, then with water, and drying. On fractionation, the fraction boiling 176–176.5° was used. Inorganic chemicals used were of analytical grade.

Method of Analysis.—The method of Tabern and Shelberg[7] using fuming sulfuric acid and 30% hydrogen peroxide was used.

Method of Mercuration.—Eighty-four grams (0.26 mole) of mercuric acetate, 80 cc. of ethyl alcohol, 30 cc. of glacial acetic acid, and 175 cc. (1.12 moles) of cymene are vigorously stirred on an oil-bath for eight to ten hours, the temperature of the reaction mixture not exceeding 135°. This has been found to be the maximum allowable temperature without having excessive polymercuration occur. The acetic acid is essential at the beginning of the reaction to prevent decomposition of the mercuric acetate, and is gradually removed by esterification during the reaction.

The reaction products are steam distilled until the rate of cymene removal becomes small. A concentrated alcoholic solution of 29 g. (0.26 mole) of calcium chloride is added to

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[1] Phillips, THIS JOURNAL, **46**, 686–94 (1924).

[2] LeFèvre, *J. Chem. Soc.*, 1501–2 (1934).

[3] Andrews, *Ind. Eng. Chem.*, **10**, 453–6 (1918).

[4] LeFèvre, *J. Chem. Soc.*, 977–84 (1933).

[5] Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., New York, 1921.

[6] Whitmore and Sobatzki, THIS JOURNAL, **55**, 1128–35 (1933).

[7] Tabern and Shelberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 401 (1932).

the contents of the flask to convert the cymylmercuric acetates to the chlorides, which are quite insoluble in the remaining cymene. The steam distillation is then continued until all the cymene and alcohol are removed. The mercurated cymene is filtered off and dried, weight of product about 70 g.

Separation of Poly- from Mono-mercurated Cymene.—The mercurated cymene is extracted with a hot solution of 50% alcohol–50% acetone, filtered, and the residue washed repeatedly with hot alcohol. The weight of residue is 5–10 g.

Anal. Calcd. for $C_{10}H_{12}(HgCl)_2$: Hg, 66.3. For $C_{10}H_{11}(HgCl)_3$: Hg, 71.6. Found: Hg, 70.8.

The polymercurated cymene is a white amorphous solid, insoluble in all solvents tried, and decomposes without melting. A low temperature and efficient agitation to keep the mercuric acetate in suspension minimizes the formation of polymercurated compounds.

The filtrate from the extraction contains the monomercurated cymene. Water is added to the solution, the compounds precipitated out, filtered and dried. The weight of product is 62 g.; m. p. 127°. The yield based on total mercuric acetate is 64% to mono-mercurated and 13% to poly-mercurated compounds.

Separation of Isomeric Mercurated Cymene.—Ten grams (0.027 mole) of the product is added to 250 cc. of alcohol containing 50 g. (0.33 mole) of sodium iodide and the solution refluxed overnight.[6] The solution is cooled and the separated crystals filtered off (weight 4 g.), washed several times with hot water to remove sodium iodide, dissolved in hot alcohol and recrystallized to constant melting point for the most insoluble fraction. The melting point 133.5–134.0° shows this to be 2-di-*p*-cymylmercury. All melting points were taken with Anschütz type thermometers and corrected for emergent stem.

2-*p*-Cymylmercuric Chloride.—The 2-di-*p*-cymylmercury is treated with a hot alcoholic solution of mercuric chloride, and the 2-*p*-cymylmercuric chloride thrown out with water. White, needle-like crystals melting at 154–154.5° are obtained. Whitmore and Sobatzki[6] give 155°. The solubility of the compound is as follows, in g. per 100 cc. of solution at 25°: ethanol, 0.385; isopropanol, 0.593; commercial methyl ethyl ketone, 2.19; acetone, 7.25.

Anal. Calcd. for $C_{10}H_{13}HgCl$: Hg, 54.3. Found: Hg, 54.5.

2-Di-*p*-cymylmercury.—Two grams of 2-*p*-cymylmercuric chloride is refluxed with 10 g. of sodium iodide in 100 cc. of alcohol, giving 1.54 g. of 2-di-*p*-cymylmercury when water is added to the solution. This is crystallized to constant melting point from alcohol; melting point 133.5–134.0°; Whitmore and Sobatzki[6] give 133–134°.

Anal. Calcd. for $(C_{10}H_{13})_2Hg$: Hg, 43.0. Found: Hg, 42.7.

3-*p*-Cymylmercuric Chloride.—The alcoholic filtrate after the separation of the 2-di-*p*-cymylmercury is slowly diluted with water. The colloidal suspensions encountered may be coagulated by heating the solutions and gradually cooling. The crystals are filtered off and recrystallized from alcohol, retaining the fractions melting below 70°, consisting mainly of 3-di-*p*-cymylmercury. These are dissolved in a hot alcoholic solution of mercuric chloride, water is slowly added and crystal fractions taken. The first fractions melt at 177–178° and on further recrystallization give white, needle-like crystals melting at 177.5–178.0°. This is pure 3-*p*-cymylmercuric chloride.

Anal. Calcd. for $C_{10}H_{13}HgCl$: Hg, 54.3. Found: Hg, 54.1.

3-Di-*p*-cymylmercury.—1.37 g. of 2-*p*-cymylmercuric chloride is refluxed overnight with 10 g. of sodium iodide in 75 cc. of alcohol. The product is thrown out of solution by the very gradual addition of water. Recrystallization from alcohol gives white, needle-like crystals melting at 102–102.2°.

Anal. Calcd. for $(C_{10}H_{13})_2Hg$: Hg, 43.0. Found: Hg, 42.9.

Melting Point–Composition Diagram.—To pure 2-*p*-cymylmercuric chloride are added small portions of pure 3-*p*-cymylmercuric chloride dissolved in acetone. Upon evaporation to dryness, the melting point is determined for this known composition. This is repeated with the further addition of 3-*p*-cymylmercuric chloride until the minimum point in the melting point curve is reached. The other portion of the curve is determined in a similar manner starting with pure 3-*p*-cymylmercuric chloride. The results are shown in Fig. 1. The range of the melting point is indicated by the size of data points, being less than one degree in most cases.

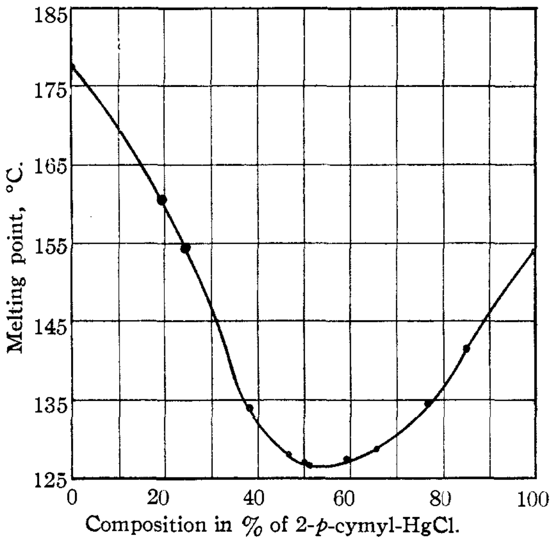

Fig. 1.—Melting point–composition diagram.

Distillation of 2- and 3-*p*-Cymylmercuric Chloride.—The mixture of 2- and 3-*p*-cymylmercuric chloride in the mercuration can be distilled at atmospheric pressure with but slight decomposition of the boiling liquid. A small amount of mercury comes over at atmospheric pressure but is reduced to a trace when distillation is conducted at reduced pressure. The distillate melts at 128–129°.

Discussion

It was not found possible to separate the 2-*p*-cymylmercuric chloride from the 3-*p*-cymylmercuric chloride by fractional crystallization in any solvent used (ethyl alcohol, acetone, methyl ethyl ketone, toluene, and mixtures of these). The separation resulted in small amounts of pure 2-*p*-cymylmercuric chloride being separated from the minimum melting mixture (126–127°). It was found that by conversion into the dicymylmercury compounds the relative solubilities were greatly changed. The 2-di-*p*-cymylmercury is much less soluble than the 2-*p*-cymylmercuric chloride, while the 3-di-*p*-cymylmercury is more soluble than the 2-*p*-cymylmercuric chloride. This causes a greater difference in solubility between the 2- and 3-derivatives, so that the 2-di-*p*-cymylmercury was almost completely removed when the alcoholic sodium iodide solution cooled. No separation was effected by simple distillation.

The orientation in the *p*-cymene molecule has been the subject of some discussion.[4] Early workers reported that the entering group went into the 2-position. However, there is a very close agreement in the physical properties for the 2- and 3-derivatives, other than mercury derivatives, so that the two can easily be confused. The correct relationships have been shown for sulfonation by Phillips[1] and LeFèvre,[2] and for nitration, chlorination and bromination by LeFèvre.[4] The orientation in the present work can be found from the data given in Fig. 1. The mixture of mono isomers melted at 127° and as this was fractionally crystallized to give pure 2-*p*-cymylmercuric chloride and the minimum melting mixture, this melting point corresponds to approximately 60% of 2-*p*-cymylmercuric chloride and 40% of 3-*p*-cymylmercuric chloride. These figures were approximately checked by a weight balance when this mixture was separated. These results may be compared with the data obtained for other substitution reagents.

Method	2-sub., %	3-sub., %	Ref.
Sulfonation	90	5	2
	85	15	1
Nitration	87	. .	4
Chlorination	63	. .	4
Bromination	57	. .	4
Mercuration	60	40	

This comparison shows that mercuration produces a larger proportion of the 3-derivative than any of the reactions previously investigated.

This work will be continued for the purpose of identifying and synthesizing derivatives.

Summary

1. *p*-Cymene has been directly mercurated with a 64% yield of mono-mercurated compounds.

2. A method of separation of the two mono derivatives is given, based on the great difference in solubility of the di-cymylmercury compounds.

3. 3-Di-*p*-cymylmercury and 3-*p*-cymylmercuric chloride are identified.

SEATTLE, WASHINGTON RECEIVED MARCH 11, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Heat Capacities and Entropies of Organic Compounds. I. A Thermodynamic Temperature Scale in Terms of the Copper–Constantan Thermocouple from 12 to 273°K.[1]

BY J. G. ASTON, EUGENE WILLIHNGANZ AND GEORGE H. MESSERLY

Introduction

For measurements in progress in this Laboratory of heat capacities from 11°K. to room temperatures, it was necessary to establish a temperature scale over this range. As Giauque and coworkers[2a,b] had obtained satisfactory results in terms of the copper–constantan couple over this same range, it was decided to establish the scale on essentially the same terms. The present paper contains a portion of the results of the comparison of copper–constantan couples with a helium thermometer.

Recently Southard and Andrews[3] have calibrated a copper–constantan thermocouple against a resistance thermometer down to 85°K. They used constantan wire which was quite different from that of G., B. and S.,[2a] but which was so like our wire that the difference corresponded to only 0.9° at 85°K. Experience has shown that most of the constantan wire now available is quite similar to that of S. and A.[3] and to our own. A

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(1) Submitted by Eugene Willihnganz in partial fulfilment of the requirements for the Ph.D. degree.

(2) (a) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2353 (1927); (b) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

(3) Southard and Andrews, *J. Franklin Inst.*, **207**, 323 (1929).