## Summary

The following reduction products have been isolated from the catalytic reduction of β-acetylpyridine: ethylpiperidine, two diastereoisomeric forms of 3-piperidylmethylcarbinol and β-pyridylmethylcarbinol.

A group of new local anesthetics has been prepared from these reduction products. The data which are presented show that these anesthetics, particularly those derived from β-pyridylcarbinol, possess unusual and interesting pharmacological properties.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SWARTHMORE COLLEGE]

# Organic Selenium Compounds. II. A New Type of Aromatic Selenium Halide

BY DUNCAN G. FOSTER

## Introduction

There are, at the present time, four types of organic selenium halides described in the literature: (1) RSeX, in which R is aromatic; (2) $RR'SeX_2$, in which R and R′ are either di-aryl or alkyl-aryl; (3) $R_3SeX$, in which R is aryl only; and (4) $RSeX_3$. The only reported case of this last type is Shaw and Reid's ethyl selenium tribromide, $C_2H_5SeBr_3$,[1] no aromatic compounds of this type and no analogous compounds in which X is another halogen than bromine having been prepared. This list does not include halogen acid addition compounds, such as $RSeO_2H{\cdot}HCl$, but only true halides.

In the course of an investigation of the reactions of the first three types of halides mentioned, to be reported in a later paper, the formation of phenyl selenium tribromide, the first example of an aromatic compound of the last-mentioned class, has been observed, the analogous phenyl selenium trichloride, $C_6H_5SeCl_3$, has also been prepared, and an unsuccessful attempt made to prepare phenyl selenium triiodide, which is too unstable to exist under ordinary conditions. The various synthetic methods employed with these compounds and some of their reactions indicate that they are halogen salts of a selenonium base, $C_6H_5Se(OH)_3$, the ortho form of ordinary benzene seleninic acid, $C_6H_5SeOOH$.

## Outline and Discussion of the Present Investigation

(1) **Phenyl selenium tribromide,** $C_6H_5SeBr_3$, was first observed as a by-product formed during the preparation of phenyl ethyl selenium dibromide, $(C_6H_5)(C_2H_5)SeBr_2$, from phenyl ethyl selenide, $(C_6H_5)Se(C_2H_5)$

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[1] Shaw and Reid, THIS JOURNAL, **48**, 525 (1926).

and bromine by the method of Edwards, Gaythwaite, Kenyon and Phillips.[2] The equation for this reaction is

$$(C_6H_5)(C_2H_5)Se + Br_2 = (C_6H_5)(C_2H_5)SeBr_2 \qquad (1)$$

When the phenyl ethyl selenide was that which had been prepared by regeneration from phenyl selenium monobromide, $C_6H_5SeBr$, by means of magnesium and ethyl bromide (the details for this reaction are given in the Experimental Part of this paper) and when the reaction mixture was allowed to become warm from the heat of the reaction, a second product was formed, which appeared from the recrystallizing solvent as rose colored needles and was identified as $C_6H_5SeBr_3$. The explanation of its formation is probably as follows. The investigators mentioned above have shown that phenyl ethyl selenium dibromide decomposes above its melting point (86°) to phenyl selenium bromide and ethyl bromide.

$$(C_6H_5)(C_2H_5)SeBr_2 = C_6H_5SeBr + C_2H_5Br \qquad (2)$$

I have observed that this reaction also takes place slowly at room temperature and fairly rapidly even at the boiling point of ether. Thus, if, during the bromination of phenyl ethyl selenide, the mixture is not cooled, some $C_6H_5SeBr$ will be formed. This can then react directly with bromine to form $C_6H_5SeBr_3$.

$$C_6H_5SeBr + Br_2 = C_6H_5SeBr_3 \qquad (3)$$

It is also possible that there was still some $C_6H_5SeBr$ in the solution used, which had not been acted upon by the magnesium, and this would also be converted to $C_6H_5SeBr_3$.

Assuming that reaction (3) really took place, I was able to prepare phenyl selenium tribromide in good yield by treating an ether solution of $C_6H_5SeBr$ with the calculated quantity of free bromine.

(2) **Phenyl Selenium Trichloride,** $C_6H_5SeCl_3$.—No chlorine compounds of this type have been prepared, but they should, since the bromine analog was found to be so stable, be easily capable of existence and of preparation by one of three different methods: (a) by the pyrolytic decomposition of phenyl ethyl selenium dichloride and treatment of the product with chlorine

$$(C_6H_5)(C_2H_5)SeCl_2 + (\text{heat}) = (C_6H_5SeCl) + C_2H_5Cl \qquad (4)$$

$$(C_6H_5SeCl) + Cl_2 = C_6H_5SeCl_3 \qquad (5)$$

(b) by the displacement with chlorine of the bromine in $C_6H_5SeBr_3$

$$2C_6H_5SeBr_3 + 3Cl_2 = 2C_6H_5SeCl_2 + 3Br_2 \qquad (6)$$

and (c) by the action of chlorine on $C_6H_5SeBr$

$$2C_6H_5SeBr + 3Cl_2 = 2C_6H_5SeCl_3 + Br_2 \qquad (7)$$

All of these reactions were tried and all gave good yields of the rather unstable, pale yellow solid, $C_6H_5SeCl_3$.

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(2) Edwards, Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 2302 (1928).

A fourth possible reaction, that of thionyl chloride on benzene seleninic acid, failed to give the same product

$$C_6H_5SeOOH + 2SOCl_2 = C_6H_5SeCl_3 + HCl + 2SO_2 \qquad (8)$$

(3) **Attempted Preparation of Phenyl Selenium Triiodide, $C_6H_5SeI_3$.**—Iodides of the type $R_2SeI_2$ have been described by Edwards, Gaythwaite, Kenyon and Phillips,[2] and those of the type $R_3SeI$ by Leicester and Bergstrom.[3] Both were prepared by the action of soluble iodide (KI) on water solutions of other halides. Potassium iodide solution was therefore added to a water solution of $C_6H_5SeBr_3$. A brown precipitate formed which decomposed within ten seconds leaving an oil which appeared to contain free iodine. Potassium iodide also reacted with $(C_6H_5)(C_2H_5)SeBr_2$, but the product was a dark oil with the odor of phenyl ethyl selenide. Free iodine was without action on organic solutions of $C_6H_5SeC_2H_5$. It seemed obvious from these experiments that phenyl selenium triiodide can have no more than a transient existence under ordinary laboratory conditions.

(4) **Properties of the Trihalides.**—Phenyl selenium tribromide, m. p. 105–106°, is a rose-red solid crystallizing in circular clumps of fine needles. It is moderately soluble in all the ordinary organic solvents except ether, petroleum ether and carbon disulfide, in which it is sparingly soluble. The solutions are brownish-red, evolve bromine at the boiling point, and, on long standing, hydrogen bromide. The residue, after removal of the solvent, is a dark oil not identified. The dry substance decomposes slowly on standing, its melting point dropping, but no definite product has been identified. The substance is very soluble in water to give a *completely colorless* solution, from which all the bromine can be precipitated by silver nitrate. It is completely stable in water. A solution which stood for more than a week evolved no hydrogen bromide, but all the water evaporated, and unchanged $C_6H_5SeBr_3$ remained. The compound has a faint disgusting odor.

Phenyl selenium trichloride is a pale yellow solid, m. p. 133–144°, probably white when perfectly pure, crystallizing in short fat prisms. It is much less stable than the tribromide, becoming gummy in a few minutes with loss of hydrogen chloride and chlorine in contact with the air. It can be kept under concd. hydrochloric acid or in a desiccator in an atmosphere of hydrogen chloride gas or of chlorine. Its solubility is similar to the tribromide, organic solutions being pale yellow and the water solution colorless. It also apparently does not hydrolyze. A small quantity on a watch glass stood in contact with water for several days. At first it dissolved until saturated. The residue changed to an oil and an oil was left when the water evaporated, the same behavior it exhibited when standing alone in a desiccator. There was no sign of $C_6H_5SeOOH$, which would be expected to be the hydrolysis product and which is rather spar-

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(3) Leicester and Bergstrom, THIS JOURNAL, 53, 4433 (1931).

ingly soluble. The trichloride is almost odorless and all three chlorine atoms can be precipitated by silver nitrate from water solution.

These trihalides might be expected to be the acyl halides of the ortho form of benzene seleninic acid, $C_6H_5Se(OH)_3$. They do not, however, behave like acyl halides of an acid as strong as benzene seleninic, nor do they seem to be formed by reactions which would be expected to give benzene seleninyl chloride. It can be said, at least, that the action of thionyl chloride and of phosphorus pentachloride on $C_6H_5SeOOH$ and on $C_6H_5SeOONa$, respectively, does not yield benzene selenium trichloride, but gives mixtures of solids melting over a rather broad range much higher than the melting point of $C_6H_5SeCl_3$ (in the neighborhood of 170°). Jackson[4] also treated *benzyl* seleninic acid with phosphorus pentachloride, but he did not investigate the product, so there is no way of knowing whether or not it was a trichloride. Although we have seen that neither trihalide hydrolyzes in water, as acyl halides would be expected to do, yet treatment of either with one equivalent of sodium hydroxide does produce benzene seleninic acid

$$C_6H_5SeX_3 + 3NaOH = C_6H_5SeOOH + H_2O + 3NaX \qquad (9)$$

It seemed possible that solutions of benzene seleninic acid might contain $C_6H_5Se(OH)_3$, formed by the addition of one molecule of water to the acid, which would then ionize as a base to give $C_6H_5Se^{+++}$ and $3\ OH^-$. If this were true, it should be possible to prepare the trihalides by the action of aqueous hydrohalogen acids on benzene seleninic acid. Some difficulty was presented by the fact that these halides are so very soluble, while the acid is only sparingly so. However, by using a large excess of ammonium bromide to provide a common ion for mass action effect, in the one case, and in the other by saturating the solution with hydrogen chloride gas, good yields of both trihalides have been obtained from $C_6H_5SeOOH$ solution and aqueous hydrogen bromide or hydrogen chloride.

$$C_6H_5SeOOH + 3HX = C_6H_5SeX_3 + 2H_2O \qquad (10)$$

This was also the manner in which Shaw and Reid[1] obtained ethyl selenium tribromide. The inference is that ortho benzene seleninic acid is a base, and if this is true the well-known acid addition products of this acid, like $C_6H_5SeOOH{\cdot}HNO_3$, would more properly be written as true *salts*, with a molecule of water of crystallization, *e. g.*, $C_6H_5SeONO_3{\cdot}H_2O$, or as *basic salts*, $C_6H_5Se(NO_3)(OH)_2$.

## Experimental Part

### I. Materials

**Phenyl Ethyl Selenide,** $C_6H_5SeC_2H_5$.—This substance was prepared by the method described in the first paper of this series,[5] and also by the Grignard reaction, without isolating selenophenol, as follows. $C_6H_5SeMgBr$ was made from 157 g. of bromobenzene,

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[4] Jackson, *Ann.*, **179**, 14 (1875).

[5] Foster and Brown, THIS JOURNAL, **50**, 1184 (1928).

24 g. of magnesium and 79 g. of selenium powder in the usual manner.[6] To the ether solution obtained was added from a dropping funnel 156 g. of ethyl iodide or 109 g. of ethyl bromide mixed with an equal volume of absolute ether. The mixture was refluxed on a water-bath for one hour, then decomposed with ice and hydrochloric acid in the usual manner and the ether layer separated. The solution was washed with a total of 60 g. of sodium hydroxide in 200 cc. of water, in three portions. By acidification and extraction with ether, some selenophenol could be recovered from this extract. The main ethereal solution was dried over calcium chloride, the ether distilled off and the residue distilled. The fraction boiling at 215–216° was collected as phenyl ethyl selenide. There were obtained 85 g. or 46% of the theoretical amount, also 25 g. of products boiling between 300 and 305°, which was mainly diphenyl selenide, and from the alkaline extracts 16 g. of selenophenol. The total yield of all products was 77%. Since all the products were of use, this compares favorably with the other method mentioned and saves much time.

$$C_6H_5SeMgBr + C_2H_5Br = C_6H_5SeC_2H_5 + MgBr_2 \qquad (11)$$

**Phenyl Ethyl Selenium Dibromide,** $(C_6H_5)(C_2H_5)SeBr_2$, was prepared by the action of bromine on phenyl ethyl selenide.[2] When this compound was recrystallized from ether it was reddish-yellow and had a melting point of 81°. From carbon tetrachloride–petroleum ether mixture it gave lemon yellow prisms, m. p. 81–83°, if melted slowly, giving a red liquid that did not solidify on cooling. If heated rather rapidly it melted sharply at 86° to give a yellow liquid that solidified on cooling. The sample investigated by Edwards, Kenyon, Gaythwaite and Phillips must have contained a small amount of the decomposition product, $C_6H_5SeBr$, accounting for the slightly lower melting point (81°) and reddish color which they report.

This compound was analyzed by dissolving in dilute nitric acid (5 cc. of concd. in 100 cc. of water) and precipitating with silver nitrate, and also by fusion in a Parr bomb.

*Anal.* I ($HNO_3$ method) Calcd. for 1 atom Br in $C_8H_{10}SeBr_2$: 23.18. Found: Br, 22.69. II (Parr bomb) Calcd. for total Br in $C_8H_{10}SeBr_2$: 46.36. Found: Br, 46.32.

These results show that only one of the two bromine atoms dissociates in water.

**Phenyl Ethyl Selenium Dibromide from Phenyl Selenium Monobromide.**—Since phenyl ethyl selenium dibromide decomposes on standing (Reaction 2), it was desirable to find a satisfactory method of recovering it. This was readily accomplished as follows: 25 g. of the decomposition product, $C_6H_5SeBr$, was dissolved in 100 cc. of absolute ether and 15 g. (50% excess) of ethyl bromide added; 2.5 g. of magnesium powder and a pinch of magnesium–copper couple were dropped in. After gentle warming, the ether refluxed spontaneously. When the reaction had subsided, the mixture was refluxed for two hours, until the dark red color had disappeared. It was then shaken with an equal volume of ice and saturated ammonium chloride solution, separated and dried over calcium chloride. When a few drops of this solution were evaporated on a watch glass, a liquid with the characteristic odor of phenyl ethyl selenide remained

$$C_6H_5SeBr + Mg + C_2H_5Br = C_6H_5SeC_2H_5 + MgBr_2 \qquad (12)$$

This ether solution was filtered and treated with a slight excess of bromine in the usual manner. The resultant yellow solid was filtered off and recrystallized from carbon tetrachloride–petroleum ether mixture (3–1); 3 g. of $C_6H_5SeBr_3$ and 32 g. or 89% of the theoretical quantity of $(C_6H_5)(C_2H_5)SeBr_2$ were obtained; m. p. of the latter, 85–86°. Mixed m. p. with a sample made as described in the previous paragraph, 84–85°.

**Phenyl ethyl selenium dichloride,** $(C_6H_5)(C_2H_5)SeCl_2$, was prepared by the method described in the earlier paper.[7]

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(6) Taboury, *Ann. chim. phys.*, **15**, 5 (1908).

(7) Ref. 5, p. 1187.

**Benzene seleninic acid** was prepared as described by Pyman.[8]

**Phenyl selenium bromide,** $C_6H_5SeBr$, results from the decomposition of phenyl ethyl selenium dibromide on standing, boiling for five to eight hours in ether or carbon tetrachloride, or heating just above the melting point.[2]

### II. Preparation of Phenyl Selenium Trihalides, $C_6H_5SeX_3$

**1. Phenyl Selenium Tribromide,** $C_6H_5SeBr_3$.—(a) The substance appeared as a by-product in the preparation of phenyl ethyl selenium dibromide described in the foregoing section; rose-red needles, m. p. 105–106°. Analysis was accomplished simply by dissolving a sample in water and 5 cc. of dilute nitric acid and precipitating the bromine with silver nitrate.

*Anal.* Calcd. for $C_6H_5SeBr_3$: Br, 60.0. Found: Br, 60.4.

(b) **From Phenyl Selenium Monobromide.**—Thirteen grams of $C_6H_5SeBr$ was dissolved in 50 cc. of dry ether and 9 grams of bromine dissolved in 20 cc. of carbon disulfide added slowly from a dropping funnel to the mixture cooled in an ice-water bath. A red solid precipitated, which was filtered off, washed with dry ether and sucked dry on the funnel; m. p. 105–106°; yield, 15.5 g. or 70% of the theoretical; mixed m. p. with sample described in the previous paragraph, 105–106°.

(c) **From Benzene Seleninic Acid and Aqueous Hydrogen Bromide.**—110 cc. of the mother liquor obtained in preparing $C_6H_5SeOOH$ from its hydronitrate was used in this reaction.[8] It contained about 4 g. of $C_6H_5SeOOH$ and 1 equivalent of ammonium nitrate; 70 g. of ammonium bromide was dissolved in it and the solution filtered free from dirt. Thirty cc. (90% excess) of constant-boiling hydrobromic acid was now added slowly. At first a yellow precipitate appeared, which rapidly turned red. The solid was filtered off, dried in a desiccator and recrystallized from carbon tetrachloride; 5.2 g. was obtained. Upon adding 50 cc. more hydrobromic acid to the filtrate, 2.8 g. more of solid was obtained; total yield, 95% of the theoretical; m. p. 105–106°; mixed m. p. with $C_6H_5SeBr_3$, 105–106°.

### 2. Phenyl Selenium Trichloride, $C_6H_5SeCl_3$

(a) **From Phenyl Selenium Tribromide.**—Five grams of $C_6H_5SeBr_3$ was dissolved in 50 cc. of dry ether and chlorine bubbled in from a tank until all the color of the liberated bromine had disappeared. Much heat was developed and the ether boiled. On cooling a yellowish granular solid came out, which was filtered off, washed rapidly with dry ether and dried in a desiccator. It was recrystallized by dissolving in boiling benzene, then cooling in ice and saturating with dry hydrogen chloride, or, by adding a little carbon disulfide to the solution, the solid slowly crystallized out in short, fat prisms without adding hydrogen chloride, but the yield was smaller; yield, 3 g. of crude material, or 91% of the theoretical; m. p. 133–134° (dec.).

Analyses were made by the same method used for the tribromide, but since the trichloride is so unstable, it was always gummy by the time it had been transferred to the weighing bottle in which it was weighed, and the analyses were always somewhat too low.

*Anal.* Calcd. for $C_6H_5SeCl_3$: Cl, 40.57. Found: Cl, 39.45, 39.47.

(b) **From Phenyl Selenium Monobromide.**—0.7 g. of $C_6H_5SeBr$ was dissolved in about 10 cc. of dry ether in a test-tube, cooled in ice and chlorine bubbled in until saturated. A yellowish granular solid appeared. On attempting to filter, the ether caught fire spontaneously as soon as it came in contact with the air and most of the product was destroyed. About 0.2 g. was saved; m. p. 133–134° (dec.); mixed m. p. with sample obtained as in above paragraph, 133–134° (dec.).

(c) **From Benzene Seleninic Acid and Aqueous Hydrochloric Acid.**—Ten grams of $C_6H_5SeOOH$ was dissolved in 120 cc. of water to make an approximately saturated

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[8] Pyman, *J. Chem. Soc.*, **115**, 166 (1919).

solution at 0°, cooled in an ice-bath and saturated with hydrogen chloride gas. Toward the end of the reaction a solid came out, which was rapidly filtered on a Buchner funnel, using a mat made of the solid instead of filter paper, and refiltering the solid that went through while the mat was being prepared. Decomposition was checked by cooling all the filtering apparatus in ice water before using. The product was washed with cold concd. hydrochloric acid and dried in a desiccator over sulfuric acid. The yield was 23 g. or upwards of 200%, but the solid was later found to be full of water saturated with hydrochloric acid, which could not be removed by further drying. From the results of a rough chlorine analysis made on this wet substance, the yield was calculated to be approximately 80% of the theoretical. Five grams was dissolved in hot benzene and separated from the water by decanting through a filter wet with benzene, then saturated with hydrogen chloride and cooled, filtered and dried; m. p. 134°; mixed m. p. with sample described above, 133–134°, both with decomposition.

*Anal.* Calcd. for $C_6H_5SeCl_3$: Cl, 40.57. Found: Cl, 39.44.

(d) **From Phenyl Ethyl Selenium Dichloride.**—Twenty-three grams of phenyl ethyl selenide was converted in a flask to $(C_6H_5)(C_2H_5)SeCl_2$[5] and the ether and excess chlorine removed by pumping. The flask was heated to 80° in a Wood's metal bath. Effervescence occurred and the escaping gas was collected over water, at 25° and 760 mm. When effervescence had ceased, 2050 cc. of gas had been collected. The gas had the characteristic odor of ethyl chloride and gave a white precipitate with alcoholic silver nitrate. This volume of gas corresponds to about 6.5 g. of ethyl chloride or 81.4% of the calculated quantity, based on 23 g. of phenyl ethyl selenide. A yellow oil remained in the flask, which was, or contained, presumably, $C_6H_5SeCl$, but no attempt was made to isolate this compound, because of the belief that it might be unstable and the supply of material was limited. It was dissolved in 100 cc. of dry ether and saturated cold with chlorine. A yellowish, granular solid came out which was filtered off and recrystallized as described above; m. p. 133–134° (dec.); mixed m. p. with sample described above, 133–134° (dec.).

### III. Treatment of Trihalides with Sodium Hydroxide

(1) **$C_6H_5SeBr_3$.**—Eight grams of $C_6H_5SeBr_3$ was added to a solution of 3.4 g. (3 moles) of sodium hydroxide dissolved in 25 cc. of water. Much heat was developed. The solution was filtered free from a trace of oily material and allowed to cool. A white crystalline solid came out which was filtered off and dried; m. p. 121–122° (m. p. $C_6H_5SeOOH$, 122–124°); yield, 3.5 g. or 87% of the theoretical. No $C_6H_5SeOOH$ was at this time available, so part of the solid was dissolved in concd. nitric acid and warmed on the steam-bath until it was colorless. On cooling and seeding with a crystal of $C_6H_5SeOOH \cdot HNO_3$, prepared by the oxidation of diphenyl diselenide with nitric acid, the whole set to a white crystalline mass. It was filtered off, washed with cold water and dried in a desiccator; m. p. 110–112°; mixed m. p. with $C_6H_5SeOOH \cdot HNO_3$, 110–112°.

(2) **$C_6H_5SeCl_3$.**—Eight and a half grams of the trichloride was treated with 4 g. of sodium hydroxide exactly as described above: 8 g. or 79% of the theoretical was obtained; m. p. 121–122°; mixed m. p. with sample described above, 121–122°.

The trihalides decompose when heated above their melting points, giving off hydrohalogen acid and leaving a dark oil which is uncrystallizable but reacts with cold water to give a very slightly soluble white crystalline solid, m. p. 162°, without decomposition. This compound is under investigation.

## Summary

1. Phenyl selenium tribromide and phenyl selenium trichloride have been prepared by a variety of methods and their properties are described. Phenyl selenium triiodide could not be prepared.

2. The methods of preparation and reactions of these substances indicate that they are halogen salts of the hypothetical ortho benzene seleninic acid, $C_6H_5Se(OH)_3$, and that this latter compound has basic properties.

SWARTHMORE, PENNSYLVANIA

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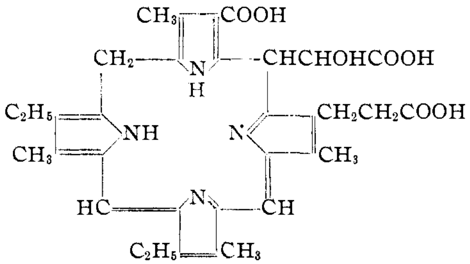
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

# Studies in the Chlorophyll Series. X. The Esters of Chlorin *e*

BY J. B. CONANT AND K. F. ARMSTRONG[1]

The structure of chlorin *e* has been established by a variety of transformations as dihydroisorhodoporphyrin glycolic acid (Formula I).[2]



I

When esterified with diazomethane, hydrochloric acid and methyl alcohol, or by the action of dimethyl sulfate on the potassium salt, a trimethyl ester is formed. The identity of these esters has been investigated by converting them into the copper and zinc complex salts and taking mixed melting points. The results indicated that all the esters are identical. The complex metal salts of the esters of chlorin *e* are very suitable for the characterization of these compounds as they have sharp melting points; however, in our opinion all identification by mixed melting points in the chlorophyll series must be accepted with some reservation. Since this work was completed, a paper by Fischer and Siebel[3] has appeared in which the identity of these same esters was concluded from the mixed melting points of the esters themselves, and from their transformations with hydrogen iodide.

On hydrolysis with alkali, the trimethyl ester regenerates chlorin *e*. The saponification was carried out at room temperature and in an atmosphere of nitrogen to avoid the possibility of oxidation. The sole

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(1) Henry Fund Fellow at Harvard University.

(2) THIS JOURNAL, **55**, 795 (1933).

(3) Fischer and Siebel, *Ann.*, **499**, 84 (1932).