

was given (showing that an excess of acetyl chloride was present) the mixture was hydrolyzed by pouring it onto cracked ice containing a small amount of hydrochloric acid. On working up the extract in the customary manner by removing the ether, there remained a liquid with a pronounced camphor-like odor. This distilled between 120 and 125°, with the last portion coming over at about 130°. In order to further characterize this water-insoluble carbinol, it was converted to the corresponding chloride by passing in hydrogen chloride until no more of this gas was absorbed. The methyldiethylchloromethane when distilled in a micro-distillation flask boiled at 115–118°. Its refractive index was 1.4037.

An authentic specimen of methyldiethylcarbinol was prepared from methyl ethyl ketone and ethylmagnesium bromide. It boiled at 120–122°. Treatment with hydrogen chloride gave the methyldiethylchloromethane boiling at 115–118°, and having a refractive index of 1.4034 as determined under the same conditions used for the unknown chloride.

The similarity of the carbinols and the chlorides obtained from them leaves no doubt as to the formation of methyldiethylcarbinol from magnesium diethyl and acetyl chloride.

Summary

Magnesium diethyl prepared by heating magnesium powder with mercury diethyl in the presence of mercuric chloride as a catalyst is a solid and not a liquid. When treated with acetyl chloride it gives methyldiethylcarbinol and not trimethylcarbinol as previously reported.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

A NEW PROCEDURE FOR THE QUANTITATIVE ESTIMATION OF SELENIUM IN ORGANIC COMPOUNDS

BY EDWIN H. SHAW, JR., AND E. EMMET REID

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Introduction

During the recent investigation of some organic selenium compounds the authors¹ felt the need of a simple and direct method of estimating selenium. Most of the methods described in the literature depend on a Carius tube combustion which is slow and tedious. As combustion with sodium peroxide in the Parr bomb has been so successful with sulfur,² and has supplanted the Carius method with halogens,³ it seemed advisable to adapt this method to the determination of selenium. The only novelty is in the use of the fusion method. Two commonly used methods have

¹ Shaw and Reid, *THIS JOURNAL*, **48**, 520 (1926).

² Parr, *ibid.*, **30**, 768 (1908).

³ Lemp and Broderson, *ibid.*, **39**, 2069 (1917).

been employed for the determination of the selenium in the solution of the melt.

Historical

Siemens⁴ determined selenium in ethyl selenomercaptan by passing its vapors over hot copper oxide and noting the change in weight, $\text{CuO} \rightarrow \text{CuSe}$. Michaelis and Röhmer⁵ heat the compound in a bomb tube with fuming nitric acid, reflux the product with excess hydrochloric acid to remove the nitric acid, and precipitate elementary selenium from the resultant solution with sodium sulfite. Bauer⁶ describes a similar process. Lyons and Shinn⁷ modify the elimination of the nitric acid by evaporating the solution to dryness with the addition of silver nitrate or zinc nitrate to prevent loss of selenious acid. The product is dissolved in dilute hydrochloric acid, and either titrated with thiosulfate or precipitated with sodium sulfite. Frerichs⁸ oxidizes in the same way but converts the selenium into silver selenite, and determines silver volumetrically as a measure of the selenium present, while Becker and Meyer⁹ weigh the silver selenite formed. Wrede¹⁰ burns the compound in oxygen in the presence of platinum as a catalyst, and titrates the selenious acid formed with centi-normal sodium hydroxide, sodium acid selenite being neutral to methyl orange.

Results

The procedure which was arrived at after many variations of the conditions, and which gave satisfactory results with all the compounds tried, was as follows. Mix the weighed sample, 0.2 to 0.4 g., with 0.4 g. of cane sugar, 0.2 g. of potassium nitrate and 14 g. of sodium peroxide and spread a thin blanket of sodium peroxide over the charge. The combustion is made in the usual manner. The melt is dissolved in water, boiled to destroy hydrogen peroxide, cooled, acidified with hydrochloric acid, filtered and diluted to 350 cc. The selenium in this solution is in the form of selenic acid, and is not reduced to the free elementary form by passing sulfur dioxide through the solution. From this solution the selenium may be precipitated by two alternative methods.

1. **Precipitation by Sulfur Dioxide.**—The sulfur dioxide precipitation was first described by Rose.¹¹ This method has the advantage of rapid and complete precipitation, and the disadvantage of possible loss of the

⁴ Siemens, *Ann.*, **61**, 360 (1874).

⁵ Michaelis and Röhmer, *Ber.*, **30**, 2827 (1897).

⁶ Bauer, *Ber.*, **48**, 507 (1915).

⁷ Lyons and Shinn, *THIS JOURNAL*, **24**, 1087 (1902).

⁸ Frerichs, *Arch. Pharm.*, **240**, 656 (1902).

⁹ Becker and Meyer, *Ber.*, **37**, 2551 (1904).

¹⁰ Wrede, *Z. physiol. Chem.*, **109**, 272 (1920).

¹¹ Rose, *Pogg. Ann.*, **113**, 472; *Z. anal. Chem.*, **1**, 73 (1862).

volatile selenium monochloride from the hot solution.¹² This loss can be reduced by shortening the time of heating the selenic acid with excess hydrochloric acid and by using a rapid stream of sulfur dioxide to bring about the reduction. To the 350 cc. of solution obtained above, 200 cc. of concentrated hydrochloric acid is added, and the solution covered with a watch glass and brought to the boiling point. Sulfur dioxide is passed into the hot, but not boiling, solution until the precipitate has entirely coagulated and the supernatant liquid is clear. The watch glass is rinsed into the solution and 200 cc. of water are added to the solution. The precipitated selenium is filtered through a Gooch crucible, the beaker is rinsed with alcohol to remove traces of adhering selenium and the precipitate is washed with alcohol and finally several times with water. The Gooch crucible is dried at 110–120° and weighed.

2. Precipitation by Potassium Iodide.—The potassium iodide precipitation has been described by Peirce.¹³ By this method the reduction of selenates is not complete unless all the iodine is boiled out of the solution, and in the presence of excess iodine some of it is strongly adsorbed by the selenium. The continued boiling of the solution to expel the iodine may lead to mechanical loss of selenium. Care to prevent too vigorous boiling will prevent this mechanical loss. To the 350 cc. of solution obtained above, 50 cc. of concentrated hydrochloric acid is added and 3 g. of potassium iodide. Boil the solution gently to remove the iodine, replacing the water lost by evaporation. This boiling out requires about two hours. The selenium is then filtered through a Gooch crucible, the beaker is rinsed with alcohol to remove traces of adhering selenium and the precipitate is washed with alcohol and finally several times with water. The Gooch crucible is dried at 110–120° and weighed.

Experimental

The organic selenium compounds used to demonstrate this analytical method are described in a previous paper by the authors.¹ Another compound was used, *p*-nitrophenylselenocyanate prepared by the method of Bauer.¹⁴ As described by Bauer, the compound is not pure, being colored light brown and melting at 136.7–137.3° (corr.). The product can be purified by dissolving in concentrated nitric acid and precipitating by the addition of water. It crystallizes in thin leaves, has a very slight yellowish color and melts sharply at 139.4° (corr.). An additional recrystallization by dissolving in concentrated nitric acid and adding water did not increase the melting point, the product melting simultaneously with the original material at 139.4° (corr.). Recrystallization from water,

¹² Lenher and Kao, *THIS JOURNAL*, **47**, 2454 (1925).

¹³ Peirce, *Z. anorg. Chem.*, **12**, 409 (1896).

¹⁴ Bauer, *Ber.*, **46**, 95 (1913).

in which the compound is sparingly soluble, produced no improvement, the product melting at 139.4° (corr.).

Table I gives results obtained in the analysis of ethyl seleninic acid hydronitrate and *p*-nitrophenylselenocyanate by means of the sulfur dioxide precipitation described above.

TABLE I
ANALYSES BY SO₂ PRECIPITATION

Compound	Weight of sample	Selenium, weight			Selenium, per cent.		
		Theory	Found	Error	Theory	Found	Error
C ₂ H ₅ SeO ₂ H.HNO ₃	0.1917	0.0743	0.0741	-0.0002	38.77	38.65	-0.12
C ₂ H ₅ SeO ₂ H.HNO ₃	.1798	.0697	.0695	-.0002	38.77	38.65	-.12
C ₂ H ₅ SeO ₂ H.HNO ₃	.2741	.1063	.1063	.0000	38.77	38.77	.00
C ₂ H ₅ SeO ₂ H.HNO ₃	.3380	.1310	.1308	-.0002	38.77	38.70	-.07
C ₂ H ₅ SeO ₂ H.HNO ₃	.3986	.1545	.1552	+.0007	38.77	38.94	+.17
C ₂ H ₅ SeO ₂ H.HNO ₃	.3723	.1443	.1436	-.0007	38.77	38.57	-.20
C ₂ H ₅ SeO ₂ H.HNO ₃	.6218	.2411	.2403	-.0008	38.77	38.65	-.12
C ₂ H ₅ SeO ₂ H.HNO ₃	.5666	.2197	.2192	-.0005	38.77	38.69	-.08
O ₂ N—C ₆ H ₄ —SeCN	.2153	.0750	.0746	-.0004	34.85	34.65	-.20
O ₂ N—C ₆ H ₄ —SeCN	.2160	.0753	.0752	-.0001	34.85	34.81	-.04

Table II gives results obtained in the analysis of *p*-nitrophenylselenocyanate by the potassium iodide precipitation described above.

TABLE II
ANALYSES OF *p*-NITROPHENYLSELENOCYANATE BY KI PRECIPITATION

Weight of sample	Theory	Selenium, weight			Selenium, per cent.		
		Found	Error	Theory	Found	Error	
0.2340	0.0815	0.0817	+0.0002	34.85	34.91	+0.06	
.2615	.0911	.0908	-.0003	34.85	34.72	-.13	
.2533	.0883	.0877	-.0006	34.85	34.62	-.23	
.2077	.0724	.0717	-.0007	34.85	34.52	-.33	
.2410	.0840	.0833	-.0007	34.85	34.56	-.29	

Table III is a collection of results previously published,¹ included here to show the applicability of the analytical method to an assortment of compounds. These compounds represent all the solid compounds described in the previous paper.

TABLE III
RESULTS PREVIOUSLY PUBLISHED, PRECIPITATION BY SO₂

Compound	Weight of sample	Selenium, weight			Selenium, per cent.		
		Theory	Found	Error	Theory	Found	Error
C ₂ H ₅ SeO ₂ H.HNO ₃	0.4463	0.1730	0.1721	-0.0009	38.77	38.56	-0.21
C ₂ H ₅ SeO ₂ H.HNO ₃	.4886	.1894	.1896	+.0002	38.77	38.80	+.03
C ₂ H ₅ SeO ₂ H.HCl	.4001	.1783	.1778	-.0005	44.56	44.44	-.12
C ₂ H ₅ SeO ₂ H.HCl	.4198	.1871	.1865	-.0006	44.56	44.42	-.14
C ₂ H ₅ SeBr ₃	.3805	.0866	.0867	+.0001	22.76	22.79	+.03
C ₂ H ₅ SeBr ₃	.4160	.0947	.0945	-.0002	22.76	22.72	-.04
O ₂ S(C ₂ H ₅ SeC ₂ H ₅) ₂	.4376	.2059	.2063	+.0004	47.05	47.14	+.09
	.4601	.2165	.2167	+.0002	47.05	47.10	+.05
C ₂ H ₅ Se—C ₁₄ H ₉ O ₂ —SO ₂ C ₄ H ₉	.4125	.0750	.0763	+.0013	18.19	18.49	+.30
	.3847	.0700	.0701	+.0001	18.19	18.22	+.03

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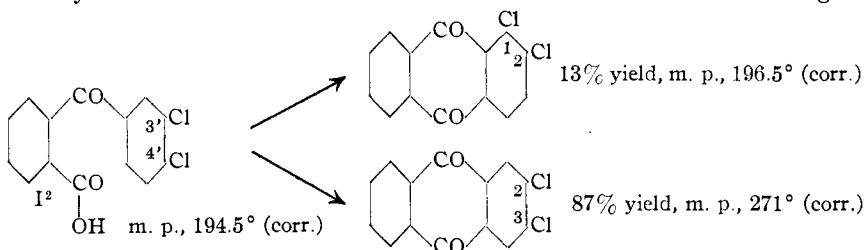
Summary

The Parr bomb fusion method has been adapted to the analysis of organic selenium compounds. The conditions for the precipitation of the selenium from the solution of the melt have been worked out.

BALTIMORE, MARYLAND

NOTES

The Formation of 1,2-Dichloro-anthraquinone and 2,3-Dichloro-anthraquinone from *o*-Dichlorobenzene.—Phillips states¹ that dichlorobenzoylbenzoic acid of the constitution shown in Formula I does not give



any 1,2-dichloro-anthraquinone on condensation with concentrated sulfuric acid. This statement is erroneous as I have shown³ that there is always formed about 13% of 1,2-dichloro-anthraquinone, which remains in the sulfuric acid after the condensation and crystallizes on diluting the acid in little leaflets. The substance melts, contrary to the statement of Ullmann,⁴ at 196.5° (corr.), and not at 207°.

I may add that Phillips' observations are, on the other hand, quite in agreement with ours. The 1,2-dichlorobenzene was quite pure, being especially made for us by the Aktiengesellschaft für Aniline Fabrikation in Berlin. I have already published this fact on page 488 of my "Künstliche Organische Farbstoffe" (Berlin, 1926). The yield of the 3',4'-dichlorobenzoylbenzoic acid was in our best experiments 35%.⁵

ZURICH ORGANIC-TECHNICAL LABORATORY
ZURICH, SWITZERLAND

HANS EDUARD FIERZ-DAVID

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¹ Phillips, *THIS JOURNAL*, **49**, 473-478 (1927).

² The sodium salt as well as the potassium salt is sparingly soluble.

³ E. Senn, *Dissertation*, Swiss Technical High School, 1923.

⁴ See Ullmann, *Encyklopaedia*.

⁵ Ref. 3, p. 29.