[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

The Preparation of Tri-Para-Tolylselenonium Chloride by Means of the Friedel–Crafts Reaction with Selenium Dioxide[1]

BY JOHN HARLAND CROWELL WITH W. E. BRADT

Introduction

In 1927 Lyons and Bradt[2] reported the results of a study upon the action of selenium dioxide and benzene in the presence of anhydrous aluminum chloride. Di-*p*-chlorophenyl selenide, diphenyl selenide, diphenyl diselenide and diphenylselenonium dichloride were obtained. They represented these substances as secondary products, and assumed the first product of the reaction to have been diphenyl selenoxide.

In the present work the authors carried out this reaction with toluene. The conditions of Lyons and Bradt were so modified that excess heating was avoided throughout both the reaction and the isolation procedure. This gave tri-*p*-tolylselenonium chloride as the chief product of the reaction.

Experimental Part

One hundred and sixty cc. of purified toluene was added to 60 g. of commercial anhydrous aluminum chloride which had been thoroughly mixed with 50 g. of freshly prepared pure selenium dioxide in a flask equipped with a reflux condenser and a means of vigorous agitation. The reaction was first cooled and then was heated for two hours on a steam-bath. The product was then hydrolyzed by pouring it into a large volume of cold water acidified with hydrochloric acid, filtered and the toluene layer removed.

The toluene layer[3] on distillation yielded small amounts of *p*-chlorotoluene (identified by a mixed melting point at 5.5–6.5° (corr.) with purified *p*-chlorotoluene).

Zinc Chloride Addition Compound.—The addition of zinc chloride solution to the warm aqueous layer caused the formation of a voluminous white crystalline precipitate which, after crystallization from alcohol, exhibited a constant melting point of 235°. It was identified as a *zinc chloride addition compound of tri-p-tolylselenonium chloride.* Molecular weight data, while not conclusive (due to partial ionization), indicated that two molecules of the selenium compound were attached to one molecule of zinc chloride, as in the formula, $ZnCl_2 \cdot 2(p\text{-}CH_3C_6H_4\text{-})_3SeCl$.

Anal. Calcd. for $C_{42}H_{42}Se_2Cl_2 \cdot ZnCl_2$: mol. wt., 912; C, 55.26; H, 4.64; Se, 17.37; Zn, 7.17. Found: mol. wt., 690; C, 54.3; H, 4.69; Se, 17.45; Zn, 7.15.

The zinc chloride addition compound was slightly soluble in ethyl alcohol, distilled water and aqueous hydrochloric acid. Its very slight solubility in aqueous hydrochloric acid made possible a fairly accurate determination of the amount of tri-*p*-tolylselenonium chloride formed. By this means 77% yields were isolated.

Tri-*p*-tolylselenonium chloride was isolated from the aqueous layer of a duplicate experiment by repeated extraction with chloroform, evaporation to a small volume and precipitation by pouring into a large volume of anhydrous ether. This, after crystalliza-

---

[1] Presented at the Regional Meeting of the Pacific Division of the American Association for the Advancement of Science at Pullman, Washington, June, 1932.

[2] Lyons and Bradt, *Ber.*, **60**, 60–63 (1927).

[3] If temperature conditions were maintained at sufficiently low levels (40–70°) the toluene layer contained either only a trace of or no selenium compounds.

tion from pyridine and subsequent crystallization from acetone or chloroform, yielded clear white rhombic needles melting at 160.0° (corr.). Analysis indicated that the substance was tri-*p*-tolylselenonium chloride carrying one mole of water of crystallization.

Anal. Calcd. for ($C_{21}H_{21}SeCl\cdot H_2O$): mol. wt., 405.8; C, 62.09; H, 5.71; Se, 19.52; Cl, 8.73. Found: mol. wt., 404.0; C, 62.24; H, 5.79; Se, 20.43; Cl, 8.72.

These data agree with the formula reported by Leicester and Bergstrom.[4] Tri-*p*-tolylselenonium chloride was soluble in water, dilute aqueous hydrochloric acid, pyridine, chloroform, aqueous sodium hydroxide and acetone, and was very slightly soluble in ether. It formed addition compounds with chlorides of the following ions: Hg^{++}, Cu^{++}, Ag^{+}, Zn^{++}, Pb^{++}, of which only the zinc chloride compound was investigated.

Further proof of the identity of this compound was furnished by the identification of its thermal decomposition products. When tri-*p*-tolylselenonium chloride was heated to a temperature of 200–235° decomposition resulted. The decomposition products were purified and identified as *di-p-tolyl selenide* and *p-chlorotoluene*.

Anal. Calcd. for ($C_{14}H_{14}Se$): C, 64.3; H, 5.40; m. p., 69–69.5°. Found: C, 63.5; H, 5.39; m. p. 68.0° (corr.).

Di-*p*-tolylselenide was moderately soluble in alcohol, chloroform, ether, carbon disulfide and insoluble in water.

The zinc chloride addition compound of triphenylselenonium chloride, $ZnCl_2 + 2(C_6H_5)_3SeCl$ (m. p. 273.5–274.0°), was prepared by using the authors' modified method with benzene. Analyses for C, H, Se, Zn and Cl completed its identification. Only traces of the products reported by Lyons and Bradt were found. This compound will be further discussed in a later paper.

Discussion

A comparison of the benzene compounds obtained by Lyons and Bradt with the toluene compounds by the authors using a procedure modified to avoid excess heating, verifies the original assumption by Lyons and Bradt that diphenyl selenide, diphenyl diselenide and di-*p*-chlorophenyl selenide were secondary products, the formation of which had been caused by the action of the heat upon the original products. The introduction of vigorous mechanical agitation, careful limitation of temperature to 40–70°, and the use of excess toluene, has avoided this thermal decomposition of the original products. Consequently, tri-*p*-tolylselenonium chloride, or triphenylselenonium chloride normally constitutes the entire reaction product. In no case were appreciable amounts of the products analogous to those identified by Lyons and Bradt found to be present. The presence of di-*p*-tolyl selenide and *p*-chlorotoluene in small amounts has been explained by the fact that they are known to be products of the thermal decomposition of tri-*p*-tolylselenonium chloride.

Summary

A method has been described for the synthesis of tri-*p*-tolylselenonium chloride by the action of selenium dioxide on toluene in the presence of anhydrous aluminum chloride. The presence of small amounts of di-*p*-tolyl selenide and *p*-tolyl chloride is due to the thermal decomposition of the

---

(4) Leicester and Bergstrom, THIS JOURNAL, 53, 4428–4436 (1931).

tri-*p*-tolylselenonium chloride which has been isolated in 77% yield as the zinc chloride addition compound.

PULLMAN, WASHINGTON

RECEIVED JULY 26, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Wildiers' Bios: The Fractionation of Bios from Yeast[1]

BY W. LASH MILLER, EDNA V. EASTCOTT AND J. E. MACONACHIE

The fractionation of the bios contained in an aqueous infusion of malt-combings was described by Dr. G. H. W. Lucas[1a] in 1924. After preliminary purification of the infusion, baryta and alcohol were added and the precipitate so formed was filtered off; to the filtrate, freed from alcohol and barium, he gave the name "crude Bios II solution." The precipitate was extracted with hot water, and the solution freed from barium; this "crude Bios I solution" was then precipitated by lead acetate and ammonia, the precipitate suspended in water and treated with carbon dioxide and sulfuric acid; the solution so obtained, after removing the last traces of lead with hydrogen sulfide, he called "Bios I solution." The physiologically active constituent of this Bios I solution was identified with *i*-inositol by Miss E. V. Eastcott[2] in 1928.

The yeast crop resulting under standardized conditions when a solution of salts and sugar is seeded with certain kinds of yeast[3] is not much increased by adding either Bios I solution (*i. e.*, a solution of *i*-inositol) or Bios II solution; but if both are added together, the crop is large—Lucas[1a] obtained counts of 15 to 25 from his Bios I solutions, 35 to 50 from his Bios II solutions purified by acetone, and 165 to 240 from the mixtures. In Wildiers' language, neither Bios I (*i*-inositol) nor Bios II contains much bios, but their mixture contains a considerable quantity of that substance; thus precipitation by alcohol and baryta "fractionated" the bios of the combings, and has subsequently been used to fractionate the bios from malt, rice polishings, tea, mushrooms (*agaricus campestris*), molasses, tomatoes, oranges and yeast. It is obvious that such a fractionation of the bios is very different from the mere removal of inactive materials,

---

[1] Financial assistance from the National Research Council of Canada is gratefully acknowledged.

[1a] G. H. W. Lucas, *J. Phys. Chem.*, **28**, 1180 (1924).

[2] E. V. Eastcott, *ibid.*, **32**, 1094 (1928); THIS JOURNAL, **51**, 2773 (1929).

[3] Dr. Helen Stantial finds that *Wildiers' yeast* and the following yeasts from the American Type Culture Collection behave with inositol and Bios II like the race with which most of our own experiments have been carried out: 2361 *Sacch, validus*, 4206 *Schizosacch, octosporus*. Mr. Maconachie found the same for 2331 (*brewers' yeast*) and for 2335 (*bakers' yeast*) and Dr. Lucas (Ref. 1a, p. 1190) for one of the yeasts used by Prof. W. H. Eddy. Miss Stantial also found that 2361 *Sacch. pastorianus* gives a large crop in media containing only salts and sugar [see Lash Miller, *J. Chem. Ed.*, **7**, 263 (1930)] like the top yeast used by Prof. Eddy (Lucas, Ref. 1a); and that the crops of 2333 *Sacch, mandschuricus* and of 2602 *Zygosacch, mandschuricus* are much increased by Bios II, but are not further increased by adding inositol to media containing Bios II. (Helen Stantial, *Trans. Roy. Soc. Canada*, Sec. III, p. 163 (1932).