

### Experimental

**Triphenyl-*p*-aminophenyllead.**—To 0.128 mole of *n*-butyllithium in 200 ml. of ether was added dropwise 6.9 g. (0.04 mole) of *p*-bromoaniline in 50 ml. of ether. After addition was completed, the solution was stirred at room temperature for thirty minutes. The low temperature ( $-60^{\circ}$ ) reported previously<sup>2</sup> for the preparation of *p*-aminophenyllithium is not necessary. A slight excess of an ether solution of anhydrous magnesium bromide, prepared by adding bromine dropwise to magnesium suspended in ether, was then added to the reaction mixture. The Grignard reagent thus formed was allowed to react with 18.4 g. (0.04 mole) of triphenyllead chloride for two hours at room temperature, and then hydrolyzed with iced ammonium chloride solution.

The ether layer was extracted with dilute hydrochloric acid. From the hydrochloric acid extract was isolated 3.5 g. of *p*-bromoaniline. The residual ether layer was dried and then evaporated under reduced pressure. The solid residue yielded, after several crystallizations from petroleum ether (b. p. 60–68°), 2.2 g. of a white crystalline solid, m. p. 166–167°.

The ether insoluble material obtained from the reaction was extracted with three 200-ml. portions of petroleum ether (b. p. 60–68°). The extractions yielded 4.8 g. of material melting at 166–167° and identical with the substance obtained from the ether soluble portion. The total yield was 7.0 g. or 66%, assuming that the unrecovered *p*-bromoaniline was converted to *p*-aminophenyllithium.

*Anal.* Calcd. for  $C_{24}H_{21}NPb$ : Pb, 39.01. Found: Pb, 39.45.

**Triphenyl-1-(2-hydroxynaphthyl)-azophenyl-4-lead.**—One gram of triphenyl-*p*-aminophenyllead was diazotized and coupled with  $\beta$ -naphthol in the usual manner. The coupling product, crystallized from dilute ethanol, decomposed at 135°, and was red in acid solution and green in the presence of base.

*Anal.* Calcd. for  $C_{34}H_{26}ON_2Pb$ : Pb, 30.02. Found: Pb, 29.65.

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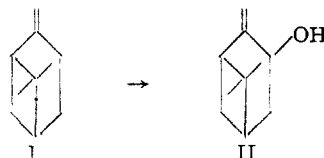
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### The Oxidation of $\beta$ -Pinene with Selenium Dioxide

BY LLOYD M. JOSHEL AND S. PALKIN

The oxidation of  $\beta$ -pinene (I) with selenium dioxide<sup>1,2</sup> has been recently reinvestigated by Stallcup and Hawkins,<sup>3</sup> who reported that no pinocarveol (II) or other alcohol could be found in the oxidation mixture. In order to make available a ready means for the preparation of pinocarveol from  $\beta$ -pinene and in view of the possible bearing on the mechanism of selenium dioxide oxidation, we are prompted to report the results of

some experiments made some time ago in this Laboratory.



Both the French workers<sup>1</sup> and Stallcup and Hawkins<sup>3</sup> used one mole (two equivalents) of selenium dioxide per mole of  $\beta$ -pinene. We found that when somewhat less than one-half a mole of selenium dioxide is used per mole of  $\beta$ -pinene, pinocarveol is readily obtained. Zacharewicz,<sup>2</sup> who used an even smaller ratio of selenium dioxide to  $\beta$ -pinene, also obtained pinocarveol but in less than one-half the yield reported below.

We are indebted to Messrs. Hawkins and Stallcup for their kindness in trying out the oxidation procedure described below. In a private communication Dr. Hawkins has informed us that they have confirmed our findings with regard to the main product, pinocarveol, and the small amount of carvopinone formed under these conditions.

### Experimental

A solution of 21 g. (0.16 mole) of c. p. selenious acid in 40 ml. of absolute ethanol was added dropwise during one-half hour, with mechanical stirring, to 54 g. (0.40 mole) of  $\beta$ -pinene. During the addition the solution became warm and turned yellow in color. After stirring another half-hour at room temperature, the solution was refluxed for four hours. The solution, which was red at this point, was then steam-distilled and the oil in the distillate was taken up in ether, washed, dried and distilled under nitrogen, furnishing, along with other fractions, 21 g. (42%) of a colorless liquid, b. p. 101.5–103° (25 mm.). The physical constants and active hydrogen determination indicated that this material was pinocarveol of about 85–90% purity. It could be further purified by conversion to the borate. The alcohol was heated with an equal volume of ethyl borate at 100–125° for one-half hour and the volatile contaminants removed by reducing the pressure gradually to 2 mm. while the bath was raised to 150°. The residual ester was then simultaneously hydrolyzed and steam distilled and the oil in the distillate taken up in ether, washed, dried, and distilled under nitrogen. In this way a colorless liquid, b. p. 101–102° (20 mm.), was obtained in 69% yield from the crude alcohol, or 29% over-all yield;  $n_D^{20}$  1.4995,  $d_4^{20}$  0.9798,  $\alpha_D^{20}$  +67.48°,  $\alpha_D^{20}$  +71.57°,  $\alpha_D^{20}$  +83.37°. Active hydrogen determination (semimicro) with methylmagnesium iodide showed 11.55% hydroxyl; calcd., 11.17%. The phenylurethan melted at 84–86°. This compares favorably with the m. p. of this derivative as usually reported,<sup>3,4</sup> although Schmidt<sup>5</sup> reported that on

(1) Dupont, Allard and Dulou, *Bull. soc. chim.*, [4] **63**, 599 (1933).

(2) Zacharewicz, *Roczniki Chem.*, **17**, 630 (1937).

(3) Stallcup and Hawkins, *THIS JOURNAL*, **63**, 3339 (1941).

(4) Schmidt, *Ber.*, **62**, 2945 (1929).

(5) Schmidt, *ibid.*, **63**, 1129 (1930).

rigorous purification the m. p. can be raised to 88–89°. On catalytic hydrogenation the alcohol absorbs 0.9–1.0 mole of hydrogen.<sup>6</sup>

Three grams of a non-alcoholic liquid were recovered from the volatile fraction obtained during the above ethyl borate treatment. The substance polymerized very rapidly on heating and this property, together with the rotation, refractive index, and method of preparation, indicates that it was probably impure carvopinone.<sup>3</sup>

(6) Joshei, Hall and Palkin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 447 (1941).

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### The Separation of Ytterbium from Accompanying Rare Earths by Means of its Amalgam

By HERBERT N. McCoy and R. PHILIP HAMMOND

The preparation of ytterbium amalgam by the electrolytic method described earlier<sup>1</sup> has been repeated, using a larger amount (4 g. of oxide) of the same starting material. The electrolyses were carried to the point where no further amalgam formation took place. The rare earths from amalgams and from residual electrolytes were then extracted as chlorides called I and II, respectively. Chloride I formed much the larger part of the material; chloride II amounted to about 0.1 g.

From chlorides I and II spectrograms were made using a replica grating of 15,000 lines per inch (5906 lines per cm.) and a graphite arc source. These spectrograms for the region 2500 to 4600 Å., accompanied by that of iron, were enlarged photographically to give prints with a dispersion of one Å. per mm. The enlarged prints were examined with the aid of Massachusetts Institute of Technology wave length tables<sup>2</sup> and more than 250 of the strong lines identified.

The spectrogram of chloride I was that of ytterbium containing a much smaller proportion of europium. No lines of other rare earths could be found on this spectrogram. That of chloride II showed in addition to some remaining ytterbium and europium, the presence of gadolinium, terbium, dysprosium, yttrium, erbium, thulium and lutecium. The presence of holmium was probable but could not be established with certainty because its strong lines were masked by those of other elements present.

(1) McCoy, *THIS JOURNAL*, **68**, 1622, 3432 (1941).

(2) "Massachusetts Institute of Technology Wave Length Tables," George W. Harrison, John Wiley and Sons, Inc., New York, N. Y., 1939.

This work shows that of the rare earths contained in the starting material only ytterbium and europium form amalgams by the method used. If the small proportion of europium present had first been removed, as might easily have been done by fractional crystallization as dimethyl phosphates,<sup>3</sup> bromates<sup>4</sup> or ethyl sulfates<sup>5</sup> the separation of ytterbium from the rare earths that usually accompany it would have been complete.

(3) Morgan and James, *THIS JOURNAL*, **36**, 10 (1914).

(4) James and Bissel, *ibid.*, **36**, 2060 (1914).

(5) Urbain, *Compt. rend.*, **126**, 833 (1898).

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### The Purification of Thorium Chloride Octahydrate

By CHESTER B. KREMER

In connection with previous researches on thorium compounds as well as in recent work in the production of thorium dioxide catalysts, the necessity of obtaining pure thorium chloride octahydrate arose. Thorium chloride "c. p." as purchased on the market contains appreciable amounts of iron and silica. Purification by simple recrystallization is difficult because of the tenacity with which iron compounds are retained by the salt and the formation of concentrated solutions, sirupy in nature, which will not deposit crystals. However, it is possible to obtain pure  $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$  by a method which in part is based upon a slight modification of the Gooch and Havens method for the determination of aluminum.

Specially prepared asbestos for the following operations is obtained by boiling a high grade variety repeatedly with concentrated hydrochloric acid until free of detectable iron and then washing thoroughly with distilled water.

Two hundred grams of the "c. p." salt is dissolved in just enough 6 *M* hydrochloric acid for complete solution, filtered through asbestos and then extracted twice with ethyl ether,<sup>1</sup> this operation removing practically all of the iron.<sup>2</sup> The solution is then evaporated to small volume on a hot plate. Excess silica precipitates out and is filtered off through asbestos. The filtrate is cooled to 0° and dry hydrogen chloride bubbled in until the solution is saturated with the gas. An equal volume of ethyl ether is

(1) Isopropyl ether may be employed; see Dodson, Forney and Swift, *THIS JOURNAL*, **68**, 2573 (1936).

(2) Langmuir, *ibid.*, **22**, 102 (1900).