

It is suggested that the name "pyrethrosin" be retained for this crystalline product obtained from *Chrysanthemum cinerariaefolium* and that all others be discarded.

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Tetraphenyllead and Diphenyllead Dihalides

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The Pfeiffer¹ procedure for the preparation of R_4Pb compounds by interaction of the Grignard reagent and lead chloride is admirably suited for laboratory purposes. However, the yields of tetraphenyllead by this method are about 50% in moderate sized runs.²

Incidental to a study on the mechanism of formation of some organometallic compounds, it has been found possible to increase the yield of tetraphenyllead to 83%. An occasional by-product is triphenyllead bromide, isolated in yields up to 6%. This compound does not owe its formation to a secondary reaction between tetraphenyllead and magnesium bromide or the binary system ($Mg + MgBr_2$), inasmuch as tetraphenyllead is unaffected by these substances under the conditions of the Pfeiffer reaction. A recent³ study showed that R_3Pb compounds react with magnesium iodide to give R_3PbI compounds. A corresponding reaction of triphenyllead and magnesium bromide suggests itself for the formation of triphenyllead bromide. Actually, we have found that triphenyllead and magnesium bromide give triphenyllead bromide. Triphenyllead is undoubtedly an intermediate in the preparation of tetraphenyllead; and when the time of reaction (in the directions which follow) is decreased, the tetraphenyllead is contaminated with some triphenyllead.

To a vigorously stirred solution of phenylmagnesium bromide (prepared from 1.5 moles of bromobenzene) in 500 cc. of ether, is added 500 cc. of dry toluene and 181 g. (0.65 mole) of dry, finely ground lead chloride. The lead chloride is added in three portions at five-minute intervals. The mixture is stirred with gentle refluxing for five hours, and thins out appreciably after the initial fifteen to thirty minutes of heating.

(1) Pfeiffer and Truskier, *Ber.*, **37**, 1125 (1904).

(2) Gilman and Robinson, *THIS JOURNAL*, **49**, 2315 (1927).

(3) Gilman and Bailie, *ibid.*, **61**, 731 (1939).

Hydrolysis is effected by pouring upon crushed ice mixed with ammonium chloride or hydrochloric acid. Vigorous stirring should be maintained during hydrolysis.

The toluene-ether layer is decanted and the water layer filtered. Distillation of the organic solvent layer leaves a residue consisting of a few grams of tetraphenyllead and triphenyllead bromide together with about 10 g. of biphenyl which probably came largely incidental to the formation of the Grignard reagent. The filtered solid from the aqueous layer is air dried, and extracted with 400 cc. of chloroform in a Soxhlet extractor to give an 82-83% yield of crystalline, pure tetraphenyllead (m. p. 225-226°). In the directions just noted, which do not necessarily give maximum yields, no inert atmosphere was used and the Grignard reagent was not filtered free of magnesium.

Diphenyllead dibromide and diphenyllead diiodide are prepared conveniently and in excellent yields in essential accordance with the procedure of Polis.⁴ To 50 cc. of *boiling* concentrated nitric acid is added slowly 10 g. (0.019 mole) of tetraphenyllead. The mixture is cooled, filtered through glass wool, and washed with a little water. The diphenyllead dinitrate is dissolved in boiling water acidulated with a little nitric acid, and to the hot solution is added a solution of sodium bromide (4.1 g., 0.04 mole). The diphenyllead dibromide precipitates immediately, and the yield is 96%. In a corresponding manner, diphenyllead diiodide is obtained in a 98% yield when sodium iodide is used. Diphenyllead dichloride is most conveniently prepared, in a 98% yield, from tetraphenyllead and hydrogen chloride.⁵ It can be prepared in a 93% yield by the addition of concd. hydrochloric acid to an aqueous solution of diphenyllead dinitrate.

Diphenyllead difluoride is obtainable in a 92% yield by the addition of an aqueous solution of potassium fluoride to an alcoholic solution of diphenyllead diiodide. Diphenyllead difluoride is insoluble in the usual organic solvents and does not melt up to 300°.

Anal. Calcd. for $C_{12}H_{10}PbF_2$: Pb, 51.88.
Found: Pb, 52.07, 51.65.

Diphenyllead difluoride and phenylmagnesium bromide give tetraphenyllead.

(4) Polis, *Ber.*, **20**, 720 (1887).

(5) Gilman and Robinson, *THIS JOURNAL*, **51**, 3112 (1929).

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The Reduction of α -Bromocyclohexanone with Aluminum Isopropoxide

BY S. WINSTEIN

The reduction of some α -bromo ketones by aluminum isopropoxide was the subject of a recent communication to the Editor by Stevens,¹ who obtained from α -bromopropiophenone a 35% yield of bromohydrin and about an equal yield of product not containing bromine. Presumably hydrogen bromide was split out. Tertiary α -bromo ketones and cyclic secondary α -bromo ketones were reported to yield not bromohydrins but products almost entirely free of bromine. What type of product he obtained was not indicated. In the course of other work the author has had occasion to reduce with aluminum isopropoxide the cyclic secondary α -bromo ketone, α -bromocyclohexanone. Since Stevens is continuing his investigation of the reaction of α -bromo ketones with aluminum isopropoxide, the results obtained with this cyclic ketone should be reported.

The reaction product from the reduction of α -bromocyclohexanone was found to be a mixture

(1) Stevens, *THIS JOURNAL*, **60**, 3089 (1938).

of bromohydrin and cyclohexanol, in yields of 30 and 33%, respectively, with no unsaturated compound being isolated. It is possible that the cyclohexanol arises from dismutation of bromocyclohexanone to cyclohexanone and dibromocyclohexanone with subsequent reduction of the cyclohexanone to cyclohexanol.

Experimental

75.8 g. (0.428 mole) of α -bromocyclohexanone, b. p. 69–71° (1.5 mm.), prepared by the method of Kötzt,² dissolved in 200 ml. of anhydrous isopropanol (Shell) was added to aluminum isopropoxide solution prepared from 7.5 g. of aluminum and 75 ml. of anhydrous isopropanol, according to the directions of Young, Hartung and Crossley.³ The mixture was refluxed for three and one-half hours. Then it was concentrated to a thick residue by distillation first of acetone, then of solvent through a 20-cm. column of glass helices for two hours at atmospheric pressure and finally with the aid of an aspirator. One hundred ml. of water and 130 ml. of 6 *N* sulfuric acid were added to the residue and all lumps were broken up. A little ether was added and the oil phase was separated, washed with bicarbonate solution and dried over sodium sulfate. Distillation and then refractionation at reduced pressure through a 40-cm. Weston⁴ column yielded 22.6 g. (30%) of 2-bromocyclohexanol, b. p. (10 mm.) 85.5–86.5°, n_D^{25} 1.5164, and 14.3 g. (33%) of cyclohexanol, b. p. (10 mm.) 61.0–61.2°, n_D^{25} 1.4649, m. p. of 3,5-dinitrobenzoate and mixed m. p. with authentic specimen, 112°.

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(2) Kötzt, *Ann.*, **358**, 195 (1907).

(3) Young, Hartung and Crossley, *THIS JOURNAL*, **58**, 100 (1936).

(4) Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

COMMUNICATIONS TO THE EDITOR

COLOR REACTIONS IN VITAMIN K CONCENTRATES

Sir:

During studies of the inactivation of vitamin K by its reaction with bases, we have detected and separated an alcohol-soluble reddish pigment. Recently, Dam, *et al.* [*Helv. Chim. Acta*, **22**, 310 (1939)] described a color reaction of vitamin K concentrates with sodium ethylate in which a transient purple color changing to a reddish-brown color developed. We have determined that our pigment is the end stage of this color reaction and that the quantity of pigment formed

is closely correlated with antihemorrhagic activity. The transient, deep purple color is considerably masked when carotenoid pigments are present; however, it is possible to employ the final, less intense but relatively stable, reddish-brown color as a quantitative measure of the vitamin.

The color reaction is carried out easily by dissolving a few milligrams of concentrate in 1 or 2 cc. of methanol and then adding 1 cc. of sodium methylate (2 to 3 g. of sodium dissolved in 50 cc. of methanol). When warmed for a few minutes, the mixture slowly develops a distinct purple