[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactions of Metallic Thallium and Metallic Lead with Organic Halides

BY HENRY GILMAN AND REUBEN G. JONES[1]

The monohalides of thallium[2] and the dihalides of lead[3] react with organolithium compounds and with Grignard reagents in accordance with equations I and II.

$$3RLi + 3TlX \longrightarrow R_3Tl + 2Tl + 3LiX \quad (I)$$

$$4RMgX + 2PbX_2 \longrightarrow R_4Pb + Pb + 4MgX_2 \quad (II)$$

The free metals formed in these reactions are in a state of fine subdivision, and it has been found that they are capable of reacting with organic halides, whereas the ordinary forms of thallium[4] and lead[5] are not.

A previous paper from this laboratory[2a] described the reaction of thallous iodide with methyllithium in the presence of methyl iodide to give a quantitative conversion to trimethylthallium according to equation III.

$$2RLi + RI + TlX \longrightarrow R_3Tl + LiI + LiX \quad (III)$$

It is the purpose of this paper to report further extensions of this reaction in the thallium series and also similar reactions with lead compounds.

That methyl iodide actually does react with metallic thallium, as postulated previously,[2a] was demonstrated by carrying out reaction III in two stages. First, thallous chloride was treated with two molar equivalents of methyllithium. After this reaction (equation I) had gone to completion methyl iodide was added. The black precipitate of metallic thallium all disappeared leaving a clear solution of trimethylthallium. This second stage of the reaction can be represented by equation IV.

$$3RLi + 3RI + 2Tl \longrightarrow 2R_3Tl + 3LiI \quad (IV)$$

Addition of equation I and IV gives equation III.

In order to determine the efficacy of different halides in a reaction like III a series of experiments was carried out in which ethyllithium was allowed to react with thallous chloride in the presence of ethyl iodide, ethyl bromide and ethyl chloride. The yields of triethylthallium were 100, 91 and 79%, respectively. A reaction between phenyllithium, thallous chloride and iodobenzene gave triphenylthallium in a yield of 79%. In all of these experiments the highly reactive R_3Tl compounds were not isolated as such but were converted to the more easily handled R_2TlX types.

$$R_3Tl + HX \longrightarrow R_2TlX$$

When a Grignard reagent was used instead of the RLi compound reaction III did not take place. This is not surprising in view of the fact that Grignard reagents do not react successfully with R_2TlX compounds to yield R_3Tl.[6]

The reaction of methyllithium with a lead halide in the presence of methyl iodide gave a quantitative yield of tetramethyllead. This process is probably best represented by the series of reactions

$$4CH_3Li + 2PbX_2 \longrightarrow (CH_3)_4Pb + Pb + 4LiX \quad (V)$$

$$2CH_3I + Pb \longrightarrow (CH_3)_2PbI_2 \quad (VI)$$

$$2CH_3Li + (CH_3)_2PbI_2 \longrightarrow (CH_3)_4Pb + 2LiI \quad (VII)$$

Addition of reactions V, VI and VII gives VIII as the over-all reaction.

$$3CH_3Li + CH_3I + PbX_2 \longrightarrow (CH_3)_4Pb + 2LiX + LiI \quad (VIII)$$

When methylmagnesium chloride or iodide was used in place of the methyllithium (reaction VIII) the yield of tetramethyllead was in the range of 70 to 80%. The tetramethyllead obtained in these experiments was not isolated as such because of the difficulty of completely separating it from ether and also because of the danger of explosion during distillation.[2a] It was converted (in about 92% yield) to dimethyllead dibromide.

Some preliminary experiments were carried out in which ethylmagnesium bromide was allowed to react with lead halides in the presence of ethyl iodide. There were indications that good yields of tetraethyllead were formed, and only a little unreacted metallic lead remained.

Experimental

Methyllithium and Thallous Chloride Followed by Methyl Iodide.—To a suspension of 4.8 g. (0.02 mole) of thallous chloride in 25 ml. of ether under a nitrogen atmosphere was added with stirring 45 ml. of an ether solution containing 0.045 mole of methyllithium. The resulting black reaction mixture was stirred for fifteen minutes, and then a solution of 4 g. (0.028 mole) of methyl iodide in 20 ml. of ether was added. After stirring for fifteen minutes the black precipitate of metallic thallium had completely disappeared. The clear ether solution was hydrolyzed with water to yield 7.15 g. (99%) of dimethylthallium iodide.[2a]

Phenyllithium, Iodobenzene and Thallous Chloride. Phenyllithium, 0.125 mole, in 105 ml. of ether was added during forty-five minutes to 13.5 g. (0.057 mole) of thallous chloride in 25 ml. of ether containing 12.8 g. (0.063 mole) of iodobenzene. The mixture darkened at first, and then as more phenyllithium was added it became lighter but never entirely white. Part of the ether was removed by distillation and the residue was heated at 55° for six hours. Water was added to the reaction mixture, and the insoluble material was thoroughly extracted with hot pyridine. When the pyridine extract was diluted with a large volume of water there was obtained 22 g. (79% yield) of diphenylthallium iodide. The pyridine-insoluble portion was converted, *via* the nitrate, to thallous iodide which weighed 3.63 g. representing 19.2% of the thallous chloride originally used.

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[1] Present address, The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana.

[2] (a) Gilman and Jones, THIS JOURNAL, **68**, 517 (1946); (b) Gilman and Jones, *ibid.*, **62**, 2357 (1940); (c) Birch, *J. Chem. Soc.*, 1132 (1934).

[3] Pfeiffer and Truskier, *Ber.*, **37**, 1125 (1904).

[4] Rochow and Dennis, THIS JOURNAL, **57**, 486 (1935).

[5] Calingaert, *Chem. Rev.*, **2**, 43 (1925).

[6] Groll, THIS JOURNAL, **52**, 2998 (1930).

Ethyllithium and Thallous Chloride in the Presence of Ethyl Iodide, Ethyl Bromide and Ethyl Chloride.—A suspension of 6.0 g. (0.025 mole) of thallous chloride in 25 ml. of ether containing 4.3 g. (0.028 mole) of ethyl iodide was cooled in an ice–salt-bath and stirred under nitrogen while 0.055 mole of ethyllithium in 75 ml. of ether was added during forty-five minutes. The resulting clear, colorless ether solution was treated with distilled water and there was obtained 9.7 g. (100% yield) of diethylthallium iodide.

The experiment was repeated except that 6.0 g. (0.055 mole) of ethyl bromide was used in place of the ethyl iodide, and the reaction was conducted at room temperature. Some black precipitate (metallic thallium) was formed during this reaction. It was separated by decanting the ether solution and washing with fresh ether. Treatment of the ether solution with water yielded 7.80 g. (91.3%) of diethylthallium bromide. The metallic thallium was converted to thallous iodide which weighed 0.80 g. representing 9.7% of the thallous chloride originally used.

The experiment was again repeated, but this time in place of the ethyl iodide gaseous ethyl chloride was bubbled into the mixture so that an excess was present throughout the course of the reaction. After four hours at room temperature there was obtained a 79% yield of diethylthallium chloride, subsequent to hydrolysis, and a 21.6% yield of metallic thallium, weighed as thallous iodide.

Methyllithium, Methyl Iodide and Lead Iodide.—A suspension of 18.5 g. (0.04 mole) of lead iodide in 40 ml. of ether containing 10 g. (0.07 mole) of methyl iodide was stirred while a solution of 0.15 mole of methyllithium in 100 ml. of ether was added during twenty minutes. The mixture gradually darkened and was quite black when about one-half of the methyllithium had been added. The black color then rapidly disappeared and at the end of the reaction the ether solution was clear and colorless indicating a quantitative conversion of the lead iodide to tetramethyllead. The ether solution was washed with dilute hydrochloric acid and then with water after which it was dried over calcium chloride. This solution was placed in a Dewar flask and solid carbon dioxide was added until the temperature had been reduced to −60°. With stirring a solution of 13.0 g. (0.08 mole) of bromine in 25 ml. of chloroform was added. The white precipitate of dimethyllead dibromide[7] was collected on a filter, washed with ether and ethyl acetate and air dried. The yield was 14.5 g. (92%).

Anal. Calcd. for $C_2H_6Br_2Pb$: Br, 40.2; Pb, 52.2. Found: Br, 39.4, 39.6; Pb, 52.6, 52.3.

Methylmagnesium Halide, Methyl Iodide and Lead Halide.—To a stirred suspension of 13.9 g. (0.05 mole) of lead chloride in 25 ml. of ether containing 8 g. (0.055 mole) of methyl iodide was added during fifteen minutes 0.164 mole of methylmagnesium chloride in 100 ml. of ether. The resulting mixture was heated under reflux for one hour and then treated with cold dilute hydrochloric acid. There remained a little insoluble black precipitate (metallic lead) together with a little yellow precipitate (lead iodide). The ether solution was dried and treated with bromine to convert the tetramethyllead to dimethyllead dibromide. The yield was 14.0 g. (70%).

The experiment was repeated using methylmagnesium iodide, methyl iodide and lead iodide. There was obtained a 26.6% yield of metallic lead and a 66% yield of tetramethyllead (weighed as dimethyllead dibromide).

Ethylmagnesium Bromide, Ethyl Iodide and Lead Halides.—A solution of 0.14 mole of ethylmagnesium bromide in 100 ml. of ether was added during twenty minutes to a stirred suspension of 0.04 mole of lead chloride in 50 ml. of ether containing 0.064 mole of ethyl iodide. The mixture was then heated under reflux for three hours after which it was treated with dilute hydrochloric acid. There was obtained a 36% yield of metallic lead. The ether soluble lead compound was presumed to be tetraethyllead. It was not isolated.

The above experiment was repeated using lead iodide in place of lead chloride. There was obtained a 14.6% yield of metallic lead in the form of large crystals. The other 85.4% of the lead was presumably converted to ether soluble tetraethyllead. No attempt was made to isolate it.

When the experiment was carried out using ethylmagnesium bromide, ethyl bromide and lead chloride 47% of the lead chloride was converted to metallic lead.

Summary

The reaction of thallous halides with organolithium compounds in the presence of organic halides has been found to give high yields of R_3Tl compounds in accordance with the equation

$$2RLi + RX + TlX \longrightarrow R_3Tl + 2LiX$$

Tetramethyllead has been prepared in excellent yields by the reaction of methyllithium or methylmagnesium chloride and methyl iodide with lead halides according to the equation

$$3CH_3Li + CH_3I + PbX_2 \longrightarrow (CH_3)_4Pb + 2LiX + LiI$$

There are indications that this type of reaction may be used to prepare other R_4Pb compounds.

AMES, IOWA RECEIVED OCTOBER 13, 1949

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[7] Grüttner and Krause, *Ber.*, **49**, 1415 (1916).

[CONTRIBUTION FROM THE FLUORINE LABORATORIES OF THE PENNSYLVANIA STATE COLLEGE]

Fluorocarbon Chemistry. III. Hydrogenolysis of Carbon–Carbon Bonds of Fluorocarbons[1]

BY W. R. JAMES,[2] W. H. PEARLSON[3] AND J. H. SIMONS

The thermal halogenolysis of carbon–carbon bonds of fluorocarbons with the resultant formation of fluorocarbon halides of shorter chain length has been reported in a previous paper.[1] The general reaction of carbon–carbon bond splitting in fluorocarbons is here extended to include the process of hydrogenolysis. The principal products isolated, shorter chain fluorocarbon derivatives containing one or two hydrogen atoms per molecule, were those to be expected from splitting of carbon–carbon bonds. Reactions involving carbon–fluorine bonds apparently resulted chiefly in complete decomposition of the molecule.

A previously reported catalytic reaction of hydrogen with fluorocarbons resulted in replacement of fluorine by hydrogen without indications of chain breaking.[4]

As in the halogenolysis experiments, the re-

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[1] For Paper No. II of this series see T. J. Brice, W. H. Pearlson and J. H. Simons, THIS JOURNAL, **71**, 2499 (1949).

[2] Present address: Merrimac Division, Monsanto Chemical Company, Everett, Mass.

[3] Present address: Minnesota Mining & Manufacturing Company, Saint Paul 1, Minn.

[4] A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 367 (1947).