TABLE VII

DISTILLATION AND ANALYTICAL DATA FOR TEST NO. 10

Fraction	B. p. at 50 mm.,[a] °C.	Number of carbon atoms in R_4Pb compounds present	Weight, g.	Pb analysis
1[b]	→ 33	4	..	1.99 g.
2[c]	78.5	4 + 5 + 6	35.5	71.09%
3	99.0	6 + 7	54.0	67.33%
4	114.7	7 + 8	66.0	64.20%
5	127.3	8 + 9	59.7	61.59%
6	132.5	9 + 10	20.3	60.07%
7	145.5	10 + 11	29.6	57.82%
Residue[d]		11 + 12	..	4.04 g.

[a] The actual boiling points were converted to 50 mm. by use of a nomogram.[2] [b] Contained some solvent hexane used for extraction of aqueous layer. [c] Estimated to contain 0.25 ml. of Me_4Pb. [d] The residue was washed from the still with carbon tetrachloride and its R_4Pb content was estimated to be 50% $EtPr_3Pb$.

metallic lead and 6 g. of tetramethyllead. The other lead alkyls were not isolated.

Tetramethyllead and Tetraphenyllead in Hexane with Aluminum Chloride Catalyst.—To a solution of 0.1 mole of tetraphenyllead and 0.2 mole of tetramethyllead in 75 ml. of hexane contained in a three-necked flask equipped with a reflux condenser and thermometer was added 1 g. of aluminum chloride. The mixture was maintained at 80° for seven hours, after which the flask was cooled and the catalyst extracted by shaking with water. After filtering the organic lead layer, two distillations yielded: tetramethyllead, 9 g., b. p. →77° (3 mm.); trimethylphenyllead, 31 g., b. p. 77–78° (3 mm.), $n^{20}D$ 1.5837 (*Anal.* Calcd. for $C_9H_{14}Pb$: Pb, 62.90. Found: Pb, 63.32); dimethyldiphenyllead, 25 g., b. p. 151–152° (2 mm.), $n^{20}D$ 1.6263 (*Anal.* Calcd. for $C_{14}H_{16}Pb$: Pb, 52.93. Found: Pb, 53.11); and a residue of 10 g., from which was obtained, by three recrystallizations from *n*-hexane, 3.5 g. of triphenylmethyllead, m. p., 62–63° (*Anal.* Calcd. for $C_{19}H_{18}Pb$: Pb, 45.69. Found: Pb, 45.65). A few crystals of tetraphenyllead, m. p. 226–228°, mixed m. p. 226–228°, also precipitated out of the equilibrium mixture prior to the distillation.

Tetraphenyllead and Tetra-*p*-tolyllead without Catalyst.—A mixture of 3 g. of tetraphenyllead and 3.3 g. of tetra-*p*-tolyllead in an air-jacketed test-tube equipped with a thermometer and stirrer was heated to melting in an oil-bath and allowed to cool slowly with stirring. Two successive cooling curves showed initial freezing points of 204.5 and 201.5°, respectively. After remelting and maintaining the mixture at 200° for three successive five-hour periods, the mixture showed initial freezing points of 177, 152.5 and 150°, respectively. Attempts to isolate the constituents by fractional crystallization and use of selective solvents were unsuccessful.

Summary

Data presented for the redistribution reaction in various R_4Pb systems show that the reaction is a general one for these compounds, and give an indication of the influence of some of the factors affecting the reaction such as the R groups, catalysts, catalyst concentration, solvents, temperature and time.

DETROIT, MICHIGAN RECEIVED AUGUST 30, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL GASOLINE CORPORATION]

The Redistribution Reaction. VI. Alkyl Lead Halides

BY GEORGE CALINGAERT, HAROLD SOROOS AND HYMIN SHAPIRO

It was stated in the first paper of this series[1] that the interchange of alkyl groups in trialkyllead halides appears to be a general reaction for which no catalyst is required other than the alkyl lead halide itself.

The present paper covers the experimental data for this interchange of alkyl groups between two trialkyllead halides, between trialkyllead halides and tetraalkyllead compounds, and in a single mixed trialkyllead halide. The six systems tested, together with the experimental conditions employed, are listed in Table I. In each system the alkyl groups involved were methyl and ethyl. In the tests involving trialkyllead halides alone, only the chlorides were used; in the systems comprising tetraalkyllead with trialkyllead halide, both the chlorides and bromides were investigated. An experimental difficulty encountered in these reactions was the instability of the salts, particularly the bromides, which tend to disproportionate to lead alkyls, dialkyllead dihalides, and even alkyllead trihalides, and yield in addition the decomposition products of the last two, namely, hydrocarbons, alkyl halides, and lead halides. These secondary reactions were minimized by operating at a relatively low temperature and, in two cases, by converting the trialkyllead halides to the stable lead alkyls by means of an appropriate Grignard reagent immediately upon completion of the redistribution reaction.

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(1) Calingaert and Beatty, THIS JOURNAL, **61**, 2748 (1939).

TABLE I

REDISTRIBUTION OF ALKYLLEAD HALIDES

No.	Compounds	Moles	Solvent	Ml.	Temp., °C.	Hours	Notes
1	$Me_2EtPbCl$	0.38	Acetone	240	60	5	*a*
2	Me_3PbCl Et_3PbCl	.30 .30	Acetone	300	60	5	*a*
3	Me_4Pb Et_3PbCl	.15 .15	Hexane	50	76	5	*b*
4	Me_4Pb Et_3PbCl	.15 .15	Hexane	50	76	5	*b, c*
5	Me_4Pb Et_3PbBr	.15 .15	Hexane	50	76	5	*d*
6	Et_4Pb Me_3PbBr	.15 .15	Hexane	50	80	5	*c, d*

[a] Complete analysis showed the product to be a random equilibrium mixture. [b] Analysis showed that both the R_3PbCl and R_4Pb in the product contained methyl and ethyl radicals in about equal proportions. [c] Added 2.5 mole per cent. of aluminum chloride catalyst to the lead compounds. [d] Analysis of R_4Pb in the product indicated a random equilibrium mixture; the R_3PbBr salts were not analyzed.

In the first two systems involving only trialkyllead chlorides, four compounds are predicted by theory and, correspondingly, by appropriate treatment with a suitable Grignard reagent, four lead alkyls were obtained which were readily separated by fractional distillation.[2]

In the systems containing tetraalkyllead, the theory predicts the formation of five lead alkyls and four trialkyllead halides. These were first separated by distillation into two groups, the liquid lead alkyls and the solid trialkyllead halides. The lead alkyls were subsequently fractionated. Although no attempt was made to separate the constituents present in the mixture of trialkyllead halides, the melting point as well as the lead and chlorine analysis of the mixture indicated the presence of both methyl and ethyl radicals. Whenever the analysis was carried to completion, the composition of the groups of compounds analyzed corresponded to the predicted random equilibrium, and these equilibrium compositions were independent of the identity of the starting materials.

Material balances for the halides could not be established as quantitatively as in the case of the catalytic redistribution of the lead alkyl systems,[3] first, because of a certain amount of decomposition of these salts, and, second, because their conversion to lead alkyls by the Grignard reaction was not quantitative.

The reactions appeared to take place readily and to reach completion in a relatively short time.[4] The compounds themselves act as catalysts, and the presence of an additional catalyst did not materially affect the rate of the reaction or alter the composition of the final product. Analytical data for the composition of three of the equilibrium mixtures are given in Tables II, III, and IV, and the distillation curves for two of the products are shown in Figs. 1 and 2.

TABLE II

PRODUCTS FROM THE REDISTRIBUTION OF $Me_2EtPbCl$

Compound	Identified as	Composition, mole per cent. Found	Composition, mole per cent. Calcd.[a] for r[b] = $^2/_3$
Me_3PbCl	Me_4Pb	30.0	29.6
$Me_2EtPbCl$	Me_3EtPb	47.2	44.5
$MeEt_2PbCl$	Me_2Et_2Pb	18.4	22.2
Et_3PbCl	$MeEt_3Pb$	4.4	3.7

[a] Calculated mole percentages are given[1] by: $Me_3PbCl = r^3$; $Me_2EtPbCl = 3r^2(1 - r)$; $MeEt_2PbCl = 3r(1 - r)^2$; $Et_3PbCl = (1 - r)^3$. [b] r is the mole fraction of methyl radicals in the starting compound.

TABLE III

PRODUCTS FROM THE REDISTRIBUTION OF Me_3PbCl WITH Et_3PbCl

Compound	Identified as	Composition, mole per cent. Found	Calculated for r[a] = 0.46	Calculated for r[b] = 0.50
Me_3PbCl	Me_4Pb	8.6	9.7	12.5
$Me_2EtPbCl$	Me_3EtPb	34.9	34.3	37.5
$MeEt_2PbCl$	Me_2Et_2Pb	41.5	40.3	37.5
Et_3PbCl	$MeEt_3Pb$	15.0	15.7	12.5

[a] r is the mole fraction of methyl radicals found in the product. [b] r is the mole fraction of methyl radicals present in the starting mixture.

TABLE IV

R_4Pb PRODUCTS FROM THE REDISTRIBUTION OF Me_4Pb WITH Et_3PbBr

Compound	Composition, mole per cent. Found	Calculated[a] for r[b] = 0.66	Calculated[a] for r[c] = 0.57
Me_4Pb	17.6	19.0	10.6
Me_3EtPb	44.0	39.1	31.9
Me_2Et_2Pb	22.6	30.2	36.0
$MeEt_3Pb$ Et_4Pb	15.8	11.7	21.5

[a] Calculated mole percentages are given[1] by: $Me_4Pb = r^4$; $Me_3EtPb = 4r^3(1 - r)$; $Me_2Et_2Pb = 6r^2(1 - r)^2$; $MeEt_3Pb = 4r(1 - r)^3$; $Et_4Pb = (1 - r)^4$. [b] r is the mole fraction of methyl radicals found in the R_4Pb portion of the product. [c] r is the mole fraction of methyl radicals present in the starting mixture.

Conclusion.—The data show that the redistribution reaction of the trialkyllead halides takes place readily in the absence of any additional catalyst other than the halides themselves. This fact elucidates several reports of anomalous be-

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[2] Calingaert, Beatty and Neal, THIS JOURNAL, **61**, 2755 (1939).

[3] Calingaert and Soroos, *ibid.*, **61**, 2758 (1939); Calingaert, Beatty and Soroos, *ibid.*, **62**, 1099 (1940).

[4] Calingaert, Beatty and Hess, *ibid.*, **61**, 3300 (1939).

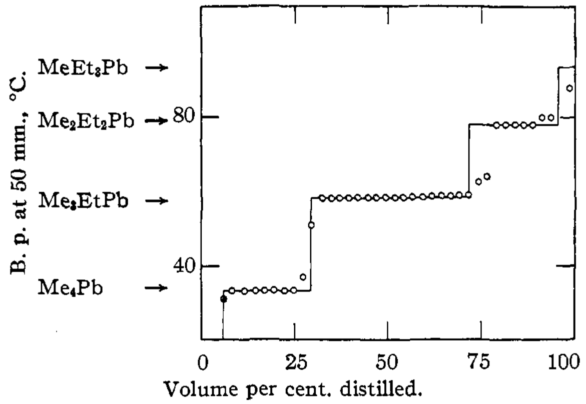

Fig. 1.—Distillation of R_4Pb compounds from reaction product of $Me_2EtPbCl$: solid line calculated for random equilibrium mixture with [Me] = 2/3.

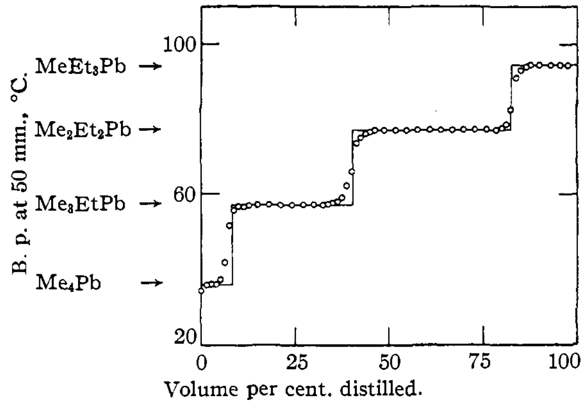

Fig. 2.—Distillation of R_4Pb compounds from reaction product of $Me_3PbCl + Et_3PbCl$: solid line calculated for random equilibrium mixture with [Me] = 0.46.

havior which have appeared in the literature, but which have received very little consideration from either their authors or others. Previous work in this Laboratory[5] has shown that in the synthesis of certain $R_3R'Pb$ compounds from the reaction of R_3PbX compounds with Grignard reagents, some R_4Pb and $R_2R'_2Pb$ compounds are also formed. Grüttner and Krause[6] have emphasized that in the preparation of $R_2R'R''Pb$ compounds from $R_2R'PbX$, great care must be exercised to use the halides only when freshly prepared, as storage for any length of time, especially of the bromides, leads to low yields and an impure product. On the basis of the disclosures made in the present paper, it seems certain that these previous results were due to the spontaneous redistribution of the trialkyllead halides containing different alkyl groups, with the result that the final lead alkyl product contained, in addition to the expected compound, the three compounds corresponding to this redistribution.

Experimental

Redistribution of Dimethylethyllead Chloride.—The salt was prepared by passing dry hydrogen chloride into a hexane solution of trimethyllead. The precipitated salt was filtered, and freed of small amounts of lead chloride and dialkyllead dichlorides by dissolving the product in benzene, filtering, and reprecipitating the salt by dilution with hexane. The material was finally filtered, washed with hexane, and dried by evacuation.

Anal. Calcd. for $C_4H_{11}PbCl$: Pb, 68.66; Cl, 11.75. Found: Pb, 68.62; Cl, 11.76.

The redistribution of dimethylethyllead chloride and the subsequent conversion of the resulting random equilibrium mixture of trialkyllead chlorides to the corresponding tetraalkyllead compounds was accomplished in the following manner. A solution of 0.38 mole of dimethylethyllead chloride in 240 ml. of dry acetone was refluxed at 60° for five hours. After cooling and filtering from 0.6358 g. of precipitated lead chloride, the acetone was distilled, the last traces being removed at reduced pressure and condensed in a dry-ice trap. The residue was washed with cold hexane. Fractionation of the acetone distillate and hexane washings yielded 2.234 g. of lead alkyls. The residue was next dissolved in 300 ml. of dry benzene, filtered from 0.1849 g. of dialkyllead chlorides, precipitated by dilution with hexane at −70°, and filtered. An additional small amount of the salts obtained by evaporation of the filtrate was combined with the main body of the material. The mixture of trialkyllead chlorides was finally suspended in 200 ml. of dry ether and treated with an ether solution of 0.7 mole of methylmagnesium bromide. After decomposing the reaction mixture with water and separating the ether layer, fractionation of the product indicated an 83% yield of tetraalkyllead compounds in the proportions corresponding to a random equilibrium mixture of the trialkyllead chlorides, as shown in Table II and Fig. 1.

Redistribution of Trimethyl- with Triethyllead Chloride.—A solution of 0.3 mole each of trimethyl- and triethyllead chloride in 300 ml. of dry acetone was refluxed at 60° for five hours. After filtering from a minute amount of lead chloride, the acetone was evaporated and the residue dried by suction. The mixture of trialkyllead chlorides was converted to the corresponding tetraalkyllead compounds by treating the salts, suspended in 300 ml. of dry ether, with an ether solution of 0.9 mole of methylmagnesium bromide. After decomposing the excess Grignard reagent with water, and separating the ether layer, fractionation of the product gave an 88% yield of lead alkyls corresponding to the random redistribution of the trialkyllead chlorides shown in Table III. The distillation curve is shown in Fig. 2. The observed 46% methyl radicals in the product agrees with the 50% taken in the starting materials as well as is to be expected.

That the redistribution of the two trialkyllead chlorides was not brought about by any catalytic effect of the Grignard reagent was demonstrated by treating an ether suspension of 0.2 mole each of trimethyl- and triethyllead chloride with an ether solution of 0.6 mole of methylmag-

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[5] Calingaert and Soroos, *J. Org. Chem.*, **2**, 535 (1938).

[6] Grüttner and Krause, *Ber.*, **50**, 202 (1917).

nesium bromide. After decomposing the excess Grignard reagent with water and separating the ether layer, fractionation of the product gave only two lead alkyls, namely, 0.18 mole of tetramethyllead and 0.123 mole of methyltriethyllead. The yield of lead alkyls was 76%.

Redistribution of Triethyllead Chloride with Tetramethyllead. (a) With no Catalyst.—A mixture of 0.15 mole each of triethyllead chloride and tetramethyllead in 50 ml. of hexane was refluxed at 77° for five hours. The mixture of liquid lead alkyls was distilled rapidly at reduced pressure (2–50 mm.) from the mixture of solid alkyllead chlorides. The residue was washed with hexane, dried on a porous plate (wt. 40 g.), and analyzed. *Anal.* Calcd. for $Me_{1.5}Et_{1.5}PbCl$: Pb, 67.10; Cl, 11.48. Found: Pb, 65.96; Cl, 11.83. A sample of the solids recrystallized from hexane decomposed at 95°; triethyllead chloride decomposes at 170°. Fractionation of the distillate of liquid lead alkyls gave 2.3 ml. of tetramethyllead, 7.7 ml. of trimethylethyllead, 4.6 ml. of dimethyldiethyllead, and 2–3 ml. of residue containing the higher lead alkyls. Although the data obtained in this and the experiments given below were not of such accuracy as to permit a complete analysis of the products of the reaction, the results were nevertheless sufficient to indicate conclusively that redistribution of the alkyl groups had occurred.

(b) With Aluminum Chloride Catalyst.—A mixture of 0.15 mole each of triethyllead chloride and tetramethyllead with 1 g. of aluminum chloride in 50 ml. of hexane, treated in the same manner as in (a), gave 40.8 g. of a mixture of solid alkyllead chlorides. *Anal.* Calcd. for $Me_{1.5}Et_{1.5}PbCl$: Pb, 67.10; Cl, 11.48. Found: Pb, 65.59; Cl, 11.68. A sample of the solid mixture recrystallized from hexane decomposed at 90°. Fractionation of the liquid lead alkyls gave 2.5 ml. of tetramethyllead, 6.9 ml. of trimethylethyllead, 3.1 ml. of dimethyldiethyllead, and 4–5 ml. of residue containing the higher lead alkyls.

Redistribution of Triethyllead Bromide with Tetramethyllead.—A mixture of 0.15 mole each of triethyllead bromide and tetramethyllead in 50 ml. of hexane was refluxed at 77° for five hours. The liquid portion of the product was filtered from the undissolved salts and the solids were washed with hexane. The lead alkyl filtrate and hexane washings were distilled rapidly at reduced pressure (2–50 mm.) from a small amount of dissolved salts. Fractionation of the distillate gave 3.8 ml. of tetramethyllead, 10.6 ml. of trimethylethyllead, 6.0 ml. of dimethyldiethyllead, and 4.6 ml. of a mixture of methyltriethyllead and tetraethyllead. The analysis of the product is given in Table IV.

The data show that considerable decomposition of the trialkyllead bromides took place, forming lead alkyls and lead bromide, since the total recovery of lead alkyls (0.161 mole) is greater than the input (0.15 mole).

Redistribution of Trimethyllead Bromide with Tetraethyllead.—The redistribution of 0.15 mole each of trimethyllead bromide and tetramethyllead with 1 g. of aluminum chloride at 80° for five hours, followed by filtration and vacuum distillation from the solid alkyllead bromide salts, and by fractionation of the liquid lead alkyls, gave 45.5 g. of lead alkyl distillate. The fractionation, although not adequate for accurate analysis, indicated a random equilibrium mixture, showing that the redistribution was probably complete.

Summary

Trialkyllead halides containing methyl and ethyl radicals undergo the redistribution reaction spontaneously and yield a random equilibrium mixture containing all four possible trialkyllead halides. Mixtures of trialkyllead halides and tetraalkyllead containing these two radicals yield the five possible lead alkyls as well as the four halides.

DETROIT, MICHIGAN RECEIVED SEPTEMBER 27, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL GASOLINE CORPORATION]

The Redistribution Reaction. VII. Alkyl Compounds of Mercury, Tin, Silicon and Zinc

BY GEORGE CALINGAERT, HAROLD SOROOS AND VINCENT HNIZDA

The first paper[1] of this series stated that the redistribution reaction takes place in a variety of metal alkyls and subsequent papers have described the reaction for R_4Pb compounds[2] and the trialkyllead halides.[3]

The present paper gives the experimental data relating to the interchange of alkyl groups in several other metal alkyls, namely, those of mercury, tin, silicon and zinc. The systems tested, together with the experimental conditions employed, are listed in Table I and comprise eleven compounds, four metals and three alkyl radicals. The results, except for zinc, were similar to those obtained for the lead compounds, the products being random equilibrium mixtures of all the possible metal alkyls for each metal and the two alkyl groups present.

Both methylethylmercury and an equimolecular mixture of dimethyl- and diethylmercury gave the same random equilibrium mixture of the three mercury alkyls, shown in Table II, when allowed to stand at room temperature in the presence of

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[1] Calingaert and Beatty, THIS JOURNAL, **61**, 2748 (1939).

[2] Calingaert, Beatty and Soroos, *ibid.*, **62**, 1099 (1940).

[3] Calingaert, Soroos and Shapiro, *ibid.*, **62**, 1104 (1940).