

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

The Redistribution Reaction. V. R_4Pb Compounds

BY GEORGE CALINGAERT, HAROLD A. BEATTY AND HAROLD SOROOS

Previous papers in this series^{1,2,3} have described the redistribution reaction for the interchange of organic radicals, and have shown that this reaction takes place quantitatively and leads to the formation of random equilibrium mixtures. The present paper covers the experimental data relating to the redistribution of tetraalkyllead and tetraaryllead compounds. In view of the novelty of the reaction, it was desired to explore the field as widely as possible before attempting a systematic or detailed study, and the data submitted here should be evaluated accordingly. The present tests were limited to an investigation of the generality of the reaction in the R_4Pb field, and to a preliminary study of how the reaction is affected by some experimental variables such as catalysts, catalyst concentration, solvents, temperature, and time. Later reports will cover more quantitative investigations of the most promising parts of the field explored.

With a few exceptions, the reactions were carried out in the same general manner, which consisted of taking the R_4Pb compound or mixture with the desired catalyst and in many cases with an inert solvent, maintaining this mixture at a given temperature for a certain length of time, removing the catalyst by extraction with water or with a suitable solvent or reagent, and finally analyzing the product by fractional distillation² or some other suitable method. In some of the cases, the analysis was carried out only far enough to indicate clearly that the reaction had taken place.

Systems Investigated.—The various R_4Pb systems tested are listed in Table I, and comprise thirteen different compounds containing six different alkyl and two different aryl radicals. With the exception of tests 12 and 14, the reaction conditions used were, as is described in the Experimental Part, essentially the same for each test, and these conditions were usually more than adequate to bring the reaction to completion. In each of the fourteen systems listed, the redistribution occurred and was judged to be complete or nearly so.

(1) Calingaert and Beatty, *THIS JOURNAL*, **61**, 2748 (1939).(2) Calingaert, Beatty and Neal, *ibid.*, **61**, 2755 (1939).(3) Calingaert and Soroos, *ibid.*, **61**, 2758 (1939).

As far as the data indicate, all the alkyl radicals tested showed a reactivity of the same order of magnitude, with the exception of the tertiary butyl radical. Indeed, the redistribution of trimethyl-*t*-butyllead was accomplished only under drastic conditions, and it was accompanied by decomposition, which is presumably due to the instability of the poly-*t*-butyllead compounds formed. Judging from tests 13 and 14, it appears that the reactivity of the aryl radicals is of an order equal to, if not greater than, that of the alkyl radicals. The result of test 14 is of interest in showing that in the case of aryl groups the presence of a catalyst is not essential, and this recalls the interchange of phenyl and tolyl radicals previously observed in triarylbismuth compounds.⁴

As shown in Table II, the products of eight of these reactions, for which complete analyses were obtained, corresponded as well as could be expected to random equilibrium mixtures. More careful analyses would doubtless have shown even closer correspondence.² In the other six tests, complete analyses were not obtained, but the results (described in the Experimental Part) were nevertheless sufficient to show that redistribution had occurred.

In the three different systems used in tests 1, 2, and 3, which contain the same proportions of methyl to ethyl radicals, the product of each is in accord with the predicted composition, namely, 6.25 mole per cent. tetramethyllead, 25 mole per cent. trimethylethyllead, 37.5 mole per cent. dimethyldiethyllead, 25 mole per cent. methyltriethyllead, and 6.25 mole per cent. tetraethyllead; whereas the compound used in test 4 containing a different proportion of methyl to ethyl radicals gave a product containing the above five methyl-ethyl-lead compounds in close to the predicted proportions of 31.6, 42.2, 21.1, 4.7, and 0.4 mole per cent. respectively. The system used in test 10 contained equal proportions of the three different radicals, methyl, ethyl and *n*-propyl, and gave a product for which the analyses and distillation curve agree very well with the data calculated for the expected mixture of the fifteen

(4) Challenger and Ridgway, *J. Chem. Soc.*, **121**, 104 (1922).

TABLE I
 REDISTRIBUTION OF R_4Pb SYSTEMS

Test	Compounds	Composition Moles	$AlCl_3$, Mole %	Solvent, ml.	Temp., °C.	Time, hr.
1	Me_4Pb	0.15	1.3	None	80	2
	Et_4Pb	.15				
2	Me_3EtPb	.215	3.5	None	80	1
	$MeEt_3Pb$	.215				
3	Me_2Et_2Pb	.3	2.5	Hexane (50)	80	5
4	Me_3EtPb	.3	2.5	Hexane (50)	85	6
5	Me_4Pb	.1	3.8	Hexane (50)	80	5
	$n-Pr_4Pb$	.1				
6	Me_4Pb	.295	1.7	None	80	5
	$n-Pr_4Pb$	.145				
7	$Me_3-i-PrPb$	.30	1.7	None	80	5
	Me_2-i-Pr_2Pb	.14				
8	Et_4Pb	.1	3.8	Hexane (50)	80	5
	$n-Pr_4Pb$	.1				
9	Et_2-n-Pr_2Pb	.16	3.7	Hexane (38)	80	5
10	Me_4Pb	.3	1.5	None	80	5
	Et_4Pb	.3				
	$n-Pr_4Pb$	.3				
11	Me_2-i-Bu_2Pb	.13	5.8	Hexane (25)	85	5
12	$Me_3-t-BuPb$	.08	9.4	Decalin (20)	100-130	5
13	Me_4Pb	.2	2.5	Hexane (75)	80	7
	Ph_4Pb	.1				
14	Ph_4Pb	.06	None	None	200	16
	$(p-MeC_6H_4)_4Pb$	.06				

 TABLE II
 OBSERVED AND CALCULATED^a COMPOSITIONS OF THE REACTION PRODUCTS

Test	Compounds	r^b		R_4Pb	$R_3R'Pb$	$R_2R'_2Pb$	RR'_3Pb	R'_4Pb
1	Me_4Pb	0.50	Obsd.	6.0	21.1	39.6	27.3	6.0
	Et_4Pb		Calcd.	6.25	25.0	37.5	25.0	6.25
2	Me_3EtPb	.50	Obsd.	4.4	25.4	44.4	17.8	8.0
	$MeEt_3Pb$		Calcd.	6.25	25.0	37.5	25.0	6.25
3	Me_2Et_2Pb	.50	Obsd.	3.5	20.4	42.7	27.4	6.0
			Calcd.	6.25	25.0	37.5	25.0	6.25
4	Me_3EtPb	.75	Obsd.	29.9	46.7	16.1	6.7	0.6
			Calcd.	31.6	42.2	21.1	4.7	.4
5	Me_4Pb	.50	Obsd.	5.0	20.6	45.4	23.0	6.0
	$n-Pr_4Pb$		Calcd.	6.25	25.0	37.5	25.0	6.25
6	Me_4Pb	.67	Obsd.	16.3	41.9	32.5	8.2	1.1
	$n-Pr_4Pb$		Calcd.	20.2	39.7	29.3	9.6	1.2
7	$Me_3-i-PrPb$	.67	Obsd.	13.2	49.2	32.7	4.5	0.4
	Me_2-i-Pr_2Pb		Calcd.	20.2	39.7	29.3	9.6	1.2
11	Me_2-i-Bu_2Pb	.50	Obsd.	8	22	48	18	4
			Calcd.	6.25	25.0	37.5	25.0	6.25

^a Calculated mole percentages of compounds are obtained by the equations: Mole fraction $R_4Pb = r^4$; $R_3R'Pb = 4r^3(1-r)$; $R_2R'_2Pb = 6r^2(1-r)^2$; $RR'_3Pb = 4r(1-r)^3$; $R'_4Pb = (1-r)^4$. ^b r , the mole fraction of the smaller alkyl group, equals $[R_4Pb] + 0.75[R_3R'Pb] + 0.5[R_2R'_2Pb] + 0.25[RR'_3Pb]$, where the brackets denote the mole fraction of the compounds used.

possible compounds in their theoretical proportions, as shown in Table III and Fig. 1.

Tests 6 and 7, each of which contains the same relative proportion of methyl to propyl radicals,

were made to determine whether the redistribution would be accompanied by the isomerization of *i*-propyl groups to *n*-propyl groups, an occurrence which might be anticipated in view of the

TABLE III

CALCULATED AND OBSERVED COMPOSITION OF RANDOM EQUILIBRIUM MIXTURE CONTAINING Me, Et, AND Pr RADICALS IN THE SAME PROPORTIONS

Carbon atoms	Compounds	Mole per cent. Calculated ^a	Observed ^b
4	Me ₄ Pb	1.23	1.3
5	Me ₃ EtPb	4.94	3.6
6	Me ₂ Et ₂ Pb	7.41	
	Me ₃ PrPb	4.94	12.35
7	MeEt ₂ Pb	4.94	
	Me ₂ EtPrPb	14.81	19.75
8	Et ₄ Pb	1.24	
	MeEt ₂ PrPb	14.81	
	Me ₂ Pr ₂ Pb	7.41	23.46
9	Et ₃ PrPb	4.94	
	MeEtPr ₂ Pb	14.81	19.75
10	Et ₂ Pr ₂ Pb	7.41	
	MePr ₃ Pb	4.94	12.35
11	EtPr ₃ Pb	4.94	5.9
12	Pr ₄ Pb	1.23	1.2
		100.00	100.0

^a Calculated concentrations are given by the general formula previously presented,¹ which in the present case is:

Mole fraction $Me_aEt_bPr_{(4-a-b)}Pb =$

$$\frac{4!}{a!b!(4-a-b)!} \left(\frac{1}{3}\right)^a \left(\frac{1}{3}\right)^b \left(\frac{1}{3}\right)^{(4-a-b)}$$

^b Observed concentrations were calculated as described in the Experimental Part.

greater stability of *n*-propyllead compounds. The distillation curves, which are illustrated in Fig. 2, clearly indicate that no isomerization takes place.

Catalysts.—The different catalysts for the redistribution reaction were tested with the system tetramethyllead-tetraethyllead. These catalysts are listed in Table IV, which also gives the concentrations and experimental conditions employed. It is believed that this list is by no means exhaustive. Bearing in mind that a large number of metallic halides have been shown to react with organo-metallic compounds to give organo-metallic halides⁵ as, for example $Et_4Pb + AlCl_3 = Et_3PbCl + EtAlCl_2$, it will be noted that most of the catalysts either belong to the class of RMX compounds or will yield such compounds under the conditions of the reaction. For this reason, the list of catalysts probably could be enlarged quite readily

(5) Goddard, Ashley and Evans, *J. Chem. Soc.*, **121**, 978 (1922); Goddard and Goddard, *ibid.*, **121**, 260 (1922); Goddard, *ibid.*, **123**, 1172 (1923); Gilman and Apperson, *J. Org. Chem.*, **4**, 162 (1939).

TABLE IV

LIST OF CATALYSTS

Conditions: 0.15 mole Me₄Pb, 0.15 mole Et₄Pb, 50 ml. solvent.

Catalyst	Mole %	Solvent	Temp., °C.	Time, hr.	Redistribution
ZnF ₂	6.5	Decalin	170	5	Complete
ZnCl ₂	4.9	Decalin	175	24	Partial ^a
HgCl ₂	2.5	Decalin	170	6	Complete
BF ₃ (gas)	..	Hexane	80	4	Complete
BF ₃ Et ₂ O	5.3	Hexane	85	5	Complete
AlCl ₃	2.5	Hexane	80	5	Complete
AlBr ₃	1.3	Hexane	80	5	Partial
AlI ₃	1.6	Hexane	80	5	Slight
MeAlCl ₂	3.0	Hexane	80	5	Complete
Me ₂ AlCl	7.2	Hexane	85	5	Complete
Bu ₃ Al ₂ I ₃	2.9	Hexane	85	5	Slight
ZrCl ₄	2.9	Decalin	175	5	Partial
SnCl ₄	8.6	Decalin	160	5	Complete ^a
Et ₃ SnBr	2.3	Hexane	80	5	Partial
Et ₃ PbCl	5.1	Hexane	80	5	Complete ^b
Et ₃ PbBr	8.9	Hexane	80	5	Complete ^b
Me ₃ PbI	11.4	Hexane	80	5	Partial ^b
PCl ₃	7.6	Decalin	160	5.5	Complete
AsCl ₃	3.7	Decalin	170	5	Complete ^c
BiCl ₃	2.1	Decalin	170	5	Complete
FeCl ₃	2.1	Decalin	160	6	Complete
PtCl ₄	2.0	Decalin	100	5	Complete

^a Some decomposition occurred, with deposition of metallic lead. ^b The catalyst was not removed before distillation. ^c A moderate amount of side reaction occurred, with deposition of lead chloride.

by further tests. The different catalysts show a

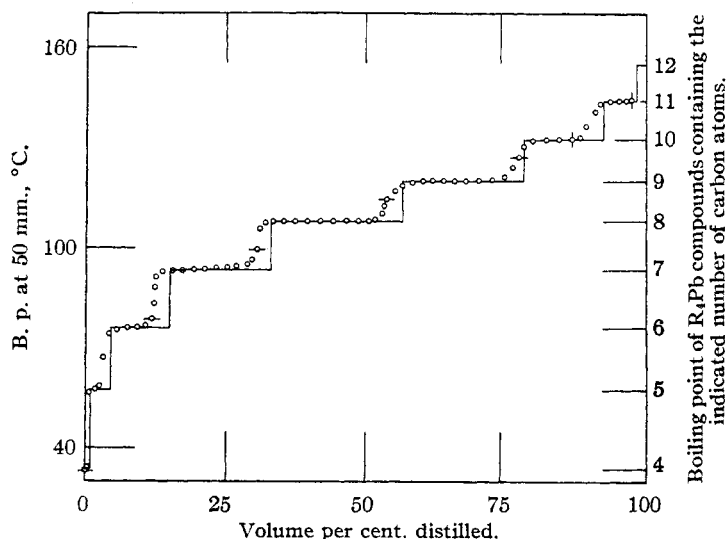


Fig. 1.—Distillation of the reaction product of Me₄Pb + Et₄Pb + Pr₄Pb: solid line calculated for random equilibrium mixture having $[Me] = [Et] = [Pr] = 1/3$; —○—, distillation cuts.

considerable variation in their activity, ranging from relatively weak catalysts such as the alkyllead halides and zirconium chloride, up to very

effective catalysts such as the methylaluminum a high temperature. Of the catalysts, the trialkylchlorides. A general idea of the influence of the lead halides increase in activity in the order:

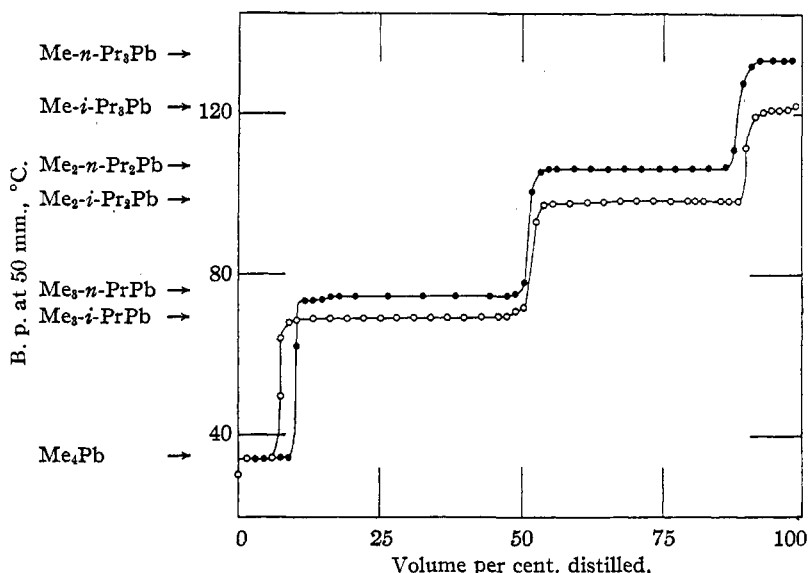


Fig. 2.—Distillation of the reaction products of test 6 ($\text{Me}_3\text{-}i\text{-PrPb} + \text{Me}_2\text{-}i\text{-Pr}_2\text{Pb}$) and test 7 ($\text{Me}_4\text{Pb} + n\text{-Pr}_4\text{Pb}$): $\circ$, $i\text{-Pr}$, $\bullet$, $n\text{-Pr}$.

kind and amount of catalyst on the reaction velocity is obtainable from the data in Table V. For the system tetramethyllead-tetraethyllead, with or without solvents, no reaction was detected in the absence of a catalyst even after a long time at

velocity is marked, as can be seen from the data for the trialkyllead halide catalysts in Table V, but no quantitative measurement of the effect has been made as yet. On the other hand, there is not the slightest indication of any effect of tem-

iodide, bromide, chloride; but they are at best relatively weak catalysts, concentrations of five to ten mole per cent. being required to bring about complete reaction in five hours at 80° . The aluminum chloride catalysts are effective at a concentration of 0.5 mole per cent., even in thirty minutes at room temperature. With smaller concentrations there was some indication that the reaction proceeded for a time at about the normal rate but then came to a halt, probably owing to the disappearance of the catalyst through decomposition reactions.

Temperature.—The effect of temperature on the reaction

TABLE V
THE EFFECT OF CATALYST CONCENTRATION, SOLVENTS AND TEMPERATURE^a

Catalyst	Mole % of catalyst	Solvent	Ml.	Temp., °C.	Time, hr.	Redistribution
None	...	Decalin	50	160	28	None
None	...	Hexane	50	85	5	None
AlCl_3	2.5	Hexane	50	25	5	Complete
AlCl_3	2.5	Hexane	500	70	5	Complete
AlCl_3	1.3	Hexane	35	90	1	Complete
AlCl_3	0.3	Hexane	50	80	5	Partial
AlCl_3	1.02	None		25	0.25	Complete ^b
AlCl_3	0.61	None		25	.5	Complete ^b
Me_2AlCl	.51	None		25	.5	Complete ^b
Me_2AlCl	.44	None		25	.5	Complete ^b
Me_2AlCl	.38	None		25	1	Partial (stops) ^b
AlCl_3	.38	None		25	1	Partial (stops) ^b
AlCl_3	.32	None		20	24	Partial
Et_3PbCl	5.0	Hexane	50	80	5	Complete ^c
Et_3PbCl	3.0	Hexane	50	80	5	None ^c
$\text{Me}_3\text{PbCl} + \text{Et}_3\text{PbCl}$	5.1	None		25	24	None
$\text{Me}_3\text{PbCl} + \text{Et}_3\text{PbCl}$	2.6	Acetone	30	25	22	Trace ^d
$\text{Me}_3\text{PbCl} + \text{Et}_3\text{PbCl}$	5.1	Acetone	75	54	18	Partial ^d
Et_3PbBr	8.9	Hexane	50	80	5	Complete ^c
Et_3PbBr	4.4	Hexane	50	80	5	Partial ^c
Me_3PbI	11.4	Hexane	50	80	5	Partial ^c

^a About 50 ml. of an equimolecular mixture of Me_4Pb and Et_4Pb was used in all cases. ^b The course of the reaction was followed by vapor pressure measurements. ^c The product was distilled directly without first extracting the catalyst.

^d The acetone was distilled and the catalyst extracted, prior to distillation.

perature on the relative proportions of the R_4Pb compounds in the product of the completed reaction of a given system.

Solvents.—The presence of any of several chemically inert solvents does not appear to exert any pronounced effect on the reaction velocity, and certainly does not alter the relative proportions of the R_4Pb compounds in the completely-reacted product. The data in Table V indicate that, for the aluminum chloride catalyst, the presence of hexane may have a moderate retarding effect on the reaction velocity, but that a ten-fold increase in the amount of hexane has no further perceptible effect.

Experimental

Tetramethyllead and Tetraethyllead with Aluminum Chloride Catalyst.—Into a three-neck flask equipped with a reflux condenser and thermometer was added successively 0.5 g. of aluminum chloride and a mixture of 0.15 mole each of tetramethyl- and tetraethyllead, while maintaining an atmosphere of nitrogen within the system and cooling the flask in ice water. The mixture was kept at 80° for two hours. After cooling, an equal volume of water was added and after shaking the alkyllead layer was separated, filtered, and fractionated.² Redistribution was complete, as shown in Table II.

Other Alkyllead Systems.—The other alkyllead systems were run in a similar manner, except for variations in temperature, kind and amount of solvent, and concentration of the particular catalyst used, as shown in Tables I, IV, and V. When a solvent was used, the catalysts, with the exception of the methylaluminum chlorides, were added directly to the solution of the lead alkyls. The methylaluminum chloride catalysts were added by breaking small sealed glass capsules of the materials beneath the surface of the liquid lead alkyls, while maintaining an atmosphere of nitrogen in the system. In the experiment using boron trifluoride catalyst, the gas was bubbled into the solution of lead alkyls for one to two minutes prior to heating. In the two tests (Table V) in which acetone was used as the solvent, after the reaction the acetone was first distilled and the mixture of trialkyllead chloride catalysts extracted from the residue of lead alkyls with concentrated ammonia solution, prior to distillation of the product. In all other tests (Tables IV and V) where the trialkyllead halides were used for catalysts (with the exception of one test (Table V) where no solvent was used) the products of the reaction were distilled without first removing the catalyst.

In five tests listed in Table V, the course of the redistribution reaction was followed by a vapor pressure method which consisted of removing samples of the reaction mixture at regular time intervals, extracting the catalyst from the samples with water and filtering, and measuring the vapor pressure of the mixtures at 60°. The apparatus used for these measurements consisted of a bulb of about 200-ml. capacity, fitted with a mercury manometer and with a side arm for evacuating the system and intro-

ducing a measured amount of the sample. The apparatus was contained in a bath maintained thermostatically at $60 \pm 0.01^\circ$. The vapor pressure of samples thus measured varied from 67 mm., indicating no redistribution, to 31 mm., indicating complete redistribution.

Trimethylisopropyllead and Dimethyldiisopropyllead with Aluminum Chloride Catalyst.—The product of the reaction of 0.3 mole of trimethylisopropyllead, 0.14 mole of dimethyldiisopropyllead and 1 g. of aluminum chloride, at 80° for five hours, on distillation gave the fractions listed in Table VI. The observed and calculated composition of the equilibrium mixture based on the lead analyses of the various fractions and the distillation curve (Fig. 2) are compared in Table II, test 7. The reaction, under the conditions used, was not entirely complete.

TABLE VI

DISTILLATION AND ANALYTICAL DATA FOR TEST No. 7

Fraction	B. p. at 50 mm., ^a °C.	Weight, g.	Lead analysis	Compounds present
1	→ 30		3.1935 g.	Me_4Pb + hexane ^b
2	49.5	9.4	76.57%	Me_4Pb + hexane ^b
3	93.0	56.0	70.22%	Me_4Pb + $Me_3-i-PrPb$
4	111.5	41.8	64.39%	$Me_3-i-PrPb$ + Me_2-i-Pr_2Pb
5	122.0	8.6	60.37%	Me_2-i-Pr_2Pb + $Me-i-Pr_3Pb$
Residue ^c			0.401 g.	$Me-i-Pr_3Pb$ + $i-Pr_4Pb$

^a The actual boiling points were converted to 50 mm. by the aid of a nomogram.² ^b Solvent hexane used for extraction of aqueous layer. ^c The residue was washed from the still with carbon tetrachloride. Its R_4Pb content was estimated to be 80% $i-Pr_4Pb$.

Tetraethyllead and Tetra-*n*-propyllead with Aluminum Chloride Catalyst.—The product of the redistribution of 0.1 mole each of tetraethyl- and tetra-*n*-propyllead in the presence of 1 g. of aluminum chloride and 50 ml. of hexane at 80° for five hours showed complete redistribution on distillation. The distillation, however, was not of such precision as to warrant making an analysis of the products.

Diethyldi-*n*-propyllead with Aluminum Chloride Catalyst.—The product of the redistribution of 0.16 mole of diethyldi-*n*-propyllead in 38 ml. of hexane in the presence of 0.8 g. of aluminum chloride at 80° for five hours was judged to be complete although the distillation was not precise enough to make an analysis of the products.

Tetramethyllead, Tetraethyllead and Tetra-*n*-propyllead with Aluminum Chloride Catalyst.—In the system tetramethyl-, tetraethyl-, tetra-*n*-propyllead, it was not possible to separate all fifteen constituents by fractionation since the boiling points of the compounds containing the same number of carbon atoms are almost identical. The analysis was therefore limited to separation into the nine groups of compounds containing, respectively, from 4 to 12 carbon atoms, as shown in Table III. This was accomplished by making eight sharp distillation cuts, and determining by lead analysis the relative amounts of two consecutive groups of isomers in each cut. These compositions are indicated in Table VII, and the quantitative summation for each group of isomers is given in Table III.

Trimethyl-*t*-butyllead with Aluminum Chloride Catalyst.—The products from the redistribution of 0.08 mole of trimethyl-*t*-butyllead with 1 g. of aluminum chloride in 20 ml. of decalin at 100–130° for five hours were 7 g. of

TABLE VII

DISTILLATION AND ANALYTICAL DATA FOR TEST NO. 10

Fraction	B. p. at 50 mm., ^a °C.	Number of carbon atoms in R ₄ Pb 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 Me₄Pb. ^d The residue was washed from the still with carbon tetrachloride and its R₄Pb content was estimated to be 50% EtPr₃Pb.

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*_D²⁰ 1.5837 (*Anal.*

Calcd. for C₉H₁₄Pb: Pb, 62.90. Found: Pb, 63.32); dimethyldiphenyllead, 25 g., b. p. 151–152° (2 mm.), *n*_D²⁰ 1.6263 (*Anal.* Calcd. for C₁₄H₁₈Pb: 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 C₁₉H₁₈Pb: 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 R₄Pb 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

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The Redistribution Reaction. VI. Alkyl Lead Halides

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It was stated in the first paper of this series¹ 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 com-

prising 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.

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