

densities and molecular weights, the mole fractions of each component of the metal alkyl portion of the product were calculated. In those relatively few cases where two or three components were expected to be present in the resi-

TABLE V
ANALYSIS OF A TETRAALKYLLEAD MIXTURE

Pressure, mm.	Vapor temp.		Distillate	
	Obsd.	Corr. to 50 mm.	Vol. obsd. at -30°	Vol. corr. to 20°
60	38.5	34.8	1.5	1.5
	41.6	37.5	3.2	3.3
	45.4	41.8	3.6	3.7
33	40.0	49.0	4.2	4.4
	45.2	54.2	5.0	5.2
	46.5	55.9	5.5	5.7
	47.0	56.1	7.5	7.8
32	47.4	56.4	11.0	11.5
	47.2	57.0	13.0	13.6
	48.5	58.2	15.6	16.3
	53.0	63.0	16.3	17.1
11	36.6	67.0	17.0	17.8
	42.5	73.3	17.3	18.1
	45.5	76.5	19.2	20.1
	46.3	77.2	21.0	22.0
	46.0	77.0	26.0	27.3
	46.0	77.0	33.0	34.6
	46.0	77.0	36.0	37.8
5.5	50.5	81.3	37.8	39.6
	45.0	88.2	38.7	40.6
	49.4	93.0	39.5	41.4
	49.5	93.0	42.0	44.1
	49.5	93.0	44.3	46.5
	50.5	94.0	49.0	51.4
	50.4	94.0	52.6	55.2
	52.5	96.0	54.0	56.7
	54.4	98.0	54.2	56.9
	59.4	103.2	54.5	57.2
4.5	59.0	106.5	56.0	58.8

Compound	Cut points, ml.	Vol., ml.	Milli- mole	Mole, %
Solvent	0			
Me ₃ Pb	1.5	2.7	20.1	5.5
Me ₃ EtPb	4.2	13.4	89.6	24.4
Me ₂ Et ₂ Pb	17.6	22.9	138.9	37.8
MeEt ₃ Pb	40.5	16.7	92.6	25.2
Et ₄ Pb dist.	57.2	5.1	26.1	7.1
Et ₄ Pb residue	59.8			
	62.3			

$$[\text{Me}] = 0.055 + (0.75 \times 0.244) + (0.5 \times 0.378) + (0.25 \times 0.252) = 0.490.$$

due, a reasonable estimate of each was made; inasmuch as the amounts of these involved were always small and their various molecular volumes did not differ greatly, this procedure introduced no significant uncertainty in computation of the total amount of each kind of metal and alkyl group present.

The observed and derived data and the distillation curve for a typical example of a satisfactory analysis of a mixture of the five methyl and ethyl tetraalkyllead compounds are given in Table V and Fig. 2.

Summary

The procedure used for the analysis of volatile metal alkyl mixtures by distillation is described, and is shown by tests to give results accurate to less than 1% of the total volume.

Analyses of a series of mixtures of methyl and ethyl lead alkyls which have undergone the redistribution reaction show, within this experimental error, exact agreement with the compositions predicted for random equilibrium mixtures; individual analyses for other systems are also in satisfactory accord with prediction.

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

The Redistribution Reaction. III. Determination of a Material Balance

BY GEORGE CALINGAERT AND HAROLD SOROOS

The first paper¹ of this series reported, as a distinctive characteristic of the redistribution reaction, its essential freedom from side reactions and decomposition. This was evidenced, for many different systems, by the absence of gas evolution, precipitation, tar formation, or heat of reaction, and by satisfactory recoveries of material. To provide a quantitative measure of this, for one case at least, the present work was undertaken, and consisted in carrying out a representative redistribution reaction in the usual

manner, obtaining an accurate material balance, and testing for secondary products.

Such a determination can be made with a high degree of accuracy for a reaction involving tetraalkyllead compounds, since any side reactions will convert the lead to other forms, which can be separated readily from the tetraalkyllead compounds constituting the bulk of the reaction mass. Accordingly, a mixture of tetramethyl- and tetraethyllead was used for this test.

Table I gives the material balance on a lead basis for two tests in which a mixture of the two

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

TABLE I
 MATERIAL BALANCE WITH ALUMINUM CHLORIDE CATALYST

Input	Test 1			Test 2		
	G.	Millimoles	%	G.	Millimoles	%
Pb as R ₄ Pb	57.864	279.25	100.00	60.7935	293.39	100.00
AlCl ₃	0.442	3.32		0.3012	2.26	
Recovery						
Pb as R ₄ Pb	56.7827	274.04	98.13	60.0334	289.72	98.75
Pb as R ₃ PbCl	0.7803	3.77	1.35	0.9053	4.37	1.49
Pb as PbCl ₂	0.0470	0.22	0.08	0.0654	0.31	0.11
Loss (or gain)	+0.2540	+1.22	+0.44	-0.2106	-1.01	-0.35
Total	57.8640	279.25	100.00	60.7935	293.39	100.00

lead alkyls was diluted with hexane and treated with aluminum chloride. The recovery of tetraalkyllead averaged 98.5%; the remaining 1.5% was principally trialkyllead chloride. A trace of lead chloride was found, as was to be expected since this is a normal decomposition product of trialkyllead chlorides. No metallic lead was formed. Aluminum chloride is known to react with tetraalkyllead,² and the trialkyllead halide found corresponded approximately to the aluminum chloride taken, in accordance with the equation $\text{AlCl}_3 + \text{R}_4\text{Pb} \rightarrow \text{RAlCl}_2 + \text{R}_3\text{PbCl}$.

These results suggested that the use of alkyl-aluminum chlorides as catalysts might reduce the formation of the lead salts, and this was found to be so. Table II gives the data for two tests in which the mixture of the two lead alkyls, without solvent, was treated with methylaluminum dichloride and dimethylaluminum chloride, respectively. In order to obtain readily-measurable quantities of the products of the reaction with the catalysts, the amounts of the latter used were very much greater than necessary for complete redistribution. Analyses were made only for the alkyllead chlorides and lead chloride formed; again, there was no metallic lead. The amount of lead thus found in the form of salts equalled only 0.10 and 0.04 mole, respectively, per mole of catalyst. A parallel test using aluminum chloride confirmed the results given in Table I, yielding 1.46 moles of lead chlorides per mole of catalyst.

 TABLE II
 TETRAALKYLLEAD CONVERTED TO LEAD CHLORIDES BY DIFFERENT ALUMINUM CATALYSTS

Pb input, as R ₄ Pb, millimoles	Catalyst		Pb output, as chlorides, millimoles	Moles Pb chlorides per mole Al
	Compound	Millimoles		
296.41	Me ₂ AlCl	16.10	0.626	0.039
300.81	MeAlCl ₂	18.84	1.965	0.104
297.19	AlCl ₃	3.12	4.540	1.455

(2) Gilman and Apperson, *J. Org. Chem.*, **4**, 162 (1939).

In these three tests, the tetraalkyllead product of the reaction was distilled as described in the preceding paper³ and the redistribution was found to be complete. In the first tests using aluminum chloride the distillation was omitted, since concurrent experiments showed that the reaction was complete, under the conditions used, with lower concentrations of the catalyst.

It is, therefore, evident that the redistribution reaction is quantitative, apart from such irreversible interaction with the catalyst as may be imposed by the selection of one particular catalyst or another.

Experimental

Determination of a Material Balance.—The determination of a material balance was carried out in the following manner.

Approximately 0.15 mole each of tetramethyl- and tetraethyllead with 40-ml. of *n*-hexane were placed in a glass-stoppered flask and weighed. After a sample was withdrawn for a lead analysis, a small amount of anhydrous aluminum chloride was added and its weight determined. A reflux condenser, the top of which was connected to a dry-ice trap, was attached to the flask and the mixture was refluxed at 80° for four hours. The contents of the trap and condenser were washed into the reaction mixture with 5-ml. of *n*-hexane. The main body of the reaction mixture, containing the tetraalkyllead compounds and dissolved trialkyllead chlorides, was filtered by nitrogen pressure through a sintered-glass filter-stick into a tared flask, using several small portions of *n*-hexane to wash the residue. Samples of the filtrate and the hexane washings were analyzed for lead. An aliquot of the filtrate was extracted with four 25-ml. portions of concentrated ammonia solution to remove the dissolved trialkyllead chlorides, and after filtering the combined extracts through a wet filter paper, the lead content was determined. The residue was washed with five 10-ml. portions of benzene, followed by filtration through the filter-stick to remove the undissolved trialkyllead chlorides, and the lead content of the washings was determined. About 100 ml. of water in small portions was next used to wash the residue free of lead chloride. The lead content of the washings was determined. The flask and filter-stick were finally washed with

(3) Calingaert, Beatty and Neal, *THIS JOURNAL*, **61**, 2755 (1939).

nitric acid and the lead was determined. The analytical data for the two experiments are given in Table III.

TABLE III
LEAD ANALYSIS

Input	Pb found, g.	
	Test 1	Test 2
R ₄ Pb (Hexane solution)	57.8640	60.7935
Recovery		
R ₄ Pb, R ₃ PbCl (Hexane solution)	55.5530	58.8735
R ₄ Pb, R ₃ PbCl (Hexane washings)	1.4430	1.5290
R ₃ PbCl (NH ₃ extraction)	0.2133	0.3691
R ₃ PbCl (Benzene washings)	.5670	.5362
PbCl ₂	.0440	.0639
Residue (HNO ₃ washings)	.0030	.0015

Determination of Lead Chlorides Formed with Different Catalysts.—The determination of the amount of tetraalkyllead compounds converted to alkyllead chlorides and lead chloride using different aluminum catalysts was carried out in the following manner.

To a weighed amount of the catalyst, contained in a 500-ml. 3-necked flask equipped with vapor-proof mechanical stirrer, thermometer, and reflux condenser, the tetraethyllead followed by the tetramethyllead was added slowly from a dropping funnel in the top of the condenser. The flask was cooled in an ice-bath and an atmosphere of nitrogen was maintained within the flask during the addition of the alkyllead compounds. Failure to follow the experimental procedure and precautions outlined above may result in violent decomposition of the tetraalkyllead, especially of the tetramethyllead. The ice-bath was then removed and replaced by an oil-bath; the mixture was stirred and maintained at 80° in an atmosphere of nitrogen for two hours.

The reaction flask was then cooled and the catalyst decomposed by shaking with 100 ml. of distilled water. The aqueous layer, containing alkyllead chlorides and lead

chloride, was separated, filtered through a wet filter paper and analyzed for lead. The alkyllead layer was extracted with four 25-ml. portions of concentrated ammonia solution, to remove trialkyllead chlorides. The extracts were combined, filtered through a wet filter paper, and analyzed for lead. The filter papers were finally washed with nitric acid to dissolve any lead residue, and the washings were analyzed for lead.

The alkyllead layers were finally distilled to ascertain the extent of redistribution. The reaction was complete in every case. Table IV gives the analyses of products for lead chlorides.

TABLE IV
LEAD ANALYSIS

Products	Catalyst		
	Me ₃ AlCl	MeAlCl ₂	AlCl ₃
Pb in Aq. layer, g.	0.1296	0.3150	0.9220
Pb in NH ₃ , g.	.0000	.0926	.0193
Pb in residue, g.	.0000	.0000	.0000
Pb (total), g.	.1296	.4076	.9413

Summary

By determination of an accurate material balance, the redistribution of a mixture of tetramethyl- and tetraethyllead in hexane solution is shown to be quantitative. When aluminum chloride is used as the catalyst, it is found to react irreversibly with the alkyllead compounds, as expected, forming alkyllead chlorides in very small quantities, equivalent to about 1.5 moles per mole of catalyst. When methylaluminum chlorides are used as catalysts, this amount becomes negligible.

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The Reaction of the Grignard Reagent with Homophthalic Anhydride

BY CHARLES C. PRICE, FREDERICK M. LEWIS AND MORRIS MEISTER

The reaction of methylmagnesium iodide with homophthalic anhydride has been investigated as a possible method for the preparation of the unreported keto acid, *o*-acetylphenylacetic acid (I), which was desired in connection with another investigation.

Bauer and Wolz,¹ in determining the products from the action of an excess of several Grignard reagents on homophthalic anhydride, obtained only the various homophthalides. Since Simonis and Arand and Weizmann, Bergmann and Bergmann² have reported keto acids as well as phthal-

ides from phthalic anhydride, the reaction with homophthalic anhydride has been studied under conditions more favorable for the formation of the desired keto acid. However, in spite of using the inverse procedure, *i. e.*, adding the Grignard reagent to a solution of the anhydride, and using just the calculated amount of reagent, one-half of the starting material was converted to dimethylhomophthalide (II), the remainder was recovered unchanged. No *o*-acetylphenylacetic acid was obtained, although in a few cases the recovered homophthalic acid had a low melting point and gave an iodoform test, indicating the possible presence of small amounts of this substance.

(1) Bauer and Wolz, *Arch. Pharm.*, **249**, 454 (1911).

(2) (a) Simonis and Arand, *Ber.*, **42**, 3721 (1909); (b) Weizmann, Bergmann and Bergmann, *J. Chem. Soc.*, 1369 (1935).