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).

TABLE I

ORGANO-METALLIC SYSTEMS TESTED

Composition Compd.	Moles	$AlCl_3$, mole per cent.	Solvent	Temp., °C.	Time, hours
Me_2Hg	0.11	1.7	None	25	18
Et_2Hg	.11				
MeEtHg	.07	4.0	None	25	66
Me_4Sn	.15	2.5	Pentane	60	5
Et_4Sn	.15		(50 ml.)		
Et_4Si	.14	2.5	None	173–181	5
Pr_4Si	.15				
Me_2Zn	.32	1.4[a]	None	About 60	5
Et_2Zn	.21				

[a] Also tested with 1.5% of a mixture of methylaluminum chlorides in addition to the aluminum chloride.

the aluminum chloride catalyst. The analytical distillation curves[4] are shown in Fig. 1. The redistribution of dimethylmercury with diethylmercury and the subsequent isolation of methylethylmercury is of particular interest, since reports in the literature[5] suggest that methylethylmercury is too unstable to exist as such for any length of time.

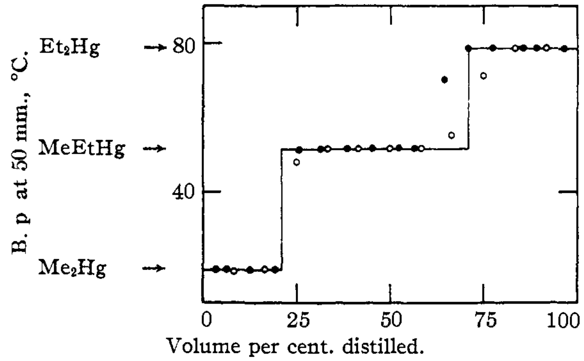

Fig. 1.—Distillation of reaction product from: ○, MeEtHg; ●, $Me_2Hg + Et_2Hg$; solid line calculated for random equilibrium in mixture having [Me] = 0.5.

Contrary to these reports, pure methylethylmercury appears to be a very stable compound, being unchanged on standing at room temperature for months, or on distillation at 127°, even after the addition of a small amount of iodine. Its isolation in a pure state can, therefore, be accomplished by fractional distillation of the random redistribution mixture of the three mercury alkyls obtained from the redistribution of a mixture of dimethylmercury with diethylmercury. In the light of the present study it now appears probable that Frankland's material contained catalytic amounts of alkylmercuric chloride which caused redistribution, and that the equilibrium was constantly displaced by the removal of dimethylmercury, thus resulting in the gradual disappearance of the methylethylmercury originally present.

TABLE II

PRODUCTS FROM THE REDISTRIBUTION OF Me_2Hg WITH Et_2Hg, AND OF MeEtHg

Original compounds		Composition, mole per cent. Me_2Hg	MeEtHg	Et_2Hg
$Me_2Hg + Et_2Hg$	Found	26	46	28
	Calcd.	25	50	25
MeEtHg	Found	28	47	25
	Calcd.	25	50	25

Random equilibrium mixtures containing the five possible metal alkyls were obtained from the redistribution reaction of tetramethyltin with tetraethyltin, and of tetraethylsilicon with tetrapropylsilicon. The analyses of the two products are given in Tables III and IV and the analytical distillations are shown in Figs. 2 and 3. The redistribution of tetraethylsilicon with tetrapropylsilicon was tested for convenience at the refluxing temperature of the mixture, and the possibility of reaction at a lower temperature was not investigated. These results for silicon recall the inter-

TABLE III

PRODUCTS FROM THE REDISTRIBUTION OF TETRAMETHYL- WITH TETRAETHYLTIN

	Mole per cent. Found	Calcd.[1] for r^a = 0.46
Me_4Sn Me_3EtSn	24.6	25.3
Me_2Et_2Sn	38.4	37.0
$MeEt_3Sn$ Et_4Sn	37.0	37.7

[a] r is the estimated mole fraction of methyl radicals in the product.

TABLE IV

PRODUCTS FROM THE REDISTRIBUTION OF TETRAETHYL- WITH TETRAPROPYLSILICON

	Mole per cent. Found	Calcd.[1] for r^a = 0.464
Et_4Si	5	4.6
Et_3PrSi	21	21.4
Et_2Pr_2Si	40	37.1
$EtPr_3Si$	24	28.6
Pr_4Si	10	8.3

[a] r is the estimated mole fraction of methyl radicals in the product.

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

(5) Frankland, *Ann.*, **111**, 57 (1859), treated ethylmercuric chloride with dimethylzinc and stated that: "It is probable that mercuric ethomethide was formed in the above reaction; but subsequent distillations gradually transformed it, more or less perfectly, into a mixture of mercuric ethide and mercuric methide." Hilpert and Grüttner, *Ber.*, **48**, 906 (1915), state that RR'Hg compounds, sealed in glass and kept for a few weeks, decompose to R_2Hg and R'_2Hg; see also Kharasch and Marker, THIS JOURNAL, **48**, 3130 (1926).

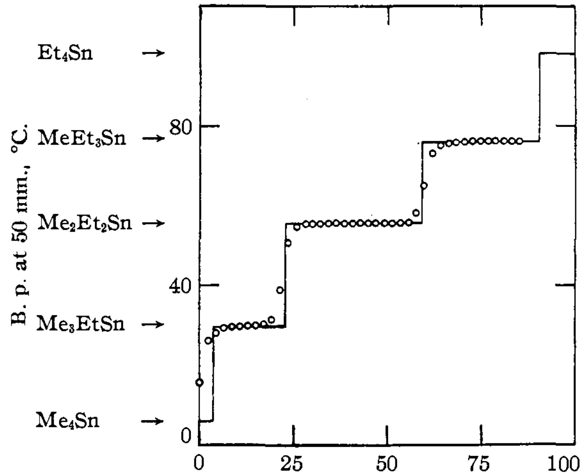
changes of radicals found at high temperatures (about 300°) by Dolgov and Volnov[6] in alkyl and alkyl–aryl $R_3R'Si$ compounds. These authors stated that the compounds rearranged according to the scheme $2R_3R'Si \rightarrow R_2R'_2Si + R_4Si$, and ascribed this to the greater stability of the symmetrical molecules. However, their analytical data are only sufficient for the identification of the new compounds so obtained, and are not adequate to determine the composition of the whole product or to demonstrate the existence of an equilibrium.

A mixture of dimethylzinc with diethylzinc did not undergo any redistribution at the boiling temperature (about 60°) in the presence of aluminum chloride or mixed methylaluminum chlorides as catalysts. The possibility that the reaction can be brought about at a higher temperature or under different operating conditions has not yet been tested.

Although only four metals and three alkyl radicals have been tested in the present study, it seems probable in the light of the results with lead[2] that the reaction will occur as well with other alkyl and aryl radicals of the present metals. It would at least with those metals which are known to form mixed compounds of the RR'M type. This supposition is borne out by the observation of Challenger and Ridgway,[7] who studied the transfer of aryl radicals in organo-metallic compounds, and stated that "a most interesting example of this type of reaction is afforded by the ready production of diphenyl-α-naphthylbismuth by the fusion of tri-α-naphthylbismuth and triphenylbismuth at 190°." Some amount of unchanged reactants was also found in the product, but the small quantities of materials and the methods of separation used obviously precluded an accurate analysis of the product, and no mention of phenyl-di-α-naphthylbismuth is made. These authors also stated that "a preliminary experiment appeared to indicate that this reaction is reversible," without giving any experimental details. It would seem probable that this reaction is an example of redistribution and that a precise analysis would have shown a random equilibrium mixture of all four R_3Bi compounds.

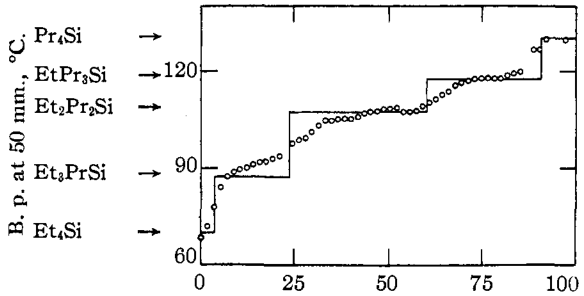
Experimental

Dimethyl- with Diethylmercury.—A mixture of 0.11 mole each of dimethyl- and diethylmercury with 1.7 mole per cent. of aluminum chloride was allowed to stand in a stoppered flask at room temperature for eighteen hours. After extracting the catalyst by shaking with water, the distillation of the product, shown by the solid circles in Fig. 1, yielded the equilibrium mixture given in Table II.



Volume per cent. distilled.

Fig. 2.—Distillation of the reaction product from $Me_4Sn + Et_4Sn$: solid line calculated for random equilibrium mixture having [Me] = 0.46.



Volume per cent. distilled.

Fig. 3.—Distillation of the reaction product from Et_4Si and Pr_4Si: solid line calculated for random equilibrium mixture having [Et] = 0.464.

Methylethylmercury.—The pure compound was obtained by fractional distillation of the random equilibrium mixture obtained from the redistribution of dimethylmercury with diethylmercury: b. p. 51.5 (50 mm.), d^{20} 2.71; $n^{20}D$ 1.5440. *Anal.* Calcd. for C_3H_8Hg: Hg, 81.98. Found: Hg, 81.24. The compound, after standing for seven months at room temperature, showed no evidence of spontaneous redistribution or decomposition to the symmetrical compounds, when redistilled at 50 mm. through a packed column in an atmosphere of nitrogen. Another sample distilled at atmospheric pressure (127.4° at 748 mm.) with no evidence of decomposition, even when the flask was almost dry. Repeating this high temperature distillation after the addition of a trace of iodine produced no change in boiling point or evidence of redistribution, although the iodine reacted immediately with the mercury compound.

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[6] Dolgov and Volnov, *Zhur. Obshchei Khim.*, **1**, 91 (1931); see also Ladenburg, *Ber.*, **7**, 387 (1874).

[7] Challenger and Ridgway, *J. Chem. Soc.*, **121**, 104 (1922).

The redistribution of the compound was effected by treating 0.07 mole with 3.5 mole per cent. of aluminum chloride at room temperature for sixty-six hours, followed by extraction of the catalyst with water. The analytical distillation of the product is shown by the open circles of Fig. 1, and its composition is given in Table II.

Tetramethyl- with Tetraethyltin.—The redistribution of a mixture of 0.15 mole each of the two tin alkyls with 2.5 mole per cent. of aluminum chloride was carried out in 50 ml. of pentane at the boiling point of the mixture, 60°, for five hours. The catalyst went into solution in the mixture and later there was formed about 1 ml. of heavy yellow oil, from which the product was decanted. After distilling off the solvent, there remained 61 g. of tin alkyls, whose analysis by distillation is given in Table III and Fig. 2.

Tetraethyl- with Tetrapropylsilicon.—The redistribution of a mixture of 0.14 mole of tetraethylsilicon and 0.15 mole of tetrapropylsilicon (48% ethyl radicals) with 2.5 mole per cent. of aluminum chloride was carried out at the boiling point of the mixture, 175–180°, for five hours. There was no visible reaction of the catalyst, which finally was extracted with water. The analytical distillation shown in Fig. 3, although not made carefully, showed that redistribution had occurred, and the estimated composition corresponded with the expected equilibrium mixture, as shown in Table IV.

Dimethyl- with Diethylzinc.—A mixture of 0.32 mole of dimethylzinc and 0.21 mole of diethylzinc, after refluxing for five hours in an atmosphere of nitrogen, was fractionated into the two original components without evidence of redistribution. After refluxing the same mixture at atmospheric pressure (temperature about 60°) for five hours in the presence of 1.4 mole per cent. of aluminum chloride, followed by vacuum distillation (20–50 mm.) from the catalyst, fractionation again gave only the symmetrical zinc alkyls. Repeating the experiment with the addition of 1.5 mole per cent. of a mixture of methylaluminum chlorides to the aluminum chloride still did not bring about redistribution.

The recovery of products in the above experiments was essentially quantitative, except for normal handling losses incurred during extraction of the catalyst, filtration, transfer, and distillation.

Summary

The alkyl compounds of mercury, tin and silicon readily undergo the redistribution reaction, yielding random equilibrium mixtures, while the zinc alkyls at 60° failed to react. Methylethylmercury was isolated and found to be stable on standing or distillation, in the absence of redistribution catalysts.

DETROIT, MICHIGAN RECEIVED OCTOBER 9, 1939

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, AND THE NATIONAL INSTITUTE OF HEALTH, WASHINGTON, D. C.]

Studies in the Phenanthrene Series. XXIV. Phenolic Amino Alcohols and Naphthisoquinolines Derived from 9,10-Dihydrophenanthrene[1]

BY ALFRED H. STUART AND ERICH MOSETTIG

Ethanolamine and propanolamine derivatives of 9,10-dihydrophenanthrene prepared in our laboratory[2] have been found to exhibit a relatively high analgesic activity, which, unfortunately, was accompanied by convulsant and emetic effects of similar or even higher degree.[3] In the hope of finding compounds with a more favorable ratio of desirable and undesirable physiological effects, it was decided to synthesize analogous amino alcohols of the dihydrophenanthrene series, containing besides the alkamine side chain also a phenolic hydroxyl group.

The choice of positions into which the phenolic hydroxyl group can be introduced appears to be limited, and the same holds true for the introduction of a second substituent that can be used for building up alkamine side chains or other desirable groups. Thus, the phenolic hydroxyl group can be conveniently introduced only into position 2 of 9,10-dihydrophenanthrene.[4] Also acyl groups enter chiefly position 2, and position 7 if 2 is already occupied by a phenolic hydroxyl group.[2,4b] We have described recently a practicable method for the preparation of 2-hydroxy-7-acetyl-9,10-dihydrophenanthrene,[4b] and this compound, indeed, became the key substance for the various syntheses described in this communication. The 2-hydroxy-7-[2-(diethylamino)-1-hydroxyethyl]-9,10-dihydrophenanthrene (I) was prepared by bromination of the above-mentioned hydroxy ketone, replacement of the bromine by the di-

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(1) This work is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia, and the University of Michigan. Publication authorized by the Surgeon General, U. S. P. H. S.

(2) Burger and Mosettig, THIS JOURNAL, **58**, 1857 (1936).

(3) Small, Eddy, Mosettig and Himmelsbach, "Studies on Drug Addiction," Supplement No. 138 to the Public Health reports, pp. 81–83 (1938).

(4) (a) Burger and Mosettig, THIS JOURNAL, **59**, 1302 (1937); (b) Mosettig and Stuart, *ibid.*, **61**, 1 (1939); (c) Krueger and Mosettig, *J. Org. Chem.*, **3**, 340 (1938).