

3. Oxidation of pyrazolines containing a bromine atom or a nitro radical in the hydrazine residue seemed to cause complete degradation of the molecule. These compounds are still being studied.

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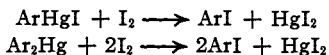
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The Interconversion of Arylmercuric Halides and Diarylmercury Compounds. I

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The reaction, $\text{Ar}_2\text{Hg} + \text{HgX}_2 \rightleftharpoons 2\text{ArHgX}$, has been the subject of many studies.²

The present investigation deals with the influence of inorganic iodides on the reaction. It was suggested by the observation that while sodium iodide in alcoholic solution reverses the reaction in the case of para tolyl compounds, giving a complete conversion to di-*p*-tolylmercury, it has no effect on phenylmercuric iodide. Early in the investigation cases were found in which the reversibility of the reaction by sodium iodide lay between these extremes. Consequently it became necessary to develop a method for analyzing mixtures of Ar_2Hg and ArHgI . This was accomplished satisfactorily by iodimetry.³ The method can best be illustrated by the two equations



Thus a given amount of mercury in a diarylmercury will react with twice as much iodine as the same amount of mercury in an arylmercuric iodide. The method was found to give satisfactory results with known mixtures of arylmercuric halides and diarylmercury compounds.

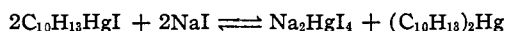
The following arylmercuric iodides were converted to the mercury diaryls by refluxing with an excess of alcoholic sodium iodide: *o*-tolyl, *m*-tolyl, *p*-tolyl, *m*-xylyl, mesitylyl, α -naphthyl and β -naphthyl. Phenylmercuric iodide showed no change even after refluxing for three hundred hours with alcoholic sodium iodide. Benzyl- and cyclohexylmercuric iodides decomposed on long heating with sodium iodide. *p*-Ethylphenyl-

(1) Research Fellow of the Public Health Institute of Chicago. This paper is abstracted from a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree at Northwestern University.

(2) Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., New York, 1921, pp. 59-67; Whitmore, THIS JOURNAL, **41**, 1841 (1919); Hein and Wagler, *Ber.*, **58B**, 1499 (1925); Jurgens, *Rec. trav. chim.*, **45**, 61 (1926); Whitmore, Hanson and Carnahan, THIS JOURNAL, **51**, 894 (1929).

(3) This method was developed at Northwestern University by Messrs. Louis Ehrenfeld and R. J. Sobatzki independently, the former for analyzing mixtures of C-Hg and O-Hg compounds and the latter for analyzing mixtures of C-Hg and C-Hg-C compounds.

mercuric iodide gave a mixture of unchanged material and di-*p*-ethylphenylmercury in which the two substances could be distinguished by their characteristic crystalline forms. When *p*-cymylmercuric chloride was refluxed with excess of alcoholic sodium iodide, crystals of the pure di-*p*-cymylmercury separated on cooling. This was proved by analysis and by reaction with mercuric chloride to give a quantitative yield of pure *p*-cymylmercuric chloride. A careful study of this reaction showed the existence of a very sensitive equilibrium. When the mixture of sodium iodide and *p*-cymylmercuric chloride was heated with alcohol a yellow solution was formed at once. When this solution was cooled crystals of di-*p*-cymylmercury separated at once. In an effort to find whether the diarylmercury existed in the hot solution, the latter was poured into a large volume of ice water. The solid which precipitated was found to be *p*-cymylmercuric iodide contaminated by about 1% of the diarylmercury compound. These results showed that the hot solution contained the following system in equilibrium.



It thus became necessary to study conditions which might influence such an equilibrium. The relative solubilities of a number of arylmercuric iodides and the corresponding diarylmercury compounds in alcohol at 25° were determined. In some cases the diarylmercury was more soluble and in others the arylmercuric iodide was more soluble, but the difference in solubilities of corresponding compounds was not more than five-fold except in the case of the phenyl compounds in which case the diarylmercury was forty times as soluble as the arylmercuric iodide. This peculiarity explains the impossibility of converting phenylmercuric iodide to diphenylmercury by means of sodium iodide. It is not possible to get a sufficient concentration of sodium iodide in alcohol to overcome the effect of the unfavorable solubility ratio. In the case of the *p*-tolyl compounds in which the formation of di-*p*-tolylmercury is so readily caused by sodium iodide, the solubility of *p*-tolylmercuric iodide is almost five times as great as that of di-*p*-tolylmercury.

The effect of the relative concentration of sodium iodide on a number of these reactions was studied. In each case the mixture was refluxed and then cooled. In the case of *p*-ethylphenylmercuric chloride a molar ratio of sodium iodide to ArHgCl of 3.5:1 gave a mixture containing 11% of the diarylmercury; a ratio of 4.5:1 gave 64% and a ratio of 9:1 gave complete conversion to di-*p*-ethylphenylmercury.

The effect of relative concentration on the reversibility of the reaction was likewise studied. A molar ratio of Na₂HgI₄ to di-*p*-ethylphenylmercury of 1:1 gave a 97% conversion to *p*-ethylphenylmercuric iodide, while molar ratios of 2:1, 4:1 and 8:1 gave conversions of 98, 99 and 99.8%, respectively.

By using a molar ratio of sodium iodide to benzylmercuric chloride of 10:1 it was possible to obtain a complete conversion to dibenzylmercury.

In the case of *m*-tolylmercuric chloride, a molar ratio of sodium iodide of 3.5:1 gave an impure product containing only 30% di-*m*-tolylmercury, while a molar ratio of 8:1 gave the pure diarylmercury. In the case of *o*-tolylmercuric chloride a molar ratio of sodium iodide of 4.5:1 was sufficient to form di-*o*-tolylmercury. With phenylmercuric chloride a molar ratio of sodium iodide of 16:1 failed to give any diphenylmercury.

The influence of the volume of alcohol and of the time of refluxing was studied with the *p*-tolylmercuric compounds. A moderate volume was found to be as effective as a large volume. The time of refluxing was reduced to an approximate limit of ten minutes without cutting down the yield of diarylmercury.⁴

A number of mixtures of arylmercuric iodides and sodium iodide in various molar ratios were brought to equilibrium in boiling alcohol and then poured into large volumes of cold water. Analyses of the precipitated products by iodimetry showed them to consist almost entirely of arylmercuric iodides. This was in spite of the fact that the same solutions on cooling gave the diarylmercury compounds, with the single exception of the phenylmercuric compounds.

Experimental

Preparation of the Mercury Compounds.—These were made by known reactions. The results are summarized in Table I.

TABLE I

Compound	Method	Yield, %	Melting point, °C.		Analysis, Hg	
			Obs.	Lit.	Calcd.	Found ^a
Phenyl-HgI	<i>e</i>	66	265–266	266		
Diphenyl-Hg	<i>d</i>		120	122–123		
<i>o</i> -Tolyl-HgCl	<i>c</i>	42	145–146	146		
<i>o</i> -Tolyl-HgBr	<i>e</i>		169.5		53.98	54.0
<i>o</i> -Tolyl-HgI	<i>e</i>		176		47.93	48.0
Di- <i>o</i> -tolyl-Hg	<i>h</i>		106.5–107	107		
<i>m</i> -Tolyl-HgCl	<i>c</i>	27 <i>f</i>	159.5–160	160		
<i>m</i> -Tolyl-HgI	<i>e</i>		161	162		
Di- <i>m</i> -tolyl-Hg	<i>h</i>		101–102	102		
<i>p</i> -Tolyl-HgCl	<i>c</i>	51	233	233		
<i>p</i> -Tolyl-HgI	<i>e</i>	90	220	220		
Di- <i>p</i> -tolyl-Hg	<i>h</i>		237	238		
Benzyl-HgCl	<i>g</i>		103–104	104		
Benzyl-HgI	<i>i</i>		117	117		
Dibenzyl-Hg	<i>d</i>		110	111		
<i>p</i> -Ethylphenyl-HgCl	<i>c</i>	65 <i>j</i>	221		58.82	58.8
<i>p</i> -Ethylphenyl-HgBr	<i>e</i>		227–228		52.02	51.9
<i>p</i> -Ethylphenyl-HgI	<i>e</i>		229		46.38	46.3
Di- <i>p</i> -ethylphenyl-Hg	<i>h, d</i>		136.5		48.86	48.8

(4) Contrast the long refluxing recommended in "Organic Syntheses," 1923, Vol. III, p. 65.

TABLE I (Concluded)

Compound	Method	Yield, %	Melting point, °C.		Analysis, Hg	
			Obs.	Lit.	Calcd.	Found ^a
Phenylethyl-HgBr	<i>g</i>	65	173 dec.	169 ^k		
Phenylethyl-HgI	<i>h</i>		154		46.38	46.3
Mesityl-HgCl	<i>l</i>		199-200	200		
Dimesityl-Hg	<i>h</i>		230	236		
<i>p</i> -Cymyl-HgCl	<i>c</i>	62 ^j	155	156		
<i>p</i> -Cymyl-HgI	<i>e</i>		169	169		
Di- <i>p</i> -cymyl-Hg	<i>h</i>		134	134		
Cyclohexyl-HgBr	<i>g</i>		152-153	153		
Cyclohexyl-HgI	<i>m</i>		143	143		
α -Naphthyl-HgCl	<i>c</i>		187-188	188-189		
Di- α -naphthyl-Hg	<i>h</i>		240-241	243		
β -Naphthyl-HgCl	<i>c</i>		268-270	271		
Di- β -naphthyl-Hg	<i>h</i>		237-238	247-248 ^b		

^a Analyses are given only for new compounds although they were performed on most of the known compounds as well. The figures given are the average of at least two analyses.

^b Beattie and Whitmore, unpublished results.

^c Sulfinic acid method of Peters, *Ber.*, 38, 2567 (1905), as modified in "Organic Syntheses," 1923, Vol. III, p. 99.

^d Copper and pyridine method of Hein and Wagler, *Ber.*, 58B, 1499 (1925).

^e Action of the R₂Hg compound with HgX₂ in boiling alcohol.

^f Yield based on the *m*-toluidine used in making toluene-*m*-sulfinic acid.

^g Action of the RMgX compound with an excess of HgX₂.

^h Action of RHgCl with excess of sodium iodide in boiling alcohol. By increasing the ratio of NaI:RHgCl, the time of refluxing could be decreased greatly; cf. "Organic Syntheses," 1923, Vol. III, p. 65.

ⁱ Action of RHgCl with 1 mole of potassium iodide or sodium iodide.

^j Yield based on the sulfonyl chloride used to make the sodium sulfinate.

^k Hill, *THIS JOURNAL*, 50, 167 (1928).

^l Direct mercuration with mercuric acetate.

^m Obtained from cyclohexylmercuric bromide even with 5 moles of sodium iodide.

Determination of C-Hg Linkage by Iodimetry.—About 0.1 g. of mercuri-bis compound or 0.2 g. of organomercuric halide, weighed accurately, is mixed with 1 g. of potassium iodide, 2 cc. of chloroform, 25 cc. of water and 25.00 cc. of approximately 0.1 *N* iodine solution in a 100-cc. Erlenmeyer flask attached to a reflux condenser by a ground joint. The flask is heated enough to cause the chloroform to reflux gently for fifteen to thirty minutes. During the refluxing 25.00 cc. of the iodine solution used is titrated

TABLE II

Ar	SOLUBILITIES OF ARHGI AND AR ₂ HG				Ratio of molar solubilities Ar ₂ Hg:ArHgI
	G. per 25 cc. of soln. in 95% alcohol at 25°		Moles per liter of solution		
	Ar ₂ Hg	ArHgI	Ar ₂ Hg	ArHgI	
Phenyl	0.359	0.009	0.0405	0.0010	40:1
<i>m</i> -Tolyl	.1862	.0616	.0149	.00588	2.5:1
<i>p</i> -Tolyl	.008	.042	.00083	.0040	1:4.8
<i>p</i> -Ethylphenyl	.0949	.0509	.00924	.00488	1.9:1
Benzyl	.040	.104	.0041	.0109	1:2.7
2- <i>p</i> -Cymyl	.020	.051	.0018	.0044	1:2.4

TABLE III
 $\text{ArHgX} + \text{NaI} \longrightarrow \text{Ar}_2\text{Hg}$

Ar	X	ArHgX(g)	Molar ratio NaI: ArHgX	Vol. 95% alcohol, cc.	Reflux- ing time	Product	M. p., °C.	Known m. p., °C.		Found av.	Crude crystals Hg(C-Hg basis)	
								Ar ₂ Hg	ArHgI		Calcd. Ar ₂ Hg	ArHgI
Phenyl	Iodide	9.0	5.5:1 ^a	300	300 hrs.	ArHgI	265-266	121- 123	266			
Phenyl	Iodide	1.0	16:1	100	3 hrs.	ArHgI	265			99.6	104.9	47.9
<i>o</i> -Tolyl	Iodide	0.5	4.4:1	50 ^b	15 min.	Mixture				103.1		
		0.5	9:1	30 ^c	15 min.	Ar ₂ Hg				64.9	104.9	47.9
<i>m</i> -Tolyl	Chloride	6.0	3.6:1	200	27 hrs.	Mixture	92-94	102	162	64.9	104.9	47.9
		2.0	9:1	125	15 min.	Ar ₂ Hg	101-102			104.9		
<i>p</i> -Tolyl	Chloride	0.50	3.5:1	25	1 hr.	Ar ₂ Hg ^d	235-237	238	220	105.6 ^e	104.9	47.9
		0.50	3.5:1	25	2 hrs.	Ar ₂ Hg ^d	232-236			104.9		
					17 hrs.		228-236			105.3		
					15 min.					103.2		
					10 min.					104.0		
					5 min.					101.7		
					10 min.					93.0		
					10 min.					102.8		
					10 min.					93.1		
					10 min.					101.4		
Benzyl	Chloride	5.0	4:1	200	10 min.	Mixture	88	111	117	88.3		
		2.0	4.5:1	160	15 min.	Mixture	89-91			67.3	104.9	47.9
		1.6	11:1	60	10 min.	R ₂ Hg	110-111			74.3		
<i>p</i> -Ethylphenyl	Chloride	10	3.5:1	250	20 hrs.	Mixture	129	136.5	229	103.1		
		0.5	4.5:1	40	5 min. ^g	Mixture				75.1	97.7	46.4
		0.5	9:1	60	5 min.	R ₂ Hg	136			89.7		
		0.5	9:1	60	5 min. ^h	R ₂ Hg	136.5			98.1		
Phenylethyl	Bromide	5.0	5:1	200	20 min.	RHgI	154	Unstable	154	97.7		
		1.0	23:1	50	1 hr.	RHgI				46.6	97.7	46.4
		1.0	23:1	50	72 hrs.	Decomp. and RHgI				46.9		
2- <i>p</i> -Cymyl	Cl	10.0	3.7:1	200	7 hrs.	R ₂ Hg	133.5	134				
?- <i>m</i> -Xylyl	Cl	4.0	4.5:1	200	17 hrs.	R ₂ Hg	140-147 ⁱ		169	96.9	97.7	46.4
Mesitylyl	Cl	1.5	4.5:1	100	24 hrs.	R ₂ Hg	230	236	178	90.3	91.5	44.9
Cyclohexyl	Br	2.0	4.9:1	150	30 min.	RHgI	143	78.9	143			
	Iodide	2.0	4.9:1	150	60 hrs.	No C-Hg cpd. Metallic Hg						
α -Naphthyl	Cl	5.0	4.8:1	250	13 hrs.	R ₂ Hg	240	243	185	87.9	88.3	44.1
β -Naphthyl	Cl	1.0	4.9:1	250	19 hrs.	R ₂ Hg	237	238	251	87.8	88.3	44.1

^a Potassium iodide used. ^b After refluxing the solution was evaporated to 10 cc. and allowed to crystallize at 20°. ^c Evaporated to 10 cc. and crystallized at 10°. ^d The yields of R₂Hg obtained in the *p*-tolyl experiments averaged 86%. ^e In the *p*-tolyl series a small amount of finely divided mercury was observed. This may account for the high results in the mercury determination. ^f Vigorous mechanical agitation during refluxing. ^g Crystallized at 5°. ^h Crystallized at 0°. ⁱ Repeated crystallization failed to separate the isomers which were present.

TABLE IV
Ar₂Hg + Na₂HgI₄ + NaI → ArHgI

Ar	G. Ar ₂ Hg	Molar ratio Na ₂ HgI ₄ : Ar ₂ Hg	Molar ratio excess NaI: Ar ₂ Hg	Alcohol, 95% used, cc.	Product	M. p., °C.	Known Ar ₂ Hg	m. p., °C. ArHgI	Hg(C-HgCl)		
									Found Average	Ar ₂ Hg	Calcd. ArHgI
Phenyl	0.885	1:1	18:1	100	RHgI	263-264	123	266			
Phenyl	1.06	1:1	3:1	75	RHgI ^a	265-266					
Benzyl	0.040	1:1	0	25	Mixture ^b						
<i>p</i> -Ethylphenyl	.205	1:1	0	30					48.2	97.7	46.4
	.205	2:1	0	30					47.3		
	.41	4:1	0	25	RHgI	228-228.5	136.5	229	46.9		
	.41	8:1	0	25	RHgI	228.5-229		229	46.5		
2- <i>p</i> -cymyl	.196	1:1	1:1	50	R ₂ Hg	133-134	134	169			

^a 94% yield. ^b This experiment was not repeated because of lack of material.

TABLE V
DATA ON FROZEN EQUILIBRIUM MIXTURES IN BOILING ALCOHOL WITH VARYING AMOUNTS OF IODIDES IN SOLUTION

Ar	Molar ratio NaI:ArHg	Hg. (C-Hg basis calcd. for)			Molar ratio ArHgI:Ar ₂ Hg at equilibrium	Ratio of molar solubilities at 25° ArHgI:Ar ₂ Hg
		Found average	Ar ₂ Hg	ArHgI		
Phenyl	16:1	50.5	113.1	49.6	50:1	1:40
<i>p</i> -Tolyl	4:1	49.2	104.9	47.9	40:1	5:1
	12:1				20:1	
Benzyl	34:1	53.4	104.9	47.9	10:1	2:1
<i>p</i> -Ethylphenyl	12:1	46.7	97.8	46.4	150:1	1:2
<i>p</i> -Cymyl	4:1	44.0	86.0	43.6	70:1	2:1

with accurately standardized sodium thiosulfate solution (approximately 0.05 *N*). The flask containing the reaction mixture is cooled, acidified with 2 drops of concd. hydrochloric acid and titrated with the standard thiosulfate. The difference in the thiosulfate used here and with the blank iodine titration gives a measure of the C-Hg linkage present, each such linkage corresponding to two equivalents of iodine or thiosulfate.

Before the method was applied in the research it was tried on several pure substances and known mixtures. Of these only three examples will be given. (a) A sample of 0.1593 g. of *o*-tolylmercuric bromide was refluxed for thirty minutes with 25.00 cc. of the iodine solution. The titration of the 25.00-cc. blank of the iodine solution required 24.80 cc. of 0.05578 *N* sodium thiosulfate solution. The unreacted iodine in the refluxed mixture required 9.38 cc. of the same thiosulfate solution for its titration. Thus the C-Hg bonds in the mercury compound reacted with iodine equivalent to 15.42 cc. of the 0.05578 *N* solution which, in turn, is equivalent to 54.06% of mercury (as C-Hg) in the *o*-tolylmercuric bromide. The calculated percentage is 53.98. If the compound analyzed had contained the C-Hg-C combination the percentage found on the C-Hg basis would have been divided by two to get the actual percentage of mercury in the compound. Thus diphenylmercury which contains 56.57% mercury would show 113.1% mercury on the C-Hg basis when determined by iodimetry. (b) A mixture was made up of 0.0423 g. of *p*-ethylphenylmercuric chloride and 0.0298 g. of di-*p*-ethylphenylmercury. This reacted with iodine equivalent to 10.90 cc. of 0.04956 *N* thiosulfate indicating 75.02% mercury (C-Hg basis). The calculated amount for the mixture is 74.9% (C-Hg basis). (c) A similar experiment using 0.0288 g. of the Ar_2HgCl and 0.0453 g. of the Ar_2Hg compounds required iodine equivalent to 12.30 cc. of the 0.04956 *N* thiosulfate, indicating 82.47% mercury (C-Hg basis) as compared with the calculated value of 82.59% for this mixture.

Solubility of the Mercury Compounds in Alcohol.—After several more complicated methods for determining the concentration of the saturated solutions were tried, the following simple procedure was adopted. A saturated solution of the mercury compound in alcohol at 60–70° was prepared. The solution and excess of solid were then stirred and cooled to 25° and kept at that temperature in a thermostat for seventy-two hours. Several 25-cc. samples were removed by means of a filter pipet and transferred to weighed beakers. The main portion of the alcohol was removed at 60–70° in an air-bath (hood). When the residual volume was 5 cc. the beakers were transferred to vacuum desiccators and dried to constant weight. The accuracy of the method was determined by dissolving in alcohol weighed amounts of a variety of arylmercuric halides and diarylmercury compounds and recovering them. In each case the weight of material after the experiment was from 0.5 to 1 mg. greater than that introduced. Thus the method was sufficiently accurate for our purposes. The results are given in Table II.

Action of Alkali Iodides with the Arylmercuric Halides.—The results of the action of varied amounts of sodium and potassium iodides in refluxing alcoholic solution with the various arylmercuric halides are given in Table III.

Action of Diarylmercury Compounds with the Complex Alkali Mercury Iodides.—The experiment with diphenylmercury is typical. A mixture of 2.25 g. (5 mols) of sodium iodide, 1.36 g. (1 mol) of mercuric iodide and 1.06 g. (1 mol) of diphenylmercury in 75 cc. of alcohol was refluxed for thirty minutes. The hot solution had the characteristic yellow color of Na_2HgI_4 solutions. On cooling, this color disappeared and platelets of phenylmercuric iodide separated; m. p. 255–256°, yield 2.42 g. or 94%.

The results of similar experiments with other mercury compounds are given in Table IV.

The Ratio of Concentrations of the Arylmercuric Iodides and the Diarylmercury Compounds in Equilibrium Mixtures in Alcohol at the Boiling Point.—The mixture of a mercury compound which had been refluxed with a known ratio of sodium iodide was poured into a large volume of cold water to precipitate all the mercury compounds present. Thus the equilibrium was essentially "frozen." The precipitate was analyzed and the ratio of $\text{ArHgI}:\text{Ar}_2\text{Hg}$ calculated. The results appear in Table V.

Failure to Produce Diphenylmercury by Means of Iodides.—A solution of 9 g. (1 mol) of phenylmercuric iodide and 20.0 g. (5.5 mols) of potassium iodide in 300 cc. of 95% alcohol was refluxed for three hundred hours. The mixture was cooled. The crystals which separated were washed and dried, m. p. 265–266°. The mother liquor was gradually evaporated to yield five crystalline fractions. The first four showed the same m. p. 265°. The last fraction, obtained by evaporating the final mother liquor to dryness, washing with alcohol and water and drying, melted at 264–265°. The m. p. of phenylmercuric iodide is 266° and that of mercury diphenyl is 120°. Thus none of the latter substance was formed. A similar experiment using sodium iodide gave the same result.

Action of Mercury Diphenyl with Cold Solutions of Mercuric Salts.—The conversion of mercuri-bis compounds to organomercuric halides is usually carried out by refluxing the former with mercuric halides in alcohol or acetone solution. In the phenyl series this vigorous treatment was found to be unnecessary. Thus the mixing of cold solutions of 0.355 g. of diphenylmercury in 50 cc. of alcohol and 0.272 g. of mercuric chloride in 20 cc. of alcohol gave an *immediate* precipitate of phenylmercuric chloride, m. p. 250–251°. The filtrate gave no test for mercuric ions with bases.

Similarly cold solutions of 0.177 g. of diphenylmercury in 20 cc. of alcohol and 0.227 g. of mercuric iodide in 40 cc. of alcohol gave an immediate precipitate of phenylmercuric iodide, m. p. 265–266°.

The tendency to the formation of ArHgX is apparently not limited to cases in which that product precipitates from the reaction mixture. Thus cold solutions of 0.048 g. of di-*p*-tolylmercury in 200 cc. of alcohol and 0.057 g. of mercuric iodide in 20 cc. of alcohol gave no precipitate on mixing but the resulting solution gave no precipitate with sodium hydroxide, showing that the mercuric iodide had reacted with the diarylmercury.

A similar experiment with cold alcoholic solutions of di-*p*-ethylphenylmercury and mercuric chloride gave a precipitate of *p*-ethylphenylmercuric chloride, m. p. 221°, yield 94%.

Summary

1. The relation of arylmercuric halides to diarylmercury compounds has been studied from the point of view of the equilibrium



2. The alkali iodide method for forcing this reaction to the right has been studied with thirteen arylmercuric iodides. With ten of these it was successful.

3. A new method for mercury analysis of organic mercury compounds has been developed. This is particularly useful in determining the proportions of R_2Hg and RHgX in a mixture of the two. It is also valuable in determining the amount of organic mercury compound in the presence of inorganic mercury compounds.