[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE DECOMPOSITION OF UNSYMMETRICAL ORGANOMERCURIC COMPOUNDS: A METHOD OF ESTABLISHING THE RELATIVE DEGREE OF ELECTRONEGATIVITY OF ORGANIC RADICALS. III*

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The previous paper[1] in this series defined the more electronegative of two organic radicals as the one cloven from the mercury atom by hydrogen chloride in the following reaction:

$$RHgR' + HCl \rightarrow RHgCl + R'H$$

That paper summarized the procedures for the preparation, proof of structure, and cleavage of unsymmetrical mercury compounds, and presented a table of the results obtained up to that time. The present work is concerned with the effects of halogens and the trifluoromethyl group on the electronegativity of the phenyl radical, and with the relative electronegativities of the benzyl and *o*-, *m*-, and *p*-chlorobenzyl radicals. Further evidence establishing the validity of the above method of determining the relative electronegativities of organic radicals is presented. It is shown in Table I that in all cases tested the cleavage of phenylethylmercury is independent of the halogen acid and solvent employed.

Phenylethylmercury was treated with halogen acid under the following conditions: with hydrogen chloride in alcohol, with hydrogen bromide in alcohol, glacial acetic acid, and benzene, and with hydrogen iodide in the two latter solvents. In all cases the product was shown by melting point to be ethylmercuric halide. It is thus shown that the phenyl radical is more easily cloven from the mercury atom than the ethyl radical, irrespective of the solvent or halogen acid used. Since the phenylmercuric halides are less soluble than the corresponding ethylmercuric halides, it is clear that the more soluble of the organomercuric halides is formed, and, therefore, that the course of the reaction is not determined by the insolubility of one of the two possible products.

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* This paper is condensed from the Doctorate Thesis of Herman Pines, the University of Chicago, 1935, and from the Master's Thesis of Janice H. Levine, the University of Chicago, 1933.

[1] KHARASCH AND FLENNER, *J. Am. Chem. Soc.*, **54**, 674 (1932).

The treatment of suitable monohalogenated diphenylmercury compounds with hydrogen chloride leads to the following conclusions: the *p*-fluorophenyl radical is somewhat more electronegative than the phenyl radical; the *p*-chlorophenyl, *p*-bromophenyl, *o*-bromophenyl, *m*-bromophenyl, and *m*-fluorophenyl radicals are somewhat less electronegative than the phenyl radical. The phenylmercury derivatives of the last three radicals gave exclusively benzene and the substituted phenylmercuric chloride on cleavage but the three *p*-halogenated diphenylmercury compounds all gave mixtures of the possible cleavage products. We conclude that the *p*-halogenated radicals are very close to the phenyl radical in electronegativity. Thus, the *p*-fluorophenyl radical (although the difference is slight) appears to be the only known exception to the rule of Kharasch and Flenner that direct substitution decreases the electronegativity of the phenyl radical.

Other experiments indicate that the *m*-(α,α,α-trifluoro)tolyl radical is less electronegative than the phenyl and *m*-chlorophenyl radicals, but mixtures of cleavage products were obtained in both cases. This result shows that such substitution in the side-chain decreases the electronegativity of the tolyl radical, and that a trifluoromethyl group in the *m*-position has a greater effect than a chlorine atom in decreasing the electronegativity of the phenyl radical.

Cleavage of *o*-, *m*-, and *p*-chlorodibenzylmercury with hydrogen chloride showed that all the chlorobenzyl radicals are less electronegative than the unsubstituted benzyl radical. 2,3′-Dichlorodibenzylmercury was cloven to give an equimolecular mixture of *o*- and *m*-chlorobenzylmercuric chlorides. 2,4′-Dichlorodibenzylmercury also gave a mixture of chlorobenzylmercuric chlorides on cleavage, but the proportion of isomers in the mixture was not determined. It is concluded that the three chlorobenzyl radicals are of approximately the same relative electronegativity and that all are less electronegative than the benzyl radical.

Subsequent papers in this series will be published soon.

EXPERIMENTAL

Analytical methods for the determination of mercury.—Three methods were used for the determination of mercury in the organomercuric compounds. Two have already been described by Kharasch and Flenner, and by Whitmore and Sobatski.[2] The third is the method of Smith[3] for inorganic compounds, modified for use in the case of organic compounds by Kharasch, Legault, and Sprowls. A quantity of the organomercuric compound (0.4 g.) is weighed into a tall, narrow beaker with a bulb in the bottom, and is dissolved in 5 cc. of glacial acetic acid by warming on the steam bath. Two cc. of bromine is added to convert the organic to inorganic mercury. The mixture is warmed again on the steam bath and then allowed to

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[2] WHITMORE AND SOBATZKI, *ibid.*, **55**, 1128 (1933).

[3] SMITH, "Electro-Analysis," P. Blakiston's Sons, Phila., **1918**, p. 99.

stand for half an hour. When the organic radical attached to mercury is weakly electronegative, overnight standing is necessary for complete conversion. Eight cc. of amylene is then added to destroy excess bromine. The amylene bromide collects in the bulb in the bottom of the beaker; otherwise it might coat and poison the electrodes. The solution is neutralized by the addition of 85 cc. of 6.67% sodium bicarbonate solution and 15 cc. of 10% sodium carbonate solution, then acidified with 8 cc. of concentrated nitric acid. The solution is then electrolyzed for two hours with a currect of 3.5 amperes. The temperature rises to (and remains at) about 80°. The mercury is deposited on a previously weighed, perforated, cylindrical gold electrode, which is washed with water, alcohol, and ether, and dried over phosphorus pentoxide. The electrode is cleaned for subsequent use by heating to 600° in an electric furnace.

TABLE I

CLEAVAGE WITH VARIOUS HALOGEN ACIDS AND SOLVENTS

GRAMS C_6H_5-Hg-C_2H_5	SOLVENT CC.	CLEAVAGE REAGENT		PRODUCT[a]		RECORDED MELTING POINTS, °C.
		Solvent, cc.	Saturated with	Softens, °C.	Melts, °C.	
1.3	Ethanol, 25–30	Ethanol, 7	HCl		192	C_2H_5HgCl, 192 C_6H_5HgCl, 251
1.5	Benzene[b], 25–30	Benzene, 15	HBr		189	C_2H_5HgBr, 193
1.0	Glacial acetic acid, 20	Glacial acetic acid, 7–10	HBr	187	189	C_6H_5HgBr, 276
1.0	Ethanol, 20	Ethanol, 7	HBr	187	189	
1.3	Benzene	HI gas from H_3PO_4 and NaI		162	175[c]	C_2H_5HgI, 182
1.3	Glacial acetic acid			179	181	C_6H_5HgI, 266

[a] Products precipitated from the reaction mixture and were washed with ether and/or petroleum ether. Benzene solutions were concentrated in an air stream to effect crystallization.

[b] Cleavage carried out at 15°; others at room temperature.

[c] Ethylmercuric iodide was separated from mercuric iodide by extraction with acetone and evaporation of acetone solution.

Preparation of halides.—The preparation of a few uncommon halides used as starting materials for the required organomercuric chlorides is indicated below.

The three isomeric bromofluorobenzenes were prepared from the corresponding bromoanilines by diazotization and formation and decomposition of the borofluorides, essentially according to the procedure of Balz and Schiemann.[4] The yields and boiling points of the bromofluorobenzenes thus obtained were: *ortho*, 37%, 157–60°; *meta*, 50%, 148–51°; *para*, 52%, 150–2°.

m-Bromochlorobenzene was prepared from *m*-bromoaniline by diazotization and treatment with cuprous chloride. The yield was 72% of a compound which boiled at 192°.

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[4] BALZ AND SCHIEMANN, *Ber.*, **60**, 1186 (1927).

Two chlorobenzyl bromides were prepared by bromination of the appropriate chlorotoluenes. Fifty grams of bromine was added slowly to 35 g. of boiling chlorotoluene. The product was washed with sodium carbonate, dried, and distilled.

TABLE II

PREPARATION AND PROPERTIES OF ORGANOMERCURIC CHLORIDES

R IN RHgCl	PREPARATION			M.P., °C.	MERCURY ANALYSIS		
	Method[a]	Starting Material	Yield, %		Calc'd	Found	Method[b]
C_6H_5-	MN	$C_6H_5NH_2$	18	252			
m-FC_6H_4-	G	m-FC_6H_4Br		243[c]	60.4	58.8 58.9	K & F
p-FC_6H_4-	G	p-FC_6H_4Br		291	60.4	58.7 58.5	K & F
p-ClC_6H_4-	N	p-$ClC_6H_4NH_2$	25	238	57.8	57.1 57.2	K & F
o-BrC_6H_4-	H	o-$BrC_6H_4NH_2$	44	155			
	N	o-$BrC_6H_4NH_2$	0[d]				
m-BrC_6H_4-	H	m-$BrC_6H_4NH_2$	50	194			
p-BrC_6H_4	H	p-$BrC_6H_4NH_2$	60	250			
	N	p-$BrC_6H_4NH_2$	28	248			
	MN	p-$BrC_6H_4NH_2$	55	255			
m-$CF_3C_6H_4$-	MN	m-$CF_3C_6H_4NH_2$	20	151	52.6	53.2	Elec.
$C_6H_5CH_2$-	G	$C_6H_5CH_2Cl$	74	107			
o-$ClC_6H_4CH_2$-	G	o-$ClC_6H_4CH_2Cl$	25	115	55.5	55.56[e]	W & S
m-$ClC_6H_4CH_2$-	G	m-$ClC_6H_4CH_2Br$	40	141	55.5	54.8 54.8	W & S
p-$ClC_6H_4CH_2$-	G	p-$ClC_6H_4CH_2Br$	55	141			

[a] G, H, N, and MN indicate the Grignard, Hanke, Nesmejanow, and modified Nesmejanow methods, respectively.

[b] Elec., K & F, and W & S indicate the electrolytic, Kharasch and Flenner, and Whitmore and Sobatzky methods, respectively.

[c] The original melting point of 239° was raised to 243° by shaking with freshly-precipitated silver chloride.

[d] Preparation in either acetone or alcohol solution gave tars from which none of the desired mercury compound could be obtained.

[e] This analysis was made on a sample melting at 111° which had been prepared from di-o-chlorobenzylmercury and mercuric chloride. Di-o-chlorobenzylmercury was prepared by the addition of mercuric chloride to three equivalents of o-chlorobenzylmagnesium bromide in ether. It was a white crystalline solid, melting at 100°, and containing 44.31% mercury by the Whitmore and Sobatzky method (calculated, 44.49% Hg).

o-Chlorobenzyl bromide, b.p.$_{10}$ 103–4°, was obtained in 72% yield; m-chlorobenzyl bromide, b.p.$_{8}$ 105–8°, in 63% yield.

Preparation and properties of the organomercuric chlorides.—(Summarized in Table II.) Three methods of preparing the organomercuric chlorides were employed. The first method involved the reaction of a sulfinic acid (prepared from a diazonium salt by Gatterman's method[5]) with mercuric acetate in glacial acetic acid to give an arylmercuric acetate.[6] Aqueous or alcoholic solutions of the acetate were converted to chloride by reaction with sodium chloride. The second method is the decomposition of an aryldiazonium chloride-mercuric chloride double salt in the presence of copper bronze, according to Nesmejanow.[7] When his procedure was followed as closely as possible, we could not attain his yield of phenylmercuric chloride, and considerable tar was obtained. Less tar and improved yields of phenylmercuric chloride were obtained in a less vigorous reaction when metallic mercury was substituted for the copper. The third method is by reaction of a Grignard reagent with mercuric chloride. One mole of Grignard reagent in ether solution was heated for one to two hours with 1.2 moles of mercuric chloride. The product was poured into water, and the solid organomercuric chloride was washed

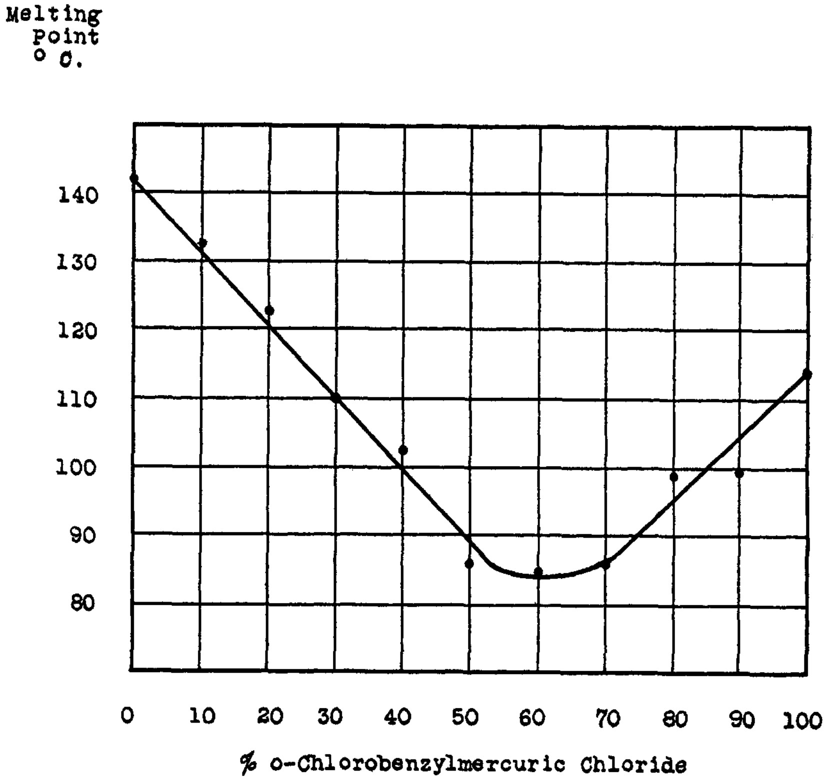

FIGURE I. MELTING POINT CURVE OF MIXTURES OF *o*- AND *m*-CHLOROBENZYLMERCURIC CHLORIDES

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[5] GATTERMAN, *ibid.*, **32**, 1136 (1899).

[6] HANKE, *J. Am. Chem. Soc.*, **45**, 1321 (1923).

[7] NESMEJANOW, *ibid.*, **62**, 1010 (1929).

TABLE III

PREPARATION AND CLEAVAGE OF UNSYMMETRICAL MERCURY COMPOUNDS

UNSYMMETRICAL MERCURY COMPOUND				ANAL. METHOD[b]	CLEAVAGE PRODUCT: RHgCl and/or R'HgCl		
R and R' in RHgR'[a]	M. p., °C.	Hg Anal. Calc'd. %	Hg Anal. Found %		Hg Anal., %	M.p., °C.	Composition
C_6H_5- *m*-FC_6H_4-	107–11	53.8	52.6 52.4	K & F	60.7 60.0	234–6	*m*-FC_6H_4HgCl
C_6H_5- *p*-FC_6H_4-	111–5	53.8	53.3 53.4	K & F	63.4 63.1	258–61	C_6H_5HgCl, 80% *p*-FC_6H_4HgCl, 20%
p-FC_6H_4- C_6H_5-	115–8	53.8	53.4 53.3	K & F	63.3 63.7	254–7	C_6H_5HgCl, 80% *p*-FC_6H_4HgCl, 20%
C_6H_5- *p*-FC_6H_4-	106–11			W & S	62.34 62.09 62.50	259–61	C_6H_5HgCl, 57% *p*-FC_6H_4HgCl, 43%
p-ClC_6H_4- C_6H_5-	165–205	51.4	50.2 50.7	K & F	59.3 59.1	250–2	*p*-ClC_6H_4HgCl, 78% C_6H_5HgCl, 22%
p-ClC_6H_4- C_6H_5-	172–200			K & F	59.5 59.6	245–9	*p*-ClC_6H_4HgCl, 70% C_6H_5HgCl, 30%
o-BrC_6H_4- C_6H_5-	73–5	46.1	45.8 45.4	K & F	52.2	145–7	*o*-BrC_6H_4HgCl
m-BrC_6H_4- C_6H_5-	Liquid	46.1	45.15	K & F	51.9 51.1	183–6	*m*-BrC_6H_4HgCl
p-BrC_6H_4- C_6H_5-	151–75	46.1	46.2 46.5	K & F	54.5 54.0	238	*p*-BrC_6H_4HgCl, 76% C_6H_5HgCl, 24%
p-BrC_6H_4- C_6H_5-	136–76			K & F	54.5 54.3	233–5	*p*-BrC_6H_4HgCl, 74% C_6H_5HgCl, 26%
m-$CF_3C_6H_4$- C_6H_5-	100–3	47.8	47.4	Elec.	53.6	159–60	*m*-$CF_3C_6H_4HgCl$, 91% C_6H_5HgCl, 9%
m-$CF_3C_6H_4$- *m*-ClC_6H_4-	130–43	43.6	44.0	Elec.	56.8 56.6	164	*m*-$CF_3C_6H_4HgCl$, 82% *m*-ClC_6H_4HgCl, 18%

m-$CF_3C_6H_4$- *m*-ClC_6H_4-	130–40	43.6	43.5 43.7	W & S	54.5 54.3	159–63	*m*-$CF_3C_6H_4HgCl$, 65% *m*-ClC_6H_4HgCl, 35%
m-$CF_3C_6H_4$- *m*-ClC_6H_4-	130–9			W & S	54.0 54.2	164–6	*m*-$CF_3C_6H_4HgCl$, 70% *m*-ClC_6H_4HgCl, 30%
$C_6H_5CH_2$- *o*-$ClC_6H_4CH_2$- *o*-$ClC_6H_4CH_2$- $C_6H_5CH_2$-	Liquid	48.09	44.47[c]	W & S	55.5	96–103	*o*-$ClC_6H_4CH_2HgCl$[d,e]
m-$ClC_6H_4CH_2$- $C_6H_5CH_2$-	Liquid			W & S	55.9	132	*m*-$ClC_6H_4CH_2HgCl$[i]
$C_6H_5CH_2$- *p*-$ClC_6H_4CH_2$-	80–2	48.09	48.41 48.29	Elec.	57.2 56.7	131–7	*p*-$ClC_6H_4CH_2HgCl$,[d,f] 75% $C_6H_5CH_2Cl$, 25%
o-$ClC_6H_4CH_2$- *m*-$ClC_6H_4CH_2$-	Liquid	44.3	42.8[c] 42.9	W & S	54.7	87	*o*-$ClC_6H_4CH_2HgCl$, 50%[d,g] *m*-$ClC_6H_4CH_2HgCl$, 50%
p-$ClC_6H_4CH_2$- *o*-$ClC_6H_4CH_2$-	90–113	44.3	43.9 43.8	W & S			
p-$ClC_6H_4CH_2$- *o*-$ClC_6H_4CH_2$-	98–129			W & S	54.9	99–110	*o*-$ClC_6H_4CH_2HgCl$[d,h] *p*-$ClC_6H_4CH_2HgCl$

[a] The unsymmetrical mercury compound was prepared from the organomercuric chloride of the first-named radical and the organomagnesium bromide of the second-named radical.

[b] Both the unsymmetrical mercury compound and the cleavage product were analyzed by the same method, designated as in Table II.

[c] Low mercury content is probably due to difficulty of removing solvents.

[d] The unsymmetrical compound was not decomposed by alcoholic hydrogen chloride at room temperature and so the reaction mixture was heated to 60° for 20 minutes.

[e] The addition of known *o*-chlorobenzylmercuric chloride to the solid cleavage product raised its melting point to 98–108°; addition of benzylmercuric chloride lowered the melting point of the cleavage product to 85–8°. These facts, together with the mercury analysis, indicate that the cleavage product is fairly pure *o*-chlorobenzylmercuric chloride.

[f] The melting point of the solid cleavage product was lowered by the addition of benzylmercuric chloride but not by the addition of *p*-chlorobenzylmercuric chloride. Thus, by melting point the product is fairly pure *p*-chlorobenzylmercuric chloride but mercury analysis indicates the presence of about 25% benzylmercuric chloride.

[g] The melting point of the product corresponds to 50–70% of *o*-chlorobenzylmercuric chloride and 30–50% of *m*-chlorobenzylmercuric chloride, as can be seen from Figure I. Addition of 10% *m*-chlorobenzylmercuric chloride to the product raised the melting point of the mixture to 100°. Hence the original cleavage product consisted of equal proportions of the two chlorobenzylmercuric chlorides.

[h] The proportion of *o*- and *p*-chlorobenzylmercuric chlorides in the cleavage product is not known.

[i] This result is taken from the Master's Thesis of Willard R. Sprowls, the University of Chicago, 1935.

with water until no trace of mercuric chloride remained (test with sodium hydroxide). When the Grignard reagent was made from an organic bromide, the product was sometimes a mixture of organomercuric bromide and chloride. This mixture was converted to chloride by shaking with freshly precipitated silver chloride.

Attempts to prepare *o*-fluorophenylmercuric chloride by treatment of *o*-bromofluorobenzene with magnesium (reaction finally took place in a sealed tube at 120°) and then with mercuric chloride failed to give any organic compound containing mercury.

Preparation, properties, and cleavage of unsymmetrical organomercuric compounds. —The unsymmetrical mercury compounds were prepared from an organomercuric chloride and a Grignard reagent, and treated with mercuric chloride and alcoholic hydrogen chloride as described by Kharasch and Flenner. The analyses and the results are summarized in Table III.

SUMMARY

1. A number of new organomercuric compounds of the type RHgCl and RHgR′ have been prepared.

2. The relative electronegativities of some halogenated phenyl radicals, the *m*-(α,α,α-trifluoro)tolyl, the benzyl, and the three chlorobenzyl radicals have been determined.