BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2574—2581 (1970)

Thermal Demercuration Reactions of Organomercurials

Naoki Inamoto and Masaaki Yoshifuji

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

(Received February 23, 1970)

Thermal demercuration reactions of organomercurials (RHgX) alone or with mercuric salts (HgY_2) were performed (where R=*n*-butyl, *s*-butyl, cyclohexyl, benzyl, phenyl, and *p*-tolyl; X,Y=Cl, Br, CN, SCN, and OAc). Alkyl chlorides were obtained in good yields in the cases of alkylmercuric chlorides. The results in the reactions of cyclohexylmercuric halides with mercuric salts suggested the exchange reaction between them. Thermal demercuration reactions of arylmercurials gave the corresponding aromatic hydrocarbons as main product, and their mechanisms which involve generation of aryl radicals were discussed. General mechanisms of demercuration reaction of organomercurials alone were also discussed, and the importance of intermolecular interaction between organic group and chlorine was suggested in the cases of aliphatic organomercuric chlorides.

French, Inamoto and Wright[1] found that mercurous salts are the most effective catalyst for redistribution reaction of the bis-organomercurials. As impure bis-organomercurials redistributed more readily than pure materials, the following mechanism

---

[1] W. E. French, N. Inamoto and G. F Wright, *Can. J. Chem.*, **42**, 2228 (1964).

was postulated for the formation of mercurous salts as a catalyst.

$$\mathrm{RHgR} \xrightarrow[\text{peroxide}]{\text{heat or}} \mathrm{R{-}R} + \mathrm{Hg} \qquad (1)$$

$$\mathrm{RHgX} \rightarrow \mathrm{RX} + \mathrm{Hg} \qquad (2)$$

$$2\,\mathrm{RHgX} \rightleftarrows \mathrm{R_2Hg} + \mathrm{HgX_2} \qquad (3)$$

$$\mathrm{HgX_2} + \mathrm{Hg} \rightarrow \mathrm{Hg_2X_2} \qquad (4)$$

The reaction (2) has not been reported except for some vinylmercuric salt,[2)] although it is well known that organomercuric salts give mercurous salts by thermal decomposition,[3)] photolysis,[4-6)] or the action of peroxide.[1,7)]

$$2\,\mathrm{RHgX} \rightarrow 2\mathrm{R}\cdot + 2\cdot\mathrm{HgX}\ (\rightarrow \mathrm{Hg_2X_2})$$

According to the reactions (2) and (4), the following reaction would be expected to occur.

$$\mathrm{RHgX} + \mathrm{HgX_2} \rightarrow \mathrm{RX} + \mathrm{Hg_2X_2} \qquad (5)$$

Inamoto and Wright[8)] carried out the reactions of organomercurials with mercuric salts and obtained the following preliminary results. Reaction of cyclohexylmercuric or *n*-butylmercuric chloride with a slight excess of mercuric chloride at 150—240°C gave cyclohexyl chloride (isolated in 68% yield under reduced pressure) or *n*-butyl chloride (isolated in 40% yield), respectively, and mercurous chloride was produced in nearly quantitative yield in both cases. Therefore, it was proved that the reaction (5) occurs. On the other hand, phenylmercuric or *p*-tolylmercuric chloride gave benzene or toluene (isolated in 20—30% yield by distillation), respectively, instead of the corresponding aryl chloride, under similar conditions, and the yields of mercurous chloride were not quantitative. These results indicate that the reaction of arylmercuric chlorides does not follow the reaction (5). Furthermore, the similar reaction of cyclohexylmercuric bromide with mercuric chloride gave no cyclohexyl bromide but cyclohexyl chloride.

In order to clarify these reactions, we investigated the thermal decompositions of organomercurials alone or with mercuric salts in more detail.

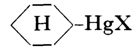
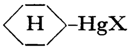
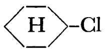
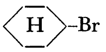
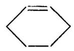
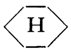
Results and Discussion

Alkylmercuric Chloride, Bromide, and Cyanide. The thermal reaction of *s*-butylmercuric chloride with a slight excess of mercuric chloride at about 260°C for 2 hr gave *s*-butyl chloride in 64% yield after distillation.

Table 1 shows the results on the thermal reactions of the cyclohexylmercuric halide-mercuric halide system. The ratio of cyclohexyl bromide to the chloride increased with the bromine content in the system. The formation of the chloride, moreover, is apparently considered to be more favorable than that of the bromide. This result suggests that an exchange reaction occurs between cyclohexylmercuric halide and mercuric halide. Formation of considerable amount of cyclohexyl bromide in the thermal reaction of cyclohexylmercuric bromide with an insufficient amount of mercuric chloride is presumably attributed to a self-decomposition of an excess cyclohexylmercuric bromide.

Some attention should be given on the de-

TABLE 1. THERMAL REACTIONS OF CYCLOHEXYLMERCURIC CHLORIDE AND CYCLOHEXYLMERCURIC BROMIDE (at 230—265°C, under a pressure of 50 mmHg for 1.5 hr)

 (I) X	$\mathrm{HgY_2}$ (II) Y	II/I mole ratio	Composition of products				Hg[a)] (%)	Recovery of R (%)	 recovered (%)
			 (mol %)						
Cl	—	0	61		34	5	67	88	12
Cl	Br	0.25	49	7	39	5	49	97	3
Cl	Br	1.14	55	12	30	3	0	98	1
Cl	Br	3.00	45	21	34	1	0	94	—
Br	Cl	1.18	70	2	27	1	0	100	—
Br	Cl	0.27	26	35	33	7	39	91	4
Br	—	0		35	41	24	24	93	7

a) Yield from RHgX used.

[2)] E. Tobler and D. J. Foster, *Z. Naturforsch., B*, **17**, 136 (1962).

[3)] M. M. Koton and F. S. Florinskii, *Zh. Obshch. Khim.*, **9**, 2196 (1939).

[4)] V. Weinmayr, *J. Amer. Chem. Soc.*, **81**, 3590 (1959).

[5)] D. H. Hey, D. A. Shingleton and G. H. Williams, *J. Chem. Soc.*, **1963**, 1958.

[6)] K. Yoshida and S. Tsutsumi, *Tetrahedron Lett.*, **1966**, 281.

[7)] J. H. Robson and G. F Wright, *Can. J. Chem.*, **38**, 1 (1960).

[8)] N. Inamoto and G. F Wright, unpublished work; see N. Inamoto, *Nippon Kagaku Zasshi*, **86**, 1223 (1965).

Table 2. Thermal reactions of phenylmercuric chloride and phenylmercuric cyanide (for 1.3 hr)

PhHgX X	HgY_2 Y	Temp. (°C)	Composition of products (mol %) PhH	PhCl	PhCN	$Hg^{a)}$ (%)	Recovery of R (%)
Cl	—	300—340	99	1		0.4	35
Cl	Cl	300—320	91	9		0	41
Cl	Cl	260—280	97	3		0	45
Cl	Cl	200—220	∼100	0.02		0	46
Cl	CN	310—320	96	1	4	29	48
CN	—	300—340	94		6	62	54
CN	CN	240—265	99.5		0.5	1	30
CN	CN	280—295b)	99		1	11	48
CN	CN	320—350	95		5	148	26
CN	Cl	300—350	94	3	3	0	50

a) Yield from PhHgX used.

b) Reaction was carried out *in vacuo* in a sealed tube.

mercuration reaction of cyclohexylmercuric chloride or bromide alone as in the following. First, the yield of mercury metal liberated in the latter was smaller than that in the former. Secondly, the yield of cyclohexane from the latter was much larger than that in the former, partly because of the formation of cyclohexyl radicals due to the weaker bond strength of C–Hg in the bromide than that in the chloride,[*1] followed by hydrogen abstraction from the surrounding organomercurials. Partial formation of cyclohexyl radicals is evident from the detection of a trace of dicyclohexyl by means of vapor phase chromatography (VPC).

Another pathway of the formation of cyclohexane is a reaction of unchanged cyclohexylmercuric bromide with hydrogen bromide generated by mercuric bromide - catalyzed dehydrobromination of cyclohexyl bromide produced during the reaction,10) because of facile dehydrobromination of organic bromide. This pathway is considered to be reasonable, because of the formation of a considerable amount of cyclohexene.

The demercuration reaction of cyclohexylmercuric cyanide alone at 240—265°C under reduced pressure gave cyclohexane (4%), cyclohexene (66%), cyclohexyl cyanide (9%), mercury metal (84%), and hydrogen cyanide.

Mechanisms of these demercuration reactions will be discussed later.

Phenylmercuric Chloride, Cyanide, and Thiocyanate. Table 2 shows the results on the thermal reactions of phenylmercuric chloride or cyanide[*2] under various conditions. In every case, the main product was benzene (25—50% yields), and the yield of chlorobenzene or/and benzonitrile was very poor, but increased at higher temperatures. The benzene formation can be explained by assuming generation of phenyl radicals, followed by hydrogen abstraction from the surrounding organomercurials. It is confirmed by the presence of diphenyl among the products.

The reaction of phenylmercuric cyanide and mercuric cyanide at 350°C gave a large amount of mercury, which might be attributed to the

Table 3. Thermal reactions of phenylmercuric thiocyanate (for 1.5 hr)

HgY_2 Y	Temp. (°C)	Composition of products (mol %) PhH	PhCN	PhSCN	$Hg^{a)}$ (%)	Recovery of R (%)
—	270—300	98	2	0	21	31
SCN	220—290	96	3	1	23	33
CN	210—285	98	1	1	76	40

a) Yield from PhHgSCN used.

[*1] *e.g.*, compare the following bond dissociation energy D(R–HgX);9) D(Et–HgCl) = 60.3 ± 3 and D(Et–HgBr) = 57.6 ± 3 (kcal/mol).

9) H. A. Skinner, in F. G. A. Stone and R. West, "Advances in Organometallic Chemistry," Vol. 2, Academic Press, New York (1964), p. 49.

10) F. Swarts, *Bull. Classe Sci., Acad. Roy. Belg.*, **22**, 784 (1936).

[*2] Our present results on the thermal reactions of phenylmercuric cyanide with mercuric cyanide were quite different from those reported by one of the authors (N. I.).8)

TABLE 4. THERMAL REACTIONS OF BIS-ORGANOMERCURIES WITH MERCURIC SALTS (for 1 hr)

R_2Hg (III) R	HgX_2 (IV) X	IV/III mole ratio	Temp. (°C)	Composition of products (mol %) RH	RX	Hg (%)	Recovery of R (%)
Ph	Cl	3.30	260—290	91	9	0	66
Ph	CN	2.28	240—290	98	2	1	25
PhC≡C-	CN	2.31	250 (50 mmHg)	98	2	96	14

decomposition of mercuric cyanide at higher temperatures.[11]

Table 3 shows the results on the thermal reactions of phenylmercuric thiocyanate. The main product was also benzene, together with a considerable amount of mercury metal and mercuric sulfide. Phenyl isothiocyanate was not detected. In the demercuration reaction of phenylmercuric thiocyanate alone, no phenyl thiocyanate was obtained.

The demercuration reaction of *p*-tolylmercuric chloride alone gave toluene (47%) as a main product, together with a trace of *p*-tolyl chloride, dibenzyl, di-*p*-tolyl, phenyl-*p*-tolylmethane and mercury metal.

Bis-organomercuries. In order to test the possibility of the reaction (3), the reactions of diphenyl mercury with mercuric salts were carried out (Table 4). The thermal reaction of diphenylmercury with mercuric chloride (or cyanide) gave almost the same products as those of phenylmercuric chloride (or cyanide) with mercuric chloride (or cyanide).

The thermal reaction of bis-phenylethynylmercury with mercuric cyanide was similar to that of diphenylmercury with mercuric cyanide, but mercury liberated was almost quantitative.

Acetoxymercurials. The results of the thermal reactions of acetoxymercurials are summarized in Table 5.

n-Butylmercuric acetate gave metallic mercury in 72% yield, but only a small amount of *n*-butyl acetate (9.6%) was obtained together with a considerable amount of very volatile material, which is supposed to be butane or butene. Other products were acetic acid (24%), a considerable amount of acetic anhydride, and a trace of methyl acetate. In the presence of a slight excess of mercuric acetate, the yield of *n*-butyl acetate was rather small (5%). A considerable amount of very volatile material was also observed in this case.

Benzylmercuric acetate gave metallic mercury in 68% yield, but only a trace of benzyl acetate was formed, together with a considerable amount of dibenzyl and acetic acid and a trace of toluene, acetic anhydride and methyl acetate. In the presence of slight excess of mercuric acetate, the amount of benzyl acetate increased and the amount of dibenzyl decreased.

The demercuration reaction of phenylmercuric acetate alone or with mercuric acetate gave acetic acid, benzene (50%), and a trace of methyl acetate, together with mercury metal. Neither phenyl acetate nor toluene were detected.

In this connection, the thermal reaction of mercuric acetate alone was performed, and the products

TABLE 5. THERMAL REACTIONS OF ACETOXYMERCURIALS (for 1—1.5 hr)

RHgOAc R	HgX_2 X	Temp. (°C)	Products (%) ROAc	RH	AcOH[a]	R-R[b]	Hg[c]	Recovery of R (%)
—	OAc	210—220	—	—	63	—	90	—
n-C_4H_9	—	215—253	10	—	24[d]	—	72	—
n-C_4H_9	OAc	250—258	5	—	56	—	80	—
$PhCH_2$	—	255—260[e]	0.2	1	44[d]	31	68	64
$PhCH_2$	OAc	250—315[e]	18	2	54	8	90	36
Ph	—	180—230	0	52	72	—	66	52
Ph	OAc	180—230	0	48	64	—	26	48

a) Yield based on acetoxy group.
b) Yield based on R group.
c) Yield based on total mercury in the system.
d) Acetic anhydride was also obtained.
e) The reaction was carried out under a pressure of 40 mmHg.

---

[11] J. P. Galvin and H. O. Pritchard, *J. Phys. Chem.*, **68**, 1035 (1964).

TABLE 6. THERMAL REACTIONS OF ORGANOMERCURIC SALT ALONE[a)]

RHgX		Temp. (°C)	Products (%)				RHgX recovered (%)
R	X		RX	R(−H)[b)]	RH	Hg	
n-C_4H_9	Br	~245	29.5	—	—	33	12
cyclo-C_6H_{11}	Cl	230—265[c)]	54	30	4	67	13
cyclo-C_6H_{11}	Br	~250[c)]	33	37.5	23	24	7
cyclo-C_6H_{11}	CN	240—265[c)]	9	66	4	84	10
C_6H_5	Cl	300—340	0.4	—	33	0.4	5
C_6H_5	CN	300—340	3.4	—	50	62	3
C_6H_5	SCN	270—300	0.5 (PhCN)	—	30.5	21	2
p-$CH_3C_6H_4$	Cl	285—310	2.4	—	47	4	1

a) Acetates were excluded.
b) Denotes the corresponding olefin.
c) The reaction was carried out under a pressure of 50 mmHg.

were metallic mercury (90%), a large amount of acetic acid and a trace of methyl acetate. Thus the thermal reactions of organomercuric acetate proved to involve the self-decomposition of mercuric acetate itself.

The formations of acetic acid and methyl acetate are reasonably explained by radical mechanism including acetoxy radicals.*3

Mechanisms of Demercuration Reactions. The results on the thermal reactions of organomercuric halides alone are very interesting: although cyclohexylmercuric chloride liberated a large amount of mercury metal and gave cyclohexyl chloride, phenylmercuric and *p*-tolylmercuric chlorides gave the corresponding aromatic hydrocarbons and only a trace of mercury (Table 6). Moreover, cyclohexylmercuric and *n*-butylmercuric bromides gave smaller amount of mercury metal than cyclohexylmercuric chloride.

These results show that the appearance of the demercuration reaction depends upon both organic and inorganic groups, and that the demercuration reactions of alkylmercuric halides are different from those of arylmercuric halides.

Three mechanisms are possible for thermal demercuration of organomercuric salt alone.

Mechanism A

$$\text{R-Hg-X} \rightarrow \text{R}\cdot + \cdot\text{HgX} \qquad (6)$$

$$\text{R}\cdot + \cdot\text{HgX} \rightarrow \text{RX} + \text{Hg} \qquad (7)$$

$$2\cdot\text{HgX} \rightarrow \text{Hg}_2\text{X}_2$$

Mechanism B

$$2\ \text{R-Hg-X} \rightleftarrows \begin{bmatrix} \text{R-Hg-X} & \\ \vdots\ \ \vdots & \\ \text{R—Hg-X} \end{bmatrix} \rightleftarrows \text{R}_2\text{Hg} + \text{HgX}_2 \qquad (8)$$

$$\text{R-Hg-R} \rightarrow 2\text{R}\cdot + \text{Hg} \qquad (1)$$

$$\text{R}\cdot + \text{HgX}_2 \rightarrow \text{RX} + \cdot\text{HgX} \qquad (9)$$

$$\text{Hg} + \text{HgX}_2 \rightarrow \text{Hg}_2\text{X}_2 \qquad (4)$$

$$2\cdot\text{HgX} \rightarrow \text{Hg}_2\text{X}_2$$

Mechanism C

$$\text{R-Hg-X} \rightleftarrows [\text{-X}\cdots\text{R-Hg-X}\cdots\text{R-Hg-}]$$

$$\text{or} \begin{bmatrix} \text{R-Hg-X} \\ \vdots\qquad\vdots \\ \text{X-Hg-R} \end{bmatrix} \rightarrow \text{RX} + \text{Hg} \qquad (10)$$

If the mechanism A is correct, organomercuric bromides would give larger amount of mercury metal than the corresponding chlorides, from a consideration of bond energy of R–HgX and ·Hg–X. However, as the results are opposite, the mechanism A seems to be unlikely.

In the mechanism B, the position of the equilibrium (reaction (8)) generally lies by far to the left-hand side, but, if at least one of the components in the right-hand side is unstable to heat, the equilibrium would shift to the right-hand side. Since bis-organomercurials are usually less stable to heat than organomercuric salts, organic free radicals would generate from bis-organomercurials thus produced, and would react according to the reaction (9), which would compete with the reaction (4). Thus the formation of mercury metal would be considerably supressed. Therefore, the formation of large amounts of mercury metal could not be explained by the mechanism B.

Kharasch *et al.*[12)] and Shoolery *et al.*[13–15)] have

---

*3 It is considered that the acetoxy radicals may be stabilized by some interaction with mercury metal, because completely free acetoxy radical would rapidly decompose into methyl radical and carbon dioxide.

12) M. S. Kharasch and M. W. Grafflin, *J. Amer. Chem. Soc.*, **47**, 1948 (1925); M. S. Kharasch and R. Marker, *ibid.*, **48**, 3130 (1926); M. S. Kharasch and A. L. Flenner, *ibid.*, **54**, 674 (1932); M. S. Kharasch, H. Pines and J. H. Levine, *J. Org. Chem.*, **3**, 347 (1938); M. S. Kharasch and S. Swartz, *ibid.*, **3**, 405 (1938); M. S. Kharasch, R. R. Legault and W. R. Sprowls, *ibid.*, **3**, 409 (1938).

13) B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.*, **77**, 3977 (1955).

14) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

15) M. A. Davis, *J. Org. Chem.*, **32**, 1161 (1967).

established the relative electronegativities of organic and inorganic groups as follows:

p-$CH_3C_6H_4 > C_6H_5 > CH_3 > n$-$C_4H_9 > C_6H_5CH_2 >$ *cyclo*-C_6H_{11}; $OAc > Cl > Br > SCN > CN$

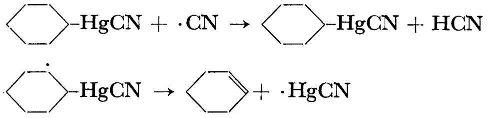
Since aryl groups are more electronegative than cyclohexyl, the intermolecular interaction between cyclohexyl and chlorine seems to be more strong than that between aryl and chlorine. From these considerations, the demercuration reactions of alkylmercuric chlorides are considered to proceed mainly through the mechanism C. Thus, the corresponding chlorides are obtained in good yields. Partial formation of alkyl radicals is attributed to the mechanisms A (may be less probable) and B.

In the cases of alkylmercuric bromides, intermolecular interaction between alkyl group and bromine is considered to be not so strong as in the alkylmercuric chlorides because of less electronegativity of bromine. Therefore, the contribution of the mechanism C decreases and both liberation of metallic mercury and the formation of organic bromide decrease.

Arylmercuric chlorides, on the contrary, might decompose on heating to generate aryl radicals mainly through mechanism B, because an intermediate complex in the reaction (8) seems favorable over that in the mechanism C from a consideration of the electronegativities of aryl group and chlorine. Formation of the corresponding aromatic hydrocarbon is presumably attributed to hydrogen abstraction from the surrounding organomercurials by aryl radicals. Thus the reaction (9), in which aryl radical is considered to be more favorable over alkyl radical, scarcely occurs.

In organomercuric cyanides, considerable amount of mercury metal was always liberated. These facts indicate that the demercuration reaction of organomercuric cyanides proceeds mainly through the mechanism B, because mercuric cyanide produced is also unstable to heat.[11]

A large amount of cyclohexene in the case of cyclohexylmercuric cyanide is presumably formed through homolytic β-elimination of aliphatic organomercurials[16] by cyano radical, which is produced by thermal decomposition of mercuric cyanide,[11] because the formation of a considerable amount of hydrogen cyanide was observed.



The demercuration reaction of phenylmercuric thiocyanate is considered to be very similar to that of the corresponding cyanide, excepting that no phenyl thiocyanate was obtained. This is explained by the following decomposition, because a large amount of mercuric sulfide was obtained and then liberated mercury metal decreased.

$$Hg(SCN)_2 \rightarrow HgS + \cdot CN + \cdot SCN$$
$$Hg + \cdot SCN \rightarrow HgS + \cdot CN$$

In the cases of organomercuric acetates, since mercuric acetate was almost decomposed to give metallic mercury under similar conditions, the demercuration reaction proceeds mainly through the mechanism B.

Phenylmercuric acetate gave neither phenyl acetate nor toluene. This fact shows that the mechanism C does not occur at all, because acetoxy group is more electronegative than chlorine. From the result, it is considered that the reaction (9) is also unlikely in other cases. Thus, the formation of a trace of RX is probably attributed to a small contribution of the mechanism C.

The following two mechanisms are possible for the demercuration reaction of organomercuric salt in the presence of mercuric salt.

Mechanism D

$$\begin{matrix} \text{R-Hg-X} \\ + \\ \text{HgY}_2 \end{matrix} \rightleftarrows \left[\begin{matrix} \text{R—Hg-X} \\ \vdots \qquad \vdots \\ \text{Y-Hg-Y} \end{matrix}\right] \rightleftarrows \text{RHgY} + \text{HgXY} \quad (11)$$

$$\text{RHgX(or RHgY)} \xrightarrow[\text{B, C or E}]{\text{Mechanism}}$$

Mechanism E

$$\text{RHgX} + \text{HgY}_2 \rightleftarrows [\cdots\text{X-Hg-R}\cdots\text{Y-Hg-Y}\cdots \text{R-Hg-X}\cdots] \rightarrow \text{RY} + \text{Hg} \quad (12)$$
$$\text{Hg} + \text{HgY}_2 \rightarrow \text{Hg}_2\text{Y}_2$$

In cyclohexylmercuric halide - mercuric halide systems, the ratio of cyclohexyl bromide to the chloride increased with the bromine content in the system, and the formation of the chloride was more favorable than that of the bromide (Table 1). These facts can be explained considering that the position of the equilibrium (11) lies to the side of cyclohexylmercuric chloride and that organomercuric salts thus produced decompose through the mechanism C or E depending on the amount of mercuric salts present.

Generally, it is concluded that alkylmercuric halides also decompose mainly through the mechanisms C and E in the presence of mercuric halides. In the cases of arylmercuric salts, the reactions presumably proceed through the mechanisms D and E. This conclusion is also supported from the facts that the results of the reactions of diphenylmercury with mercuric salts were very similar to those of phenylmercuric salts with mercuric salts.

In organomercuric acetate, the demercuration reaction proceeds through the mechanism B as described before. Thus, n-butylmercuric or benzylmercuric acetate gave the corresponding organic acetate only in a poor yield. In the case of n-butylmercuric acetate, the yield of n-butyl acetate

---

16) F. R. Jensen and H. E. Guard, *J. Amer. Chem. Soc.*, **90**, 3250 (1968).

decreased from 10% to 5% in the presence of mercuric acetate. This fact can be reasonably explained by a large contribution of homolytic *β*-elimination16) similarly to that of cyclohexylmercuric cyanide.

On the other hand, in the case of benzylmercuric acetate, the yield of benzyl acetate increased considerably and the yield of dibenzyl decreased in the presence of mercuric acetate. Since benzyl group is much less electronegative and acetoxy group is much more electronegative, the observed results can be explained by the absence of homolytic *β*-elimination and by the contribution of the mechanism E in the presence of mercuric acetate.

Experimental[*4]

Materials. Organomercurials were prepared by usual methods: *n*-butylmercuric bromide, mp 129.5—131°C (lit,17) 136°C); *n*-butylmercuric acetate, mp 54—55.5°C (lit,17) 56°C); *s*-butylmercuric chloride, mp 26.5—29.5°C (lit,18) 28°C); benzylmercuric acetate, mp 124—125°C (lit,19) 128—128.8°C); cyclohexylmercuric bromide, mp 151—153°C (lit,20) 153°C); cyclohexylmercuric chloride, mp 160—161.5°C (lit,21) 163°C); cyclohexylmercuric cyanide, mp 147—148.5°C (lit,21) 146°C); phenylmercuric acetate, mp 148.5—150°C (lit,22) 149°C); phenylmercuric chloride, mp 249.4—249.7°C (lit,21) 251°C); phenylmercuric cyanide, mp 203—205°C (lit,21) 209°C); phenylmercuric thiocyanate, mp 230—231°C (decomp.) (lit,23) 231—232.5°C (decomp.)); diphenylmercury, mp 125—127°C (lit,24) 122—124°C); *p*-tolylmercuric chloride, mp 232.5—234.5°C (lit,21) 233°C); bis-phenylethynylmercury, mp 123—124°C (lit,25) 124.5—125°C).

Mercuric thiocyanate was prepared by the usual method.26) Other inorganic mercuric salts were obtained commercially.

Authentic samples were prepared by the methods described in the literature: cyclohexyl cyanide,27) bp 183—187°C (lit,28) 184—185°C); dicyclohexyl, bp 110°C/15 mmHg, n_D^{19} 1.4800 (lit, bp 233°C/750 mmHg,29) n_D^{20} 1.4795426)); phenyl thiocyanate, bp 104—106°C/15.5 mmHg (lit,23) 232—233°C), IR: 2150 cm^{-1} (–S–C≡N); *p*-tolyl chloride, bp 155—156.5°C, n_D^{16} 1.5231 (lit, bp 162—162.2°C,30) $n_D^{18.20}$ 1.519931)); di-*p*-tolyl, mp 118—120°C (lit,32) 121°C); phenyl-*p*-tolylmethane, bp 141°C/13 mmHg (lit,33) 144°C/16 mmHg); phenylethynyl cyanide, bp 101°C/12 mmHg, mp 37.5—39°C (lit,34) bp 105—106°C/13 mmHg, mp 41°C); benzyl acetate, bp 104°C/17 mmHg, n_D^{21} 1.5008 (lit,35) bp 213°C, $n_D^{19.93}$ 1.50324).

Other samples were obtained commercially.

General Methods for Thermal Reactions. About 2 g of organomercurial or a mixture of about 2 g of organomercurial and an appropriate amount of mercuric salt, which was softly covered with glass wool to prevent from sublimation of mercurials, was placed without a solvent in a reaction tube equipped with a thermometer and a cold trap, and heated at 200—300°C for 1—2 hr under ordinary or/and reduced pressure. Volatile liquid was collected in the cold trap cooled with dry ice-ethanol, weighed, and submitted to VPC[*5] or distilled. Nonvolatile material in the reaction tube was extracted with ether or petroleum ether, with ethanol, methanol or acetone, and with water, successively, and each extract after evaporation was submitted to determination of melting point and/or to thin layer chromatography for identification. Metallic mercury liberated was isolated from the residual material and weighed.

Some typical examples are described below, and the results are summarized in Tables 1—6.

s-Butylmercuric Chloride with Mercuric Chloride. A mixture of 4.917 g (16.7 mmol) of *s*-butylmercuric chloride and 6.091 g (22.4 mmol) of mercuric chloride was heated at 250—260°C under ordinary pressure for 2 hr. Generation of hydrogen chloride was observed. Volatile liquid (1.420 g) was distilled, and 0.977 g (10.6 mmol, 63.5%) of *s*-butyl chloride, bp 61—68°C, was obtained.

Cyclohexylmercuric Chloride with Mercuric Bromide. A mixture of 2.003 g (6.27 mmol) of cyclohexylmercuric chloride and 2.579 g (7.18 mmol) of mercuric bromide (mole ratio 1 : 1.14) was heated at 240—265°C under a pressure of 50 mmHg for 1.5 hr. Volatile liquid (0.683 g) was submitted to VPC, and cyclohexane (0.20 mmol), cyclohexene (1.87 mmol), cyclohexyl chloride (3.36 mmol) and cyclohexyl bromide (0.74 mmol) were determined. A trace of dicyclohexyl was also detected. From the ethanol extract of nonvolatile material 0.302 g (11.7%) of unchanged mercuric bromide was recovered. The residue consisted of 2.828 g of white insoluble material, and no metallic mercury was observed.

[*4] All the melting points and boiling points described here were not corrected.

17) K. H. Slotta and K. R. Jacobi, *J. Prakt. Chem.*, **120**, 249 (1929).

18) H. B. Charman, E. D. Hughes and C. Ingold, *J. Chem. Soc.*, **1959**, 2523.

19) G. H. Coleman, L. A. Weed and C. D. Myers, *J. Amer. Chem. Soc.*, **59**, 2703 (1937).

20) G. Grüttner, *Ber.*, **47**, 1651 (1914).

21) E. Carr, I. B. Johns and R. M. Hixson, *J. Amer. Chem. Soc.*, **60**, 891 (1938).

22) J. L. Maynard, *ibid.*, **46**, 1510 (1924).

23) E. Söderbäck, *Ann. Chem.*, **419**, 267 (1919).

24) W. E. Bachmann, *J. Amer. Chem. Soc.*, **55**, 2827 (1933).

25) J. R. Johnson and W. L. McEwen, *ibid.*, **48**, 469 (1926).

26) A. A. Blanchard, J. W. Phelan and A. R. Davis, "Synthetic Inorganic Chemistry," John Wiley, New York (1936), p. 234.

27) C. H. Tilford, M. G. Van Campen and R. S. Shelton, *J. Amer. Chem. Soc.*, **69**, 2902 (1947).

28) M. Godchot, *Bull. Soc. Chim. Fr.*, **1911**, 261.

29) J. H. Gardner and P. Borgstrom, *J. Amer. Chem. Soc.*, **51**, 3375 (1929).

30) W. H. Perkin, *J. Chem. Soc.*, **1896**, 1203.

31) K. Seubert, *Ber.*, **22**, 2519 (1889).

32) L. Gattermann, *ibid.*, **23**, 1223 (1890).

33) K. V. Auwers and A. Frühling, *Ann. Chem.*, **422**, 192 (1921).

34) Ch. Moureu and I. Lazennec, *Bull. Soc. Chim. Fr.*, **1906**, 520.

35) S. T. J. Tromp, *Rec. Trav. Chim. Pays-Bas*, **41**, 278 (1922).

[*5] Diisodecyl phthalate, Apiezon "L" grease, di-2-ethylhexyl sebacate and succinic polyester of diethylene glycol were used as liquid phase.

Phenylmercuric Thiocyanate with Mercuric Thiocyanate. A mixture of 2.003 g (5.96 mmol) of phenylmercuric thiocyanate and 2.013 g (6.34 mmol) of mercuric thiocyanate was heated at 220—290°C under atmospheric pressure for 1 hr and then under a pressure of 20 mmHg at 270°C for 45 min. The volatile liquid (0.327 g) was submitted to VPC, and benzene (1.92 mmol, 32.3%), benzonitrile (0.471 mmol), and phenyl thiocyanate (0.0232 mmol) were determined. No phenyl isothiocyanate was detected. From the petroleum ether extract of nonvolatile material, 6 mg (0.036 mmol) of diphenyl was obtained, and from the ethanol extract 20 mg (1%) of unchanged phenylmercuric thiocyanate was recovered. The residue consisted of a considerable amount of insoluble black material and 243 mg (1.21 mmol) of metallic mercury. The black material proved to contain mercuric sulfide by the usual analytical method.

The authors wish to express their thanks to Professor G. F Wright, The University of Toronto, Canada, for his valuable comments throughout this work.