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THE MECHANISM OF BIMOLECULAR ELECTROPHYLIC SUBSTITUTION AT A SATURATED CARBON ATOM

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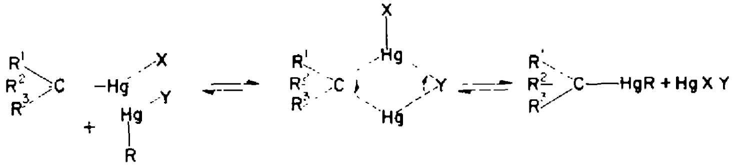
Abstract—The reaction between ArHgAlk and $Hg^{203}X_2$ was investigated. In all the cases only $ArHg^{203}X$ and AlkHgX were obtained.

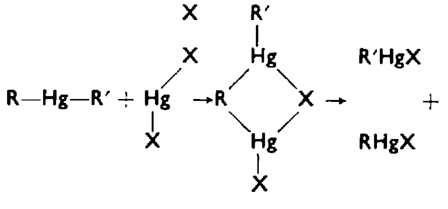
ON the basis of the reaction kinetics and stereochemistry of electrophilic substitution at the saturated carbon (Reactions 1–5), it was suggested earlier that these reactions involve similar mechanisms and transition states:[1–4]

1. $2R^1R^2R^3CHgX \rightarrow (R^1R^2R^3C)^2Hg + HgX_2$
2. $R^1R^2R^3CHgX + Hg^{203}X_2 \rightleftarrows R^1R^2R^3CHg^{203}X + HgX_2$
3. $R^1R^2R^3CHgX + RHg^{203}X \rightleftarrows R^1R^2R^3CHg^{203}X + RHgX$
4. $(R^1R^2R^3C)_2Hg + HgX_2 \rightarrow 2R^1R^2R^3CHgX$
5. $(R^1R^2R^3C)_2Hg + R^1R^1R^3CHg^{203}X \rightleftarrows (R^1R^2R^3C)_2Hg^{203} + R^1R^2R^3CHgX$



1. R = R¹R²R³C, Y = X = Hal
2. R = Y = X = Hal
3. Y = X = Hal
4. X = R¹R²R³C, R = Y = Hal
5. R = X = R¹R²R³C, Y = Hal

Ingold *et al.*,[5–10] suggested a similar mechanism for desymmetrization of organomercury compounds. In asymmetric compounds, RHgR′, two transition states are possible, one shown in the following scheme and the other where R and R′ are interchanged:



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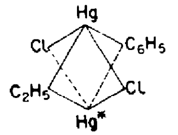
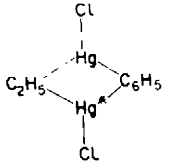
[1] O. A. Reutov, *Acta Chem. Acad. Sci. Hung.* **18,** 439 (1959).
[2] O. A. Reutov and I. P. Beletskaya, *Dokl. Akad. Nauk SSSR* **131,** 853 (1960).
[3] O. A. Reutov, *Angew. Chem.* **72,** 198 (1960).
[4] O. A. Reutov, *Record of Chem. Progr.* No **1,** 1 (1961).
[5] H. B. Charman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 2523 (1959).
[6] H. B. Charman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 2530 (1959).
[7] H. B. Charman, E. D. Hughes, C. K. Ingold and F. G. Thorpe, *J. Chem. Soc.* 1121 (1961).
[8] E. D. Hughes, C. K. Ingold, F. G. Thorpe and H. C. Volger, *J. Chem. Soc.* 1133 (1961).
[9] H. B. Charman, E. D. Hughes, C. K. Ingold and H. C. Volger, *J. Chem. Soc.* 1142 (1961).
[10] E. D. Hughes and H. C. Volger, *J. Chem. Soc.* 2359 (1961).

Kharash postulated a series of radicals in order of their electronegativity in terms of their affinity to proton; aromatic radicals proved to be more electronegative than aliphatic. Thus, protolysis of arylalkylmercury leads to a quantitative yield of alkylmercuric chloride. Evidently replacement of hydrogen chloride by mercuric halide, in spite of a possible similarity in mechanism, may give different results due to the considerably larger volume of the mercury atom and the lower polarity of the reagent. This can be proved only by using labelled mercury.

Three diametrically opposite results for this reaction were published during 1961–62 by Dessy *et al.*,[11] Brodersen and Schlenker[12] and the present workers.[13]

Dessy *et al.*, reported that desymmetrization of ethylphenylmercury with mercuric chloride gives a 50% distribution of the starting labelled mercury in the reaction products. Accordingly, they proposed mechanisms involving either a six-centred transition state with each mercury atom simultaneously bonded to the four remaining centres (phenyl, ethyl and two chlorines), or an alternative transition state.[11]





Dessy's observation casts a doubt on the mechanism suggested[1–4] at least as far as desymmetrization reactions are concerned. However, we are inclined to ascribe this result to the secondary exchange between the reaction products, though corresponding blanks have been made. We have observed that even traces of impurities may catalyse such an exchange.* Repeating the experiment of Dessy *et al.*, the labelled Hg was found in the phenylmercury halide.[13]

Brodersen and Schlenker assert that desymmetrization of butylphenylmercury with labelled mercuric bromide results in radioactive butylmercuric bromide and inactive phenylmercuric bromide, implying rupture of the bond between mercury and alkyl and not between mercury and phenyl. Such a result, besides contradicting known facts, is paradoxical in that it represents a third way out whereas theoretically there should be only one.

Borisov and Osipova[14] have shown that thallium trichloride reacts with asymmetrical mercury compounds of this type according to the Kharash's rule. The reaction proceeds as follows:

$$2RHgR' + TlCl_3 \rightarrow R_2TlCl + 2R'HgCl$$

The action of thallium trichloride on ethylphenylmercury gives rise to diphenylthallium chloride and ethylmercuric chloride, and it is the phenylmercury bond and not the alkylmercury bond that is broken. The reactions of ethylnaphthylmercury and butylanisylmercury with thallium trichloride proceed similarly.

$$Alk\text{–}Hg\text{–}Ar + TlCl_3 \rightarrow Ar_2TlCl + Alk_2HgCl$$

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* Amines and I^- appear to catalyse the reaction:

$$ArCH_2HgX + Hg^*X_2 \rightleftarrows ArCH_2Hg^*X + HgX_2.$$

[11] R. E. Dessy, Y. K. Lee and Iin-Young Kim, *J. Amer. Chem. Soc.* **83**, 1163 (1961).

[12] K. Brodersen and U. Schlenker, *Chem. Ber.* **94**, 3304 (1961).

[13] Nic. A. Nesmeyanov and O. A. Reutov, *Dokl. Akad. Nauk SSSR* **144**, 126 (1962).

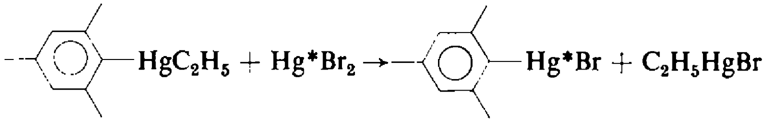
[14] A. E. Borisov and M. A. Osipova, *Izvest. A.N. SSSR, Otdel. Khim. Nauk* 1039 (1961).

Further, symmetrization, desymmetrization and protolysis by acid and other reactions proceed faster with diarylmercury than with dialkylmercury, and according to Dessy *et al.*, the reaction between diphenylmercury and mercuric iodide is considerably faster than the analogous reaction with diethylmercury.

Desymmetrization of organomercury compounds of the type arylalkylmercury have been investigated and the following reactions observed:

1. $C_6H_5HgC_2H_5 + Hg^*Br_2 \rightarrow C_6H_5Hg^*Br + C_2H_5HgBr$
2. $C_6H_5HgC_2H_5 + Hg^*Cl_2 \rightarrow C_6H_5Hg^*Cl + C_2H_5HgCl$
3. $C_6H_5HgC_4H_9\text{-n} + Hg^*Br_2 \rightarrow C_6H_5Hg^*Br + \text{n-}C_4H_9HgBr$

4.



In all instances arylmercury halide was practically 100% active and alkylmercury halide inactive. This being the case in Reaction 3 (in which Brodersen and Schlenker obtained the contrary result) and even in Reaction 4, where the mesityl radical through steric hindrance may have changed the reaction course.

Since evidence presented in this paper indicates that the reaction of alkylarylmercury with mercuric halide substitution takes place at an aromatic rather than a saturated carbon; there is no need to postulate any new mechanism for electrophilic substitution at saturated carbon other than that already suggested by C. K. Ingold and by one of us.

EXPERIMENTAL

Compounds of the type ArHgAlk were obtained by the interaction of alkylmercuric bromides and arylboric acids. This procedure is more convenient than the phenyl lithium method[11] in that the reaction takes place readily and the products are not contaminated by diaryl which if produced is difficult to remove completely.

The purity of the ArHgAlk was confirmed and according to the method of Kharash, AlkHgX being produced in almost theoretical yield and therefore excluding the possibility of mixtures of 2 symmetric organo Hg compds.

Protolysis of ArHgAlk

To 0·2–0·3 g organomercury compound in 1·0 ml methanol, 0·15–0·20 ml 20% HCl or HBr was slowly added in 30 min. After 10 min, 5–7 ml water was added to the reaction mixture, and the resulting precipitate of AlkHgX collected. Yields and m.ps of alkylmercuric salts are given in Table 1.

Butylphenylmercury

Solutions of 6·0 g phenylboric acid in 20 ml methanol and 5·0 g NaOH in 10 ml water were added to a hot methanolic solution of 12·0 g butylmercuric bromide, and the mixture further heated for 5 min. After allowing to stand for 1 hr, it was poured in water and the resulting oily layer was extracted with ether. The ethereal extracts were dried over $MgSO_4$ and the ether removed *in vacuo*. The product was purified by distilling twice *in vacuo*, yield 90%, b.p. 113–116°/2–2·5 mm, n_D^{20} 1·5913. (Found: C, 36·12, 36·13; H, 4·23, 4·20; Hg, 59·58, 59·41. $C_{10}H_{14}Hg$ requires: C, 35·85; H, 4·21; Hg, 59·85%.)

Ethylphenylmercury

Ethylmercuric bromide under the same conditions gave ethylphenylmercury in 80% yield, b.p. 105–108°/5 mm. (Found: C, 31·55, 31·40; H, 3·27, 3·31; Hg, 65·01, 65·10. $C_8H_{10}Hg$ requires: C, 31·32; H, 3·29; Hg, 65·39%.)

TABLE 1

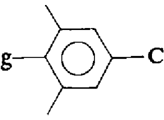
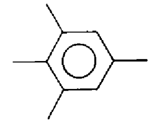
Compound	Salt	Yield	m.p.	Lit. m.p. and ref.
$C_2H_5HgC_6H_5$	C_2H_5HgCl	95%	193–194°	190–193°[15]
C_2H_5Hg 	C_2H_5HgBr	90%	193·5°	193·5°[16]
$C_4H_9HgC_6H_5$	C_4H_9HgBr	85%	130–131°	129°[17] 136°[18]

TABLE 2

Products	m.p.	Lit. m.p. and ref.
1. C_2H_5HgBr	193–194	193·5[16]
C_6H_5HgBr	272–273	275[19]
2. C_2H_5HgCl	—	
C_6H_5HgCl	249	250[20]
3. HgBr 	196	194[21]
C_2H_5HgBr	192–193	193·5[16]
4. C_6H_5HgBr	274–276	275[19]
C_4H_9HgBr	129–131	129[17] 136[18]

Ethylphenylmercury

This was obtained by the phenyllithium method[11] in 60% yield. (Found: C, 31·81, 31·99; H, 3·28, 3·32; Hg, 64·35, 64·01. $C_8H_{10}Hg$ requires: C, 31·32; H, 3·29; Hg, 65·39%.)

Ethylmesitylmercury

A solution of 4·9 g mesitylboric acid and 2 g NaOH in a minimum volume of methanol was added to a solution of 8 g ethylmercuric bromide in boiling abs. methanol. After heating for 30 min, the reaction mixture was allowed to stand for 1 hr and then poured into ice-water. The precipitate formed was collected, yield almost quantitative, m.p. 28–29°. After recrystallization from methanol m.p. 30–31°. (Found: C, 37·85, 37·94; H, 4·67, 4·62; Hg, 57·87, 57·90. $C_{11}H_{16}Hg$ requires: C, 38·09; H, 4·71; Hg, 57·47%.)

Reactions between ArHgAlk *and* $Hg^{203}X_2$

Desymmetrization of ArHgAlk *with radioactive mercuric bromide and chloride.* A solution of 2–5 mmol mercuric halide, labelled with Hg^{203}, in the minimum volume of methanol was added

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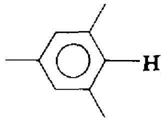
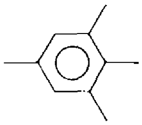
[15] C. Willgerodt, *Chem. Ber.* **31**, 921 (1898).
[16] C. S. Marvel, C. G. Gaurke and E. L. Hill, *J. Amer. Chem. Soc.* **47**, 3010 (1925).
[17] C. S. Marvel and V. L. Gould, *J. Amer. Chem. Soc.* **44**, 157 (1922).
[18] K. H. Slotta and K. R. Jacobi, *J. Pract. Chem.* **120**, 276 (1929).
[19] R. Otto, *J. Pract. Chem.* **2, 1**, 186 (1870).
[20] E. Dreher and R. Otto, *Liebigs Ann.* **154**, 112 (1870).
[21] A. Michaelis, *Chem. Ber.* **28**, 592 (1895).

TABLE 3. RELATIVE RADIOACTIVE CONTENT OF HgX_2 AND REACTION PRODUCTS

No.	Reaction	AlkHgX	ArHgX	HgX_2
1	$C_6H_5HgC_2H_5 + Hg^*Br_2$	C_2H_5HgBr 1·7%	C_6H_5HgBr 95%	$HgBr_2$ 100%
2	The same without steam distill.	— not isolated	C_6H_5HgBr 92%	$HgBr_2$ 100%
3	$C_6H_5HgC_2H_5 + Hg^*Cl_2$	— not isolated	C_6H_5HgCl 95-98%	$HgCl_2$ 100%
4	$C_6H_5HgC_4H_9 + Hg^*Br_2$	C_4H_9HgBr 0·8%	C_6H_5HgBr 102%	$HgBr_2$ 100%
5	 $-HgC_2H_5 + Hg^*Br_2$	C_2H_5HgBr 5%	 $-HgBr$ 97%	$HgBr_2$ 100%

rapidly to a solution of an equivalent quantity alkylarylmercury in 2–3 ml methanol. A white crystalline precipitate formed immediately, which was collected after 15 min and washed with water. Alkylmercuric bromide was steam distilled and recrystallized from methanol twice. The crystalline residue in the distillation vessel was washed with water, methanol and ether and recrystallized from xylene. In Table 2 the m.ps of four pairs of products obtained in four such reactions are listed.

Reaction between ethylphenylmercury and mercuric halide (according to Dessy *et al.*)

$Hg^{203}Cl_2$ (0·44 mmoles in 3 ml methanol) was added to 0·44 mmoles of ethylphenylmercury in 2 ml methanol. The resulting precipitate was dissolved in 15 ml abs. methanol by heating for about 20 min and the solution filtered hot. After cooling and recrystallization from methanol (m.p. 249°), the radioactivity of phenylmercuric chloride was measured.

Radioactive measurements

Radioactive mercury bromide was prepared from labelled Hg^{203} and bromine, and recrystallized from water and ethanol. The radioactivity of HgX_2, ArHgX and AlkHgX samples was measured by dissolving 20·00–30·00 mg of the substance in 20 ml dioxan and placing the solution in a standard vessel on a gamma counter MS-4 for liquids. The range of error was about 7%. The data is given in Table 3.

Acknowledgement—We wish to thank Mr. V. N. Nicolskiy for assistance in experimental work.