methyl 4-bromocrotonate, a liquid product was obtained and all attempts to crystallise this were unsuccessful.

Reactions

(*a*) *Thermal decomposition.* A quantity of the tetraethylammonium tri-μ-chloro-bis(π-allyldicarbonylmolybdenum) was heated to 350° and the gases which were formed were analysed by infrared and vapour phase chromatographic techniques. Ethylene, triethylamine, propene, carbon monoxide and allyl chloride were found. The proportions of the different gases were not determined. However, the CO evolved was determined accurately; 4 CO/mole complex were found.

(*b*) *With lithium iodide.* Reaction of the bromo complex corresponding to the above complex in tetrahydrofuran with a large excess of lithium iodide failed to cause any displacement of the bromine bridges by iodine, the starting material being recovered unchanged.

(*c*) *With pyridine.* To a suspension of the tetraethylammonium tri-μ-chloro-bis(2-methyl-π-allyldicarbonylmolybdenum) (0.5 g) in carbon tetrachloride (25 ml) sufficient pyridine to effect solution was added (5 ml). After 1 h the reaction mixture was filtered free from the tetraethylammonium chloride which was precipitated and the solution was evaporated to dryness. The yellow solid obtained was crystallised from methylene chloride–petroleum ether as yellow plates, m.p. 115–7° (decomp.) (0.54 g, 88 %). (Found: C, 48.06; H, 4.17; Mo, 23.13. $C_{16}H_{17}ClMoN_2O_2$ calcd.: C, 47.96; H, 4.27; Mo, 23.94 %.)

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SUMMARY

The reaction of the tetraethylammonium salts of the anionic halopentacarbonyl complexes of molybdenum and tungsten with allyl halides gives novel dimeric π-allyl complexes whose structures are discussed on the basis of spectroscopic, chemical and analytical data.

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ALOMETHYL–METAL COMPOUNDS

. PREPARATION OF PHENYL(TRIHALOMETHYL)MERCURY COMPOUNDS

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The first trihalomethylmercury compound, CBr_3HgBr, was prepared in 1926[2]. his compound class aroused no further interest until recently, when Russian workers ported three new synthetic routes to trihalomethylmercurials:

$$CCl_3Br + Hg \xrightarrow{UV} CCl_3HgBr \text{ (ref. 3)}$$

$$C_6H_5HgX + CHX_3 + \textit{tert}\text{-BuOK} \longrightarrow C_6H_5HgCX_3 + KX + \textit{tert}\text{-BuOH (ref. 4)}$$

$$2CCl_3COONa + HgCl_2 \xrightarrow{CH_3OCH_2CH_2OCH_3} (CCl_3)_2Hg + 2CO_2 + 2NaCl \text{ (ref. 5)}^{****}$$

Our discovery that phenyl(trihalomethyl)mercurials are valuable reagents for e synthesis of *gem*-dihalocyclopropanes[1a,c,f] led us to investigate more closely the nthesis of this class of organomercury compounds. Of the three newer procedures, at of Reutov and Lovtsova seemed the most versatile. Furthermore, our interest the latter procedure was sharpened considerably by the mechanism which these thors claimed was operative in the C_6H_5HgCl/haloform/potassium *tert*-butoxide action. We report here the results of our studies concerning the preparation of enyl(trihalomethyl)mercurials by the Reutov–Lovtsova method and concerning e mechanism of this most useful reaction.

ENYL(TRIHALOMETHYL)MERCURIAL PREPARATION

neral comments

The preparation of $C_6H_5HgCX_3$ compounds in good yield by the Reutov–vtsova procedure can be accomplished in a reproducible manner, but certain cautions must be observed. A detailed procedure will be given in the EXPERIMENTAL tion, but it may be mentioned here that the rate of stirring of this heterogeneous ction mixture is a critical factor. *High speed stirring is required.*

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*We have reported on results obtained in this area in 10 preliminary communications . 1a–j).
** Alfred P. Sloan Foundation Fellow, 1962–66.
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**** Further investigated by Logan[6].

TABLE 1

CONDITIONS FOR PREPARATION OF PHENYL(TRIHALOMETHYL)MERCURIALS[a]

Expt. No.	HCX_3	C_6H_5HgX'[b]	*Base*	*Moles* C_6H_5HgX	*Molar ratio* HCX_3/*Base*/ C_6H_5HgX	*Base addn. time (h)*	*Volume solvent (ml)*	*Crude yield (%)* $C_6H_5HgCX_3$
1	$HCCl_3$	C_6H_5HgCl[c]	*tert*-C_4H_9OK (s)	0.016	4/2.5/1	½	100	0g
2[h]	$HCCl_3$	C_6H_5HgCl[c]	*tert*-C_4H_9OK (s)	0.016	4/2.5/1	½	100	66
3	$HCCl_3$	C_6H_5HgBr[c]	*tert*-C_4H_9OK (s)	0.016	4/2.5/1	½	150	58
4	$HCCl_3$	C_6H_5HgCl	*tert*-C_4H_9OK (soln.)	0.25	4/2.5/1	½	450	58
5	$HCCl_3$	C_6H_5HgCl	*tert*-C_4H_9OK (soln.)	0.25	8/4/1	1½	700	57
6[h]	$HCCl_3$	C_6H_5HgBr	*tert*-C_4H_9OK (s)	0.25	4/2/1	½	1200	74
7	$HCCl_3$	C_6H_5HgBr	*tert*-C_4H_9OK (s)	0.1	1/1.3/5	½	200	13
8	$HCCl_3$	$C_6H_5HgO_2CCH_3$[d]	*tert*-C_4H_9OK (soln.)	0.1	4/2/1	⅓	400	0–25[i]
9	$HCCl_2Br$	C_6H_5HgCl	*tert*-C_4H_9OK (soln.)	0.1	4/2/1	2	400	46
10	$HCCl_2Br$	C_6H_5HgBr	*tert*-C_4H_9OK (soln.)	0.1	4/2/1	2	400	50
11	$HCCl_2Br$	$C_6H_5HgO_2CCH_3$[d]	*tert*-C_4H_9OK (soln.)	0.1	4/2/1	¾	250[e]	0g
12[h]	$HCCl_2Br$	C_6H_5HgBr	*tert*-C_4H_9OK (s)	0.25	4/2/1	½	1200	81 (80)
13	$HCCl_2Br$	C_6H_5HgBr	*tert*-C_4H_9OK (soln.)	0.25	4/2/1	½	1200	19
14[h]	$HCCl_2Br$	C_6H_5HgCl	*tert*-C_4H_9OK (s)	0.25	4/2/1	½	1200	81
15	$HCCl_2Br$	C_6H_5HgCl	*tert*-C_4H_9OK (s)	0.5	2/2/1	½	1800	61
16	$HCCl_2Br$	C_6H_5HgCl	*tert*-C_4H_9OK (s)	0.5	2.2/2/1	1½	1800	41[j]
17	$HCCl_2Br$	C_6H_5HgCl	*tert*-C_4H_9OK (s)	0.5	2.2/2/1	1	1500	40[k]
18	$HCCl_2Br$	C_6H_5HgBr	$NaOCH_3$ (s)[f]	0.1	4/2/1	½	500	7
19	$HCCl_2Br$	C_6H_5HgBr	*tert*-C_4H_9OK (s)[f]	0.25	4/1.7/1	½	1200	3.6
20	$HCCl_2Br$	C_6H_5HgBr	*tert*-$C_5H_{11}OK$ (s)[f]	0.5	4/2.2/1	½	1200	0
21	$HCClBr_2$	C_6H_5HgCl[f]	*tert*-C_4H_9OK (soln.)	0.1	4/2/1	1½	400	3[l]
22	$HCClBr_2$	C_6H_5HgBr[f]	*tert*-C_4H_9OK (soln.)	0.1	4/2/1	2	400	9
23	$HCClBr_2$	C_6H_5HgBr	*tert*-C_4H_9OK (soln.)	0.1	3.3/2/1	1¾	400	66
24	$HCBr_3$	C_6H_5HgBr	*tert*-C_4H_9OK (soln.)	0.2	4/3/1	¾	750	7
25[h]	$HCBr_3$	C_6H_5HgBr	*tert*-C_4H_9OK (s)	0.25	4/2/1	½	1000	90
26	$HCBr_3$	C_6H_5HgBr	*tert*-C_4H_9OK (s)	0.25	2/2/1	½	1200	76
27	$HCCl_2F$	C_6H_5HgBr	*tert*-C_4H_9OK (soln.)	0.10	4/2/1	2½	400	0

[a] All experiments were carried out in benzene at 4–10° (ice bath) with high speed stirring unless noted otherwise. [b] Prepared from tetraphenyltin and the respective halide unless specified otherwise. [c] Prepared from diphenylmercury and the respective mercuric halide. [d] Prepared from diphenylmercury and mercuric acetate. [e] Solvent, tetrahydrofuran. [f] Commercial product. [g] Mechanical stirring used. [h] Described in detail in the experimental section. [i] Crude product very impure. [j] Temperature, 2° (salt–ice bath). [k] Temperature, 25–35° (no cooling). [l] No pure product obtained.

A summary of the various experimental conditions used in the preparation of $C_6H_5HgCCl_3$, $C_6H_5HgCCl_2Br$, $C_6H_5HgCClBr_2$ and $C_6H_5HgCBr_3$ is given in Table 1. This mmary reveals several additional factors upon which the yields of $C_6H_5HgCX_3$ pend. (*1*) A solution of potassium *tert*-butoxide in *tert*-butanol is easier to prepare d handle, but use of the solid base in the form of its solvate[7], *tert*-$C_4H_9OK \cdot$ *tert*-H_9OH, consistently gave higher yields, especially in the case of the bromine-ntaining haloforms (compare experiments 4 and 6; 12 and 13; 24 and 25). Further-ore, the use of commercial *tert*-C_4H_9OK resulted in only very low yields of product. The optimum molar ratio of the starting materials (haloform/base/C_6H_5HgX) was nd to be 4/2/1. Reutov and Lovtsova had used these reagents in 4/2.2/1 ratio. ttle was gained by having a very large excess of haloform and butoxide (experiments nd 5), while a decrease in the ratio of haloform/base to C_6H_5HgX generally resulted a substantial decrease in yield (experiments 6 and 7, 14 and 15; 25 and 26). (*3*) The lds of $C_6H_5HgCX_3$ were essentially independent of which halogen (Cl or Br) was sent in the starting phenylmercuric halide, but the purity of the latter was quite portant. Available commercial products, which melted over a wide range several grees below the correct m.p., gave only poor yields of product, while use of pure enylmercuric chloride or bromide, prepared by phenylation of mercuric chloride bromide with tetraphenyltin or diphenylmercury, resulted in good product yields. Control of temperature is important; an increase from the usual 4–10° to 25–35° external cooling) resulted in a considerable decrease in $C_6H_5HgCX_3$ yield.

Schweizer and O'Neill have described an improved method for the preparation $C_6H_5HgCCl_3$ by the reaction of phenylmercuric bromide with ethyl trichloroacetate d sodium methoxide in benzene solution[8]. The method of Razuvaev *et al.*[5] based on lium trichloroacetate, which Logan[6] reported gave $C_6H_5HgCCl_3$ in 77 % yield, also rits consideration as an alternative to the chloroform/potassium butoxide route. wever, neither of these procedures is readily applicable to the preparation of the re useful bromine-containing mercurials, since the required $CBrCl_2COOH$,

BLE 2

NYL(TRIHALOMETHYL)MERCURY COMPOUNDS

pound	M.p. (°C)	IR (CS_2) (cm^{-1})	Analysis: Calcd. (Found), %				
			C	H	Cl	Br	Hg
$_5HgCCl_3$	116.5–118[a]	c	21.22 (21.30)	1.27 (1.51)	26.85 (26.71)		50.64 (50.91)
$_5HgCCl_2Br$	110–111 (dec.)	d	19.08 (19.03)	1.14 (1.18)	16.09 (15.96)	18.14 (17.90)	45.53 (45.82)
$_5HgCClBr_2$	110–112 (dec.)	e			7.30 (7.07)	32.95 (32.71)	41.36 (41.36)
$_5HgCBr_3$	119–120 (dec.)[b]	f	15.90 (15.96)	0.95 (0.93)		45.28 (45.20)	37.88 (38.05)

[a] M.p. in ref. 4: 114–116°. [b] M.p. in ref. 4: 98° (dec.). [c] 3020 (w), 1020 (w), 996 (w), 726 (s), (s), 690 (s). [d] 3050 (w), 1023 (w), 998 (w), 765 (w), 726 (s), 700 (m), 691 (m), 635 (w), 590 (w). 2 (w), 1021 (w), 998 (w), 750 (w), 725 (s), 690 (m), 661 (m). [f] 3075 (m), 3060 (m), 1076 (vw), (vw), 1023 (m), 997 (m), 903 (w), 726 (s), 694 (s), 612 (s).

$CBr_2ClCOOH$ and CBr_3COOH or their esters either are not commercially available or are quite expensive. Also, they are more difficult to prepare than the haloforms.

The properties and analyses of the phenyl(trihalomethyl)mercurials are summarized in Table 2. These $C_6H_5HgCX_3$ compounds readily formed dense, highly reflective needle-like crystals (from hexane/chloroform), with the exception of $C_6H_5HgCBr_3$, which normally crystallized as short prisms from this solvent system. All of these compounds were very soluble in benzene, chloroform, carbon tetrachloride, methylene chloride and ether, but were only slightly soluble in aliphatic hydrocarbons and ethanol. All, especially those containing bromine, were found to be thermally unstable, and they slowly decomposed with the formation of phenylmercuric halide on standing as solids or in solution at 25°. Consequently they were stored at −5°, at which temperature they could be kept without deterioration. All of the $C_6H_5HgCX_3$ compounds are easily distinguishable from the light, flaky phenylmercuric halides by their appearance and solubility and by thin-layer chromatography. For qualitative and semi-quantitative analytical purposes it was found convenient to cleave the $C_6H_5HgCX_3$ compounds with an excess of bromine in carbon tetrachloride at 25°; C_6H_5Br and $BrCX_3$ then were determined by gas chromatography (g.l.c.).

THE MECHANISM OF THE PHENYLMERCURIC HALIDE/HALOFORM/POTASSIUM *tert*-BUTOXIDE REACTION

Reutov and Lovtsova[4] expressed the opinion that the formation of aryl(trihalomethyl)mercurials by their procedure involves the insertion of a dihalocarbene into the mercury–halogen linkage. It must be noted that such a reaction, $:CX_2$ insertion

$$C_6H_5HgY + :CX_2 \longrightarrow C_6H_5HgCX_2Y \text{ (X and Y = halogen)}$$

into a metal–halogen bond, was without precedent and that no experimental evidence was offered by the authors in support of their postulated mechanism. The basis for their favoring a carbene insertion mechanism appeared to be the fact that the haloform/potassium *tert*-butoxide reagent system was that used by Doering and Hoffmann[9] in their preparation of *gem*-dihalocyclopropanes by dihalocarbene addition to olefins. The Russian authors apparently neglected to consider that the formation of dihalocarbenes by the reaction of haloform and base proceeds via intermediate formation of trihalomethide ion[10]. The lifetime of such carbanion intermediates (relative to their decomposition to carbenes) is sufficiently long to allow other reactions, such as addition to ketones and aldehydes[11], to be observed. Our experience[12] with the ease of nucleophilic substitution at mercury, *e.g.*, the reaction

$$C_6H_5HgCl + NaI \longrightarrow C_6H_5HgI + NaCl$$

suggested to us that the phenylmercuric halide/haloform/potassium *tert*-butoxide reaction might lead to $C_6H_5HgCX_3$ by nucleophilic displacement of halogen from mercury by trihalomethide ion,

$$C_6H_5HgY + CX_3^- \longrightarrow C_6H_5HgCX_3 + Y^-$$

rather than by a carbene insertion mechanism, and we carried out the experiments described below in order to answer this question.

If a carbene insertion into the Hg–X linkage actually were taking place, then one would expect, in the absence of complicating halogen exchange reactions, that reaction of phenylmercuric *bromide* with the $CHCl_3$/*tert*-C_4H_9OK system to give $C_6H_5HgCCl_2Br$. When this reaction was carried out using the Reutov–Lovtsova procedure *only* $C_6H_5HgCCl_3$ (74 %) was formed. Identification of the product was made by m.p. and mixed m.p. with an authentic sample. Unreacted phenylmercuric bromide was recovered in 26 % yield. When a small sample of the product was treated with excess bromine, the only volatile products formed were bromotrichloromethane and bromobenzene. No dibromodichloromethane was detected by g.l.c. However, phenyl(trichloromethyl)mercury would have been formed in this reaction by a carbene insertion mechanism if the insertion had been preceded by a rapid $C_6H_5HgBr + Cl^-$ exchange, the chloride ion coming from decomposition of CCl_3^- to CCl_2. In a separate experiment, in which C_6H_5HgBr was treated with potassium chloride in a solvent mixture consisting of *tert*-butyl alcohol, chloroform and benzene for 4 h with high-speed stirring, no halide exchange producing C_6H_5HgCl was observed. The absence of detectable quantities of phenylmercuric chloride in this experiment still left open the possibility that an extremely small equilibrium yield of C_6H_5HgCl could have been present. This could have accounted for the observed formation of $C_6H_5HgCCl_3$ by a CCl_2 insertion mechanism. However, this alternative would have required the extremely unlikely possibility that CCl_2 insertion into Hg–Cl was highly preferred over insertion into Hg–Br.

The possibility that the initial CCl_2 insertion product, $C_6H_5HgCCl_2Br$, might have exchanged with chloride ion to give the observed $C_6H_5HgCCl_3$ also was investigated. No such exchange was found to occur.

These results speak strongly against a dihalocarbene insertion mechanism and for a mechanism involving nucleophilic attack by CX_3^- on mercury.

The intermediacy of the trichloromethyl anion introduced other complications. When phenyl(bromodichloromethyl)mercury was treated with an excess of chloroform and potassium *tert*-butoxide in the absence of another reactive substrate such as C_6H_5HgX, partial substitution of CCl_2Br by CCl_3 occurred and a 5:1 mixture of $C_6H_5HgCCl_3$ and $C_6H_5HgCCl_2Br$ (determined by bromine cleavage) was obtained.

$$C_6H_5HgCCl_2Br + CCl_3^- \longrightarrow C_6H_5HgCCl_3 + CCl_2Br^-$$

While such an exchange might account for the observed formation of $C_6H_5HgCCl_3$ from the reaction of C_6H_5HgBr and $CHCl_3$/*tert*-C_4H_9OK via the carbene mechanism (*i.e.*, initial formation of $C_6H_5HgCCl_2Br$, followed by its reaction with CCl_3^-), we do not believe this to be the case. It is to be noted that in the experiment described above ca. 17 % of the $C_6H_5HgCCl_2Br$ survived the reaction conditions. In contrast, as already stated, in the $CHCl_3$/*tert*-C_4H_9OK/C_6H_5HgBr experiment *only* $C_6H_5HgCCl_3$ was obtained. If a carbene mechanism were operative, then at least some $C_6H_5HgCCl_2Br$ should have been present.

When phenylmercuric chloride was treated with bromodichloromethane and potassium *tert*-butoxide, the product was that expected from the displacement mechanism, $C_6H_5HgCCl_2Br$. However, the interpretation of this result is complicated by the fact that exchange between bromide ion (from the haloform/base reagent mixture, which is used in twofold excess) and phenylmercuric chloride does occur.

In summary, the evidence which has accumulated in this study contradicts the carbene insertion mechanism of Reutov and Lovtsova and supports a mechanism in which the trihalomethide ion attacks at the mercury atom of C_6H_5HgX, displacing X^- and forming the phenyl(trihalomethyl)mercurial.

Subsequent papers in this series will deal with the reactions of phenyl(trihalomethyl)mercury compounds.

EXPERIMENTAL

General comments

All phenyl(trihalomethyl)mercurial syntheses were carried out under an atmosphere of prepurified nitrogen. Melting points are corrected. Elemental analyses were performed by Dr. S. M. NAGY (M.I.T. Microchemical Laboratory) and by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Potassium *tert*-butoxide was prepared by the procedure of Speziale and Ratts[9]. The preparation of the phenylmercuric halides by the tetraphenyltin route is described below.

Preparation of phenylmercuric bromide from tetraphenyltin

To a boiling solution of 156.5 g (0.367 mole) of tetraphenyltin (M & T Chemicals, Inc.) in 1800 ml of benzene that was stirred in a 3-l beaker on a magnetic stirrer-hotplate, was added a hot solution of 360.4 g (1.0 mole) of mercuric bromide in 500 ml of tetrahydrofuran over a period of 2 minutes, during which time rapid precipitation of a white flaky solid occurred. The mixture was stirred and heated for 5 minutes, then stirred without heating for 3 h. The mixture, the volume of which had been reduced to *ca.* 1200 ml, was stored at 5° overnight and filtered. The residue was washed with two 100 ml portions of benzene and dried *in vacuo* at 55° for 4 h. This afforded 247 g (69 %) of flaky, white phenylmercuric bromide, m.p. 283–285°. A second crop of 12 g (3 %), m.p. 283–286° was obtained by evaporation of the filtrate to 750 ml and cooling to 5° overnight. The phenylmercuric bromide was used without further purification in the following reactions.

Preparation of phenylmercuric chloride from tetraphenyltin

Phenylmercuric chloride, from 156 g (0.367 mole) of tetraphenyltin in 1800 ml of benzene and 271.5 g (1.0 mole) of mercuric chloride in 300 ml of tetrahydrofuran, was prepared as described in the previous experiment. The first crop afforded 310 g (99 %) of a flaky, white solid, m.p. 256–258°, after drying at 55° *in vacuo*. The phenylmercuric chloride was used in subsequent experiments without further purification.

Preparation of phenyl(bromodichloromethyl)mercury

Into a dry 2-l Morton flask, equipped with a high-speed stirrer, under an atmosphere of prepurified nitrogen were placed 89.4 g (0.25 mole) of phenylmercuric bromide, 163.8 g (1.0 mole) of freshly distilled bromodichloromethane (Dow Chemical Co.) and 1200 ml of reagent-grade benzene (freshly dried by molecular sieves or by distillation from calcium hydride). Solid potassium *tert*-butoxide[from 19.5 g (0.5 g-atom) of potassium] was added with vigorous stirring and cooling (ice bath), through a 1 inch diameter rubber connecting tube, over a 35 minute period. The reaction

ixture was stirred for an additional hour at 0° and then poured into 1.5-l of distilled ater.

After having stood for 1.5 h, the mixture was filtered and the residue washed ith 60 ml of warm benzene. Subsequent drying of the washed residue *in vacuo* forded 12.3 g (14 % recovery) of phenylmercuric bromide, m.p. 283–285°. The enzene phase of the filtrate was extracted with two 250-ml portions of distilled ater, while the aqueous phase was extracted with two 150-ml portions of benzene. he benzene washings and extracts, combined with the benzene phase, were dried ($MgSO_4$) for 4 h and then evaporated at 25°/30 mm. There remained 88.5 g (81 % rude yield) of a cream-white solid of m.p. 80–95° (resolidified after having partially elted). Recrystallization of the latter from a mixture of 600 ml of *n*-hexane and 150 l of chloroform at 50° yielded 64.7 g (59 %) of phenyl(bromodichloromethyl)-ercury, m.p. 108–110° (with instantaneous decomposition after having melted). igorous stirring of the crude product/solvent mixture during recrystallization was ecessary to effect rapid solution of the solid and to prevent local overheating. The roduct was collected as white needle-like crystals in three crops: (*a*) after filtration 50°) from a small amount of flaky, white solid and cooling to room temperature; *b*) after storage of the filtrate from (*a*) for 6 h at 5°; (*c*) after rotary evaporation of the iltrate from (*b*) to *ca.* 300 ml at reduced pressure, followed by refrigeration at —10° vernight.

An analytical sample obtained in another preparation after recrystallization rom *n*-hexane and *n*-hexane/chloroform mixtures gave m.p. 110–111° (dec.)*.

A similar experiment on the same scale using phenylmercuric chloride, solid otassium *tert*-butoxide and bromodichloromethane under the conditions described bove resulted in a crude yield of $C_6H_5HgCCl_2Br$ of 81 %.

Preparation of phenyl(tribromomethyl)mercury

The addition of solid potassium *tert*-butoxide [from 19.5 g (0.5 g-atom) of potassium] to a mixture of 89.4 g (0.25 mole) of phenylmercuric bromide and 252.7 g (1.0 mole) of freshly distilled bromoform in 1 liter of benzene was carried out as described in the previous experiment for phenyl(bromodichloromethyl)mercury. The light yellow reaction mixture was poured into 1.5 l of distilled water, and after standing for 7 h at 25°, filtered from 2 g of an off-white solid. The benzene(lower)** phase of the filtrate was extracted with 500 ml of distilled water, while the aqueous phase was extracted with two 150-ml portions of benzene. The combined benzene phase and extracts were dried ($MgSO_4$) for 4 h and rotary evaporated at 25°/20 mm to *ca.* 250 ml. Filtration gave 59.5 g of a white, crystalline solid, m.p. 110–113° (decomposed instantaneously after having partially melted). The yellow filtrate was similarly concentrated to *ca.* 50 ml, and the slow addition of 300 ml of *n*-hexane caused precipitation of a white, very finely crystalline solid, 52 g, m.p. 114–116° (decomposed instantaneously after having partially melted). The filtrate from the latter was cooled to 0° overnight and on filtration afforded 8 g of a cream-colored solid, m.p. 110–111° (decomposed on melting). The total crude yield was 119.5 g (90 %).

* In order to obtain an accurate m.p. of the thermally unstable bromine-containing phenyl-(trihalomethyl)mercurials the sample was placed in the oil bath at 85° and the m.p. observed with a heating rate of *ca.* 10°/minute.

** When a low yield of the phenyl(tribromomethyl)mercurial was obtained the benzene phase was found above the aqueous layer.

Recrystallization of the crude product from a pentane/methylene chloride mixture failed to alter the melting point significantly.

An analytical sample obtained in another preparation after four recrystallizations from pentane/methylene chloride gave material of m.p. 119–120° (dec.); lit.[4] m.p. 98°.

Reaction of phenyl(bromodichloromethyl)mercury with excess bromine

Into a dry 50-ml three-necked flask, equipped with a magnetic stirrer, reflux condenser and 60-ml addition funnel were placed 2.20 g (5.0 mmoles) of phenyl(bromodichloromethyl)mercury and 15 ml of reagent grade benzene (freshly distilled from calcium hydride) under an atmosphere of dry argon. After stirring the mixture briefly to dissolve the solid mercurial, 11 ml of a 1 *M* solution (11.0 mmoles) of bromine in carbon tetrachloride was added dropwise with stirring over a 45 minute interval. During this time the bromine color was rapidly discharged and a white solid precipitated. The mixture was filtered from 1.6 g of a white powder, m.p. 236–238° (with slight decomposition) into a 50-ml separatory funnel and the filtrate extracted with 20 ml of a 5 % aqueous sodium thiosulfate solution and then with 25 ml of distilled water. The aqueous phase was extracted with 10 ml of benzene and the combined organic phases dried ($MgSO_4$) and trap-to-trap distilled at 30°/0.05 mm. Quantitative gas–liquid chromatographic (g.l.c.) analysis of the distillate using a General Electric Co. SE 30 (25 % on Chromosorb W) column at 160° and *n*-butyrophenone as an internal standard indicated that dibromodichloromethane and bromobenzene had formed in 87.6 and 91.4 % yield respectively. The volatile products were identified by their g.l.c. retention times and by their infrared spectra. Sublimation of the solid at 120°/0.01 mm afforded 1.6 g (89 %) of white mercuric bromide, m.p. 232–237°. A mixed m.p. with an authentic sample was not depressed.

Analysis of a synthetic mixture of phenyl(trichloromethyl)mercury and phenyl(bromodichloromethyl)mercury

The addition of 11 ml of a 1 *M* solution (11 mmoles) of bromine in carbon tetrachloride to a stirred solution of 1.18 g (2.98 mmoles) of phenyl(trichloromethyl)mercury and 0.89 g (2.02 mmoles) of phenyl(bromodichloromethyl)mercury in 20 ml of anhydrous benzene was carried out at 25° over a 30 minute interval as described above. The orange-colored mixture was stirred for an additional hour at 25°, filtered from 1.68 g (94%) of crude mercuric bromide, m.p. 235–240° (to a brown liquid) and the filtrate was extracted and distilled as described previously for phenyl(bromodichloromethyl)mercury. Quantitative gas–liquid chromatographic analysis of the distillate, using *p*-chlorotoluene as an internal standard, indicated that 2.8 mmoles (95 %) of bromotrichloromethane, 1.78 mmoles (88 %) of dibromodichloromethane and 4.44 mmoles (89 %) of bromobenzene had formed. Thus the molar ratio of $BrCCl_3$ to Br_2CCl_2 was 1.60 compared with 1.48 for the molar ratio of $C_6H_5HgCCl_3$ to $C_6H_5HgCCl_2Br$.

Preparation of phenyl(trichloromethyl)mercury from phenylmercuric bromide

The addition of solid potassium *tert*-butoxide[from 19.5 g (0.5 g-atom) of potassium] to a mixture of 89.4 g (0.25 mole) of phenylmercuric bromide and 119.4 g (1.0 mole) of freshly distilled chloroform in 1200 ml of anhydrous benzene was carried

ut as described above for the preparation of phenyl(bromodichloromethyl)mercury. fter having been stirred for an additional hour at 0°, the grey-colored reaction mixre was poured into 1.5 l of distilled water and permitted to stand overnight. Workup llowing that described previously afforded 23.7 g (26 %) of crude phenylmercuric romide, m.p. 282–286° and 73 g (74 %) of crude phenyl(trichloromethyl)mercury, .p. 90–100°. The former was extracted (Soxhlet) with benzene over a 5 day period nd a yield of 22 g (24.6 %) of pure white phenylmercuric bromide, m.p. 284–286°, as obtained on filtration of the extracts at 25°. The latter product was recrystallized om a chloroform/*n*-hexane mixture and a total of 65 g (66 %) of phenyl(trichloroethyl)mercury, m.p. 115–117°, was obtained. A mixed m.p. with an authentic mple was not depressed.

The addition of 11 ml of a 1 *M* solution (11 mmoles) of bromine in carbon tetrahloride to a stirred solution of 1.98 g (5.0 mmoles) of phenyl(trichloromethyl)mercury btained above in 20 ml of anhydrous benzene was carried out at 25° over a 30 minute nterval as described above for phenyl(bromodichloromethyl)mercury. The resulting ixture of white solid in an orange solution was stirred for an additional 30 minutes nd filtered directly into a 50-ml separatory funnel from 1.65 g (91.5 %) of crude ercuric bromide, m.p. 235–240° (to a dark brown liquid). The orange filtrate was xtracted with 20 ml of distilled water to which was added dropwise enough 20 % queous sodium thiosulfate solution to decolorize the organic phase. The aqueous hase was extracted with 5 ml of benzene and the combined organic phases were ried ($MgSO_4$) and trap-to-trap distilled at 40°/0.05 mm. Gas-chromatographic nalysis of the clear distillate using an SE 30 column at 100° and *p*-chlorotoluene as n internal standard showed that bromotrichloromethane and bromobenzene had ormed in 90 and 86 % yield respectively. No dibromodichloromethane was detected y g.l.c. The volatile products were identified by comparison of their g.l.c. retention imes and infrared spectra (of collected samples) with those of authentic samples.

ttempted reaction of phenylmercuric bromide with potassium chloride

Into a 500-ml Morton flask were placed 7.14 g (0.02 mole) of phenylmercuric romide, 5.0 g (0.067 mole) of finely ground potassium chloride, 7.15 g (0.06 mole) of hloroform, 20 ml of *tert*-butanol and 100 ml of reagent-grade benzene. After the eaction mixture had been stirred at high speed for 4 h at 0°, 100 ml of distilled water as added with slow stirring, and the mixture filtered, leaving a white powder-like esidue of phenylmercuric bromide, 7.05 g (99 % recovery), m.p. 283–285°. Analysis f the residue by thin-layer chromatography showed that it consisted of only phenylercuric bromide; no phenylmercuric chloride was detected. The benzene phase of the iltrate was dried ($MgSO_4$) and evaporated at reduced pressure, leaving a very small mount of flaky, white phenylmercuric bromide, m.p. 283–285°. In a similar experiment where 6.26 g (0.02 mole) of phenylmercuric chloride was stirred at high speed with 7.2 g (0.06 mole) of potassium bromide a mixture of phenylmercuric bromide and henylmercuric chloride, m.p. 262–270°, was obtained, as analyzed by thin-layer hromatography.

Attempted reaction of phenyl(bromodichloromethyl)mercury with potassium chloride

Into a 200-ml Morton flask that was equipped with a high-speed stirrer were placed 8.80 g (20.0 mmoles) of phenyl(bromodichloromethyl)mercury, 2.98 g (40.0

mmoles) of finely powdered potassium chloride, 9.55 g (80.0 mmoles) of reagent-grade chloroform, 5.93 g (80.0 mmoles) of *tert*-butyl alcohol and 100 ml of anhydrous benzene. The mixture was stirred briefly at low speed to dissolve the mercurial, then cooled to 0° and stirred at high speed for 1.5 h. The mixture which contained a small amount of flaky, white solid was poured into 250 ml of distilled water and the aqueous phase washed with 25 ml of benzene. The combined organic phases were dried ($MgSO_4$) and rotary evaporated to dryness at reduced pressure. There remained 8.9 g of a white, finely crystalline solid, m.p. 95–100° (resolidified after having partially melted). A 2.0-g sample of the latter was treated with an excess of bromine as described in the previous experiment and gas chromatographic analysis of the volatile products showed that 4.00 mmoles of bromobenzene, 3.78 mmoles of dibromodichloromethane and 0.165 mmoles of bromotrichloromethane* had formed. These values when recalculated on the basis of the entire sample, indicated that it was at least 95 % phenyl(bromodichloromethyl)mercury, and that very little, if any, halogen exchange had occurred.

Reaction of phenyl(bromodichloromethyl)mercury with chloroform and potassium tert-butoxide

A dry 500-ml Morton flask that was equipped with a high-speed stirrer and cooling bath was charged with 22.0 g (0.050 mole) of phenyl(bromodichloromethyl)mercury, 23.8 g (0.20 mole) of chloroform (reagent grade, redistilled) and 250 ml of anhydrous benzene under an atmosphere of nitrogen. Then 0.10 mole of solid potassium *tert*-butoxide [from 3.9 g (0.10 g-atom) of potassium] was added with high-speed stirring and cooling (ice bath) over a 30 minute interval. Stirring was continued for 1 h at 0° and then the mixture was poured into 1 liter of distilled water and filtered from 1 g of phenylmercuric bromide, m.p. 282–284°. The organic phase of the filtrate was extracted with 100 ml of water and the aqueous phase was extracted with 100 ml of benzene. The combined organic phases were dried ($MgSO_4$) and rotary evaporated to dryness at 25°/30 mm. There remained 17.2 g of a cream-colored crystalline solid, m.p. 113–115° (slowly resolidified after having melted). A small sample of the latter was analyzed for bromine and was found to contain 3.32 % Br, from which a $C_6H_5HgCCl_3/C_6H_5HgCCl_2Br$ molar ratio of 4.96 was calculated.

A 2.0 g sample of the solid product was treated with an excess of bromine as described above. Gas-chromatographic analysis of the volatile products showed that 4.45 mmoles of bromobenzene, 3.88 mmoles of bromotrichloromethane and 0.64 mmoles of dibromodichloromethane had formed.

The molar ratio of tetrahalomethanes was 3.88/0.640 = 6.0. As shown previously by the analysis of a synthetic mixture of $C_6H_5HgCCl_3$ and $C_6H_5HgCCl_2Br$ the molar ratio of the respective tetrahalomethanes was somewhat higher than that of the mercurials. This implies that the molar ratio of $C_6H_5HgCCl_3$ to $C_6H_5HgCCl_2Br$ in the product was 5.0–5.5 to 1.

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* Previous experience has shown that the $C_6H_5HgCCl_2Br$ was contaminated with 1–3 % $C_6H_5HgCCl_3$ due to a $CHCl_3$ impurity in the starting $CHBrCl_2$.

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Detailed procedures for the preparation of $C_6H_5HgCCl_3$, $C_6H_5HgCCl_2Br$, $H_5HgCClBr_2$ and $C_6H_5HgCBr_3$ by the Reutov–Lovtsova method are given. Evidence presented which indicates that the reaction of phenylmercuric halide, haloform and tassium *tert*-butoxide forms $C_6H_5HgCX_3$ by way of nucleophilic displacement of lide ions from mercury by the trihalomethyl anion.

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