MERCURY

ANNUAL SURVEY COVERING THE YEAR 1973

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CONTENTS

1. REVIEWS

Reviews covering the following aspects of organomercury chemistry have appeared:

- The stability of organomercury complexes with anionic and neutral ligands (1)
- The stereochemistry and mechanism of the oxymercuration of cyclopropanes (2)
- The autoxidation of organo-Group IV-mercury compounds (3).

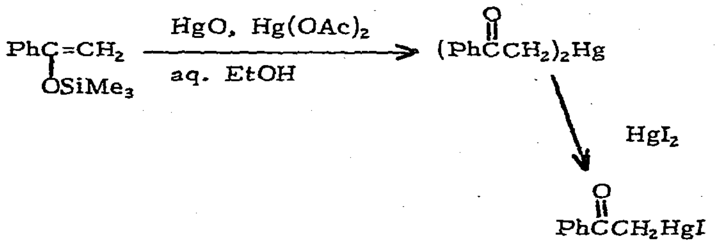
2. PREPARATION OF ORGANOMERCURY COMPOUNDS

The reactions of organic compounds of other metals with mercuric halides or carboxylates have found useful application in organomercurial synthesis in the past. In recent years the now readily accessible organoboranes have served well in this application. The use of gem-diboronalkanes has been reported by Larock as a good route to gem-dimercurialkanes (4):

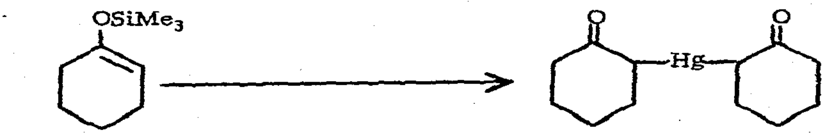
$$RC\equiv CH \xrightarrow{2\ BH_3,\ THF} RCH_2CH(BH_2)_2 \xrightarrow{MeOH} RCH_2CH[B(OMe)_2]_2 \xrightarrow{HgCl_2/NaOH} RCH_2CH(HgCl)_2 \quad (58\text{-}77\%)$$

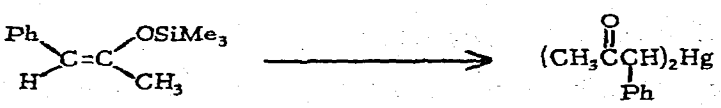
Examples in which 1-pentyne, 1-hexyne, 1-decyne, 3,3-dimethyl-1-butyne and phenylacetylene were used are described. The resulting 1,1-bis-(chloromercuri)alkanes were soluble only in the more polar organic solvents such as DMF, DMSO and HMPT.

Silyl enolates reacted with mercuric oxide and a catalytic amount of mercuric acetate in aqueous ethanol to give α-mercuriketones (5):

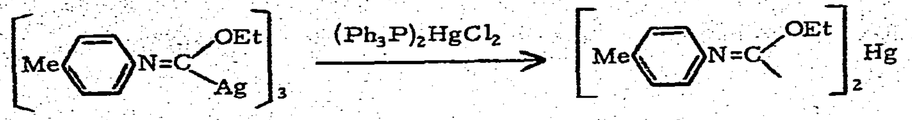


$$PhC(OSiMe_3)=CH_2 \xrightarrow[aq.\ EtOH]{HgO,\ Hg(OAc)_2} (PhCOCH_2)_2Hg \xrightarrow{HgI_2} PhCOCH_2HgI$$

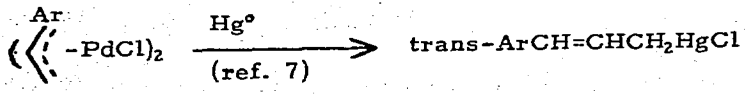




A silver derivative has been used to prepare a novel mercurial (6):



The cleavage of other transition metal-carbon bonds by mercury(II) salts or by elemental mercury has been reported to yield organomercurials, but most of these reactions are not of synthetic utility, e.g.:

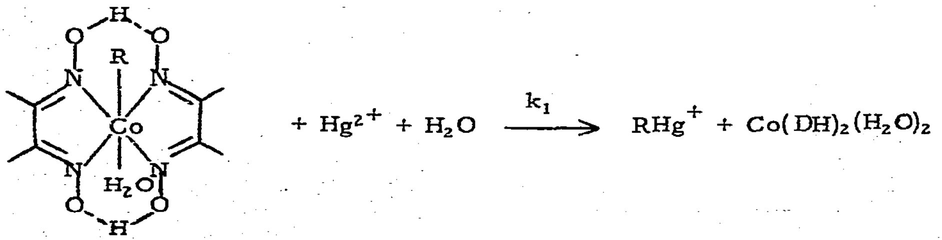


(Ar = fluoro- and chlorophenyl)

$$RC(B_{10}H_{10})CFe(CO)_2C_5H_5 \xrightarrow[\text{(ref. 8)}]{HgCl_2} RC(B_{10}H_{10})CHgCl$$

(o- and m-carboranyl compounds)

The alkylation of Hg(II) species by alkylcobalt compounds has received further attention. This reaction is of some importance since it appears to provide a route to the formation of $CH_3Hg(II)$ compounds in mercury-polluted waters. Kinetic studies have been reported in two papers. For the reaction shown below, the second order rate constants shown in



$RCo(DH)_2(H_2O)$

Table 1 were obtained as R was varied (9). Electrophilic attack by mercuric ion was indicated by the k_1 values for the arylcobaloximes which gave a linear correlation with Hammett σ constants ($\rho = -6.3$). The cleavage of trans-4-tert-butylcyclohexylcobaloxime-pyridine complex with

TABLE 1. Kinetic Data for the Reactions of $RCo(DH)_2(H_2O)$ with Hg^{2+} at 25° ($\mu = 1.0$)

R	k_1, M^{-1} sec^{-1}
CH_3	54
C_2H_5	1.2×10^{-1}
n-C_3H_7	9.4×10^{-2}
$C_6H_5CH_2$	7.5×10^{-2}
p-$NO_2C_6H_4CH_2$	6.5×10^{-3}
p-$FC_6H_4CH_2$	2.8×10^{-2}
p-$CH_3C_6H_4CH_2$	9.0×10^{-2}
p-$CH_3OC_6H_4CH_2$	11.3×10^{-2}
C_6H_5	4.0×10^{2}
p-FC_6H_4	2.5×10^{2}
p-$CH_3C_6H_4$	4.5×10^{3}
p-$CH_3OC_6H_4$	3.0×10^{4}

mercuric acetate gave only the cis-4-tert-butylcyclohexylmercurial, and a similar experiment with cis-2-hydroxycyclohexylcobaloxime confirmed this result (10). Thus these S_E2 cleavages appear to proceed with inversion at the carbon atom. Similar cleavage of the carbon-cobalt bond by mercuric ion in alkylcobaloximes has been the subject of extensive kinetic studies (11).

Catalyzed (UV or benzoyl peroxide) decarboxylation of mercury(II) carboxylates has been used in the synthesis of some new organomercurials (12):

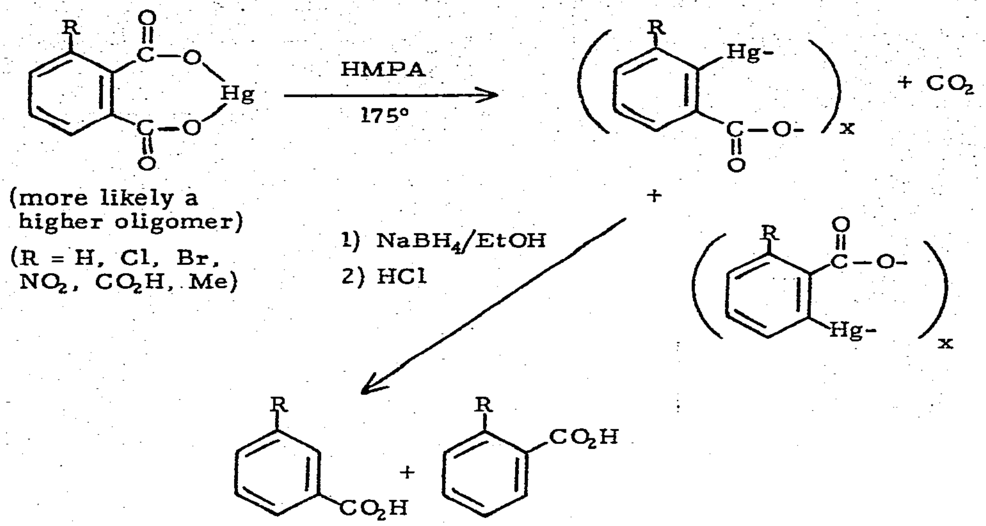
$$(RCH_2CH_2CO_2)_2Hg \longrightarrow \xrightarrow{X^-} RCH_2CH_2HgX$$

(R = Ph, $PhCH_2$, $Cl(CH_2)_3$)

The compounds where R = EtS and $PhCONH(CH_2)_3$, and also Hg(II) nicotinate and isonicotinate, were unreactive under these conditions, while Hg(II) levulinate gave mainly mercury oxides.

The conversion of Hg(II) salts of unsymmetrical 1,2-dicarboxylic acids to monocarboxylic acids (Pesci reaction) has been studied by

Newman and Vander Zwan (13) and an improved procedure was developed:



(more likely a higher oligomer)
(R = H, Cl, Br, NO_2, CO_2H, Me)

The organomercury intermediates were not isolated.

The decarboxylation of mercury(II) trifluoroacetates, which has been shown previously to be effected only with difficulty at higher (300°) temperatures, was shown to proceed much more readily in the presence of fused potassium carbonate at 180-200° (14):

$$Hg(O_2CCF_3)_2 \xrightarrow{-2CO_2} Hg(CF_3)_2 \qquad (93\%)$$

$$PhHgO_2CCF_3 \xrightarrow{-CO_2} PhHgCF_3 \qquad (70\%)$$

Further examples of the extrusion of SO_2 and SO_3 from mercury (II) sulfinates and sulfonates, to give organomercurials, have been reported.

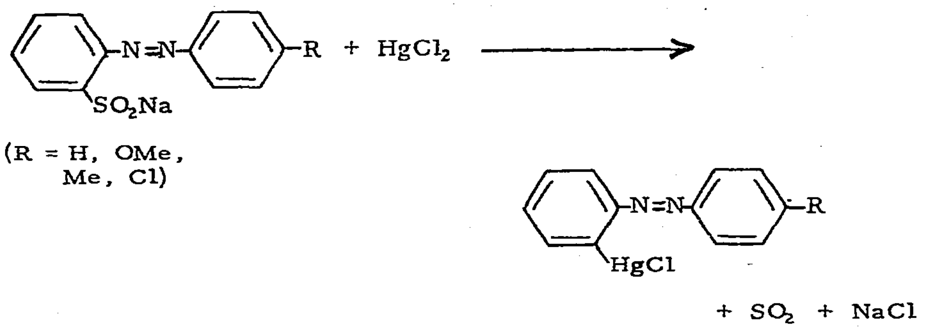
$$HgX_2 + C_6F_5SO_2^-Li^+ \xrightarrow[\text{(ref. 15)}]{H_2O} C_6H_5HgX + SO_2 + LiX$$

(X = Cl, Br, OAc, O_2SPh)

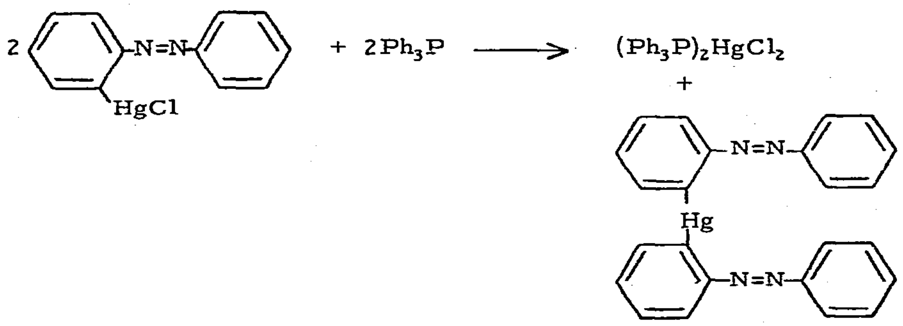
$$HgX_2 + 2\,C_6F_5SO_2^-Li^+ \xrightarrow[\text{(ref. 15)}]{t\text{-}BuOH/H_2O} (C_6F_5)_2Hg + 2SO_2 + 2LiX$$

These reactions proceeded rapidly when the reactants were mixed at room temperature. Very clever use has been made of this chemistry in the analysis of low levels of mercury in waters, in urine, etc., by Mushak et al. (16). Treatment of the aqueous solution containing mercuric ion with $C_6F_5SO_2Li$ and subsequently with sodium chloride gave C_6F_5HgCl whose concentration then was determined by gas chromatography.

Another example of SO_2 extrusion was provided by Cross and Tennent (17):



The symmetrical mercurial (R = H) was prepared by treatment of the chloromercuri derivative with triphenylphosphine:

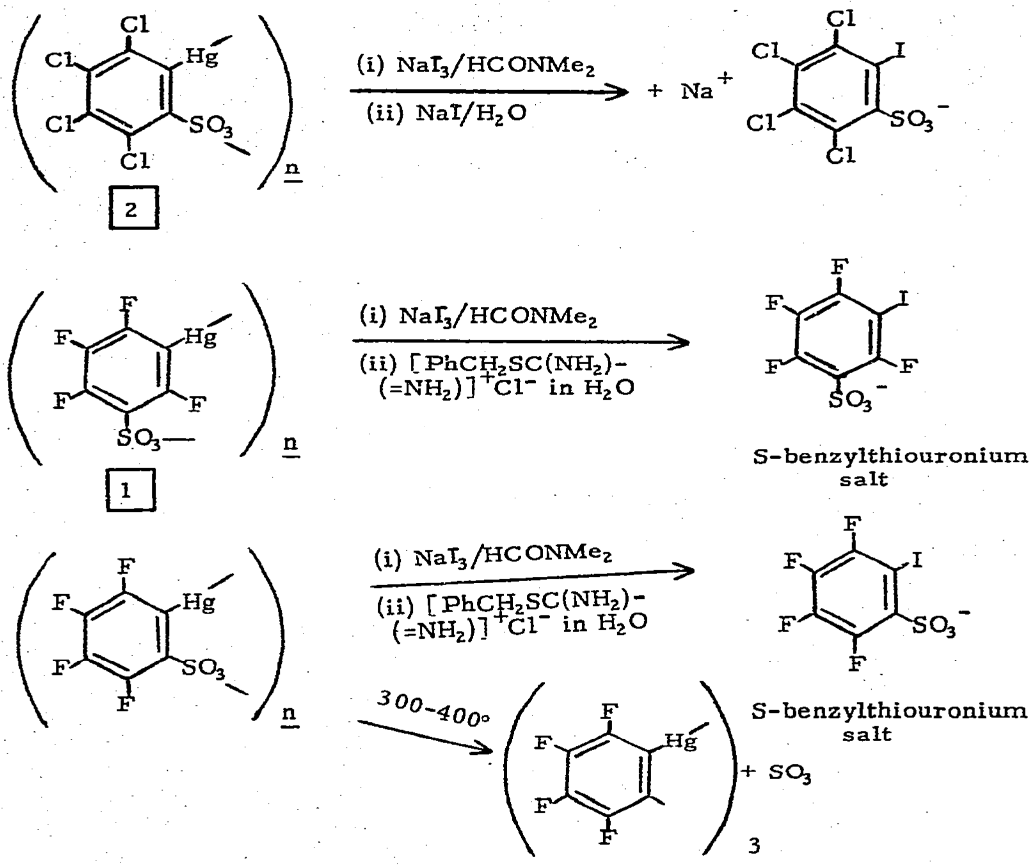


Sulfur trioxide extrusion could be effected from mercury (II) arenesulfonate dihydrates (18) or pyridinates (19):

$$Hg(O_3SAr)_2 \cdot 2H_2O \xrightarrow{130-240^\circ} Ar_2Hg + SO_3 + 2H_2O$$

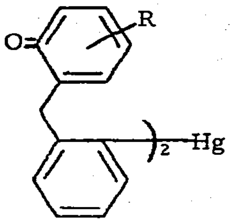
($Ar = C_6Cl_5$, 2,3,5,6-Cl_4C_6H, 2,3,4,6-Cl_4C_6H, C_6F_5, 2,3,5,6-F_4C_6H)

Milder reaction conditions resulted in formation of $ArHgO_3SAr$ when Ar = C_6Cl_5 and 2,3,5,6-Cl_4C_6H. In some cases, e.g., Ar = 2,3,4,5-Cl_4C_6H, 2,3,4,5-F_4C_6H and 2,3,4,6-F_5C_6H, polymeric mercuritetrahalobenzenesulfonates were formed in an aromatic mercuration process. These products were characterized by the chemical conversions shown below.

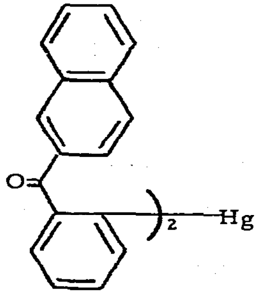


In these reactions with the dihydrates considerable competition from hydrolysis and hydrolytic desulfonation was encountered. Thermolysis of the dipyridinates, $Hg(O_3SAr)_2 \cdot 2C_5H_5N$, at 130-240° was quite satisfactory in the cases where Ar = C_6Cl_5, p-HC_6Cl_4, m-HC_6Cl_4, C_6F_5, p-HC_6F_4 and m-HC_6F_4, but with Ar = o-HC_6F_4 and o-HC_6Cl_4 the mercuration products $\boxed{1}$ and $\boxed{2}$ again were the sole organomercury products. Such specific ortho-metalation processes are of special interest and this effect in organomercury chemistry merits further investigation.

Functional diarylmercurials of types $\boxed{3}$ and $\boxed{4}$ have been prepared in 35-65% yield by the electrolysis (mercury cathode) of the diazonium salts derived from 2-amino-R-benzophenones (R = H, p-Me, p-MeO, m-O_2N) and 2-amino-β-benzoylnaphthalene (20).



$\boxed{3}$



$\boxed{4}$

UV irradiation at 20° of aqueous mercuric chloride in the presence of organic acids ($MeCO_2H$, $EtCO_2H$) or alcohols (MeOH, EtOH) gave methyl- and ethylmercury derivatives (by TLC, GLC) in low to trace yields (21) in reactions that may be of interest to the environmental chemist but not to the synthetic chemist.

3. USE OF ORGANOMERCURIALS IN SYNTHESIS

A. Organometallic Synthesis

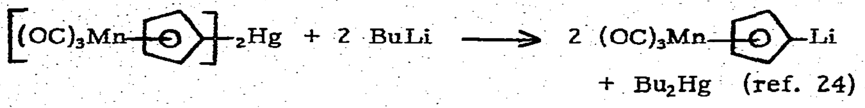
Further examples of the application in synthesis of the metal displacement reaction involving organomercurials have been recorded:

$$Ar_2Hg + Ca \xrightarrow{THF} Ar_2Ca + Hg \qquad \text{(ref. 22)}$$

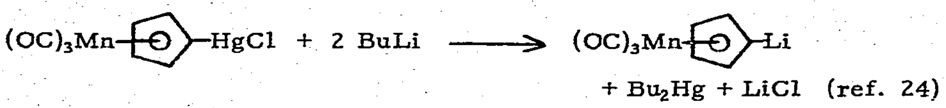
(Ar = Ph, o-MeC_6H_4, ~~m-MeC_6H_4~~, p-MeC_6H_4, p-$MeOC_6H_4$, 2-thienyl, 1-naphthyl, 1-indenyl, Ph_3C, Ph_2CH)

$$3\ Me_2Hg + 2\ In \longrightarrow 2\ Me_3In + 3\ Hg \qquad \text{(ref. 23)}$$

The transmetalation reaction also has found application:



+ Bu_2Hg (ref. 24)

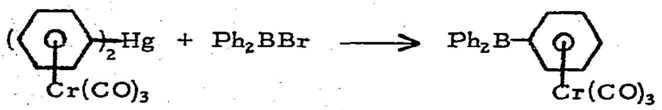


+ Bu_2Hg + LiCl (ref. 24)

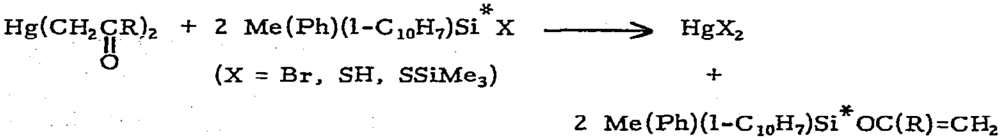
Organomercury compounds also have found further use as weak alkylating and arylating agents in reactions with metal halides:

$$ArHgCl + BCl_3 \xrightarrow{\text{benzene, reflux}} ArBCl_2 + HgCl_2$$

(Ar = o- and m-tolyl) (ref. 25)



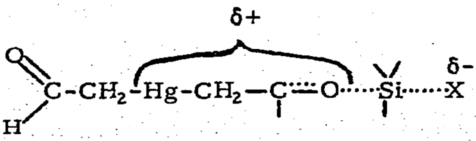
(ref. 26)



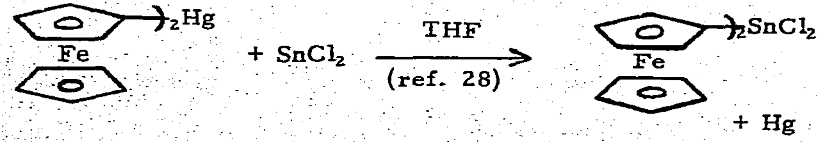
$$Hg(CH_2\overset{}{\underset{\underset{O}{\|}}{C}}R)_2 + 2\ Me(Ph)(1\text{-}C_{10}H_7)Si^*X \longrightarrow HgX_2 + 2\ Me(Ph)(1\text{-}C_{10}H_7)Si^*OC(R){=}CH_2$$

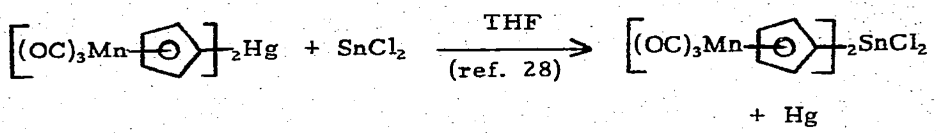
(X = Br, SH, $SSiMe_3$)

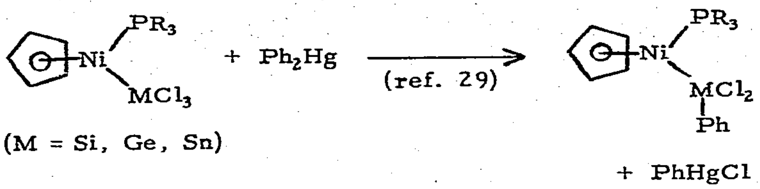
(These reactions are of the S_N2-Si type and proceeded predominantly with inversion of configuration at silicon (27). Transition state $\boxed{5}$ was suggested.



$\boxed{5}$

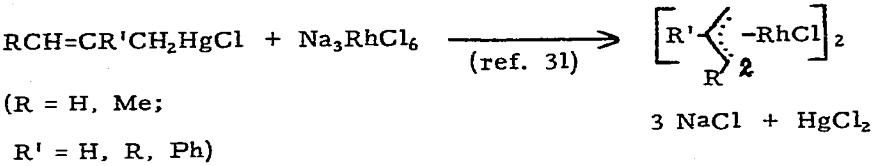


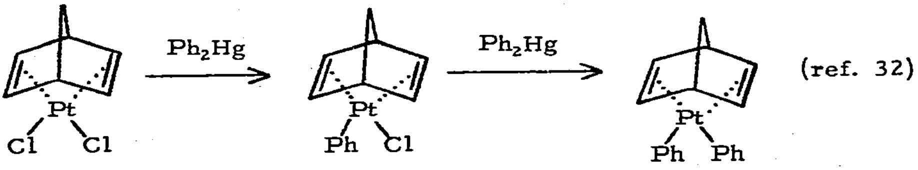


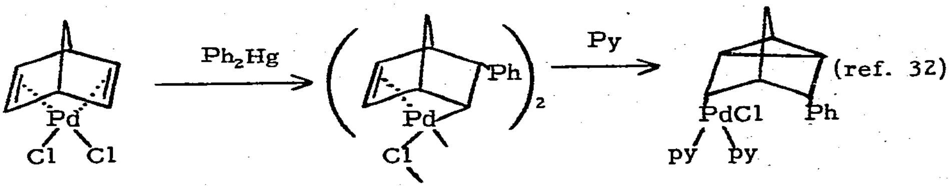


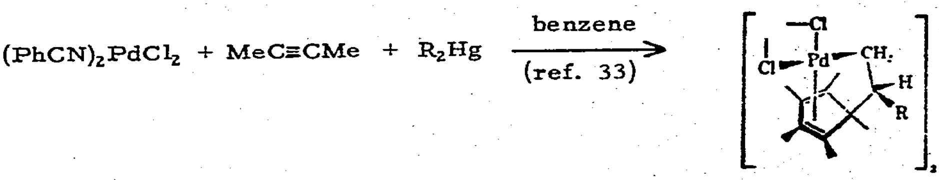
$$\mathrm{Me_2Hg + 2\ NbCl_5 \xrightarrow[\text{(ref. 30)}]{CH_2Cl_2} CH_3NbCl_4 + HgCl_2}$$

$$\mathrm{Me_2Hg + 2\ TaCl_5 \xrightarrow[\text{(ref. 30)}]{CH_2Cl_2} CH_3TaCl_4 + HgCl_2}$$





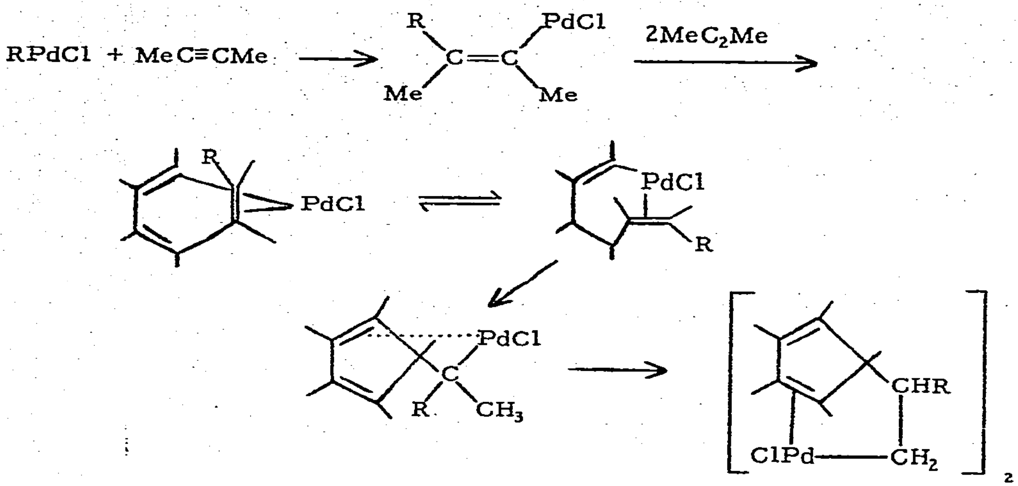


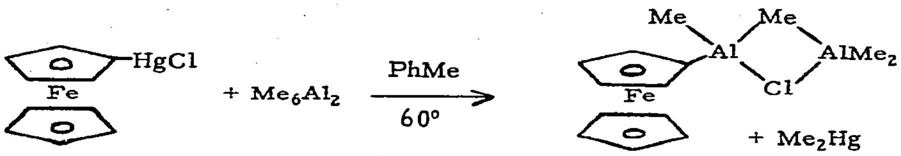


R = phenyl
R = *p*-tolyl

The following reaction course was suggested for this conversion:

$$PdCl_2 + R_2Hg \longrightarrow RPdCl + RHgCl$$

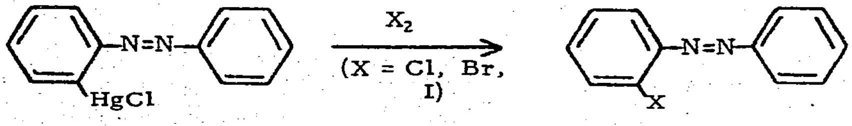




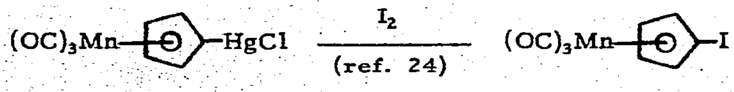
(ref. 34)

B. Organic Synthesis

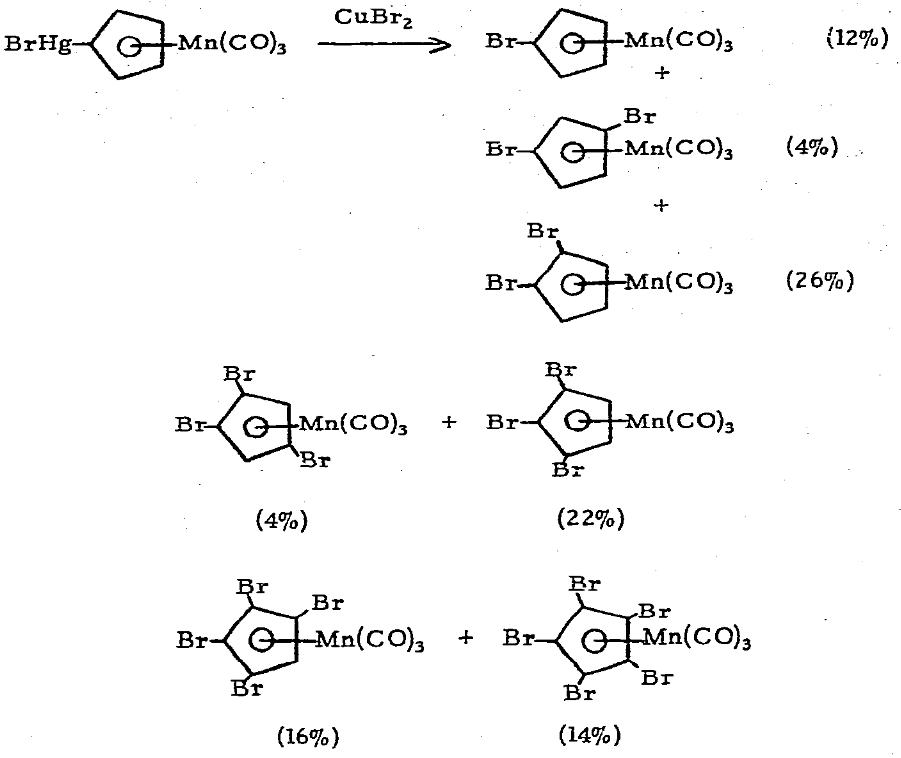
The conversion of organomercurials to organic halides by halogenolysis of the C-Hg bond has been used preparatively in the past, and some new examples have been reported.



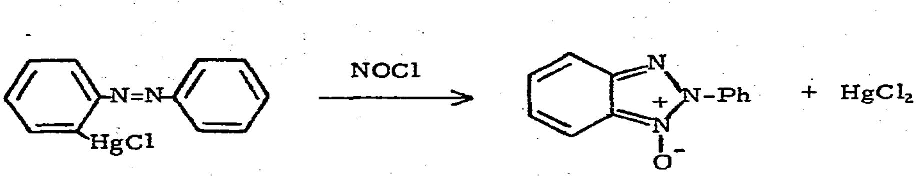
(ref. 17)



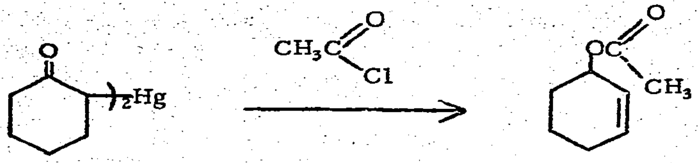
However, brominolysis with copper(II) bromide gave all possible brominated cymantrenes (35):



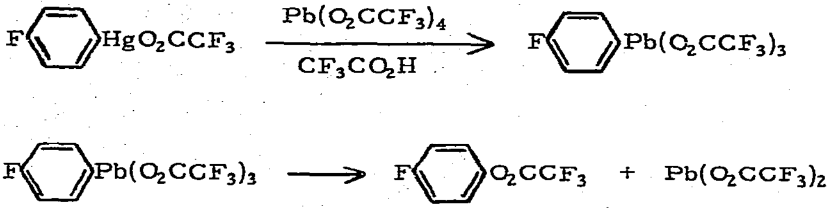
The reaction of ortho-mercurated azobenzene with nitrosyl chloride gave a triazole 1-oxide via replacement of the chloromercuri group with a nitroso function (17):



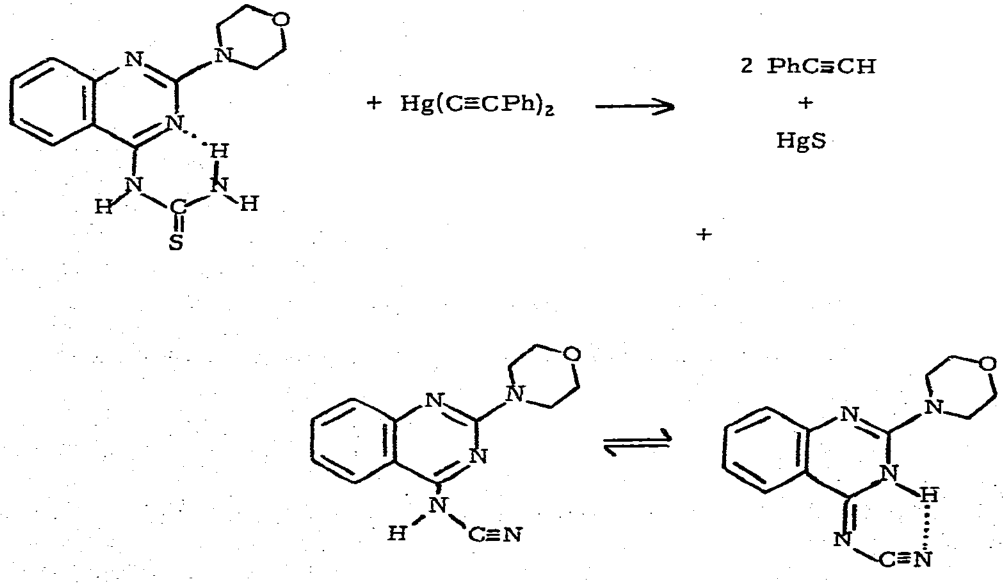
Treatment of α-mercurated ketones with acetyl chloride resulted in formation of allylic esters (5), e.g.:



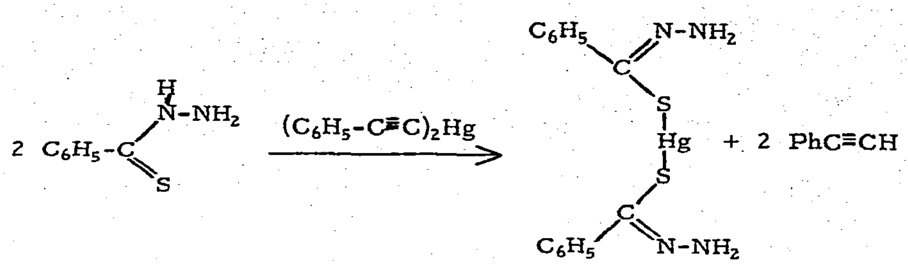
Aryl esters of trifluoroacetic acid were prepared by reaction of arylmercuric trifluoroacetates with lead(IV) trifluoroacetate (36):



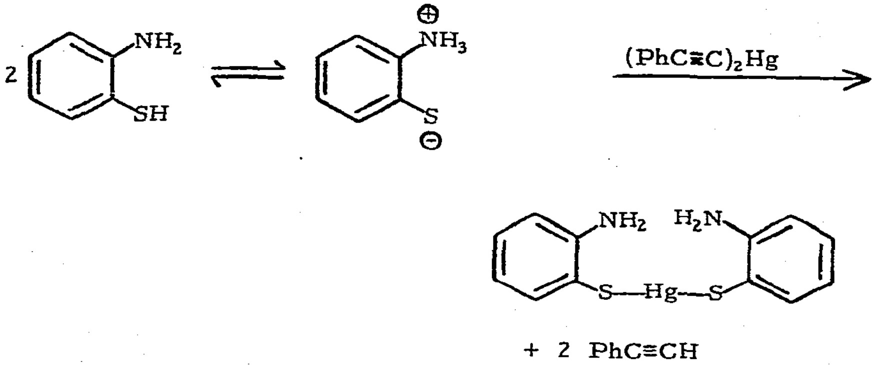
Ried and his coworkers have reported more synthetic applications of acetylenic mercurials. Bis(phenylethynyl)mercury is a desulfurization agent, as indicated in the reaction below (37):



Another reaction in which $Hg(C\equiv CPh)_2$ attacks at a C=S linkage is (38):



With 2-aminothiophenol a mercury(II) mercaptide also is obtained (38):



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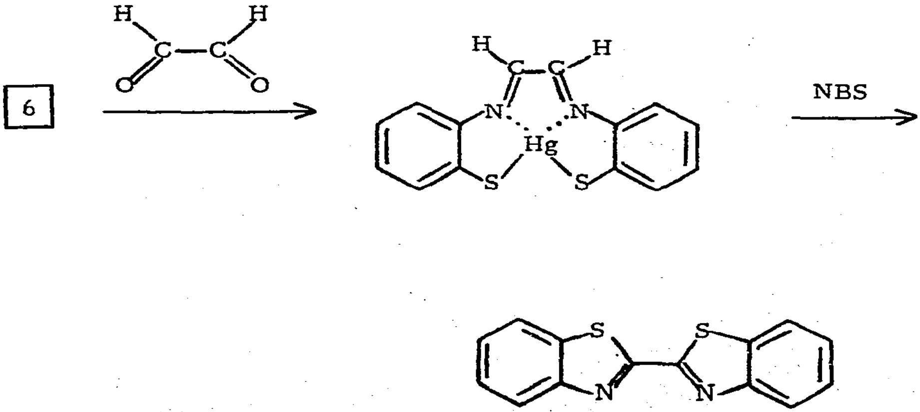
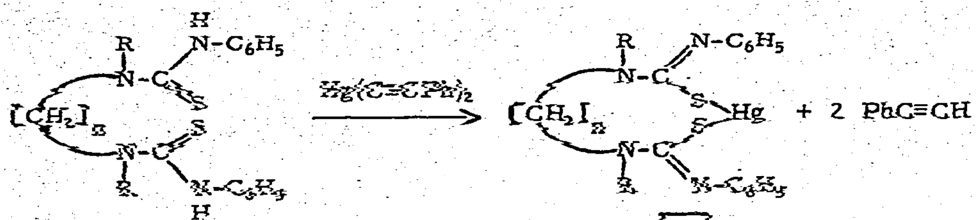
The latter provides a good entry into heterocyclic chemistry:



Bis-thioureas also were converted to various heterocyclic systems. Here mercury(II) mercaptides were formed in the initial reaction between Hg-$(C{\equiv}CPh)_2$ and the bis-thioureas (38):

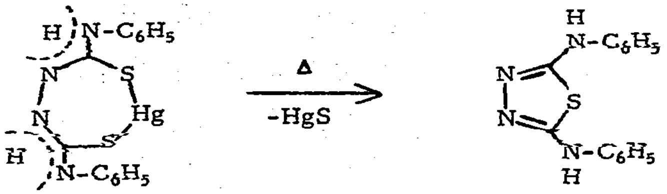


7

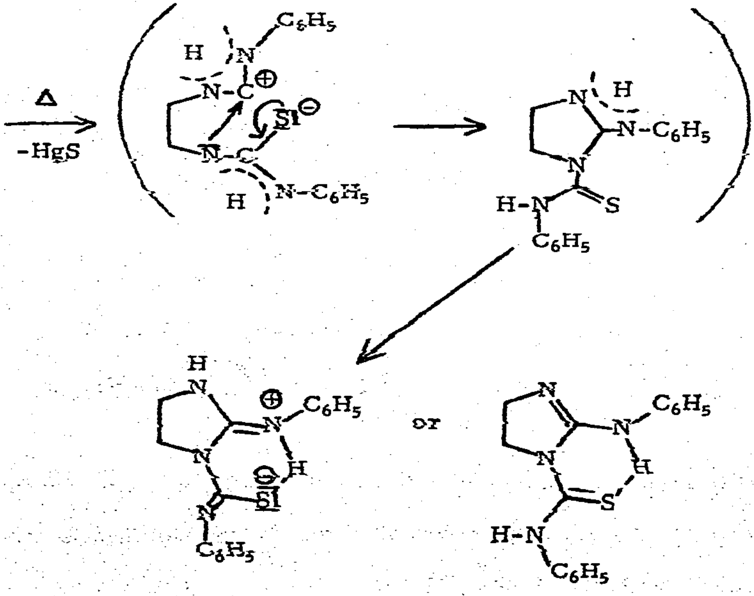
	n	R
a	0	H
b	2	H
c	2	CH_3

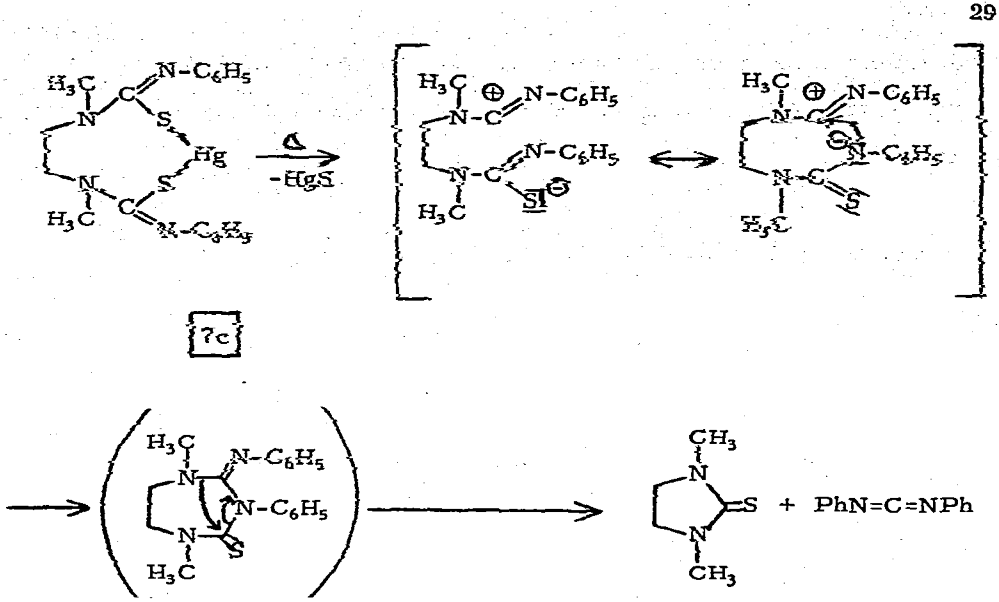
The pyrolysis of these mercaptides was studied:

7a :



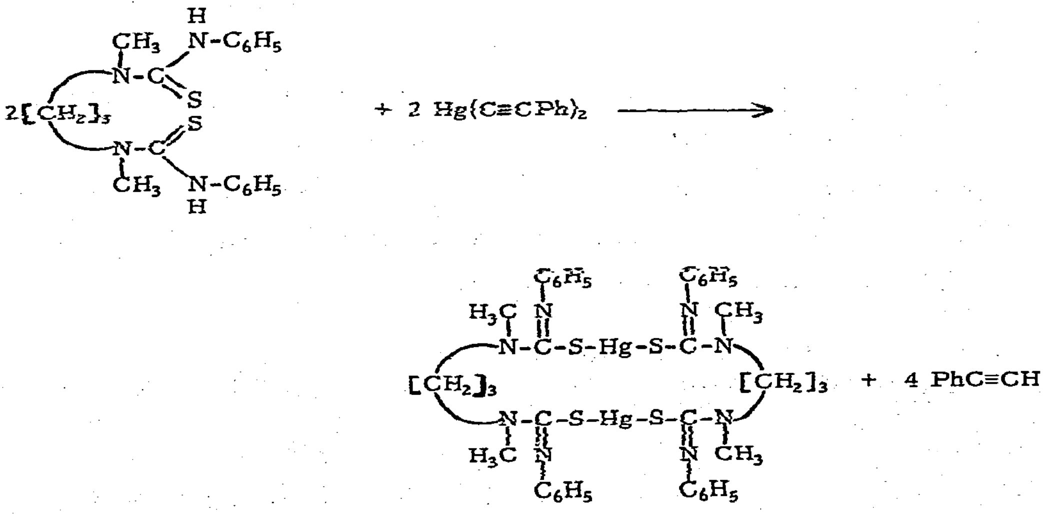
7b :



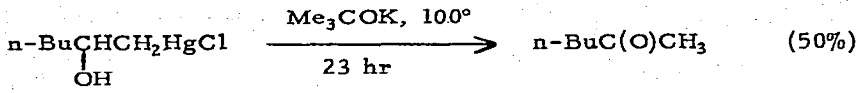


7c

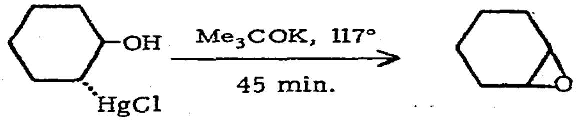
The "dimeric" mercaptide, obtained as shown below, gave no definite decomposition products on pyrolysis.



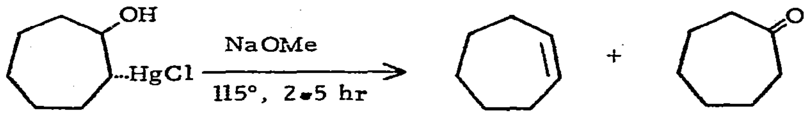
A new synthetic application of the hydroxymercuration products of olefins has been reported (39). Treatment of β-hydroxyalkylmercuric chlorides with a variety of bases (NaOMe, $KOCMe_3$, Na_2CO_3, NaH) in diglyme at elevated temperature was found to give epoxides and/or ketones. For instance:



$$\underset{OH}{n\text{-}BuCHCH_2HgCl} \xrightarrow[23\ hr]{Me_3COK,\ 100^\circ} n\text{-}BuC(O)CH_3 \qquad (50\%)$$



(99%)



(58%) (10%)

The action of base on the mercurial was believed to give a zwitterion, $\underset{O^-}{RCHCH_2Hg^+}$, for whose decomposition conformation-dependent routes to the ketone or the epoxide were available.

Nefedov, Sergeeva and Eidus have continued their studies of aspects of the carbonylation of organomercurials and other mercury compounds. The carbonylation of alkoxymercuration products of ethylene, $ROCH_2CH_2HgOAc$, proceeded in fair yields when R was n-propyl or a larger n-alkyl group, but not when R = Me or Et (40, 41):

$$ROCH_2CH_2HgOAc \xrightarrow[ROH,\ 150-250^\circ]{CO\ (50-150\ atm.)} ROCH_2CH_2CO_2R + Hg + ROAc$$

$(R = n\text{-}C_3H_7, \sim 45\%\ yield)$
$(R = n\text{-}C_4H_9, \sim 50\%\ yield)$
$(R = n\text{-}C_6H_{13}, \sim 20\%\ yield)$

In this reaction, $ROCH_2CH_2HgCO_2R$ is formed first and decomposes with extrusion of mercury in a subsequent step. This carbonylation reaction may be carried out without prior isolation of the β-alkoxyethylmercuric acetate by heating a suspension of mercuric acetate in the appropriate alcohol under a pressure (70-80 atm. total) of carbon monoxide and ethylene (41). However, considerably better yields of $ROCH_2CH_2CO_2R$ products were obtained when these reactions were carried out in two steps: (1) treatment of the mercuric acetate suspension in the alcohol with carbon monoxide (40 atm. at 230° for 3 hr.) and (2), after cooling and venting, treatment of the resulting mixture with ethylene (35 atm. at 230° for 3 hr.). The $ROCH_2CH_2CO_2R$ yields were in the 70-80% range when this procedure was used (41). It was shown, by interception and reduction of the intermediates with sodium borohydride, that the two step procedure does not involve the intermediacy of $ROCH_2CH_2HgOAc$, rather that the reaction sequence shown below is operative (42):

$$Hg(O_2CCH_3)_2 + ROH + CO \longrightarrow CH_3CO_2HgCO_2R + CH_3OH$$

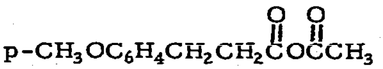
$$CH_3CO_2HgCO_2R + CH_2{=}CH_2 + ROH \longrightarrow ROCH_2CH_2HgCO_2R + CH_3CO_2H$$

$$ROCH_2CH_2HgCO_2R \longrightarrow Hg + ROCH_2CH_2CO_2R$$

Similar carbonylation of the arylation products of alkoxy mercurated olefins was possible, but competing processes predominated (43):

$$\begin{tikzcd} CH_2{=}CH_2 + Hg(OAc)_2 \arrow[r] & AcOCH_2CH_2HgOAc \arrow[d, "PhOCH_3,\ H_2SO_4"] \\ & p\text{-}CH_3OC_6H_4CH_2CH_2HgOAc \end{tikzcd}$$

$$p\text{-}CH_3OC_6H_4CH_2CH_2HgOAc + HCO_2H + ROH \xrightarrow{H_2SO_4}$$



$$p\text{-}CH_3OC_6H_4CH_2CH_2\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 \qquad (16\%)$$

$$(+ p\text{-}CH_3OC_6H_4CH_2CH_3 \quad (28\%)$$

$$+ p\text{-}CH_3OC_6H_4CH_2CH_2C_6H_4OCH_3\text{-}p\ (22\%))$$

(The required carbon monoxide in these reactions was produced by the sulfuric acid-induced decomposition of formic acid).

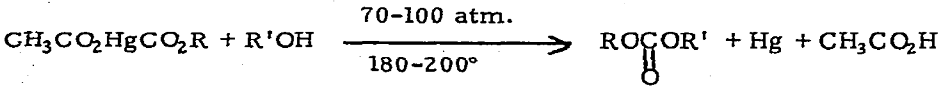
The synthesis of symmetrical dialkyl carbonates by mercuric acetate-induced carbonylation of alcohols has been reported by the same group (44-47):

$$Hg(O_2CCH_3)_2 + CO + ROH \longrightarrow CH_3CO_2HgCO_2R + CH_3CO_2H$$

$$CH_3CO_2HgCO_2R + ROH \longrightarrow (RO)_2C{=}O + Hg + CH_3CO_2H$$

These reactions were carried out at 150-250° and 50-150 atm. Unsymmetrical dialkyl carbonates were obtained in a two-step procedure (46):

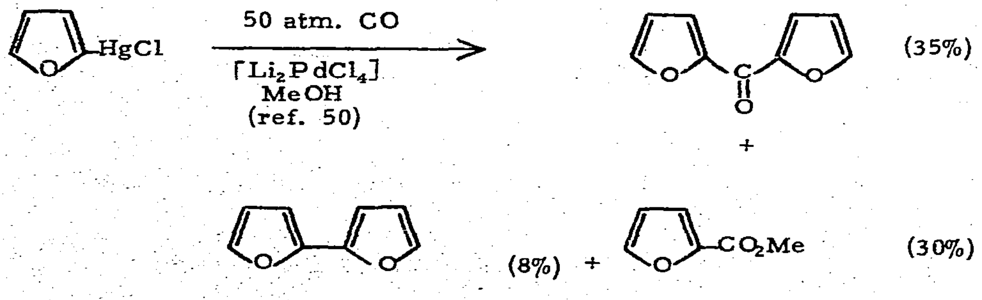
$$Hg(O_2CCH_3)_2 + ROH + CO \xrightarrow[25\text{-}60^\circ]{20\text{-}120\ \text{atm.}} CH_3CO_2HgCO_2R + CH_3CO_2H$$

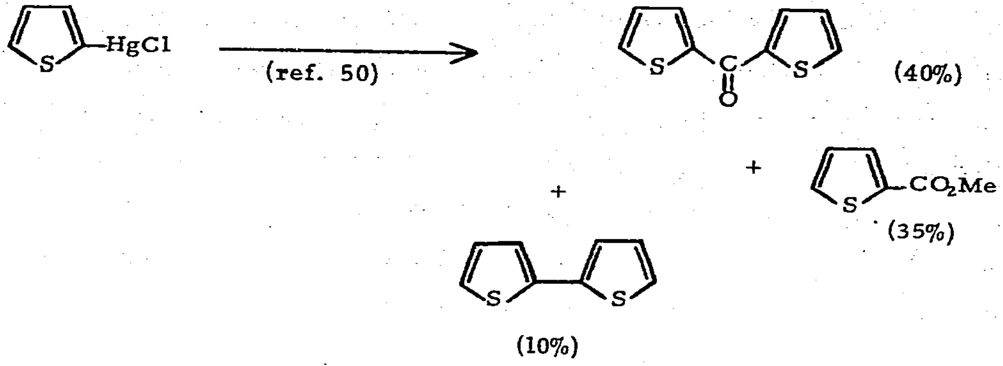


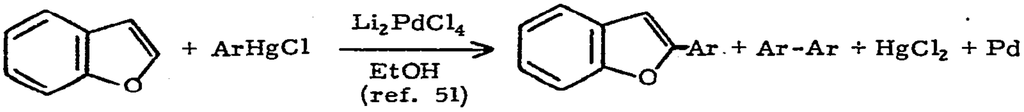
$$CH_3CO_2HgCO_2R + R'OH \xrightarrow[180\text{-}200^\circ]{70\text{-}100\ \text{atm.}} RO\underset{\underset{O}{\|}}{C}OR' + Hg + CH_3CO_2H$$

Similar mercuric acetate-induced carbonylation of primary and secondary amines also was found to be possible (48,49). These reactions, carried out at 150-200° and 90-100 atm., gave N-alkylformamides in good yields. However, such a reaction with aniline gave N,N'-diphenylurea.

Previous Annual Surveys have given examples of the use of organomercurials in the <u>in situ</u> generation of σ-organopalladium intermediates whose further conversions gave organic products. Further examples have been reported:





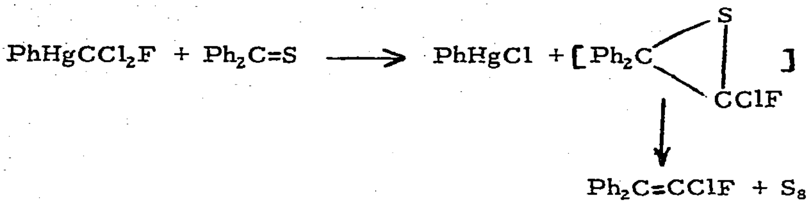


C. Halomethyl-Mercury Compounds

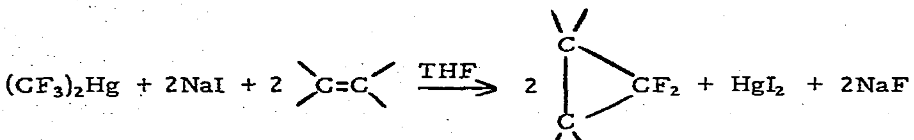
New halomethylmercurials have been reported; improved syntheses of some known halomethylmercurials have been developed and new divalent carbon transfer reactions of this class of reagents have been recorded.

Phenyl(trihalomethyl)mercury compounds ($PhHgCCl_3$, $PhHgCCl_2Br$ and $PhHgCBr_3$) can be prepared in a two-phase system in a reaction which involves the addition of an aqueous solution containing 20% by weight each of sodium hydroxide and potassium fluoride to a suspension of phenylmercuric chloride in the haloform (or in a diluent containing the haloform) and a small amount of triethylbenzylammonium chloride (52). This procedure has advantages over the THF method (Seyferth and Lambert, 1969) in that potassium tert-butoxide is not required as the base and the reaction can be carried out at room temperature. It has the disadvantages that the yields of mercurial product are lower and that an excess of the haloform appears to be required. The room temperature reaction of $PhHgNEt_2$ with chloroform to give $PhHgCCl_3$ in 75% yield has been recorded (53).

An improved synthesis of $PhHgCCl_2F$ has been developed and as a result, this compound may now be considered a practical reagent for the generation of fluorochlorocarbene (54). A noteworthy observation made during the course of this work is that $PhHgCCl_2F$ is about four times more reactive than believed originally (Seyferth and Darragh, 1970). New examples of its synthetic utility were provided (Table 2). The reaction with thiobenzophenone proceeded as shown below.



Improved preparations of $PhHgCF_3$ and of $(CF_3)_2Hg$ (14) have been mentioned in Section 2. The ready availability of the former mercurial directly from the easily prepared phenylmercuric trifluoroacetate should make it a much more practical CF_2 generator (55). The results of the Russian workers (14) suggested that $(CF_3)_2Hg$ was not a good CF_2 precursor (via the sodium iodide procedure):

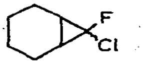
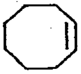
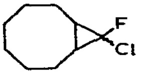
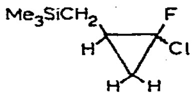
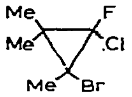
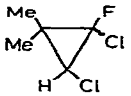
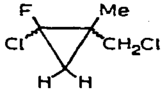
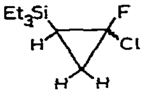
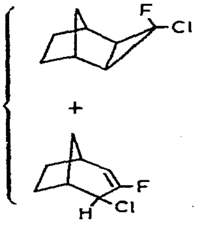
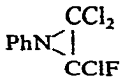


(~ 35% for cyclohexene and $CH_3CO_2CMe=CH_2$)

However, $(CF_3)_2Hg$ can serve well as a CF_2 transfer agent, as work at M. I. T. has shown (56). Thus, the $(CF_3)_2Hg/2NaI$ combination reacted

TABLE 2

REACTIONS OF PHENYL(FLUORODICHLOROMETHYL)MERCURY[a]

Reactant	*(mmol)*	*$PhHgCCl_2F$ (mmol)*	*Product*	*(Yield %)*[b]	*PhHgCl yield (%)*
	(62)	18.6		(84)	86
	(650)	216.0		(78)	85
$Me_3SiCH_2CH{=}CH_2$	(32)	14.0		(91;	90
$Me_2C{=}C(Br)CH_3$	(60)	18.2		(80)	92
$Me_2C{=}CHCl$	(74)	17.3		(72)	85
$CH_2{=}C(CH_3)CH_2Cl$	(75)	16.1		(80)	86
$Et_3SiCH{=}CH_2$	(24.4)	15.1		(65)	81
	(65)	20.3		(42) (42)	88
Et_3SiH	(50)	18.3	$Et_3SiCHClF$	(80)	84
$PhN{=}CCl_2$	(39)[c]	21.2		(74)	87
$Ph_2C{=}S$	(15.7)[d]	14.8	$Ph_2C{=}CClF$	(75)	85

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[a] Reactions carried out in benzene solution at reflux, with stirring under nitrogen, for 20 h unless otherwise specified. [b] Yields were calculated assuming that the mercurial charged was pure $PhHgCCl_2F$; because of the inert Ph_2Hg contaminant in the mercurial, these yields are somewhat lower than the actual yields based on $PhHgCCl_2F$ in the mercury starting material. [c] 40 h reaction time. [d] 48 h reaction time.

(from D. Seyferth and G.J. Murphy, J. Organometal. Chem., 49 (1973) 117)

(20 hr. at reflux) with an excess of cyclohexene in benzene solution to give 7,7-difluoronorcarane in 79% yield. A similar reaction with allyltrimethylsilane gave 1,1-difluoro-2-trimethylsilylmethylcyclopropane in 89% yield. The decisive factor in these reactions, as in those of $PhHgCF_3$, is the choice of solvent: much better results are obtained when these reagents, in combination with NaI, are used in benzene rather than in the ethers which serve well in the case of the $PhHgCCl_3/NaI$ system.

Full details have been provided concerning the synthesis of phenyl-(fluorodibromomethyl)mercury, a reagent which releases CFBr under exceptionally mild conditions (57). This compound must be prepared at low temperatures:

$$\mathrm{PhHgCl + Me_3COK + \underset{(2\ equiv.)}{CHFBr_2} \xrightarrow{THF,\ -65^\circ} \underset{(35\text{-}40\%)}{PhHgCFBr_2}}$$

$$\mathrm{PhHgCl + NaOMe + \underset{(2\ equiv.)}{CHFBr_2} \xrightarrow{THF,\ -25^\circ} \underset{(50\text{-}55\%)}{PhHgCFBr_2}}$$

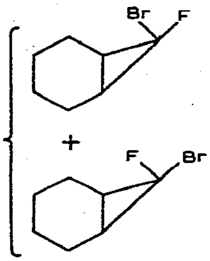
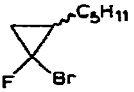
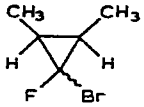
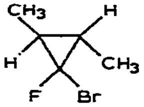
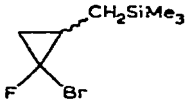
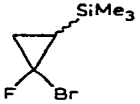
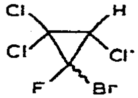
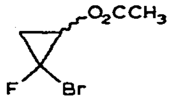
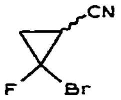
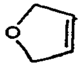
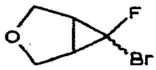
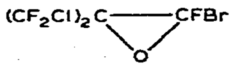
As a solid, this mercurial is stable for longer periods of time at 0°, but it decomposes slowly at room temperature. In solution, it is quite unstable. Oxygenated solvents (ketones, alcohols, ethers) induce its spontaneous, exothermic decomposition. This general instability results in high reactivity as a CFBr reagent (Table 3).

A new mercury reagent has been prepared which provides a route to tetrafluoroethylidene, CF_3CF (58):

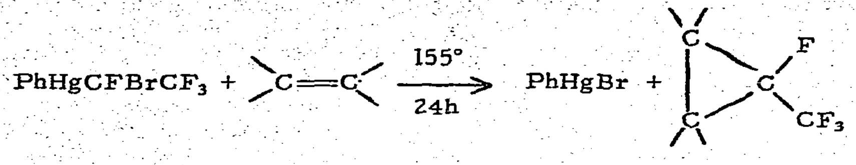
$$\mathrm{PhHgCl + CF_3CHFBr + NaOMe\ (in\ MeOH) \xrightarrow{THF,\ -35^\circ} PhHgCFBrCF_3 + NaCl + MeOH}$$

Addition of this carbene to olefins and its insertion into the Si-H bond of triethylsilane were described:

TABLE 3-REACTIONS OF PHENYL(FLUORODIBROMOMETHYL)MERCURY

Carbenophile	*Product*	*Yield (%)*		*Isomer ratio*
		4 days at room temp.	*20 min at 80°*	
Cyclohexene		58 32	58 30	
n-$C_5H_{11}CH{=}CH_2$		78	72	
cis-$CH_3CH{=}CHCH_3$		99		1.70
trans-$CH_3CH{=}CHCH_3$		98		
$Me_3SiCH_2CH{=}CH_2$		60	70	
$Me_3SiCH{=}CH_2$		55		2.5
$CCl_2{=}CHCl$			58	1.95
$CH_3CO_2CH{=}CH_2$			95	1.5
$CH_2{=}CHCN$		33	24	1.9
			57	
$(CF_2Cl)_2C{=}O$		74		
Et_3SiH	$Et_3SiCHFBr$	87	68	

(from D. Seyferth and S.P. Hopper, J. Organometal. Chem., 51 (1973) 77)



$$PhHgCFBrCF_3 + Et_3SiH \xrightarrow[24h]{155^\circ} PhHgBr + Et_3SiCHFCF_3$$

Some examples are given in Table 4.

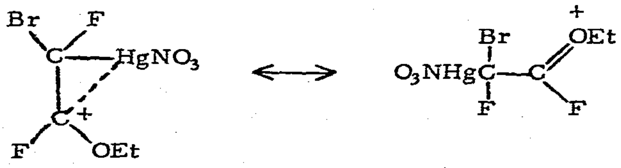
The new compounds $PhHgCFClCO_2R$ (R = Me, Et) and $PhHgCFBrCO_2Et$ also have been prepared by reaction of the respective alkyl dihaloacetate with potassium tert-butoxide and phenylmercuric chloride or by the mercuration of the respective ethyl trihalovinyl ether with mercuric nitrate in ethanol, followed by redistribution of the mercuration product (59):

$$PhHgCl + HCClFCO_2CH_3 \xrightarrow[THF/-60^\circ]{1.5\ \underline{t}\text{-BuOK}} \xrightarrow{HCl\text{-}H_2O}$$

$$PhHgCClFCO_2CH_3\ (44\%) + \underline{t}\text{-BuOH} + KCl$$

and:

$$CBrF{=}CFOEt + Hg(NO_3)_2 \xrightarrow{EtOH}$$



$$\downarrow EtOH$$

$$O_3NHgCFBrCO_2Et + EtF + HNO_3$$

$$\downarrow \text{aq NaCl}$$

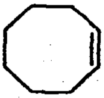
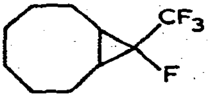
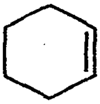
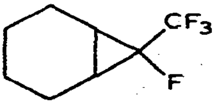
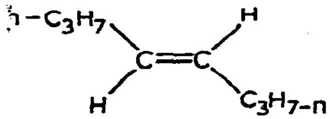
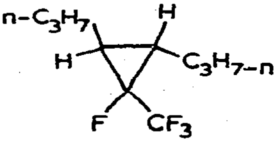
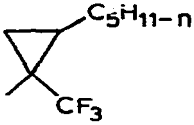
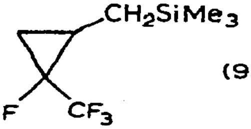
$$ClHgCFBrCO_2Et$$

$$\downarrow Ph_2Hg \text{ in } C_6H_6$$

$$PhHgCFBrCO_2Et + PhHgCl(s)$$

TABLE 4

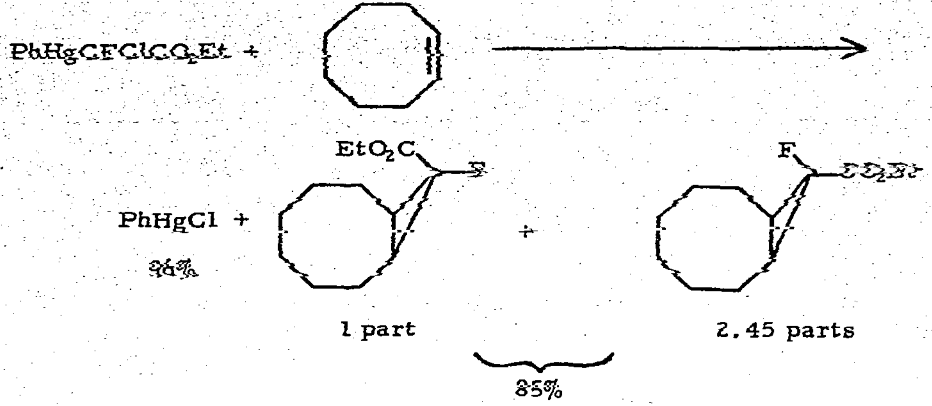
REACTIONS[a] OF PHENYL(1-BROMO-1,2,2,2-TETRAFLUOROETHYL)MERCURY

Carbenophile	*Product (% yield)*	*Isomer ratio*	*C_6H_5HgBr (% yield)*
	 (98)	3.4	96
	 (87)	3.6	87
	 (80)		92
n-$C_5H_{11}CH{=}CH_2$[b]	 (70)	1.9	80
$Me_3SiCH_2CH{=}CH_2$[c]	 (93)	1.8	99
Et_3SiH	$Et_3SiCHFCF_3$ (53)		61

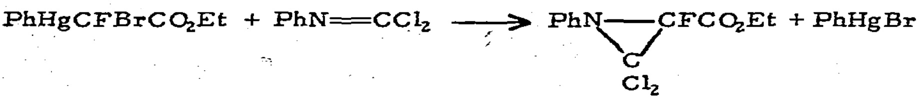
Reactions at 155° for 24 h in a sealed tube, carbenophile to mercurial ratio of 3, benzene diluent, unless otherwise noted. [b] 72 h reaction time. [c] OLefin (10 ml) used as solvent.

from D. Seyferth and G.J. Murphy, J. Organometal. Chem., 52 (1973) C1)

These mercurials were found to be effective $FCCO_2R$ transfer agents at temperatures above 125°, reacting with olefins to give gem-fluorocarboalkoxycyclopropanes and inserting $FCCO_2R$ into the Si-H bond of triethylsilane. Addition of $FCCO_2Et$ to a C=N bond also could be achieved.



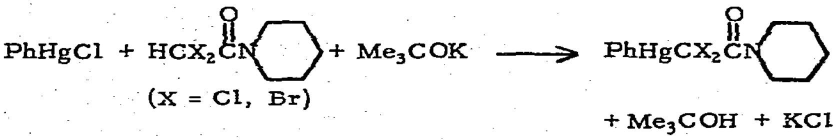
$$\mathrm{PhHgCFClCO_2R + Et_3SiH \longrightarrow Et_3SiCHFCO_2R + PhHgCl}$$



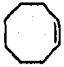
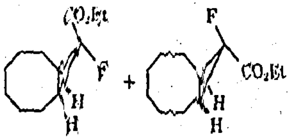
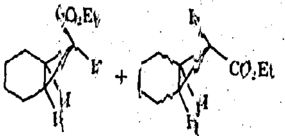
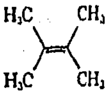
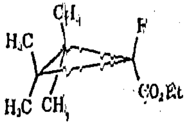
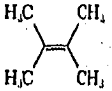
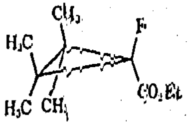
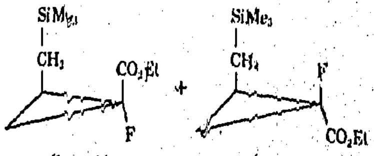
This work is summarized in Tables 5 and 6. Also noteworthy is a reaction which implied the insertion of FCCO$_2$Et into the Hg-Cl bond:

$$\mathrm{PhHgCFBrCO_2Et + PhHgCl \xrightarrow{PhCl,\ 133^\circ} PhHgCFClCO_2Et + PhHgBr}$$

The first halomethylmercurials containing an amide function have been described (60, 61):



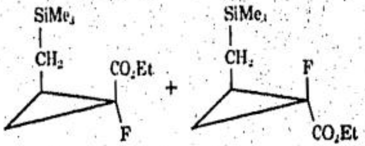
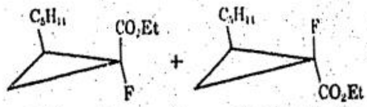
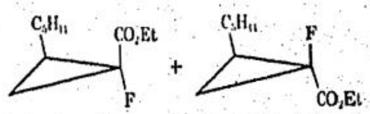
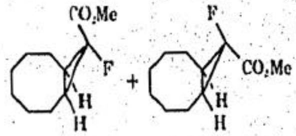
The decomposition of these mercurials in refluxing bromobenzene gave the isomeric halo-β-lactams via the novel intramolecular insertion of the carbene center into an α C-H bond of the piperidino substituent:

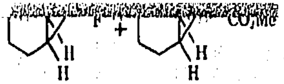
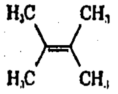
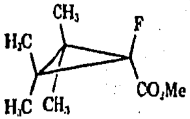
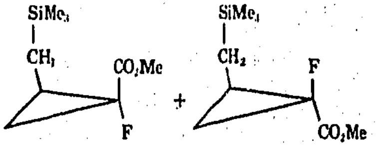
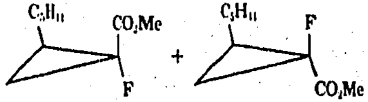
Substrate (mmol)	Mmol of mercurial	Solvent (ml)	Reaction temp, °C	Reaction time, hr	Yield PhHgCl, %	Recovered starting material, %	Products (% yield based on consumption of starting mercurial)
			Reactions of $PhHgCFClCO_2Et$				
 (neat)	12.0	Olefin (20)	144	36	96		 (1 part) (2.4 parts) (85%)
 (neat)	12.0	Olefin (20)	132 (sealed tube)	24	79	10	 (1 part) (2.39 parts) (69%)
 (36)	12.0	Benzene (12)	135 (sealed tube)	24	26	64	 (22%)
 (72)	12.0	Benzene (12)	155 (sealed tube)	72	72 +Hg^0 (21)		 (38%)
$Me_3SiCH_2CH{=}CH_2$ (neat)	12.0	Olefin (20)	129 (sealed tube)	36	66 +Hg^0 (19)		 (1 part) (1.85 parts) (24%)

(Table continued)

TABLE 5 (continued)

TABLE 5 (continued)

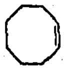
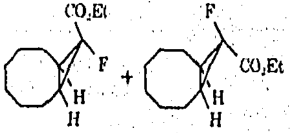
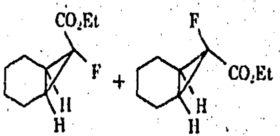
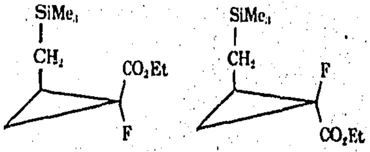
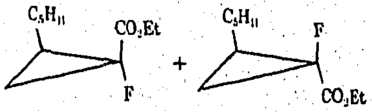
Substrate (mmol)	Mmol of mercurial	Solvent (ml)	Reaction temp. °C	Reaction time, hr	Yield PhHgCl, %	Recovered starting material, %	Products (% yield based on consumption of starting mercurial)
$Me_3SiCH_2CH{=}CH_2$ (neat)	12.0	Olefin (20)	133 (sealed tube)	62	55 + Hg^0 (21)		 (1 part) + (1.9 parts) (55%)
$CH_2{=}CHC_5H_{11}$-n (neat)	12.0	Olefin (20)	134 (sealed tube)	48	37 + Hg^0 (18)	9	 (1 part) + (2.5 parts) (15%)
$CH_2{=}CHC_5H_{11}$-n (neat)	10.3	Olefin (12)	145 (sealed tube)	24	33 + Hg^0 (14)	18	 (1 part) + (2.6 parts) (18%)
Et_3SiH (neat)	12.0	Et_3SiH (20)	108–110	50	25 + Hg^0 (54)		$Et_3SiCHFCO_2Et$ (71%)
Reactions of $PhHgCClFCO_2Me$							
 (22)	7.2	Benzene (7.0)	135 (sealed tube)	48	58	38	 (1 part) + (1.8-1.9 parts)

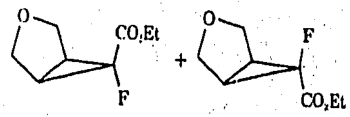
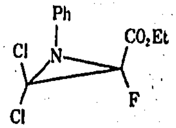
 (24)	8.0	Benzene (8)	135 (sealed tube)	[illegible]	[illegible]		 (1 part) (1.9 parts) (47%)
 (60)	10.0	Benzene (10)	155 (sealed tube)	72	54 +Hg⁰ (29)		 (48%)
$Me_3SiCH_2CH{=}CH_2$ (24)	8.0	Benzene (8)	135 (sealed tube)	60	71	10	 (1 part) (1.4 parts) (61%)
$CH_2{=}CHC_5H_{11}$-n	8.0	Benzene (8)	135 (sealed tube)	60	47		 (1 part) (1.9 parts) (24%)
Et_3SiH (24)	8.0	Benzene (8)	135 (sealed tube)	60	63 +Hg⁰ (25)		$Et_3SiCHFCO_2Me$ (72%)

(from D. Seyferth and R.A. Woodruff, J. Organometal. Chem., 38 (1973) 4031)

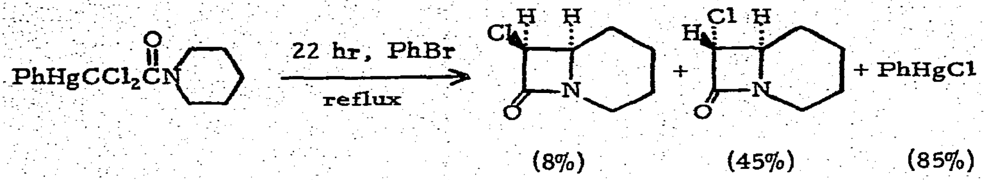
TABLE 6

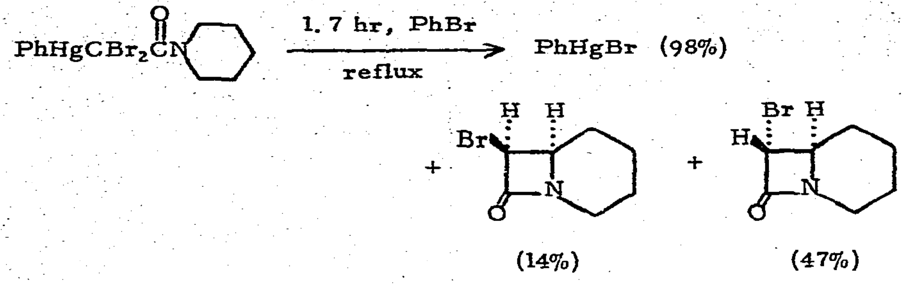
FLUOROCARBOETHOXYCARBENE TRANSFER REACTIONS OF $PhHgCBrFCO_2Et$

Substrate (mmol)	Mmol of mer-curial	Solvent (ml)	Reaction temp, °C	Reac-tion time, hr	Yield PhHgBr, %	Recov-ered start-ing mate-rial, %	Products (% yield based on starting material consumed)
 (21)	7.0	Benzene (7)	125 (sealed tube)	20	83		 (1 part) (2.2 parts) (74%)
 (21)	7.0	Benzene (7)	125 (sealed tube)	20	80		 (1 part) (2.2 parts) (59%)
$Me_3SiCH_2CH{=}CH_2$ (18)	6.0	Benzene (6)	135 (sealed tube)	24	80		 (1 part) (1.6 parts) (72%)
$CH_2{=}CHC_5H_{11}\text{-}n$ (18)	6.0	Benzene (6)	135 (sealed tube)	24	77		 (1 part) (2.9 parts)

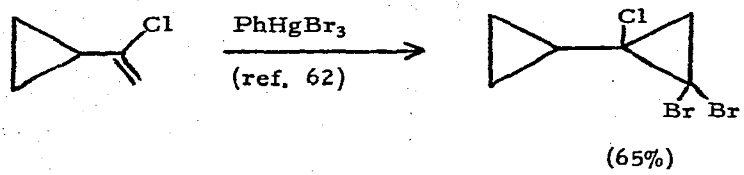
Et_3SiH (21)	7.0	Benzene (7)	125 (sealed tube)	20	93		$Et_3SiCHFCO_2Et$ (74%)
 (neat)	6.0	Olefin (6)	125 (sealed tube)	24	Mixed with polymer and Hg^0		 (1 part) (13 parts) (ca. 15%)
$PhN{=}CCl_2$ (6.0)	6.0	Benzene (6)	125 (sealed tube)	24	38	36	 (40-55)

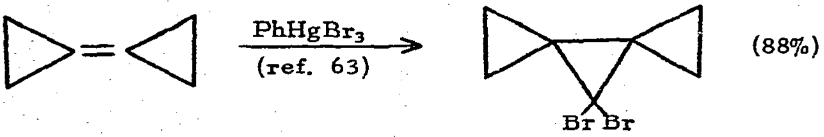
(from D. Seyferth and R.A. Woodruff, J. Organometal. Chem., 38 (1973) 4031)

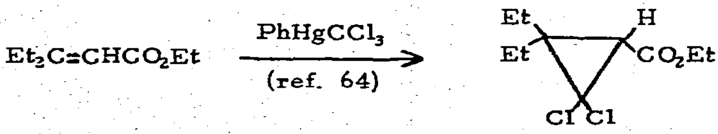


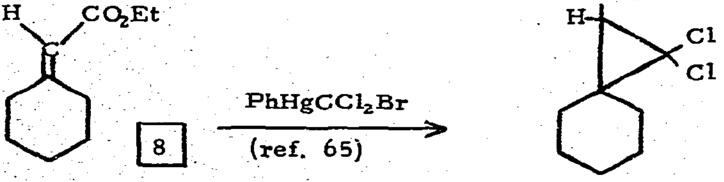


Further examples of the use of phenyl(trihalomethyl)mercurials in cyclopropane synthesis have been published:

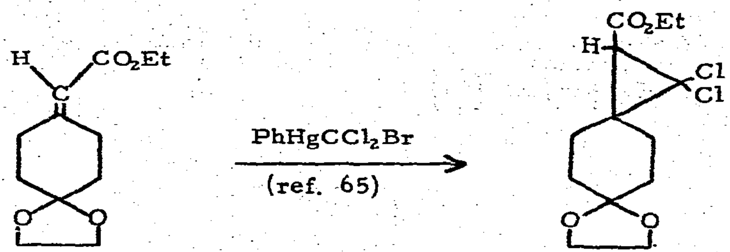






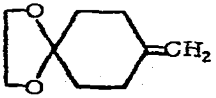


8

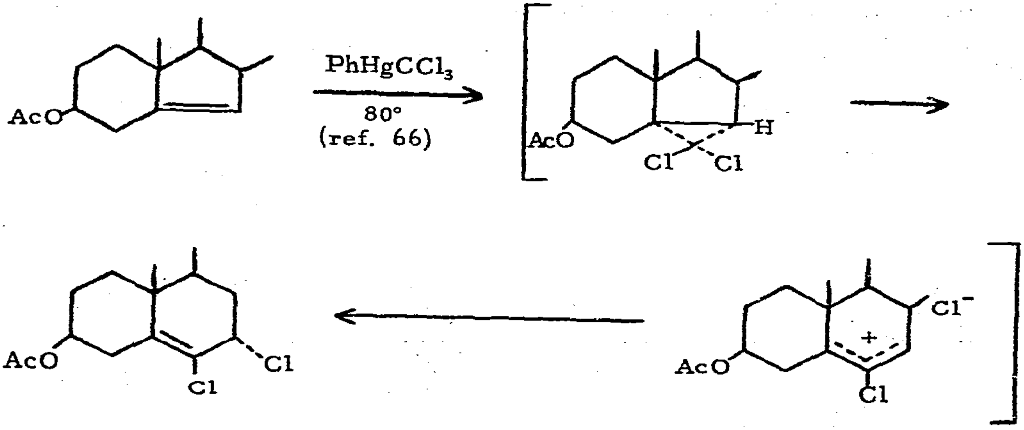


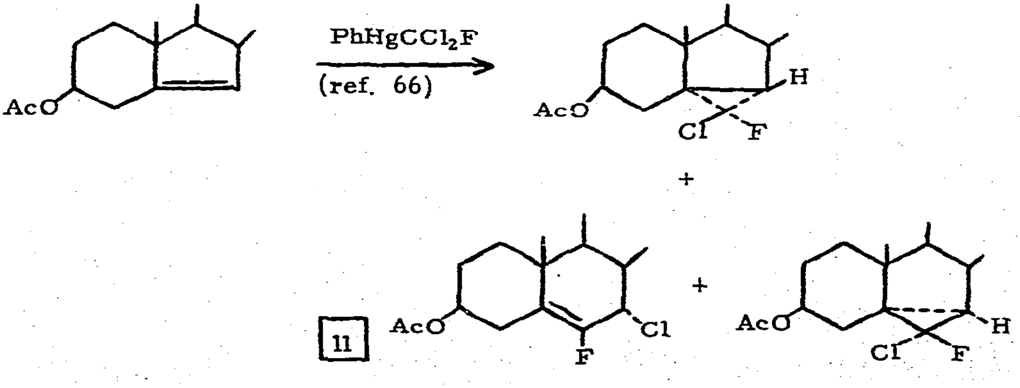
9

(The relative reactivities toward $PhHgCCl_2Br$-derived dichlorocarbene of olefins 8 (0.264 vs cyclohexene), 9 (0.204), methylenecyclohexane (4.57) and 10 (2.95) showed that the ketal oxygen atoms in 9 and 10 have no synergistic effect on the addition of CCl_2 to the C=C bonds in this series of olefins.)



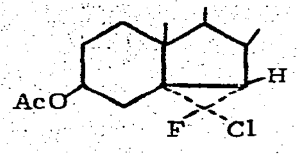
10



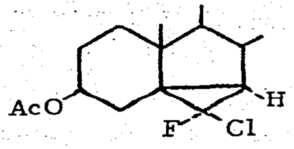


11

Compound $\boxed{11}$ was formed by ring opening of the other cyclopropane products formed initially, $\boxed{12}$ and $\boxed{13}$.



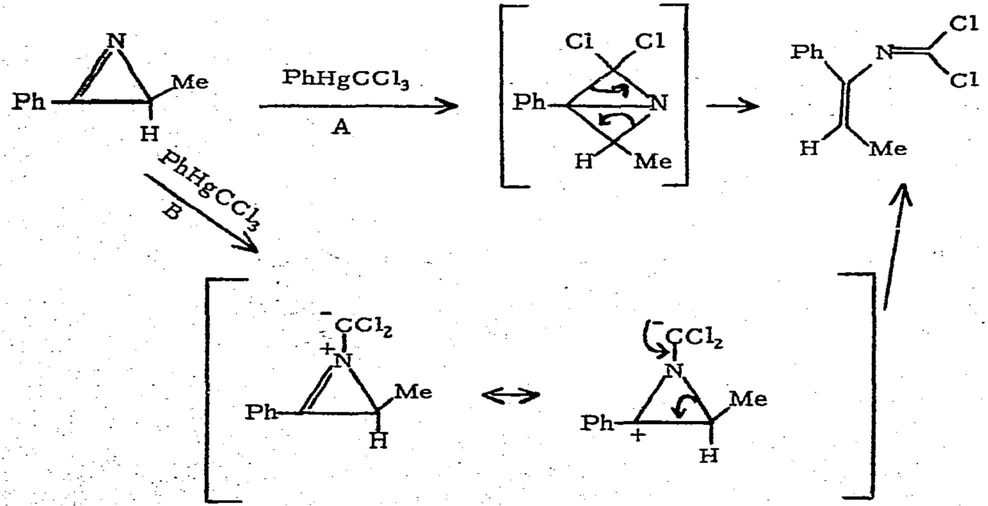
$\boxed{12}$



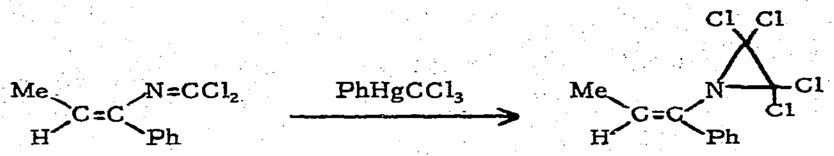
$\boxed{13}$

Not all olefins react with $PhHgCX_3$ compounds; steric hindrance can inhibit C=C addition. Thus trans-β-pinene did not react with $PhHgCCl_3$, nor with other CCl_2 sources (67).

There have been reported new examples of reactions of $PhHgCX_3$ compounds with C≡N and N=N containing compounds. 3-Methyl-2-phenyl-1-azirine reacted with $PhHgCCl_3$ in refluxing benzene to give N-(dichlorovinylidene)-1-(1-phenylpropenyl)amine, presumably by one of the two routes shown below (68).

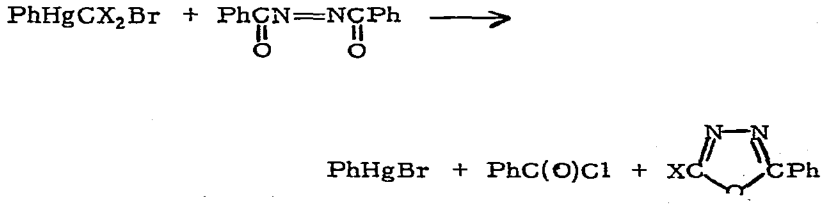


Route B was favored by the authors. A minor by-product arose from addition of further CCl_2 to the C=N bond (not the C=C bond) of the product:

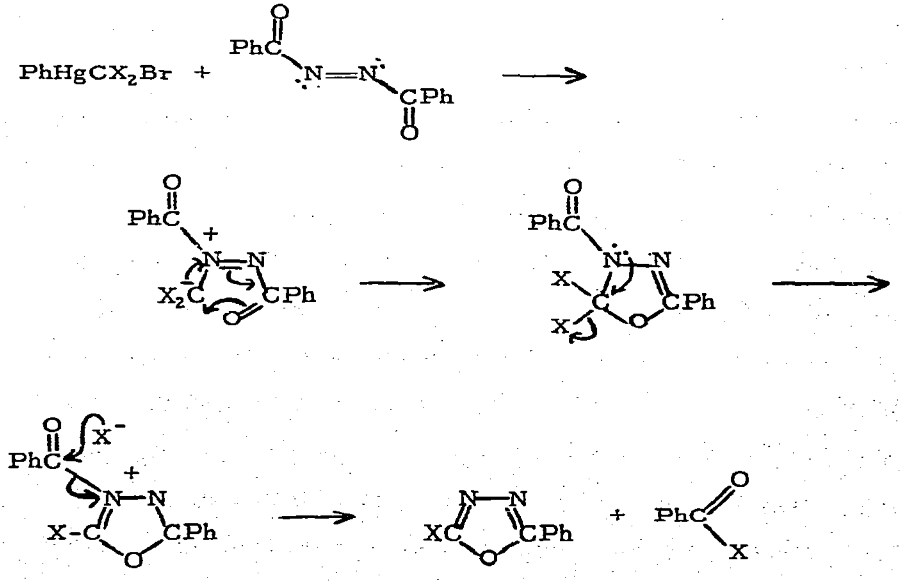


The action of the $PhHgCCl_2Br/NaI$ reagent on 2,3-diethyl-1-aziridine in benzene/DME at room temperature proceeded similarly, giving N-(dichlorovinylidene)-3-(3-hexenyl)amine.

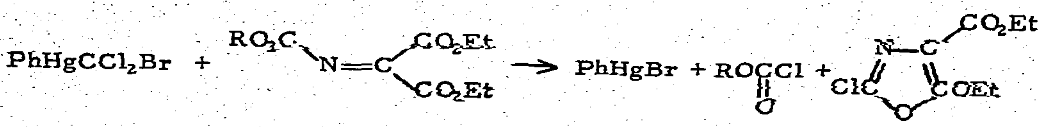
Formal 1,4 addition of CCl_2 to compounds containing the N=N-C=O (azodibenzoyl) and N=N-C=O systems [$(RO_2CN{=}C(CO_2Et)_2$] has been reported for reactions utilizing phenyl(bromodichloromethyl)mercury as CCl_2 source (69):



via:

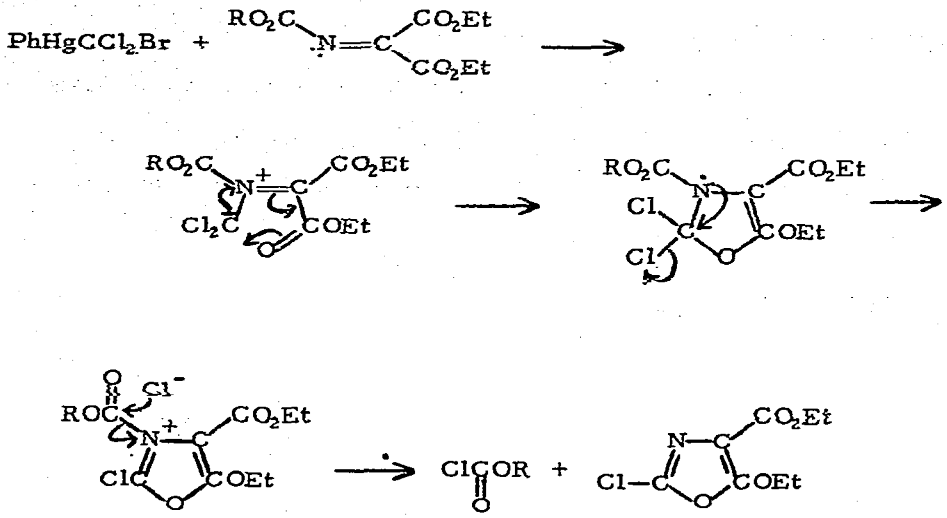


and



(R = Me, Et)

via:



(1,4 Addition of CCl_2 has never been observed with C=C-C=O or C=C-C=C systems).

More papers have been concerned with insertion reactions of $PhHgCCl_2Br$-derived dichlorocarbene. A study of the stereochemistry of the insertion of CCl_2 (via $PhHgCCl_2Br$) into the benzylic C-H bond of (+)-2-phenylbutane has shown that this reaction occurs with predominant retention of configuration (70). This result, as well as those of a Hammett study of reactions of this mercurial with substituted cumenes, $ZC_6H_4CMe_2H$ (Z = p-Me, p-F, p-Cl, m-CF_3, H), indicated that this insertion of CCl_2 is a concerted process in which only a small partial positive charge is developed at the carbon atom into whose bond to hydrogen CCl_2 is being inserted. In another stereochemical study it was found that the insertions of $PhHgCCl_2Br$-derived CCl_2 into the β-C-H bond and the Si-C bond of silacyclobutanes are stereoselective processes which proceed with overall retention of configuration (71).

Dichlorocarbene has been inserted into the Si-Cl bond of hexachlorodisilane by reactions of phenyl(trihalomethyl)mercurials (72):

$$\begin{array}{lcl} PhHgCCl_3 + NaI + Cl_3SiSiCl_3 & \xrightarrow{120^\circ} & Cl_3SiSiCl_2CCl_3 + PhHgX \\ (\text{or } PhHgCCl_2Br) & & \quad (\sim 30\%) \end{array}$$

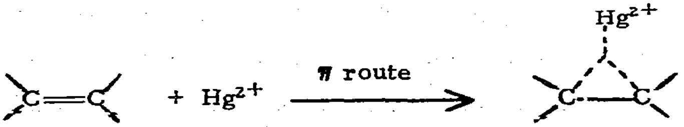
Halomethylmercurials also can be sources of halomethyl radicals, provided enough energy for homolytic C-Hg bond rupture is supplied. In this connection, we note that the $Cl_3C\cdot$ radical (whose ESR spectrum was studied) has been generated from $Hg(CCl_3)_2$ (73).

4. MERCURATION OF UNSATURATED COMPOUNDS

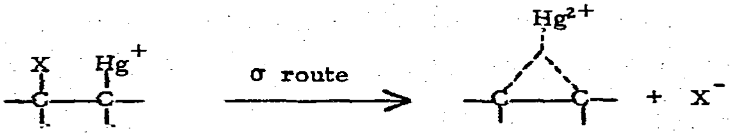
A. Olefins and Acetylenes

The general scope and regio- and stereoselectivity of the solvomercuration processes, notably oxymercuration, now are reasonably well understood. However, research activity devoted to the mechanism of this reaction and its stereochemical principles continues.

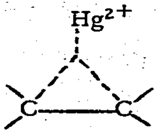
Olah and Clifford (74) have published full details of their characterization by ^1H and ^{13}C NMR of stable mercurinium ions in superacid media at low temperatures. Two procedures served in their preparation:



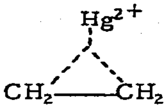
and

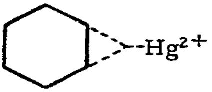


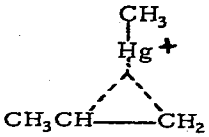
The primary bonding is believed to be one involving overlap of the mercury 6s orbital with the π cloud of the olefin:

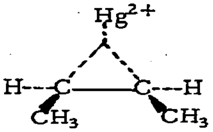


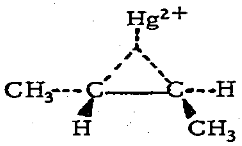
The possibility of rapidly equilibrating β-mercury-substituted carbonium ions was rejected on the basis of the available data. Among the ions studied were the following:

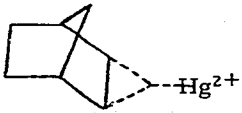


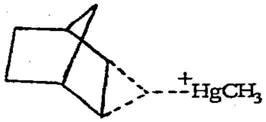




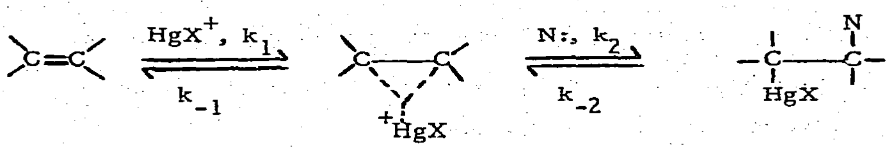








The superacids used as ionizing media in this study included FSO_3H/-SbF_5/SO_2, SbF_5/SO_2, $FSO_3H/SbF_5/SO_2ClF$ and SbF_5/SO_2ClF. As the authors point out, the successful generation of such mercurinium ions under these very special conditions has no direct bearing on the question of whether or not such mercurinium ion intermediates are involved in solvomercuration of olefins under the more usual conditions. Many workers seem to accept as the preferred mechanism of the solvomercuration reaction one that involves reversible formation of a bridged π-complex, i.e., the mercurinium ion (k_1), followed by rate-limiting attack by the nucleophile (usually, but not always, the solvent) on this intermediate (k_2):



Others, however, consider the mercurinium ion an unproven and unneeded intermediate. Thus Bach and Richter (75) argue strongly in favor of the mercurinium ion intermediate in their paper on the oxymercuration of cis- and trans-di-tert-butylethylene. On the other hand, Brown and Kawakami (76) in their paper on the oxymercuration-demercuration of 7,7-dimethylnorbornene and related olefins state emphatically: "We discard the symmetrical mercurinium ion in interpreting our results. We prefer the concept of electrophilic attack by the mercury species, ^+HgX, at the least substituted carbon atom of the double bond. This produces a mercury-substituted carbonium ion which reacts rapidly with the solvent from the trans direction, if that is unhindered, but from the cis direction in molecules such as norbornyl in which the endo direction is strongly hindered."

When the acetoxymercuration of cyclopentadiene in glacial acetic acid was followed by conductometric measurement, it was found that the conductivity increased as the olefin was added. This behavior was ascribed by the authors to the formation of a mercurinium ion intermediate (77).

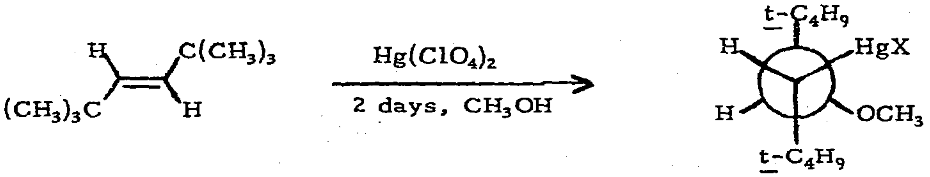
The stereochemistry and relative rates of oxymercuration of cyclic, bicyclic and a few hindered olefins have been studied (78: Table 7) (79: Table 8). The rate of the oxymercuration reaction is not increased by an increase in the strain energy of the olefin, and it is steric effects which appear to be of importance. This confirms that k_2, the attack by the nucleophile on the positively charged intermediate, is the rate-determining step. This work by Bach and Richter (75, 78) is noteworthy in that it provides the first example of the syn addition of the elements of XHg-OR to a noncyclic olefin:

Table 7. Relative Rates and Stereochemistry of Oxymercuration of Some Strained Olefins (from R. D. Bach and R. F. Richter, Tetrahedron Lett. (1973) 4099)

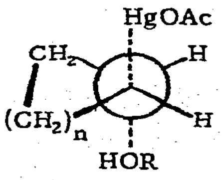
Alkene	Mode of Oxymercuration	Relative Rate	Strain Energy
norbornadiene	syn	27.0	31.59
trans-cyclooctene	syn	10.1	17.85
1-octene	anti	9.5	
norbornene	syn	4.5	23.62
1-methylcyclohexene	anti	2.2	2.68
benzonorbornadiene	syn	1.1	
cyclohexene	anti	1.0	2.61
4-*t*-butylcyclohexene	anti	0.96	
cyclobutene	anti	0.40	
bicyclo[4.2.0]oct-7-ene	syn/anti	0.17	
bicyclo[3.2.1]oct-2-ene	syn/anti	0.065	
bicyclo[2.2.2]octene	syn/anti	0.030	15.99
cis-cyclooctene	anti	0.004	8.81
cis-di-*t*-butylethylene	anti	0.001	16.37
trans-di-*t*-butylethylene	syn	no reaction	6.01
cis-cyclodecene	anti	slow	11.63
trans-cyclodecene	syn	slow	11.95
dibenzobicyclo[2.2.2]octatriene	syn/anti	slow	
[4.4.2]propell-11-ene	anti	no reaction	
adamantylidene adamantane		no reaction	

Table 8. Stereochemistry of Oxymercuration of Some Cyclic Olefins (from W. L. Waters, T. G. Traylor and A. Factor, J. Org. Chem., 38 (1973) 2306)

Cycloalkene	Stereochemistry of hydroxymercuration	Stereochemistry of methoxymercuration
Cyclobutene	Trans	Trans
Cyclopentene	Trans	Trans
Cyclohexene	Trans	Trans
Cycloheptene	Trans	Trans
cis-Cyclooctene	Trans	Trans
trans-Cyclooctene	Cis	Cis
cis-Cyclononene	Trans	Trans
trans-Cyclononene	Cis	Cis

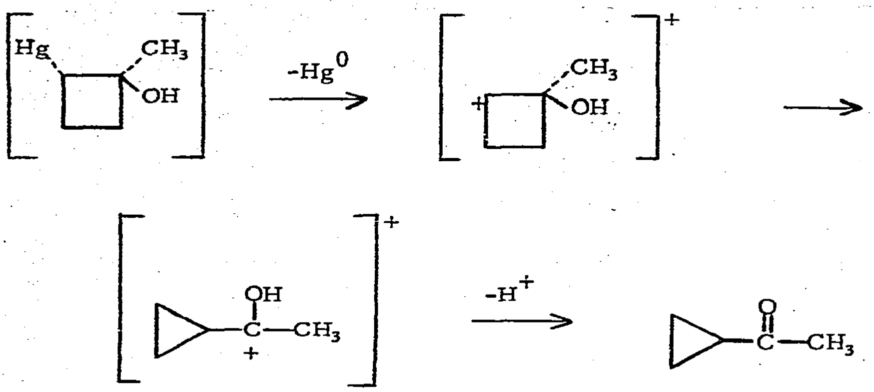


Waters et al (79) relate the tendency of an olefin to be oxymercurated *via* a *trans* mechanism to its ability to form the normal *anti* transition state:

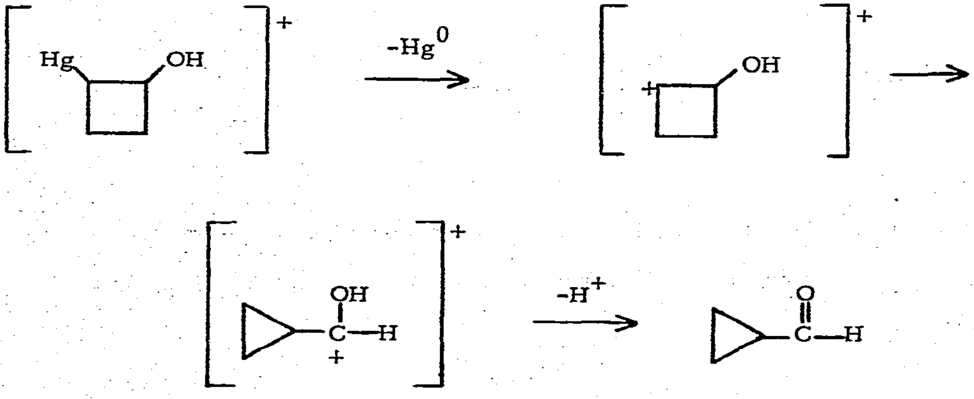


If this transition state is energetically unfavorable, because of steric or twist strain reasons, cis addition will occur.

The kinetics of hydroxymercuration of various cycloalkenes and methylenecycloalkanes were determined by Halpern et al. (80). Of interest in this study is the facile decomposition in strong acid solution of the hydroxymercuration product of 1-methylcyclobutene:

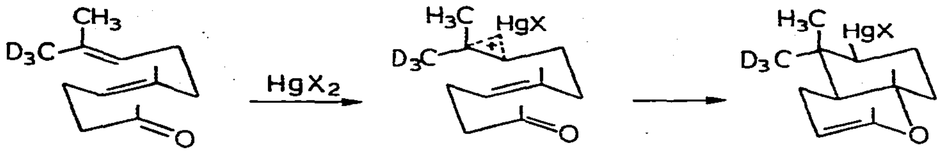


The hydroxymercuration product of cyclobutene was much more stable but did decompose slowly to cyclopropanecarboxaldehye, especially in strong acid solution:



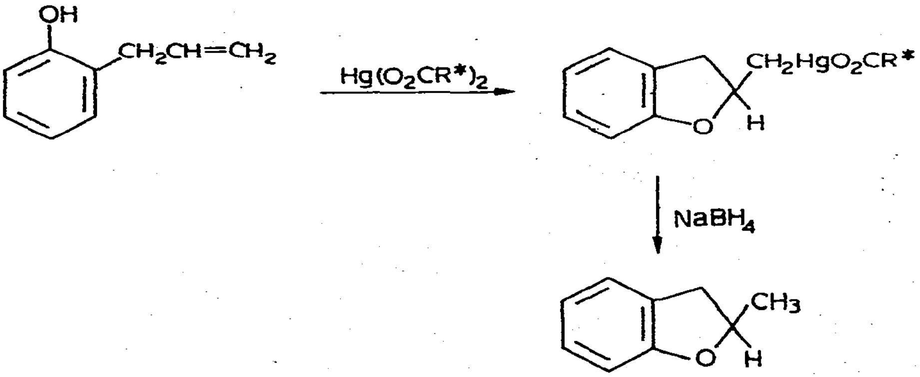
Results obtained in studies of the kinetics and mechanism of α,β-unsaturated ketones (81), esters (81, 82) and acids (82) also have been interpreted using the mercurinium ion intermediate hypothesis.

As indicated above, the stereochemical course of oxymercuration of acyclic olefins usually involves *anti* addition. A thorough study of the methoxymercuration of *trans*- and *cis*-ethylene-1,2-d_2 by NMR has provided full confirmation of this (83): the *trans* compound gave *erythro*-1,2-dideuterio-2-methoxyethylmercuric chloride; the *cis* compound gave the *threo* isomer. Such *anti* stereochemistry was observed in a case where the nucleophile attacking the positively charged intermediate was a C=C unit within the same molecule (84):



Further examples of more synthetically oriented solvomercurations or of the solvomercuration-demercuration sequence may be mentioned.

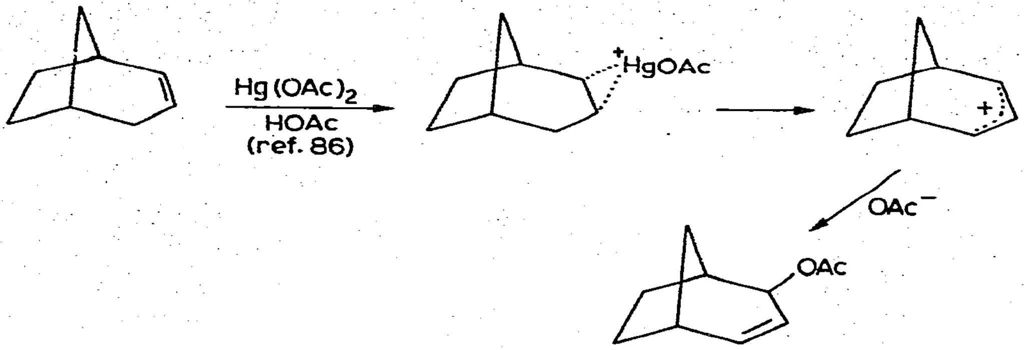
It has been found that the cyclizing oxymercuration of *o*-allylphenol with mercuric salts of chiral carboxylic acids, followed by demercuration of the products with sodium borohydride, gave optically active 2,3-dihydro-2-methylbenzofuran (85):



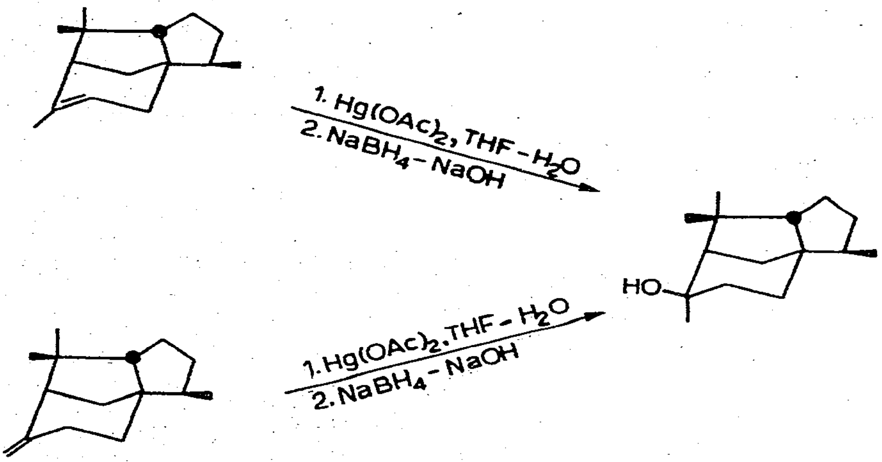
The extent of asymmetric induction was low (< 5% excess of enantiomer). DMSO (4 moles per mole of mercuric carboxylate) favors this process and the highest optical yields were obtained with mercury(II) salts of amino acids (e.g., Hg[(S)-valinate]$_2$.

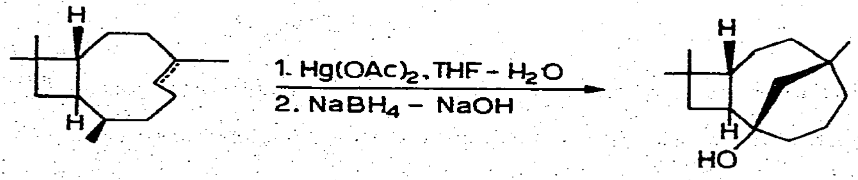
Other organic compounds which were investigated:

bicyclic olefins (86):

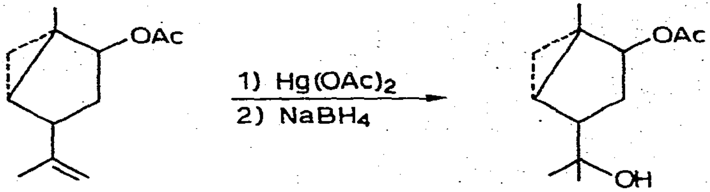


terpenes (87):

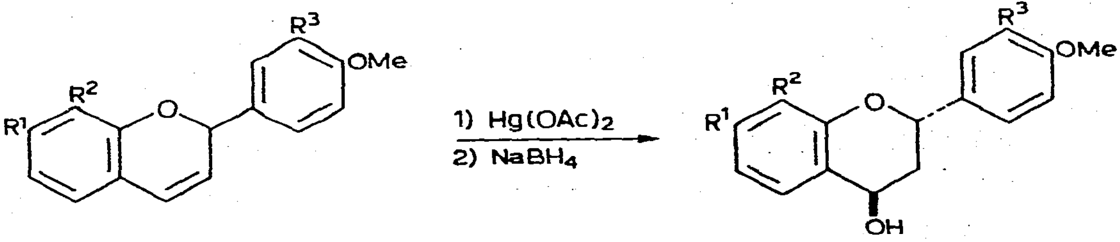




and (88):

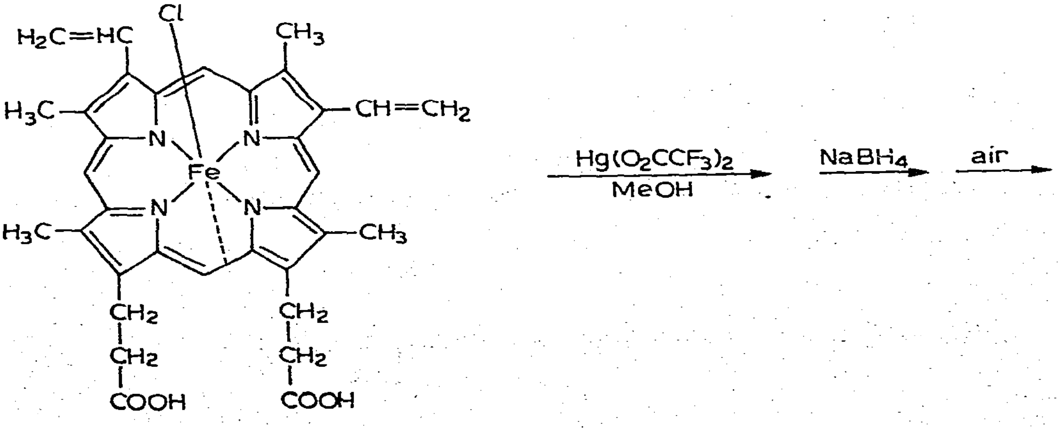


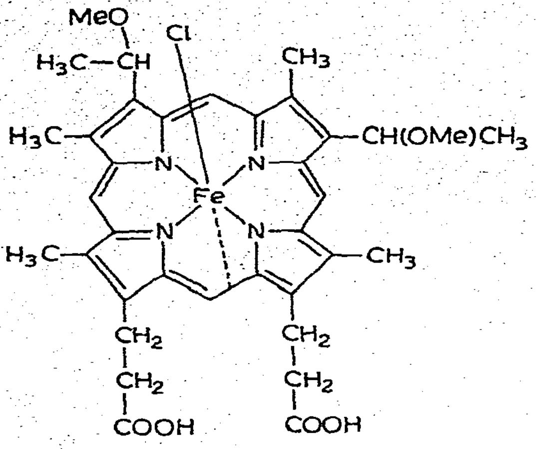
flavenes (89):



	R^1	R^2	R^3
(2)	H	H	H
(3)	OMe	H	H
(4)	Me	H	H
(5)	OMe	OMe	OMe
(6)	OMe	OMe	H

vinylprotohemins (90):





<u>long chain unsaturated esters</u> (91): Examples of the methoxy- acetoxy-, and acetylamino-mercuration of methyl oleate, with subsequent demercuration with $NaBH_4$.

<u>vinyl ethers</u> (92):

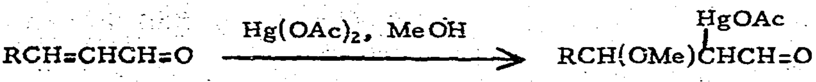
$$ROCH{=}CH_2 + Hg(OAc)_2 \longrightarrow AcOHgCH_2CH(OR)OAc$$

$$ROCH{=}CH_2 + Hg(OAc)_2 \xrightarrow{MeOH} AcOHgCH_2CH(OR)\ (OMe)$$

(R = Ac, Et, n-Bu, c-C_6H_{11},
Ph, p-$O_2NC_6H_4$)

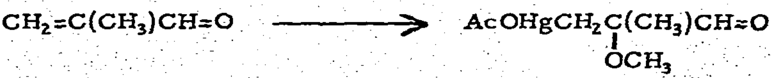
(These adducts were stable only below 0°. Treatment with aqueous NaCl converted them to $ClHgCH_2CH{=}O$).

<u>α, β-unsaturated aldehydes</u> (93):

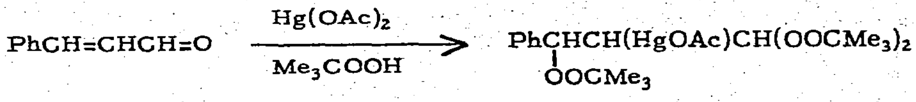


$$RCH{=}CHCH{=}O \xrightarrow{Hg(OAc)_2,\ MeOH} RCH(OMe)\overset{\displaystyle HgOAc}{C}HCH{=}O$$

(R = CH_3, C_6H_5)

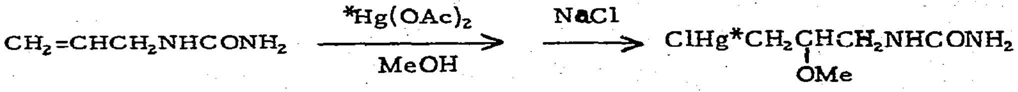


$$CH_2{=}C(CH_3)CH{=}O \longrightarrow AcOHgCH_2\underset{\displaystyle OCH_3}{C}(CH_3)CH{=}O$$



$$PhCH{=}CHCH{=}O \xrightarrow[Me_3COOH]{Hg(OAc)_2} Ph\underset{OOCMe_3}{CH}CH(HgOAc)CH(OOCMe_3)_2$$

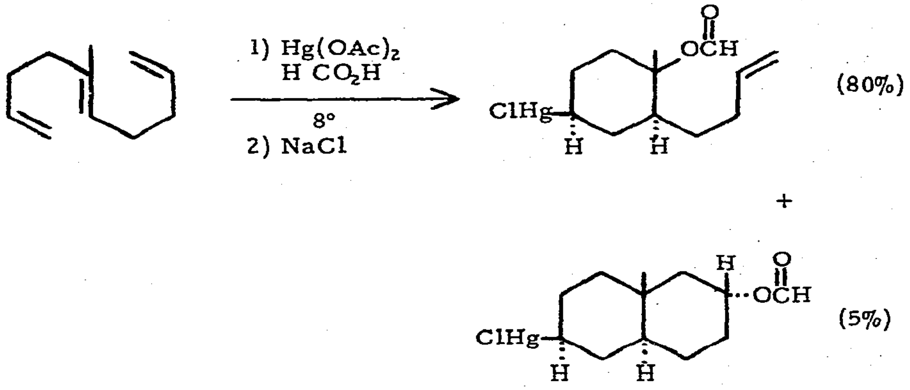
allyl urea (labelled mercury) (94):



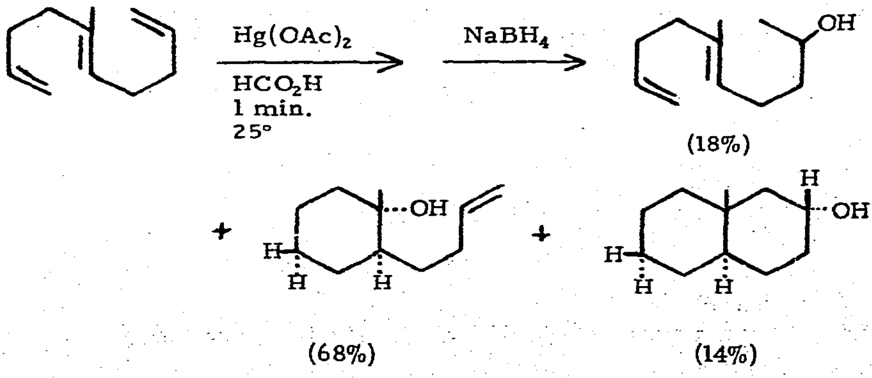
$$CH_2{=}CHCH_2NHCONH_2 \xrightarrow[MeOH]{^*Hg(OAc)_2} \xrightarrow{NaCl} ClHg^*CH_2\underset{OMe}{CH}CH_2NHCONH_2$$

(with ^{197}Hg and ^{203}Hg)

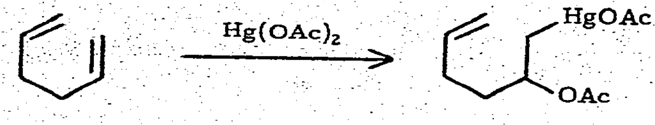
a triene (95):



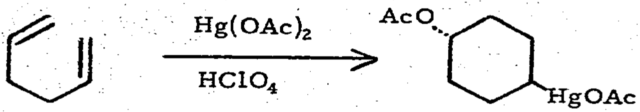
Also carried out were mercuration-demercuration sequences:



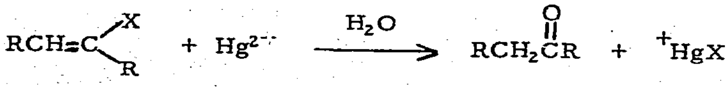
Similar cyclizations were observed with dienes (96), but only in the presence of an acid catalyst:



but



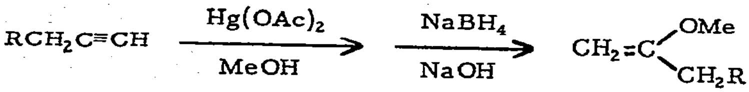
vinyl halides (97):



$$RCH{=}C(X)R + Hg^{2+} \xrightarrow{H_2O} RCH_2\overset{O}{\overset{\|}{C}}R + {}^{+}HgX$$

(via $R\underset{Hg^{+}}{CH}$-CH(OH)XR and β-elimination of HgX^{+} from this intermediate).

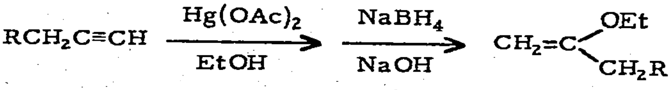
terminal acetylenes (98):



$$RCH_2C\equiv CH \xrightarrow[MeOH]{Hg(OAc)_2} \xrightarrow[NaOH]{NaBH_4} CH_2{=}C(OMe)CH_2R$$

(65%)

(R = n-C_5H_{11})

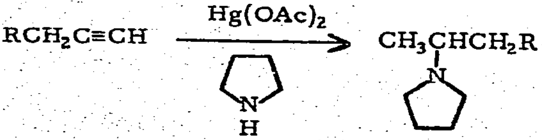


$$RCH_2C\equiv CH \xrightarrow[EtOH]{Hg(OAc)_2} \xrightarrow[NaOH]{NaBH_4} CH_2{=}C(OEt)CH_2R$$

(36%) + $(RCH_2C\equiv C)_2Hg$

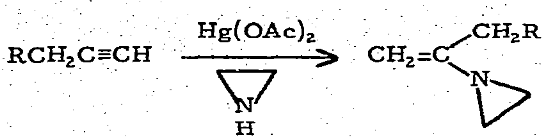
but:

$RCH_2C\equiv CH \xrightarrow[Me_3COH]{Hg(OAc)_2}$ only $(RCH_2C\equiv C)_2Hg$



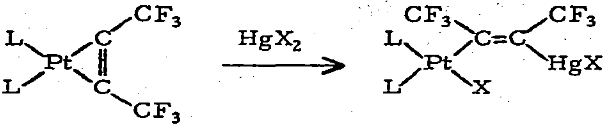
(not the enamine)

(80%)



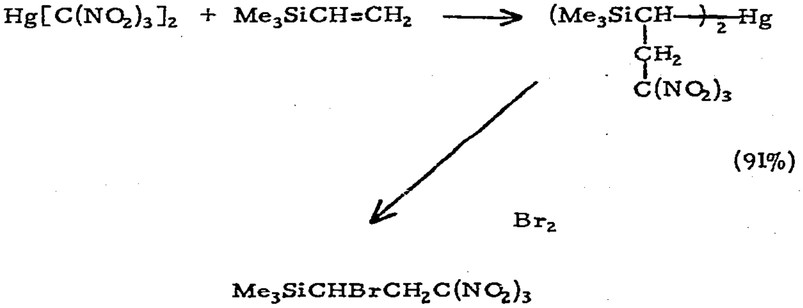
(18%)

Of special interest is the mercuration of an acetylene while it is coordinated to a transition metal (99):

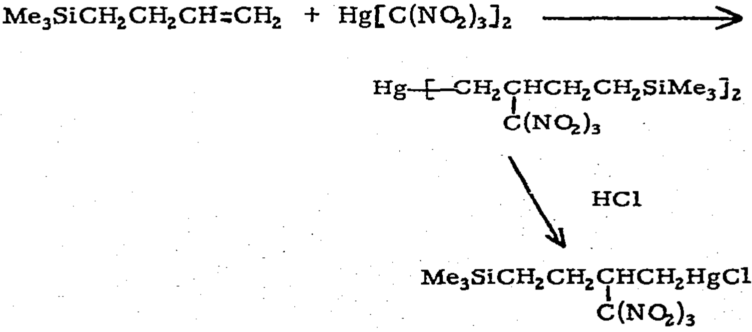


(L = Ph_3P, Ph_2MeP; X = Cl, Br)

The addition of mercurials containing only Hg-C bonds to unsaturated systems has been reported. Alkenylsilanes have been mercurated with $Hg[C(NO_2)_3]_2$ (100):

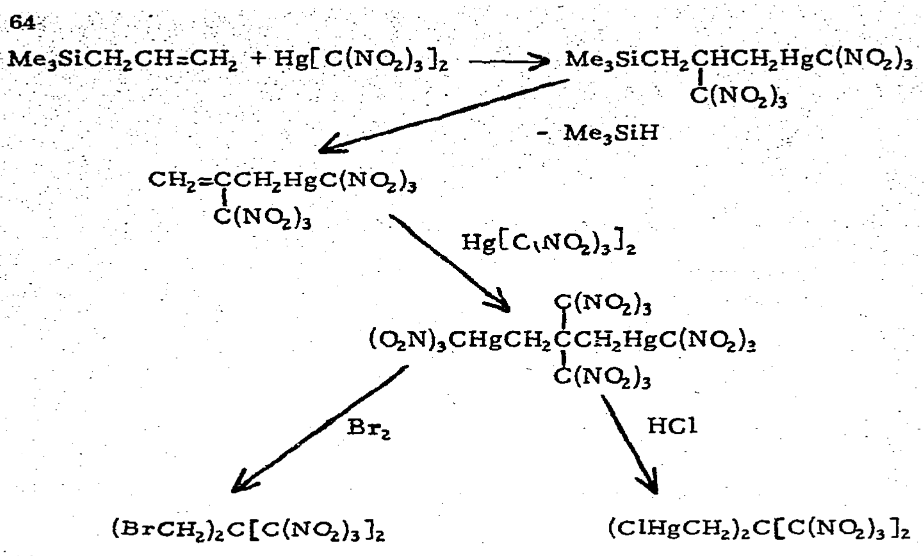


$$Hg[C(NO_2)_3]_2 + Me_3SiCH{=}CH_2 \longrightarrow (Me_3SiCH(CH_2C(NO_2)_3))_2Hg \xrightarrow{Br_2} Me_3SiCHBrCH_2C(NO_2)_3$$

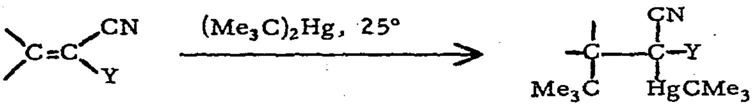


$$Me_3SiCH_2CH_2CH{=}CH_2 + Hg[C(NO_2)_3]_2 \longrightarrow Hg[CH_2CH(C(NO_2)_3)CH_2CH_2SiMe_3]_2 \xrightarrow{HCl} Me_3SiCH_2CH_2CH(C(NO_2)_3)CH_2HgCl$$

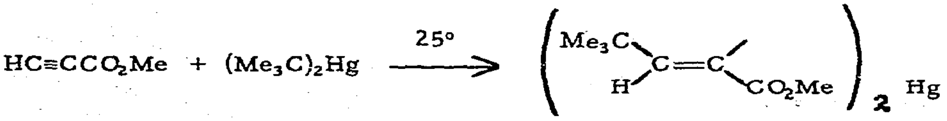
With allyltrimethylsilane loss of the trimethylsilyl group was observed, giving $[(O_2N)_3CHgCH_2]_2C[C(NO_2)_3]_2$ as final product:

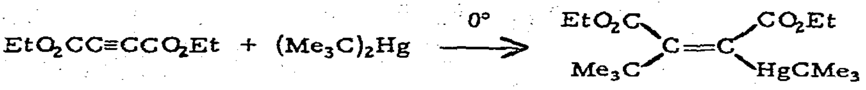


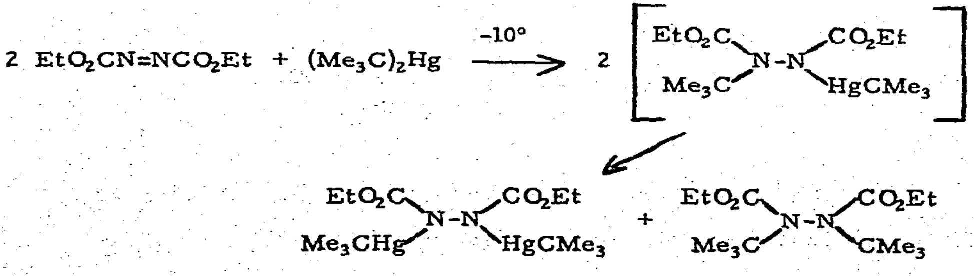
While such additions of the very polar $Hg[C(NO_2)_3]_2$ are not surprising, the addition reactions of di-tert-butylmercury to strongly activated C=C linkages, as well as to some C≡C and N=N bonds are noteworthy (101):



(Occurs with $Me_2C{=}C(CN)_2$, $Me_2C{=}C(CN)CO_2Et$, $PhCH{=}C(CN)_2$, $p\text{-}MeC_6H_4\text{-}CH{=}C(CN)_2$, $p\text{-}ClC_6H_4CH{=}C(CN)_2$)







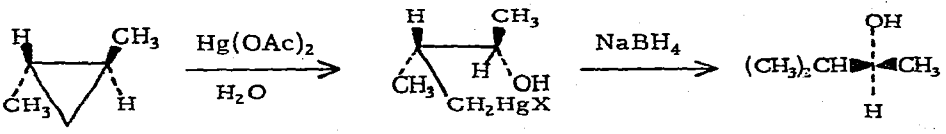
Demercuration of the products was easily effected with organotin hydrides:

$$Me_3CHgZ + R_3SnH \xrightarrow[\text{(exothermic)}]{\text{benzene, 0°}} R_3SnZ + Hg + i\text{-}C_4H_{10}$$

For most of these addition reactions the authors assumed a polar, 4-center transition state, but radical processes occurred as well.

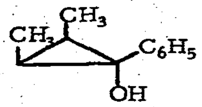
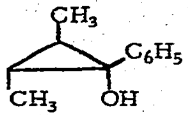
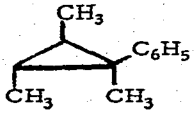
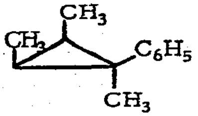
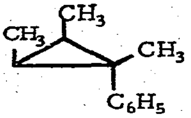
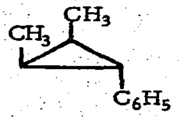
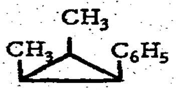
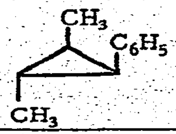
B. Cyclopropanes and Cyclopropenes

The stereochemistry of the oxymercuration of cyclopropanes, which results in opening of the three-membered ring, has been studied by two groups (review: ref. 2). Sokolov et.al. (102) established that during hydroxymercuration of optically active trans-1,2-dimethylcyclopropane the nucleophilic attack by OH^- occurs with predominant inversion of configuration:



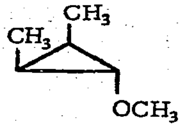
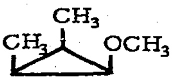
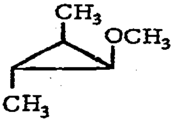
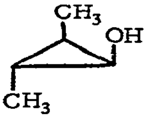
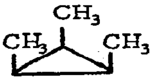
A more comprehensive study of the methoxymercuration of cyclopropanes has been reported by DePuy and McGirk (103). This work showed that the stereochemistry of the reaction of the RCO_2Hg^+ species is generally determined by its attack at the least substituted C-C bond of the ring; that the nucleophile reacts almost exclusively with inversion; that in a completely symmetrical system (all ring bonds identical), inversion predominates slightly in the attack by RCO_2Hg^+. The results obtained with cis, cis-1,2,3-trimethylcyclopropane demonstrate the latter point:

Table 9. The Stereochemistry of Cyclopropane Ring Opening by Mercuric Acetate (from C. H. DePuy and R. H. McGirk, J. Amer. Chem. Soc., 95 (1973) 2366)

Compound	Stereochemistry of electrophilic attack (% inversion)[a]	Stereochemistry of nucleophilic attack (% inversion)[a]
	100[b]	
	100[b]	
	100	100
	100	100
	100	100
	72	75
	82	91
	12	90

(continued)

Table 9. (Continued)

	95	
	40	
	10	
	<5	
	62	100

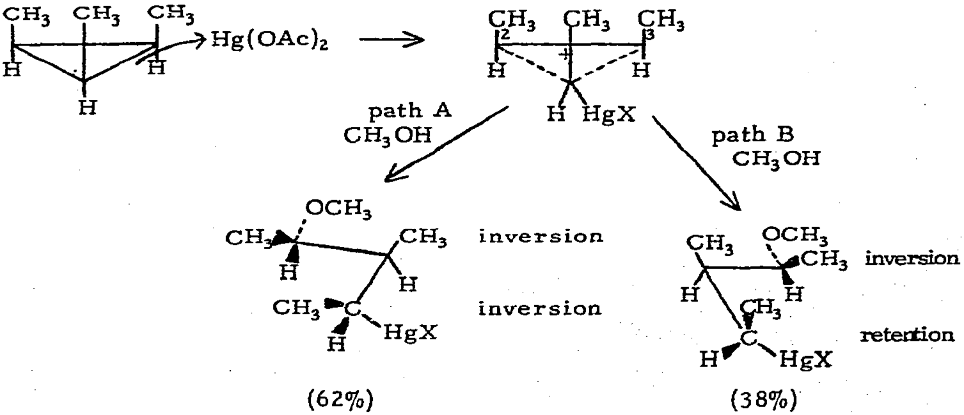
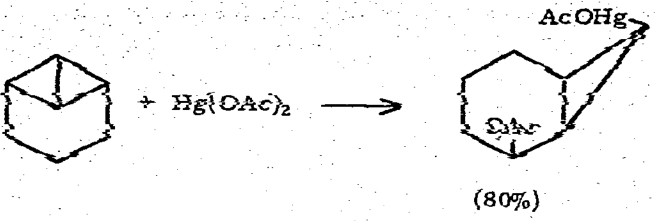


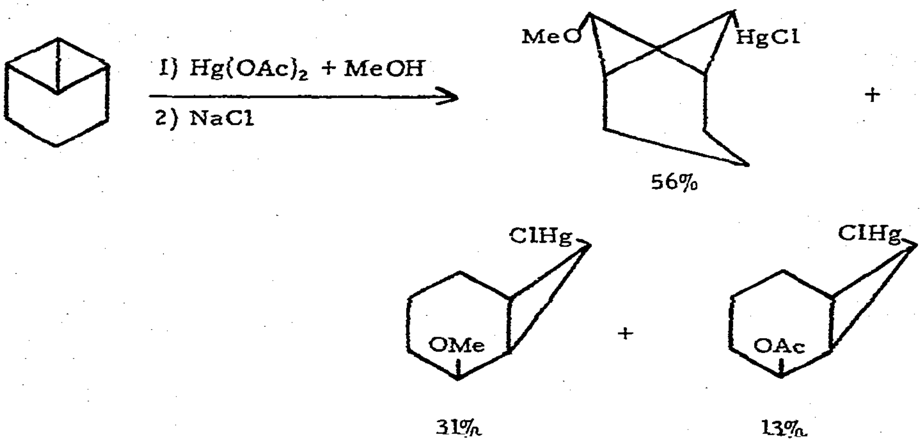
Table 9 shows the stereochemical results.

Ring opening of tricyclo[4.1.0.$0^{2,7}$]heptane by Hg(II) compounds has been described by Müller (104, 105). Oxymercuration was carried out under various condition:

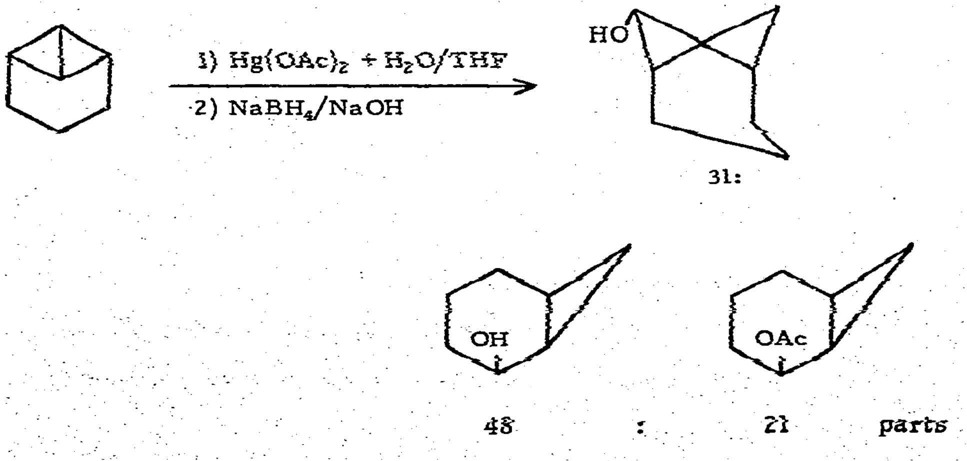
Mercuric acetate in CCl_4 or THF:



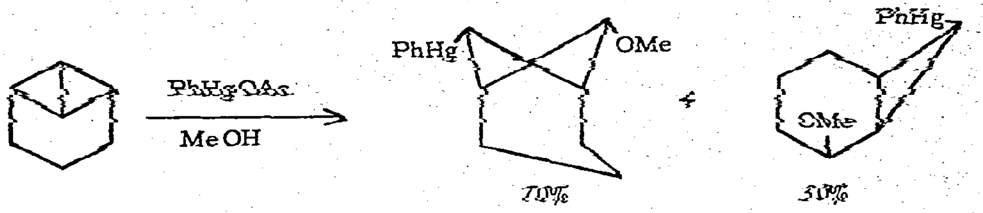
Mercuric acetate in methanol:



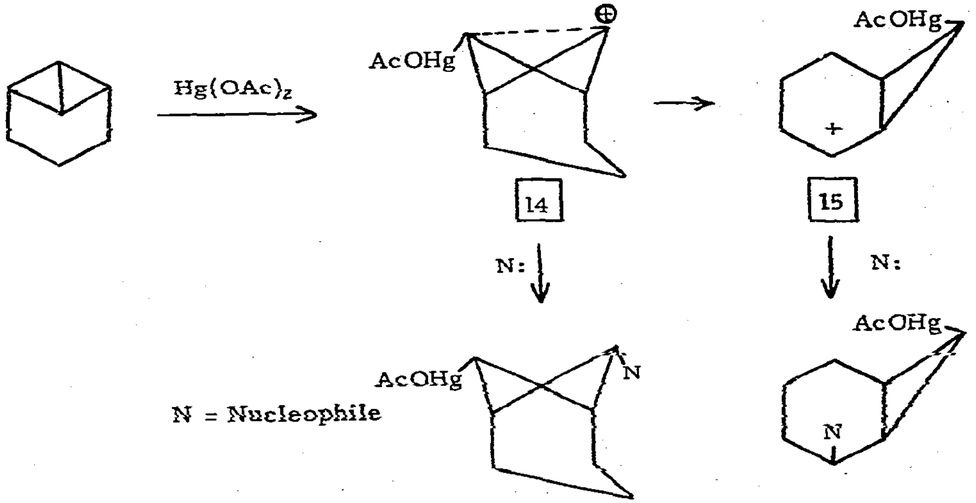
Mercuric acetate in aqueous tetrahydrofuran:



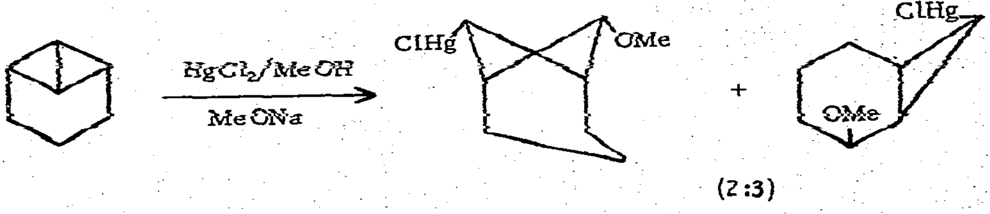
Phenylmercuric acetate in methanol:



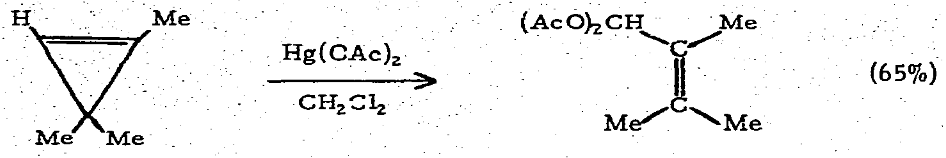
The suggested mechanism is as follows:



Ion $\boxed{14}$ rearranges rapidly to $\boxed{15}$ and thus can be intercepted only by strong nucleophiles such as methanol. In the absence of strong nucleophiles, products derived from $\boxed{15}$ are obtained. Other reactions studied included:

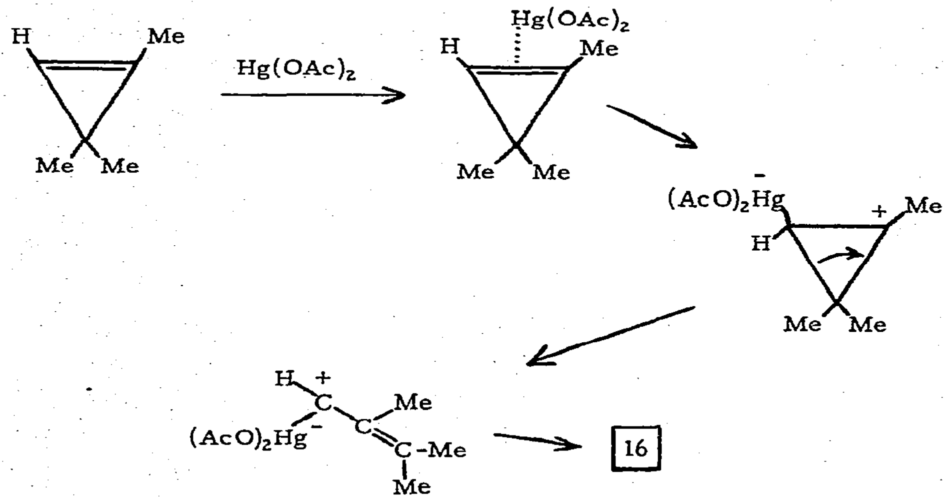


The oxidative cleavage of cyclopropenes has been investigated by Japanese workers (106):



16

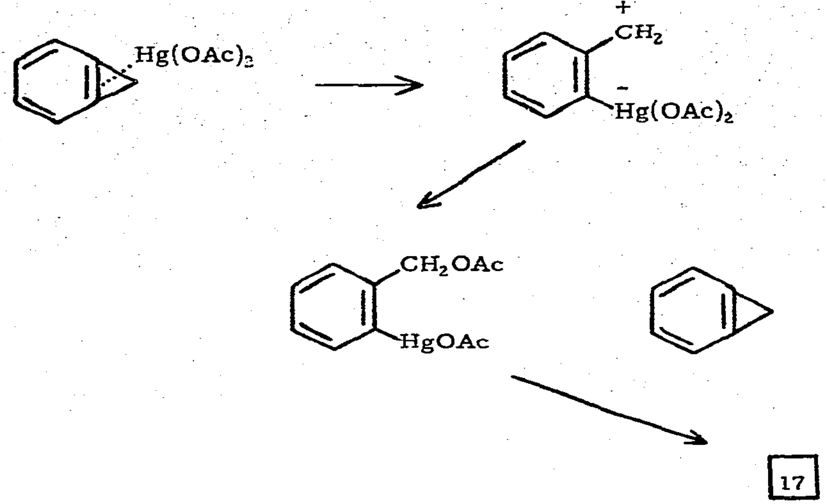
The following reaction course was postulated:



The reaction of benzocyclopropene with mercuric acetate also was examined:

17

This reaction was postulated to proceed <u>via</u>:



C. Aromatic Compounds

The mercuration of benzene with mercuric trifluoroacetate is an excellent route to $PhHgO_2CCF_3$ (107):

$$Hg(O_2CCF_3)_2 + C_6H_6 \xrightarrow[\substack{[BF_3\cdot OEt_2] \\ 1\text{ hr., } 20^\circ}]{ClCH_2CH_2Cl} \underset{(99\%)}{C_6H_5HgO_2CCF_3} + CF_3CO_2H$$

The reaction is first order in each reactant and the activation energy is 13.2 kcal/mol. The direct mercuration of tetrafluorobenzenes with mercuric trifluoroacetate was found to be a good route to tetrafluorophenylmercurials (108):

$$ArH + Hg(O_2CCF_3)_2 \xrightarrow{160-200^\circ} ArHgO_2CCF_3 + CF_3CO_2H$$

(Ar = o-HC_6F_4, m-HC_6F_4, p-$MeOC_6F_4$, o-$O_2NC_6F_4$)

Dimercuration also was possible:

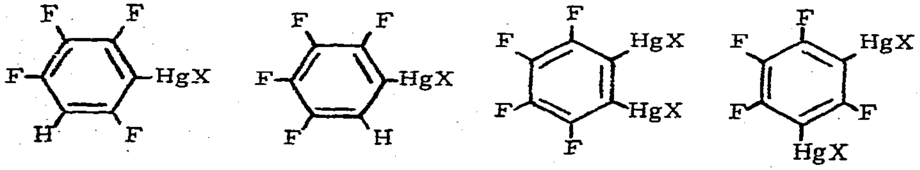
$$\text{o- or m-}H_2C_6F_4 + 2\ Hg(O_2CCF_3)_2 \longrightarrow 2\ CF_3CO_2H + \text{o- or m-}(CF_3CO_2Hg)_2C_6F_4$$

Mercuration of p-$MeOC_6F_4H$ with $HgBr_4^{2-}$ under basic conditions in aqueous tert-butanol gave a good yield of (p-$MeOC_6F_4)_2Hg$, but this procedure proved not to be a useful synthetic route to other tetrafluorophenylmercurials. The tetrafluorophenylmercuric trifluoroacetates prepared during the course of this study were symmetrized:

$$ArHgO_2CCF_3 + 4\ X^- \xrightarrow{MeOH} Ar_2Hg + HgX_4^{2-} + 2\ CF_3CO_2^-$$

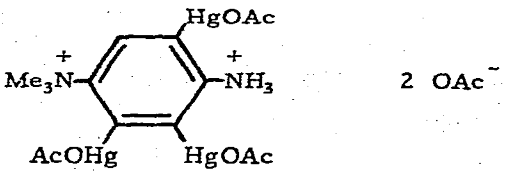
$$(X = Cl,\ Br)$$

and converted to the respective arylmercuric halides and acetates by diverse metathesis reactions. Among the compounds prepared were:



(X = Cl and Br)

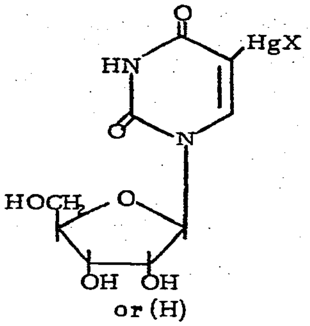
The action of aqueous mercuric acetate on (trimethylammonium)-anilinium diacetate gave a trimercurated product, $\boxed{18}$ (109).



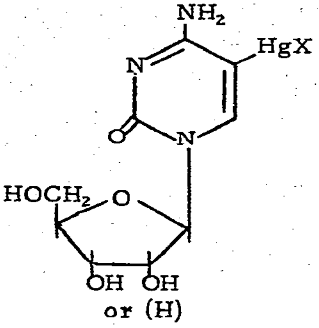
$\boxed{18}$

This synthesis was carried out as part of a program for the localization of pharmacological receptor sites by electron microscopy. Another group has prepared several 5'-triphosphates of the mercuri-nucleotides

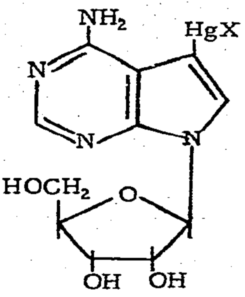
$\boxed{19}$ $\boxed{20}$ and $\boxed{21}$ by direct mercuration with mercuric acetate (110).



$\boxed{19}$



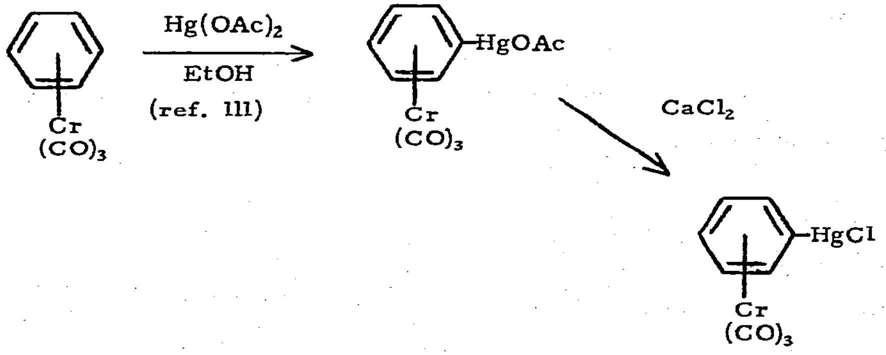
$\boxed{20}$



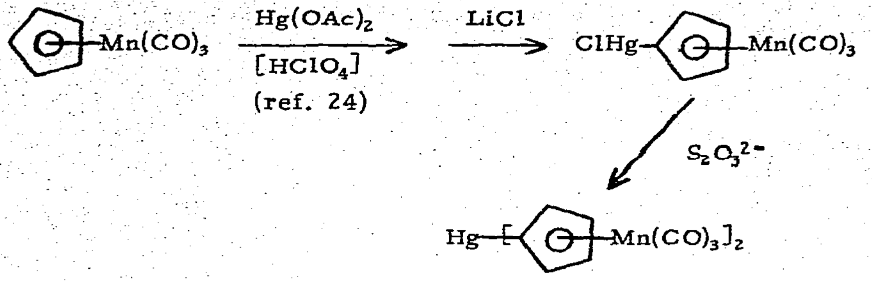
$\boxed{21}$

These compounds (X = OAc), in the absence of added mercaptan, were not polymerized. Addition of mercaptans gave the thiomercuri analogs (X = SR) which were found to be excellent substrates for all polymerases tested. Important biological applications of these novel mercurials were suggested.

The direct mercuration of transition metal complexes of aromatic molecules is a known reaction. New examples have been reported:



As expected, benzenechromium tricarbonyl is less reactive toward (electrophilic) mercuration than is uncomplexed benzene.



Detailed directions for the preparation (by direct mercuration of ferrocene) and purification of chloromercuriferrocene and 1,1'-bis(chloromercuri)ferrocene have been provided by Rausch et al. (112).

5. ORGANOFUNCTIONAL ORGANOMERCURY COMPOUNDS

A. Highly Halogenated Organomercurials

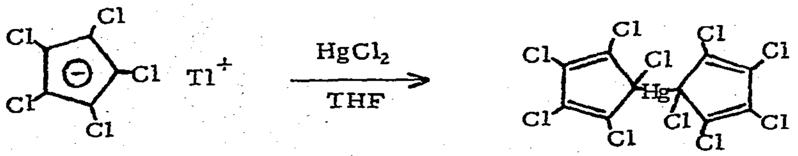
Reference already has been made to some compounds of this class in previous sections:

polyfluoroarylmercurials (15, 16, 18, 19)

polychloroarylmercurials (18, 19)

halomethylmercurials (Section 3C)

Wulfsberg, West and Rao have prepared pentachlorocyclopentadienyl mercury compounds (113):



or better:

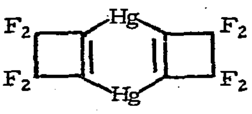
$$Hg(OAc)_2 \xrightarrow{LiOMe} (MeO)_2Hg \xrightarrow{3\ C_5Cl_5H,\ 0^\circ} (C_5Cl_5)_2Hg$$

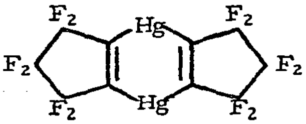
$$PhHgOH \xrightarrow[Me_2C(OMe)_2]{C_5Cl_5H} PhHgC_5Cl_5$$

$$(C_5Cl_5)_2Hg + HgX_2 \longrightarrow 2\ C_5Cl_5HgX \qquad (X = Cl, Br)$$

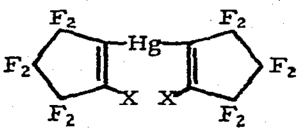
This work was complicated by the formation of several different crystalline modifications of some of these compounds, of adducts with THF, DME and diglyme, of adducts of the C_5Cl_5HgX compounds with mercuric halides. The presence of a σ-bonded pentachlorocyclopentadienyl group in these compounds was indicated by IR, NQR and UV spectral data. The electronic spectra provided evidence for σ-π conjugation between the C-Hg bond and the cyclopentadienyl π orbitals. Thermolysis of the pentachlorocyclopentadienyls proceeded by homolytic C-Hg bond scission, not by α-elimination of Hg-Cl to give the tetrachlorocyclopentadienylidene carbene. Also, nucleophilic displacement of the pentachlorocyclopentadienide anion from mercury was a facile process, with even chloride ion being a sufficiently strong nucleophile. Transfer of C_5Cl_5 from these mercurials to transition metals, to make perchlorometallocenes, could not be realized.

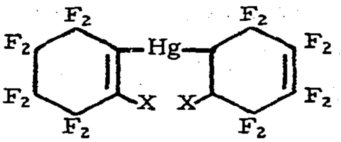
Mercury derivatives of polyfluorinated cycloalkenes also were accessible by the organolithium route (114):





(These most likely are oligomeric - possibly trimeric - so that the mercury atoms can maintain their preferred colinear bonds).





B. Carboranyl-Mercurials

Russian workers have continued their studies of carborane-substituted organomercury compounds. Methylmercury derivatives of 1,6- and 1,10-dicarba-closo-decaboranes (10) have been prepared by reaction of the appropriate lithio-carborane derivative with methylmercuric chloride or mercuric bromide (115). The compounds prepared included:

1-Ph-6-MeHg-1,6-$B_8C_2H_8$	1-Ph-10-MeHg-1, 10-$B_8C_2H_8$
(1-Ph-1, 6-$B_8C_2H_8$-6-$)_2$Hg	(1-Ph-1, 10-$B_8C_2H_8$-10-$)_2$Hg

The action of bromine (in benzene at 25°) resulted in cleavage of the methyl, not the carboranyl, group from mercury. Reactions of these carboranes were studied:

$$(1\text{-Ph-1, 10-}B_8C_2H_8\text{-10-})_2Hg + HgBr_2 \xrightarrow{\text{PhCl, reflux}} 2\ 1\text{-Ph-10-BrHg-1, 10-}B_8C_2H_8$$

$$(1\text{-Ph-1, 10-}B_8C_2H_8\text{-10-})_2Hg + 2\ BuLi \longrightarrow Bu_2Hg + 2\ 1\text{-Ph-10-Li-1, 10-}B_8C_2H_8$$

$$1\text{-Ph-10-MeHg-1, 10-}B_8C_2H_8 \xrightarrow[\text{reflux}]{KOH,\ H_2O/C_6H_6} 1\text{-Ph-1, 10-}B_8C_2H_8$$

$$1\text{-Ph-10-MeHg-1, 10-}B_8C_2H_8 \xrightarrow[78°]{HCl,\ EtOH} 1\text{-Ph-1, 10-}B_8C_2H_8 + MeHgCl$$

Halomercury derivatives of 1,2-dicarba-closo-dodecaboranes (12) (ortho-carboranes) could not be symmetrized by standard methods (NaCN, KI, NH_3), but anion radicals achieved this transformation (116):

$$B_{10}H_{10}(PhC_2HgCl) \xrightarrow[THF]{} [B_{10}H_{10}(PhC_2\text{-})]_2Hg$$

The required chloromercury derivatives were prepared in high yield by chlorinolysis of $B_{10}H_{10}(PhC_2HgEt)$. Chloromercury derivatives of o- and m-carborane also were obtained by cleavage of σ-$Fe(CO)_2C_5H_5$-substituted carboranes (8).

Carboranes containing $Me_2C=CHHg$ substituents also have been synthesized (117): $B_{10}H_{10}(MeC_2HgCH=CMe_2)$ and $1,7$-$MeCB_{10}H_{10}CHgCH=CMe_2$.

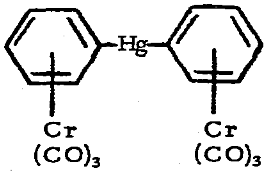
Simple organoboron compounds containing chloromercury substituents have been studied by Matteson (118):

$$[(MeO)_2B]_2CH_2 + HgCl_2 \xrightarrow{NaOAc} ClHgCH_2B(OMe)_2$$

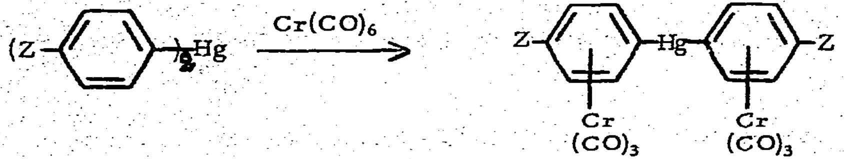
The mechanism of such mercurideboronations was studied (cleavage rates of $RCH_2B(OMe)_2$ by $HgCl_2$ in acetate-buffered methanol; R = H, $(MeO)_2B$, ClHg, Ph, n-Pr) and a direct interaction of the neighboring (non-displaced) boron atom with attacking $HgCl_2$ was suggested.

C. Metallocene-Mercurials

Mercury derivatives of ferrocene and cyclopentadienylmanganese tricarbonyl already have been mentioned in previous sections (24, 28, 34, 35). Also mentioned has been the mercuration of benzenechromium tricarbonyl (111). The compound $\boxed{22}$ can be prepared by reaction of diphenylmercury with chromium hexacarbonyl, as indicated in last year's Survey (J. Organometal. Chem., 62 (1973) 117). Further work has shown this to be a general reaction (119):



$\boxed{22}$



(Z = Me_2N, MeO, Me,
H, F)

As expected, electron-releasing substituents facilitate this reaction.

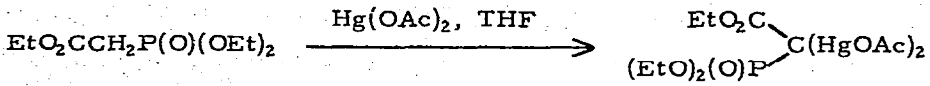
D. Organophosphorus-substituted Mercurials

Direct reaction of phosphonic acid esters containing activating groups with mercuric acetate gave a series of mercurated phosphonate esters (120):

$$[(EtO)_2P(O)]_2CH_2 + 2Hg(OAc)_2 \xrightarrow{EtOH} [(EtO)_2P(O)]_2C(HgOAc)_2 \ (95\%) + 2\ HOAc$$

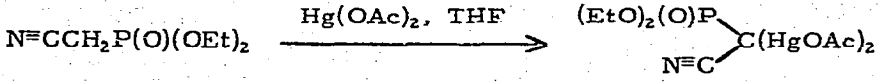
$$[(EtO)_2P(O)]_2CHCl + Hg(OAc)_2 \longrightarrow [(EtO)_2P(O)]_2CClHgOAc + HOAc$$

(55%)



$$EtO_2CCH_2P(O)(OEt)_2 \xrightarrow{Hg(OAc)_2,\ THF} (EtO_2C)((EtO)_2(O)P)C(HgOAc)_2$$

(39%)



$$N{\equiv}CCH_2P(O)(OEt)_2 \xrightarrow{Hg(OAc)_2,\ THF} ((EtO)_2(O)P)(N{\equiv}C)C(HgOAc)_2$$

(99%)

Reactions of $\boxed{23}$ were examined briefly:

$$[(EtO)_2P(O)]_2C(HgOAc)_2 \xrightarrow{HgX_2/THF} [(EtO)_2P(O)]_2C(HgX)_2$$

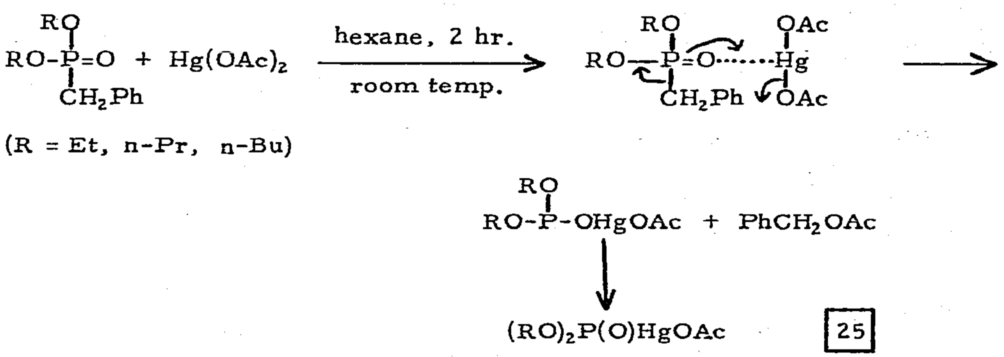
$\boxed{24}$

$$\boxed{24} \xrightarrow{2\ Ph_2Hg} [(EtO)_2P(O)]_2C(HgPh)_2$$

$$\xrightarrow{Cl_2} [(EtO)_2P(O)]_2CCl_2\cdot HgCl_2$$

$$\xrightarrow{H_2S/EtOH} [(EtO)_2P(O)]_2CH_2 + HgS + 2\ HOAc$$

Such mercuration was found not to occur with $PhCH_2P(O)(OEt)_2$. This reaction was studied in detail by Egyptian workers (121). The reaction course found was:

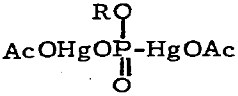


$$(RO)_2P(O)CH_2Ph + Hg(OAc)_2 \xrightarrow[\text{room temp.}]{\text{hexane, 2 hr.}} (RO)_2P(CH_2Ph){=}O\cdots Hg(OAc)_2 \longrightarrow (RO)_2P{-}OHgOAc + PhCH_2OAc \longrightarrow (RO)_2P(O)HgOAc$$

(R = Et, n-Pr, n-Bu)

25

Compounds of type $\boxed{25}$ are known and their reaction with mercuric acetate in acetic acid at 100° led to a dimercurated product:



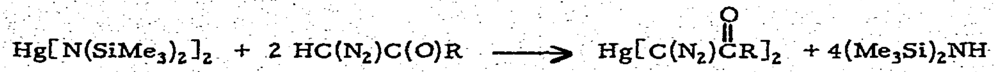
$$AcOHgOP(O)(OR){-}HgOAc$$

E. Mercurated Diazoalkanes and Carbenes

The chemistry of mercurated diazoalkanes, which has been the subject of much study in the last few years, has continued to receive attention. Organomercury-diazoketones have been prepared:

$$RHgN(SiMe_3)_2 + HC(N_2)C(O)R' \longrightarrow RHgC(N_2)C(O)R' + (Me_3Si)_2NH$$

(R = Me, Et; R' = Me, Ph)



$$Hg[N(SiMe_3)_2]_2 + 2\ HC(N_2)C(O)R \longrightarrow Hg[C(N_2)\overset{O}{\overset{\|}{C}}R]_2 + 4(Me_3Si)_2NH$$

All four compounds were obtained in the form of yellow crystals; their mass, proton NMR and vibrational spectra were discussed in detail (122).

Another synthesis of mercurated diazoalkanes is based on reactions of organomercuric alkoxides and hydroxides (123):

$$RHgCl \xrightarrow[EtOH]{EtOK} RHgOEt \xrightarrow{HC(N_2)Y} RHgC(N_2)Y + EtOH$$

$$RHgOH + HC(N_2)Y \xrightarrow{EtOH} RHgC(N_2)Y + H_2O$$

Examples: (1) R = Me, Et, i-Pr, Me_3C, $PhCH_2$, Ph; Y = CO_2Me

(2) R = Me, Ph; Y = CO_2Et

(3) R = Ph; Y = C(O)Me

(4) R = Me; Y = CN

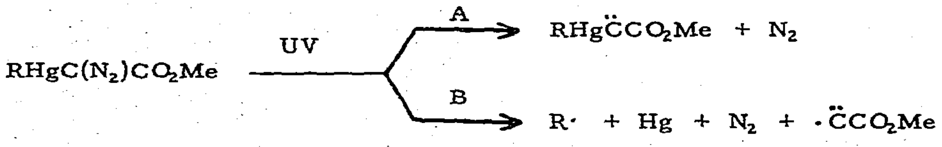
(5) R = Me; Y = Ph

(6) R = Me; Y = Me

(7) R = Me; Y = HgMe

(These compounds also were characterized by their mass, IR, UV and NMR spectra).

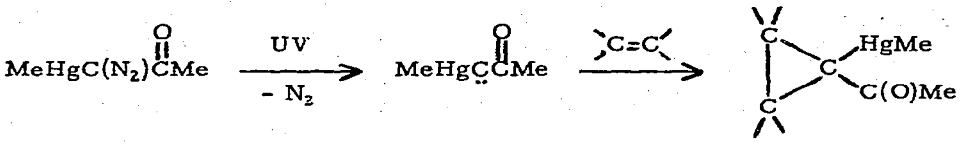
The photolysis of these mercurials proceeds by two pathways (123):



The relative extent to which they occur depends on R, with process B increasing in the order of the R· radical stability: $Me<Et<Ph<Me_2CH \lesssim PhCH_2<Me_3C$. Also, higher energy irradiation favors the fragmentation process. Nearly quantitative yields of the CH_3Hg-substituted carbene were obtained upon irradiation of the long wavelength absorption band of the $CH_3HgC(N_2)Y$ compounds at temperatures below 0°. The most labile tert-

butylmercuri-substituted diazo ester was the best carbyne $(\cdot\ddot{C}CO_2Me)$ source.

The direct photolysis of methylmercuridiazoacetone in olefin medium (>335 nm irradiation) gave 1-methylmercuri-1-acetylcyclopropanes in 70-90% yield (124):



(Olefin: <u>cis</u>- and <u>trans</u>-2-butene, isobutylene, butene-1 and 1,3-butadiene)

Little, if any, of the Wolff rearrangement product was formed and no C-H insertion products were detected. The addition to <u>cis</u>- and <u>trans</u>-2-butene was stereospecific. A singlet ground state thus was suggested for $CH_3Hg\ddot{C}C(O)CH_3$. Similar cyclopropanations could be achieved with $MeHgC(N_2)CO_2Me$, stereospecifically and in high yield. On the other hand, $CH_3Hg\ddot{C}C{\equiv}N$, obtained by photolysis of $MeHgC(N_2)CN$, did not add stereospecifically to <u>cis</u>-butene, and 1,3-butadiene was found to be much more reactive toward this carbene than butene-2 (125). The explanation given for these observations was that the carbene was generated in the singlet state, but that in this case the presence of the α-CH_3Hg group greatly accelerated intersystem crossing to the triplet state (relative to $H\ddot{C}CN$, where the triplet state is less accessible).

The methylmercuri-substituted cyclopropanes were easily converted to the respective halocyclopropanes by halogen cleavage of the C-Hg bond.

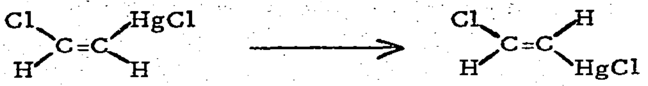
Insertion of $CH_3HgCCO_2CH_3$ into the O-H bond of methanol also occurred readily (123):

$$\begin{tikzcd}
MeHgC(N_2)CO_2Me + MeOH \arrow[r, "UV"] & MeHgCH(OMe)CO_2Me \arrow[d, "NaBH_4"] & (98\%) \\
& CH_2(OMe)CO_2Me &
\end{tikzcd}$$

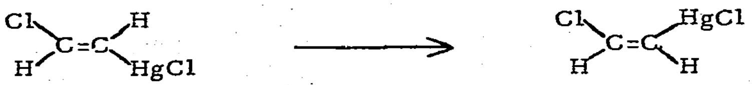
The Wolff rearrangement was shown not to occur in this system.

F. Olefinic Mercurials

The interconversions of cis- and trans-β-chlorovinylmercuric chloride have been studied (126):



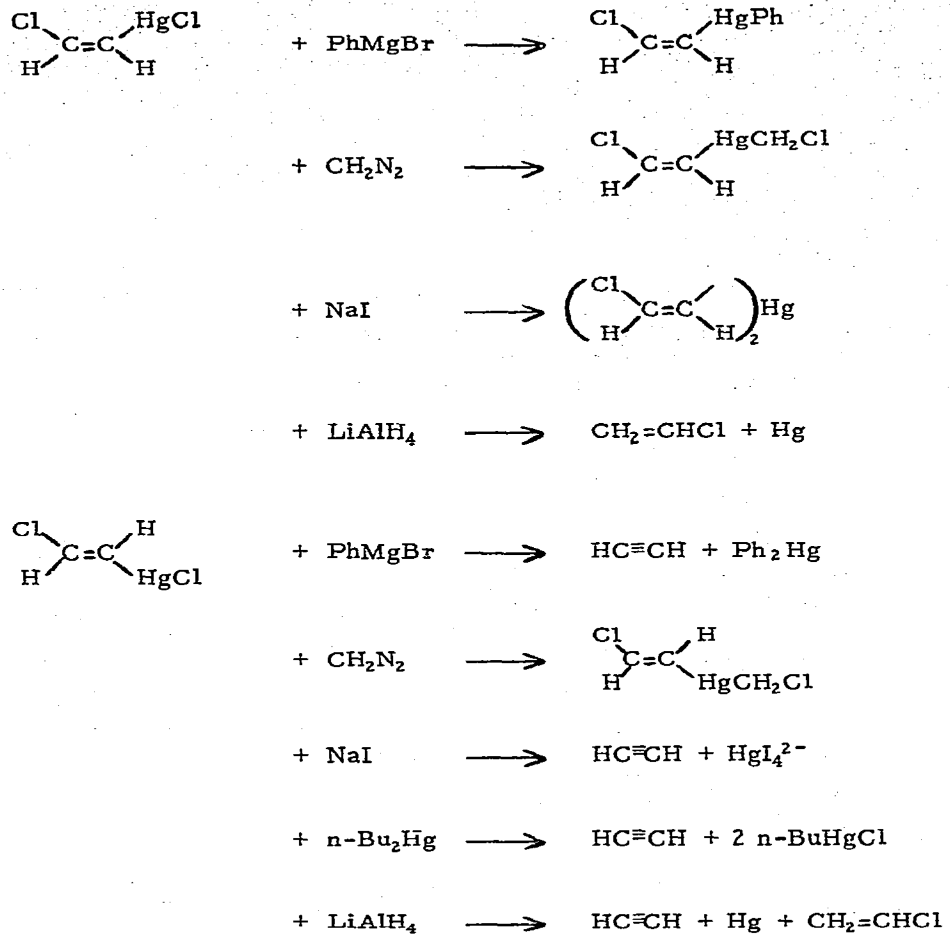
Conditions: 56% after 25 min. at 75-85°;
44% after 3.5 hr. in refluxing benzene;
44% after 50 min. in refluxing benzene containing benzoyl peroxide.



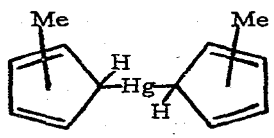
Conditions: 50% after 7 min. at 140-150°;
32% after 10 hr. in refluxing toluene;
57% after 30 min. in refluxing octane

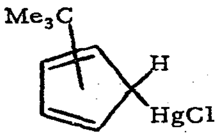
Such thermal isomerizations are believed to involve β-elimination of mercuric chloride followed by its nonstereospecific readdition to acetylene. No isomerization of trans-ClCH=CHHgCl occurred during vacuum sublimation at 100°, on prolonged standing at room temperature in organic solvents or in benzene at 80°. Slow cis ⇌ trans isomerization did take place in THF at room temperature in the presence of 20 mole % of mercuric chloride. Thus, after 24 hr. in separate experiments pure trans-ClCH=CHHgCl was converted to a 68/32 trans/cis mixture and the pure cis isomer to a 61/39 trans/cis mixture.

Some reactions of these compounds were studied (126, 127). Considerable differences were found, with the trans isomer being very prone to undergo β-elimination induced by nucleophiles.

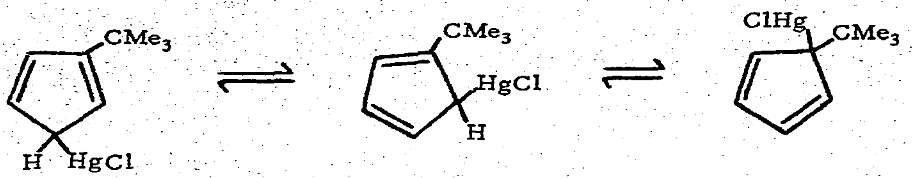


New cyclopentadienylmercury compounds have been prepared by the organolithium route (128):





Variable temperature NMR spectroscopy showed both to have fluxional behavior. Thus there is rapid interconversion among the following forms in the case of tert-butylcyclopentadienylmercuric chloride at room temperature:



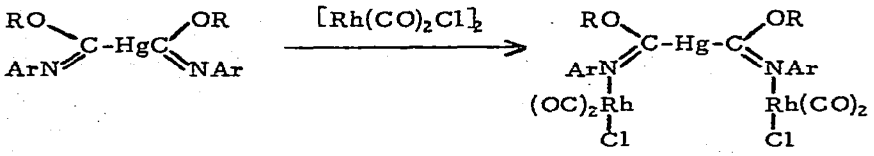
$\boxed{26}$ $\boxed{27}$ $\boxed{28}$

At -96°, however, the molecule is frozen into one of its lowest free energy configurations, either $\boxed{26}$ or $\boxed{27}$; $\boxed{28}$ being unfavorable because of the steric crowding resulting from the geminal substitution.

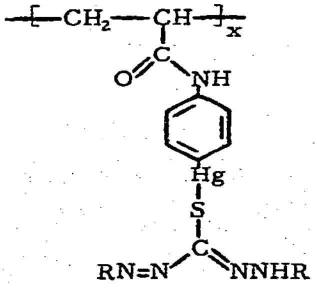
G. Miscellaneous Organofunctionals

The mercurated nucleotides $\boxed{19}$, $\boxed{20}$ and $\boxed{21}$ and their potentially important biological applications (110) have been mentioned in a previous section.

The imino-mercurial $\boxed{29}$ has been found to form complexes, through nitrogen, with transition metal species (129):



Mercurated photochromic polymers of type $\boxed{30}$ have been studied by Japanese workers (130).



$\boxed{30}$

6. C-Hg BOND REACTIONS OF ORGANOMERCURIALS

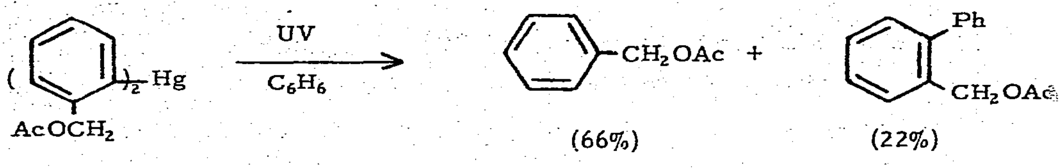
The pyrolysis or photolysis of organomercurials are classical routes to free radicals, and both have been the subject of detailed study by Zhil'tsov and Druzhkov (131). Such decompositions of R_2Hg (R = Me, Et, i-Pr) were carried out in the absence of solvent and in solution (benzene and isopropanol). From the product distributions it was concluded that the "cage effect" is not very important. Methyl radicals generated by pyrolysis of dimethylmercury have been allowed to react with various chlorosilanes and chlorohydrosilanes at 450° (132). It was found that the Si-H bond is much more reactive toward the methyl radical than are the C-H bonds of a CH_3-Si system. Of interest was the formation of silylmethylmercurials during these reactions:

$$Me_2Hg + MeSiCl_3 \xrightarrow{450^\circ} \text{some } (Cl_3SiCH_2)_2Hg$$

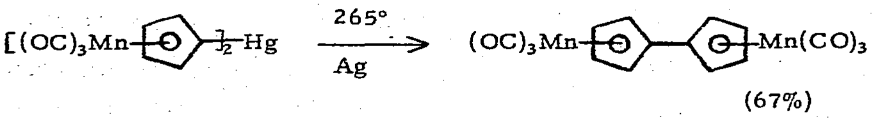
$$Me_2Hg + Me_2SiCl_2 \xrightarrow{450^\circ} \text{some } (MeCl_2SiCH_2)_2Hg$$

These silylmethylmercury compounds were not isolated as such, rather were converted to the known $(Me_3SiCH_2)_2Hg$ by the Grignard reaction. Thermolysis and photolysis of this mercurial also has been investigated by another group (133). It is much more stable than diethyl- or diisopropylmercury. After a heating period of 100 hr at 200° over 95% of the $(Me_3SiCH_2)_2Hg$ was recovered unchanged. The decomposition products which were identified were tetramethylsilane and $Me_3SiCH_2HgCH_2SiMe_2CH_2CH_2SiMe_3$. Photolysis of this mercurial also was not easily effected and gave tetramethylsilane, $(Me_3SiCH_2)_2$, $Me_3SiSiMe_3$, n-$Me_{10}Si_4$, $(Me_3SiCH_2CH_2SiMe_2CH_2)_2$ and $Me_3SiCH_2HgCH_2SiMe_2CH_2CH_2SiMe_3$, all products of $Me_3SiCH_2\cdot$, $Me_3Si\cdot$ and $CH_3\cdot$ radicals generated in the photolysis.

The pyrolysis of $ClHgCH_2CH{=}O$ above 200° gave ketene in an apparently radical process which was facilitated by added benzoyl peroxide (134). The photolysis of a functional arylmercurial also was studied (106):



The pyrolysis of metallocenyl-substituted mercurials in the presence of silver powder gave novel coupling products (24):



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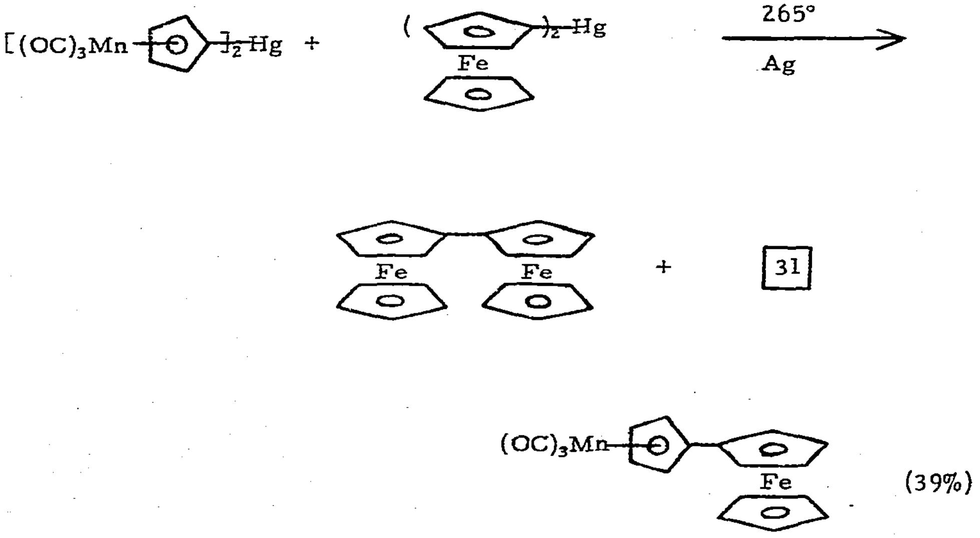


31

The oxidation of organomercurials with various oxidizing agents has been the subject of several investigations.

Ozonization of dimethylmercury in aqueous solution was found to be too fast to allow kinetic studies, almost all of the dimethylmercury present being destroyed within 10 min. at room temperature (135). Similar ozonolysis of aqueous methyl-and ethylmercuric chloride in the ppm range has been reported (136). Thus, ozonization is a possible means of destroying organomercurials in environmental waters.

The action of nitronium tetrafluoroborate on RHgX compounds (R = alkyl or aryl; X = R or Br) in sulfolane results in an oxidation-reduction reaction in which the arene together with some nitroarene are formed when R = aryl (137, 138). On the other hand, the nitroarene was the major product when the oxidizing agent used was nitric acid in acetic anhydride (138, 139). With alkylmercurials, one of the products of reaction with $NO_2{}^+BF_4{}^-$ is the nitroalkane, and with both RHgBr and ArHgBr some organic bromide was formed as well. The initial formation of a cation radical, $[RHgX]^{+\bullet}$ was suggested, whose further "in-cage" or "out-of-cage" reactions gave the observed products.

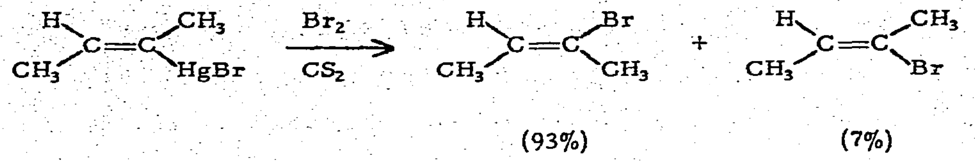
The reactions of organomercurials with triphenylmethane derivatives also proceeds via an initial electron transfer step in many cases (Reutov et al, 1969). Further work by this group has shown that a peroxide is formed when such an interaction is allowed to occur in the presence of oxygen (140):

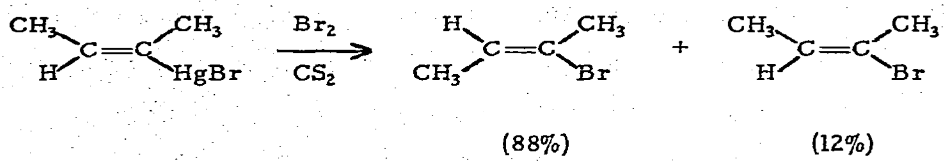
$$\mathrm{Ph_3CBr + R_2Hg \xrightarrow{O_2} Ph_3COOR} \quad (50\text{-}70\%)$$

$$(\mathrm{R = Me,\ Me_3CH_2})$$

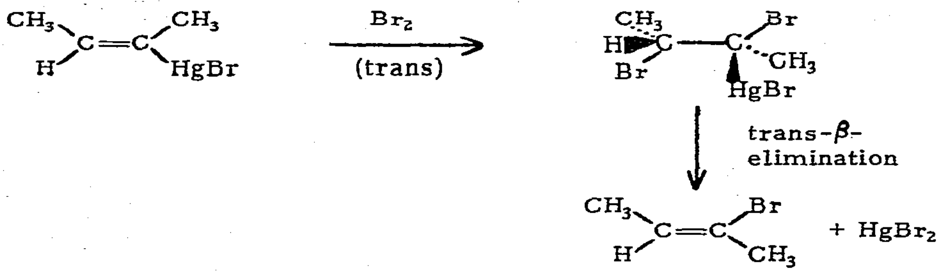
The reactions of various alkylmercuric bromides with β hydrogen substituents (R = $n\text{-}C_3H_7$, Me_2CHCH_2, EtMeCH, but not C_2H_5) reacted with triphenylbromomethane to give low yields of triphenylmethane, presumably via a hydride abstraction mechanism (141).

The stereochemistry of the cleavage of the C-Hg bond by halogens has been the subject of many studies in the past. In general, radical cleavage (Br_2 in CS_2 or CCl_4) results in loss of stereochemistry at the carbon atom to which the mercury is bonded, while ionic cleavage (Br_2 in methanol or pyridine) results in retention of configuration at carbon. It therefore was surprising to find that brominolysis of cis- and trans-propenyl- and 2-butenylmercuric bromide in carbon disulfide resulted in predominant inversion of configuration at carbon (142):





In pyridine, on the other hand, such cleavage proceeded with retention of configuration at carbon. The results of the experiments in CS_2 were explained in terms of an addition-elimination sequence, rather than a direct cleavage of the C-Hg bond:



trans-Butenylmercuric bromide was found to be about 75 times more reactive toward bromine in carbon disulfide than n-propylmercuric bromide, but only about 34 times more reactive in pyridine solution. Other studies (143) have implicated carbonium ion intermediates in the bromodemercuration of certain organomercurials, especially of benzyl derivatives, in DMF solution.

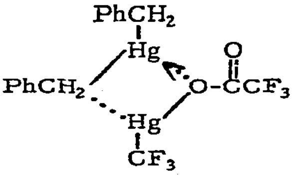
The results of isotope positional scrambling obtained in a study of the reaction of 1-propyl-1-^{14}C-mercuric perchlorate with trifluoroacetic acid (reflux for 8 hr.) suggested that some of the $CH_3CH_2CH_2O_2CCF_3$ obtained as the minor product was formed via edge-protonated cyclopropane (144). The major (93%) product of this reaction was $Me_2CHO_2CCF_3$. A detailed kinetic study of the protolysis (HCl in EtOH) of 2-acetyl-3-chloromercuri-

1-methylindole has been reported (145). Cleavage of trans-ClCH=CHHgCl with $CuCl_2$-KCl and NH_4Cl-HCl has been studied (146).

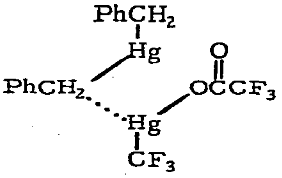
Reutov and his group have continued their investigations of substituent exchanges in organomercury chemistry. In one study, the redistribution of dibenzylmercury with mercuric halides in pyridine was followed by proton NMR spectroscopy (147). This second order reaction was most rapid with $HgCl_2$ ($k = 4.05\mathrm{x}10^{-3}$ l/mol. sec at 46°). Mercuric bromide ($k = 3.33\mathrm{x}10^{-3}$) and iodide ($k = 1.19\mathrm{x}10^{-3}$) were less reactive. The energies of activation for these reactions were: with $HgCl_2$, 12.2; $HgBr_2$, 15.5; HgI_2, 20.1 kcal/mol. The kinetics of the three-alkyl exchange between dibenzylmercury and trifluoromethylmercuric trifluoroacetate in pyridine also were determined (148):

$$(PhCH_2)_2Hg + CF_3HgO_2CCF_3 \longrightarrow PhCH_2HgCF_3 + PhCH_2HgO_2CCF_3$$

Again, a second order process was found ($k = 1.75\mathrm{x}10^{-3}$ l/mol. sec at 48°; E_{act} 12.1 kcal/mol). Transition states $\boxed{32}$ or $\boxed{33}$ were favored. The



$\boxed{32}$



$\boxed{33}$

substituent exchange reaction between dibenzylmercury and trichloromethylmercuric bromide to give benzyl(trichloromethyl)mercury and benzylmercuric bromide also was reported (148), but a kinetic study was not possible, due to the instability of $PhCH_2HgCCl_3$ (→Hg°).

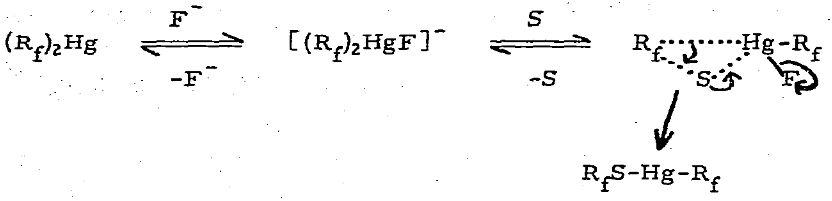
In a more preparative vein, it was found that o-tolylmercuric halides undergo symmetrization to di-o-tolylmercury and mercuric halide on chromatography columns of active basic alumina or magnesium oxide (149). Presumably the usual nucleophilic process is involved. Symmetrization of ethylmercuric iodide could not be achieved in good yield by this procedure. As the authors pointed out, this method has only very limited practical applicability.

Among miscellaneous reactions we note the formal insertion of sulfur into the C-Hg bonds of bis(perfluoroalkyl)mercury compounds (150):

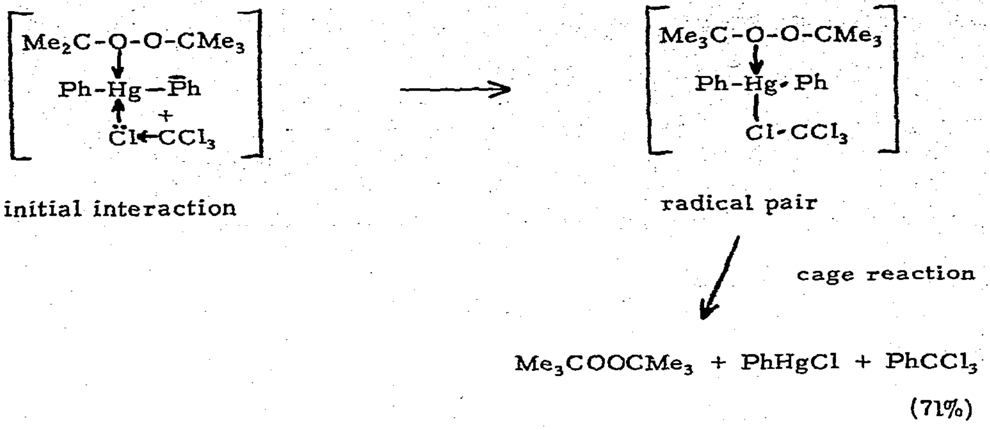
$$(R_f)_2Hg \ + \ S_8 \ \xrightarrow[70\text{-}100^\circ]{\text{KF in DMF}} \ (R_fS)_2Hg$$

$(R_f = (CF_3)_3C$
and $(CF_3)_2CF)$

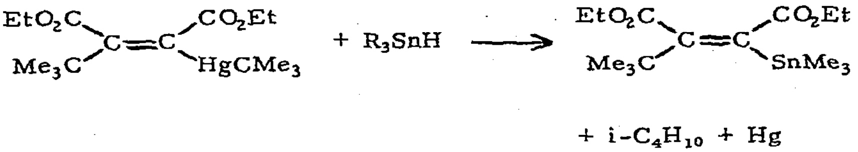
The following mechanism was favored:



The reactions of alkylmercuric alkoxides with carbon tetrachloride at 50-60° do not form $RHgCCl_3$ (as does the $RHgOR' + HCCl_3$ reaction). Instead, the products are (in the case of $RHgOCMe_3$) $RHgCl$, Hg°, Me_3COH, $CHCl_3$, RCl and the olefin derived from R (151). Also studied were <u>tert</u>-butyl peroxide-catalyzed reactions of Ph_2Hg, $i\text{-}Pr_2Hg$ and $i\text{-}PrHgCl$ with carbon tetrachloride at 100°. The results were explained in various ways in terms of electron transfer processes in which subsequent in-cage and out-of-cage steps produce the observed products. E.g.:



The reaction of organotin hydrides with R_2Hg compounds containing electronegative or unsaturated groups resulted in reduction (101, 175):



$$(PhC{\equiv}C)_2Hg + (Me_3C)_2Hg + 2Me_3SnH \longrightarrow 2\ PhC{\equiv}CSnMe_3 + 2\ Hg + 2\ i\text{-}C_4H_{10}$$

$$(CH_2{=}CHCH_2)_2Hg + Me_3SnH \xrightarrow{20^\circ} Me_3SnCH_2CH{=}CH_2 + CH_3CH{=}CH_2 + Hg$$

$$(CCl_3)_2Hg + Me_3SnH \xrightarrow{0^\circ} Me_3SnCCl_3 + HCCl_3 + Hg$$

7. MERCURY-FUNCTIONAL MERCURIALS

Diverse methylmercury compounds of type CH_3HgXR (X = O, S, O_2C and R = aryl) have been prepared for an NMR study by Sytsma and Kline (152) (Table 10). Preparative methods A and B in Table 10 are straightforward, involving reaction of the appropriate RXH compound with

Table 10. New CH_3HgXR Compounds

(Sytsma and Kline, ref. 152)

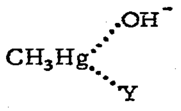
Parent Acid RXH	Method of preparation	Recryst. solvent	Melting point (°C)
A. X=O			
Phenol	A	Hexane/methylene chloride	129(130)
p-Chlorophenol	A	None	125(dec.)
1-Naphthol	A	Hexane/methylene chloride	91(dec.)
p-Bromophenol	A	None	130(dec.)
m-Bromophenol	C	Hexane/methylene chloride	101
o-Bromophenol	B	Hexane/methylene chloride	88
2,4-Dichlorophenol	A	Hexane/methylene chloride	135
8-Hydroxyquinoline	A	Hexane	99(90)
p-Formylphenol	A	None	135(dec.)
p-Nitrophenol	A	None	167(dec.)
5-Acetyl-8-hydroxyquinoline	B	None	163
Pentafluorophenol	B	Hexane/methylene chloride	134
B. X=S			
Cyclohexylmercaptan	B	Water/acetone	65
p-t-Butylthiophenol	B	Hexane	89
p-Methylthiophenol	B	Hexane	75
o-Methylthiophenol	B	Hexane	75
Thiophenol	A	Water/ethanol	92(87)
p-Fluorothiophenol	B	Hexane	81
2-Mercaptonaphthalene	B	Hexane	93
p-Chlorothiophenol	B	Hexane	63

Table 10. (Continued)

p-Bromothiophenol	A	Hexane/methylene chloride	71
1-Mercaptonaphthalene	B	Hexane	97
o-Mercaptobenzoic acid	A	Hexane/methylene chloride	168(171)
2-Mercaptopyridine	A	Water/ethanol	53
2-Mercaptoquinoline	B	Hexane	132
8-Mercaptoquinoline	B	Water/acetone	163
Thiobenzoic acid	B	Water/acetone	61
Pentafluorothiophenol	B	Water/acetone	102
Dithizone (diphenylthiocarbazone)	B	Methanol	144(dec.) (146)
2-Mercaptopyridine-N-oxide	B	Water/ethanol	117
C. $X=CO_2$			
Myristic acid	B	Methanol	82
p-Hydroxybenzoic acid	B	Hexane/methylene chloride	205(dec.)
trans-Cinnamic acid	B	Water/ethanol	157
Benzoic acid	B	Hexane/methylene chloride	113(110)
Salicylic acid	A	Methanol	118(114)

methylmercuric hydroxide or methylmercuric acetate, respectively, in aqueous methanol solution. Method C, however, deserves more discussion. In this procedure, methylmercuric hexacyanocobaltate(III) was treated with the RXH compound in methanol (48 hr. at reflux). Ether was added to precipitate the etherate of hexacyanocobaltic acid and unreacted methylmercuric hexacyanocobaltate. These were filtered to leave a solution of the desired MeHgXR compound. This is a good procedure for the preparation of very soluble methylmercury salts. The formation of methylmercuric chloride from $MeHg^+$ and Cl^-, and its distribution between aqueous and organic phases has been studied using radioactive ^{203}Hg labelling (153).

The temperature jump method has been used to study the kinetics and mechanisms of $MeHgOH + Y^-$ reactions (153a). Transition state $\boxed{34}$ was suggested for these rapid processes.

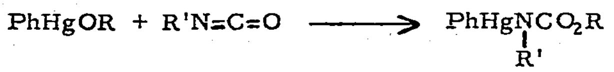


$Y = Py, Cl^-, SCN^-, Br^-, I^-, Ph_2PC_6H_4SO_3^-,$
$p\text{-}O_2NC_6H_4O^-, CN^-, OH^-$, and others

$\boxed{34}$

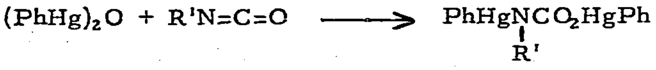
A striking analogy with proton transfer reactions was noted.

Bloodworth has continued his investigations of organomercury oxy-derivatives with a study of the reactions of organomercury alkoxides, oxides and hydroxides with organic isocyanates (154).



$$PhHgOR + R'N{=}C{=}O \longrightarrow PhHg\underset{R'}{N}CO_2R$$

$(R = Me, Me_3C)$

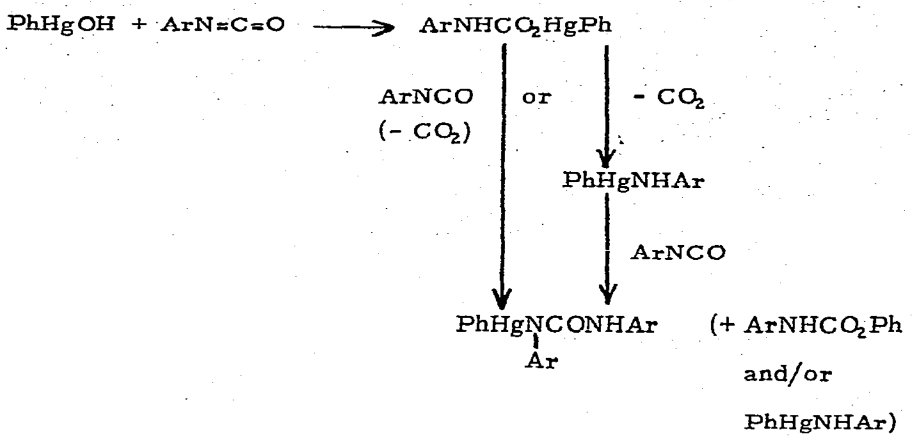


$$(PhHg)_2O + R'N{=}C{=}O \longrightarrow PhHg\underset{R'}{N}CO_2HgPh$$

$$PhHgOH + R'N{=}C{=}O \longrightarrow R'NHCO_2HgPh$$

$(R' = Et, Me_3C)$

Reactions of aryl isocyanates with phenylmercuric hydroxide were more complicated, giving the secondary products indicated, presumably <u>via</u> the pathway shown:



Some new organomercury peroxides, $PhMe_2COOHgC_6H_4Z$-p (Z = Cl and MeO), have been prepared. They appeared to be quite stable but were readily hydrolyzed by atomospheric moisture (155).

Two groups have reported on the preparation of organomercury amides. These may be prepared from the alkoxides (53, 154):

$$RHgOCMe_3 + Et_2NH \xrightarrow[\text{(ref. 53)}]{} RHgNEt_2 \text{ (not isolated)} + Me_3COH$$

(R = n-Pr, i-Pr)

$$PhHgOCMe_3 + Et_2NH \text{ (large excess)} \xrightarrow[\text{(ref. 53)}]{} PhHgNEt_2 + Me_3COH$$

(mp 93-95°)

$$PhHgOH + PhNH_2 \xrightarrow[\text{(ref. 154)}]{\text{benzene}} PhHgNHPh + H_2O$$

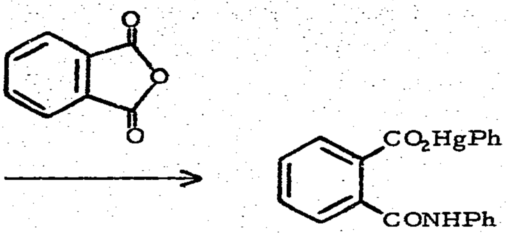
$$PhHgOH + Ph_2NH \xrightarrow{\text{benzene}} PhHgNPh_2 + H_2O$$

Removal of the water formed during these reactions by azeotropic distillation was required.

Some reactions of PhHgNHPh were studied (154):

$$PhHgNHPh \xrightarrow{PhN=C=O} PhHg(Ph)CONHPh$$

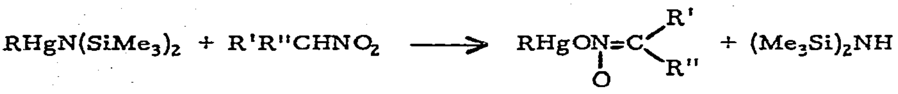
$$\xrightarrow{CO_2} PhNHCO_2HgPh \text{ (viscous oil)}$$



The compound $[(CF_3)_2N]_2Hg$ has found use in synthesis (156):

$$
\begin{array}{lcl}
[(CF_3)_2N]_2Hg + H_3SiI & \longrightarrow & H_3SiN(CF_3)_2 \quad (37\%) \\
 & & \quad \Big\downarrow \text{ room temp.} \\
 & & H_3SiF + CH_3N{=}CF_2
\end{array}
$$

Nitronate esters of organomercurials have been described (157):



$$RHgN(SiMe_3)_2 + R'R''CHNO_2 \longrightarrow RHgO\underset{\underset{O}{\downarrow}}{N}{=}C\!\begin{smallmatrix}R'\\R''\end{smallmatrix} + (Me_3Si)_2NH$$

(R = Me, Et)   (R', R'' = H, H
                         H, Me
                         Me, Me)

These crystalline solids are not very stable. $MeHgON(O){=}CH_2$ readily converted to the fulminate, MeHgCNO, in solution.

Several papers have dealt with Hg-SR compounds. Reaction of methylmercuric chloride with N-acetyl-L-cysteine gave $MeC(O)NHCH(CO_2H)CH_2SHgCH_3$, and an NMR study of the formation of this compound was reported (158).

The $(R_fS)_2Hg$ compounds mentioned already (150) were found to undergo the following reactions:

$$[(CF_3)_3CS]_2Hg \xrightarrow{Cl_2} (CF_3)_3CSCl$$

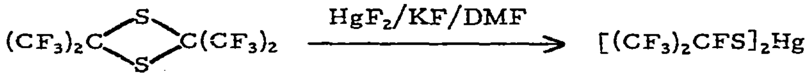
$$\xrightarrow{HCl} (CF_3)_3CSH$$

$$[(CF_3)_2CFS]_2Hg \xrightarrow{Cl_2} (CF_3)_2CFSSCF(CF_3)_2$$

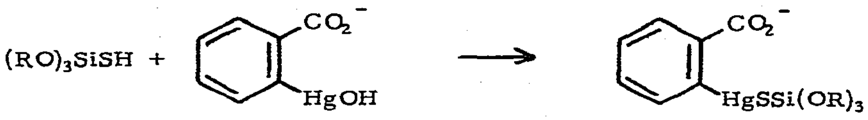
$$\xrightarrow{H_2O} (CF_3)_2C(OH)_2$$

$$\xrightarrow{CH_3I} (CF_3)_2CFSCH_3$$

The second of these thiomercurials could be prepared by another route:

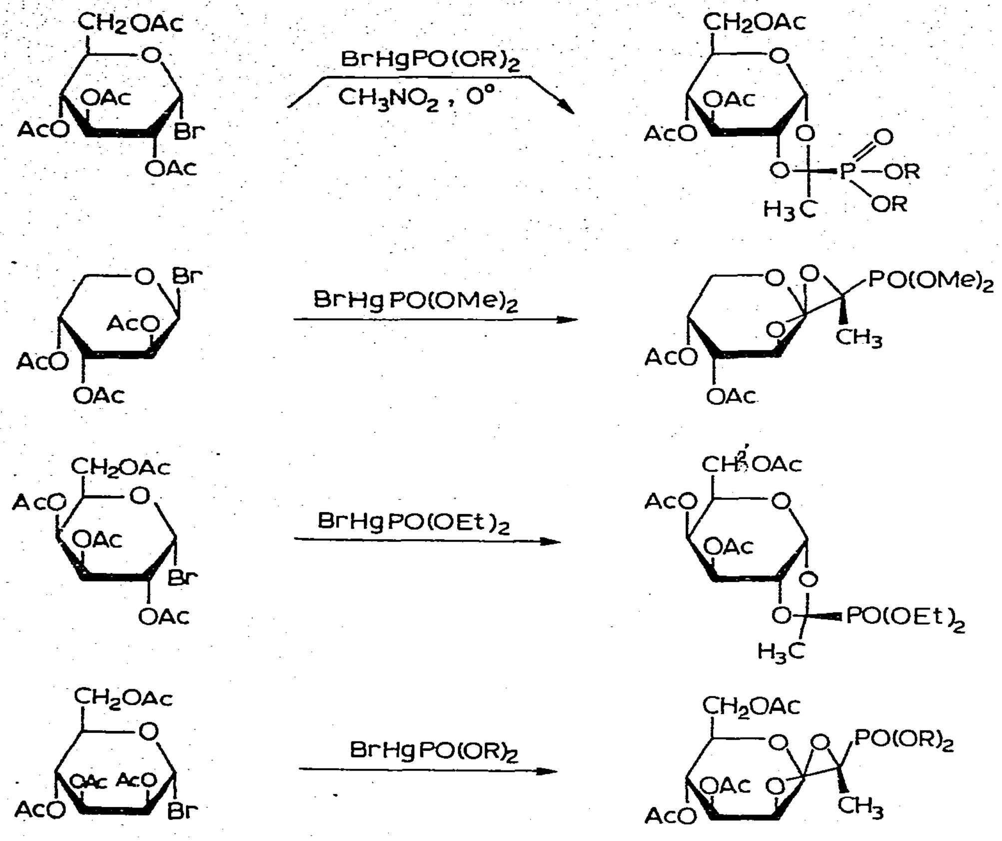


The reaction of o-hydroxymercuribenzoic acid with silanethiols of type $(RO)_3SiSH$ and $(RO)_2Si(SH)_2$ gave products containing Hg-S bonds (159), e.g.:



These products, however, were not isolated. The kinetics and mechanism of the reaction of PhHgSPh with picryl halides were examined by Italian workers (160).

Compounds containing a P-Hg bond have found application in carbohydrate synthesis (161, 162):



Mercurials with mercury-transition metal bonds have received further study by Roberts (163):

$$\mathrm{Me_3SnFe(CO)_2C_5H_5\text{-}\pi + MeHgCl \xrightarrow{DMSO} MeHgFe(CO)_2C_5H_5\text{-}\pi + Me_3SnCl}$$

$$\searrow$$

$$\mathrm{Me_2Hg + Hg[Fe(CO)_2C_5H_5]_2}$$

(but $\mathrm{PhHgFe(CO)_2C_5H_5\text{-}\pi}$ is stable).

$$\mathrm{Me_3SnMn(CO)_5 + MeHgCl \xrightarrow{Me_2CO} MeHgMn(CO)_5 + Me_3SnCl}$$

(but $\mathrm{PhHgMn(CO)_5}$ is unstable to disproportionation).

8. MERCURY-GROUP IV COMPOUNDS

A new silylaluminum complex has been used to prepare bis(triphenylsilyl)mercury (164):

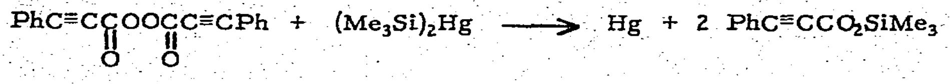
$$(Ph_3Si)_2AlEt \cdot 2LiBr \cdot 2THF \xrightarrow{Hg(OAc)_2} (Ph_3Si)_2Hg + Et_2Hg$$

Optically active (but not optically pure) (-)-bis[methyl(1-naphthyl)phenylsilyl]mercury has been prepared by reaction of $(Me_3C)_2Hg$ with the appropriate (+)-R_3Si^*H (165). The reactions of this mercurial with various substrates gave optically active products, presumably via predominant retention of configuration at silicon:

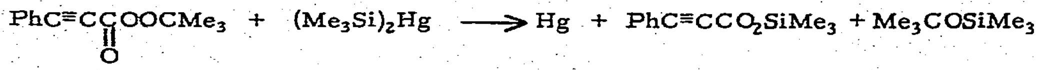
$$\begin{array}{lll} (1)\text{-}(R_3Si^*)_2Hg & \xrightarrow{LiAlH_4} & (+)\text{-}R_3Si^*H \\ & \xrightarrow{BrCH_2CH_2Br} & (+)\text{-}R_3Si^*Br \\ & \xrightarrow{UV} & (-)\text{-}(R_3Si^*)_2 \end{array}$$

Russian workers (166) have prepared optically active (-)-bis[methyl(1-naphthyl)phenylgermyl]mercury by a similar procedure. Its reaction with $Hg(CH_2CO_2Me)_2$ gave optically active (+)- $R_3Ge^*CH_2CO_2Me$.

The decomposition of Group IV-mercury compounds has been investigated. Bis(trimethylsilyl)mercury was found to decompose by a second-order process in benzene or cyclohexane, but more complicated kinetics were observed in toluene or anisole (167). In any case, homolytic scission of the Si-Hg bond is not involved as a major process in its decomposition, rather bimolecular reactions with itself or with the solvent. A small first-order contribution detected in cyclohexane medium allowed the estimation of $D(Me_3Si\text{-}HgSiMe_3)$ as 47.8 kcal/mol as a rough lower limit. Bis(trimethylsilyl)mercury was found to induce the decomposition of peresters (168):



$$PhC{\equiv}C\overset{}{\underset{\underset{O}{\|}}{C}}OO\underset{\underset{O}{\|}}{C}C{\equiv}CPh + (Me_3Si)_2Hg \longrightarrow Hg + 2\ PhC{\equiv}CCO_2SiMe_3$$



$$PhC{\equiv}C\underset{\underset{O}{\|}}{C}OOCMe_3 + (Me_3Si)_2Hg \longrightarrow Hg + PhC{\equiv}CCO_2SiMe_3 + Me_3COSiMe_3$$

Bis(trimethylstannyl)mercury reacted similarly, but with the difference that a part of the $PhC{\equiv}CCO_2SnMe_3$ produced underwent decarboxylation under the reaction conditions.

Exchange reactions of bis(triethylsilyl)mercury with bis(perfluoroalkyl)-mercurials gave stable products of type Et_3SiHgR_f ($R_f = CF_3, CF_2CF_3$), but $[(Me_3SiCH_2)_3Sn]_2Hg$ reacted only with $Hg[C(CF_3)_3]_2$, not with $Hg(CF_3)_2$ or $Hg[CF(CF_3)_2]_2$ (169):

$$[(Me_3SiCH_2)_3Sn]_2Hg + Hg[C(CF_3)_3]_2 \xrightarrow{THF,\ 20^\circ}$$

$$2\ (Me_3SiCH_2)_3SnHgC(CF_3)_3 \text{ (unstable)}$$

$$\downarrow$$

$$2\ (Me_3SnCH_2)_3SnF + 2\ Hg + 2\ (CF_3)_2C{=}CF_2$$

Full details of the preparation and reactions of $[(C_6F_5)_3Ge]_2Hg$ have been published (170). Three methods served in its preparation:

$$2\ (C_6F_5)_3GeH + HgR_2 \xrightarrow{140^\circ} [(C_6F_5)_3Ge]_2Hg + 2\ RH$$

$(R = Et,\ Et_3Ge,\ (Me_3Si)_2N)$

$$[(C_6F_5)_3Ge]_2Cd + Hg \xrightarrow{100^\circ} [(C_6F_5)_3Ge]_2Hg + Cd$$

$$(Et_3Ge)_2Hg + (C_6F_5)_3GeBr \xrightarrow{UV/benzene} [(C_6F_5)_3Ge]_2Hg + 2Et_3GeBr$$

Reactions of this germylmercurial were studied:

$$[(C_6F_5)_3Ge]_2Hg \xrightarrow{UV/PhMe} Hg + (C_6F_5)_6Ge_2\ (52\%) + (C_6F_5)_3GeH\ (32\%) + (C_6F_5)_3GeCH_2Ph\ (24\%)$$

$$\xrightarrow[100^\circ\ 49\%]{HCl} (C_6F_5)_3GeH + (C_6F_5)_3GeBr$$

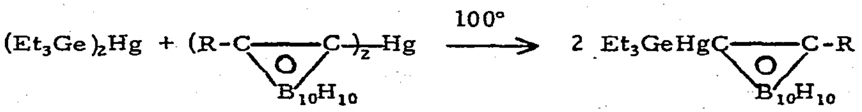
$$\xrightarrow{HgCl_2} \underset{\text{(unstable)}}{[(C_6F_5)_3GeHgCl]} \longrightarrow (C_6F_5)_3GeCl + Hg$$

$$\xrightarrow[20^\circ]{(Et_3Ge)_2Hg} (C_6F_5)_3GeHgGeEt_3$$

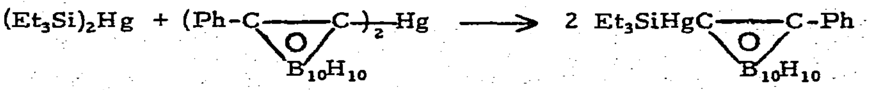
$$\xrightarrow{Br_2} (C_6F_5)_3GeBr + HgBr_2$$

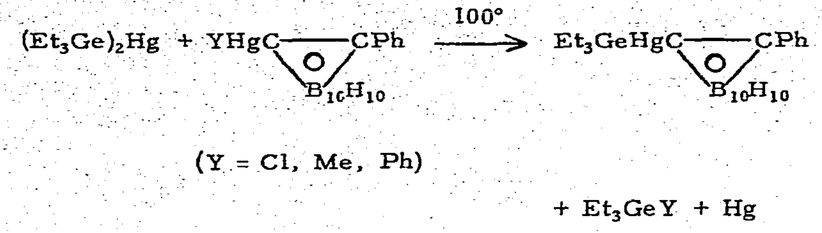
Bis(triethylgermyl)mercury, via its reactions with alkali metals in ethers and in hydrocarbons, is an excellent source of Et_3GeNa and Et_3GeK (171).

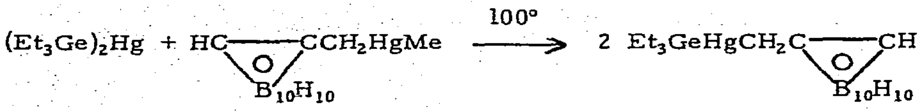
Triethylgermyl- and triethylsilylmercury derivatives of carboranes have been prepared by redistribution reactions (172):



(R = Ph, H)

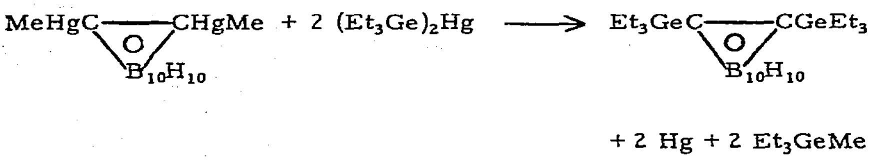




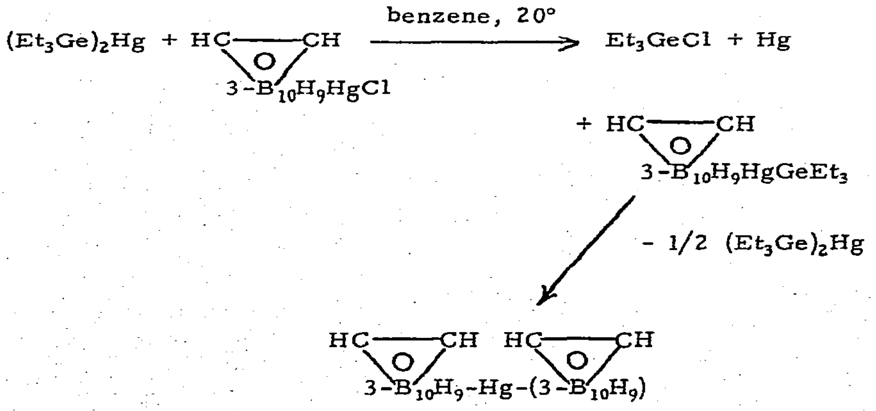


$$1,7\text{-}MeC(B_{10}H_{10})CHgCl + (Et_3Ge)_2Hg \longrightarrow 1,7\text{-}MeC(B_{10}H_{10})CHgGeEt_3 + Et_3GeCl + Hg$$

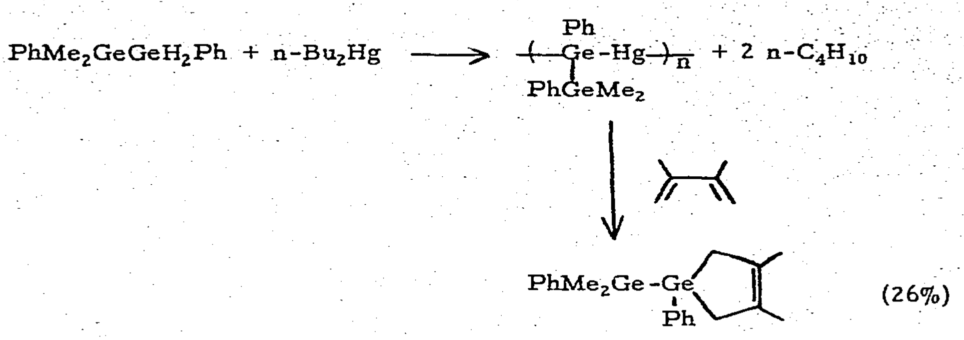
However:



A carborane with B-HgCl subsitution also reacted:

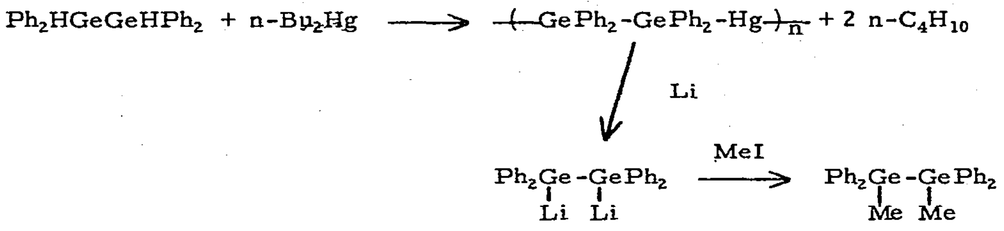


Mercury derivatives of digermanes have been used to good advantage by Rivière, Satgé and Soula in the generation of germylgermylenes (173):



(via $PhMe_2Ge\text{-}\ddot{G}ePh$)

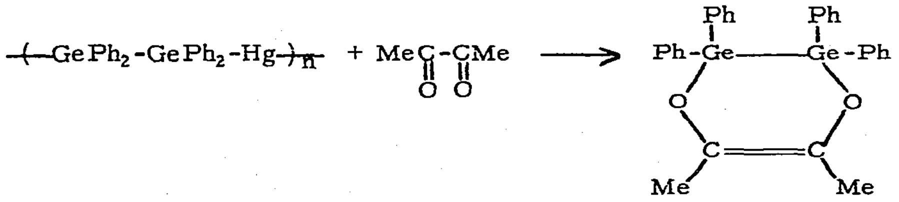
digermyl-lithium reagents (174):



$$Ph_2HGeGeHPh_2 + n\text{-}Bu_2Hg \longrightarrow -\!\!(GePh_2\text{-}GePh_2\text{-}Hg)_n\!\!- + 2\ n\text{-}C_4H_{10}$$

$$\xrightarrow{Li} Ph_2Ge(Li)\text{-}Ge(Li)Ph_2 \xrightarrow{MeI} Ph_2Ge(Me)\text{-}Ge(Me)Ph_2$$

and heterocyclic organodigermanes (174):

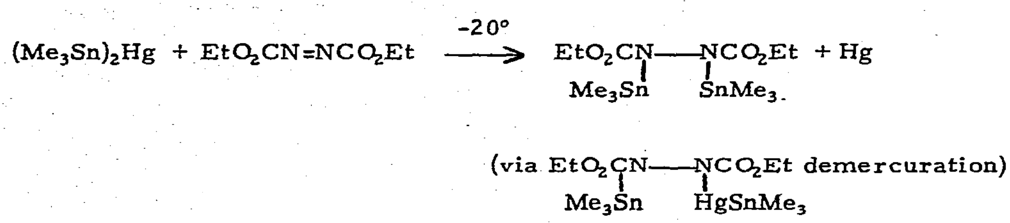


Blaukat and Neumann (175) have published full details concerning the synthesis of bis(triorganostannyl)mercurials, $(R_3Sn)_2Hg$, with R = Me, Et, n-Pr, t-Bu, Ph, via reactions of di-t-butylmercury with the appropriate triorganotin hydride. The bis(trialkylstannyl)mercury compounds where R = Me, Et and n-Pr are rather unstable, decomposing at ca. -10° ($\longrightarrow$ R_6Sn_2 + Hg) and are rapidly oxidized by air ($\longrightarrow$ $R_3SnOSnR_3$). The stannylmercurials with bulky R groups such as $[(Me_3C)_3Sn]_2Hg$ (mp 196°) and the previously reported $[(Me_3SiCH_2)_3Sn]_2Hg$ are much more stable. The latter can be prepared by the hydride route and also by metal displacement from the thallium compound (176):

$$2\ [(Me_3SiCH_2)_3Sn]_3Tl + 3\ Hg \xrightarrow{20°,\ 30\ hr} 3\ [(Me_3SiCH_2)_3Sn]_2Hg + 2\ Tl$$

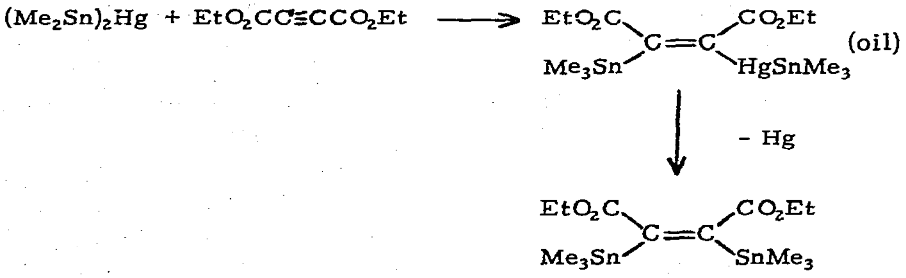
$(Ph_3Sn)_2Hg$ also is more stable thermally. Dialkyltin dihydrides also react with di-t-butylmercury, but of the intermediate stannylmercurials only $[(Me_3C)_2SnHg]_n$ is stable. All others(R = Et, n-Bu, i-Bu, cyclo-C_6H_{11}, Ph) decompose immediately to metallic mercury and the cyclostannanes, $(R_2Sn)_n$.

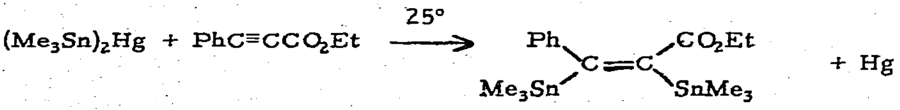
Some reactions of bis-stannylmercurials were examined:



$$(Me_3Sn)_2Hg + EtO_2CN{=}NCO_2Et \xrightarrow{-20°} EtO_2C\underset{Me_3Sn}{N}{-}\underset{SnMe_3}{N}CO_2Et + Hg$$

$$\left(\text{via } EtO_2C\underset{Me_3Sn}{N}{-}\underset{HgSnMe_3}{N}CO_2Et \text{ demercuration}\right)$$





$$(Me_3Sn)_2Hg + HC{\equiv}CCO_2Et \longrightarrow Me_3SnHgC{\equiv}CCO_2Et + Me_3SnH$$

$$\downarrow$$

$$(EtO_2CC{\equiv}C)_2Hg + (Me_3Sn)_2Hg$$

$$\downarrow Me_3SnH$$

further reaction

Other stannylmercurials have been prepared (177):

$$Et_3GeHgGe(C_6F_5)_3 + (C_6F_5)_3SnBr \xrightarrow{UV,\ 20^\circ} (C_6F_5)_3SnHgGe(C_6F_5)_3 + Et_3GeBr$$

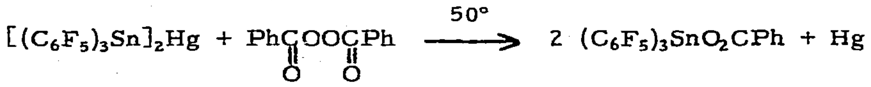
$$(Et_3Ge)_2Hg + 2\ (C_6F_5)_3SnBr \xrightarrow{UV,\ 20^\circ} [(C_6F_5)_3Sn]_2Hg + 2Et_3GeBr$$

but:

$$(Et_3Ge)_2Hg + 2\ (C_6F_5)_3SnBr \xrightarrow{no\ UV,\ 20^\circ} (C_6F_5)_6Sn_2 + Hg + 2\ Et_3GeBr$$

Two reactions of the bis-stannylmercurial were described:

$$[(C_6F_5)_3Sn]_2Hg + HgCl_2 \longrightarrow 2\ [(C_6F_5)_3SnHgCl] \longrightarrow 2\ (C_6F_5)_3SnCl + 2\ Hg$$



$$[(C_6F_5)_3Sn]_2Hg + PhC(=O)OOC(=O)Ph \xrightarrow{50^\circ} 2\ (C_6F_5)_3SnO_2CPh + Hg$$

9. COORDINATION CHEMISTRY OF ORGANOMERCURIALS

Halide ion complexes of organomercuric halides are well known (cf. another report of $CH_3HgCl_3^{2-}$ (178)), but stable complexes of RHgX and R_2Hg compounds with neutral donor molecules are quite rare. In the case of R_2Hg compounds, such adduct formation is restricted to those mercurials with rather electronegative substituents such as C_6F_5. Of many Lewis bases tried, diphenylmercury only formed crystalline adducts of type $Ph_2Hg \cdot 2L$ with 1,10-phenanthroline and its 2,9-dimethyl and 2,4,7,9-tetramethyl derivatives (179). Even these were very weak complexes which were completely dissociated in solution and whose solid state IR and UV spectra gave no evidence of covalent Hg-N bond formation. The crystal structures of the latter two complexes did not unambiguously define the role of the phenanthroline ligands because of disorder problems (180). Each mercury atom was found to be adjacent to and approximately equidistant from two nitrogen atoms. Calorimetry confirmed this weak Lewis acidity of diphenylmercury in its interaction with pyridine in carbon tetrachloride solution (181). For the process:

$$Ph_2Hg + C_5H_5N \overset{CCl_4}{\rightleftharpoons} Ph_2Hg \cdot C_5H_5N \qquad K = {\sim}0.3\ l/mol$$

$$H_f^\circ = {\sim}{-2.9}\ kcal/mol$$

Bis(pentafluorophenyl)mercury was found to be a stronger Lewis acid than diphenylmercury, but in the absolute sense, it is rather weak:

$$(C_6F_5)_2Hg + C_5H_5N \rightleftharpoons (C_6F_5)_2Hg \cdot C_5H_5N$$

in CCl_4: $K = 20.1 \pm 1.0\ l/mol$

$H_f^\circ = -5.40 \pm 0.11\ kcal/mol$

in C_6H_6: $K = 2.1 \pm 0.1\ l/mol$

$H_f^\circ = -4.32 \pm 0.11\ kcal/mol$

$$(C_6F_5)_2Hg + bipy \rightleftharpoons (C_6F_5)_2Hg \cdot bipy$$

in CCl_4: $K = 55.5 \pm 3.0\ l/mol$

$H_f^\circ = -7.28 \pm 0.12\ l/mol$

in C_6H_6: $K = 19.2 \pm 2.1\ l/mol$

$H_f^\circ = -4.19 \pm 0.25\ kcal/mol$

It was considered likely that 2,2'bipyridine is acting as a bidentate ligand.

Crystalline 1:1 complexes of $Hg[CF(NO_2)_2]_2$ with 1,2-dimethoxyethane, diglyme and sulfolane, and 1:2 complexes with $(Me_2N)_3PO$, 1,4-dioxane and DMSO have been prepared (182). IR spectroscopy indicated that these were covalent adducts. Complexes of this mercury compound with pyridine, Et_3N and TMED were unstable. Liquid, water-insoluble products were formed when $Hg[CF(NO_2)_2]_2$ was treated with THF, MeCN, $Me_2NCONMe_2$, DMF and N-methylpyrrolidine. A study of complexes of $Hg[C(NO_2)_3]_2$ with various Lewis bases in solution by means of ^1H, ^{13}C and ^{14}N NMR spectroscopy has been reported (183).

A crystalline complex was found to form when trans-ClCH=CHHgCl was treated with hexamethyl phosphoramide in petroleum ether. This 1:1 adduct, trans-$ClCH{=}CHHgCl\cdot OP(NMe_2)_3$, dissociated in solution (DMSO, dioxane, excess HMPA) (184). A trimethylphosphine complex of methylmercuric chloride, $[Me_3PHgMe]Cl$, has been prepared (185). In solution, this compound undergoes rapid ligand exchange with excess trimethylphosphine. (Other complexes of trimethylphosphine with Hg(II) compounds (HgX_2, $Hg(CN)_2$, $Hg(SCN)_2$, $Hg(OAc)_2$, $Hg(NO_3)_2$) also were studied.)

Visible absorption spectroscopy failed to provide evidence in favor of a ground state complex between dimethylmercury and 1-chloronaphthalene. (In the presence of this mercurial the first singlet to triplet absorption band of 1-chloronaphthalene is strongly enhanced.) (186). In a related study, quenching of the 1,2-benzanthracene fluorescence by dimethylmercury via an exiplex has been reported (187). Again, a ground state complex of any stability between dimethylmercury and the aromatic compound was not considered probable.

Arene complexes of the mercurous ion have been prepared by the action of arenes on sulfur dioxide solutions of mercury(I) hexafluoroarsenate (188):

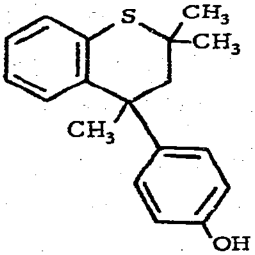
$$m\ Hg_2(AsF_6)_2 + n\ ArH \xrightarrow{SO_2} m\ Hg_2(AsF_6)_2\cdot nArH$$

1:1 complexes with benzene, biphenyl, naphthalene, m-dinitrobenzene

2:1 and 1:3 complexes with 9,10-benzophenanthrene

Raman spectroscopy showed that the Hg-Hg bond was retained in the complexes. The fact that the position of this band was dependent on the arene confirmed the arene-Hg_2^{2+} interaction. Such complexes also could be detected in sulfur dioxide solution by ^{13}C NMR in those cases where they were soluble (e.g., hexamethylbenzene). The structure of these complexes remains unknown, although it was guessed that they are similar to the dipalladiumarene complexes.

Finally, although a chemical bond is not involved, we note the first clathrate compound of dimethylmercury. The host molecule is 4-p-hydroxyphenyl-2,2,4-trimethylthiochroman $\boxed{35}$, and the host-to-guest



$\boxed{35}$

ratio is 6:1 (189). This adduct is prepared by crystallization of $\boxed{35}$ from neat dimethylmercury. It is stable to vacuum but releases dimethylmercury when its crystals are ground up or dissolved in a solvent. This clathrate is recommended as a practical means of handling dimethylmercury, although the chemist who must prepare the adduct in the first place may not quite appreciate this advantage.

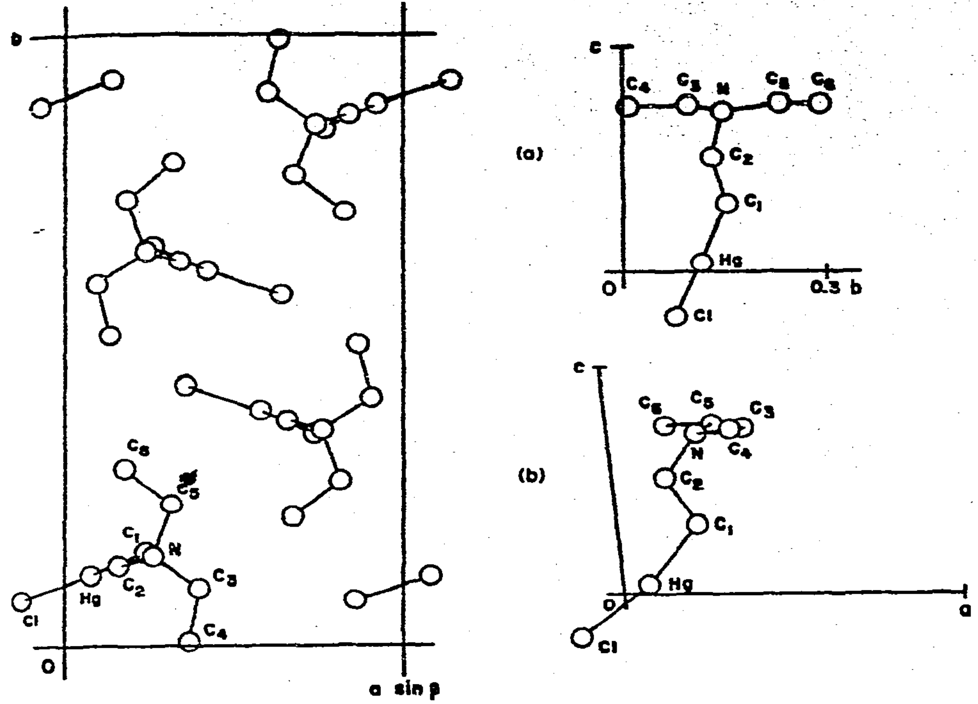
10. STRUCTURAL, SPECTROSCOPIC and PHYSICAL STUDIES

A. Structural Studies

An electron diffraction study of gaseous dimethylmercury gave 2.083 ±0.005 Å for the C-Hg bond distance (190). (A Hg-Cl distance of 2.252± 0.005 Å and a linear structure within an error of 16° were determined for gaseous $HgCl_2$ by the same method (191)).

Several X-ray diffraction studies of organomercurials and various mercury compounds without mercury-carbon bonds that might be of interest to the organometallic chemist have been reported:

$(CH_3CH_2)_2NCH_2CH_2HgCl$ (192) (Fig. 1). Of interest is the intermolecular

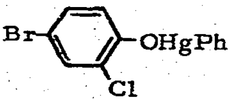


Projection of the unit cell of the *N*-[2-(chloromercuri)ethyl]diethylamine crystal along the *C* axis.

Projections of one molecule of *N*-[2-(chloromercuri)ethyl]diethylamine. (a) Along the *A* axis. (b) Along the *B* axis.

Figure 1. Structure of $Et_2CH_2CH_2HgCl$ (from K. Toman and G. G. Hess, J. Organometal. Chem., 49 (1973) 133)

N-Hg distance of 2.77(2) Å, which is less than the van der Waals contact distance of 3.0 Å and suggests weak intermolecular N→Hg coordination. The observed nonlinear C-Hg-Cl angle of 167.1(8)° may be a consequence of such intermolecular coordination.



(193) (Fig. 2). In this molecule the intramolecular

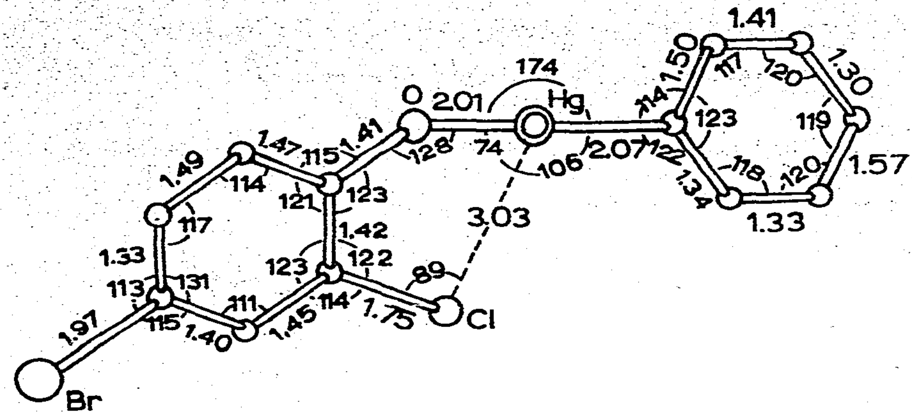


Figure 2. Structure of Phenyl(2-chloro-4bromophenoxy)mercury (from L. G. Kuz'mina et al, Zh. Strukt. Khim., 14 (1973) 508)

Hg·····Cl distance is 3.03 Å, which is smaller than the van der Waals contact distance. This suggests the occurence of weak intramolecular O→Hg coordination.

<u>$(Me_3CCO)_2CHHgOAc$</u> (194) (Fig. 3 and 4). This structure confirms the C-Hg bonded constitution of dipivaloylmethanemercuric acetate as determined spectroscopically.

<u>The 1:1 (195) and the 2:1 (196) methylmercuri derivatives of DL-penicillamine</u>. (Fig. 5 and 6). This study is of special interest in that it demonstrated the ability of CH_3Hg^+ to coordinate to nitrogen in such nitrogen-containing bases.

<u>$[(MeO)_2P(O)]_2Hg$</u> (197) (Fig. 7). The P-Hg-P angle was determined to be 165.9°. Two phosphoryl oxygen atoms from neighboring molecules interact weakly with mercury (Hg·····O distance~2.54 Å), which results in the formation of chains parallel to the a axis.

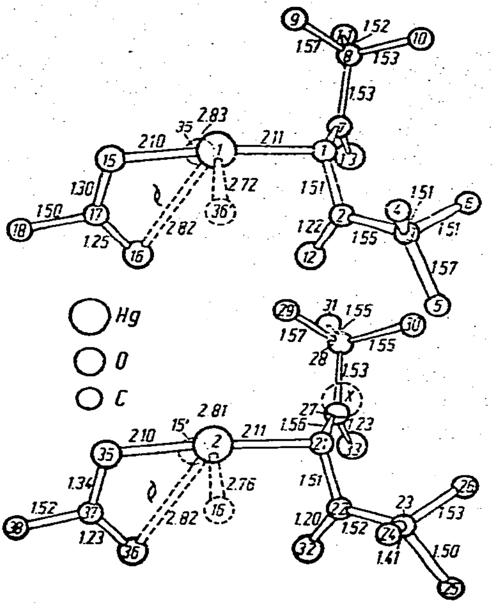


Figure 3. Structure of $(Me_3CCO)_2CHHgOAc$ (from R. Allmann and H. Musso, Chem. Ber., 106 (1973) 3001)

Projection of the two symmetry-independent $(Me_3CCO)_2CHHgOAc$ molecules on the x, y plane.

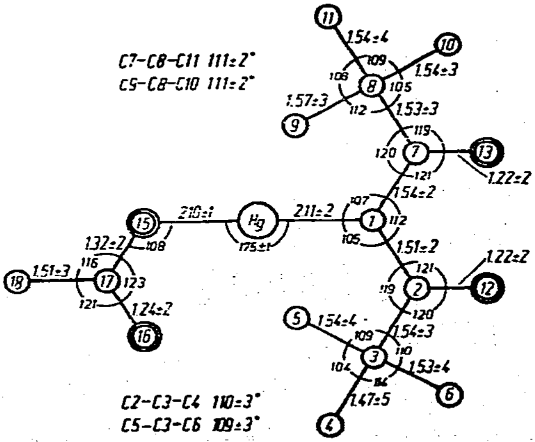


Figure 4. Bond distances and Bond Angles in $(Me_3CCO)_2CHHgOAc$ (from R. Allmann and H. Musso, Chem. Ber., 106 (1973) 3001)

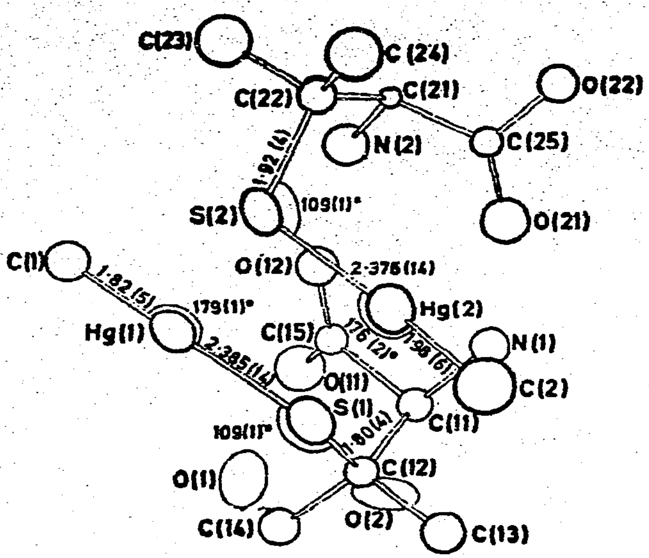


Figure 5. Structure of DL-Penicillaminatomethylmercury (II), MeHg[SC(Me)$_2$CH(NH$_3$)CO$_2$] (from Y. S. Wong, P. C. Chieh and A. J. Carty, Chem. Commun. (1973) 741)

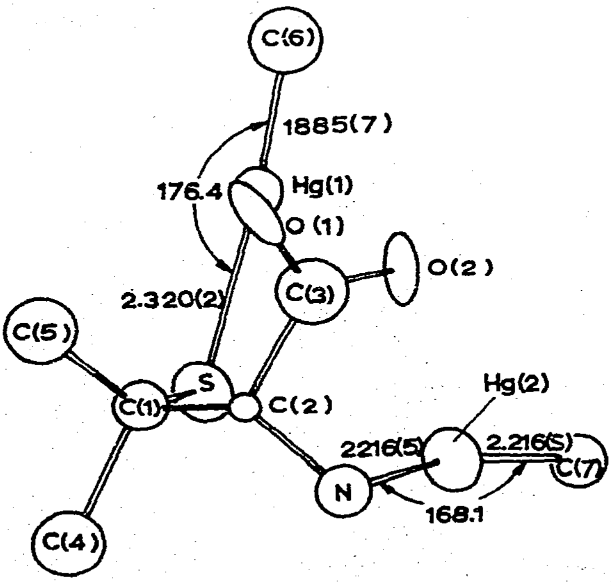


Figure 6. Structure of DL-bis(methylmercuri)penicillamine (from Y. S. Wong, P. C. Chien and A. J. Carty, Can. J. Chem.,, 51 (1973) 2597). MeHgSCMe$_2$CH(COO)NH$_2$HgMe.

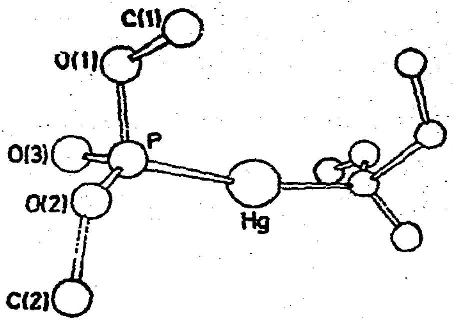


Figure 7. Structure of $Hg[P(O)(OMe)_2]_2$ (from G. G. Mather and A. Pidcock, J. Chem. Soc. Dalton (1973) 560)

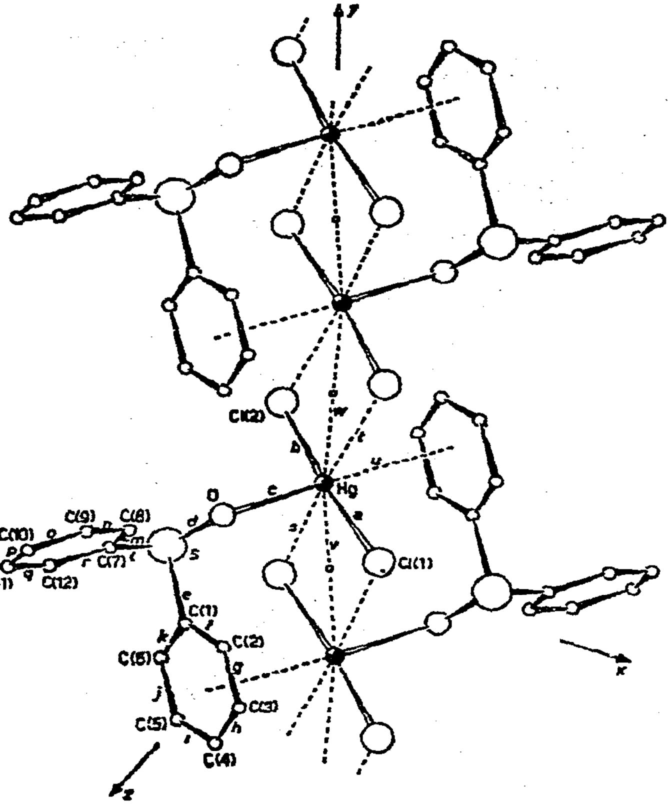


Figure 8. Structure of $Ph_2SO \cdot HgCl_2$ (from P. Biscarini et al., J. Chem. Soc. Dalton (1973) 159)

Ph$_2$SO·HgCl$_2$ (198) (Fig. 8). Of interest in this compound is the possible weak π interaction between the mercury atom and one of the phenyl rings of the diphenyl sulfoxide ligand. (⊥Hg-C$'_6$H$_5$ distance 3.51 Å).

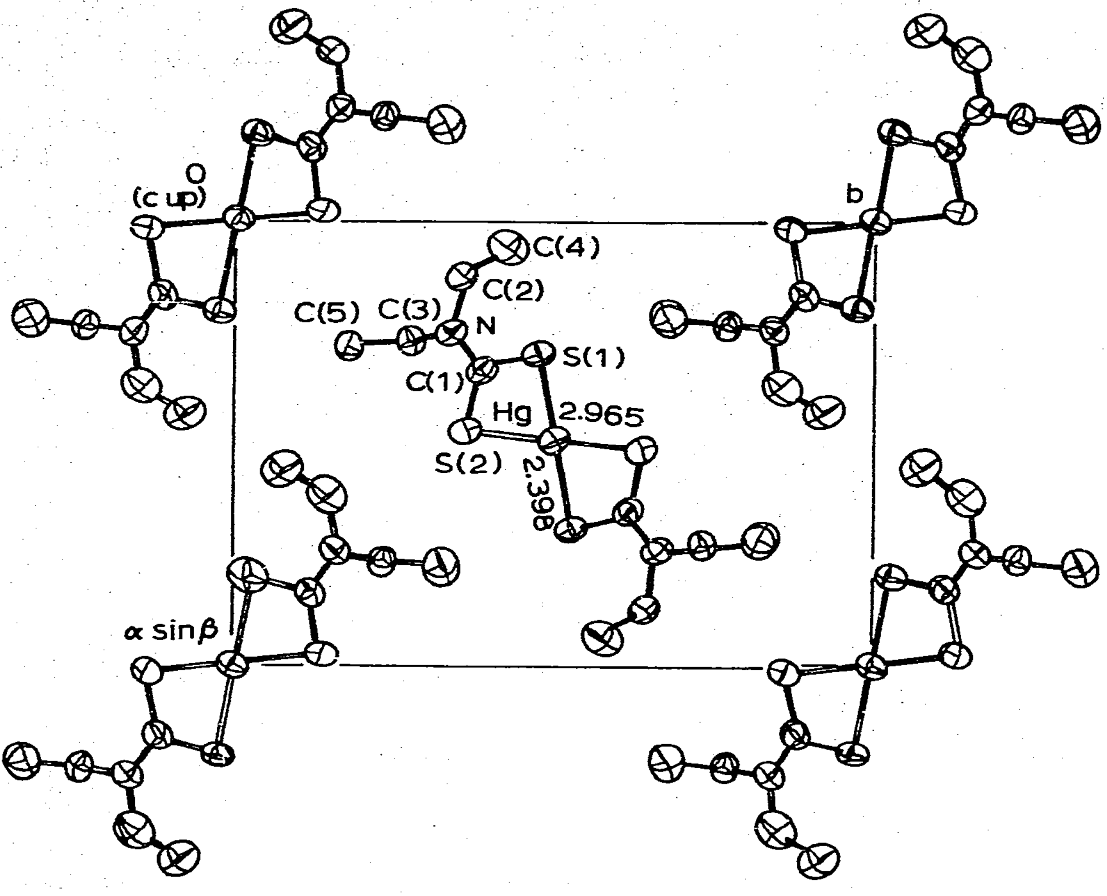


Figure 9. Structure of β-mercury(II) N,N-diethyldithiocarbamate (from H. Iwasaki, Acta Cryst., 29B (1973) 2115)

N,N-Diethyldithiocarbamato derivatives of mercury(II) (199, 200).

See Fig. 9 and 10.

The two-dimensional structure of 2,3,4,5-tetrakis(acetoxymercuri) thiophene, 36, was determined by dark field transmission electron microscopy (201). Not only the four mercury atoms, but also the sulfur

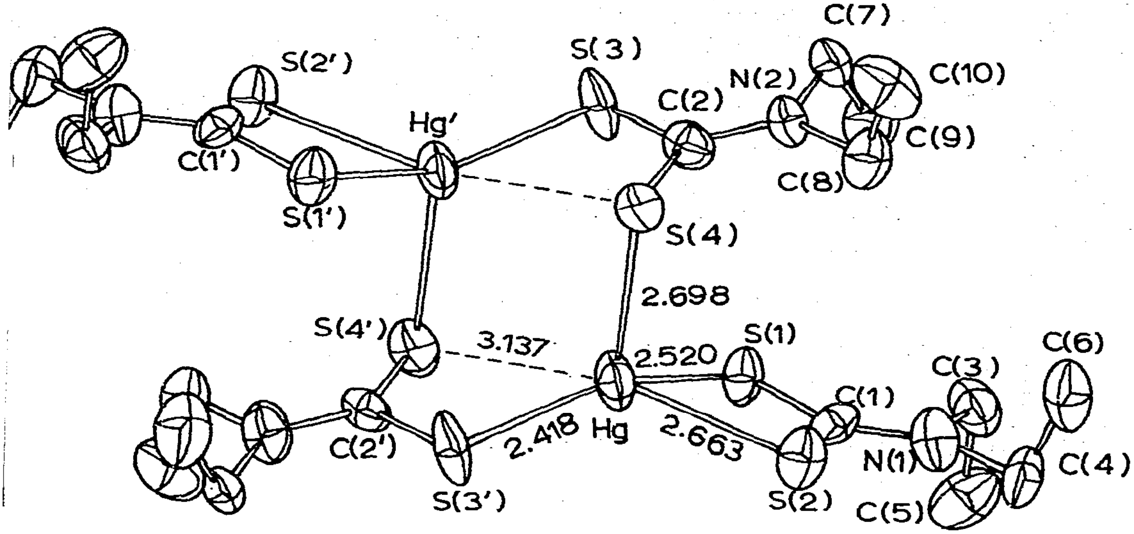
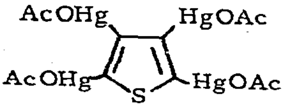


Figure 10. Structure of the Mercury(II) N,N-diethyldithiocarbamate Dimer (from H. Iwasaki, Acta Cryst., 29B (1973) 2115)



36

atom, were clearly revealed in the composite image resulting from the photographic superposition of 64 individual images.

B. Spectroscopic Studies

i. Vibrational Spectroscopy

The vibrational spectra of Me_3SiCH_2HgX and $(Me_3SiCH_2)_2Hg$ (133) and of pentachlorocyclopentadienylmercurials (113) have been reported.

ii. Nuclear Magnetic Resonance Spectroscopy

Proton NMR studies of Me_3SiCH_2HgX and $(Me_3SiCH_2)_2Hg$ (133), $Me_2C{=}CHHg$-substituted carboranes (117) and methylmercury compounds (152) have been reported. Of special interest in the latter study was the change in magnitude of $J(^{199}Hg-^1H)$ as Y in CH_3HgY was varied. This coupling constant decreased with Y in the order $OR > O_2CR > SR$, that is, with increasing covalent character of the Hg-Y bond.

Table 11. Carbon-Mercury Coupling Constants in R_2Hg Compounds (in Hz) (ref. 202)

Substituent	$^1J_{CHg}$	$^2J_{CCHg}$	$^3J_{CCCHg}$	$^4J_{CCCCHg}$
Methyl	692			
Ethyl	648	24		
n-Propyl	659	-25.2	102.6	
n-Butyl	656	26.3	100	0
Isopropyl	633.6	32.2		
Vinyl	+1159 ± 2			
Phenyl	1186	88	101.6	17.8

Table 12. $J(^{13}C-^{199}Hg)$ in R_2Hg Compounds (ref. 203).

Compound	Solvent	$J(^{13}C-^{199}Hg)$	$J(^{13}C-C-^{199}Hg)$
$(PhCH_2)_2Hg$	$CHCl_3$	631 Hz	
	C_5H_5N	669	
$(CH_3CH_2)_2Hg$	CCl_4	642	25 Hz
	$CHCl_3$	648	25
	DME	663	25
	C_5H_5N	679	25
	DMSO	688	25
$(CH_3)_2Hg$	CCl_4	687.4	
$(CH_3O_2CCH_2)_2Hg$	$CHCl_3$	753	
	C_5H_5N	820	
$(CF_3CH_2)_2Hg$	$CHCl_3$	896	
	C_5H_5N	1023	
$(CH_2{=}CH)_2Hg$	$CHCl_3$	1133	38
	DME	1162	41
	C_5H_5N	1200	42
	DMSO	1202	42
(trans-$ClCH{=}CH)_2Hg$	$CHCl_3$	1256	191
(cis-$ClCH{=}CH)_2Hg$	$CHCl_3$	1330	53
$(C_6H_5)_2Hg$	$CHCl_3$	1176	87
	C_5H_5N	1254	85
$(PhC{\equiv}C)_2Hg$	$CHCl_3$	2584	
	C_5H_5N	2694	

Spin-spin coupling between ^{13}C and ^{199}Hg nuclei in organomercurials has been studied by two groups (202, 203) (Tables 11 and 12). Noteworthy is the increase in the magnitude of this coupling as the carbon atom hybridization goes from sp^3 to sp^2 to sp and as the solvating power of the solvent is increased.

Pulse Fourier transform ^{199}Hg NMR spectra of several organic and inorganic mercury compounds have been reported by Maciel and Borzo (204) (Table 13). This technique should find useful application in organomercury chemistry.

Table 13. Some ^{199}Hg Chemical Shifts (Ref. 204)

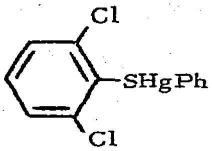
Sample	$-\delta^{199}Hg$[a]	Line width[b]
$(C_6H_5CH_2CH_2)_2Hg$	0	9
CH_3HgCl 0.52 M in pyridine	474.72	12
CH_3HgCl 0.51 M in DMSO	537.34	12
CH_3HgBr 0.50 M in pyridine	589.22	23
CH_3HgBr 0.49 M in DMSO	654.69	21
$Hg(CN)_2$ 2.0 M in pyridine	764.42	8
$Hg(CN)_2$ 0.41 M in pyridine	768.09	10
CH_3HgI 0.50 M in pyridine	791.86	34
CH_3HgI 0.49 M in DMSO	842.23	37
$HgCl_2$ 0.25 M in ethanol	1187.79	3
$HgCl_2$ 1.39 M in ethanol	1205.93	3
$Hg(NO_3)_2$ 2.0 M in 0.84 M HNO_3	2055.26	4
$Hg(NO_3)_2$ 4.0 M in 70% HNO_3	2280.06	4

[a] Chemical shift in ppm with respect to $(C_6H_5CH_2CH_2)_2Hg$, increasing magnitudes correspond to increasing shielding. All spectra were recorded at approximately 298°K. Bulk susceptibility corrections have been made.

[b] Approximate line width at half height.

iii. Nuclear Quadrupole Resonance and Mössbauer Spectroscopy

The ^{35}Cl NQR spectra of several pentachlorocyclopentadienylmercurials have confirmed other spectroscopic evidence that these compounds contain covalently bound C_5Cl_5 groups(113). The ^{35}Cl NQR spectrum of $\boxed{37}$ has been reported (205), as has an ^{129}I Mössbauer study of p-ZC_6H_4HgI (Z = F, Cl, H, MeO) (206). Effects due to the para substituents were slight as a result of the strong damping effect of the mercury atom.



$\boxed{37}$

iv. Photoelectron Spectroscopy

The photoelectron spectrum of allylmercuric iodide gave evidence for Hg-C bond hyperconjugation (interaction of the Hg-C σ_u and ethylene $\pi(b_{1u})$ orbitals) (207).

v. Mass Spectroscopy

Mass spectra of Me_3SiCH_2HgX and $(Me_3SiCH_2)_2Hg$ have been reported (133). McLaughlin and Rozett (208) have described a computer technique which calculates a least-squares fit monoisotopic mass spectrum restricted to positive solutions from polyisotopic measurements. This useful procedure was applied to the mass spectrum of dimethylmercury.

C. Other Physical Studies

A magneto-optical investigation of liquid dialkyl derivatives of zinc, cadmium and mercury gave results which were interpreted in terms of nonlinear dialkylmercury molecules (209). An inverse correlation between orientation and atom polarizations has been found for β-oxyalkylmercuric salts (210), and the electrical polarizations of dimethylmercury and mercuric chloride have been studied in the temperature range 8.5-50° C (211). Dipole moments of alkylmercuric halides have been determined (212, 213).

The polarographic reduction of RHgX compounds in acetonitrile, DMF and ethanol/benzene has been studied by Denisovich and Gubin (214). Effects of R, X and the solvent on the reduction process were examined. Polarographic reduction of various RHgCl and R_2Hg compounds, including metallocenylmercurials, was used to estimate the pK_a values of the metallocenes via the now well-known linear correlation between $E_{1/2}$ and pK_a (215). Detailed studies were carried out of the polarographic reduction of these metallocenylmercurials (diferrocenylmercury, ferrocenylmercuric chloride, bis(cyclopentadienylmanganese tricarbonyl)mercury and the rhenium analog, chloromercuricyclopentadienylmanganese (and rhenium) tricarbonyl), as well as of twelve carboranylmercurials (216). The potential utility of $E_{1/2}$ value determinations in the assessment of gross electronic properties of substituents was pointed out. Japanese workers (217) have reported on the polarography of o-hydroxyphenylmercuric chloride in aqueous nitric acid.

11. MISCELLANEOUS

A few miscellaneous items remain.

Dimethylmercury, when used as a solvent, has been found to be a spin-forbidden transition enhancer which allows the measurement of phosphorescence spectra in fluid medium at room temperature. This enabled the study of the $T_1 \rightarrow S_0$ radiative transition of a number of polynuclear aromatic hydrocarbons (218).

Among items from the analytical chemistry of organomercurials we note a study of the extraction and GLC determination of RHgX compounds (R = Me, Et, $MeOCH_2CH_2$) using ^{203}Hg-tagged materials (219). The procedure developed was useful for determining low levels of organomercurials in biological materials. Techniques for the collection and separation of metallic mercury and organomercury compounds in air have been described (220).

Finally, a detailed account has been given of methylmercury poisoning (via seed grain) in Iraq (221).

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