MERCURY

ANNUAL SURVEY COVERING THE YEAR 1972

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CONTENTS

1. REVIEWS AND BOOKS

The volume entitled "Organometallic Compounds of the Main Group Elements" of the Inorganic Chemistry Series of the "MTP International Review of Science" (University Park Press, 1972) contains a chapter by K. C. Bass on "Organic Derivatives of Zinc, Cadmium and Mercury". Recent developments (1966-1970, especially 1969-1970) of organomercury chemistry are reviewed.

Two books dealing in general with mercury and its compounds, including organomercurials, in the environment have appeared:

"Mercury in the Environment - a Toxicological and Epidemiological Approach", edited by L. T. Friberg and J. J. Vostal, CRC Press, Cleveland, Ohio, 1972.

"The Environmental Mercury Problem", by F. M. D'Itri, CRC Press, Cleveland, Ohio, 1972.

Other books or reviews published recently have covered the following topics:

- The divalent carbon transfer chemistry of phenyl(trihalomethyl)-mercury compounds (1)
- Free radical substitution reactions of organomercurials (2)
- The history, properties and analytical aspects of organomercury chemistry, in Hungarian (3).

2. PREPARATION OF ORGANOMERCURY COMPOUNDS

A new and potentially very useful synthesis of diorganomercurials uses the reduction of benzylic sulfonium salts, electrolytically at a mercury cathode (4), e.g.:

$$[p\text{-}Me_2EtCC_6H_4CH_2\overset{+}{S}Me_2]\ Cl^- \xrightarrow[\text{Hg cathode}]{\text{electrolysis}} (p\text{-}Me_2EtCC_6H_4CH_2)_2Hg$$

or with sodium amalgam (5), e.g.:

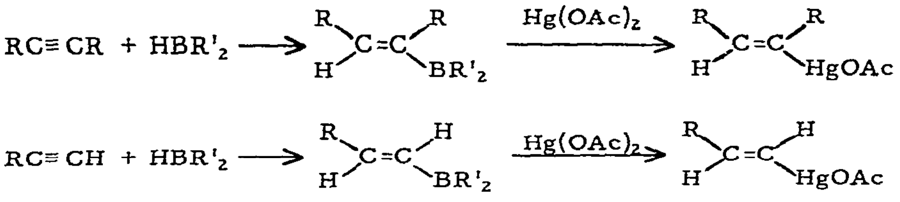
$$[PhCH_2\overset{+}{S}Me_2]\ [O_3SC_6H_4CH_3\text{-}p]^- \xrightarrow{Na/Hg} (PhCH_2)_2Hg$$

In another radical process, the oxidation of N-phenyl-N'-(tri-n-butylstannyl)hydrazine with mercuric oxide at room temperature resulted in vigorous evolution of nitrogen and formation of diphenylmercury (65%) and some biphenyl (35%) (6). Mercury (II) acetamide also oxidized this hydrazine.

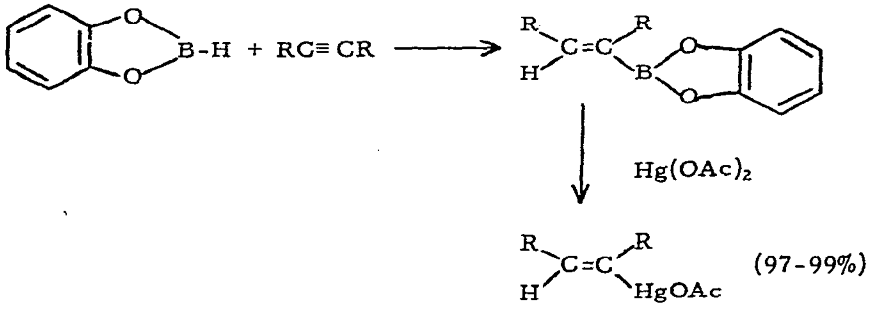
Organic derivatives of other metals or metalloids continue to serve in the preparation of organomercurials. Organoboranes are particularly useful in this connection, according to studies of H. C. Brown and his coworkers. The use of appropriate stoichiometry and reaction conditions allows the conversion of olefins, via hydroboration and reaction with mercuric acetate, to diorganomercurials (7). Thus when tri-n-butylborane was allowed to react with 1.5 molar equivalents of mercuric acetate in THF for 4 hr at reflux, di-n-butylmercury was obtained in 76% yield. Examples of such R_2Hg preparations starting with 1-butene, isobutylene, 1-dodecene, 3,3-dimethyl-1-butene, 2-methyl-1-pentene, β-pinene and 1,1-diphenylethylene were given. sec-Alkylboranes were inert under these conditions, and this allowed selective mercuri-deboronation of mixed trialkylboranes:

$$2\ (\text{cyclo-}C_6H_{11})_2BCH_2CHMe_2 + Hg(OAc)_2 \xrightarrow{\text{THF, room temp.}} \underset{(95\%)}{(Me_2CHCH_2)_2Hg} + 2\ (\text{cyclo-}C_6H_{11})_2BOAc$$

This procedure was used to prepare the dialkylmercurials starting with 1-dodecene, methyl 10-undecenoate, 5-bromo-1-pentene, 2-vinylnaphthalene, 3,3-dimethyl-1-butene and 2-methyl-1-pentene. Vinylic mercurials could be prepared in similar manner (8) (9):



(R' ≡ cyclo-C_6H_{11})



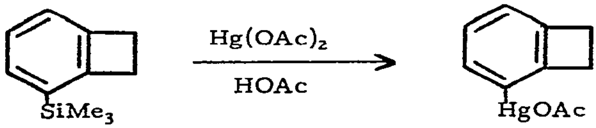
The utility of these reactions is enhanced by the fact that both steps are stereospecific.

Sodium tetraphenylborate phenylates organomercuric chlorides (at 100-150° in dioxane medium) (9a).

$$\mathrm{PhCH_2HgCl} \xrightarrow{\mathrm{NaBPh_4}} \mathrm{Ph_2Hg} + \mathrm{(PhCH_2)_2Hg} + \mathrm{PhHgCH_2Ph}$$

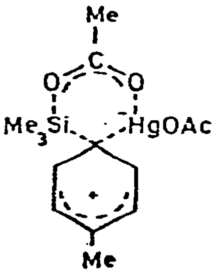
Similar reactions were observed with n-C_3H_7HgCl and i-C_3H_7HgCl.

Cleavage of the Si-C bond by Hg(II) derivatives also is possible. Such reactions can be used in synthesis, e.g. (10):



They have been studied with respect to rate and mechanism (11) and can be a nuisance (12).

A rate study (11) showed that the mercuridesilylation of p-tolyltrimethylsilane by mercuric acetate in glacial acetic acid involves both $Hg(OAc)_2$ and $HgOAc^+$ as reacting electrophiles. The latter is at least 15 times more reactive than the unionized species. The rate of mercuridesilylation was found to increase with increasing water content of the medium and also was affected by the silane concentration. The activation parameters for this reaction ($\Delta H^{\ddagger}$=13.8 kcal/mol, $\Delta S^{\ddagger}$=-30.4 cal/mol/°K) indicated a highly ordered activated complex, $\boxed{1}$



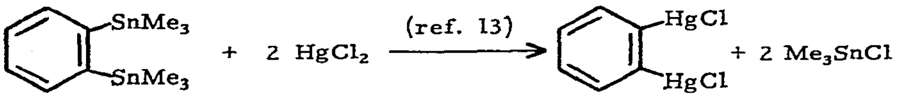
$\boxed{1}$

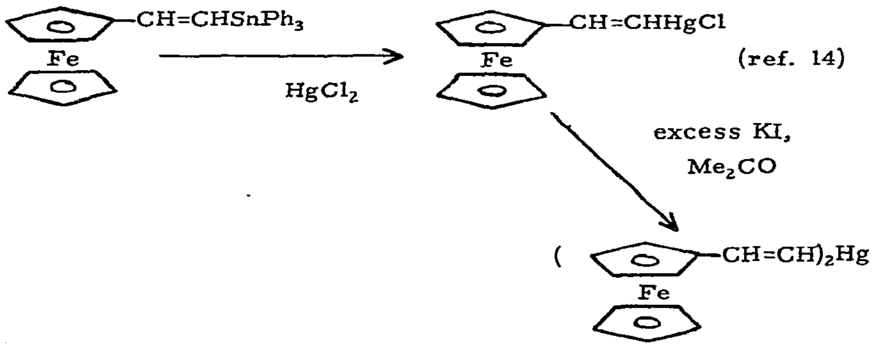
Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was found to methylate Hg(II) salts in aqueous solution (12):

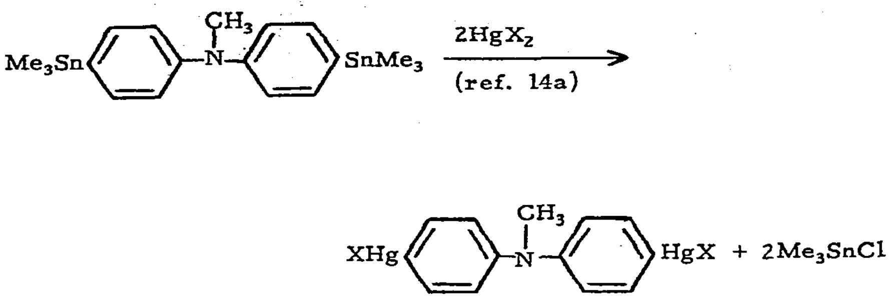
$$Me_3Si(CH_2)_3SO_3^{-}Na^{+} + HgX_2 \xrightarrow{H_2O} Me_2XSi(CH_2)_3SO_3^{-}Na^{+} + CH_3HgX$$

Since this silicon compound is used as an NMR reference standard in aqueous solution, this incompatibility with mercuric salts (which gives a silicon product with a CH_3-Si resonance 0.15 ppm downfield from the standard) must be kept in mind. These reactions proceed at room temperature, and the reactivity order is: $HgCl_2 << Hg(OAc)_2 < Hg(NO_3)_2$.

Organotin compounds also transfer organic groups to mercury, e.g.:

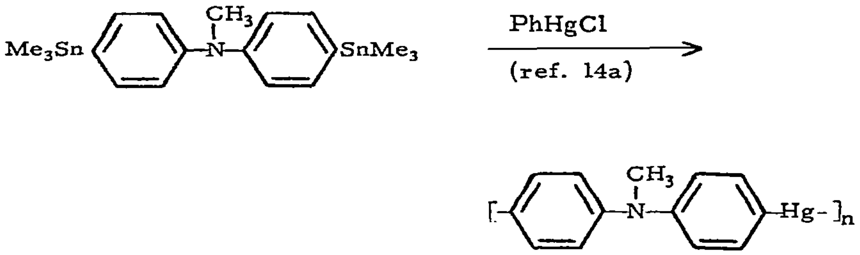






(X = Cl, OAc)

however:



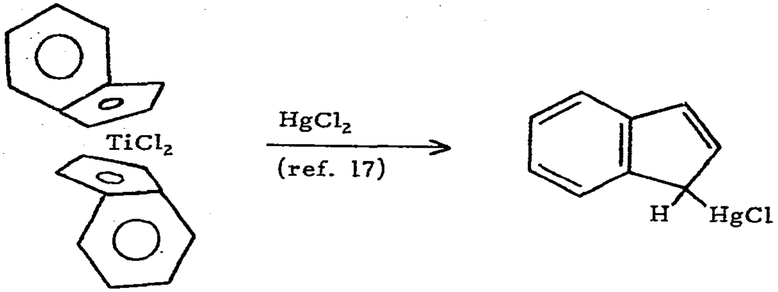
(m.p. 310° (dec); sol. in pyridine and DMF; no mol. wt. data)

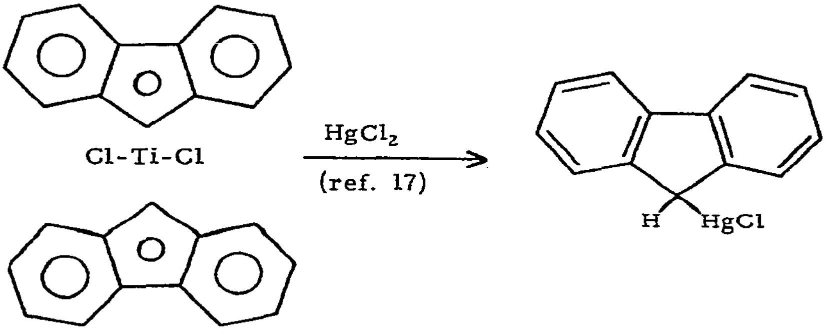
A major rearrangement was observed in such cleavage of a 3-butenyltin compound (15):

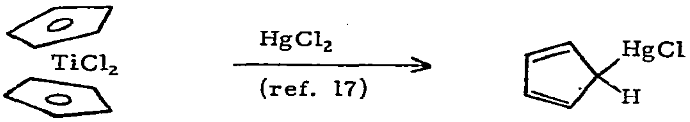
(73%)

Several examples of the transfer of organic groups from transition metal compounds to Hg(II) derivatives have been described, but few of them can be considered to be of synthetic utility.

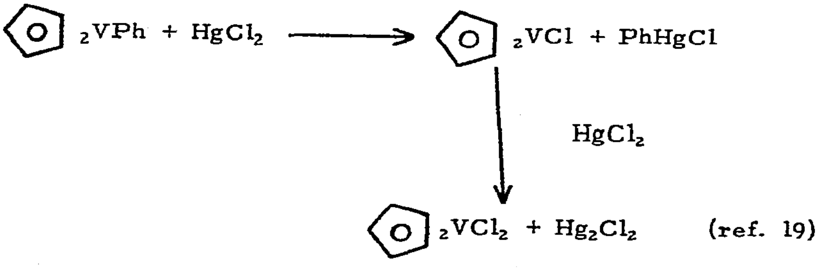
$$2\ PhC{\equiv}CAg + HgCl_2 \xrightarrow{\text{(ref. 16)}} (PhC{\equiv}C)_2Hg + 2\ AgCl$$

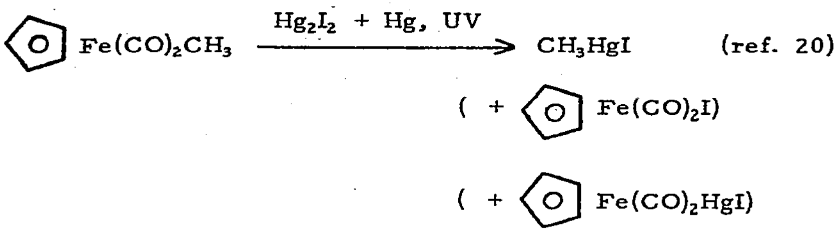


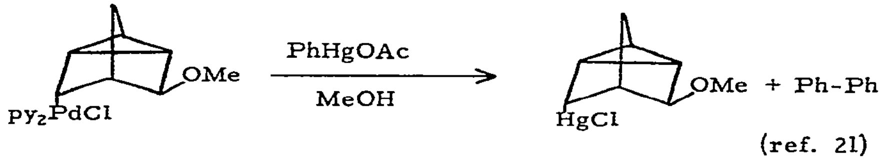


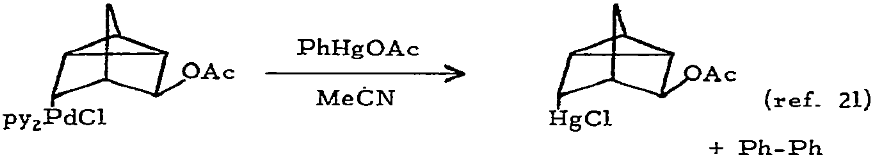


$$(C_6F_5)_4V + 2\ HgCl_2 \longrightarrow 2\ (C_6F_5)_2Hg + VCl_4 \quad \text{(ref. 18)}$$

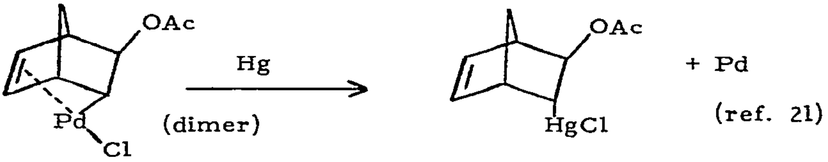


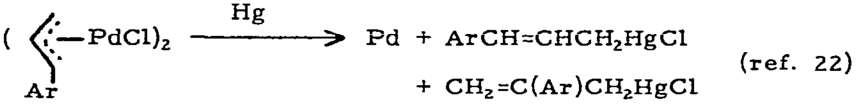






New examples of the displacement of metals from organometallic compounds by metallic mercury also have been described.





(Ar = m- and p-FC_6H_4 and ClC_6H_4)

$(C_6F_5)_3Bi \xrightarrow{Hg} (C_6F_5)_2Hg$ (ref. 23)

Ol'dekop and Maier have continued their studies of the radical-initiated decarboxylation of Hg(II) salts of organic acids. Such acyl peroxide-initiated decarboxylation of cis- and trans-4-methylcyclohexane mercury carboxylates in each case gave an approximately equimolar mixture of cis- and trans-4-methylcyclohexylmercury derivatives (24). A similar observation was made in the case of the UV-induced decarboxylation of cis- and trans-$(4\text{-}CH_3C_6H_{10}CO_2)_2Hg$. These results are in harmony with the proven radical mechanism of such decarboxylations. In other experiments, the effect of branching in the R group of $(RCO_2)_2Hg$ was examined (25):

$$(Me_3CCH_2CO_2)_2Hg \xrightarrow[\text{or UV}]{(RCO)_2O_2} Me_3CCH_2HgO_2CCH_2CMe_3$$

(fast reaction, high yield)

$$(Me_3CCH_2CH_2CO_2)_2Hg \xrightarrow[\text{or UV}]{(RCO)_2O_2} Me_3CCH_2CH_2HgO_2CCH_2CH_2CMe_3$$

(slow, nonquantitative reaction, equimolar amount of peroxide required)

Mercury(II) oxalates of type $(RO_2C\text{-}CO_2)_2Hg$ were found to be rather resistant to thermally-induced or UV-initiated decarboxylation (26). On the other hand, radical-induced decarboxylation of $Hg(O_2CCH_2\text{-}CH_2OR)_2$ to give $ROCH_2CH_2HgO_2CCH_2CH_2OR$ ($R \equiv CH_3$ through $n\text{-}C_5H_{11}$) occurred readily in yields of 43-89% (27). When $R \equiv Ph$, ethylene was the principal product. Attempted decarboxylation of $Hg(O_2CCH_2OMe)_2$ was not successful; the mercurous carboxylate, $Hg_2(O_2CCH_2OMe)_2$, was obtained instead in 87% yield.

The reported (28) decarboxylation of m- and p-$FC_6H_4O_2CCF_3$ in refluxing 1,2-dimethoxyethane (to give the respective $FC_6H_4HgCF_3$) was shown (29) to be incorrect.

The synthesis of highly halogenated arylmercurials by thermal sulfur trioxide extrusion from mercury(II) arenesulfonates was reported in 1971 by Cookson and Deacon (30), but was inadvertently not included in last year's annual survey:

$$Hg(O_3SAr)_2 \cdot H_2O \xrightarrow{160-270^\circ} Ar_2Hg + 2\ SO_3 + H_2O$$

(Ar = C_6F_5, 49% yield; Ar = C_6Cl_5, 51% yield; Ar = 2,3,5,6-C_6F_4H, 7% yield)

The Peters reaction:

$$RSO_2M + HgCl_2 \xrightarrow{H_2O,\ 100^\circ} MCl + SO_2 + RHgCl$$

has been shown to proceed via RSO_2HgCl intermediates or their complexes with mercuric chloride (31). Such intermediates, which IR spectroscopy indicated to be S-bonded to mercury, were isolated at lower temperatures. Their pyrolysis at 100-200° resulted in extrusion of sulfur dioxide:

$$2\ ArSO_2HgCl \cdot HgCl_2 \longrightarrow 2\ ArHgCl + SO_2 + HgCl_2$$

3. USE OF ORGANOMERCURIALS IN SYNTHESIS

A. Organometallic Synthesis

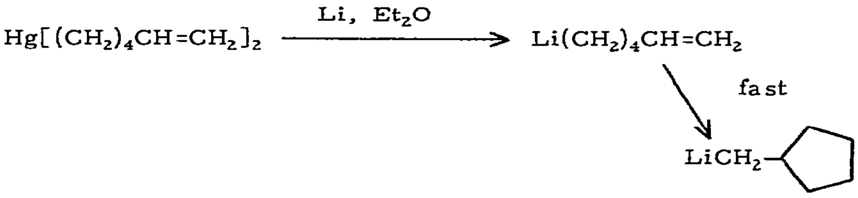
The metal displacement reaction and transmetalation processes continue to be of importance in the synthetic utilization of organomercurials. Examples of the metal displacement reaction reported in 1972 include:

$$(p\text{-}Me_2EtCC_6H_4CH_2)_2Hg \xrightarrow{Li} p\text{-}Me_2EtCC_6H_4CH_2Li$$ (ref. 4)

$$(PhCMe_2CH_2)_2Hg \xrightarrow{Li,\ pentane} PhCMe_2CH_2Li$$ (ref. 32)

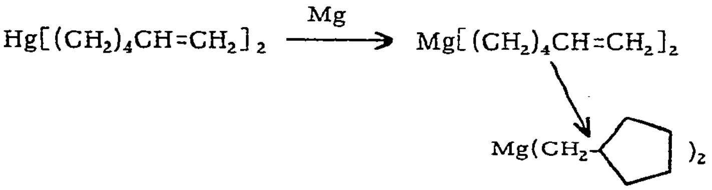
(prepared via the
Grignard reagent)

$$n\text{-}Bu_2Hg \xrightarrow{^6Li} n\text{-}Bu^6Li$$ (ref. 33)



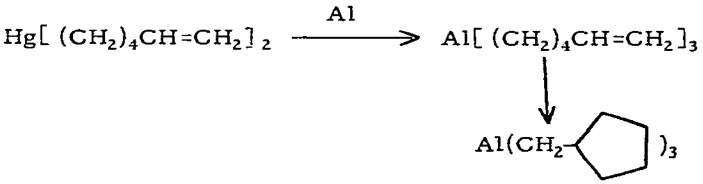
$$Hg[(CH_2)_4CH{=}CH_2]_2 \xrightarrow{Li,\ Et_2O} Li(CH_2)_4CH{=}CH_2$$

(ref. 34)



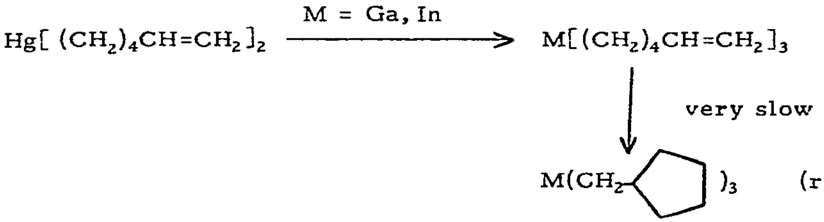
$$Hg[(CH_2)_4CH{=}CH_2]_2 \xrightarrow{Mg} Mg[(CH_2)_4CH{=}CH_2]_2$$

(ref. 34)



$$Hg[(CH_2)_4CH{=}CH_2]_2 \xrightarrow{Al} Al[(CH_2)_4CH{=}CH_2]_3$$

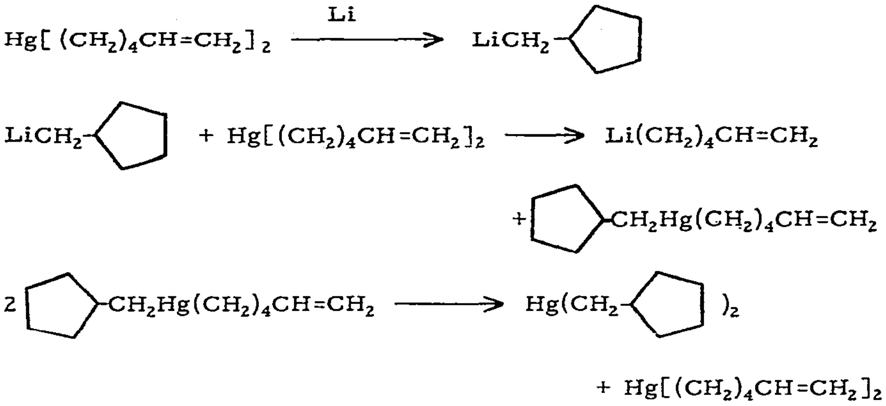
(Ref. 34)



$$Hg[(CH_2)_4CH{=}CH_2]_2 \xrightarrow{M\ =\ Ga,\ In} M[(CH_2)_4CH{=}CH_2]_3$$

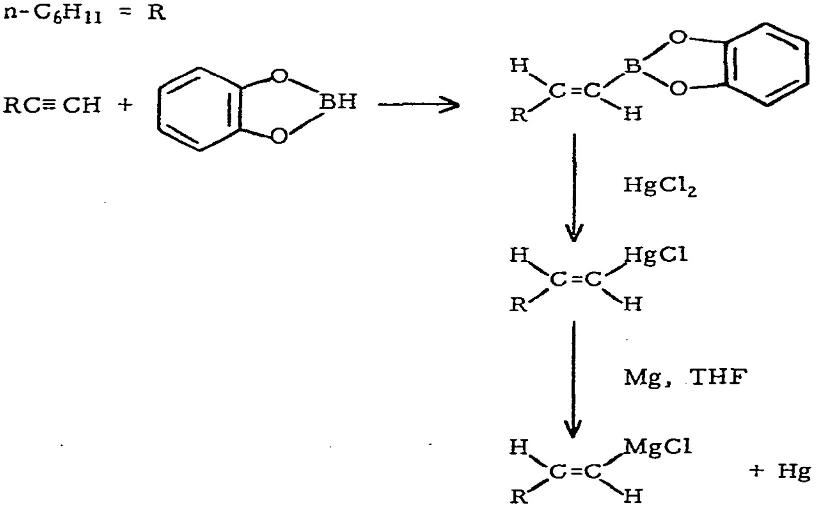
(ref. 34)

The action of the lithium or magnesium present in the first two reactions on this page on di-5-hexenylmercury also caused cyclization of the substituents on mercury via transmetalation processes:



Such a magnesium displacement reaction with a vinylic mercurial was an essential step in the synthesis of some prostaglandin analogs (35):

$n\text{-}C_6H_{11} = R$

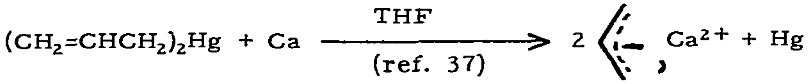


Organomercurials also have served in the synthesis of organocalcium compounds via the metal displacement reaction (36, 37):

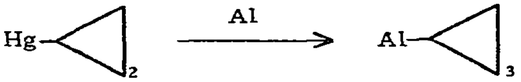
$$Ar_2Hg + Ca/Hg \xrightarrow[\text{(ref. 36)}]{\text{THF}} Ar_2Ca + Hg$$

$$R_2Hg + Ca \xrightarrow[\text{(ref. 37)}]{\text{THF}} R_2Ca + Hg$$

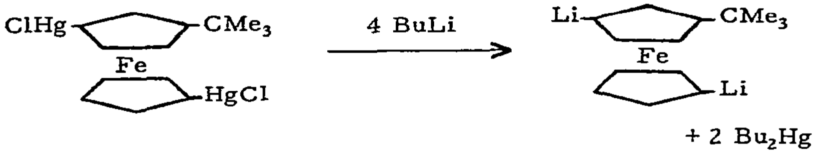
($R = C_1$ to
C_{25} alkyl)



and in the preparation of tricyclopropylaluminum (38):



Several examples of the application of the transmetalation reaction in organometallic synthesis have been reported:



(ref. 39)

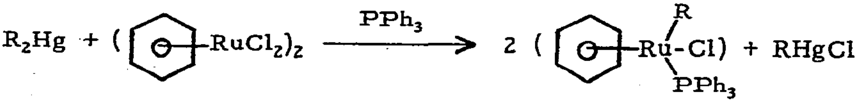
$$Ar_2Hg + Et_2Be \longrightarrow Ar_2Be + HgEt_2 \qquad \text{(ref. 40)}$$

Alkylation of halides with organomercurials has been used in the synthesis of organophosphorus (41), organoboron (42) and organometallic compounds of titanium (43) and ruthenium (44):

$$Hg(CH_2CH{=}O)_2 + 2\ (BuO)(ViO)P(O)Cl \longrightarrow (BuO)(ViO)P(O)(OCMe{=}CH_2) + HgCl_2$$

$$(CH_3C{\equiv}C)_2Hg + BF_2Cl \longrightarrow CH_3C{\equiv}CBF_2$$

$$(C_6F_5)_2Hg + 2\ TiCl_4 \longrightarrow C_6F_5TiCl_3 + HgCl_2$$

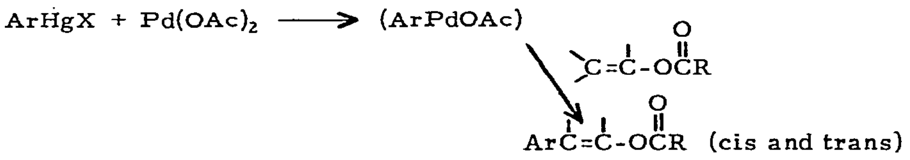


Finally, alkylation of transition metal anions, $[M_2(CO)_{10}]^{2-}$ (M = Cr, W, Mo) with $(PhC{\equiv}C)_2Hg$ to give the $[M(CO)_5C{\equiv}CPh]^-$ anions and elemental mercury has been reported (45). On the other hand, the action of phenylmercuric chloride on $[W_2(CO)_{10}]^{2-}$ proceeded differently:

$$PhHgCl + W_2(CO)_{10}^{2-} \longrightarrow Ph_2Hg + Hg + W(CO)_5Cl^-$$

B. Organic Synthesis

More examples of the indirect use of organomercurials in organic synthesis have been described; in these cases, of reactions in which an organomercurial is used to generate in situ an organopalladium derivative, further reactions of which give the final organic products. R. F. Heck, who has been a prime contributor to this area, has described the preparation of enol esters by such a process (46):



$$ArHgX + Pd(OAc)_2 \longrightarrow (ArPdOAc) \xrightarrow{\;>C{=}\overset{|}{C}{-}O\overset{\overset{O}{\|}}{C}R\;} Ar\overset{|}{C}{=}\overset{|}{C}{-}O\overset{\overset{O}{\|}}{C}R \text{ (cis and trans)}$$

A similar reaction was observed in alkylmercurial/$Pd(OAc)_2$ systems (47):

$$RHgOAc + Pd(OAc)_2 \longrightarrow (RPdOAc) \xrightarrow{CH_2{=}CHY} RCH{=}CHY$$

Table 1 shows the reactions reported. Phenylation of indene and 1,2-dihydronaphthalene also could be achieved by such a reaction (48):

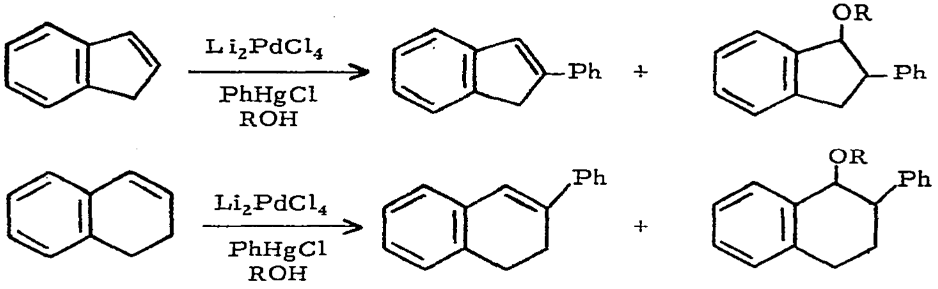
TABLE 1

OLEFIN ALKYLATIONS WITH ORGANOPALLADIUM COMPLEXES[a] (47)

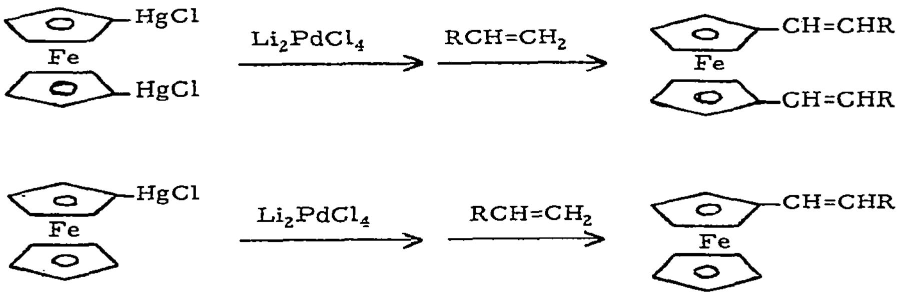
Alkylating agent	*Olefinic compound*	*Palladium salt*	*Solvent*	*Product*
5 mmoles CH_3HgOAc	2 ml $C_6H_5C(CH_3)=CH_2$	5 mmoles $Pd(OAc)_2$	10 ml CH_3CN	78% $CH_2=C(C_6H_5)CH_2CH_3$
1.67 mmoles $(CH_3)_3PbOAc$	2 ml $C_6H_5C(CH_3)=CH_2$	5 mmoles $Pd(OAc)_2$	10 ml CH_3CN	91% $CH_2=C(C_6H_5)CH_2CH_3$
1.67 mmoles $(CH_3)_3PbOAc$	2 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$	10 ml CH_3CN	44% *trans*-$CH_2CH=CHCOOCH_3$
5 mmoles CH_3HgOAc	2 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$	10 ml CH_3CN	84% *trans*-$CH_3CH=CHCOOCH_3$
1.25 mmoles $Sn(CH_3)_4$	2 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$	10 ml CH_3CN	94% *trans*-$CH_3CH=CHCOOCH_3$
5 mmoles $C_6H_5CH_2HgOAc$	2 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$	8 ml CH_3CN	20% $C_6H_5CH_2OAc$ 13% *trans*-$C_6H_5CH_2CH=CHCOOCH_3$
50 mmoles $C_6H_5CH_2HgOAc$	100 ml $CH_2=CHCOOCH_3$	50 mmoles $Pd(OAc)_2$		10% $C_6H_5CH_2OAc$ 60% (41%)[b] *trans*-$C_6H_5CH_2CH=CHCOOCH_3$
5 mmoles $C_6H_5CH_2HgOAc$	2 ml $CH_2=CHCH_2OAc$	5 mmoles $Pd(OAc)_2$	8 ml CH_3CN	78% $C_6H_5CH_2OAc$ 8% $C_6H_5CH_2CH=CHCH_2OAc$
5 mmoles $C_6H_5CH_2HgOAc$	10 ml $CH_2=CHCH_2OAc$	5 mmoles $Pd(OAc)_2$		18% $C_6H_5CH_2OAc$ 23% $C_6H_5CH_2CH=CHCH_2OAc$
5 mmoles $(CH_3)_3CCH_2HgOAc$	2 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$	8 ml CH_3CN	94% *trans*-$(CH_3)_3CCH_2CH=CHCOOCH_3$
5 mmoles $(CH_3)_3CCH_2HgOAc$	10 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$		68% $(CH_3)_3CCH_2CH=CHCOOCH_3$
50 mmoles $C_6H_5C(CH_3)_2CH_2HgOAc$	20 ml $CH_2=CHCOOCH_3$	50 mmoles $Pd(OAc)_2$	100 ml CH_3CN	41% *trans*-$(CH_3)_2C(C_6H_5)CH_2CH=CHCOOCH_3$ 19% *trans*-2-$(CH_3)_3CC_6H_4CH=CHCOOCH_3$
20 mmoles $C_6H_5C(CH_3)_2CH_2HgOAc$	8 ml $C_6H_5CH=CH_2$	20 mmoles $Pd(OAc)_2$	40 ml CH_3CN	46% $C_6H_5CH=CHOAc$ 50% *trans*-2-$(CH_3)_3CC_6H_4CH=CHC_6H_5$

[a] Reactions carried out at room temperature for about 15 h.

[b] Yield of isolated product.



The addition of ferrocenes to olefins by the mercurial-palladium route was reported by Japanese workers (49):



In all reactions with ferrocenylmercuric chloride small amounts of biferrocenyl were formed as well, while 1,1'-biferrocenylene was a minor by-product in the case of 1,1'-bis-(chloromercuri)ferrocene reactions. Some results are given in Table 2. When 1,3-dienes were used in such reactions in place of monoolefins, the products were π-allylpalladium derivatives (50):

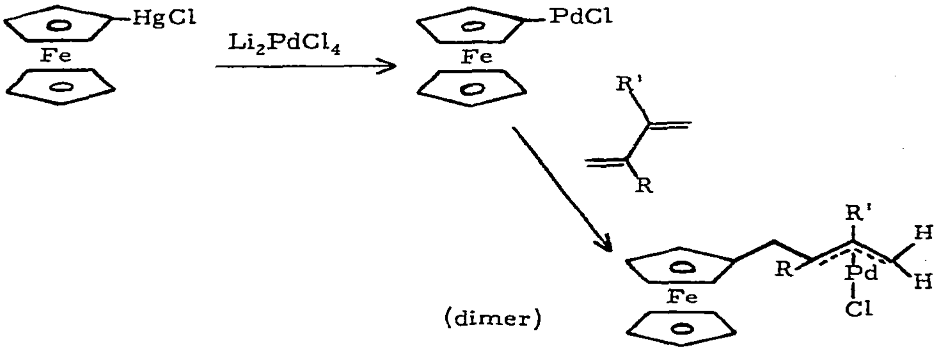


Table 2. Ferrocenylation of Olefins *via* Mercurials (49)

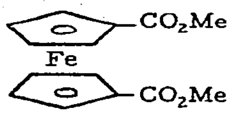
Olefin	Solvent	Product	Yield (%)[a]
(a) Reactions with Chloromercuriferrocene			
Ethylene	C_2H_5OH	Vinylferrocene	45
Styrene	CH_3OH	Styrylferrocene	52
Styrene	C_2H_5OH	Styrylferrocene	50
Styrene	CH_3COCH_3	Styrylferrocene	45
Styrene	CH_3COOH	Styrylferrocene	47
Styrene	CH_3CN	Styrylferrocene	43
Ethyl acrylate	C_2H_5OH	Ethyl-3-ferrocenyl acrylate	58
Ethyl crotonate	C_2H_5OH	Ethyl-3-ferrocenyl-crotonate	52
Methyl methacrylate	CH_3OH	Methyl 3-ferrocenyl-methacrylate	48
Acrylonitrile	C_2H_5OH	3-Ferrocenylacrylonitrile	49
Acrolein	C_2H_5OH	3-Ferrocenyl-2-propenal	45
Methyl vinyl ketone	C_2H_5OH	4-Ferrocenyl-3-buten-2-one	46
Phenyl vinyl ketone	C_2H_5OH	3-Ferrocenyl-1-phenyl-2-propen-1-one	45
3-Buten-2-ol	C_2H_5OH	4-Ferrocenyl-2-butanone	31
2-Methyl-2-propenol	C_2H_5OH	2-Methyl-3-ferrocenylpropionaldehyde	34
5-Phenyl-2-cyclohexenol	CH_3CN	3-Ferrocenyl-5-phenylcyclohexanone	14
5,5-Dimethyl-2-cyclohexenol	CH_3CN	3-Ferrocenyl-5,5-dimethylcyclohexanone	12
Isopropenyl acetate	C_2H_5OH	α-Ferrocenylacetone	27
Acetophenone enol acetate	C_2H_5OH	α-Ferrocenylacetophenone	16

Table 2 (cont'd)

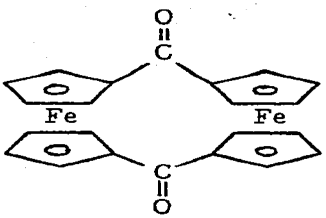
Olefin	Solvent	Product	Yield (%)[a]
2-Methylallyl chloride	C_2H_5OH	3-Chloro-1-ferrocenyl-2-methylpropene	21
(b) Reaction with 1,1'-bis(chloromercuri(ferrocene			
Styrene	C_2H_5OH	1,1'-Distyrylferrocene	37
Ethyl acrylate	C_2H_5OH	1,1'-Bis(2-ethoxycarbonylvinyl)ferrocene	28
Ethyl crotonate	C_2H_5OH	1,1'-Bis(2-ethoxycarbonyl-1-methylvinyl)ferrocene	25
Methyl methacrylate	C_2H_5OH	1,1'-Bis(2-methoxycarbonyl-2-methylvinyl)ferrocene	31
Acrylonitrile	C_2H_5OH	1,1'-Bis(2-cyanovinyl)-ferrocene	28
Acrolein	C_2H_5OH	1,1'-Bis(2-formylvinyl)-ferrocene	22
Methyl vinyl ketone	C_2H_5OH	1,1'-Bis(2-acetylvinyl)-ferrocene	27
Phenyl vinyl ketone	C_2H_5OH	1,1'-Bis(2-benzoylvinyl)-ferrocene	25

[a] Yields are based upon the ferrocenylating agent.

This type of behavior was observed with butadiene, isoprene, and 2,3-dimethylbutadiene, but with methyl sorbate the product was $C_5H_5FeC_5H_4C(CH_3){=}CH{-}CH{=}CHCO_2CH_3$. Carbonylation in methanol of the organopalladium intermediate from the reaction of 1,1'-bis-(chloromercuri)ferrocene with Li_2PdCl_4 gave $\boxed{2}$ and $\boxed{3}$. With ferrocenylmercuric chloride, the products of carbonylation were $C_5H_5FeC_5H_4CO_2Me$ and $\boxed{4}$ (51).



2



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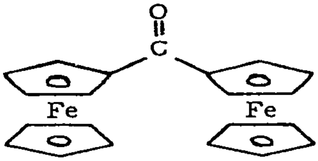
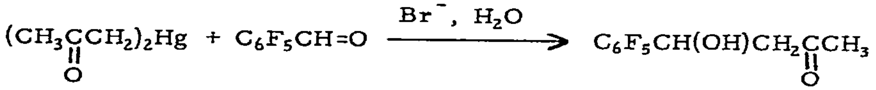


4

β-Ketoalkylmercurials have found use in synthesis in new reactions in which they show carbanion reactivity in the presence of a halide ion catalyst:

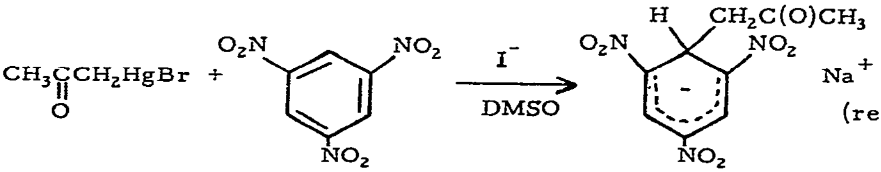


$$(CH_3\underset{\underset{O}{\|}}{C}CH_2)_2Hg + C_6F_5CH{=}O \xrightarrow{Br^-,\ H_2O} C_6F_5CH(OH)CH_2\underset{\underset{O}{\|}}{C}CH_3$$

(ref. 52)

$$(CH_3\underset{\underset{O}{\|}}{C}CH_2)_2Hg + CCl_3CH{=}O \xrightarrow{DME} CCl_3CH(OH)CH_2\underset{\underset{O}{\|}}{C}CH_3$$

(ref. 52)



(ref. 53)

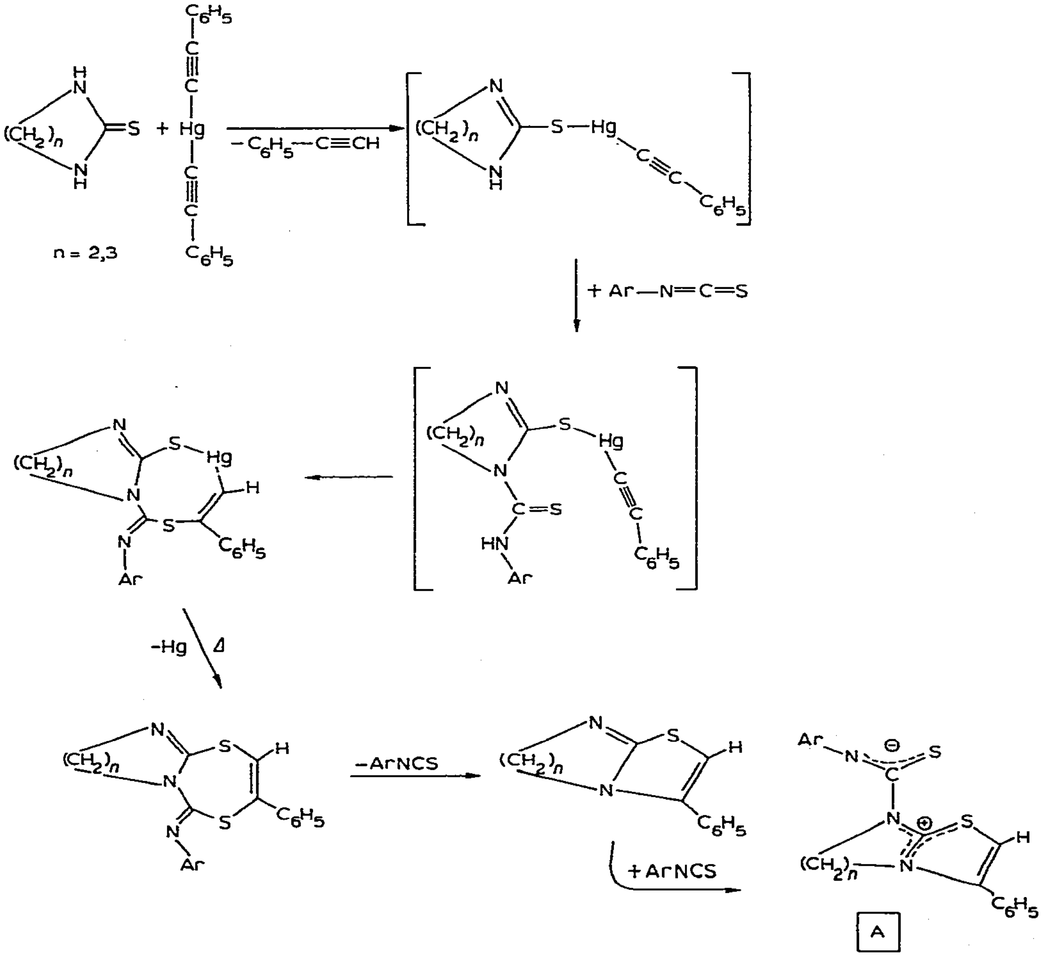
5

Similar additions to give Jackson-Meisenheimer complexes of type 5 were observed with other mercurials, R_2Hg and RHgX, with electron-withdrawing substituents, e.g., R = C_6F_5, PhC≡C, $(CF_3)_2CH$, $Ph(CO_2Et)CH$, o-carboranyl, but not Ph and alkyl (53).

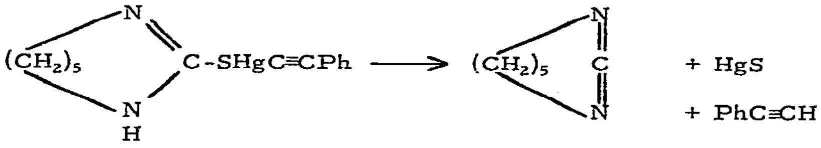
Further studies of the carbonylation of mercurials have been reported (54). A reaction of $BuOCH_2CH_2HgOAc$ with carbon monoxide in butanol at 100 atmospheres pressure and 200° gave $BuOCH_2CH_2CO_2Bu$ in 51-6% yield, in addition to minor amounts of butyl acetate.

Bis(phenylethynyl)mercury has been used in a synthesis of betaines of type $\boxed{A}$ as shown in Scheme 1 (55). This procedure works with 5- and 6-membered cyclic thiourea derivatives and when an aryl isothiocyanate is used. Mild heating serves to effect mercury

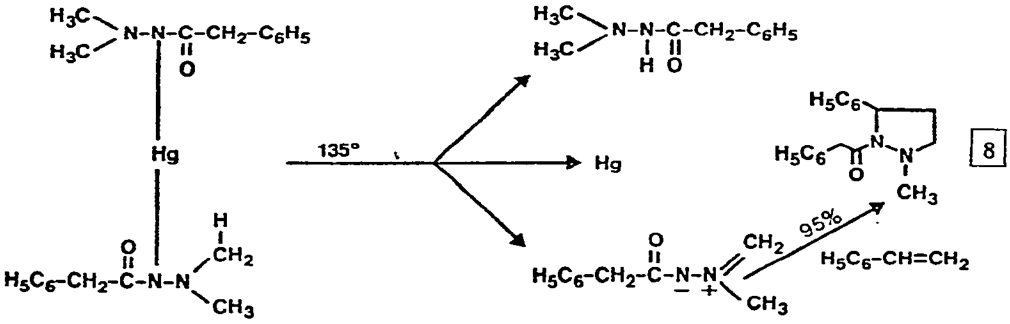
Scheme 1



extrusion from the organomercury intermediate. The 7-membered cyclic thiourea (n = 4) reacted with $Hg(C\equiv CPh)_2$ to give the cyclic carbodiimide:



A few examples of synthetic applications of mercury compounds which do not contain a Hg-C bond are worth mentioning. The reaction of N,N-dimethyl-N'-phenacetylhydrazine with mercuric oxide gave mercurial $\boxed{6}$, whose structure was determined by X-ray crystallography (fig. 1). Its pyrolysis at 135° resulted in extrusion of mercury and formation of the dipolar intermediate $\boxed{7}$ The latter could be trapped with styrene to give $\boxed{8}$ (56). Analogous adducts were obtained with use of benzonorbornadiene, acrylonitrile and 1,1-diphenylethylene in place of styrene, thus establishing a general pyrazolidine synthesis.



6 7

Mercury(II) carboxylates have been shown to be intermediates in the synthesis of alkyl halides by reaction of carboxylic acids with mercuric oxide and halogens (57).

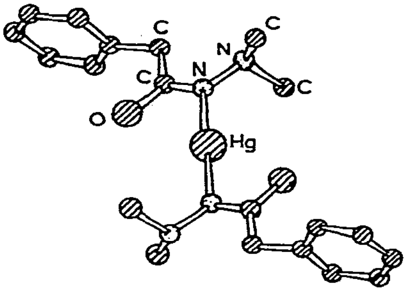


Figure 1. Structure of Mercury-bis(N, N-dimethyl-N'-phenacetylhydrazine (ref. 56).

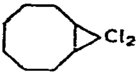
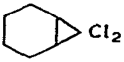
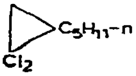
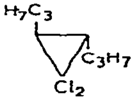
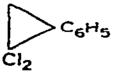
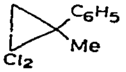
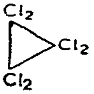
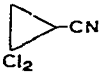
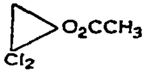
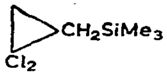
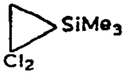
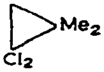
C Halomethylmercury Compounds

Further development of halomethylmercury compounds as useful divalent carbon transfer reagents may be noted and a review dealing with the scope and mechanism of the dihalocyclopropanation of olefins with phenyl(trihalomethyl)mercurials now is available (1). Several of these reagents ($PhHgCCl_2Br$, $PhHgCBr_3$, $PhHgCF_3$) now are commercially available (58).

More research has been devoted to the utilization of trihalomethylmercurials as room temperature dihalocarbene sources (cf. J. Organometal. Chem., 41 (1972) 178-181). Phenyl(trihalomethyl)mercury compounds transferred CX_2 to olefins very smoothly at room temperature, but long reaction times were required, e.g., 18 days in the case of $PhHgCCl_2Br$. The product yields obtained were excellent (Table 3) (59). Further work at M. I. T. showed the cyclohexyl(trihalomethyl)mercurials to be exceptionally reactive CX_2 sources, reacting with olefins and with triethylsilane within a few minutes at 80° and within 2-3 days at room temperature (Table 4) (60). These reagents, prepared by reaction of cyclohexylmercuric chloride, potassium tert-butoxide and the appropriate haloform in THF

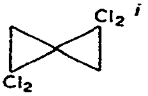
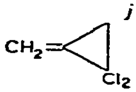
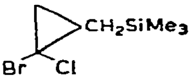
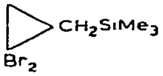
TABLE 3

REACTIONS OF $PhHgCCl_nBr_{3-n}$ ($n = 0$–2) WITH OLEFINS AT ROOM TEMPERATURE [a,b] (ref. 59)

Olefin	Product	Yield (%)	PhHgBr (%)
a. With $PhHgCCl_2Br$ [c]			
		95	100
		72	92
$n\text{-}C_5H_{11}CH{=}CH_2$		62	88
trans-$n\text{-}C_3H_7CH{=}CHC_3H_7\text{-}n$		98	100
$C_6H_5CH{=}CH_2$		80	95
$C_6H_5CMe{=}CH_2$		80	95
$Cl_2C{=}CCl_2$		80	90
$CH_2{=}CHCN$		85	92[d]
$CH_3CO_2CH{=}CH_2$		86	91
$Me_3SiCH_2CH{=}CH_2$		99	100
$Me_3SiCH{=}CH_2$		74	88
$Me_2C{=}CH_2$[e]		75	90

(continued)

TABLE 3 *(continued)*

Olefin	Product	Yield (%)	PhHgBr (%)
$CH_2{=}C{=}CH_2$[e,f]	 [i]	60	89
$CH_2{=}C{=}CH_2$[e]	 [j]	90	98
b. With $PhHgCClBr_2$[g]			
		71	90
$Me_3SiCH_2CH{=}CH_2$		72	97
c. With $PhHgCBr_3$[h]			
		69	89
$Me_3SiCH_2CH{=}CH_2$		65	85

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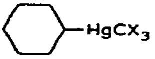
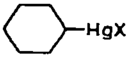
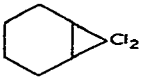
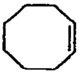
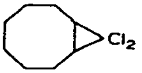
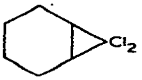
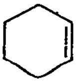
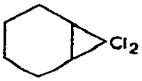
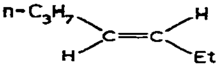
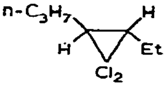
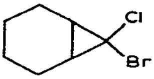
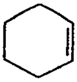
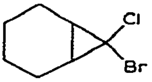
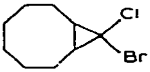
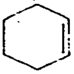
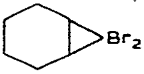
[a] At 26 ±2° at atmospheric pressure, unless otherwise specified. [b] Olefin/mercurial ratio = 10 unless otherwise specified. [c] 18 day reaction time. [d] PhHgBr slightly brown; in other reactions it was white. [e] Sealed-tube reaction. [f] Olefin/mercurial ratio 1/3. [g] 16 day reaction time. [h] 15 day reaction time.

solution at -65°, are crystalline solids which are stable at room temperature as the solid and, furthermore, the cyclohexylmercuric halides formed in their decomposition are crystalline solids which are not very soluble in organic solvents at room temperature or below.

Isopropyl(trichloromethyl)mercury was found to be equal in reactivity to cyclo-$C_6H_{11}HgCCl_3$ (cf. Table 4) and n-$C_3H_7HgCCl_3$ (Shcherbakov, cf. J. Organometal. Chem. 41 (1972) 181), reacting

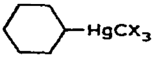
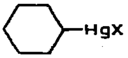
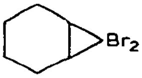
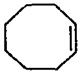
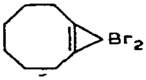
TABLE 4 (ref. 60)

REACTIONS OF CYCLOHEXYL (TRIHALOMETHYL) MERCURIALS

CX_3 in 	Reactant	Reaction conditions [a]	Product (% yield) [b]	 (% yield) [c]
CCl_3		6.5h / 80°	 (92)	
CCl_3		8h/80°	 (90)	98
CCl_3	Et_3SiH	8h/80°	Et_3SiCCl_2H (88)	97
CCl_2Br		6 min/80°	 (96)	95
CCl_2Br		49 h / 25°	 (95)	85
CCl_2Br		50h/25°	 (88)	80
CCl_2Br	Et_3SiH	50h/25°	Et_3SiCCl_2H (80)	89
$CClBr_2$		7min/80°	 (85)	90
$CClBr_2$		3 days/25°	 (87)	91
$CClBr_2$		3days /25°	 (83)	90
$CClBr_2$	Et_3SiH	3days/25°	$Et_3SiCBrClH$ (70)	90
CBr_3		10min/80°	 (40)	90

(to be continued)

TABLE 4 *(continued)*

CX$_3$ in 	Reactant	Reaction conditions [a]	Product (% yield) [b]	 (% yield) [c]
CBr$_3$		48h/25°	 (50)	80
CBr$_3$		48h/25°	 (34)	80

[a] In general, reactions were carried out with 10 mmol of the mercury reagent and 30 mmol of the reactant in 7–10 ml of dry benzene, with stirring under nitrogen. In room temperature experiments and in the 80° experiments with cyclo-$C_6H_{11}HgCCl_3$, the benzene solution of the reactants simply was stirred for the stated length of time. In the other 80° experiments, the mercury reagent, dissolved in benzene, was added during 3 min to the preheated substrate and the resulting mixture was heated for the remaining part of the stated reaction time.

[b] Determined by GLC.

[c] Obtained by filtration of the reaction mixture after it had been cooled to 5°.

with cyclohexene at 80° within 3 hr to give isopropylmercuric chloride (90%) and 7,7-dichloronorcarane (71%) (61). Such an increase in the divalent carbon transfer reactivity of a halomethylmercurial on replacement of phenyl as the "inert" substituent on mercury by an alkyl group also was found in the case of the CH_2 transfer system. Benzyl(iodomethyl)mercury was considerably more reactive in its reactions with olefins than were the previously known $Hg(CH_2Br)_2$/Ph_2Hg or ICH_2HgI/Ph_2Hg systems (62). However, the reported preparation of benzyl(iodomethyl)mercury:

$$PhCH_2HgI + CH_2N_2 \longrightarrow PhCH_2HgCH_2I + N_2$$

is not practical compared with the route to the equally reactive $(PhCH_2)_2Hg/Hg(CH_2I)_2$ reagent which does not require the use of diazomethane for its preparation (63).

Full details have been published concerning the preparation of phenyl(trifluoromethyl)mercury and its use in the generation of difluorocarbene (29, 64, 65). Of the several routes described, the most direct and practical is that summarized by the equations below (29, 64):

$$HgO + 2CF_3CO_2H \longrightarrow Hg(O_2CCF_3)_2 + H_2O$$

$$Hg(O_2CCF_3)_2 \xrightarrow{300^\circ} CF_3HgO_2CCF_3 + CO_2$$

$$CF_3HgO_2CCF_3 + Ph_2Hg \longrightarrow PhHgCF_3 + PhHgO_2CCF_3$$

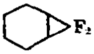
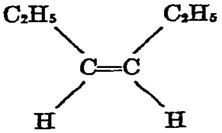
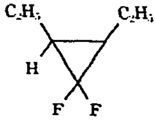
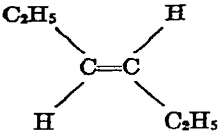
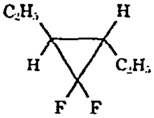
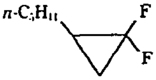
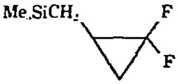
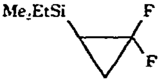
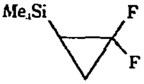
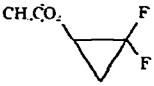
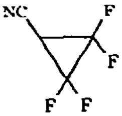
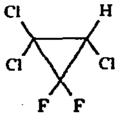
$$PhHgO_2CCF_3 + NH_4^+Cl^- \xrightarrow{H_2O} PhHgCl\downarrow + NH_4^+O_2CCF_3^-$$

Phenyl(trifluoromethyl)mercury also may be prepared by the fluorination of phenyl(tribromomethyl)mercury with phenylmercuric fluoride (as the HF adduct) in benzene at room temperature in the presence of 48% aqueous hydrofluoric acid (65). Phenyl(trichloromethyl)mercury could be fluorinated to $PhHgCF_3$ in this manner, but a reaction temperature of 90° was required. Partial fluorination of $PhHgCCl_2Br$ to give $PhHgCCl_2F$ in good yield could be achieved at room temperature, but attempted partial fluorination of $PhHgCBr_3$, $PhHgCClBr_2$ and $PhHgCFBr_2$ was unsuccessful, $PhHgCF_3$ being the major product obtained. The mechanism of this remarkable fluorination process remains a subject of conjecture.

Phenyl(trifluoromethyl)mercury is too stable to serve as a thermal CF_2 source, but in the presence of molar quantities of sodium iodide in benzene medium it transfers CF_2 to olefins, giving

TABLE 5 (ref. 64)

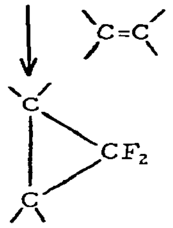
REACTIONS OF THE $PhHgCF_3/NaI$ REAGENT WITH OLEFINS

Olefin	Product	(% yield)
		(83)
		(83)
		(93)
		(94)
$n\text{-}C_5H_{11}CH{=}CH_2$		(70)
$Me_3SiCH_2CH{=}CH_2$		(100)
$Me_2EtSiCH{=}CH_2$		(44)
$Me_3SiCH{=}CH_2$		(53)
		(67)
$CH_3CO_2CH{=}CH_2$		(84)
$CH_2{=}CHCN$		(26)
$CCl_2{=}CHCl$		(72)

gem-difluorocyclopropanes in high yield (64). Presumably, the reaction course shown below is involved.

$$PhHgCF_3 + Na^{+}I^{-} \longrightarrow PhHgI + Na^{+}\overset{:}{C}F_3^{-}$$

$$Na^{+}CF_3^{-} \longrightarrow NaF + CF_2$$

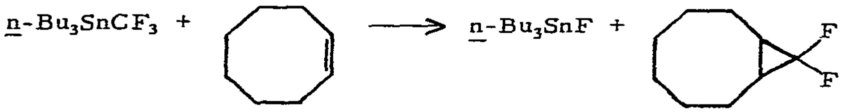


Some of the reactions carried out with the $PhHgCF_3/NaI$ system are summarized in Table 5.

Trifluoromethylmercuric iodide also reacted with sodium iodide in this manner, but CF_3HgCl and CF_3HgBr did not, appearing to form stable halide complexes instead.

A thermal transfer of CF_2 to an olefin could be effected when phenyl(trifluoromethyl)mercury was heated at about 140° with cyclooctene for 3 days in the presence of three molar equivalents of tri-n-butyltin bromide or chloride (64). A reaction course involving intermediate formation of n-Bu_3SnCF_3 was indicated:

$$PhHgCF_3 + \underline{n}\text{-}Bu_3SnX \rightleftharpoons PhHgX + \underline{n}\text{-}Bu_3SnCF_3$$



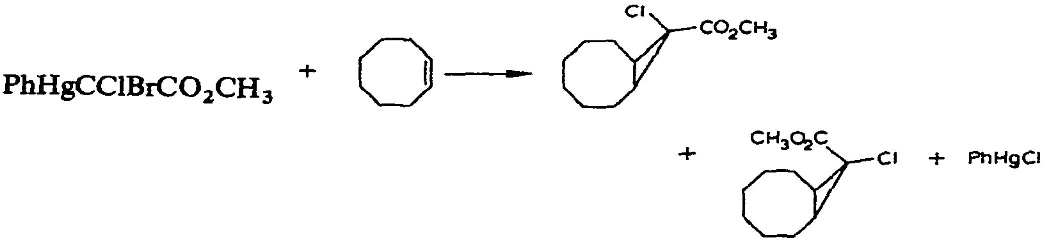
Organomercurials which transfer $FCCO_2Et$, $ClCCO_2Me$ and $BrCCO_2Me$ have been reported:

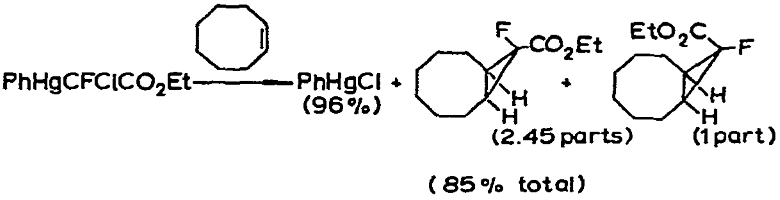
$$PhHgCl + HCXYCO_2CH_3 + Me_3COK \xrightarrow[-50^\circ]{THF} PhHgCXYCO_2CH_3 + KCl + Me_3COH \quad \text{(ref. 66)}$$

(X, Y = Cl, Cl; Cl, Br; Br, Br)

$$CClF{=}CFOEt \xrightarrow[EtOH]{Hg(NO_3)_2} \xrightarrow{HgCl_2} \begin{array}{l} Hg(CFClCO_2Et)_2 \\ + \\ ClHgCFClCO_2Et \\ \quad \Big\downarrow Ph_2Hg \\ PhHgCFClCO_2Et \quad \text{(ref. 67)} \end{array}$$

All four of these carboalkoxy-substituted mercurials reacted with olefins at temperatures of 130-150° (with multiday reaction times, usually in sealed tubes) to give the expected 1-halocyclopropanecarboxylic acid esters, e.g.:

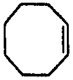
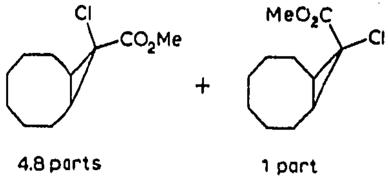
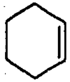
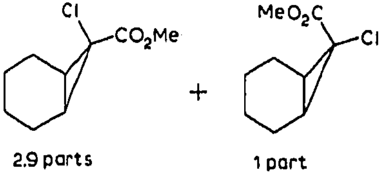
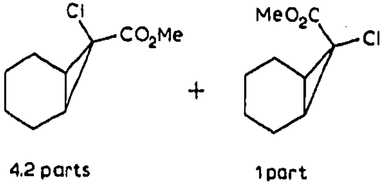
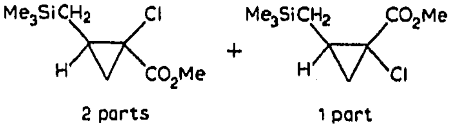
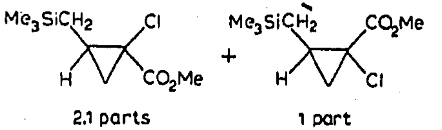


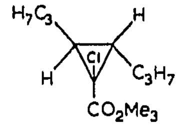
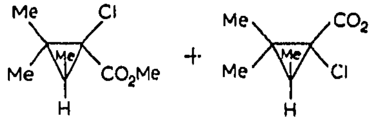
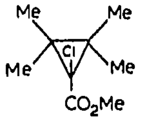
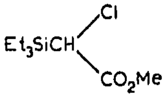
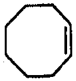
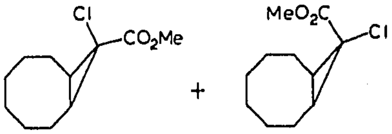
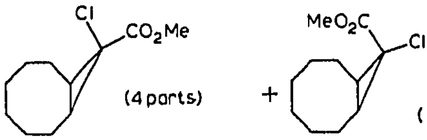
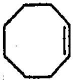
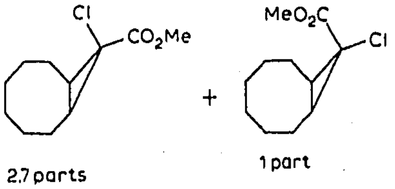


Because of the strenuous reaction conditions required, yields were variable, running from poor to excellent, depending on the olefin used. Table 6 summarizes the results obtained with $PhHgCCl_2CO_2Me$, $PhHgCClBrCO_2Me$ and $PhHgCBr_2CO_2Me$ (66). The insertion of the

TABLE 6 (ref. 66)

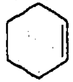
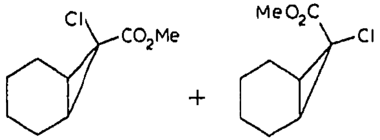
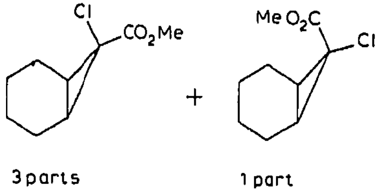
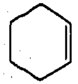
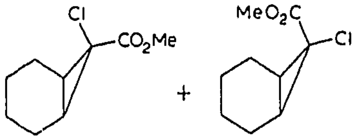
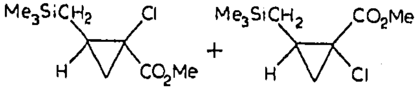
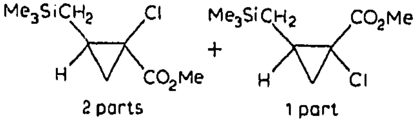
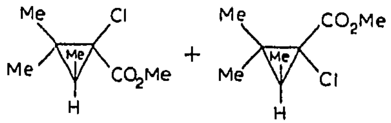
DIVALENT CARBON TRANSFER REACTIONS OF $PhHgCCl_2CO_2CH_3$, $PhHgCClBrCO_2CH_3$ AND $PhHgCBr_2CO_2CH_3$

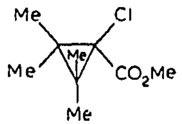
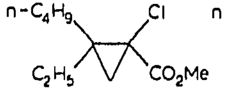
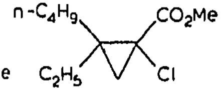
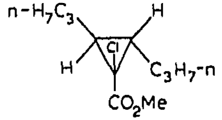
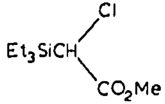
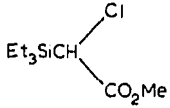
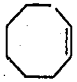
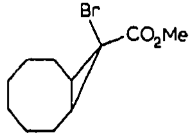
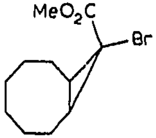
Substrate (mmol)	*mmol of mercurial*	*Solvent*	*Reaction temperature (°C)*	*Reaction time*	*Yield of PhHgX (%)*	*Products (% yield)*
Reactions of $PhHgCCl_2CO_2CH_3$						
 (38)	5	none	130°	3 days	86	 (59)
 (100)	18.4	C_6H_6 (5.0 ml)	110–135^b (sealed tube)	7 days	76 (+8% Hg)	 (42)
 (100)	15	PhCl (5.0 ml)	124–125° (sealed tube)	7 days	74 (+9% Hg)	 (36)
$Me_3SiCH_2CH{=}CH_2$ (16.6)	10.15	PhCl (20 ml)	reflux	47 h	93	 (71)
$Me_3SiCH_2CH{=}CH_2$ (100)	15	PhCl (5 ml)	124–125° (sealed tube)	7 days	87 (+8% Hg)	 (73)

$n\text{-}C_3H_7CH=CHC_3H_7\text{-}n$ (100)	15	PhCl (5 ml)	~125° (sealed tube)	7 days	67 (+8% Hg)	 (20)
$Me_2C=CHMe$ (103)	10	PhCl (28 ml)	~135° (sealed tube)	6 days	96 (+5% Hg)	 (20)
$Me_2C=CMe_2$ (22.6)	9.56	PhCl (10 ml)	~135° (sealed tube)	6 days	64 (+15% Hg)	 (~4%)
Et_3SiH (26.5)	20.1	PhCl (60 ml)	reflux	62 h	86 (+18% Hg)	 $Et_3SiCH(Cl)CO_2Me$ (42)
Reactions of $PhHgCClBrCO_2CH_3$						
 (15.6)	4.6	PhCl (20 ml)	reflux	27 h	90	 (56)
 (50)[a]	5	PhCl (2.5 ml)	127–128° (sealed tube)	24 h	92	 (67) (1 part)
 (38)	9.7	C_6H_6 (10 ml)	95°	6.5 h	74	 (27)

(*continued*)

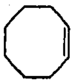
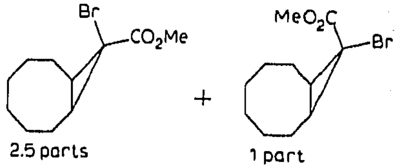
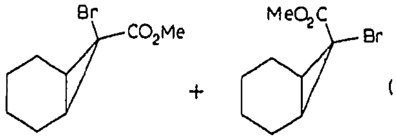
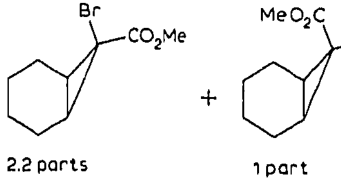
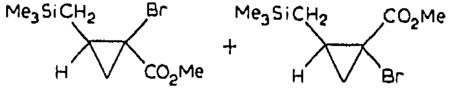
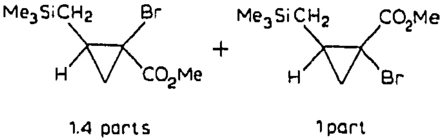
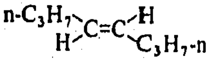
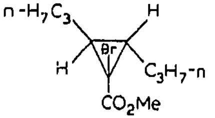
TABLE 6 *(continued)*

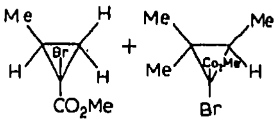
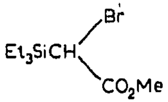
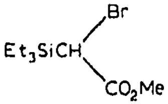
Substrate (mmol)	*mmol of mercurial*	*Solvent*	*Reaction temperature (°C)*	*Reaction time*	*Yield of PhHgX (%)*	*Products (% yield)*	
 (22.8)	10	PhCl (25 ml)	reflux	25 h	90		(32)
 (50)	5	PhCl (2.5 ml)	128° (sealed tube)	24 h	91		(12)
 (100)	10	PhCl (10 ml)	101°	8 h^b	67		(44)
$Me_3SiCH_2CH{=}CH_2$ (12.3)	4.9	PhCl (5 ml)	reflux	22 h	95		(48)
$Me_3SiCH_2CH{=}CH_2$ (50)	5	PhCl (2.5 ml)	125–126° (sealed tube)	24 h	98		(64)
$Me_2C{=}CHMe$ (21.2)	5	PhCl (10 ml)	~134° (sealed tube)	52 h	78		(19)

$Me_2C{=}CMe_2$ (11.4)	7.45	PhCl (5 ml)	~130° (sealed tube)	69 h	85	 (9)
(18.5)	1.57	125 ml	reflux	44 h	53	(8)
$n\text{-}C_4H_9(C_2H_5)C{=}CH_2$ (33)	18.6	PhCl (20 ml)	120°	20 h	89	 (1.7 part)  (1 part) (~30)
$n\text{-}C_3H_7(H)C{=}C(H)C_3H_7\text{-}n$ (50)	5	PhCl (2.5 ml)	125°	24 h	87	 (~6)
Et_3SiH (21.4)	9.5	PhCl (20 ml)	reflux	12 h	81	 (24)
Et_3SiH (50)	5	PhCl (5 ml)	125–126° (sealed tube)	24 h	66 (+26% Hg)	 (40)
Reactions of $PhHgCBr_2CO_2Me$						
 (38)	10	PhCl (20 ml)	reflux	43 h	87	 +  (50) 2.33 parts : 1 part

(continued)

TABLE 6 *(continued)*

Substrate (mmol)	*mmol of mercurial*	*Solvent*	*Reaction temperature (°C)*	*Reaction time*	*Yield of PhHgX (%)*	*Products (% yield)*
 (50)	10	PhCl (5 ml)	130°	48 h	73	 (19)
 (22)	4.8	PhCl (20 ml)	reflux	4 h	78	 (11)
 (100)	10	PhCl (10 ml)	101°	24 h	84	 (12) [+22% HCBr$_2$–CO$_2$Me]
$Me_3SiCH_2CH{=}CH_2$ (13)	5.5	PhCl (20 ml)	reflux	21 h	95	 (62)
$Me_3SiCH_2CH{=}CH_2$ (100)	10	PhCl (10 ml)	100°	24 h	94	 (25)
 $n\text{-}C_3H_7CH{=}CHC_3H_7\text{-}n$ (50)	10	PhCl (5 ml)	125°	48 h	97	 (5)

$Me_2C{=}CHMe$ (12)	4	PhCl (10 ml)	130°	24 h	92		(9) [+9% $HCBr_2CO_2Me$]
Et_3SiH (21)	8.8	PhCl (20 ml)	reflux	12 h	89		(35)
Et_3SiH (100)	10	PhCl (10 ml)	118°	24 h	81		(8)

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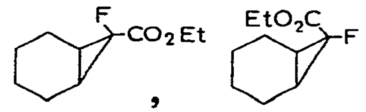
[a] When 25 mmol of the olefin and 7.5 ml of PhCl were used, a 4.2/1 mixture of products was obtained in 56% yield. A reaction with 10 mmol of the olefin in 15 ml of PhCl gave a 3.7/1 isomer ratio in 63% yield.

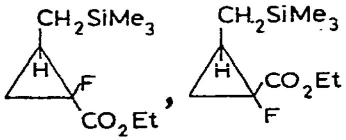
[b] C_6Cl_6 internal standard monitored by GLC.

derived carbenes into the Si-H bond of triethylsilane is to be noted Similar insertion chemistry was found with $PhHgCCFClCO_2Et$:

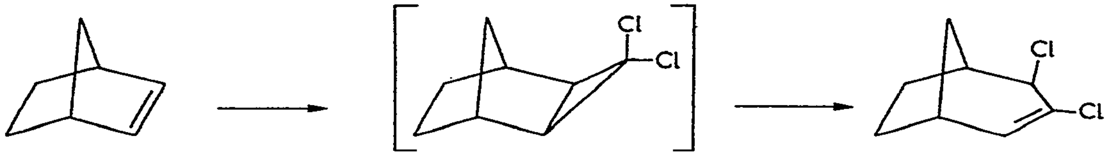
$$\underset{}{PhHgCFClCO_2Et} + \underset{(excess)}{Et_3SiH} \xrightarrow{110°,\ 50\ h} \underset{(71\%)}{Et_3SiCHFCO_2Et} + PhHgCl$$

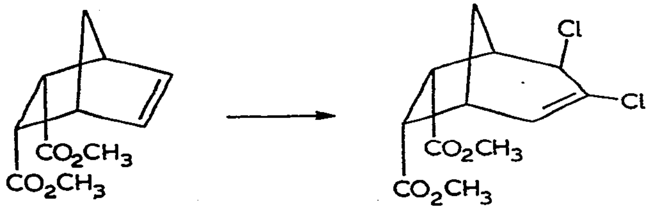
Other cyclopropanes prepared with this mercurial include (67):

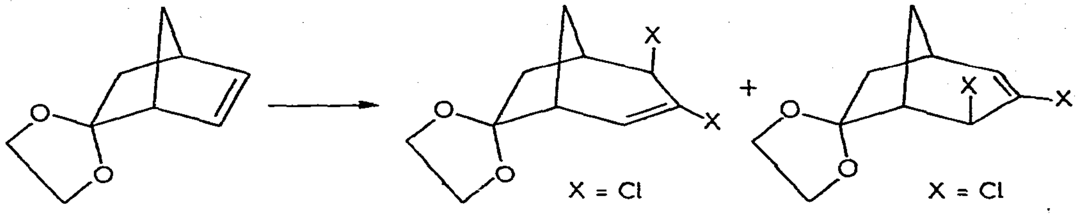


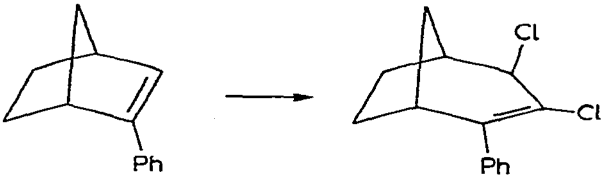


Further synthetic applications of phenyl(trihalomethy)-mercurials may be recorded. $PhHgCCl_3$-derived CCl_2 has been added to five substituted norbornadienes, to give, under the reaction conditions, the products expected from the thermal rearrangement of the initially formed gem-dichlorocyclopropane intermediates (68):

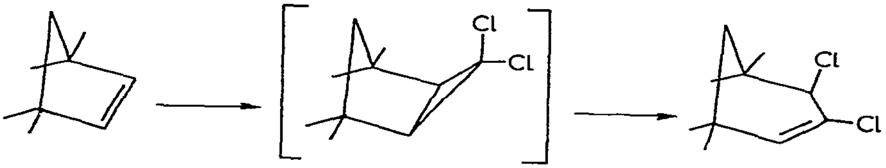




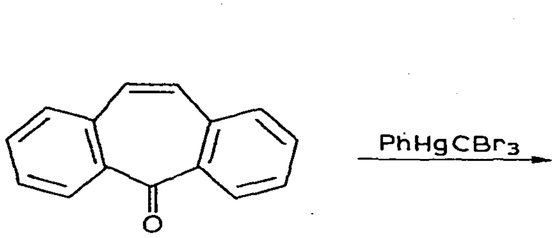




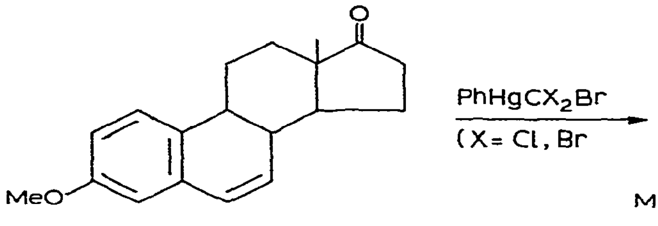
Other, related reactions were reported (68):



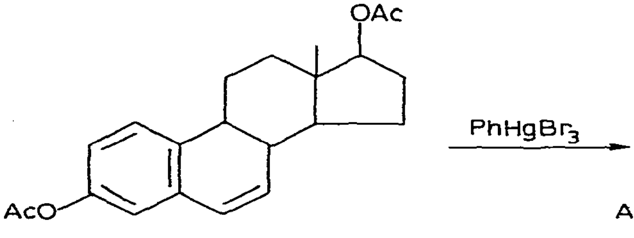
It may be noted that the latter olefin, 3,3,5,5-tetramethylcyclopentene, was unreactive toward chloroform/base-derived CCl_2 but did react with phenyl(trichloromethyl)mercury. Other dihalocarbene additions using phenyl(trihalomethyl)mercury compounds as reagents include:



(ref. 6

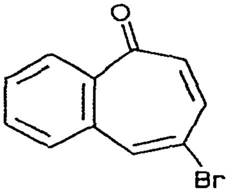


(ref. 7

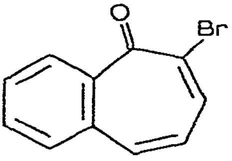


(ref. 70)

The reaction of 1-methoxynaphthalene with phenyl(tribromomethyl)-mercury gives $\boxed{9}$ (71), not $\boxed{10}$, previously claimed by Saraf in 1969. While PhHgCCl$_2$Br and PhHgCBr$_3$ added dihalocarbene to the

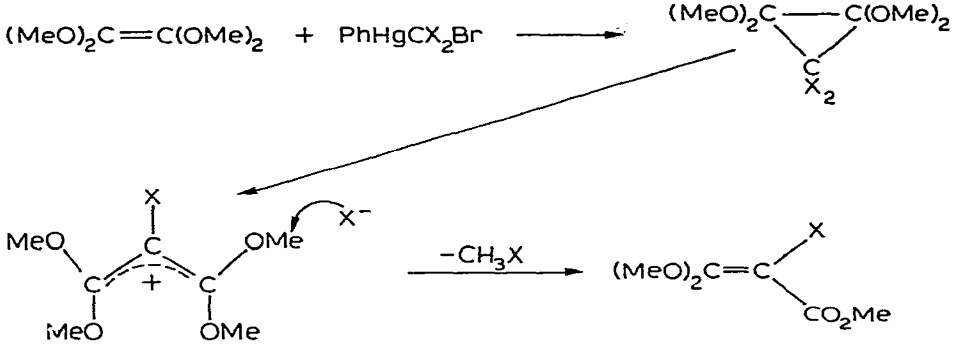


$\boxed{9}$



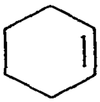
$\boxed{10}$

C=C bond of tetramethoxyethylene in refluxing benzene, the cyclopropanes underwent electrocyclic ring opening under the reaction conditions (72):

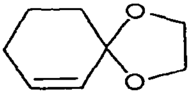


Phenyl(bromodichloromethyl)mercury has been used as CCl$_2$ reagent in several relative rate studies. Moss (73) has determined the relative reactivities of the group of olefins shown below toward PhHgCCl$_2$Br-derived CCl$_2$ in refluxing benzene solution. It was concluded from these results that CCl$_2$ is added directly to the C=C bond in these compounds, without prior interaction with the oxygen functions in these molecules. Relative rate constants for CCl$_2$ addition (via PhHgCCl$_2$Br) to methylvinylchlorosilanes, CH$_2$=CHSiMe$_{3-n}$Cl$_n$, (74) and methylvinylfluorosilanes,

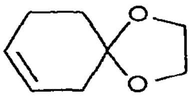
Olefin
(k_{rel}) :



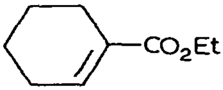
(1.00)



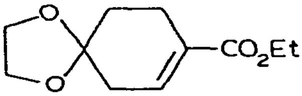
(0.012)



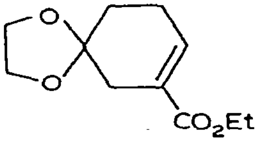
(0.44)



(0.11)



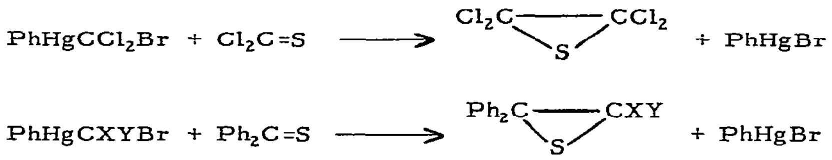
(0.028)



(0.11)

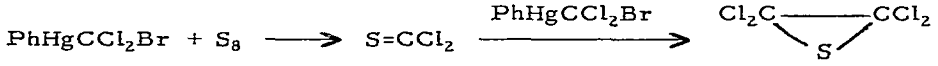
$CH_2{=}CHSiMe_{3-n}F_n$, (75) also have been determined and discussed in terms of the electronic effects in these molecules.

Reactions of phenyl (trihalomethyl)mercury-derived dihalocarbenes with other multiple bond systems have been described. Addition to the C=S bond gives thiiranes (76):

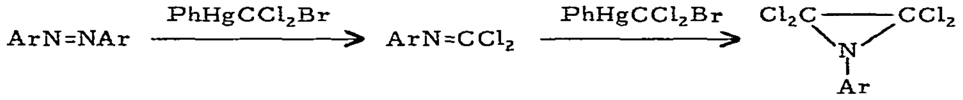


(X, Y = Cl, Cl
Cl, Br
Br, Br)

The remarkable reaction of elemental sulfur also produced tetrachlorothiirane:



With azoarenes, the expected diaziridines were not obtained. Instead, fragmentation occurred as shown below (77):

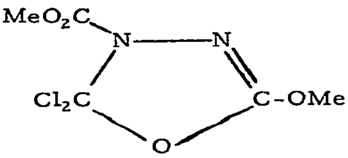


Which of these compounds was the major product depended on the PhHgCCl₂Br/ArN=NAr ratio used, but in either case, the yields were not high. With azo carboxylate esters, the final product was not the diaziridine (77):

$$\mathrm{PhHgCCl_2Br + RO_2CN{=}NCO_2R \xrightarrow{80^\circ} PhHgBr + (RO_2C)_2N\text{-}N{=}CCl_2}$$

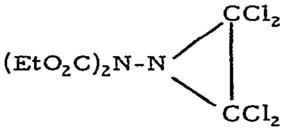
(87%)

A room temperature proton NMR study of the $PhHgCCl_2Br$/$MeO_2CN{=}NCO_2Me$ reaction demonstrated the intervention of an intermediate with nonequivalent methoxy groups which spectroscopic evidence suggested to be $\boxed{11}$, i.e., formal 1,4 addition of CCl_2 to the azodicarboxylate ester had occurred.



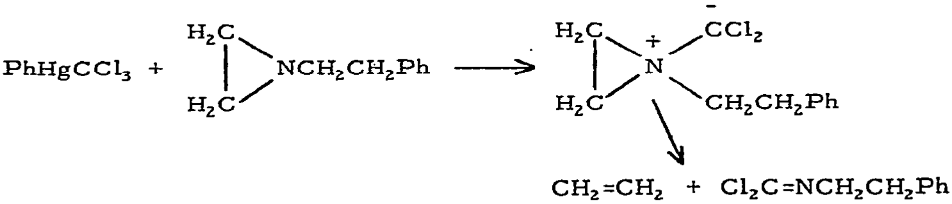
$\boxed{11}$

Among the reactions of $(EtO_2C)_2NN{=}CCl_2$ which were studied was that with phenyl(bromodichloromethyl)mercury to give $\boxed{12}$.



$\boxed{12}$

An $-N{=}CCl_2$ compound also was produced in the reaction of $PhHgCCl_3$ with N-phenethylaziridine (78):



The reaction of $PhHgCBr_3$ with sodium thiophenoxide in benzene at 80° gave $(PhS)_3CH$ as final product (79), probably by the pathway shown below:

$$\begin{tikzcd}
PhHgCBr_3 + PhS^- \arrow[r] & PhSCBr_2^- \arrow[r, "(H)"] & PhSCBr_2H \arrow[d, "2\ PhS^-"] \\
 & & HC(SPh)_3
\end{tikzcd}$$

Sommer et al. (80) have published details concerning the stereochemistry of the insertion of CCl_2 and CBr_2 (via $PhHgCCl_3$ and $PhHgCBr_3$, respectively) into the Si-H bond of optically active α-naphthylphenylmethylsilane, reactions which proceed with predominant (>90%) retention of configuration. Further studies on β-metal activated insertion of CCl_2 into aliphatic C-H bonds have been concerned with the question of the nature of the β-metal effect (81). Experiments in which $Me_3MCD(Me)CH_2CH_3$ (M = Si and Sn) were treated with $PhHgCCl_2Br$ gave $Me_3MCD(Me)CHMeCCl_2H$ as the only product. This speaks in favor of stabilization of the transition state of the insertion reaction by metal-carbon bond hyperconjugation.

The rapid, exothermic reaction of n-propyl(trichloromethyl)-mercury with diethylzinc gave a mixture of products:

$CH_3CH{=}CHCl$	$EtZnCl$	$n\text{-}PrHgCl$
$CH_3CH_2CH_3$ (minor)	$ZnCl_2$	Et_2Hg, $n\text{-}Pr_2Hg$ (minor)

A similar reaction of diethylzinc with $PhHgCCl_3$ produced 1-chloropropene, phenylmercuric chloride and zinc chloride (82). Formation of the major products may be accounted for by the reactions shown below:

$$n\text{-}PrHgCCl_3 + Et_2Zn \longrightarrow n\text{-}PrHgCl + EtZnCCl_2CH_2CH_3$$

$$\begin{tikzcd}
EtZnCCl_2CH_2CH_3 \arrow[r, "\alpha\text{-elimination}"] & EtZnCl + & CH_3CH_2CCl \arrow[d] \\
 & & CH_3CH{=}CHCl
\end{tikzcd}$$

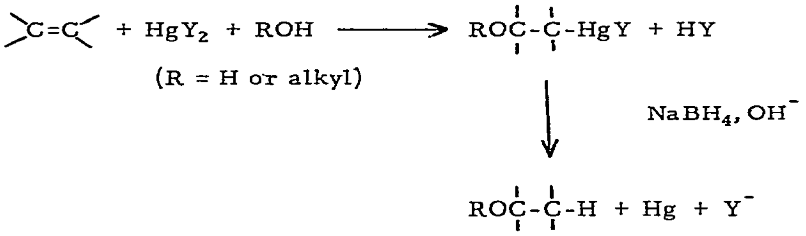
$$\begin{tikzcd}
n\text{-}PrHgCl + Et_2Zn \arrow[r] & n\text{-}PrHgEt \arrow[d] & + EtZnCl \\
 & 1/2\ n\text{-}Pr_2Hg + 1/2\ Et_2Hg &
\end{tikzcd}$$

The oxidation of n-propyl- and isopropyl(trichloromethyl)-mercury with tert-butylhydroperoxide in cyclohexane at 80° has been described. The major products isolated were the RHgCl and ROHgCl compounds. Autoxidation of isopropyl(trichloromethyl)mercury gave $Me_2CHOHgCl$ (61).

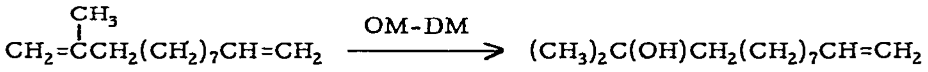
4. MERCURATION OF UNSATURATED COMPOUNDS

A. Olefins and Acetylenes

The oxymercuration-demercuration (OM-DM) procedure finds increasing use in organic synthesis, principally as a result of the studies of H. C. Brown and his coworkers. This group (83) has studied the OM-DM of nonconjugated and conjugated dienes which



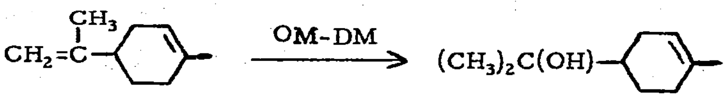
gives either enols or diols. Conditions were defined which served to optimize enol yields. The advantages of using the more soluble $Hg(O_2CCF_3)_2$ over $Hg(O_2CCH_3)_2$ were demonstrated in several cases. Among the conversions reported were:

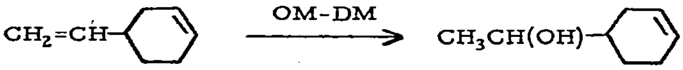


$$CH_2=\overset{CH_3}{\overset{|}{C}}CH_2(CH_2)_7CH=CH_2 \xrightarrow{\text{OM-DM}} (CH_3)_2C(OH)CH_2(CH_2)_7CH=CH_2$$

$$(CH_3)_2C=CH(CH_2)_7CH=CH_2 \xrightarrow{\text{OM-DM}} (CH_3)_2C=CH(CH_2)_7CH(OH)CH_3$$

$$CH_2=CH(CH_2)_8CH=CH_2 \xrightarrow{\text{OM-DM, }0^\circ} CH_3CH(OH)(CH_2)_8CH=CH_2\ (46\%) + CH_3CH(OH)(CH_2)_8CH(OH)CH_3\ (18\%)$$

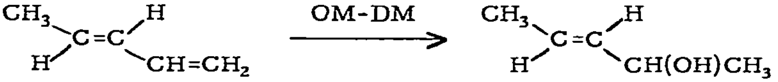




$$CH_2{=}C(CH_3)\text{-}C(CH_3){=}CH_2 \xrightarrow{\text{OM-DM}} CH_2{=}C(CH_3)\text{-}C(OH)(CH_3)_2 \text{ (49\%)}$$

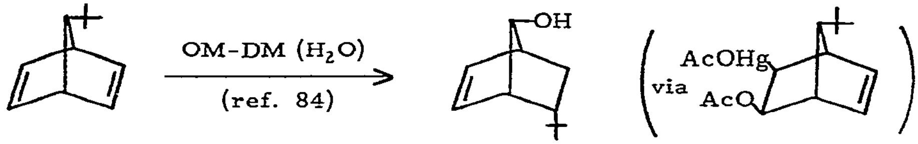
$$+$$

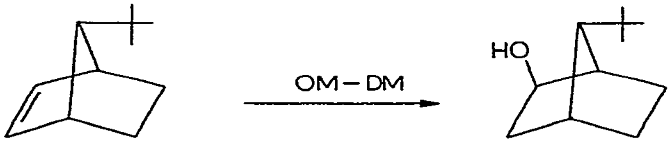
$$CH_2{=}C(CH_3)CH_2CH(OH)CH_3 \text{ (6\%)}$$



$$CH_3CH{=}CHCH{=}CH_2 \xrightarrow{\text{OM-DM}} CH_3CH{=}CHCH(OH)CH_3 \quad \text{(56\%)}$$

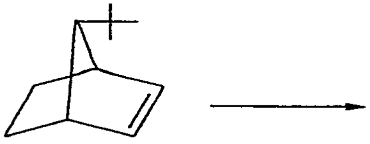
Other examples reported in 1972 include the following:



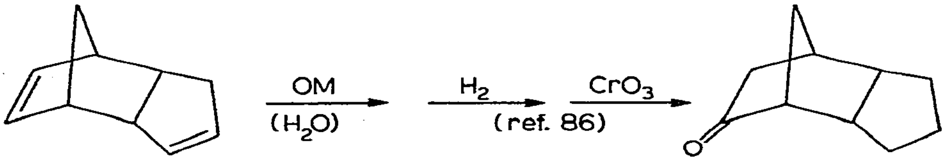


(ref. 85)

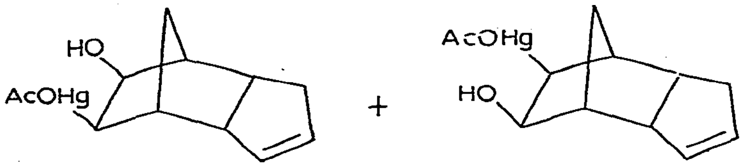
but:

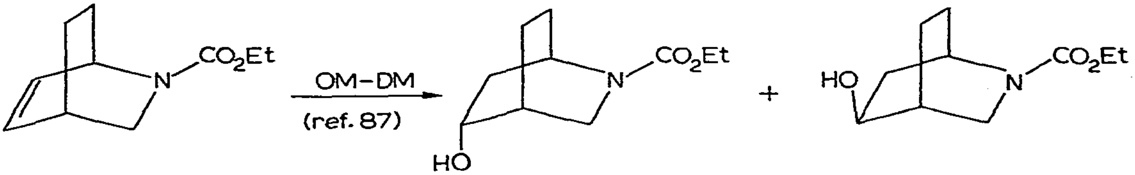


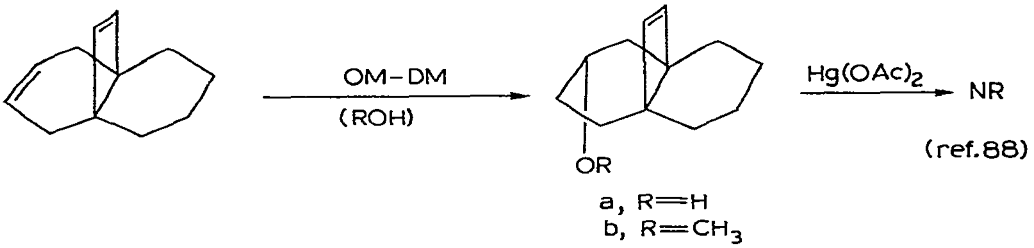
No reaction (ref. 85)
(steric factor)



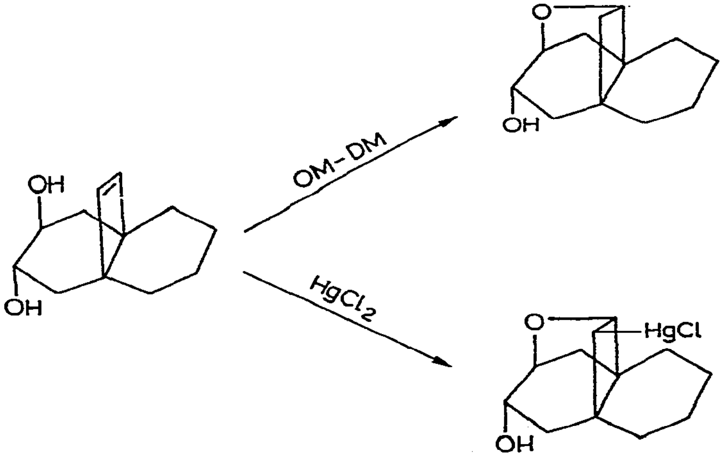
(via



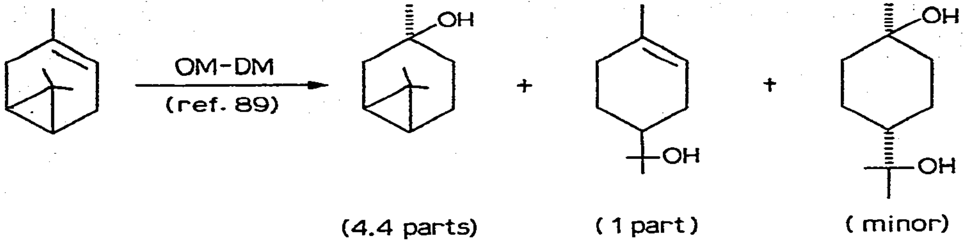


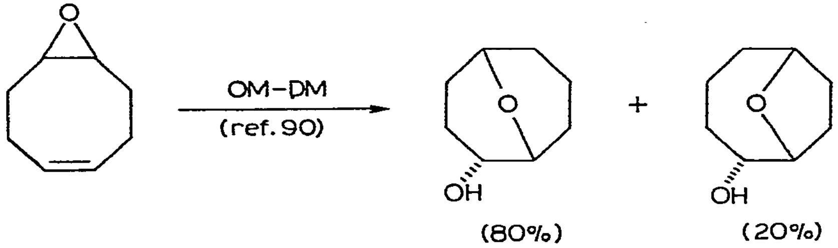


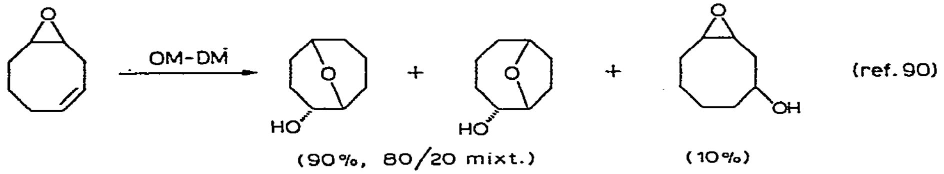
(ref. 88)

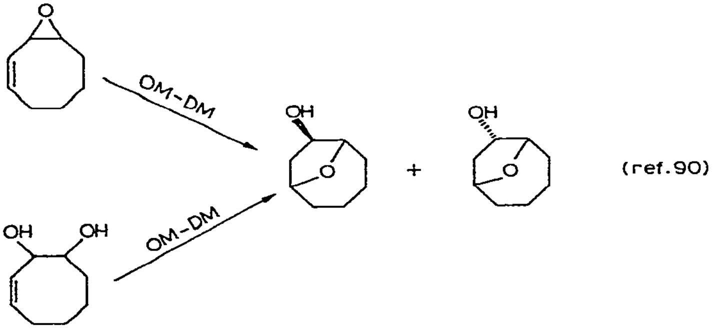


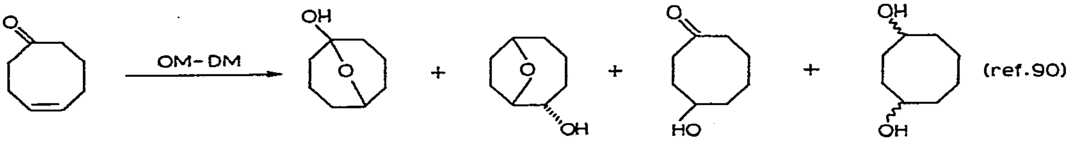
(ref.88)

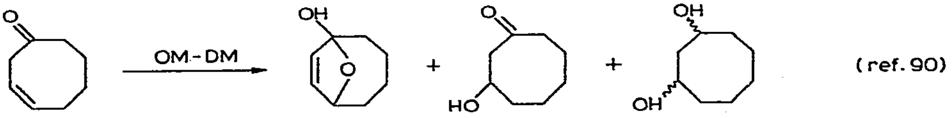

OM-DM
(ref. 89)
OH
+
OH
+
OH
OH
(4.4 parts)
(1 part)
(minor)

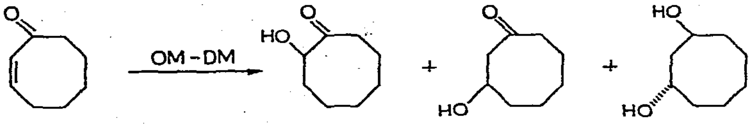

O
OM-DM
(ref.90)
O
+
O
OH
OH
(80%)
(20%)


O
OM-DM
O
+
O
+
O
(ref. 90)
HO
HO
OH
(90%, 80/20 mixt.)
(10%)

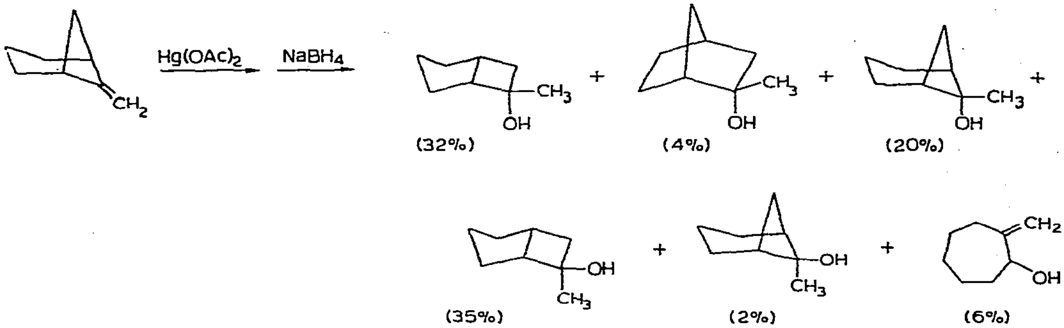

O
OM-DM
OH
OH
+
O
O
(ref.90)
OH
OH
OM-DM


O
OM-DM
OH
O
+
O
OH
+
O
HO
+
OH
OH
(ref.90)

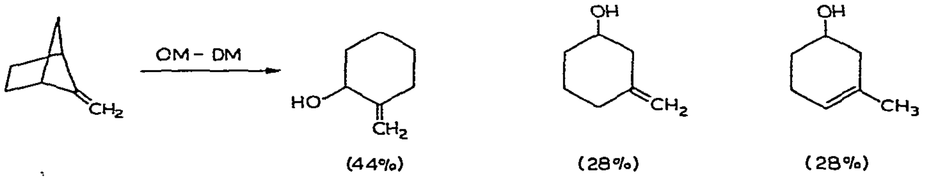

O
OM-DM
OH
O
+
O
HO
+
OH
OH
(ref. 90)



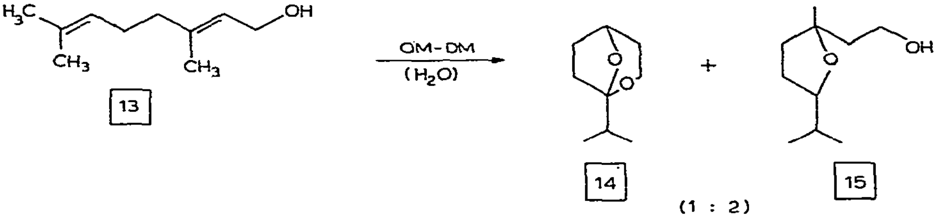
(ref.90)



(ref. 91)

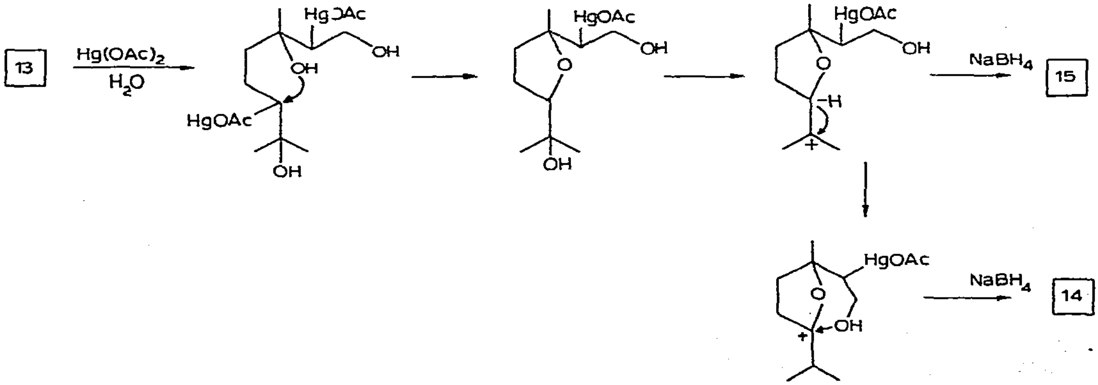


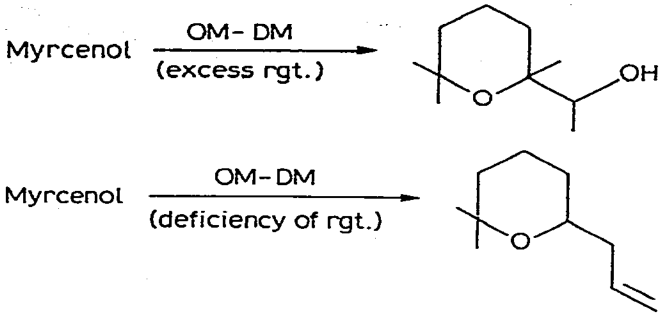
(ref.91)



(ref.92)

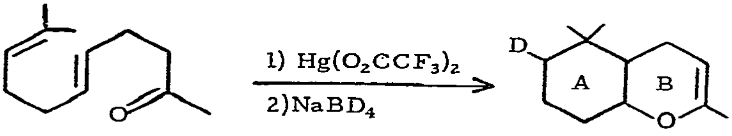
(The reaction course shown below was suggested)





(ref. 92)

(Farnesol and linalool were resistant to OM-DM).[92]



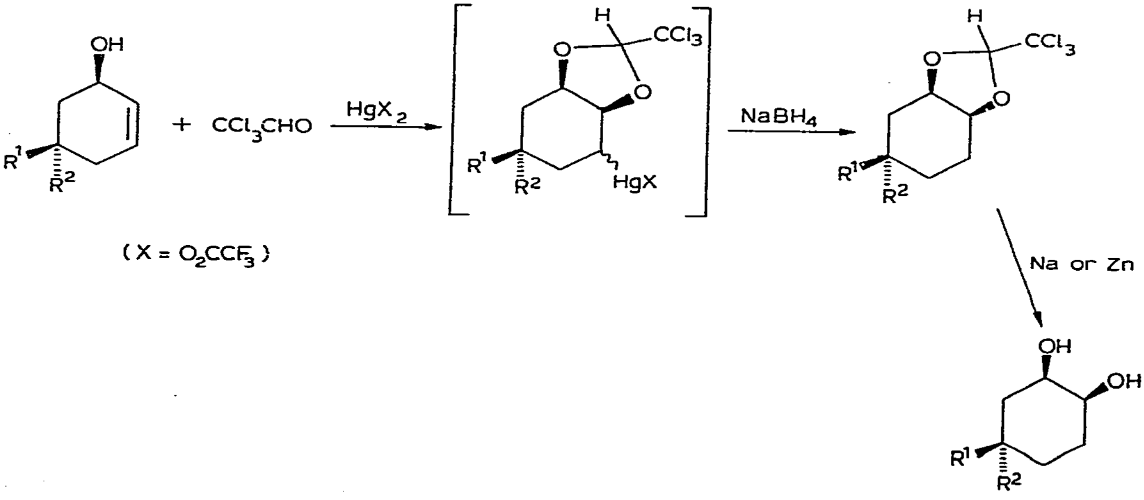
(ref. 93)

(trans-6,7-) → (trans-A/B)

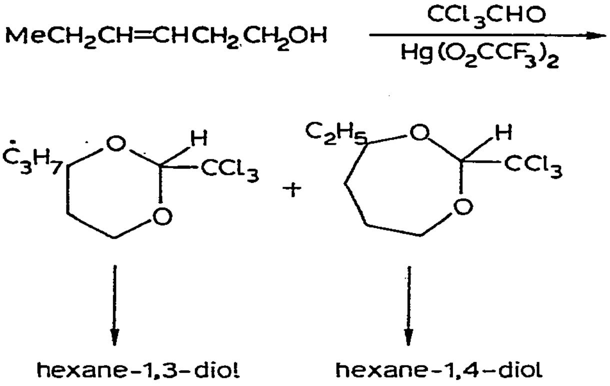
(cis-6,7-) → (cis-A/B)

Other isoprenoid compounds (cis-geranylacetone ethylene ketal, geranic acid methyl ester and ethyl trans-6,7-trans-10,11-farnesylate) were cyclized in this manner (93).

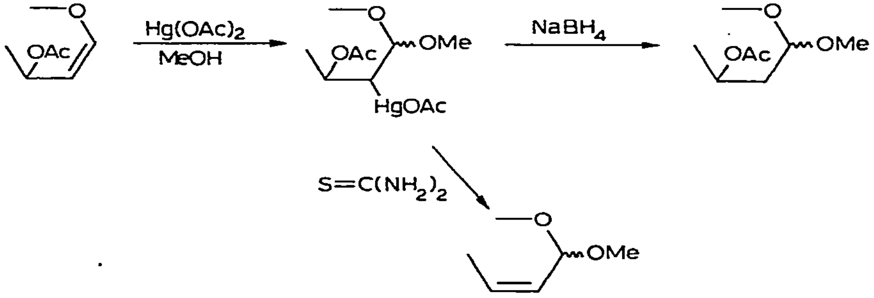
Oxymercuration-demercuration played a role in the conversion of cyclic allylic alcohols to cis vicinal diols (94):



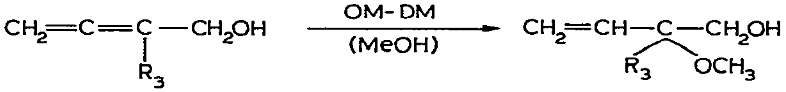
An acyclic allylic alcohol reacted similarly, but with little regiospecificity:



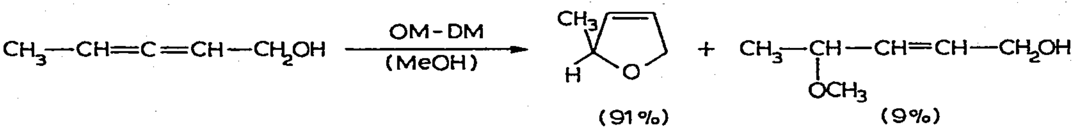
The methoxymercuration-demercuration procedure was applied to the acetates of D-glucal, D-galactal, L-arabinal and D-xylal (95); 2-deoxy sugar derivatives were obtained in high yield. Demercuration with thiourea gave pseudoglycal derivatives:

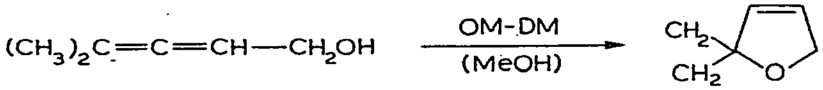


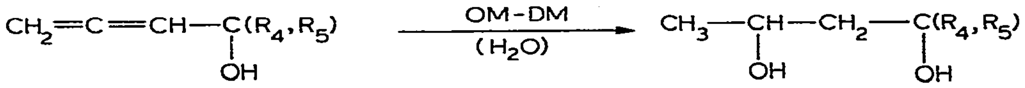
α-Allenic alcohols have been oxymercurated-demercurated (96):



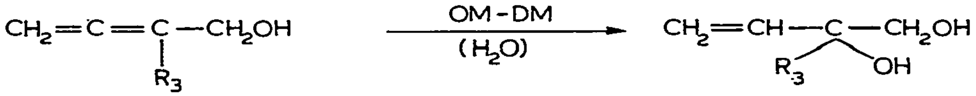
$$CH_2{=}C{=}\underset{\displaystyle R_3}{C}{-}CH_2OH \xrightarrow[\text{(MeOH)}]{\text{OM-DM}} CH_2{=}CH{-}\underset{R_3\quad OCH_3}{C}{-}CH_2OH$$



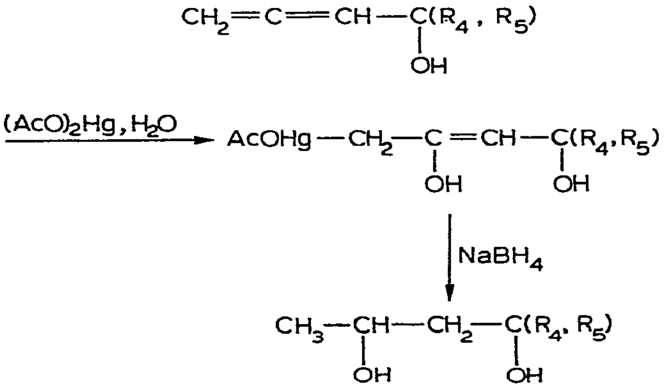




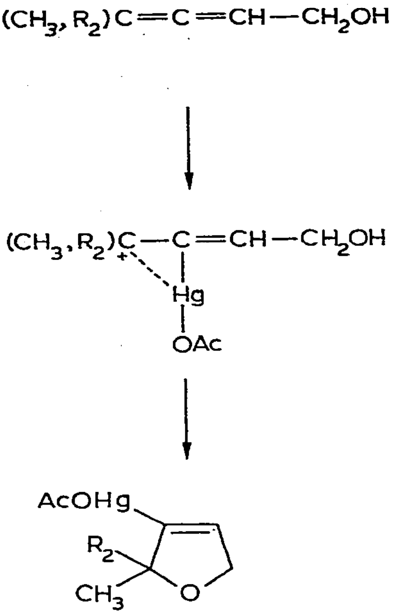
$$CH_2{=}C{=}CH{-}\underset{OH}{C}(R_4,R_5) \xrightarrow[(H_2O)]{OM\text{-}DM} CH_3{-}\underset{OH}{CH}{-}CH_2{-}\underset{OH}{C}(R_4,R_5)$$

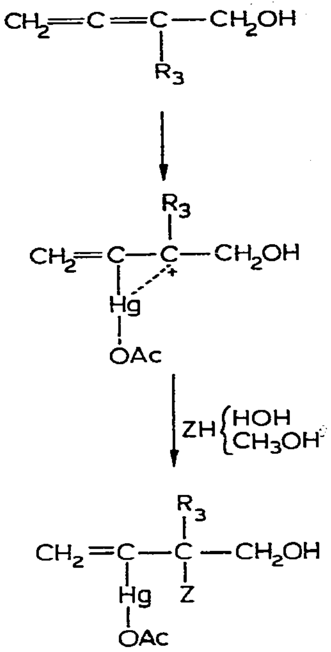


The reaction courses shown below were suggested:



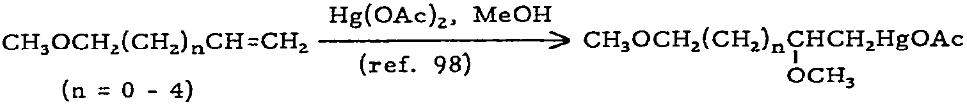
$$CH_2{=}C{=}CH{-}\underset{OH}{C}(R_4,R_5) \xrightarrow{(AcO)_2Hg,\,H_2O} AcOHg{-}CH_2{-}\underset{OH}{C}{=}CH{-}\underset{OH}{C}(R_4,R_5) \xrightarrow{NaBH_4} CH_3{-}\underset{OH}{CH}{-}CH_2{-}\underset{OH}{C}(R_4,R_5)$$





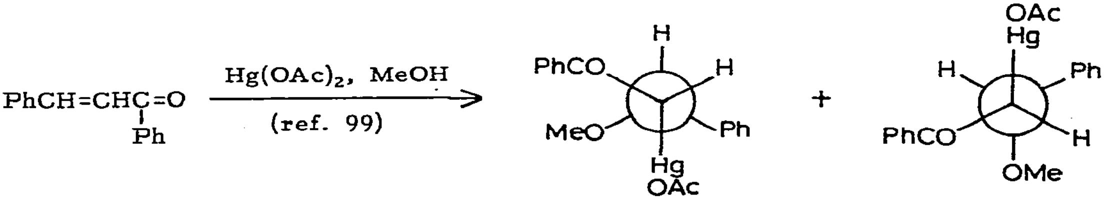
The OM-DM procedure has provided a clever and useful method for the identification, analysis and isolation of long chain alcohols and acids with C=C bonds at positions 3, 4 or 5 (97).

Other studies have dealt with oxymercuration of olefins, stopping at the organomercurial stage:



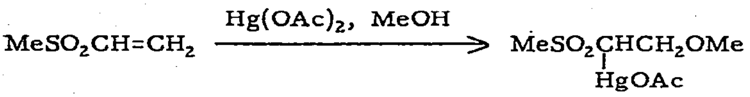
$$\mathrm{CH_3OCH_2(CH_2)_nCH{=}CH_2}\ \xrightarrow[\text{(ref. 98)}]{\mathrm{Hg(OAc)_2,\ MeOH}}\ \mathrm{CH_3OCH_2(CH_2)_n\underset{\displaystyle OCH_3}{CH}CH_2HgOAc}$$

(n = 0 - 4)



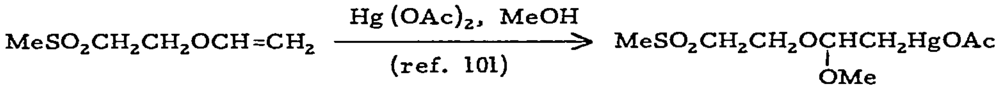
(S,R) (R,R)

(7 : 3)

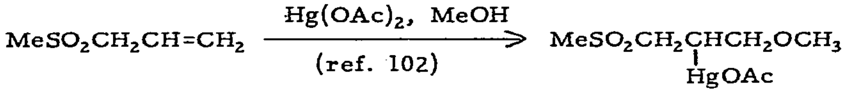


$$\mathrm{MeSO_2CH{=}CH_2} \xrightarrow{\mathrm{Hg(OAc)_2,\ MeOH}} \mathrm{MeSO_2\underset{\displaystyle HgOAc}{C}HCH_2OMe}$$

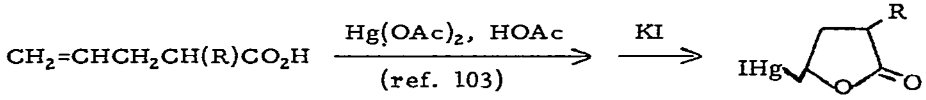
(ref. 100)

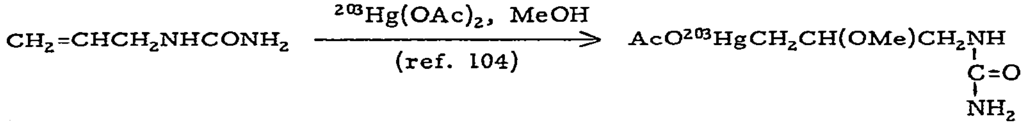


$$\mathrm{MeSO_2CH_2CH_2OCH{=}CH_2} \xrightarrow[\text{(ref. 101)}]{\mathrm{Hg(OAc)_2,\ MeOH}} \mathrm{MeSO_2CH_2CH_2O\underset{\displaystyle OMe}{C}HCH_2HgOAc}$$

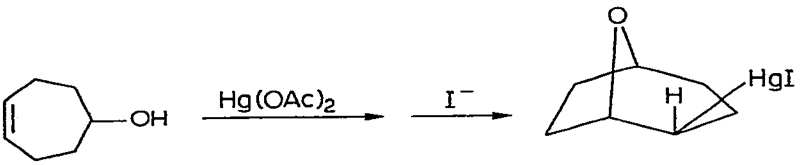


$$\mathrm{MeSO_2CH_2CH{=}CH_2} \xrightarrow[\text{(ref. 102)}]{\mathrm{Hg(OAc)_2,\ MeOH}} \mathrm{MeSO_2CH_2\underset{\displaystyle HgOAc}{C}HCH_2OCH_3}$$

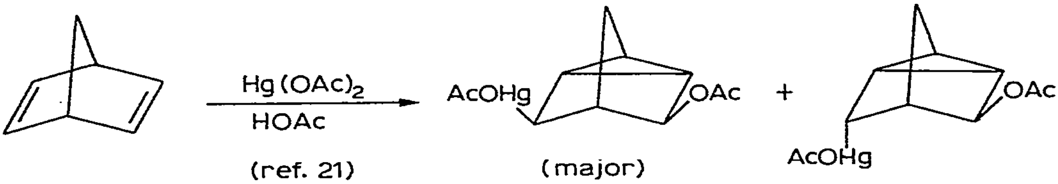




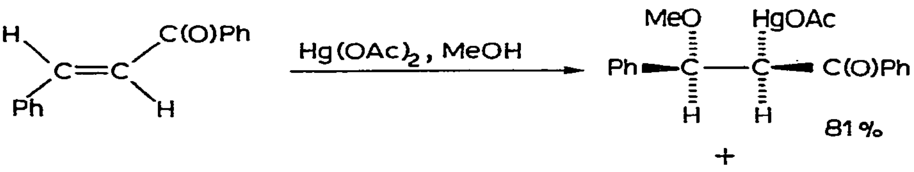
$$\mathrm{CH_2{=}CHCH_2NHCONH_2} \xrightarrow[\text{(ref. 104)}]{\mathrm{^{203}Hg(OAc)_2,\ MeOH}} \mathrm{AcO^{203}HgCH_2CH(OMe)CH_2\underset{\displaystyle \underset{\displaystyle NH_2}{C{=}O}}{N}H}$$

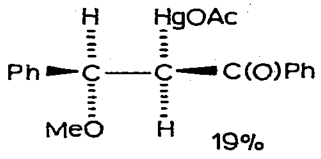


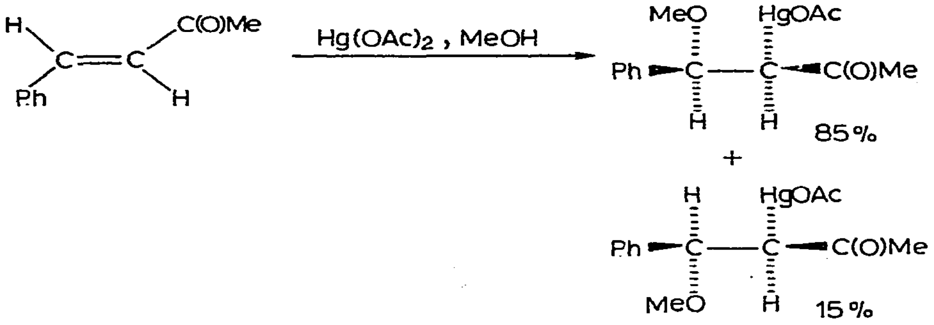
(ref. 105)



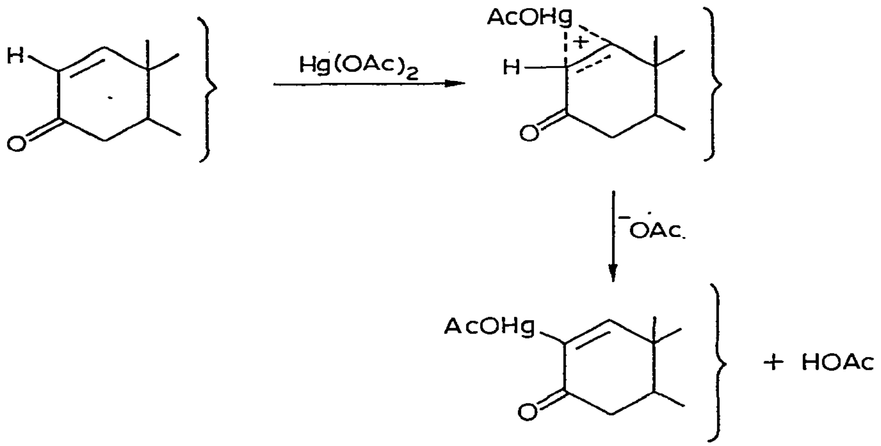
A major study has dealt with the oxymercuration of α,β-unsaturated systems, including steroids (106). Simple α,β-unsaturated compounds were oxymercurated smoothly:





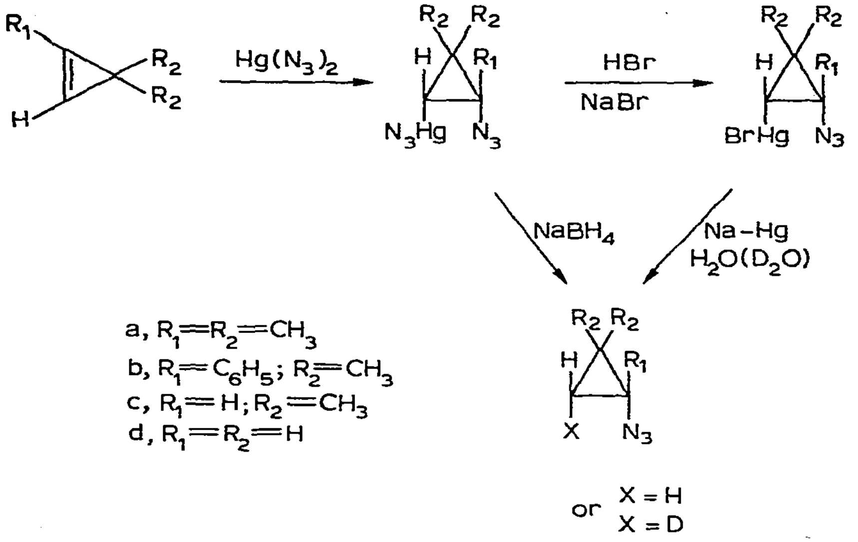


The reaction course is shown below:

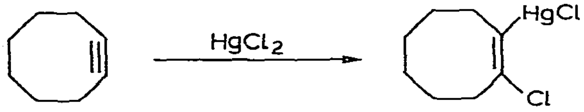


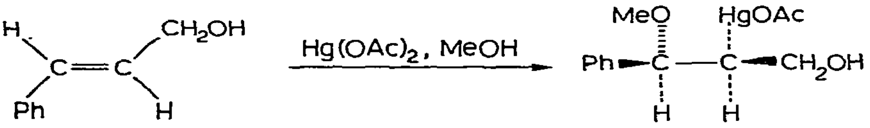
The rates of acetoxymercuration of 1,4,6-androstatriene-3,17-dione and of 1,4,6-pregnatriene-3,20-dione were measured using NMR techniques.

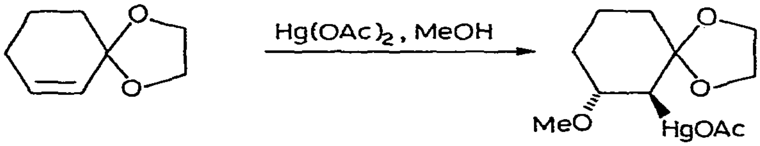
The addition of mercuric azide to cyclopropenes provided a synthesis of cyclopropyl azides (107):



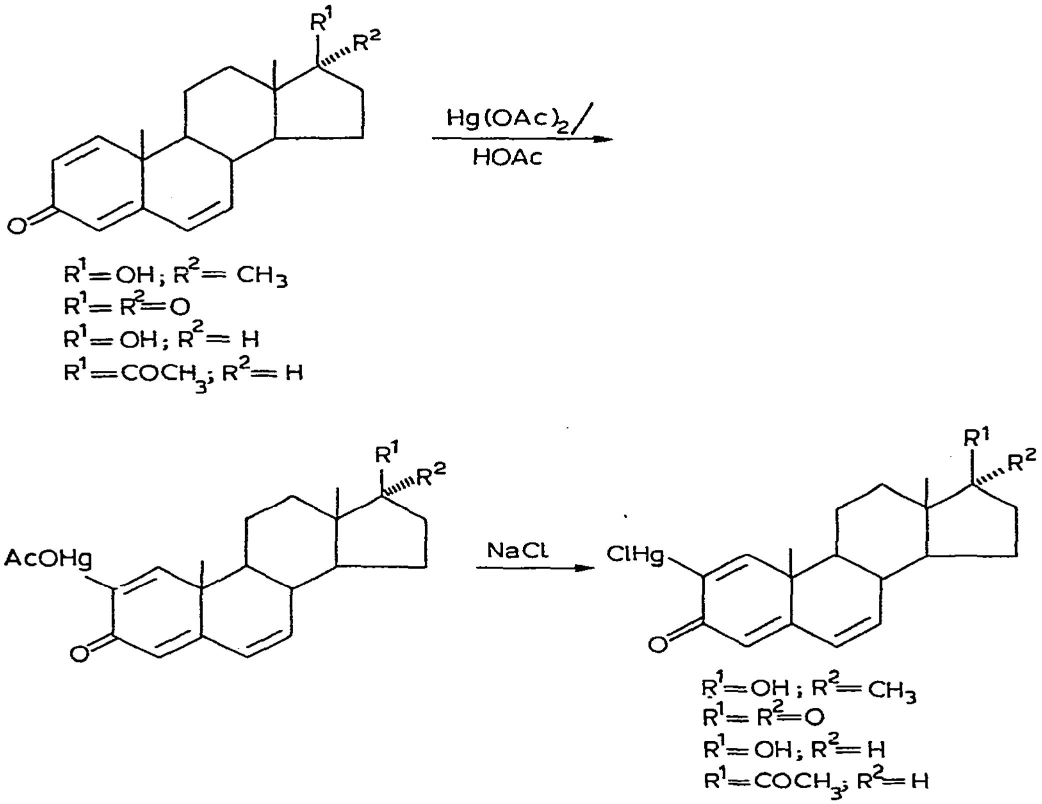
Mercuric chloride was found to add to the C≡C bond of cyclooctyne (108):



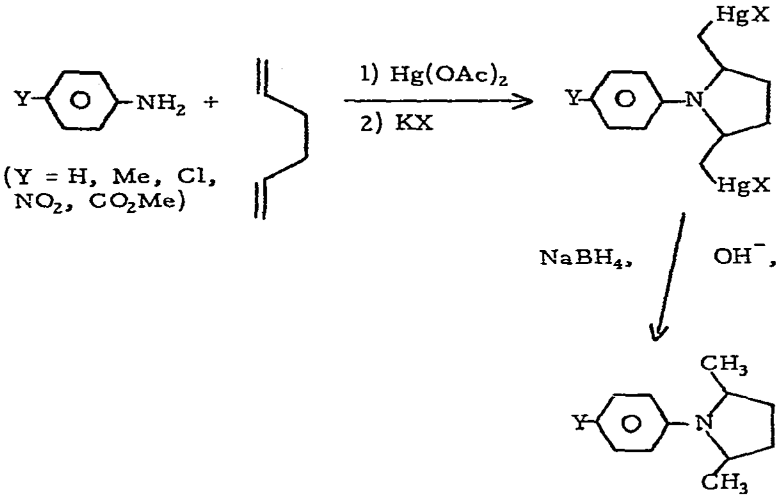




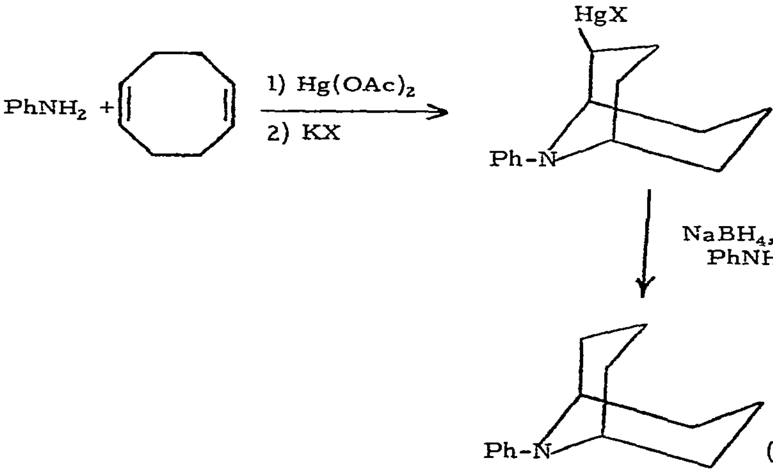
3-Keto steroids with an abstractable allylic hydrogen were not oxymercurated by mercuric acetate in methanol or acetic acid: mercurous acetate was formed, presumably as a result of the oxidation of the steroid. 3-Keto steroids without such allylic protons and with a C-1 double bond reacted with mercuric acetate. Addition of $HgOAc^+$ occurred at the α side of the C-1 double bond; proton abstraction at C-2 then resulted in formation of 2-acetoxymercuri-1-en-3-one:



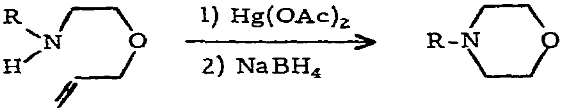
The aminomercuration of olefins has received continued attention, and this subject has been reviewed (in Spanish) by Lattes (109), one of the most active researchers in this area. The aminomercuration reaction has found application in the synthesis of nitrogen heterocyclic systems:



(ref. 110)

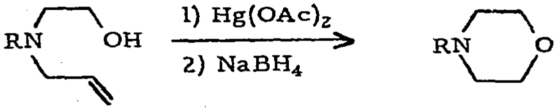


(ref. 111)

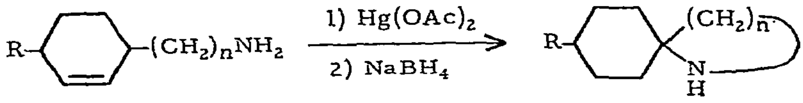


(ref. 112)

An oxymercuration route led to similar products (112):



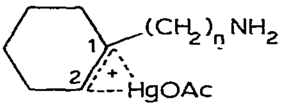
A number of variously substituted morpholines was prepared by these procedures. Heterocyclic monospiro compounds also were accessible via aminomercuration (113):



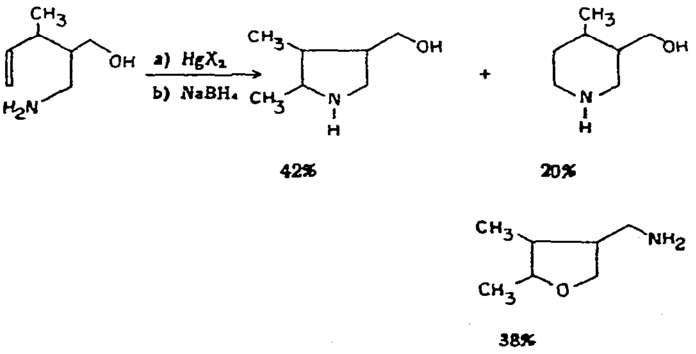
(n=3,4;
R=H, Me_3C)

but:

In the former case, intramolecular nucleophilic attack occurs at position 1, in the latter, at position 2:

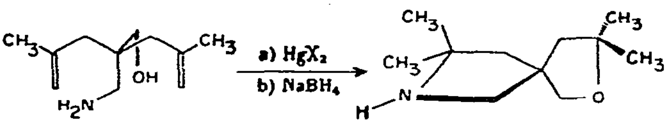


In the case of one functional olefin in which both aminomercuration and oxymercuration was possible, the former was the preferred process:



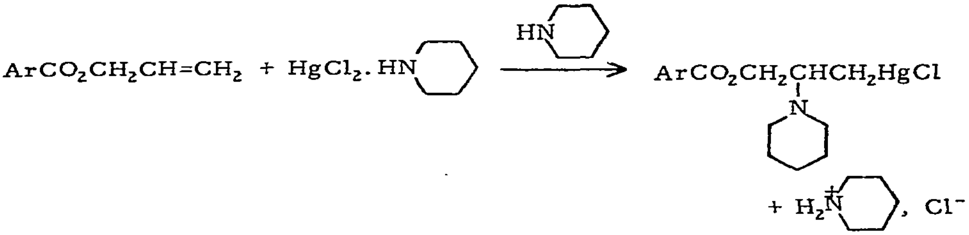
(ref. 113)

Note also:

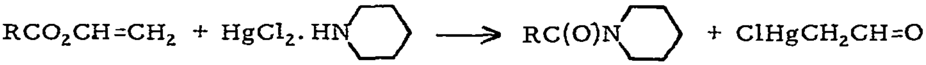


Further detailed studies by Lattes and his coworkers (114, 115) have shown that the intramolecular mercuration reaction proceeds stereospecifically by a nitrogen-assisted process.

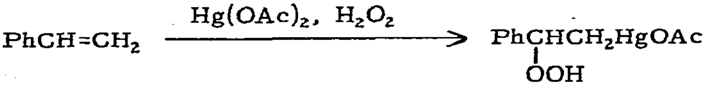
Investigations of the aminomercuration of functional olefins have been described by other workers (116):



Other olefins used included allyl urea, allyl carbamate, 3-cyclohexenyl benzoate, allyl acetate, methyl allylacetate, allylic alcohols and ethers. In addition to piperidine, the amines used included substituted piperidines, morpholine and hexamethyleneimine. Vinyl esters underwent an aminolysis-oxidation reaction:

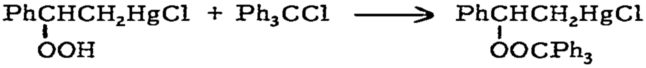


The reaction of olefins with mercuric acetate in the presence of hydrogen peroxide is another variation of the solvomercuration reaction (117):



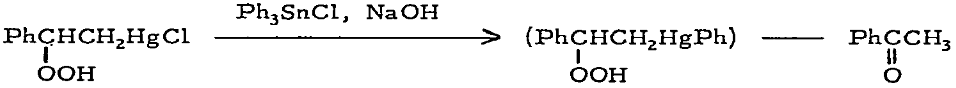
$$PhCH{=}CH_2 \xrightarrow{Hg(OAc)_2,\ H_2O_2} Ph\underset{\displaystyle OOH}{\underset{|}{C}}HCH_2HgOAc$$

Such reactions also were carried out with cyclohexene, dihydropyran, norbornene, 1,1-diphenylethylene, and 1-phenylcyclohexene. Crystalline O-trityl derivatives were prepared:



$$PhCH(OOH)CH_2HgCl + Ph_3CCl \longrightarrow PhCH(OOCPh_3)CH_2HgCl$$

The polarographic behavior of such organomercury hydroperoxides was examined. Attempted phenylation of mercury in such compounds led to fragmentation:

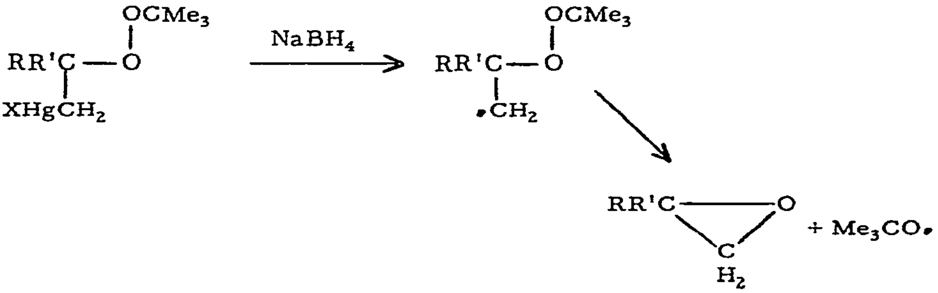


$$PhCH(OOH)CH_2HgCl \xrightarrow{Ph_3SnCl,\ NaOH} (PhCH(OOH)CH_2HgPh) \text{———} PhC(=O)CH_3$$

The reduction of t-butylperoxymercurated products of type RR'C-($OOCMe_3$)CH_2HgX by sodium borohydride gave dialkyl peroxides, $RR'MeCOOCMe_3$, and also epoxides, $\boxed{16}$. The amount of epoxide

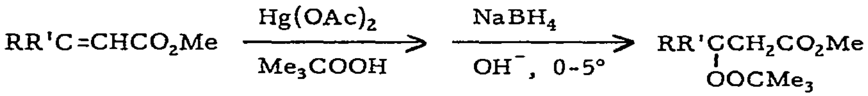
$\boxed{16}$

formed was found to increase with increasing alkylation of the terminal olefin used. A radical pathway was suggested (118):



$$RR'C(CH_2HgX)-O-OCMe_3 \xrightarrow{NaBH_4} RR'C(\cdot CH_2)-O-OCMe_3 \longrightarrow RR'C(-O-CH_2-) + Me_3CO\cdot$$

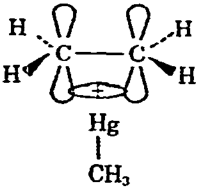
Similar reduction of the t-butylperoxymercuration products of α, β-unsaturated esters and ketones was investigated (119). The esters reacted as expected:

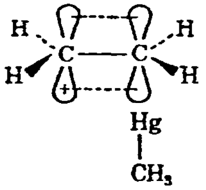


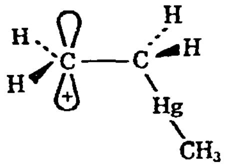
$$RR'C{=}CHCO_2Me \xrightarrow[Me_3COOH]{Hg(OAc)_2} \xrightarrow[OH^-,\ 0\text{-}5^\circ]{NaBH_4} RR'\underset{\displaystyle OOCMe_3}{C}CH_2CO_2Me$$

However, no β-ketoperoxides could be isolated from similar reactions with α, β-unsaturated ketones. In the case of trans-PhCH=CHC(O)Ph, the major product (75%) was chalcone oxide.

Further investigations have dealt with the rate, mechanism and stereochemistry of oxymercuration. The mercurinium ion, the postulated intermediate in the oxymercuration reaction, was detected by NMR in strong acid medium in 1971. Now such a species has been observed in the gas phase by ion cyclotron resonance (120). The ionization of dimethylmercury in the presence of ethylene in an ICR mass spectrometer produced a rather stable ion with the mass of $C_3H_7Hg^+$. Of the three possible structures, $\boxed{17}$, $\boxed{18}$ and $\boxed{19}$, for the ion, the first was favored on the basis of supporting MO



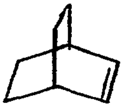




$\boxed{17}$ $\boxed{18}$ $\boxed{19}$

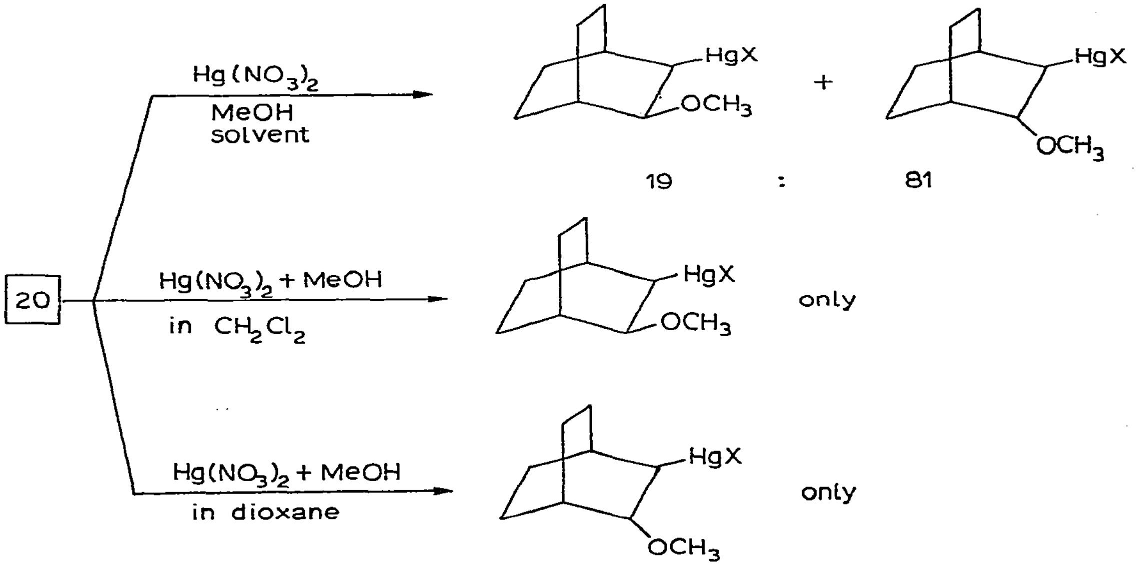
calculations.

New results concerning the stereochemical course of the oxymercuration of $\boxed{20}$ under differing experimental conditions were



$\boxed{20}$

explained by Bach and Richter (121) in terms of a mercurinium ion intermediate in both trans and cis oxymercuration. The stereochemistry of the oxymercuration of $\boxed{20}$ is strikingly affected by the solvent medium used:



Much effort has been devoted to the elucidation of the mechanism of the oxymercuration of olefins. Electrophilic attack by a charged species, HgX^+, at the olefinic C=C bond gives an intermediate with cation-like properties, but details of the nature of this intermediate and of the transition state leading to it are still unsettled (cf. previous mercury annual surveys and W. Kitching, Organometal. Chem. Rev. 3 (1968) 61). In a previous study, a linear correlation between log k_{rel} for oxymercuration of substituted styrenes and Hammett σ constants had been observed, giving $\rho = -2.25$ (OCR-B, 6 (1970) 277). This speaks against an open carbonium ion intermediate in which all the charge is centered at carbon, and one may discuss either a mercury-stabilized ion of type $\boxed{18}$ or a mercurinium ion intermediate,

TABLE 7

RELATIVE REACTIVITIES OF OLEFINS IN THE OXYMERCURATION REACTION (MERCURIC ACETATE IN THF/WATER). k_r (CYCLOHEXENE) = 1 (Ref. 122)

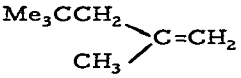
Olefin	Rel. reactivity k_r	k_{cis}/k_{trans}	Acyclic analog	Rel. reactivity k_r
1. Effect of increased alkyl branching on the relative reactivity				
1-Pentene	6.6			
1-Hexene	4.8			
3-Methyl-1-butene	2.5			
3,3-Dimethyl-1-butene	0.15			
2. Effect of the position of the double bond				
1-Pentene	6.6			
cis-2-Pentene	0.56	3.29		
trans-2-Pentene	0.17			
cis-1-Methyl-2-pentene	0.090	3.46		
trans-1-Methyl-2-pentene	0.026			
3. Effects of substituents on the double bond				
1-Pentene	6.6			
2-Methyl-1-pentene	48			
cis-2-Pentene	0.56			
trans-2-Pentene	0.17			
2-Methyl-2-pentene	1.24			
2,4-Dimethyl-2-pentene	0.056			
2,4,4-Trimethyl-2-pentene	0.020			
2,3-Dimethyl-2-butene	0.061			
4. Effect of ring systems				
Cyclopentene	0.78		*cis*-2-pentene	0.56
Cyclohexene	1.00			
1-Methylcyclopentene	1.86		2-Methyl-2-pentene	1.24
Methylenecyclopentane	59		2-Methyl-1-pentene	48
Cyclooctene	0.002			
Norbornene	3.7			
Bicyclo[2.2.2]octene	0.01			
5. Effect of conjugation of the double bond to a benzene ring				
Styrene	0.28			
α-Methylstyrene	1.18			
cis-Propenylbenzene	<0.02			
trans-Propenylbenzene	<0.02			

$\boxed{17}$. In 1972, several groups have reported relative rate studies of olefin oxymercuration. Those of Brown and Geoghegan (122) were preparatively oriented, defining scope and selectivity of such processes. Some results are presented in Table 7. Steric factors were seen to play a major role in determining reactivity of hydrocarbon olefins. The more stable the carbonium ion intermediate ($\boxed{18}$ -type structure assumed) and the lower the stability of the olefinic ground state (as a result of increased cis interactions or constraint in a bicyclic ring system), the faster the oxymercuration rate. A German group (123) has determined relative rates of oxymercuration of 28 acyclic hydrocarbon olefins (mercuric acetate in methanol): Table 8. A 5-membered Taft equation was used in the evaluation of the data. Obviously, steric factors in the olefin play a very important role. Electronic factors were examined by other workers who measured rates of methoxymercuration of substituted cinnamic acids at 40° (124). A linear correlation of log k_{rel} vs. Hammett σ values gave $\rho = -1.57 \pm 0.1$. Studies of the correlation of catalytic rate constants of the alkoxymercuration of cinnamic acid and its methyl, ethyl and phenyl esters with the pK_a (in water) values of the acid catalysts used (which included $HClO_4$, HNO_3, the chloroacetic acids, HOAc, $PhCO_2H$ and $o\text{-}HOC_6H_4CO_2H$) and with the dielectric constants of the solvents used (MeOH, EtOH, i-PrOH, n-PrOH, n-BuOH, i-BuOH, n-AmOH, i-AmOH) and their Taft σ^* constants (125).

Russian workers (126) have carried out a potentiometric study of the equilibria in the systems $C_2H_4/Hg(ClO_4)_2/HClO_4$ and $C_2H_4/$-$Hg(ClO_4)_2/NaClO_4/HClO_4$. At 25° the rate constant of the formation of $C_2H_4Hg^{2+}$ was 1.5×10^4 l/mol.

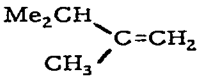
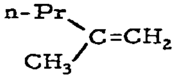
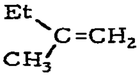
A review on the mechanism of hydration of acetylene, catalyzed by mercuric ion, has been published (127). The hydrolysis

TABLE 8. Relative Reactivities of Olefins Toward Mercuric
(ref. 123) Acetate in Methanol at Room Temperature (ref. 123)
(k_{rel} (cyclohexene) = 1)

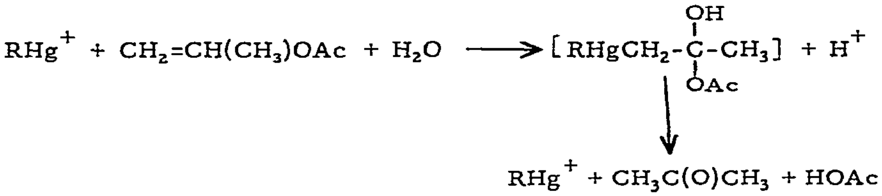
$MeC{=}CMe_2$	0.007
trans-n-$PrCH{=}CHPr$-n	0.015
$Me_3CCH{=}C(CH_3)_2$	0.019
trans-$CH_3CH{=}CHCH_2Cl$	0.027
trans-$EtCH{=}CHEt$	0.04
$CH_2{=}CHCH_2Cl$	0.06
$Me_3CCH{=}CH_2$	0.07
$Et_2C{=}CHCH_3$	0.08
cis-n-$PrCH{=}CHPr$-n	0.10
trans-$CH_3CH{=}CHCH_2OMe$	0.11
$CH_2{=}C(CH_3)CH_2Cl$	0.12
 $(Me_3CCH_2)(CH_3)C{=}CH_2$	0.24
cis-$EtCH{=}CHEt$	0.25
$PhCH_2CH{=}CH_2$	0.41
$CH_3OCH_2CH{=}CH_2$	0.46
$ClCH_2CH_2CH{=}CH_2$	0.47
$Me_2C{=}CHEt$	1.05
sec-$BuCH{=}CH_2$	1.3
$Me_2C{=}CHMe$	1.57
$CH_2{=}C(CH_3)CH_2OCH_3$	1.68
n-$C_5H_{11}CH{=}CH_2$	3.95
n-$C_6H_{13}CH{=}CH_2$	3.95
n-$C_4H_9CH{=}CH_2$	4.13

(continued)

TABLE 8 (continued)

	5.2
	5.9
$EtCH=CH_2$	6.2
	7.3
$Me_2C=CH_2$	8.7

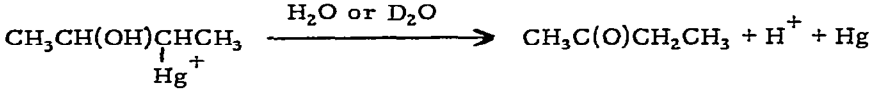
of isopropenyl acetate was found to be catalyzed by Hg^{2+} and by RHg^+ (R = Me, Ph, etc.) (128):



$$RHg^+ + CH_2=CH(CH_3)OAc + H_2O \longrightarrow [RHgCH_2\text{-}\overset{OH}{\underset{OAc}{C}}\text{-}CH_3] + H^+ \longrightarrow RHg^+ + CH_3C(O)CH_3 + HOAc$$

Kinetic and equilibrium measurements were reported for the reactions catalyzed by RHg^+, where R = CH_3COCH_2, CH_3, $p\text{-}CH_3C_6H_4$, Ph, $p\text{-}H_2NC_6H_4$, $p\text{-}ClC_6H_4$, $m\text{-}CF_3C_6H_4$ and $p\text{-}O_2NC_6H_4$.

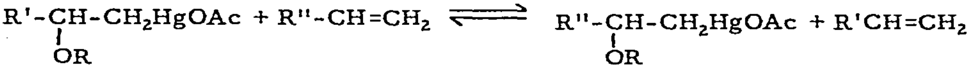
The mechanism of the redox decomposition of oxymercurated cis-2-butene in aqueous solution:



$$CH_3CH(OH)\underset{Hg^+}{C}HCH_3 \xrightarrow{H_2O \text{ or } D_2O} CH_3C(O)CH_2CH_3 + H^+ + Hg$$

has been studied by NMR spectroscopy (129). Essentially no deuterium was incorporated into the ketone product.

Other reactions of mercurated olefins have been studied from the mechanistic point of view. The transmercuration reaction is an equilibrium process:



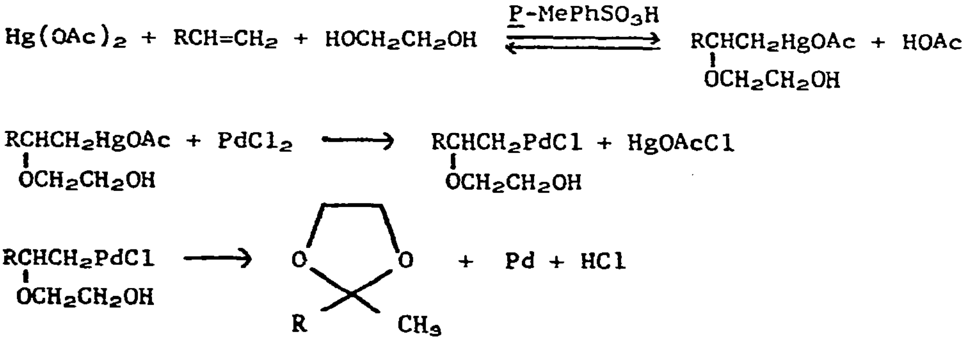
$$R'\text{-}\underset{\displaystyle OR}{CH}\text{-}CH_2HgOAc + R''\text{-}CH{=}CH_2 \rightleftharpoons R''\text{-}\underset{\displaystyle OR}{CH}\text{-}CH_2HgOAc + R'CH{=}CH_2$$

Equilibrium constants for 21 olefins (with respect to cyclohexene as a reference) were determined by a group of German workers (Table 9) (130). Further mechanistic studies established that the transmercuration is first order in oxyalkylmercurial and zero order in olefin and that its rate is equal to that of the deoxymercuration in the presence of EDTA. The mechanism indicated is a two-step process:

$$R'CH(OR)CH_2HgOAc \rightleftharpoons R'CH{=}CH_2 + AcOHg^+ + OR^-$$

$$R''CH{=}CH_2 + AcOHg^+ + OR^- \rightleftharpoons R''CH(OR)CH_2HgOAc$$

More preparatively oriented have been other investigations devoted to the oxidation of olefins via oxymercuration processes. Olefins may be converted to ethylene ketals by the process shown below (131):



$$Hg(OAc)_2 + RCH{=}CH_2 + HOCH_2CH_2OH \xrightleftharpoons{\underline{p}\text{-}MePhSO_3H} \underset{\displaystyle OCH_2CH_2OH}{RCH}CH_2HgOAc + HOAc$$

$$\underset{\displaystyle OCH_2CH_2OH}{RCH}CH_2HgOAc + PdCl_2 \longrightarrow \underset{\displaystyle OCH_2CH_2OH}{RCH}CH_2PdCl + HgOAcCl$$

TABLE 9

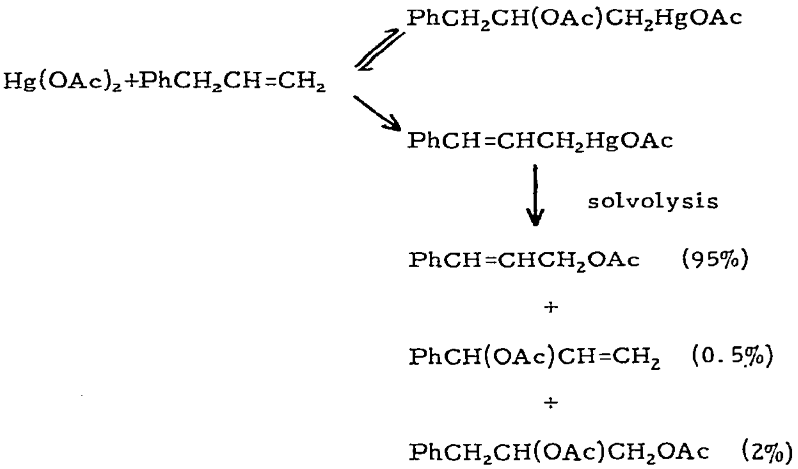
RELATIVE EQUILIBRIUM CONSTANTS OF TRANSMERCURATION OF β-METHOXYALKYL-MERCURIC ACETATES WITH OLEFINS IN METHANOL AT 50° (Ref. 130).

Olefin	K_{rel}	k_{rel} [a]	K_{AgNO_3} [b]
Cyclooctene	0.007	0.004	4.0
2,3-Dimethyl-2-butene	0.02	0.007	0.03
3-Ethyl-2-pentene	0.03	0.08	–
trans-4-Octene	0.04	0.015	0.14
2-Methyl-2-butene	0.06	1.57	0.22
Cycloheptene	0.1	0.25	3.6
Cyclopentene	0.3	0.73	2.0
cis-4-Octene	0.5	0.10	–
2,3-Dimethyl-1-butene	0.9	5.2	0.67
Cyclohexene	1	1	1
2-Methyl-1-pentene	1.4	1.05	0.58
3,3-Dimethyl-1-butene	2.4	0.07	1.0
Bicyclo[2,2,2]octene	4.0	0.03	–
2-Methyl-1-butene	5.3	7.3	0.83
3-Methyl-1-pentene	9.0	1.3	–
3-Methyl-1-butene	22.1	–	–
1-Hexene	38	4.13	1.2
1-Pentene	60	–	1.4
1-Heptene	60	3.95	0.89
1-Octene	60	3.95	0.72
Norbornene	800	1.0	17.0

[a] Relative rate constants for methoxymercuration of these olefins at 25° are given for comparison.

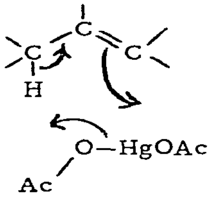
[b] Equilibrium constants for complex formation with silver nitrate in ethylene glycol.

Allylic oxidation of olefins using mercuric acetate is a well-known reaction. An investigation by Rappaport, Winstein and Young (132) indicated that allylic mercuric acetates are intermediates in such oxidations:

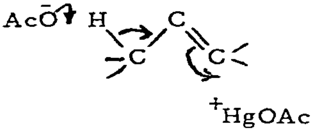


$$\begin{tikzcd}[column sep=small] & \mathrm{PhCH_2CH(OAc)CH_2HgOAc} \\ \mathrm{Hg(OAc)_2+PhCH_2CH{=}CH_2} \arrow[ur, shift left] \arrow[dr] & \\ & \mathrm{PhCH{=}CHCH_2HgOAc} \arrow[d, "\text{solvolysis}"] \\ & \mathrm{PhCH{=}CHCH_2OAc}\ (95\%) + \mathrm{PhCH(OAc)CH{=}CH_2}\ (0.5\%) + \mathrm{PhCH_2CH(OAc)CH_2OAc}\ (2\%) \end{tikzcd}$$

The oxidation of allylbenzene by mercuric acetate and the solvolysis of cinnamylmercuric acetate were compared: both gave 40% α-phenylallyl acetate and 60% cinnamyl acetate. The rate-determining formation of the allylic mercuric acetate occurs via an S_Ei' or S_E2' process:



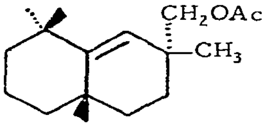
S_Ei'



S_E2'

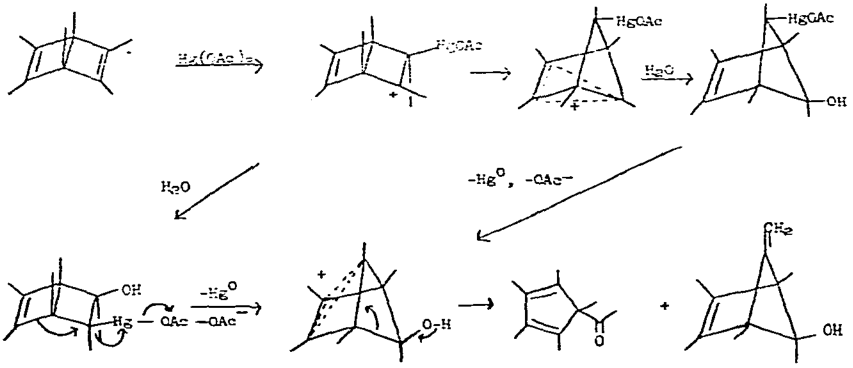
Such allylic oxidation was encountered in the reaction of thujopsene with mercuric acetate (133):

+

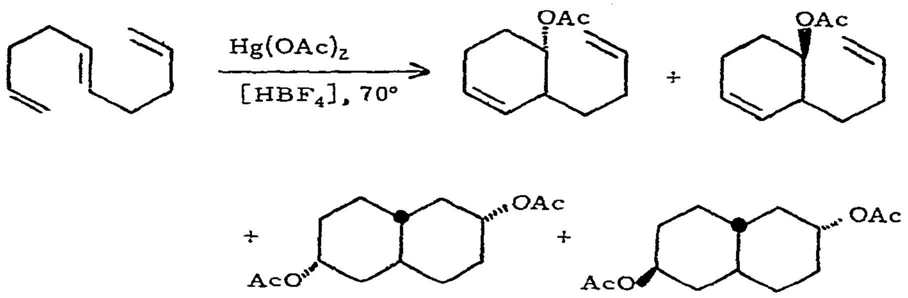


(minor)

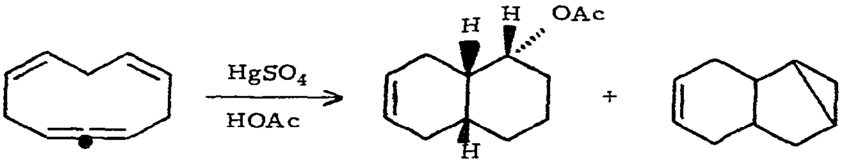
and in the reaction of 3- and 4-carene with mercuric acetate (134). Mercuric acetate oxidation (via presumed organomercury intermediates) of hexamethyl-Dewar-benzene has been reported (135, 136). The scheme below was suggested (136). The observed facile demercuration presumably is due to the homoallylic anchimeric assistance provided by the neighboring C=C bond.



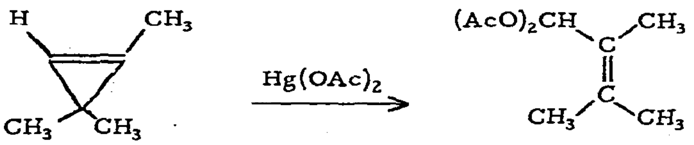
Oxidative cyclization of trans-1,5,9-decatriene with mercuric acetate in strong acid medium has been described (137): Both mono- and bicyclic products were obtained:



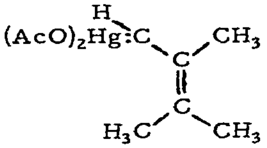
Similar oxidative cyclization was observed in the reaction of alkenylbenzenes of type 4-phenylbutene-1 and 5-phenylpentene-1 (138). Attempted oxymercuration of cyclodeca-1,2,5,8-tetraene gave mercury-free products (139):



and reaction of 1,3,3-trimethylcyclopropene with mercuric acetate resulted in oxidative ring cleavage (140):



An intermediate carbene complex, $\boxed{21}$, which subsequently underwent demercuration, was proposed, on the basis of rather unconvincing evidence.

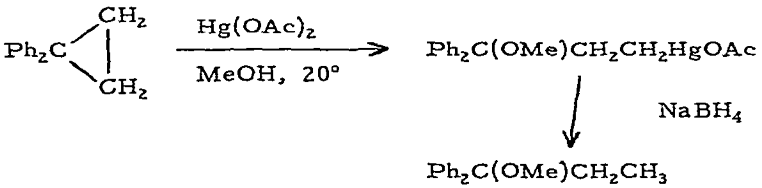


21

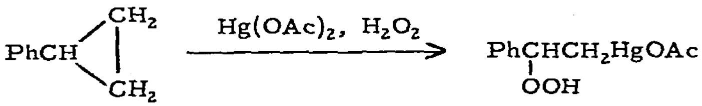
A kinetic study has been made of the oxyalkylation of aromatics with olefin oxymercuration products (141).

B. Cyclopropanes

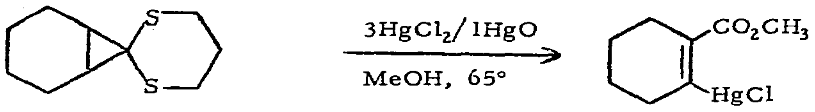
1,1-Diphenylcyclopropane underwent facile oxymercuration in methanol (142):



but its oxymercuration in acetic acid medium required the presence of added sodium acetate. In the absence of this additive, 1,1-diphenylcyclopropane was stable toward $Hg(OAc)_2/HOAc$ at 50°, but at 75-80° reacted with loss of mercury, giving $Ph_2C{=}CHCH_2OAc$ and $Ph_2C{=}CHCH_2OH$. trans-1,2-Diphenylcyclopropane did not undergo oxymercuration at 20° and was inert to $Hg(OAc)_2/HOAc$ at 75-80°. Peroxymercuration of cyclopropanes has been described by Sokolov (117):



Also reported has been the reaction of $\boxed{22}$ with mercuric chloride (143):



$\boxed{21}$

C. Isonitriles

The redox reactions of isonitriles with mercuric acetate and other mercuric salts in the presence of water, amines, ethanol and phenol produced ureas and urethanes in high yield (144):

$$Hg(OAc)_2 + ArN{\equiv}C + 3\ RNH_2 \longrightarrow ArNHC(O)NHR + Hg + CH_3C(O)NHR$$

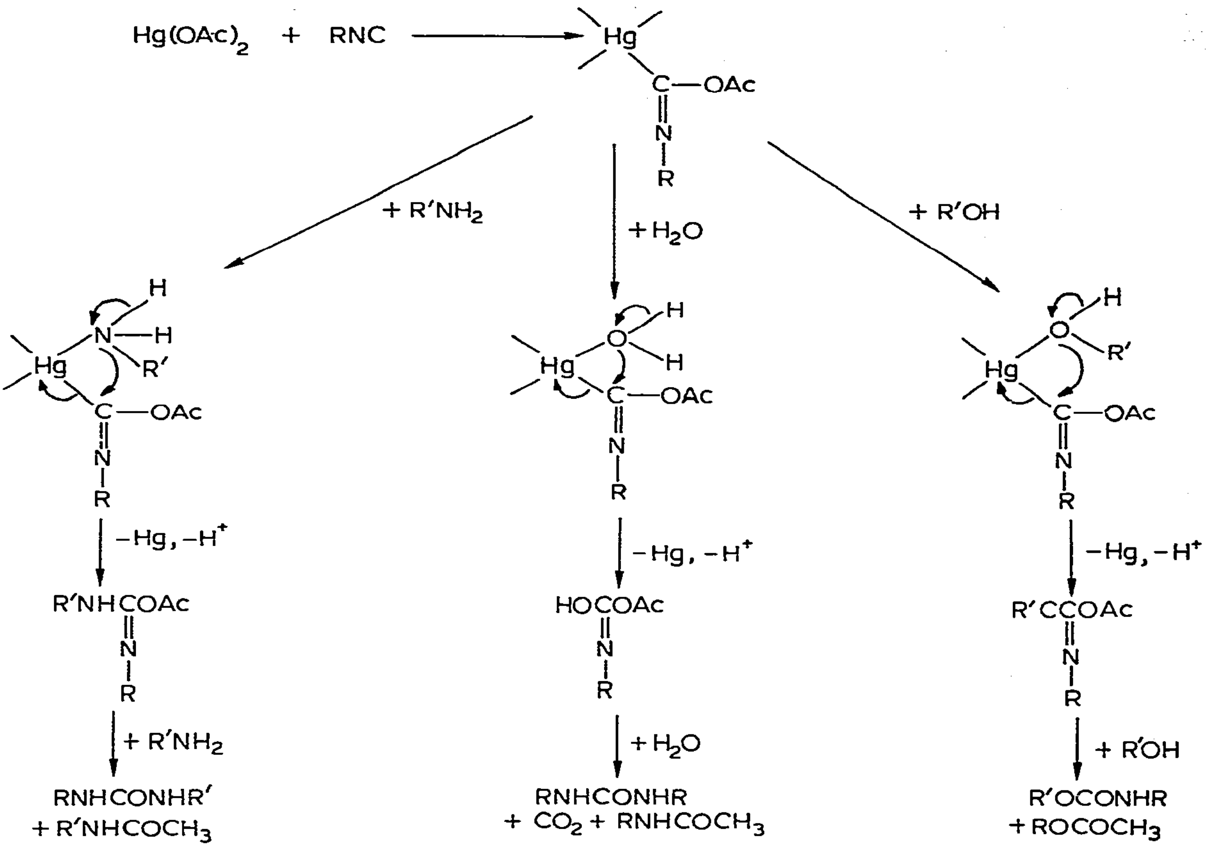
$$Hg(NO_3)_2 + ArN{\equiv}C + RNH_2 \longrightarrow ArN{=}C(NHR)_2 + ArNHC(O)NHR$$

$$Hg(OAc)_2 + ArN{\equiv}C + H_2O \longrightarrow Hg + ArNHCONHAr$$

The following reaction course involving mercuration of the isonitrile (i.e., insertion of $RN{\equiv}C$ into the Hg-OAc bond) was proposed.

D. Aromatic Compounds

A powerful new procedure for the mercuration of unreactive aromatic compounds involving the use of mercuric fluoride in liquid hydrogen fluoride has been patented (145). An example (146) will serve to illustrate the unique applicability of this method. A reaction of 10.8 g of mercuric oxide with 20 ml of liquid HF in a polyethylene bottle generated HgF_2. The addition of 10 ml of nitrobenzene



and a 10 hr reaction time at room temperature followed. The reaction mixture was poured slowly in a solution of 15 g of KBr in 500 ml of water in a polyethylene bottle. This mixture was treated with 56 g.of KOH pellets. Filtration (water and methanol washes) gave m-nitrophenylmercuric bromide in 91% yield. This procedure also served well in the mercuration of benzoic acid.

The direct mercuration of highly halogenated benzenes has been described by Deacon et al. 1,2,4,5-Tetrafluorobenzene was monomercurated when heated at 140-160° in a Carius tube with a deficiency of mercuric acetate or $Hg(O_2CCF_3)_2$ (147):

$$1,4\text{-}H_2C_6F_4 + HgY_2 \xrightarrow{150^\circ} p\text{-}HC_6F_4HgY + HY$$

Dimercuration to give $1,4\text{-}(ClHg)_2C_6F_4$ (after ion exchange with NaCl) was observed when the $Hg(O_2CCF_3)_2$/tetrafluorobenzene ratio used was two. This dimercurial also was prepared by a decarboxylation reaction:

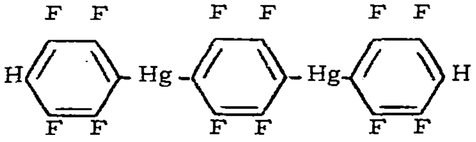
$$1,4\text{-}(TlO_2C)_2C_6F_4 + HgCl_2 \xrightarrow{120^\circ} 1,4\text{-}(ClHg)_2C_6F_4 + 2\ TlCl + 2\ CO_2$$

Mercuration under basic reaction conditions (i.e., via <u>nucleophilic</u> substitution at mercury) also was applied:

$$1,4\text{-}H_2C_6F_4 + HgBr_4^{2-} + 2\ OH^- \longrightarrow (p\text{-}HC_6F_4)_2Hg + 4\ Br^- + 2\ H_2O$$

A byproduct of this reaction, $\boxed{23}$, indicated the occurence of a secondary process:

$$(p\text{-}HC_6F_4)_2Hg + 1,4\text{-}H_2C_6F_4 + 2\ OH^- + HgBr_4^- \longrightarrow$$



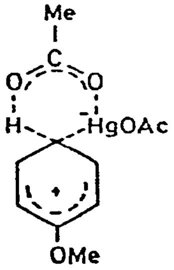
$+ 4\ Br^- + 2\ H_2O$

$\boxed{23}$

Similar direct mercuration of pentachlorobenzene and other polychlorobenzenes with mercuric trifluoroacetate at high temperature gave the symmetrical mercurials $(C_6Cl_5)_2Hg$, $(2,3,4,5\text{-}Cl_4C_6H)_2Hg$, $(2,3,4,6\text{-}Cl_4C_6H)_2Hg$, $(2,3,5,6\text{-}Cl_4C_6H)_2Hg$, $(2,3,4\text{-}Cl_3C_6H_2)_2Hg$, $(2,4,6\text{-}Cl_3C_6H_2)_2Hg$ and $(2,5\text{-}Cl_2C_6H_3)_2Hg$ (148). At these higher temperatures, the initially formed $ArHgO_2CCF_3$ disproportionate to

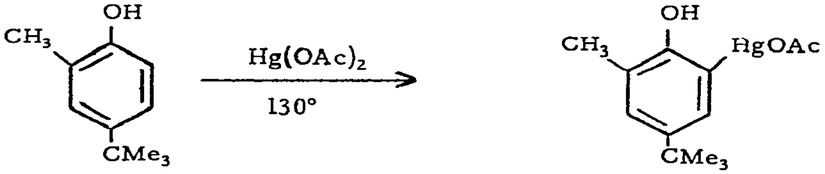
Ar_2Hg and $Hg(O_2CCF_3)_2$, but at lower temperature they can be isolated, e.g., $C_6Cl_5HgO_2CCF_3$. Mercuric difluoro- and monofluoroacetate also mercurated pentachlorobenzene at higher temperature.

A physical organic study of the mercuration of anisole with mercuric acetate in glacial acetic acid showed that this reaction involves two electrophiles: $Hg(OAc)_2$ and $AcOHg^+$ (11). The latter is at least twice as reactive as molecular mercuric acetate in this process. The activation parameters for this mercuration process indicated a highly ordered activated complex, suggested to be $\boxed{24}$.

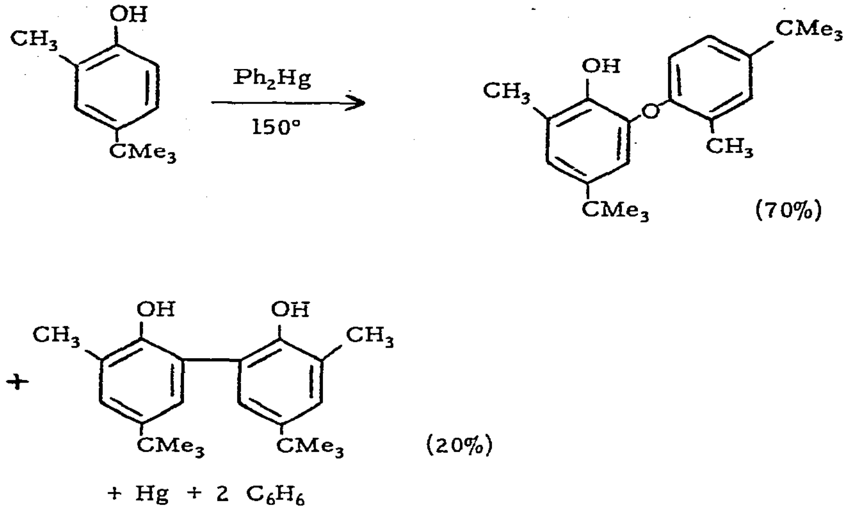


$\boxed{24}$

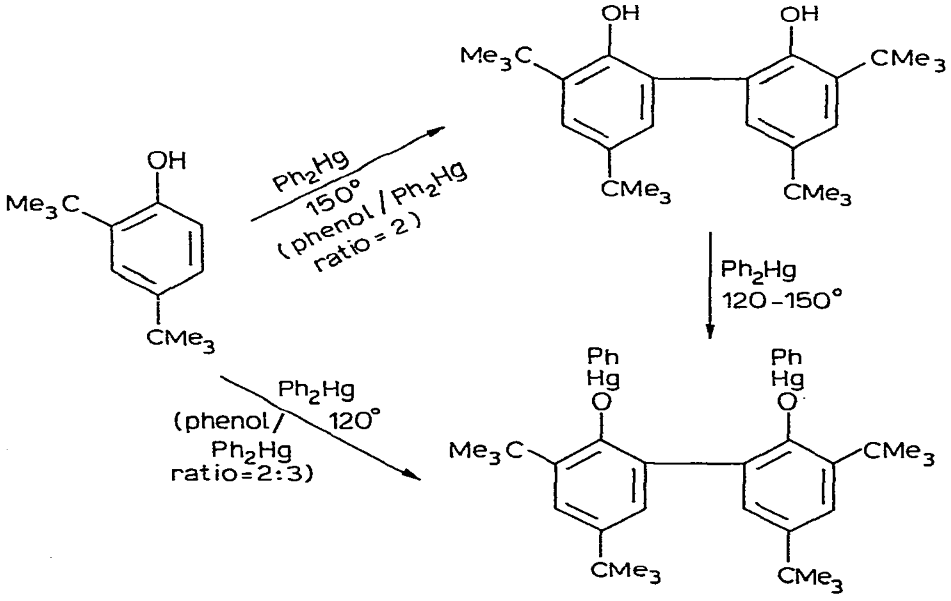
Mercuration of alkylated phenols has been described (148a):

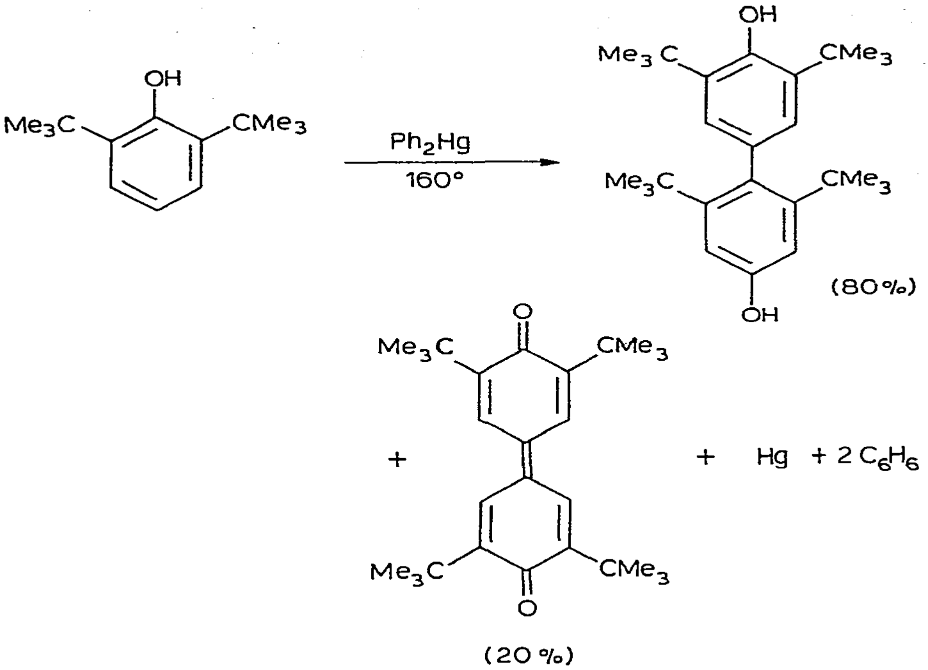


Unexpectedly, the same product was obtained when phenylmercuric acetate was used in place of mercuric acetate. The reaction of this phenol derivative with diphenylmercury gave dimeric, mercury-free products, presumably via a free radical process:

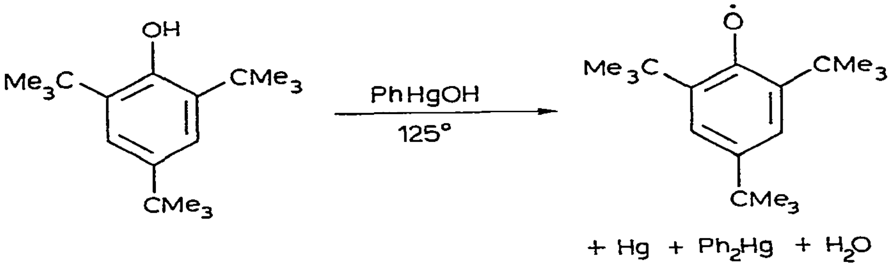


Reactions of diphenylmercury with 2,4- and 2,6-di-tert-butylphenol also were studied:





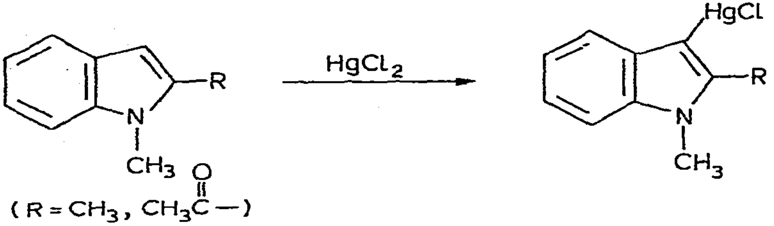
Finally, the action of phenylmercuric hydroxide on the fully blocked 2,4,6-tri-tert-butylphenol produced the corresponding phenoxy radical (ESR):

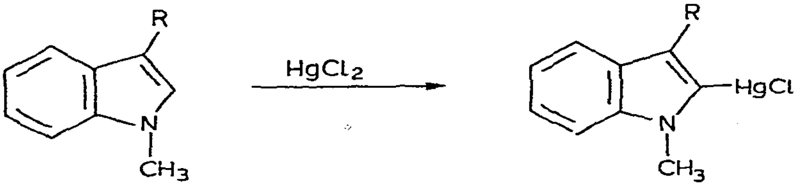


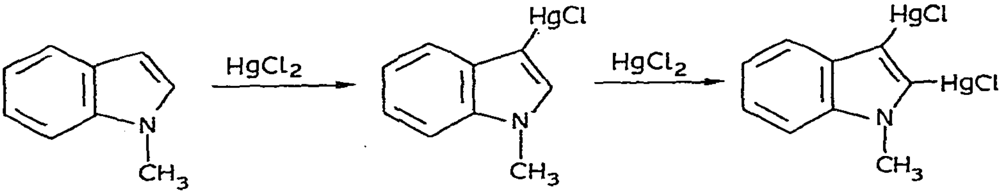
Other preparative studies include:

The mercuration (in the para position) of aniline, N,N-dimethyl- and N,N-diethylaniline with ^{197}Hg(OAc)$_2$ and ^{203}Hg(OAc)$_2$ (149).

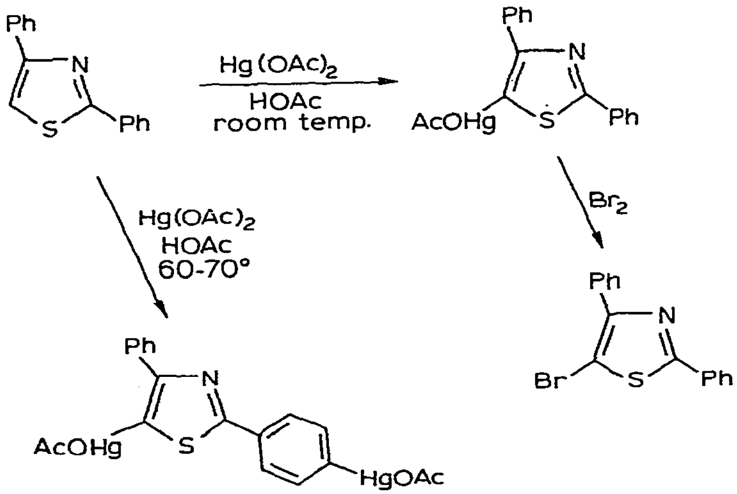
The mercuration of substituted indoles with mercuric chloride (150), for instance:





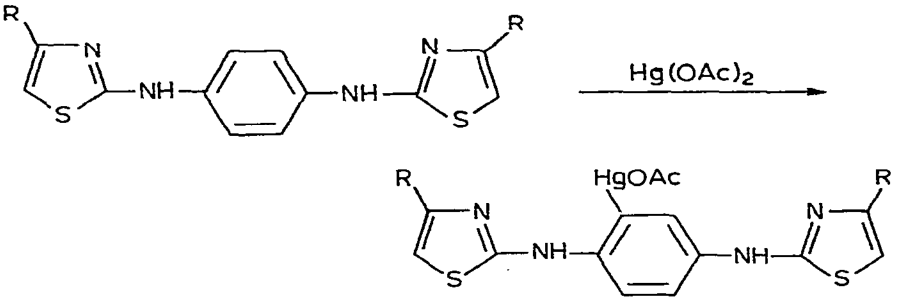


The mercuration of thiazole derivatives (151):



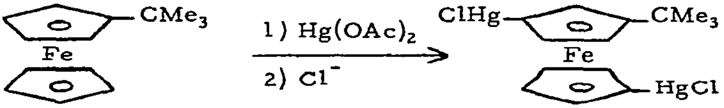
The relative reactivity of thiazoles toward $Hg(OAc)_2/HOAc$ was found to be: 2-Ph > 2-Ph-4-Me > 2-Me > 2-Ph-4,5-Me_2. 4,5-Dimethyl- and 2,4,5-trimethylthiazole were not mercurated under these conditions.

Also reported was (152):



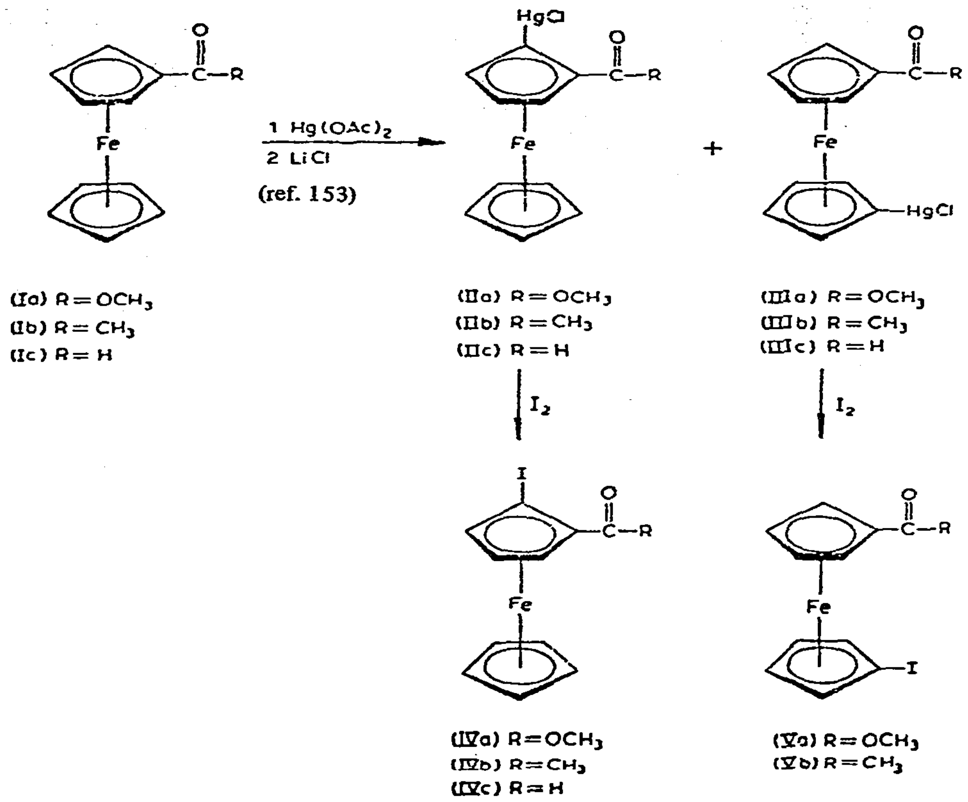
(assumed product structure)

New examples of the mercuration of metallocene derivatives have been reported:



(ref. 39)

The formation of appreciable amounts of 1,2-disubstituted product in these reactions is noteworthy and was explained in terms of intermolecular coordination of $Hg(OAc)_2$ at the carbonyl oxygen which directs reagent attack to the 2-position. Anamolous chromatographic properties of the 1,2-disubstituted products also were ascribed to similar intramolecular cooridination, $\boxed{25}$ (153).



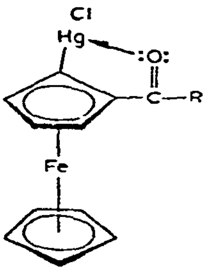
(Ia) R = OCH$_3$
(Ib) R = CH$_3$
(Ic) R = H

(IIa) R = OCH$_3$
(IIb) R = CH$_3$
(IIc) R = H

(IIIa) R = OCH$_3$
(IIIb) R = CH$_3$
(IIIc) R = H

(IVa) R = OCH$_3$
(IVb) R = CH$_3$
(IVc) R = H

(Va) R = OCH$_3$
(Vb) R = CH$_3$



25

The transmercuration reaction occurs also in the aromatic series (Kooyman et al., 1965):

$$\text{PhHgOAc} + \text{ArH} \xrightarrow{150^\circ} \text{Ar-HgOAc}_{(o,m,p)} + \text{PhH}$$

Further studies have now been reported concerning isomer equilibria among 1,2-disubstituted phenylmercuric acetates (154). The latter included 1,2-dimethyl-, 1,2-diethyl-, 1,2-dimethoxy- and 1,2,3-trimethylbenzene, tetralin and indane. A reaction of naphthalene with phenylmercuric acetate (24 hr at 150°) gave a 75% conversion to α- and β-naphthylmercuric acetate in a ratio of 60:40. The mechanism of such transmercuration processes remains unknown.

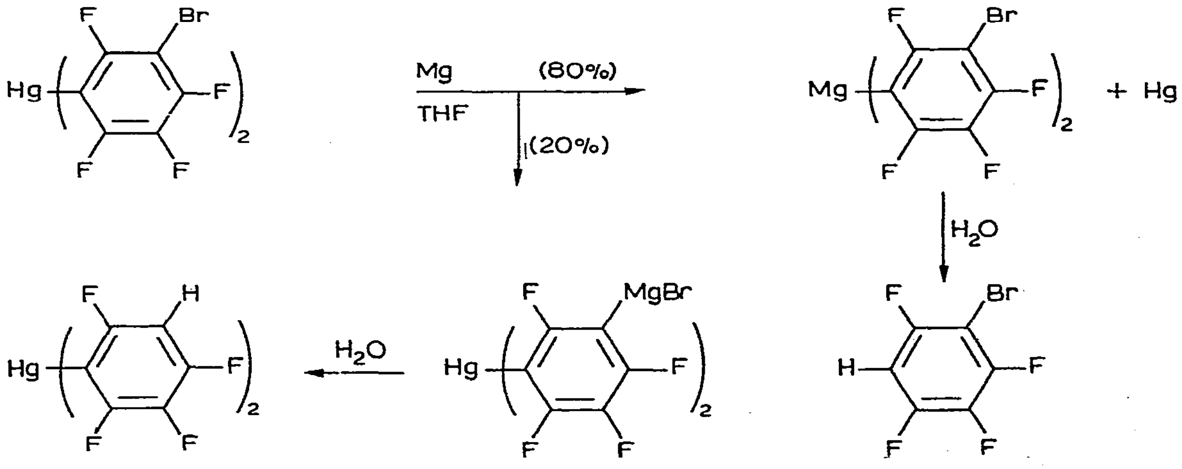
5. ORGANOFUNCTIONAL ORGANOMERCURY COMPOUNDS

A. Highly Halogenated Organomercurials

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

C_6F_5-Hg compounds (18, 23, 30, 43, 53)
C_6F_4H-Hg compounds (30, 147)
C_6Cl_5-Hg compounds (30, 148)
Halomethyl-mercury compounds (Section 3C)

The action of magnesium metal in THF on bis(3-bromotetrafluorophenyl)mercury resulted in two modes of reaction, metal displacement and Grignard reagent formation (155):

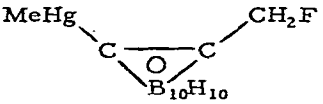


Also reported was:

$$\begin{tikzcd}(C_6F_5)_2Hg + Mg \arrow[r, "THF"] & (C_6F_5)_2Mg + Hg \arrow[d, "Me_3SiCl"] \\ & Me_3SiC_6F_5\end{tikzcd}$$

B. Carboranyl-Mercurials

New organomercury derivatives of carboranes have been described:



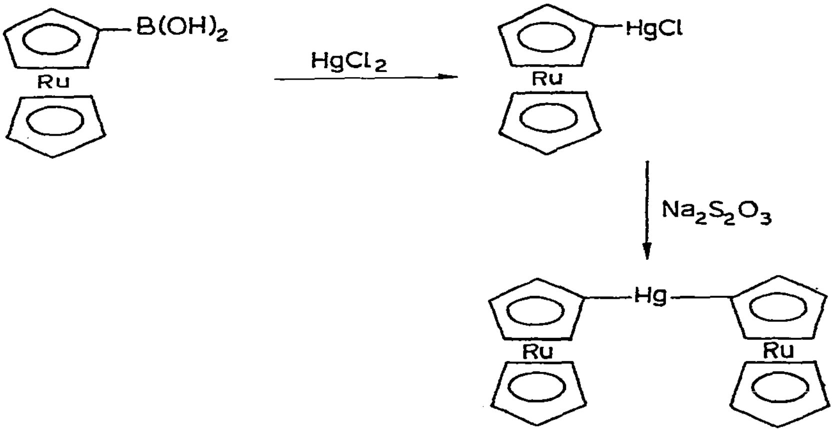
(via the Li reagent (156))

1,6- and 1,10-$PhCB_8H_8CHgMe$ and $(PhCB_8H_8C)_2Hg$, via $PhCB_8H_8CLi$ (157), and organomercury derivatives of phospha-and arsacarboranes, "m"- and "p"-$MeHgCB_{10}H_{10}P$ and $MeHgCB_{10}H_{10}As$, prepared via $LiCB_{10}H_{10}P$ and $LiCB_{10}H_{10}As$ (158).

C. Metallocene-Mercurials

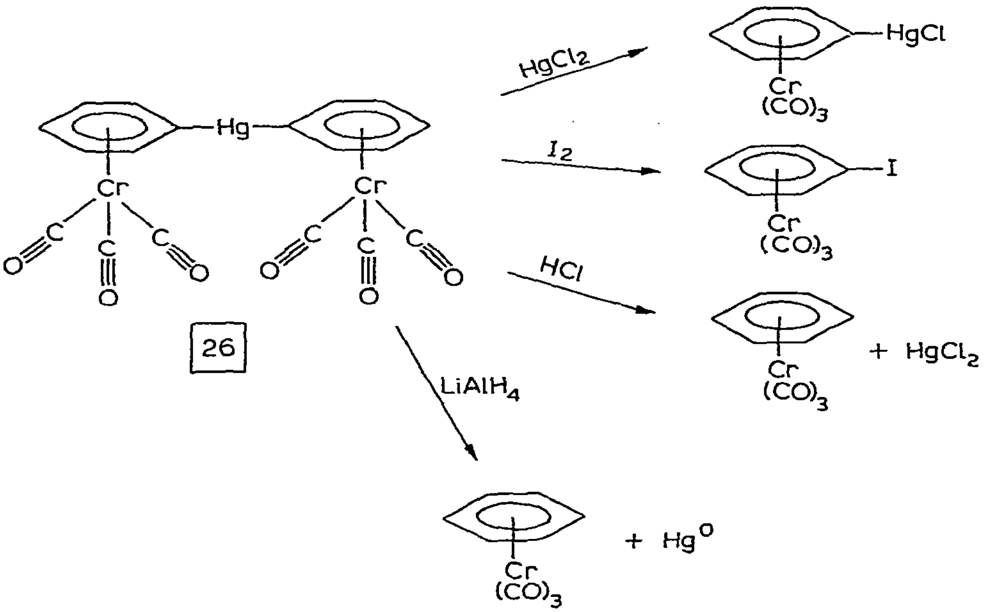
Mentioned in previous sections has been the synthesis and reactions of various ferrocenylmercurials (14, 39, 49, 50, 51).

Ruthenocenyl-mercurials have now been prepared (159):



In contrast, reaction of ruthenocene with alcoholic mercuric chloride gave $(C_5H_5)_2Ru.HgCl_2$. The same adduct was obtained on treatment of ruthenocene with mercuric acetate in acetic acid, followed by addition of KCl solution, together with an insoluble material which treatment with sodium thiosulfate converted to $C_{20}H_{18}RuHg$.

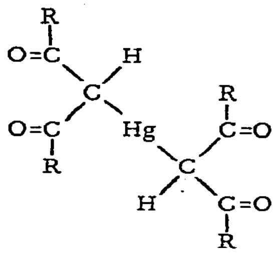
The action of chromium hexacarbonyl on diphenylmercury gave $\boxed{26}$ in 70% yield (160). Reactions of this complex were studied:



D. Organomercurials with Keto Functions

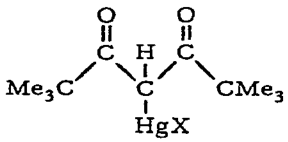
Various mercurials containing organic substituents with C=O functions have been mentioned in previous sections (41, 52, 53, 106).

Full details have been reported by Musso et al. (161) of their studies of mercury(II) derivatives of 1,3-diketones. IR and NMR studies showed these to involve C-Hg rather than O-Hg linkages:



(R=Me, Me$_3$C)

Final confirmation was provided by an X-ray crystal structure determination of bis(dipivaloylmethane)mercury (Fig. 2). Mercury-oxygen interaction occurs between neighboring molecules, as the bond distances given in Fig. 3 indicate. Two of the compounds discussed by Musso et al. were reported independently by other workers (162):



(X = OAc and Cl)

Compounds of type $RC(O)CH_2HgCl$ were found to react with potassium diphenylphosphide to give $Ph_2POC(R)=CH_2$ (163).

E. Organomercurials with Nitrogen-Containing Functions

Aminomercuration and azidomercuration reactions provide mercury compounds of this type (Section 4A).

Bis(trinitromethyl)mercury forms 1:1 complexes with a wide variety of Lewis bases (164). Those with dioxane and THF were found to be the strongest, those with nitroalkanes and acetonitrile among the weakest. Pyridine reacted to form an ionic product, $[py_2Hg^{2+}]\,[C(NO_2)_3^-]_2$. The aqueous solution chemistry of bis(trinitromethyl)mercury involves ionization:

$$\begin{tikzcd}
Hg[C(NO_2)_3]_2 \arrow[r, shift left] & {}^{+}HgC(NO_2)_3 \arrow[l, shift left] \arrow[d, shift left] & + \; C(NO_2)_3^- \\
 & Hg^{2+} + C(NO_2)_3^- \arrow[u, shift left] &
\end{tikzcd}$$

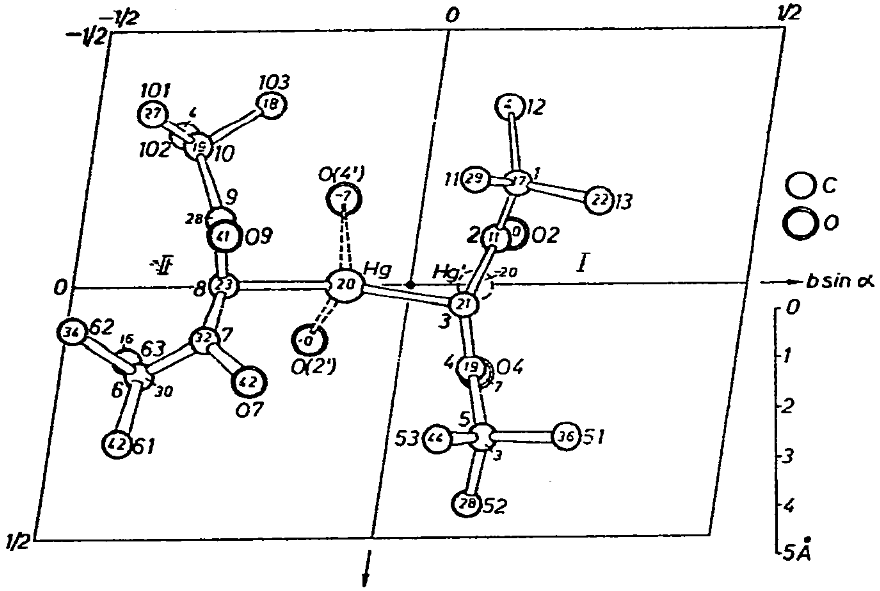


Figure 2. Structure of Bis(dipivaloylmethane)mercury. (Musso et al., Chem. Ber., 105 (1972) 3067)

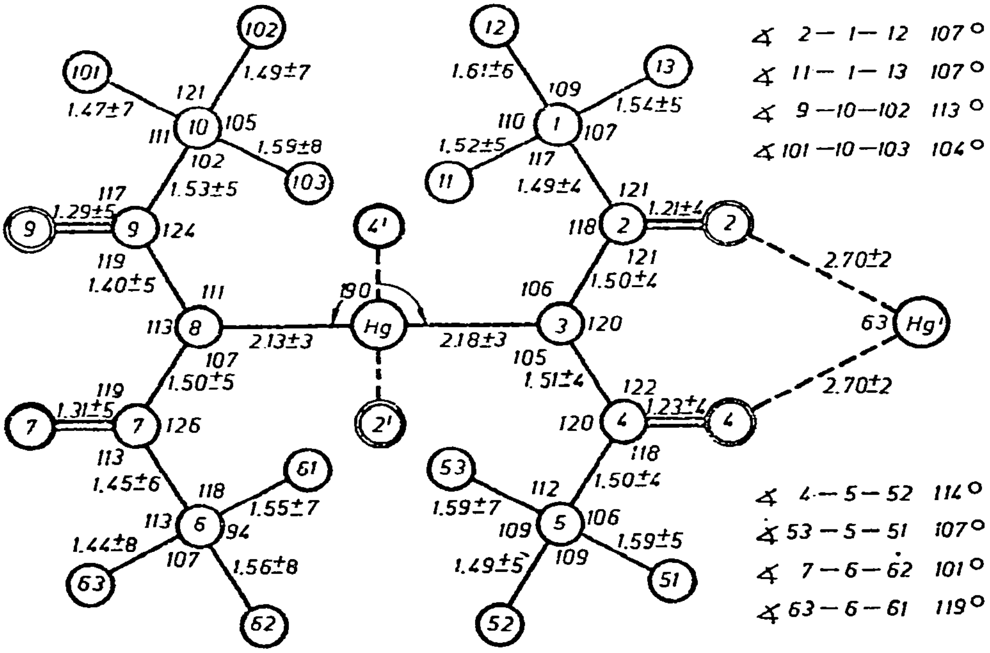


Figure 3. Bond distances and angles in Bis(dipivaloylmethane)-mercury. (Musso et al., Chem. Ber., 105 (1972) 3067)

and hydrolysis:

$$^{+}HgC(NO_2)_3 + H_2O \rightleftharpoons HOHgC(NO_2)_3 + H^+$$

From the first apparent hydrolysis constant, K_b for $HOHgC(NO_2)_3$ was calculated to be 5.6×10^{-12} (165). Also determined were the apparent dissociation constants of $Hg[C(NO_2)_3]_2$ in DMF, CH_3CN, Me_2CO, MeOH and EtOH. In contrast to the ionization of this compound observed in these organic solvents, $Hg[CF(NO_2)_2]_2$ was found to be practically unionized under the same conditions.

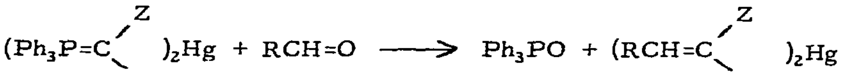
The reaction of $LiCH_2CN$ with mercuric chloride in THF gave a white, air stable solid which was insoluble in all common solvents (166). IR spectroscopy showed that Hg-C, C-H and C≡N bonds were present, hence it is likely that this material is a polymer with coordination of nitrile nitrogen to mercury.

F. Olefinic Mercurials

In previous sections mention has been made of:

vinylic mercurials (8, 9, 14, 35)
other alkenylmercurials (22, 34, 37)

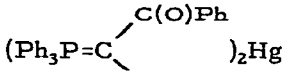
The Wittig reaction of mercurated phosphorus ylides with aldehydes is a novel route to vinylic mercurials (N. A. Nesmeyanov, Kalinin and Reutov, 1969):



$$(Ph_3P{=}C(Z)\!\!<\;)_2Hg + RCH{=}O \longrightarrow Ph_3PO + (RCH{=}C(Z)\!\!<\;)_2Hg$$

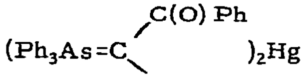
(Z = CO_2Me
and CN)

In further work (167), ylides $\boxed{27}$ and $\boxed{28}$ have been prepared. $\boxed{27}$ was not sufficiently nucleophilic to undergo a Wittig reaction, but



$(Ph_3P{=}C(C(O)Ph))_2Hg$

$\boxed{27}$

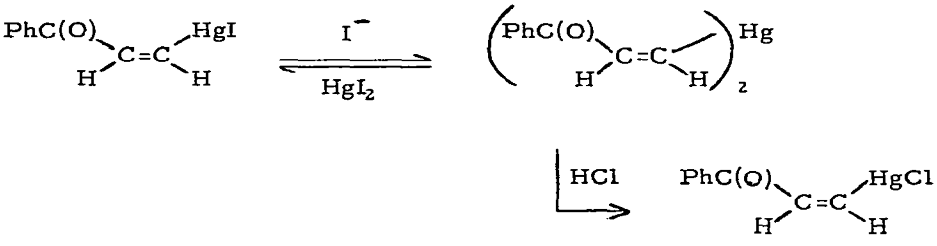


$(Ph_3As{=}C(C(O)Ph))_2Hg$

$\boxed{28}$

$\boxed{28}$ did react with p-nitrobenzaldehye to give the expected vinylic mercurial. NMR studies established the stereochemical course of such Wittig reactions.

The question of geometric isomerization at the C=C bond in PhC(O)CH=CH-Hg compounds has been examined (168):



No isomerization occurred during the conversions indicated above or when the compounds were heated in organic solvents. However, when they were kept in ethereal solution in diffuse sunlight, slow conversion to the less soluble trans isomers occurred. (Detailed NMR studies provided the basis for the isomer assignments.)

6. C-Hg BOND REACTIONS OF ORGANOMERCURIALS

The second step of the solvomercuration-demercuration sequence (Section 4A) involves reduction of the Hg-C bond (→ H-C) with sodium borohydride in basic medium. Previous workers provided convincing evidence that this reduction involves a free radical process (cf. the organomercury annual surveys of the previous two years). Further work on the $NaBH_4$ reduction of organomercurials is in agreement with a free radical mechanism.

A noncage process seems indicated since such reduction of Ph_3CCH_2HgCl in the absence of oxygen gave mostly rearranged product (169):

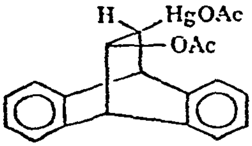
$$Ph_3CCH_2HgCl \xrightarrow{NaBH_4,\ OH^-} \underset{(92\%)}{Ph_2CHCH_2Ph} + \underset{(8\%)}{Ph_3CCH_3} + \underset{(99\%)}{Hg}$$

When this reduction was carried out in the presence of oxygen, the intermediate free radicals reacted to give alcohols:

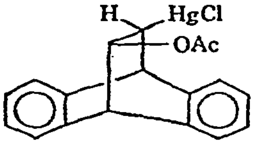
$$Ph_3CCH_2HgCl \xrightarrow{NaBH_4,\ OH^-;\ O_2} \underset{(13\%)}{Ph_3CCH_3} + \underset{(3\%)}{Ph_2CHCH_2Ph}$$

$$+ \underset{(58\%)}{Ph_2C(OH)CH_2Ph} + \underset{(19\%)}{Ph_3CCH_2OH}$$

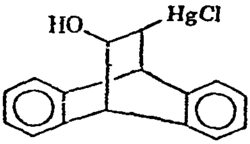
The reduction of this mercurial with lithium aluminum hydride, $NaAlH_2(CH_2CH_2OMe)_2$ and sodium amalgam gave only unrearranged. product, Ph_3CCH_3, in nearly quantitative yield. This suggests that these reactions do not involve intermediate free radicals. The sodium amalgam reduction of $\boxed{29}$, $\boxed{30}$, $\boxed{31}$, $\boxed{32}$, $\boxed{33}$ and $\boxed{34}$ in alkaline D_2O gave products with stereospecific retention during



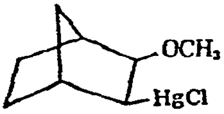
$\boxed{29}$



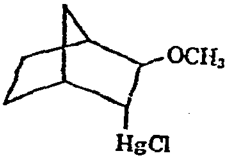
$\boxed{30}$



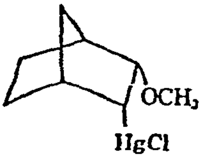
$\boxed{31}$



$\boxed{32}$

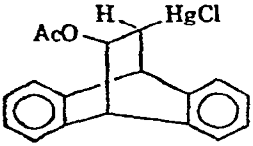


$\boxed{33}$



$\boxed{34}$

replacement of HgX by D (170). Reduction of these compounds, as well as of $\boxed{35}$, with $NaBD_4$ in alkaline medium gave the same



$\boxed{35}$

products as did Na/Hg, but without stereospecific deuterium incorporation. For the sodium borohydride reduction a radical chain process was favored:

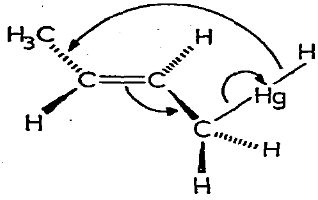
$$\begin{aligned} &RHgX + BH_4^- \longrightarrow RHgH \\ &RHgH \longrightarrow R\cdot + Hg + H\cdot \\ &R\cdot + RHgH \longrightarrow RH + RHg\cdot \\ &RHg\cdot \longrightarrow R\cdot + Hg, \text{ etc.} \end{aligned}$$

while the sodium amalgam reduction was suggested (170) to proceed via a mechanism involving two closely linked one-electron transfer steps at the amalgam surface, followed by hydrolysis of the anionic intermediate:

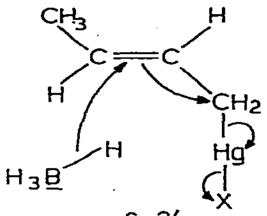
$$\begin{tikzcd} RHgCl + Na \arrow[r] & NaCl + RHg\cdot \arrow[r, "Na"] & RHg^- \arrow[d, "H_2O,\ OH^-"] \\ & & Hg + RH \end{tikzcd}$$

The last step would be expected to proceed with retention of configuration, in analogy with known organomercury chemistry.

Crotylmercuric derivatives, $CH_3CH{=}CHCH_2HgX$ (X = Cl, Br, OAc), reacted with sodium borohydride and with trimethyltin hydride to give 1-butene as sole organic product (171). As possible mechanisms, an S_Ni' and an S_N2' pathway were suggested in view



S_Ni'



S_N2'

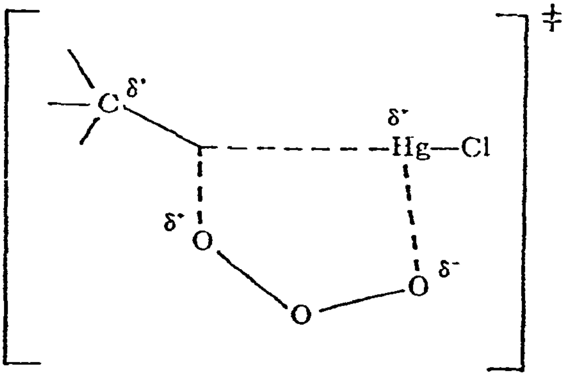
of this high specificity, which is not indicative of free butenyl radicals. In aqueous THF, sodium borohydride was found to convert benzylmercuric chloride to dibenzylmercury. Partial reduction could be achieved with tetramethylammonium borohydride and complete reduction to toluene with trimethyltin hydride.

The polargraphic reduction of $CF_3CH(HgCl)CH_2OMe$, $CF_3CH(HgCl)CH_2OH$, $Hg[CH(CF_3)CH_2OMe]_2$ and $CF_3CH(HgCl)CH_2OAc$ has been studied (172). Processes proceeding via RHg· radicals led either to symmetrization or to fragmentations, giving a fluoroolefin.

Radicals also are generated in the thermolysis of organomercurials, and in this connection we note the generation of the neophyl radical by pyrolysis of dineophylmercury (32):

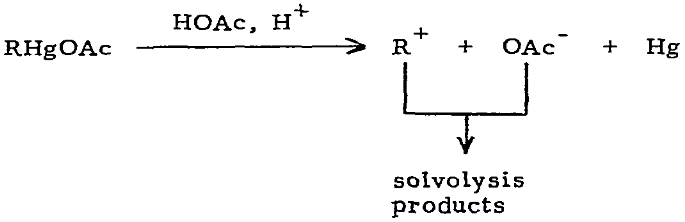
$$\begin{aligned}(PhCMe_2CH_2)_2Hg \xrightarrow[\text{in heptane}]{235^\circ} \; & PhCMe_3\ (29.3\%) + PhCH_2CHMe_2\ (12.5\%) \\ & + PhCH_2CMe{=}CH_2\ (12.1\%) \\ & + PhCH{=}CMe_2\ (8.3\%) + \\ & \quad (PhCH_2CMe_2)_2\ (21.2\%) + \\ & \text{other dimers } (< 0.1\%)\end{aligned}$$

Reactions of organomercurials with oxidizing agents also have been investigated. Ozonolysis of R_2Hg and RHgX compounds was the subject of a thorough study by Waters et al. (173). Primary alkylmercurials gave carboxylic acids; secondary alkylmercurials, ketones; tertiary alkylmercurials, alcohols. In addition to the major process of C-Hg bond cleavage, some C-C cleavage also occurred (Table 10). Kinetic studies also were carried out; a concerted process, $\boxed{36}$, was favored. The action of tert-butyl hydroperoxide on dialkylmercurials (174) and alkylmercuric chlorides (175) resulted in formation of a wide variety of organic products, probably via radical processes.



$\boxed{36}$

Another reaction that has been much used in organomercury chemistry is solvolytic demercuration as a source of carbonium ions:



$$\mathrm{RHgOAc} \xrightarrow{\mathrm{HOAc,\ H^+}} \mathrm{R^+} + \mathrm{OAc^-} + \mathrm{Hg}$$

Two groups have reported examples of ring expansions in such processes:

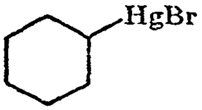
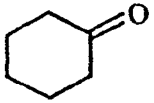
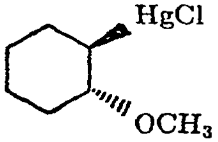
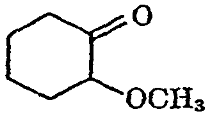
TABLE 10.

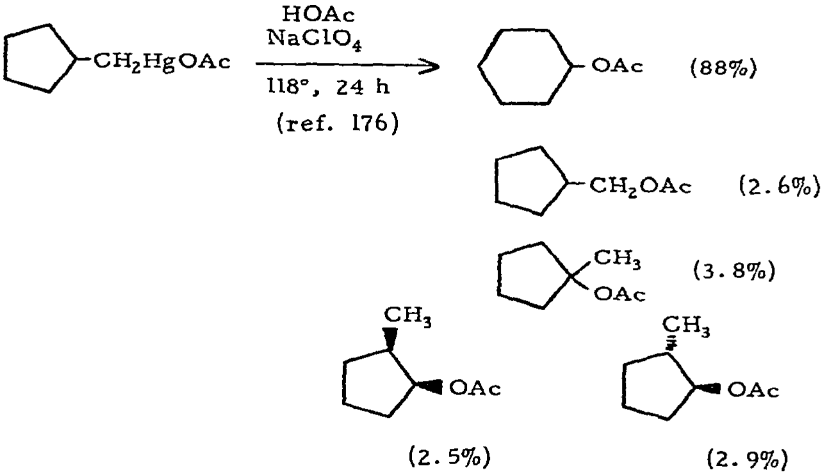
Reaction of Ozone with Alkylmercurials (Ref. 174)

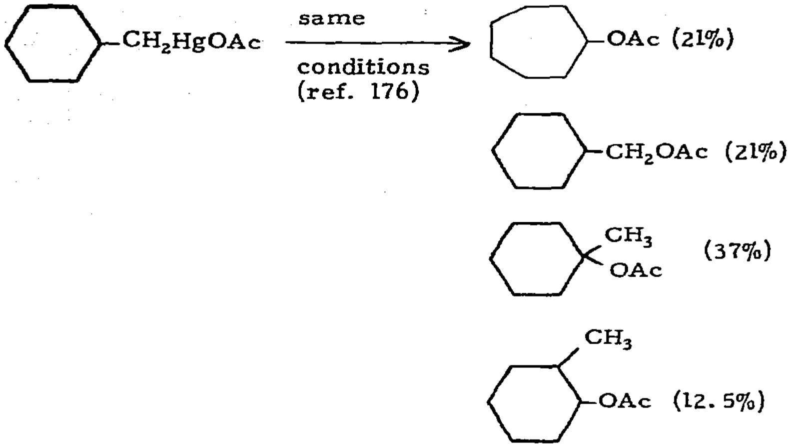
Organomercurial	*Reaction Temperature, °C*	*Inorganic Products*	*Organic Products*
$CH_3CH_2CH_2HgBr$	10	—	44% CH_3CH_2COOH 54% CH_3COOH
$CH_3CH_2CH_2HgBr$	0	—	48% CH_3CH_2COOH 50% CH_3COOH
$(CH_3CH_2CH_2)_2Hg$	10	45% $HgCl_2$ 35% Hg_2Cl_2 20% HgO	64% CH_3CH_2COOH 20% CH_3COOH 15% $HCOOH$
$(CH_3CH_2CH_2)_2Hg$	0	—	67% CH_3CH_2COOH 19% CH_3COOH 14% $HCOOH$
$(CH_3CH_2CH_2)_2Hg$	−76	—	72% CH_3CH_2COOH 16% CH_3COOH 12% $HCOOH$
$CH_3(CH_2)_5HgBr$	10	—	30% $CH_3(CH_2)_4COOH$ 40% $CH_3(CH_2)_3COOH$ 10% $CH_3(CH_2)_2COOH$ 5% CH_3COOH
$CH_3(CH_2)_5HgBr$	10	—	30% $CH_3(CH_2)_4COOH$ 40% $CH_3(CH_2)_3COOH$ 10% $CH_3(CH_2)_2COOH$ 5% CH_3COOH
$[CH_3(CH_2)_5]_2Hg$	10	—	50% $CH_3(CH_2)_4COOH$ 25% $CH_3(CH_2)_3COOH$ 10% $CH_3(CH_2)_2COOH$ 10% CH_3CH_2COOH 5% CH_3COOH
$[CH_3(CH_2)_5]_2Hg$	0	—	70% $CH_3(CH_2)_4COOH$ 10% $CH_3(CH_2)_3COOH$ 5% $CH_3(CH_2)_2COOH$ $<$5% CH_3CH_2COOH $<$5% CH_3COOH
$[CH_3(CH_2)_5]_2Hg$	−76	—	80% $CH_3(CH_2)_4COOH$ 5% $CH_3(CH_2)_3COOH$ $<$5% other acids
$(CH_3)_3CCH_2HgCl$	10	—	— $(CH_3)_2CO$ — $(CH_3)_3COH$ — $(CH_3)_3CCOOH$

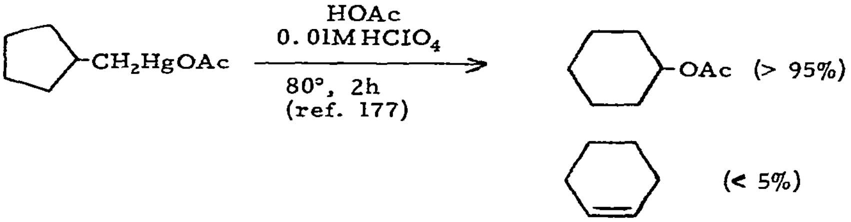
(continued)

TABLE 10 (Continued)

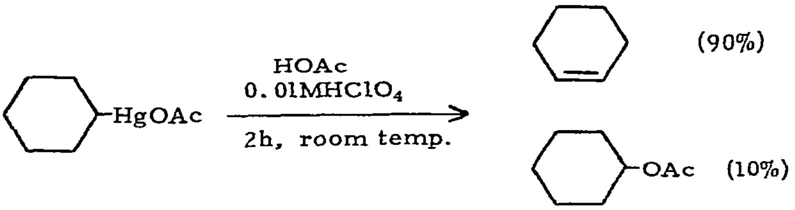
Organomercurial	*Reaction Temperature, °C*	*Inorganic Products*	*Organic Products*
$(CH_3)_2CH(CH_2)_2HgBr$	10	—	Complex mixture
$(CH_3)_2CHHgCl$	10	77% $HgCl_2$ 23% Hg_2Cl_2	79% $(CH_3)_2CO$ 19% CH_3COOH
$[(CH_3)_2CH]_2Hg$	10	55% $HgCl_2$ 35% Hg_2Cl_2 10% HgO	89% $(CH_3)_2CO$ 10% CH_3COOH
	10	—	60%  38% $HOOC(CH_2)_4COOH$
	10	—	—[b] 
$(CH_3)_3CHgCl$	10	—	50% $(CH_3)_3COH$ 22% $(CH_3)_2CO$ 28% HCOOH







Such solvolytic demercuration was much more facile with cyclohexylmercuric acetate (177):



(75% total yield)

Other reactions of organomercurials to be noted include the following:

The interesting β H^- abstraction from alkylmercurials by triphenylmethane derivatives has received further study by Reutov et al. (178). With appropriate R_2Hg compounds ($R = n\text{-}C_3H_7$, $i\text{-}C_4H_9$, $sec\text{-}C_4H_9$, C_2H_5), $Ph_3C^+Y^-$ ($Y = ClO_4^-$, BF_4^-, $HgBr_3^-$) reacted as shown:

$$(RR'CHCH_2)_2Hg + Ph_3C^+Y^- \xrightarrow{ClCH_2CH_2Cl} RR'C{=}CH_2 + Ph_3CH + RR'CHCH_2HgY$$

(isolated as the bromide)

With trityl halides, alkylation products, Ph_3CCH_2CHRR', also were formed, in small amount when Y = Br, in larger amounts when Y = Cl. With trityl iodide only triphenylmethane was produced. The reaction rate was found to increase as the ionic nature of the trityl compound increased, for Y in Ph_3CY, in the following order: $BF_4 \sim HgBr_3 > I > Cl$. Added halide ion was found to retard these reactions of the trityl halides. Polar solvents facilitate such β H^- abstraction. A mechanism involving Ph_3C^+ as the active agent is indicated.

Wurtz-type reactions of diorganomercurials with reactive organic halides have been found to occur in the presence of aluminum halides (179):

$$Ph_2Hg + RX \xrightarrow[CH_2Cl_2]{AlX_3} \underset{(35\text{-}60\%)}{Ph\text{-}R} + PhHgX$$

($RX = CH_3OCH_2Cl$, EtBr, Ph_2CHBr, $PhCH_2Br$, $p\text{-}O_2NC_6H_4CH_2Br$)

$$(PhCH_2)_2Hg + CH_3I \xrightarrow{AlX_3} PhCH_2CH_3 + PhCH_2HgI$$

$$n\text{-}Bu_2Hg + PhC(O)CH_2Br \xrightarrow{AlX_3} PhC(O)C_5H_{11}\text{-}n$$

$$Ph_2Hg + p\text{-}ZC_6H_4SO_2Cl \xrightarrow{AlBr_3} p\text{-}ZC_6H_4SO_2Ph \quad (Z = Me, H, Br)$$

The mechanism of these reactions remains unknown.

Abnormal byproducts which appear to be solvent-derived have been detected in the bromodemercuration reactions of benzylmercuric chloride, cyclohexylmercuric bromide and cyclohexylcarbinylmercuric bromide (180).

Sulfur trioxide insertion into the C-Hg bonds of R_2Hg ($R = Et$, n-Bu, Ph, p-MeC_6H_4, p-ClC_6H_4) and RHgBr compounds was found to be a facile process (181):

$$R_2Hg + SO_3 \text{ (or } SO_3\cdot\text{dioxane)} \xrightarrow[-30^\circ \text{ to } 20^\circ]{CH_2Cl_2 \text{ or } ClCH_2CH_2Cl} Hg(O_3SR)_2 \text{ (up to 99\%)}$$

Various conversions of RHgX to R_2Hg (symmetrization reactions) have been described in the past year. A new and useful procedure for such a conversion was developed by Brown and Buhler (7) as a result of a systematic evaluation of methods for RHgX symmetrization:

$$RHgOAc \xrightarrow[\text{Lewis acid}]{\text{Zn dust in THF}} R_2Hg$$

The Lewis acid used may be $BF_3\cdot OEt_2$ (25 mole % for good results), but in the one-pot sequence:

$$\begin{tikzcd}RR'C{=}CH_2 \arrow[r, "BH_3\text{, THF}"] & (RR'CHCH_2)_3B \arrow[r, "Hg(OAc)_2"] & RHgOAc + B(OAc)_3 \arrow[d, "\text{Zn dust}"] \\ & & R_2Hg\end{tikzcd}$$

an added Lewis acid is not necessary, boron acetate serving that function. The following overall yields were achieved by this procedure:

$$CH_3CH_2CH{=}CH_2 \longrightarrow (CH_3CH_2CH_2CH_2)_2Hg \quad (88\%)$$

$$Me_2C{=}CH_2 \longrightarrow (Me_2CHCH_2)_2Hg \quad (90\%)$$

$$n\text{-}C_{10}H_{21}CH{=}CH_2 \longrightarrow (n\text{-}C_{12}H_{25})_2Hg \quad (70\%)$$

$$Ph_2C{=}CH_2 \longrightarrow (Ph_2CHCH_2)_2Hg \quad (65\%)$$

A patent reports that if CO_2 is bubbled into a mixture of metallic magnesium and phenylmercuric bromide in THF medium at reflux (3 hr), diphenylmercury (76%) and metallic mercury (50%) are produced (182). Di-n-butylmercury was prepared from a butylmercuric halide in 41% yield by this procedure.

Treatment of $CF_3CH_2CH_2HgCl$ and $(O_2N)_3CCH_2CH_2HgCl$ either with an excess of potassium cyanide or potassium iodide resulted in symmetrization to the respective R_2Hg compound (183). The authors considered the possibility that in these reactions β-elimination of the relatively stable anions, CF_3^- or $(O_2N)_3C^-$, might take place, but such was not the case.

Two groups have provided more information concerning mercury atom exchange between diarylmercurials and between organomercurials and metallic mercury. For the reaction:

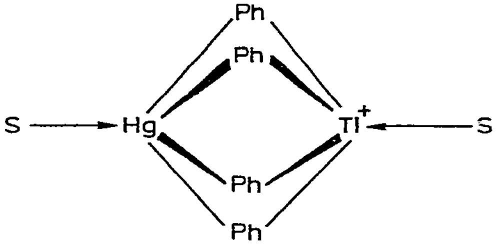
$$Ph_2{}^{203}Hg + (p\text{-}ClC_6H_4)_2Hg \xrightarrow{35\text{-}60^\circ} Ph_2Hg + (p\text{-}ClC_6H_4)_2{}^{203}Hg$$

an octahedral transition state was proposed on the basis of a kinetic study and observed solvent effects. However, such mercury atom exchange between diphenylmercury and PhHgX compounds (X = Cl, OAc, OH, OPh, OBz) was even more facile and the possibility that the exchange proceeds via the ArHgX impurities in the Ar_2Hg/Ar'_2Hg system thus was a very real one (184). A galvanostatic technique served to indicate that the mercury exchange reaction between diethylmercury and metallic mercury proceeds via organomercury radicals (185):

$$Et_2Hg + Hg^* \rightleftharpoons EtHg\cdot + EtHg\overset{*}{\cdot} \rightleftharpoons Et_2Hg^* + Hg$$

Further work using this approach showed that relative stabilities of RHg· radicals to such disproportionation decreased in the order RHg· > ArHg· > ViHg· >> $PhCH_2Hg\cdot$, with lifetimes of such radicals on a mercury surface ranging from less than 10^{-4} sec (benzyl) to $5x10^{-2}$ sec (alkyl) (186).

Phenyl group exchange between diphenylmercury and diphenylthallium bromide in pyridine was the subject of a kinetic study using ^{14}C labelling (187). A bimolecular S_Ei transition state, $\boxed{37}$, was proposed.



$\boxed{37}$

7. MERCURY-FUNCTIONAL MERCURIALS

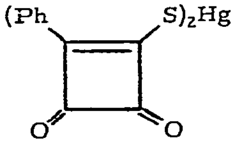
Anion exchange equilibria between methylmercuric acetate and phenylmercuric thiophenoxide in pyridine, DMSO and chloroform have been studied by NMR spectroscopy (188). For the reaction:

$$MeHgOAc + PhHgSPh \rightleftharpoons MeHgSPh + PhHgOAc$$

K = 0.5 in pyridine, 0.4 in DMSO and 0.15 in chloroform at 22°. Halogen exchange was found to occur between organomercuric halides and various organic halides, e.g., between t-butyl bromide and methylmercuric chloride (189). It appears that the tendency in such exchanges is to form the organomercuric halide with the higher stability constant.

Some new organomercury peroxides, i-$PrHgOOCMe_2Ph$ and $EtHgOOCMe_3$, were found to be relatively stable at 0-10° (190).

The preparation of $\boxed{38}$ (191) and the use of mercury mercaptides in synthesis (192):



$\boxed{38}$

$$M_2(CO)_{10}^{2-} + Hg(SR)_2 \longrightarrow 2\ M(CO)_5SR^- + Hg$$

$(M = Cr,\ Mo,\ W)$

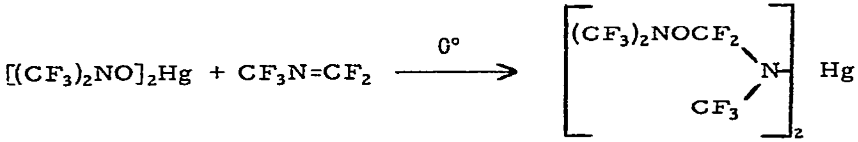
is to be noted.

Organomercury selenides have been studied (193):

$$\begin{tikzcd}(Et_3Si)_2Se + EtHgCl \arrow[r] & {[EtHgSeSiEt_3]} + Et_3SiCl \arrow[d] \\ & (EtHg)_2Se + (Et_3Si)_2Se\end{tikzcd}$$

Decomposition of bis(ethylmercuri)selenide gave mercuric selenide and diethylmercury.

The preparation of a mercury derivative of a carbodiimide, $(PhN{=}C{=}N)_2Hg$, has been described (194). Bis[bis(trifluoromethyl)-aminooxy]mercury was found to react with a perfluoroimine (195):



$$[(CF_3)_2NO]_2Hg + CF_3N{=}CF_2 \xrightarrow{0^\circ} \left[\begin{array}{r}(CF_3)_2NOCF_2\diagdown\\ N-\\ CF_3\diagup\end{array}\right]_2 Hg$$

Exchange reactions between some substituted N-methylbenzenesulfonamides and their N-phenylmercuri derivatives were studied by ^{1}H NMR spectroscopy (196). Among the exchange processes observed, in some cases metal-metal exchange was faster than proton-proton exchange.

Some new mercurials containing mercury-transition metal bonds have been isolated, but none of these was very stable.

$$[V(CO)_5L]^- + EtHgCl \xrightarrow{CH_2Cl_2} EtHgV(CO)_5L \quad \text{(ref. 197)}$$

$(L = CO \text{ or } PPh_3)$

$$[Ta(CO)_5L]^- + EtHgCl \xrightarrow{CH_2Cl_2} EtHgTa(CO)_5L \quad \text{(ref. 197)}$$

$(L = CO \text{ or } PPh_3)$

$$[Nb(CO)_5PPh_3]^- + EtHgCl \xrightarrow{CH_2Cl_2} EtHgNb(CO)_5PPh_3 \quad \text{(ref. 197)}$$

$$[Rh(CO)_3PPh_3]^- + RHgCl \xrightarrow{THF} RHgRh(CO)_3PPh_3 \quad \text{(ref. 198)}$$

$$[Ir(CO)_3PPh_3]^- + RHgCl \xrightarrow{THF} RHgIr(CO)_3PPh_3 \quad \text{(ref. 198)}$$

$(R = Ph,\ p\text{-}CH_3C_6H_4,\ PhCH_2)$

The rhodium and iridium compounds are air, moisture and light sensitive, decomposing as follows:

$$2\ RHgIr(CO)_3PPh_3 \xrightarrow{light} [Ir(CO)_3PPh_3]_2Hg + Hg + R\text{-}R$$

i.e., a reaction more complicated than simple disproportionation.

$$Me_3SnMo(CO)_3C_5H_5\text{-}\pi + RHgCl \longrightarrow RHgMo(CO)_3C_5H_5\text{-}\pi + Me_3SnCl$$

$(R = Me,\ Ph)$ (ref. 199)

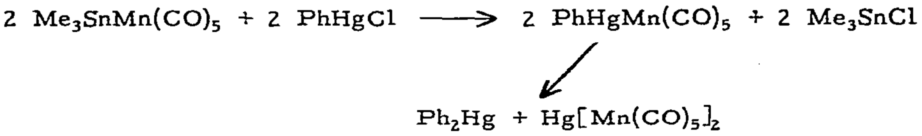
$$Me_3SnW(CO)_3C_5H_5\text{-}\pi + MeHgCl \longrightarrow MeHgW(CO)_3C_5H_5\text{-}\pi + Me_3SnCl$$

(ref. 199)

These molybdenum and tungsten complexes decomposed via disproportionation rather readily:

$$2\ RHgM(CO)_3C_5H_5\text{-}\pi \longrightarrow R_2Hg + Hg[M(CO)_3C_5H_5\text{-}\pi]_2$$

Analogous $RHgMn(CO)_5$ compounds were even less stable and could not be isolated (200):



$$\begin{tikzcd}[column sep=small] 2\ Me_3SnMn(CO)_5 + 2\ PhHgCl \arrow[r] & 2\ PhHgMn(CO)_5 + 2\ Me_3SnCl \arrow[d] \\ & Ph_2Hg + Hg[Mn(CO)_5]_2 \end{tikzcd}$$

A novel mercury-titanium derivative, $[(\pi\text{-}C_5H_5)_2TiPh_3]_2Hg$, has been prepared by Razuvaev et al. (201) by reaction of $[(\pi\text{-}C_5H_5)_2TiPh_3]Li$ with mercuric chloride in 3:1 Et_2O/THF at -40°. The compound was thermally unstable, decomposing at room temperature to give diphenylmercury and $(\pi\text{-}C_5H_5)_2TiPh_2$. Its reaction with methanol at -40° resulted in formation of $(\pi\text{-}C_5H_5)_2TiPh_2$, benzene and mercuric methoxide. Reaction of $(\pi\text{-}C_5H_5)_2TiPh_2$ with diphenylmercury at 60° in ethereal medium caused reduction of the latter to metallic mercury and of the titanium compound to "$(C_5H_5)_2Ti$".

Some work has been devoted to coordination complexes of organomercurial ions and molecules.

The ions $CH_3Hg\cdot py^+$ and $CH_3HgNH_3^+$ resulted when methylmercuric perchlorate was dissolved in pyridine and liquid ammonia, respectively, according to Raman spectroscopic measurements (202). Methylmercuric iodide also gave $CH_3HgNH_3^+$ upon solution in liquid ammonia, but when dissolved in pyridine, resulted in the neutral iodo complex. A variety of nitrate and tetrafluoroborate salts of complex organomercury cations has been prepared and studied by Raman, IR and NMR spectroscopy (203):

$[Me_3P\text{-}HgY]^+$ (Y = CH_3, CN, Cl, Br, I); $[Me_3As\text{-}HgY]^+$ (Y = CH_3, Cl); $[(Me_3P)_2Hg]^{2+}$; $[(Me_3As)_2Hg]^{2+}$; $[Me_2S\text{-}HgCH_3]^+$; $[py\text{-}HgCH_3]^+$, mostly via:

$$\left.\begin{array}{l} CH_3HgI + AgNO_3\cdot L \\ \text{or} \\ CH_3HgNO_3 + L \end{array}\right\rangle \longrightarrow CH_3HgL^+ NO_3^- + AgI$$

Anion exchange studies on CH_3HgCl in aqueous HCl and LiCl solutions suggested the retention in the resin phase of the complex anion $CH_3HgCl_3^{2-}$. Stability constants for this species and for $CH_3HgCl_2^-$ were determined (204). Laser Raman, IR and NMR studies have established the formation of $CH_3Hg(SCN)_3^{2-}$ in the CH_3HgSCN/SCN^- system. These spectroscopic measurements suggested that this species is an ion-dipole complex rather than a predominantly covalent one (205).

8. MERCURY-GROUP IV COMPOUNDS

Among interesting new compounds of this class reported in 1972 are:

Optically active (but not optically pure) bis(methyl-1-naphthylphenylsilyl)mercury as a brilliant lemon-yellow solid (206):

$$2\ Me(1\text{-}Np)(Ph)Si^{*}H + (PhCH_2)_2Hg \xrightarrow{130^\circ} [Me(1\text{-}Np)(Ph)Si]_2Hg + 2\ PhCH_3$$

This compound racemized without decomposition when heated to 150°. Preliminary evidence suggested that the photolytic and oxidative demercuration of this silylmercurial occur stereospecifically.

Bis(triphenylsilyl)mercury (207):

$$2\ Ph_3SiH + (PhCH_2)_2Hg \xrightarrow{125\text{-}130^\circ} (Ph_3Si)_2Hg + 2\ PhCH_3$$

Its chemical transformations were studied briefly:

$$\begin{tikzcd}(Ph_3Si)_2Hg \arrow[r, "250°"] & Hg + 2\ Ph_3Si\cdot \arrow[d] \\ & Ph_3SiSiPh_3 \\ & \text{(+ other products)}\end{tikzcd}$$

$$(Ph_3Si)_2Hg + O_2 \longrightarrow Ph_3SiOSiPh_3 + Hg$$

$$(Ph_3Si)_2Hg + 2H_2O \longrightarrow 2\ Ph_3SiOH + H_2 + Hg$$

Bis[tris(pentafluorophenyl)silyl]mercury (208) and the analogous germyl derivative (209):

$$2\ (C_6F_5)_3SiH + [(Me_3Si)_2N]_2Hg \xrightarrow{150\text{-}170°} [(C_6F_5)_3Si]_2Hg + 2\ (Me_3Si)_2NH$$

$$2\ (C_6F_5)_3GeH + R_2Hg \xrightarrow{100°} [(C_6F_5)_3Ge]_2Hg + 2\ RH$$

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

$$(Et_3Ge)_2Hg + 2\ (C_6F_5)_3GeBr \xrightarrow{100°} [(C_6F_5)_3Ge]_2Hg + 2\ Et_3GeBr$$

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

also:

$$(C_6F_5)_3GeH + Et_2Hg \xrightarrow{100°} EtHgGe(C_6F_5)_3 + C_2H_6$$

The kinetic stability of $[(C_6F_5)_3Si]_2Hg$ was greater than that of $[(C_6H_5)_3Si]_2Hg$. Thus, temperatures of 70-75° were required in order for its oxidation with molecular oxygen to proceed at an appreciable rate, and its reaction with benzoyl peroxide required prolonged heating:

$$[(C_6F_5)_3Si]_2Hg + Bz_2O_2 \xrightarrow{\text{toluene, } 70^\circ} 2\ (C_6F_5)_3SiOBz + Hg$$

The $(C_6F_5)_3Si\cdot$ radical formed in its photodegradation was observed to show marked preference for H atom abstraction (rather than for dimerization). Reaction of this silylmercurial with bromine gave $(C_6F_5)_3SiBr$, with mercuric chloride, $(C_6F_5)_3SiCl$ via decomposition of intermediate $(C_6F_5)_3SiHgCl$.

Full details have been provided concerning the first stable stannylmercurial, $[(Me_3SiCH_2)_3Sn]_2Hg$ (210) (cf. J. Organometal. Chem., 41 (1972) 248). Its reactions may be summarized as follows (with $R = Me_3SiCH_2$):

$$\begin{array}{lll}
(R_3Sn)_2Hg & \xrightarrow{150^\circ} & Hg + Sn + R_4Sn \\
\quad + O_2 & \longrightarrow & (R_3Sn)_2O + Hg \\
\quad + BrCH_2CH_2Br & \longrightarrow & 2\ R_3SnBr + C_2H_4 + Hg \\
\quad + 2\ EtBr\ (UV) & \longrightarrow & 2\ R_3SnBr + Et_2Hg \\
\quad + 2\ Li & \longrightarrow & 2\ R_3SnLi + Hg \\
\quad + HgX_2 & \longrightarrow & 2\ Hg + R_3SnX \\
\quad (X = Cl,\ CH_2CO_2Me, & & \\
\quad\ PhC{\equiv}C,\ Co(CO)_4) & & (\text{via } R_3SnHgX) \\
\quad + Hg[CF(CF_3)_2]_2 & \longrightarrow & Hg + 2\ R_3SnF + 2\ (CF_3)_2C{=}CF_2 \\
 & & (\text{via } R_3SnHgCF(CF_3)_2
\end{array}$$

An intermediate $(Me_3SiCH_2)_3SnHgGeEt_3$, which decomposed to give mercury and $(Me_3SiCH_2)_3SnGeEt_3$, was generated by reaction of bis-(triethylgermyl)mercury with $(Me_3SiCH_2)_3SnCl$ (210). Compounds of type $R_3SnHgCMe_3$ (R = Me, Et), in contrast, were quite unstable and extremely sensitive to light and atmospheric oxidation (211). They were prepared via:

$$Me_3CHgSiMe_3 + R_3SnOR' \longrightarrow Me_3CHgSnR_3 + Me_3SiOR'$$

and isolated as unpurifiable yellow oils. Evidence (chemical and observation of CIDNP) was presented which showed that they decompose by a free radical pathway. This same general preparative route has been used to prepare mixed Group IV mercurials (212):

$$(Me_3Si)_2Hg + Me_3GeOMe \longrightarrow Me_3SiHgGeMe_3 + Me_3SiOMe$$

$$(Me_3Ge)_2Hg + Me_3MOMe \longrightarrow Me_3GeHgMMe_3 + Me_3GeOMe$$

$$(M = Si,\ Sn)$$

These unsymmetrical mercurials are in equilibrium with the respective pairs of symmetrical mercurials, as NMR studies showed. These equilibria were found to be independent of temperature in the range of -30° to +37°, implying that $\Delta H \sim 0$.

Some calorimetric studies (213) have provided the following thermochemical data:

	$\Delta H_f(l)$	$\Delta H_f(g)$	$\bar{D}(M\text{-}Hg)$	kcal/mol
$(Et_3Si)_2Hg$	42 ± 1	28 ± 1.5	20 ± 3	
$(Et_3Ge)_2Hg$	31 ± 1	16 ± 1.5	8 ± 3	
$(iPr_3Ge)_2Hg$	73 ± 1	60 ± 1.5	17 ± 3	

Further and more extensive studies of the chemistry of silyl- and germyl-mercury compounds have been reported.

The autoxidation of $EtHgSiEt_3$ was found to be a free radical process (214):

Initiation:

$$2\ EtHgSiMe_3 \longrightarrow Et_2Hg + Et_3SiHg\cdot + Et_3Si\cdot$$

Chain Propagation:

$$Et_3Si\cdot + O_2 \longrightarrow Et_3SiOO\cdot$$

$$Et_3SiHg\cdot \longrightarrow Et_3Si\cdot + Hg$$

$$\begin{tikzcd} & \mathrm{Et_3SiOHgEt + Et_3SiO\cdot} \\ \mathrm{Et_3SiOO\cdot + EtHgSiEt_3} \arrow[ur] \arrow[dr] & \\ & \mathrm{(Et_3Si)_2O + EtHg\cdot} \end{tikzcd}$$

$$\mathrm{Et_3SiO\cdot + EtHgSiEt_3 \longrightarrow (Et_3Si)_2O + EtHg\cdot}$$

$$\mathrm{EtHg\cdot + O_2 \longrightarrow CH_3CH{=}O + HOHg\cdot}$$

$$\mathrm{HOHg\cdot + EtHgSiEt_3 \longrightarrow Et_3SiOH + EtHg\cdot + Hg}$$

$$\mathrm{2\ Et_3SiOH \longrightarrow (Et_3Si)_2O + H_2O}$$

The rate of autoxidation of $(Et_3Ge)_2Hg$ was accelerated by addition of large amounts of tert-butyl alcohol (215). Oxidation of $(Me_3Si)_2Hg$ also could be effected with lead tetra-acetate (216):

$$\mathrm{(Me_3Si)_2Hg + Pb(OAc)_4 \xrightarrow{\text{benzene, } 60^\circ} 2\ Me_3SiOAc + Hg + Pb(OAc)_2}$$

The insertion of sulfur and selenium into silyl- and germylmercury bonds was found to occur readily at 0-20° (217), e.g.:

$$\mathrm{(Et_3Si)_2Hg + 1/8\ S_8 \longrightarrow Et_3SiHgSSiEt_3}$$

$$\mathrm{EtHgGeEt_3 + 1/8\ Se_8 \longrightarrow EtHgSeGeEt_3}$$

Also prepared in this manner were:

$Et_3GeHgSGeEt_3$, $Et_3SiHgSeSiEt_3$, $Et_3GeHgSeGeEt_3$, $EtHgSSiEt_3$, $EtHgSeSiEt_3$, $Et_3GeSeHgSiEt_3$, $Et_3GeSHgSiEt_3$, and others.

Their photochemical decomposition proceeded with extrusion of mercury, e.g.:

$$\mathrm{Et_3SiHgSSiEt_3 \xrightarrow{UV} Et_3SiSSiEt_3 + Hg}$$

Lithium metal also effected their cleavage:

$$\mathrm{Et_3SiHgSSiEt_3 + 2Li \longrightarrow Et_3SiLi + Et_3SiSLi + Hg}$$

$$\mathrm{EtHgSSiEt_3 + 2Li \longrightarrow EtLi + Et_3SiSLi + Hg}$$

The silyl- and germylmercurials also react with disulfides and ditellurides, but give mercury-free products (217):

$$EtSSEt + (Et_3Si)_2Hg \xrightarrow{\text{UV or } 50\text{-}95^\circ} 2\ Et_3SiSEt + Hg$$

$$EtTeTeEt + (Et_3Ge)_2Hg \xrightarrow{20^\circ} 2\ Et_3GeTeEt + Hg$$

With triethylsilylhydroselenide and -hydrotelluride, bis(triethylgermyl)mercury reacted very readily as shown below (193):

$$Et_3SiSeH + (Et_3Ge)_2Hg \xrightarrow{\text{hexane, } -20^\circ} Et_3SiSeHgGeEt_3 + Et_3GeH$$

$$Et_3SiTeH + (Et_3Ge)_2Hg \xrightarrow{\text{hexane, } -78^\circ} Et_3SiTeHgGeEt_3 + Et_3GeH$$

and:

$$2\ Et_3SiYH + (Et_3Ge)_2Hg \xrightarrow{\text{hexane, } 50^\circ} (Et_3SiY)_2Hg + 2\ Et_3GeH$$

(Y = Se or Te)

Triethylsilylhydrosulfide requires more drastic conditions:

$$Et_3SiSH + (Et_3Ge)_2Hg \xrightarrow{70^\circ} Et_3SiSHgGeEt_3 + Et_3GeH$$

The compounds $Et_3SiYHgGeEt_3$ (Y = S, Se, Te) could be isolated by low temperature crystallization techniques but decomposed at 20° to give $Et_3SiYGeEt_3$ and elemental mercury.

Bis(triethylgermyl)mercury was found to react with bis-(polyfluoroalkyl)mercurials as follows (218; 219):

$$(Et_3Ge)_2Hg + (R_f)_2Hg \longrightarrow 2\ Et_3GeHgR_f$$

$$\boxed{39}$$

(R_f = CF_3, $CF(CF_3)_2$, CH_2CF_3, $CHFCF_3$, C_2F_5,
$CFClCF_3$, $CH(CF_3)_2$)

In some cases (R_f = $C(CF_3)_3$, $CHFCO_2Et$, CF_2CO_2Et, $CFClCO_2Et$, $CF(CF_3)CO_2Et$), products of type $\boxed{39}$ were not stable, decomposing instead to give metallic mercury and the germanes Et_3GeR_f. Such decomposition of the stable Et_3GeHgR_f compounds could be induced by a catalytic quantity of cesium fluoride at room temperature.

The reaction of bis(triethylgermyl)mercury with trityl chloride is believed to proceed via a four-center mechanism (220):

$$(Et_3Ge)_2Hg + 2\ Ph_3CCl \xrightarrow{\text{toluene}} Hg + 2\ Et_3GeCl + \text{"}Ph_6C_2\text{"}$$

With triethyltin compounds, the following reaction took place (221):

$$(Et_3Ge)_2Hg + Et_3SnY \xrightarrow{UV} Et_3GeSnEt_3 + [Et_3GeHgY]$$

(Y = Cl, OMe, OAc, CN,
NEt_2, CH_2CO_2Me)

$$Et_3GeY + Hg$$

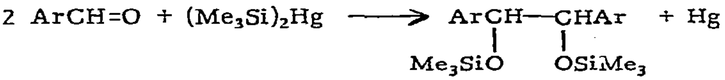
also:

$$2\ (Et_3Ge)_2Hg + Et_2SnY_2 \xrightarrow{UV} (Et_3Ge)_2SnEt_2 + 2\ Et_3GeY + 2\ Hg$$

(Y = Cl, OMe)

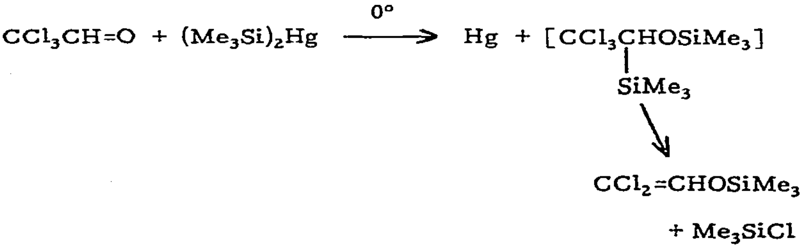
Reactions of bis(trimethylsilyl)mercury with organic substrates have been studied. Different types of behavior were observed with carbonyl-containing compounds (222):

<u>Reductive dimerization</u>:



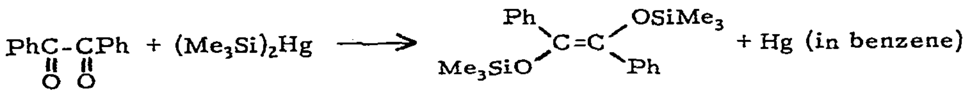
$$2\ ArCH{=}O + (Me_3Si)_2Hg \longrightarrow \underset{Me_3SiO}{ArCH}{-}\underset{OSiMe_3}{CHAr} + Hg$$

With aliphatic aldehydes there was no (or at best a slow) reaction, but the more polar chloral did react:



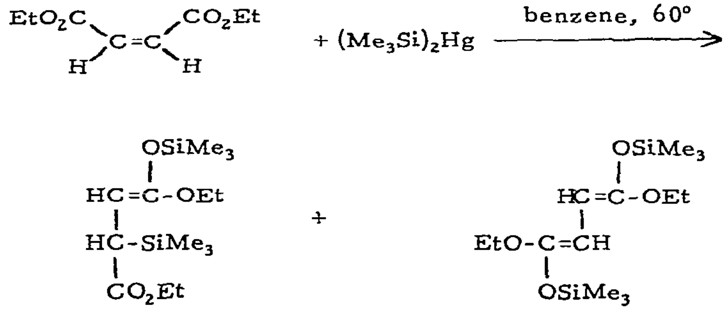
$$CCl_3CH{=}O + (Me_3Si)_2Hg \xrightarrow{0^\circ} Hg + [CCl_3\underset{SiMe_3}{C}HOSiMe_3] \longrightarrow CCl_2{=}CHOSiMe_3 + Me_3SiCl$$

1,4-Addition:

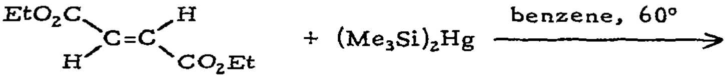


A similar reaction occurred with biacetyl when HMPA was used as solvent.

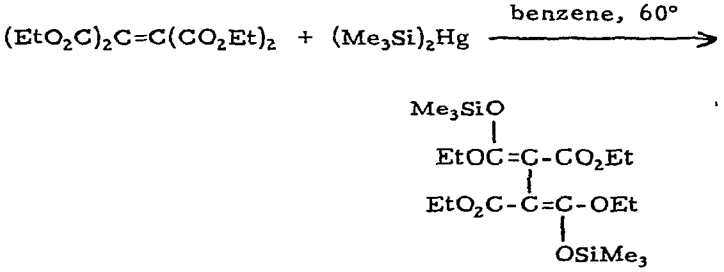
1,4- and 1,6-Addition:

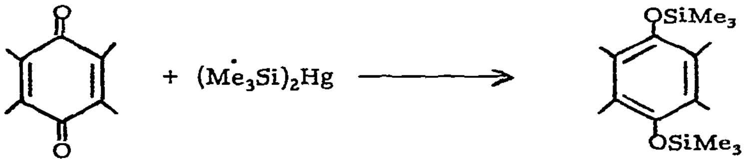


70% 1,4 20% 1,6 [40]



only [40]





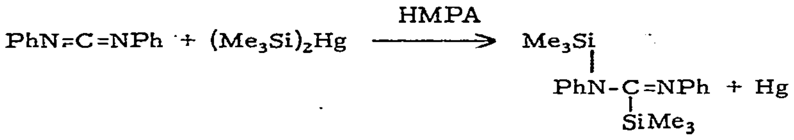
The authors appear to favor molecular rather than free radical mechanisms for these reactions.

Reactions with heteroatom cumulenes were examined (223):

$$ArN_3 + (Me_3Si)_2Hg \xrightarrow{\text{room temp.}} [Ar\text{-}N{=}N\text{-}N(SiMe_3)_2]? + Hg$$

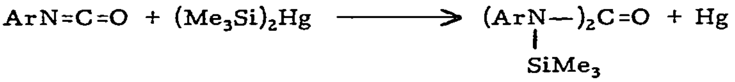
$$\downarrow$$

$$ArN(SiMe_3)_2 + N_2$$



$$PhN{=}C{=}NPh + (Me_3Si)_2Hg \xrightarrow{\text{HMPA}} PhN(SiMe_3)\text{-}C(SiMe_3){=}NPh + Hg$$

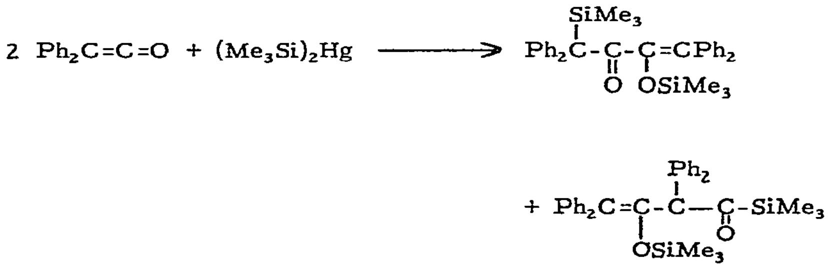
(but no reaction with dicyclohexylcarbodiimide).



$$ArN{=}C{=}O + (Me_3Si)_2Hg \longrightarrow (ArN(SiMe_3)\text{—})_2C{=}O + Hg$$

(via a rather complicated reaction course)

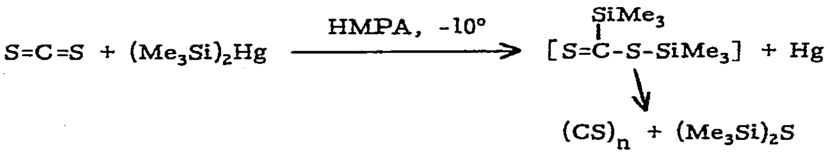
(No reaction was observed with ArN=C=S).



$$2\ Ph_2C{=}C{=}O + (Me_3Si)_2Hg \longrightarrow Ph_2C(SiMe_3)\text{-}C({=}O)\text{-}C(OSiMe_3){=}CPh_2$$

$$+\ Ph_2C{=}C(OSiMe_3)\text{-}CPh_2\text{—}C({=}O)\text{-}SiMe_3$$

$$O{=}C{=}O + (Me_3Si)_2Hg \xrightarrow{\text{HMPA, 80°}} Hg + CO + (Me_3Si)_2O$$



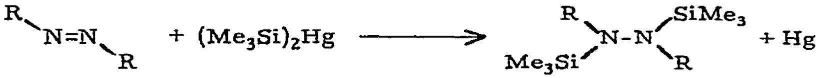
$$S{=}C{=}S + (Me_3Si)_2Hg \xrightarrow{\text{HMPA, -10°}} [S{=}C(SiMe_3)\text{-}S\text{-}SiMe_3] + Hg$$

$$\downarrow$$

$$(CS)_n + (Me_3Si)_2S$$

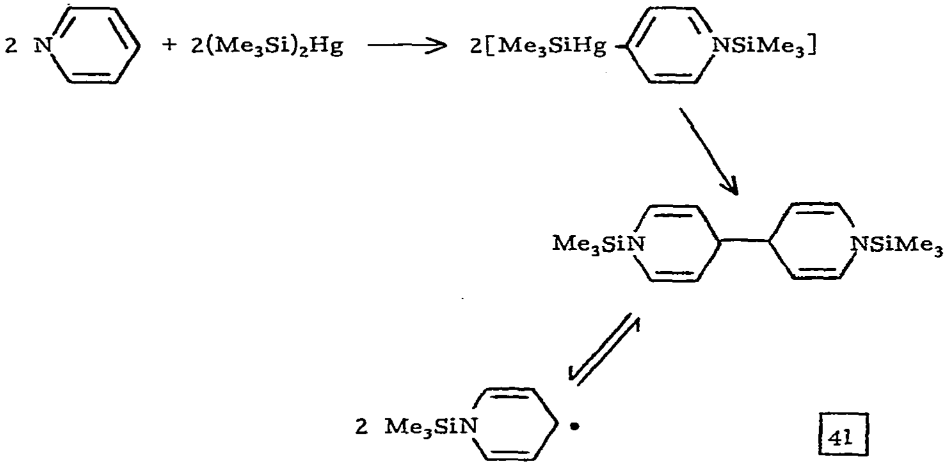
$$SO_2 + (Me_3Si)_2Hg \xrightarrow{-20°} Me_3Si\text{-}OSO\text{-}SiMe_3 + Hg$$

Bis(trimethylsilyl)mercury was found to add to azo compounds (224):



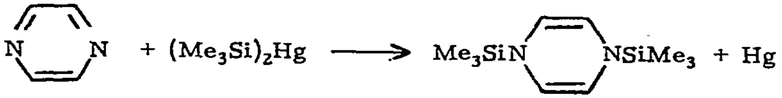
(R = CO_2Et, Ph, 2-C_5H_4N)

Reductive N-silylation occurred in the case of various aromatic N-heterocycles (224):



$\boxed{41}$

The dimeric products were found to dissociate reversibly into very stable free radicals $\boxed{41}$ when heated in the absence of air, and the reaction of 4-cyanopyridine in benzene with bis(trimethylsilyl)-mercury gave such a radical species directly (225). Reductive dimerization on reaction with $(Me_3Si)_2Hg$ also was observed with quinoline and isoquinoline. Pyrazine reacted differently (224):



For most of these reactions, the initial addition of $(Me_3Si)_2Hg$ as $Me_3SiHg—SiMe_3$ is believed to be followed by rapid extrusion of mercury from the product.

Bis(trimethylsilyl)mercury also is known to react with fluoroolefins, and more examples of such reactions have been reported (226):

$$\begin{tikzcd}
CF_2{=}CFCl + (Me_3Si)_2Hg \arrow[r, "UV"] & Me_3SiCF_2CFClHgSiMe_3 \arrow[d, "\text{UV or heat}"] \\
& Me_3SiCF{=}CFCl + Hg + Me_3SiF
\end{tikzcd}$$

A small amount of $Me_3SiCF{=}CF_2$ also was formed, presumably via reaction of $(Me_3Si)_2Hg$ at the C-Cl bond of $CF_2{=}CFCl$ to give $CF_2{=}CFHgSiMe_3$ which undergoes subsequent extrusion of mercury. Trifluoroethylene reacted more slowly with bis(trimethylsilyl)-mercury:

$$\begin{array}{c} CF_2{=}CHF \\ + \\ (Me_3Si)_2Hg \end{array} \xrightarrow{UV} \left[\begin{array}{c} Me_3SiHgCF_2CFHSiMe_3 \\ + \\ Me_3SiCF_2CFHHgSiMe_3 \end{array}\right] \longrightarrow \begin{array}{c} CF_2{=}CHSiMe_3 \\ \\ CFH{=}CFSiMe_3 \end{array}$$

Finally, we mention two new Hg-P compounds whose mode of synthesis and reactivity justifies their inclusion in this section.

Bis(di-t-butylphosphino)mercury has been prepared (227):

$$2\ (Me_3C)_2PH + Hg(CMe_3)_2 \xrightarrow{80^\circ} Hg[P(CMe_3)_2]_2 + 2\ C_4H_{10}$$

This compound, a yellow-green solid, is air stable and can be heated to 400° without decomposition. Its photolysis gives $(Me_3C)_4P_2$ and metallic mercury. Other less bulky secondary phosphines reacted with di-t-butylmercury without giving isolable $Hg(PR_2)_2$ intermediates:

$$2\ R_2PH + Hg(CMe_3)_2 \xrightarrow{0^\circ} R_2P\text{-}PR_2 + Hg + 2\ C_4H_{10}$$

Less stable than $Hg[P(CMe_3)_2]_2$ is $Hg[P(CF_3)_2]_2$ (228):

$$2\ (CF_3)_2PH + (CH_2{=}CH)_2Hg \longrightarrow Hg[P(CF_3)_2]_2 + 2\ C_2H_4$$

This compound inflames in air and decomposes to $(CF_3)_4P_2$ and elemental mercury on being heated. It reacts with $(CF_3)_2AsH$ to give the less stable $Hg[As(CF_3)_2]_2$, whose decomposition provides $(CF_3)_2As\text{-}As(CF_3)_2$.

9. STRUCTURAL, SPECTROSCOPIC AND PHYSICAL STUDIES

A. Structural Studies

The structure of cis-β-chlorovinylmercuric chloride has been determined by electron diffraction in the vapor state (229). The following bond distances and angles were recorded for this planar molecule:

d(Hg-Cl)	2.27±0.01Å	<Cl-C-C	123±2°
d(Hg-C)	2.14±0.02Å	<C-C-Hg	117±1°
d(C-Cl)	1.69±0.02Å	<C-Hg-Cl	168.5±1.5°
d(C=C)	1.33±0.03Å		

The Hg...Cl(cis) distance (3.27Å) is such as to permit a weak Cl—Hg interaction, but this study does not provide unambiguous proof for such coordination.

Several X-ray crystal structures of organomercury compounds have been reported.

Phenylmercuric acetate is composed of discrete molecules in the solid (Fig. 4) (230). The bond distances and angles are: d(Hg-C), 1.92±0.06Å, d(Hg-O), 2.11±0.04Å, <C-Hg-O, 170±2°. The intramolecular C=O...Hg distance is 2.85Å, and thus a CH_3CO_2 chelate structure is not present.

cis-β-Benzoylvinylmercuric chloride also does not show evidence of significant O→Hg coordination (C=O...Hg distance, 2.88Å) (231). The structure is shown in Fig. 5.

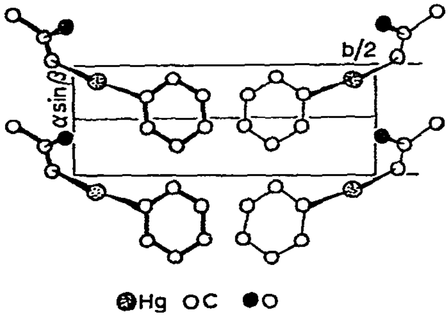


FIGURE 4. Structure of phenylmercuric acetate (B. Kamenar and M. Penavić, Inorg. Chim. Acta, 6 (1972) 191)

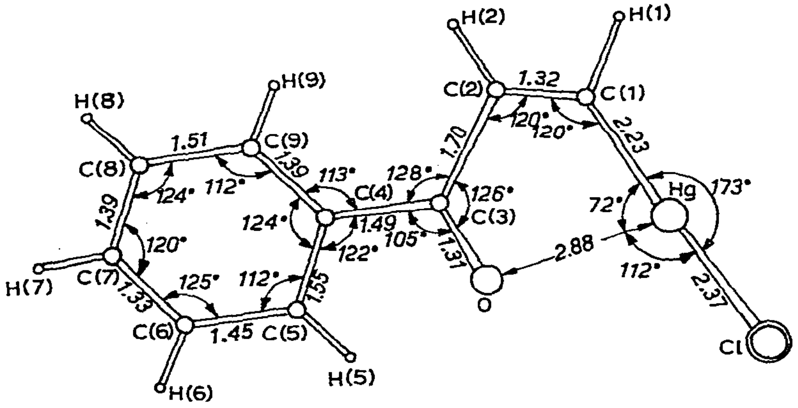


FIGURE 5. Structure of cis-β-benzoylvinylmercuric chloride (L. G. Kuzmina et al., Zh. Strukt. Khim., 12 (1971) 1026)

Full details of the structure of $[(C_6F_5)_2Hg]_2\cdot Ph_2AsCH_2AsPh_2$ have been provided (232). The Hg...As interaction is very weak, with d(Hg-As) = 3.40±2Å. This may be compared with the Hg-As distance of 2.60 and 2.82Å in $Br_2Hg\cdot o\text{-}(Me_2As)_2C_6H_4$ (Powell et al., 1966). In $[(C_6F_5)_2Hg]_2\cdot Ph_2AsCH_2AsPh_2$, d(Hg-C) = 2.15±0.04Å and 2.07±0.04Å and <C-Hg-C = 176.2±1.2°.

The structure of the adduct $CCl_3HgCl\cdot 1,10$-phenanthroline has been determined (233). Two crystallographically independent molecules were found to be present (Fig. 6).

Determination of the crystal and molecular structure of mercury(II) thiocyanate showed linear S-Hg-S and planar $\mathrm{N{=}C{\diagdown}S}$ unites and indicated a weak intermolecular Hg-N interaction (234).

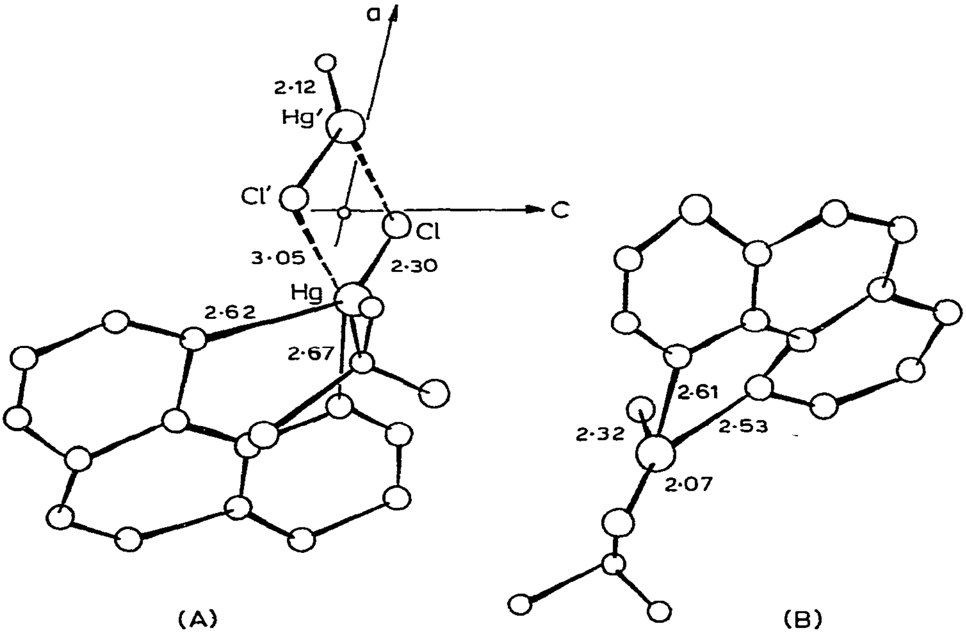


FIGURE 6. Structure of $CCl_3HgCl\cdot 1,10$-phenanthroline (A. D. Redhouse, Chem. Commun. (1972) 1119)

B. Spectroscopic Studies

i. Vibrational Spectra

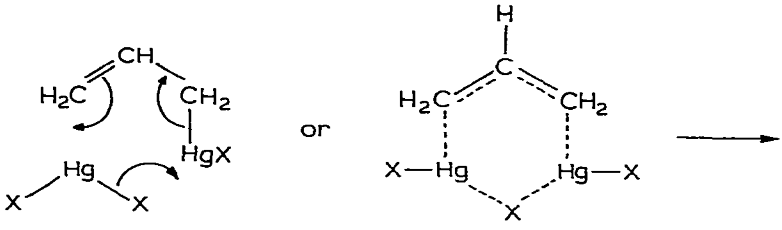
The vibrational spectra of dimethylmercury (and of Me_2Zn and Me_2Cd) (235) and of CH_3HgSCH_3 (236) have been studied, and force field calculations for CH_3HgCl and CD_3HgCl have been reported (237). The infrared spectra of ClCH=CHHgX (X = Cl, Br) and $(ClCH{=}CH)_2Hg$ (238) and the vibrational spectra of liquid and solid diallylmercury (239), the allylmercuric halides (X = Cl, Br, I) in the liquid and solid state (240), dibenzylmercury (241), diphenylmercury, diphenylmercury-$d_{10}$and the phenylmercuric halides (X = Cl, Br, I) (242) and the bis(halomethyl)mercurials, $Hg(CH_2X)_2$ (X = Cl, Br, I) in the molten and solid state (243) have been reported and discussed. IR evidence was presented supporting a charge-transfer interaction between benzene and $Hg(CH_2X)_2$.

Examination of the vibrational spectra of $(C_5H_5)_2Hg$ and $(C_5D_5)_2Hg$ provided further confirmation that σ-bonded cyclopentadienyl groups are present (244).

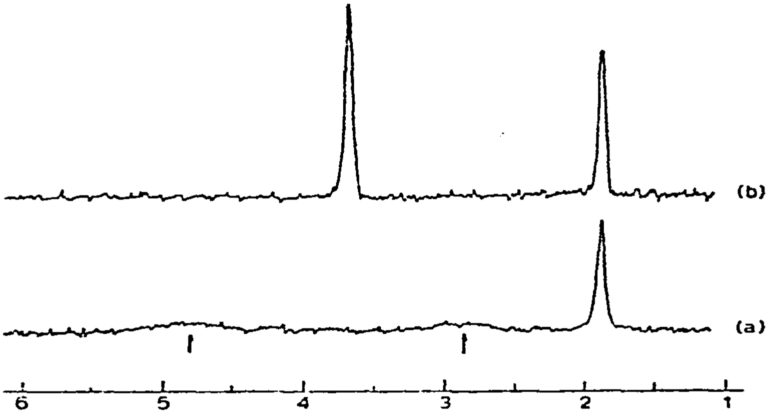
Raman and infrared spectra below 400cm^{-1} have been reported for $Hg(O_2CCH_3)_2$, $Hg(O_2CCD_3)_2$, $NCHgO_2CCH_3$, $Hg(O_2CCH_3)_2/NaO_2CCH_3$, $Hg_2(O_2CCH_3)_2$ and $Hg_2(O_2CCD_3)_2$ (245). The spectra of mercuric acetate in aqueous solution were interpreted in terms of a covalent molecular model.

ii. Nuclear Magnetic Resonance Spectra

To be noted are proton NMR studies of divinylmercury (246) and the allylic mercurials $CH_2{=}CHCH_2HgY$, $CH_3CH{=}CHCH_2HgY$, $CH_2{=}C(CH_3)CH_2HgY$ and $PhCH{=}CHCH_2HgY$ (Y = OAc and halide) (247). Added mercuric halides had dramatic effects on the spectra of allylic mercury halides (cf. Fig. 7) and this behavior was shown to be due to very rapid redistribution proceeding via an $S_E i'$-type mechanism:



$CH_2{=}CH{-}CH_2HgX + HgX_2$



(a). The 100 MHz spectrum of $CH_2{=}C(CH_3){-}CH_2HgCl$ in $CDCl_3$, showing broad resonances for vinyl and methylene protons; (b). The effect of added $HgCl_2$, with the emergence of a four-proton singlet. The $C{-}CH_3$ resonance is essentially unaffected, and no ^{199}Hg coupling is visible.

Fig. 7. (From W. Kitching et al., J. Organometal Chem., 34(1972) 233)

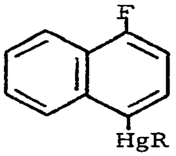
Also reported have been a ^1H and ^{13}C NMR study of neopentylmercury compounds (248), a ^{13}C NMR study of $C_5H_5HgCH_3$ (249), the metal satellite NMR spectra of diethyl and dicyclopropylmercury (250) and heteronuclear double magnetic resonance studies of ^{199}Hg nuclear shielding constants in organomercurials (Table 11) (251).

TABLE 11. (ref. 251)

^{199}Hg CHEMICAL SHIFTS FOR ORGANOMERCURY COMPOUNDS

Compound	Solvent (concentration of the organomercurial, mole/liter)	Chemical shift (δHg)
$Hg(CH_3)_2$	neat	0
$Hg(C_2H_5)_2$	CCl_4, 2	+304
$Hg(C_3H_7)_2$	CCl_4, 2	+210
$Hg(iso\text{-}C_3H_7)_2$	CCl_4, 2	+597
$Hg(C_4H_9)_2$	CCl_4, 2	+205
$Hg(C_6H_5)_2$	CH_2Cl_2, 1	+742
$(C_6H_5)Hg(C_6F_5)$	CH_2Cl_2, 1	+829
$Hg(CH_2C_6H_5)_2$	CH_2Cl_2, 1	+700
$Hg(CH_2COOCH_3)_2$	CH_2Cl_2, 2	+769
$Hg(CH{=}CH_2)_2$	CH_2Cl_2, 2	+648
$Hg(CCl{=}CH_2)_2$	CH_2Cl_2, 2	+1142

Particular attention has been paid to ^{19}F NMR studies of organomercurials: fluoroarylmercurials of type m- and p-FC_6H_4HgY (Y = $C{\equiv}CPh$, O_2CCF_3, CN, SCN, SPh, OPh, Cl, Br, I, OAc, NHAc) (28), fluoronaphthylmercurials of type 42, 43 and 44 (252),



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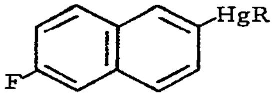

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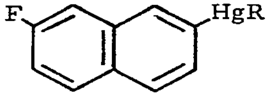
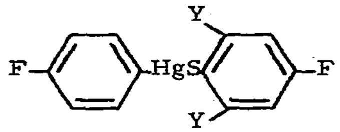


44

mercury derivatives of phenols and thiophenols of type m- and p-FC_6H_4OHgPh and m- and p-FC_6H_4SHgR (R = Et, Ph, p-$O_2NC_6H_4$, p-$Me_2NC_6H_4$, p-FC_6H_4) (253) and 45 and 46 (254), and some



$\boxed{45}$ Y = CH_3

$\boxed{46}$ Y = Br

fluoroalkylmercurials, $(C_2F_5)_2Hg$, $(CF_3CFCl)_2Hg$, $(CF_3CH_2)_2Hg$, $(CF_3CHF)_2Hg$, $[(CF_3)_2CF]_2Hg$ and $[(CF_3)_2CH]_2Hg$ (255), and CF_3-Hg compounds (29). Most of these investigations were undertaken to obtain information on the bonding in organomercurials, but strong solvent effects appeared to limit the value of these studies. From the results obtained in the case of the naphthalene systems (252), it would appear that the aryl-mercury bond has a π component. In the case of bis(polyfluoroalkyl)mercurials with C-F bonds α to the mercury (255) and the mercurial $\boxed{46}$ (254), evidence was presented for weak $X \rightarrow Hg$ (X = F, or Br in the case of $\boxed{46}$) interaction.

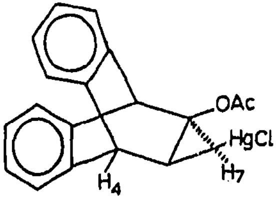
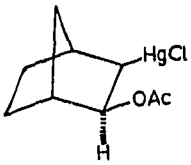
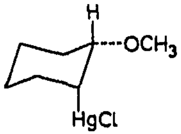
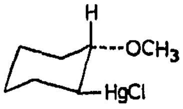
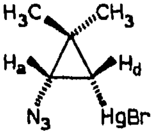
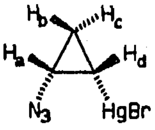
NMR spectroscopy has provided a useful means of configurational assignment of oxymercuration products of cyclic olefins (256). Another NMR study has considered the variation of vicinal ^{199}Hg-^{1}H spin-spin coupling constants with dihedral angle (Table 12) as a means of configurational assignments (107). A semiempirical MO study of ^{199}Hg-^{1}H spin-spin coupling has been published (257).

Bromine NMR relaxation measurements were used to determine relative stability constants and to define a softness scale for RHg groups (258).

Wide-line proton NMR studies have shown that in the solid state, cyclopentadienylmercurials, C_5H_5HgY (Y = Cl, Br, I, C_5H_5), undergo reorientation. Movement of the cyclopentadienyl rings which involves a simultaneous rotation and distortion of the ring, together with σ-bond rupture and reformation, was suggested to be the dynamic process occurring (259).

TABLE 12

Variation of Vicinal ^{199}Hg–^{1}H Coupling Constants with Dihedral Angle

									
	H_7	H_4				H_a	H_a	H_b	H_b
Approx dihedral angle	120°	60°	120°	180° (?)	60°	130°	130°	130°	0°
J,(Hz)	106	75	93.2	425	99	80	85	195	305

iii. Nuclear Quadrupole Resonance Spectra

The quadrupole coupling constants of halogens in CH_3HgX (X = Cl, Br, I) in the vapor and in the solid state have been determined (260). A comparison of these data together with a consideration of the known X-ray crystal structure of CH_3HgCl indicated the presence of intermolecular R-Hg-X. . . . Hg coordination.

C. Other Physical Studies

Polarographic electroreduction of organomercurials containing heterocyclic substituents (furyl, thienyl, pyrazolyl, indolyl) (261) and of trans-oxymercurated allenes (262) has been studied.

Theoretical studies of the importance of σ-π conjugation effects in the acid cleavage of allylic mercuric halides have been reported (263).

10. MISCELLANEOUS

A few miscellaneous items remain.

The thin layer chromatographic behavior of some organomercurials of type RHgY has been described (264). The selectivity of a microwave discharge detector in the gas chromatographic determination of dimethylmercury has been studied (265).

The condensation of aniline and acetylene to give quinaldine, tetrahydroquinaldine and N-ethylaniline was found to be catalyzed by trans- and cis-ClCH=CHHgCl (266).

The aggregate state of mercurated polystyrene has been investigated (267).

The chemistry of mercarbide, mercuroform and related compounds has been discussed (268, 269).

Finally, we call attention to a series of letters to the editor of Science concerning the biological effects of organomercurials (270).

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