MERCURY

ANNUAL SURVEY COVERING THE YEAR 1974

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CONTENTS

Mercury, Annual Survey covering the year 1973 see J. Organometal. Chem., 75(1974)13-134.

1. REVIEWS AND BOOKS

The organomercury volume of the Houben Weyl series on organometallic compounds has appeared (1). Covered in great detail are the preparation and reactions of organomercurials of all types, but tables of individual compounds and their properties are not given. For a review of this book, see ref. 2.

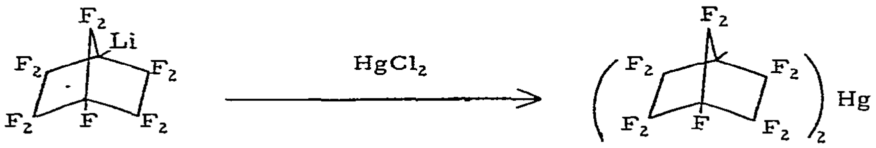
Reviews have covered the following aspects of organomercury chemistry:

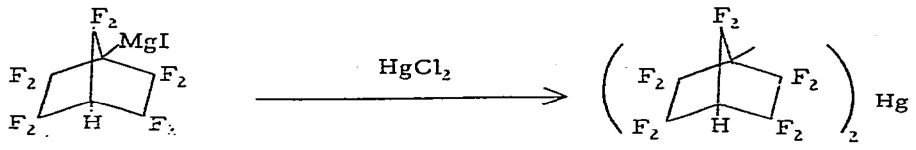
- NMR spectra and structures of organomercury compounds (3)
- Vibrational spectra of organomercurials (in Russian) (4)
- The reactions of mercuric salts with organoboranes and boronic acids (5)
- The biological activity of organomercurials (6)
- The biological cycles of mercury in the environment (7)
- The chemistry of organomercurials in aquatic systems (8)

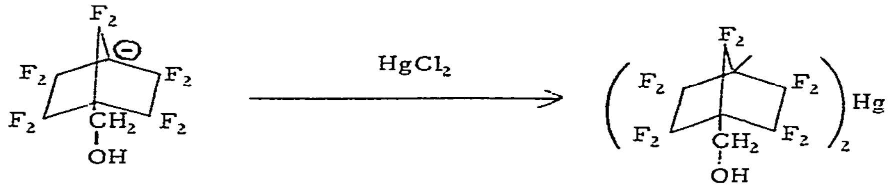
2. PREPARATION OF ORGANOMERCURY COMPOUNDS

Organometallic reagents have been used widely in the synthesis of organomercurials during the course of their development, and new examples of such syntheses were reported during the past year.

Organolithium and organomagnesium reagents served in the preparation of novel mercurials containing bicyclic fluorocarbon substituents (9):

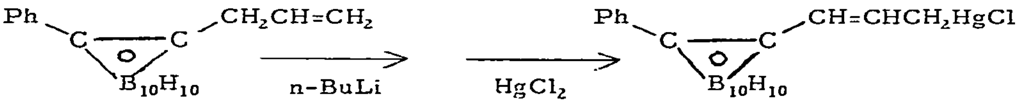






(via KOH in DMSO)

The lithium reagent derived from an allylcarborane reacted with mercuric chloride to place the mercury atom on the γ carbon atom (10):



gem-Dichloroallyllithium reacted with mercuric chloride to give exclusively the γ,γ-dichloroallylmercurial (11):

$$Ph_3PbCH_2CH{=}CCl_2 \xrightarrow[-80°]{n\text{-}BuLi} Li(CCl_2CHCH_2) \xrightarrow{HgCl_2} CCl_2{=}CHCH_2HgCl$$

A sulfur-functional mercurial was prepared by the organolithium route (12):

$$2\ PhSCH_2Li \xrightarrow{HgCl_2} Hg(CH_2SPh)_2$$

An anionic intermediate also must have been involved in the mercuration of polyfluorobenzenes in basic medium (13):

$$2\ C_6F_5H + HgBr_4^{2-} + 2\ OH^- \longrightarrow (C_6F_5)_2Hg + 4\ Br^- + 2\ H_2O$$

This reaction, which was carried out in aqueous tert-butanol, also was used to prepare unsymmetrical mercurials, $ArHgC_6F_5$, with Ar = Ph and $p\text{-}CH_3C_6H_4$. Perfluoroalkyl-carbanions reacted with mercury (II) trifluoroacetates to give bis(perfluoroalkyl)mercury compounds (14):

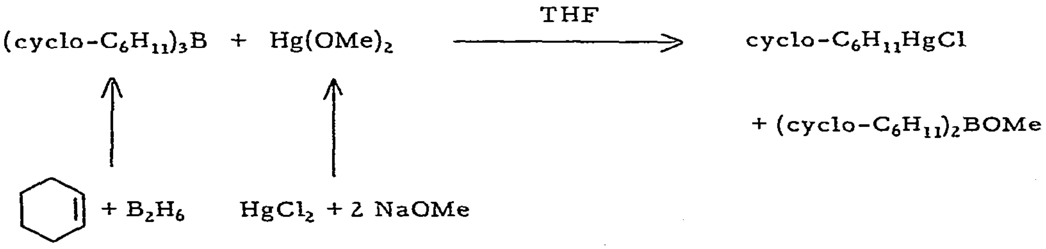
$$Hg(O_2CCF_3)_2 + 2\ (CF_3)_2C{=}CF_2 + 2\ KF \xrightarrow{DMF} [(CF_3)_3C]_2Hg$$

$$CF_3HgO_2CCF_3 + (CF_3)_2{=}CF_2 + KF \xrightarrow{THF} CF_3HgC(CF_3)_3$$

$$CF_3HgO_2CCF_3 + CF_3CBr{=}CF_2 + CsF \longrightarrow CF_3HgCBr(CF_3)_2$$

$$Hg(O_2CCF_3)_2 + CF_3C{\equiv}CCF_3 + 2F^- \longrightarrow Hg[C(CF_3){=}CFCF_3]_2$$

In previous surveys the useful conversion of organoboranes to organomercurials by reaction with mercuric acetate has been mentioned, and this subject has been reviewed (5). This reaction worked well with primary alkylboranes, but the transfer of secondary alkyl groups was not effective under the reaction conditions used. Larock now has developed conditions which serve reasonably well in the preparation of secondary alkylmercury compounds from boranes. The reaction of a tri-sec-alkylborane with mercuric methoxide in THF was rapid, but only one of the three alkyl groups was transfered to mercury (15), e.g.:



A considerable excess of mercuric methoxide was required because of extensive reduction of this reagent to metallic mercury under the reaction conditions. Mercuric methoxide is much more stable in methanol than in THF, and a suspension of this reagent in MeOH reacted with tri-sec-alkylboranes to give monoalkylmercurials. However, all three alkyl groups on boron were not utilized. In the case of tricyclohexylborane, one-half of the cyclohexyl groups was transfered to mercury when four molar equivalents of mercuric methoxide for one of the borane were used. This stoichiometry in the case of tricyclopentyl- and tri-exo-norbornylborane, however, led to transfer of only one organic group from boron to mercury. A free radical mechanism was proposed for these reactions on the basis of rather indirect evidence:

$$Hg(OMe)_2 \longrightarrow MeOHg^{\cdot} + MeO^{\cdot}$$

$$MeOHg^{\cdot} \longrightarrow MeO^{\cdot} + Hg$$

$$MeO^{\cdot} + R_3B \longrightarrow MeOBR_2 + R^{\cdot}$$

$$R^{\cdot} + Hg(OMe)_2 \longrightarrow RHgOMe + MeO^{\cdot} \qquad \text{etc.}$$

Mercury(I) tert-butoxide in tert-butanol proved to be a more effective reagent, reacting with tri-sec-alkylboranes to transfer two of the alkyl groups on boron to mercury (16):

$$(RR'CH)_3B + 3\ Hg(OCMe_3)_2 \xrightarrow{Me_3COH} 2RR'CHHgOCMe_3$$

The results of this work are summarized in Table 1. The stereochem-

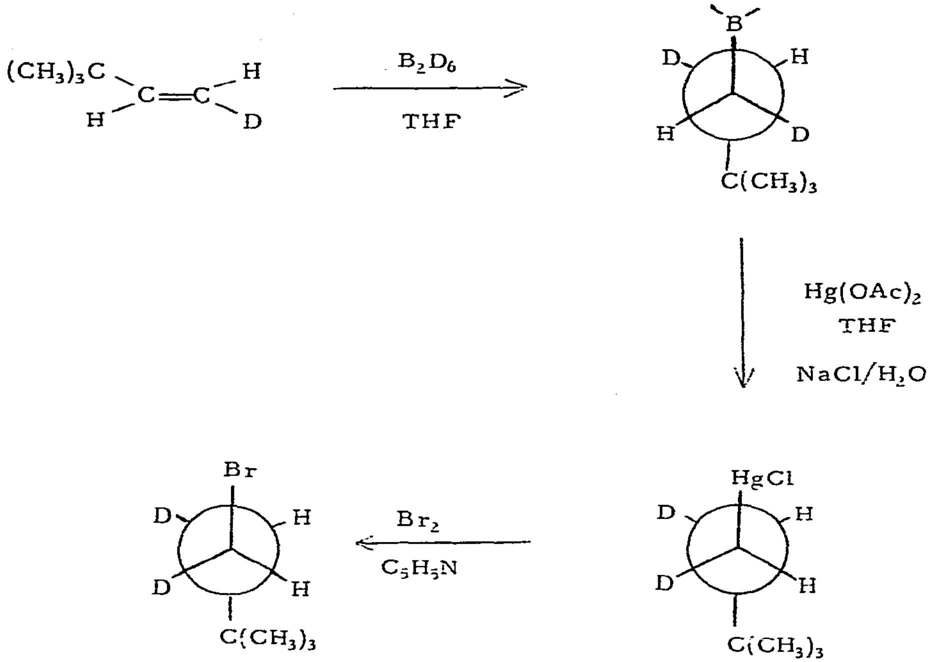
TABLE 1. The Reaction of Mercury(I) Alkoxides and Tri-sec-Alkylboranes (ref. 16)

$$R_3B + nHg_2(OR')_2 \xrightarrow{HCl} 2\ RHgCl$$

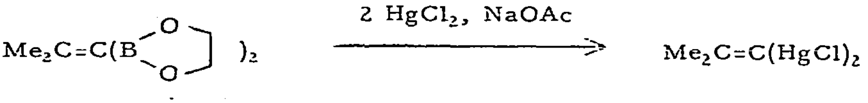
Tri-sec-alkylborane	Mercury(I) alkoxide	Equiv.[a] n =	Solvent	Isolated yield of RHgCl[b] (%)
Tricyclohexylborane	Methoxide	1	THF	7-37
		2		17-53
		3		60-70[c]
		1	Methanol	11-16
		2		63
		3		78
		3	Pentane	5-14
Tricyclopentylborane	Methoxide	3	Methanol	59
Tri-exo-2-norbornylborane	Methoxide	3	Methanol	59
Tricyclohexylborane	tert-Butoxide	3	THF	26-36
Tricyclohexylborane	tert-Butoxide	3	tert-Butanol	83
Tricyclopentylborane	tert-Butoxide	3	tert-Butanol	91
Tri-exo-2-norbornylborane	tert-Butoxide	3	tert-Butanol	82

[a] Equiv. of mercury(I) alkoxide. [b] Yield based on reaction of two alkyl groups. [c] Wildly exothermic reaction.

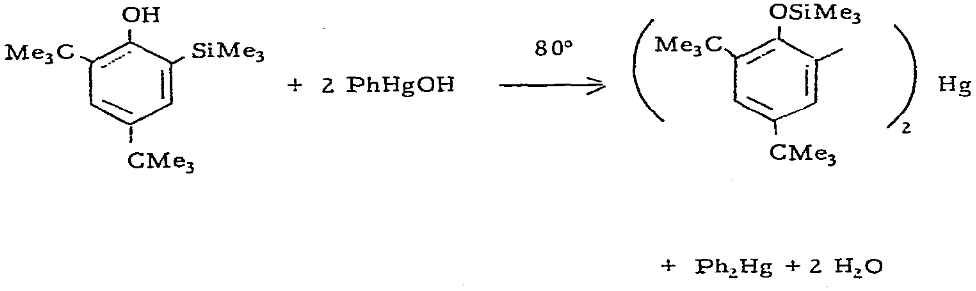
istry of this process has been studied in THF solution and found to involve reaction with inversion of configuration at carbon (17):



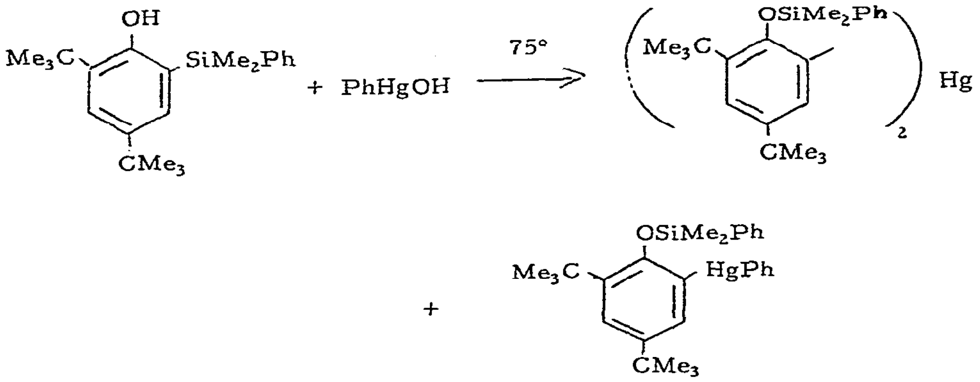
An interesting vinylic mercurial has been prepared by cleavage of an alkene-1,1-diboronic acid ester (18):



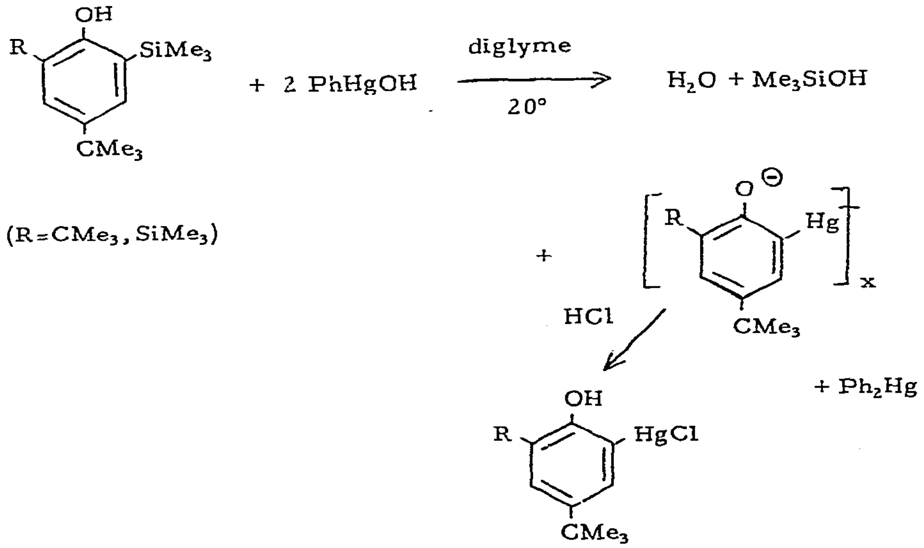
Silicon-carbon bond cleavage also has been used in mercurial preparation (19):



This reaction proceeds _via_ initial formation of the 2-trimethylsilyl-4, 6-di-tert-butylphenoxy radical (ESR evidence), which subsequently undergoes (formal) mercuridesilylation. Other examples were given, including:



In diglyme at 20°, aryl mercoxides can be formed:



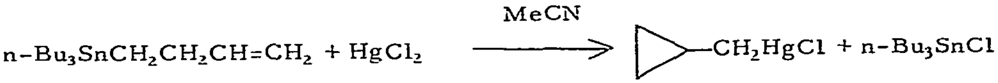
(R=CMe$_3$, SiMe$_3$)

Tin-carbon bond cleavage also serves in mercurial preparation:

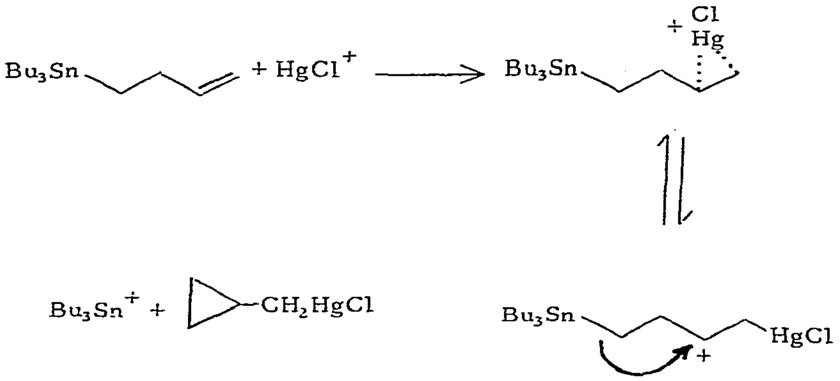
$$Ar_2SnEt_2 + Hg(OAc)_2 \xrightarrow{CHCl_3} Ar_2Hg + Et_2Sn(OAc)_2 \quad \text{(ref. 20)}$$

($Ar=Ph$, $p\text{-}MeC_6H_4$, $p\text{-}ClC_6H_4$,

$p\text{-}BrC_6H_4$, $\alpha\text{-}C_{10}H_7$)



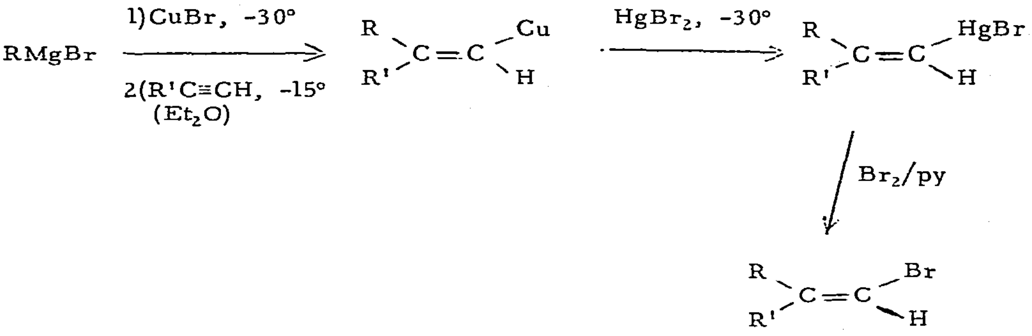
Here the attack occurs at the C=C bond (21):



A small amount of $CH_2{=}CHCH_2CH_2HgCl$ was formed in this reaction as well. (Cyclopropylcarbinylmercuric chloride was found to rearrange on standing (75% after 6 days) to $CH_2{=}CHCH_2CH_2HgCl$).

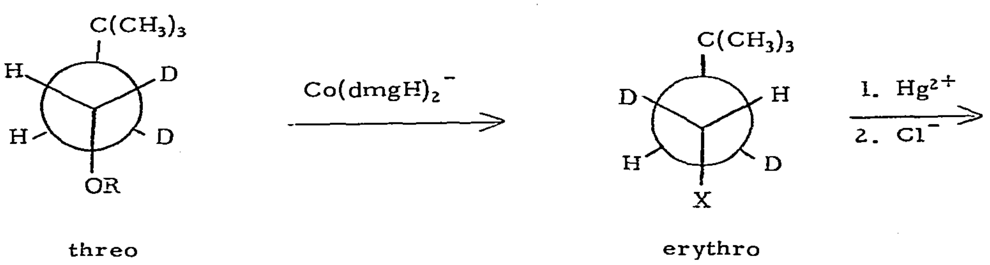
An NMR study has shown that $CF_3HgO_2CCF_3$ reacts with trimethyl(trifluoromethyl)tin in benzene at room temperature to give CF_3HgCH_3 and $Me_2(CF_3)SnO_2CCF_3$. The organotin but not the organomercury product was isolated (22). Similarly, cis-$Me_2Pt(PPh_3)_2$ readily methylated CF_3HgCl in chloroform solution (22).

Organocopper reagents have been used in the synthesis of vinylic mercurials, which in turn were used in vinyl halide preparations (23). The reaction proceeds with retention of configuration at the C=C bond:



This sequence represents a new, stereospecific route to vinylic bromides.

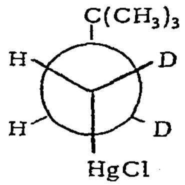
More examples of the transfer of alkyl groups from σ -alkyl-transition metal complexes to mercury have been described. Such reactions usually are of no synthetic value, and, in fact, when they occur in nature are very objectionable since by such reactions the highly toxic methylmercury(II) species is generated by the action of methylcobalamin on mercuric ion (7). As a result, the alkyl transfer from alkylcobalt compounds has received considerable attention. Thus Espenson and his coworkers have shown that such alkyl transfer from alkylcobaloximes to Hg(II) proceeds with inversion of configuration at carbon by studying the reaction of erythro- $Me_3CCHDCHDCo(dmgH)_2py$ with mercuric perchlorate in 0.20<u>F</u> aqueous perchloric acid (24). Deuterium-decoupled proton NMR measurements served to establish this stereochemical course:



R = H

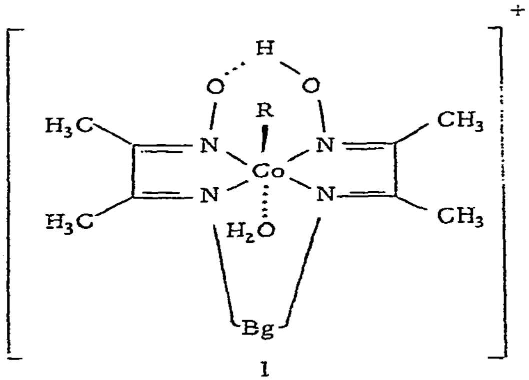
R = p-$SO_2C_6H_4Br$

X = $Co(dmgH)_2py$



threo

It is unusual for electrophilic metal-alkyl cleavage by Hg(II) to proceed with inversion; almost all other cases examined involved reaction with retention of configuration at carbon. For instance, the cleavage of cyclopentadienyl(threo-3,3-dimethylbutyl-1,2-d_2)dicarbonyliron by mercuric chloride in benzene was found to proceed with retention of configuration at carbon (25). An explanation in terms of the rather severe steric factors associated with the macrocyclic ligand of the cobaloxime was offered. The dealkylation of another type of σ-alkylcobalt complex, 1, has been studied by Magnuson and Weber (26).

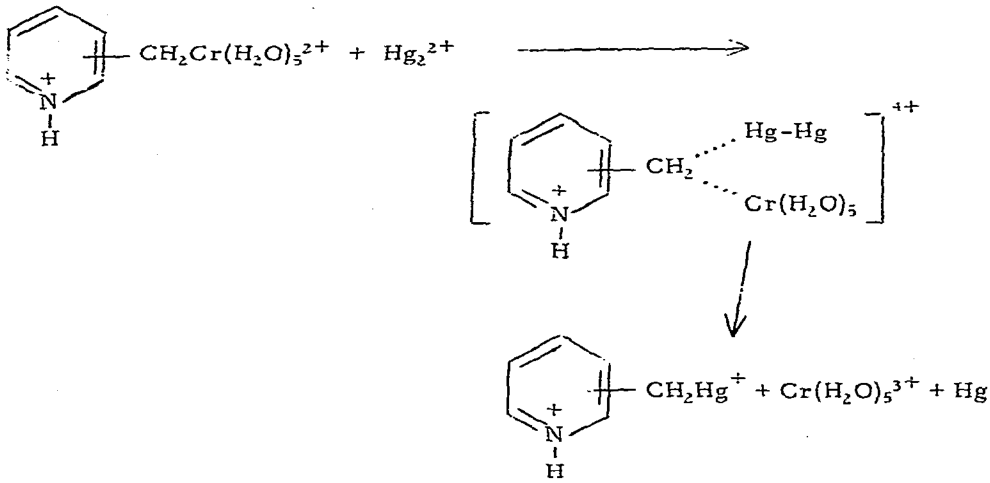


1

R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, $CH_2C_6H_5$

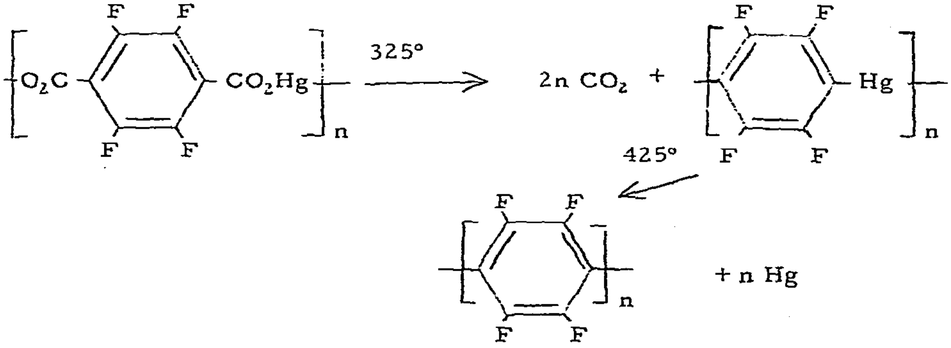
Bg = $(CH_2)_3$, $(CH_2)_2$

The relative rates of alkyl transfer to Hg(II) were found to be: Me >> Et > $PhCH_2$ > n-Bu ~ n-Pr, and an S_E2 mechanism was suggested to be operative. The dealkylation of pentaaquo(pyridinomethyl)chromium(III) ions by mercurous ion in aqueous medium also is an S_E2 process, with direct attack of Hg_2^{2+} at the methylene carbon atom (27).

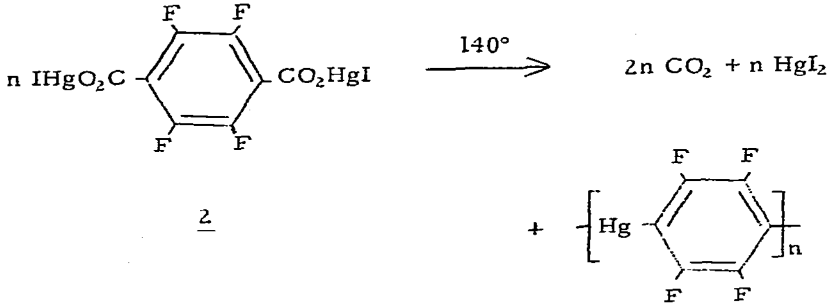


In contrast, the reaction of mercurous ion with pyridinomethyl derivatives of $Fe(CO)_2C_5H_5$ and $Mn(CO)_5$ and of methylcobaloxime involve a cleavage process in which the small concentration of mercuric ion in the $Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg^\circ$ equilibrium is the active reagent (27).

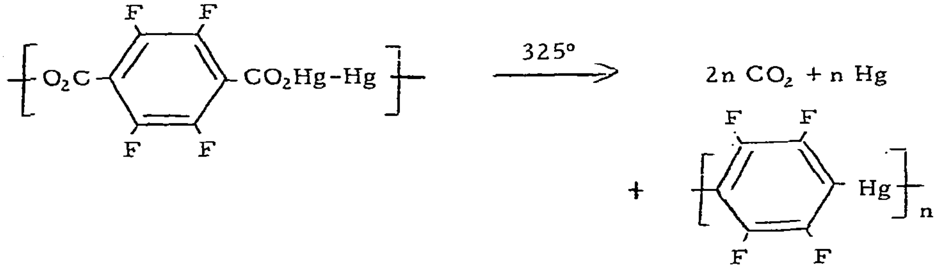
Extrusion of CO_2 and SO_2 from mercury(II) carboxylates and sulfinates continues to play a role in the synthesis of organomercurials. The mercury(II) salt of tetrafluoroterephthalic acid was found to undergo exothermic decarboxylation at around 325° in vacuum (28a); around 425° demercuration took place:



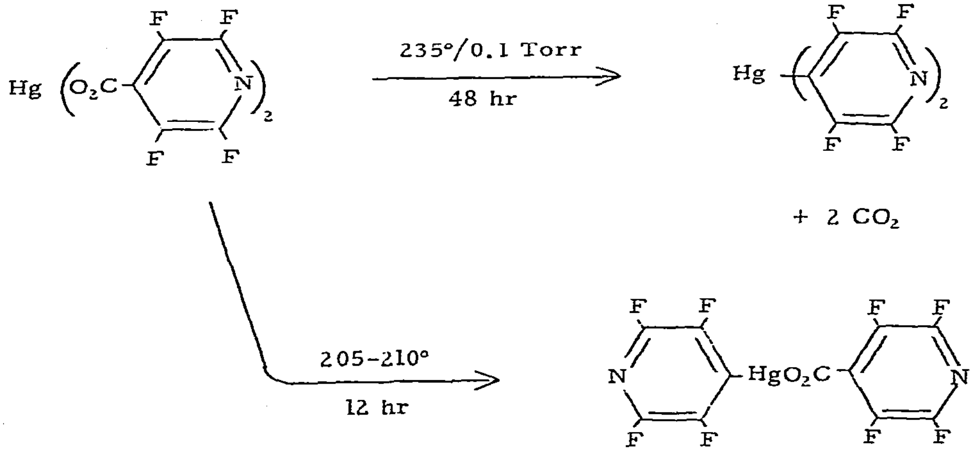
The decarboxylation of 2 was much more facile:



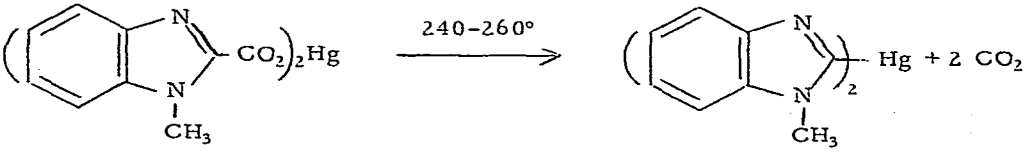
The Hg(I) tetrafluoroarylene polymer expected from the decarboxylation of the Hg(I) salt of tetrafluorophthalic acid was not stable:



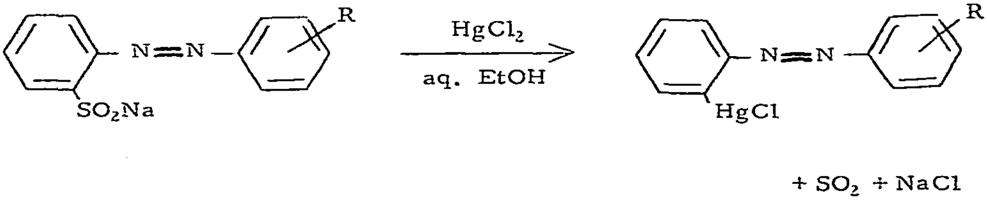
The thermal decarboxylation of mercuric tetrafluoronicotinate also has been described (28b):



Decarboxylation also served in the preparation of bis(benzimidazolyl)-mercury (29):



Thermal elimination of sulfur dioxide from a mercury(II) sulfinate was used in the preparation of o-mercurated azobenzenes (30):



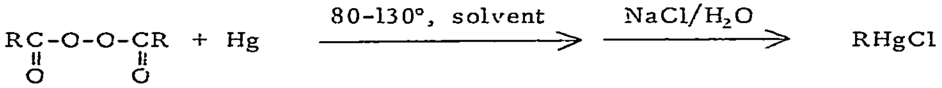
The following 2-(arylazo)arylmercury compounds were prepared by this route: 2-($ArN_2C_6H_4$)HgCl, with Ar=2'-MeC_6H_4, 3'-MeC_6H_4, and 3',5'-$Br_2C_6H_3$, and 2-($ArN_2C_6H_3$-4-Cl)HgCl, with Ar=2'-MeC_6H_4, 4'-MeC_6H_4 and 3',5'-$Br_2C_6H_3$.

Electrochemical syntheses of organomercurials are based on reactions of elemental mercury with electrochemically generated free radicals. Brown and Taylor have demonstrated that virtually quantitative yields of dialkylmercurials result on cathodic reduction of ethyl and n-butyl iodides at mercury in ethanol solution at low current densities (31). Rapid linear potential scan voltammetry following reduction at constant potential confirmed the intermediacy of adsorbed ethyl radicals in the case of ethyl iodide. Diphenylmercury could not be prepared by this procedure since further reduction of phenyl radicals occurs too readily. Other workers found that the controlled potential electroreduction of α,ω-dibromoalkanes ($Br(CH_2)_nBr$, with $n \geq 4$), using a stirred mercury cathode, resulted in excellent yields of symmetrical dialkylmercurials (32).

$$Br(CH_2)_nBr \xrightarrow{e^-,\ Hg,\ DMF} [CH_3(CH_2)_{n-1}]_2Hg$$

($n = 4, 5, 6, 7, 12$)

Radicals generated by diacyl peroxide decomposition also alkylate metallic mercury (33):



$$\underset{\substack{\| \\ O}}{RC}-O-O-\underset{\substack{\| \\ O}}{CR} + Hg \xrightarrow{80\text{-}130°,\ \text{solvent}} \xrightarrow{NaCl/H_2O} RHgCl$$

($R = n\text{-}Pr,\ n\text{-}C_5H_{11},\ n\text{-}C_8H_{17}$, some aryl)

RHgCl yields, however, were not high.

Mercuration of functional organic compounds has long been used to prepare organomercurials, but in many cases, especially those reported before the advent of modern physical and spectroscopic methods, the nature and structure of the products was uncertain. One such product was the so-called "ethane hexamercarbide", the product of the mercuration of ethanol by alkaline mercuric oxide (Hofmann, 1898). This now has been shown to be a methane derivative by Grdenić and his co-workers (34). The ethanol mercuration product was found to dissolve completely in aqueous carboxylic acids. Crystalline products were obtained from acetic and trifluoroacetic acid solutions and these were shown to be the respective $C(HgO_2CR)_4$ compounds by X-ray crystallography (Fig. 1 shows the structure of $C(HgO_2CCF_3)_4$). Thus "ethane hexamercarbide"

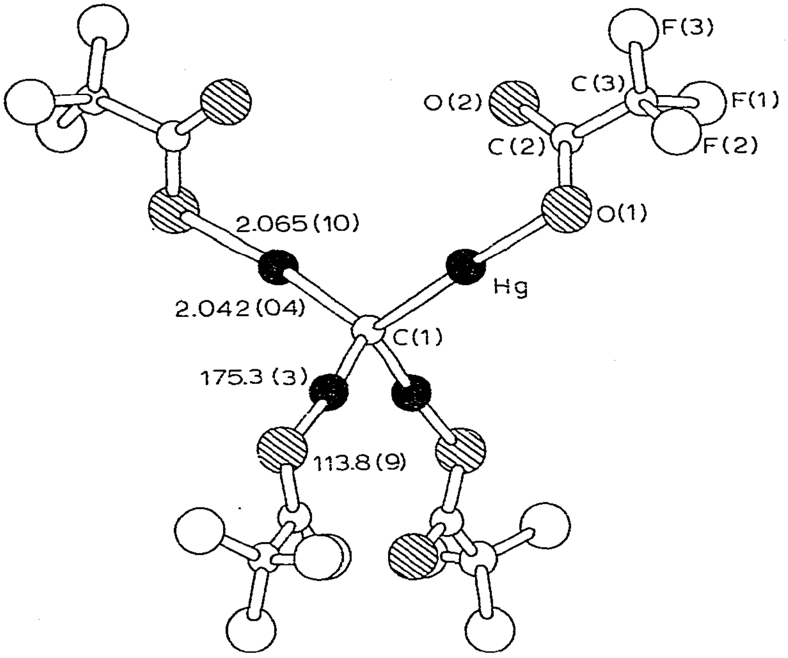


Figure 1. The structure of $C(HgO_2CCF_3)_4$. From D. Grdenič, B. Kamenar, B. Korpar-Čolig, M. Sikirica and G. Jovanovski (J. Chem. Soc., Chem. Commun. (1974) 646).

is the hydroxide of a polymeric oxonium ion containing $C\text{-}Hg\text{-}(OH)^+\text{-}Hg\text{-}C$ bridges formed by condensation of $C(HgOH)_4$. It is not clear by what reaction course this material is produced by the alkaline mercuration of ethanol.

The mercuration of acetonitrile by mercuric acetate above 120° gave polymercurated products, in particular $(AcOHg)_3CCN$ (35). The monomercurated acetonitrile also mercurates acetonitrile:

$$AcOHgCH_2CN + CH_3CN \xrightarrow{\text{reflux}} (AcOHg)_2CHCN + (AcOHg)_3CCN$$

Monomercurated acetonitriles were prepared by the organolithium route:

$$2\ LiCH_2CN + HgCl_2 \xrightarrow[THF]{-70^\circ} \underset{(20\%)}{Hg(CH_2CN)_2} + \underset{(60\%)}{ClHgCH_2CN}$$

and by a dehydration reaction:

$$Hg(CH_2CH{=}O)_2 \xrightarrow{H_2NOH\cdot HCl} ClHgCH_2CH{=}NOH \xrightarrow[(R = \text{cyclohexyl})]{RN{=}C{=}NR,\ DMF,\ 20^\circ} ClHgCH_2CN$$

$$ClHgCH_2CN \xrightarrow[120\text{-}130^\circ]{CH_3CN} Hg(CH_2CN)_2$$

Mercuration of the more acidic $(CF_3)_2CHCN$ was considerably more facile (36):

$$2\ (CF_3)_2CHCN + Hg(OAc)_2 \xrightarrow{H_2O,\ 20^\circ} \underset{(96\%)}{[(CF_3)_2C(CN)]_2Hg} + 2\ HOAc$$

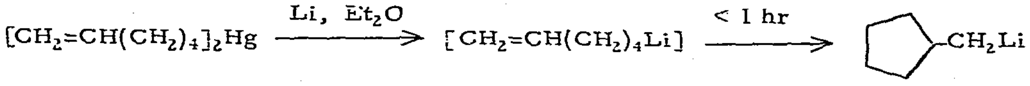
Finally, it has been found that the photomethylation of inorganic mercury species is photosensitized by basic mercuric sulfate (37). The latter is formed in a redox process when solid sulfur is present in the mercuric ion-containing aqueous solution.

3. USE OF ORGANOMERCURY COMPOUNDS IN SYNTHESIS

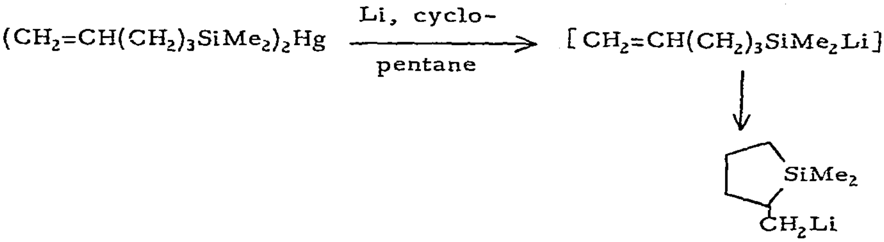
A. Organometallic Synthesis

More examples of the metal displacement reaction, in which the action of the more electropositive metals on diorganomercury compounds results in formation of mercury (or of an amalgam) and the organic derivative of the electropositive metal, have been described:

$$(CH_2{=}CHCH_2CH_2)_2Hg \xrightarrow{Li} CH_2{=}CHCH_2CH_2Li \qquad \text{(ref. 38)}$$



(ref. 39)



(ref. 40)

$(PhSCH_2)_2Hg \xrightarrow{Li,\ THF} PhSCH_2Li$ (ref. 12)

$(Me_3SiCH_2)_2Hg \xrightarrow{M,\ cyclohexane} Me_3SiCH_2M$ (ref. 41)

(M = Na, K, Rb, Cs)

$(Me_3CCH_2)_2Hg \xrightarrow{Mg,\ THF} (Me_3CCH_2)_2Mg$ (ref. 42)

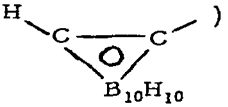
$(PhSCH_2)_2Hg \xrightarrow[reflux]{Zn,\ xylene} (PhSCH_2)_2Zn$ (ref. 12)

$[CH_2{=}CH(CH_2)_nCH_2]_2Hg \xrightarrow{M} [CH_2{=}CH(CH_2)_nCH_2]_2M$ (ref. 43)

(n = 0, 1, 2; M = Mg, Zn)

(The magnesium compound where n=3 cyclized totally to form bis-(cyclopentylmethyl)magnesium, while the analogous zinc compound contained 10% of bis(cyclopentylmethyl)zinc).

$R_2Hg \xrightarrow{M} R_2M$ (M = Ca, Sr, Ba) (ref. 44)

(R = $PhCH_2$, $CH_2{=}CHCH_2$, cyclopentadienyl, indenyl, $PhC{\equiv}C$, Ph, p-tert-$C_5H_{11}C_6H_4$ and $CH_2{=}CH$ )

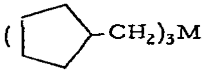
$$(Me_3SiCH_2)_2Hg \xrightarrow{\text{Al, toluene, 110°}} (Me_3SiCH_2)_3Al \qquad \text{(ref. 45)}$$

$$(CH_2{=}CHCH_2CH_2)_2Hg \xrightarrow{Al} (CH_2{=}CHCH_2CH_2)_3Al \qquad \text{(ref. 46)}$$

$$(CH_2{=}CHCH_2CH_2CH_2)_2Hg \xrightarrow{M} (CH_2{=}CHCH_2CH_2CH_2)_3M \quad (M{=}Al,\ Ga)$$

(ref. 46)

$$[CH_2{=}CH(CH_2)_4]_2Hg \xrightarrow[(M=Al,\ Ga,\ In)]{M} [CH_2{=}CH(CH_2)_4]_3M \longrightarrow$$



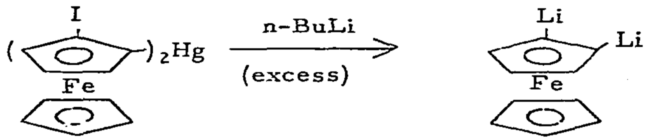
(ref. 39)

$$R_2Hg \xrightarrow{Al} R_3Al \quad (R = n\text{-}Bu,\ n\text{-}C_5H_{11}) \qquad \text{(ref. 46)}$$

$$R_2Hg \xrightarrow{\text{In, xylene, 100°}} R_3In \quad (R = CH_3,\ Ar) \qquad \text{(ref. 47)}$$

(An especially reactive grade of metallic indium, obtained via alkali metal reduction of indium trichloride, was used).

The transmetalation reaction was used to prepare 1,2-dilithioferrocene (48):



Metal hydrides also react with organomercury compounds to give organometallic products:

$\mathrm{Ar_2Hg + B_2H_6 \xrightarrow{THF} \xrightarrow{H_3O^+} ArB(OH)_2}$ (ref. 49)

$\mathrm{ArHgCl + B_2H_6 \xrightarrow{THF} \xrightarrow{H_3O^+} ArB(OH)_2}$

(Ar = Ph, p-$\mathrm{MeOC_6H_4}$, p-$\mathrm{CH_3C_6H_4}$, p-$\mathrm{ClC_6H_4}$, 2-furyl, 2-thienyl)

The high yields (generally better for the diarylmercurials) obtained make these very useful preparative reactions.

$\mathrm{(ClCH{=}CH)_2Hg + \textit{n}\text{-}Bu_3SnH \longrightarrow \textit{n}\text{-}Bu_3SnCH{=}CHCl}$ (86%) (ref. 50)

$\mathrm{(ClCH{=}CH)_2Hg + \textit{n}\text{-}Bu_3GeH \longrightarrow \textit{n}\text{-}Bu_3GeCH{=}CHCl}$ (ref. 50)

$\mathrm{(Me_2CHO)_3PCuH + R_2Hg \longrightarrow (Me_2CHO)_3PCuR + RH + Hg}$ (ref. 51)

(R = $\mathrm{CH_2CH{=}O}$, $\mathrm{CH_2C(O)}$alkyl, p-$\mathrm{Me_2NC_6H_4}$)

More examples of the well-known ability of diorganomercurials to partially alkylate metal and metalloidal halides have been reported:

$\mathrm{(PhCH_2)_2Hg + SnX_4 \xrightarrow{benzene} PhCH_2SnX_3 + PhCH_2HgX}$ (ref. 52)

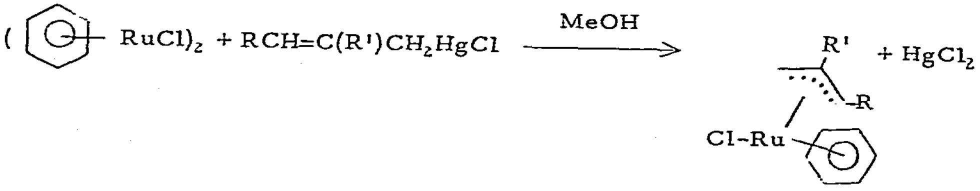
(X = Cl, Br, I; an NMR study)

$\mathrm{(CH_2{=}CH)_2Hg + F_2PBr \longrightarrow CH_2{=}CHPF_2 + CH_2{=}CHHgBr}$ (ref. 53)

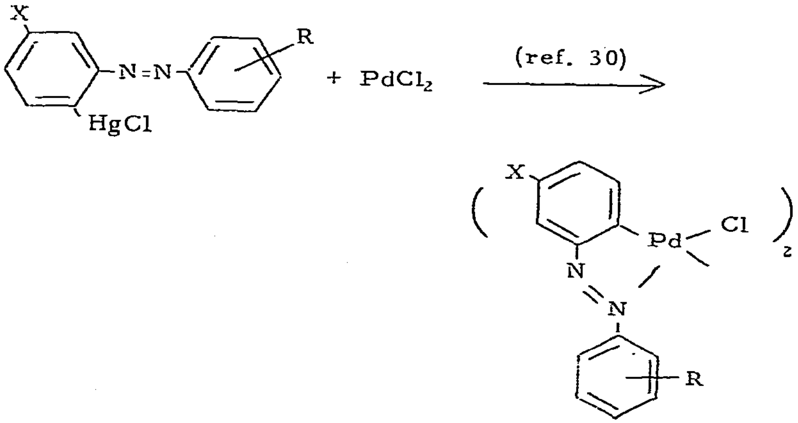
$\mathrm{(Me_2CH)_2Hg + F_2PCl \longrightarrow Me_2CHPF_2 + Me_2CHHgCl}$ (ref. 54)

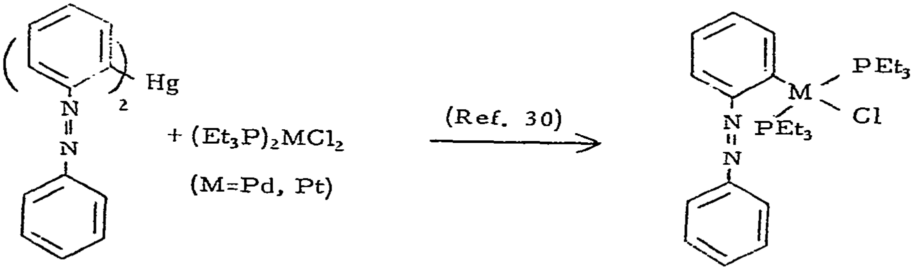
$\mathrm{Me_2Hg + 2\ WCl_6 \xrightarrow{CH_2Cl_2,\ -35^\circ} 2\ MeWCl_5 + HgCl_2}$ (ref. 55)

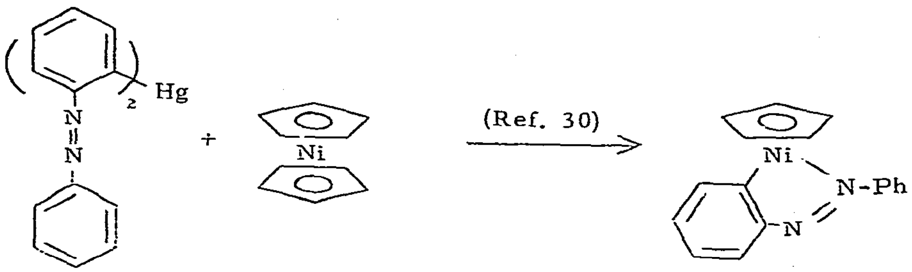
$$Me_2Hg + 2\ WOCl_4 \xrightarrow{CH_2Cl_2,\ -25°} 2\ MeWOCl_3 + HgCl_2$$ (ref. 55)

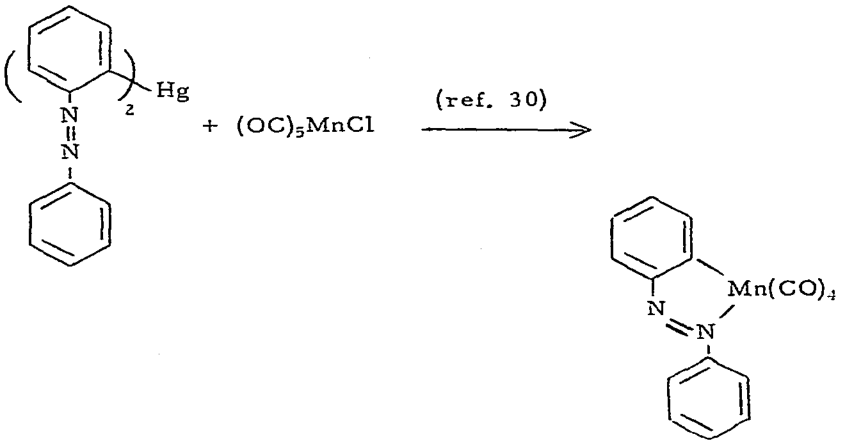


In this series of reactions, R, R' = H, H; Me, H; H, Me; Ph, H; H, Ph; Me, MeC(O) (56).









In contrast to the above reactions with $PdCl_2$, reaction of $ClHgCH_2CN$ and $Hg(CH_2CN)_2$ with palladium(II) chloride gave stable donor-acceptor complexes ($-C{\equiv}N{\rightarrow}Pd$ bonding mode) without cyanoalkyl group transfer from mercury to palladium (35).

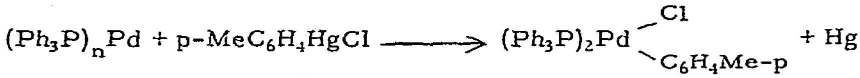
Other reactions of transition metal compounds with organomercurials which do not involve halide displacement have been reported:

$$(Ph_3P)_nPt + RHgX \longrightarrow (Ph_3P)_2PtRX + Hg + (n-2)\ Ph_3P \qquad \text{(ref. 57)}$$

$(n = 3,\ 4)$

$(R = Me,\ MeO_2CCH_2,\ p\text{-}MeC_6H_4,\ (p\text{-}MeOC_6H_4)_2C{=}CH,\ \text{ferrocenyl})$

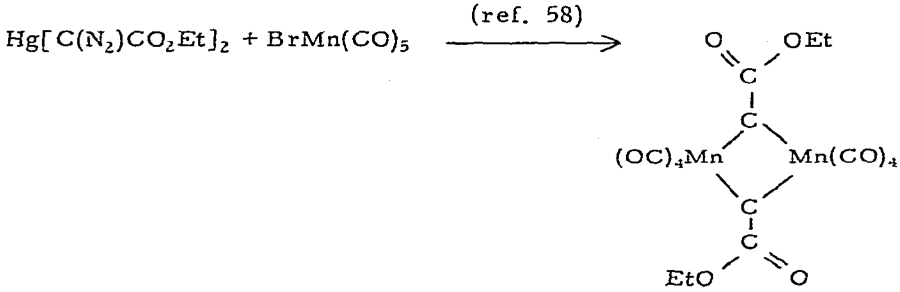
Reaction with diphenylmercury gave $(Ph_3P)_2PtPh_2$.

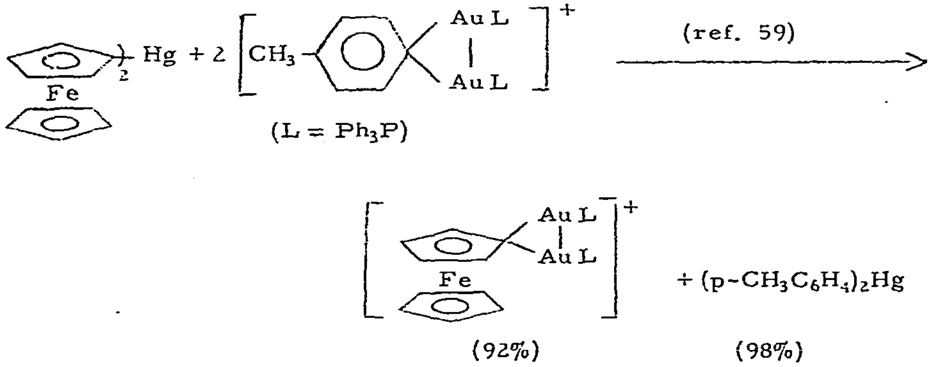


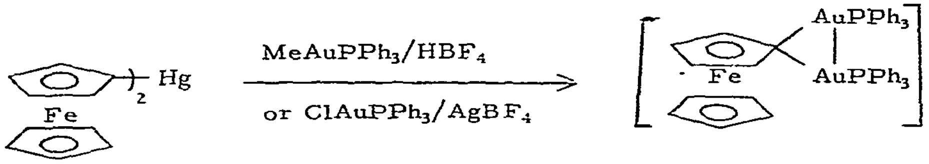
$$(Ph_3P)_nPd + p\text{-}MeC_6H_4HgCl \longrightarrow (Ph_3P)_2Pd\begin{matrix}Cl\\ C_6H_4Me\text{-}p\end{matrix} + Hg$$

(ref. 57)

These reactions proceed by way of oxidative addition, giving initially $(Ph_3P)_2Pt(X)HgR$, which extrudes mercury under the reaction conditions.

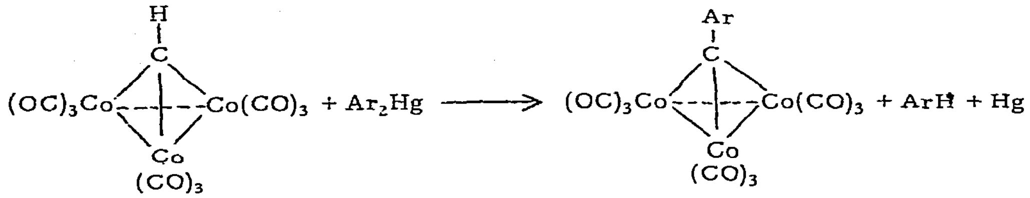




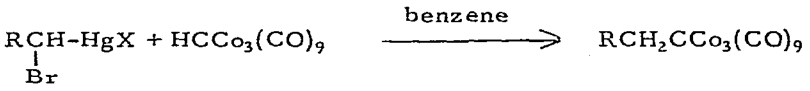


(ref. 59)

The reaction of methylidynetricobalt nonacarbonyl with arylmercurials, preferably under an atmosphere of carbon monoxide, resulted in arylation of the apical carbon atom of the cluster complex (60):



Typical results are shown in Table 2. Alkylation of the apical carbon atom using dialkylmercurials was much less favorable, requiring very long reaction times to give, at best, moderate yields. A remarkable carbon-halogen bond reduction occurred when α -haloalkylmercury compounds were allowed to react with $HCCo_3(CO)_9$ (60):



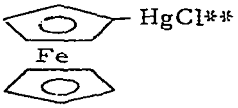
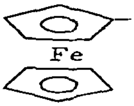
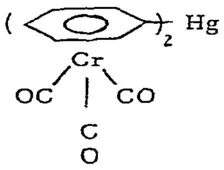
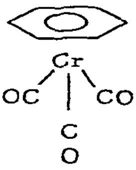
$$\underset{\substack{| \\ Br}}{RCH}\text{-}HgX + HCCo_3(CO)_9 \xrightarrow{\text{benzene}} RCH_2CCo_3(CO)_9$$

(R = H, 59% product yield; R = Me_3Si, 70% product yield)

TABLE 2. Preparation of $RCCo_3(CO)_9$ Complexes by Reactions of Organomercurials with $HCCo_3(CO)_9$ (ref. 60)

Organomercurial *	R in $RCCo_3(CO)_9$ Produced	% Yield
$(C_6H_5)_2Hg$	C_6H_5	93
$(p\text{-}CH_3OC_6H_4)_2Hg$	$p\text{-}CH_3OC_6H_4$	64
$(p\text{-}CH_3C_6H_4)_2Hg$	$p\text{-}CH_3C_6H_4$	92
$(m\text{-}CH_3C_6H_4)_2Hg$	$m\text{-}CH_3C_6H_4$	96

TABLE 2 - continued

$(o\text{-}CH_3C_6H_4)_2Hg$	$o\text{-}CH_3C_6H_4$	49
$(p\text{-}ClC_6H_4)_2Hg$	$p\text{-}ClC_6H_4$	83
$(m\text{-}ClC_6H_4)_2Hg$	$m\text{-}ClC_6H_4$	93
$(o\text{-}ClC_6H_4)_2Hg$	$o\text{-}ClC_6H_4$	57
$(m\text{-}FC_6H_4)_2Hg$	$m\text{-}FC_6H_4$	85
$(p\text{-}BrC_6H_4)_2Hg$	$p\text{-}BrC_6H_4$	86
$(p\text{-}IC_6H_4)_2Hg$	$p\text{-}IC_6H_4$	51
$(C_6F_5)_2Hg$	C_6F_5	69
$(C_6H_5CH_2)_2Hg$	$C_6H_5CH_2$	75
C_6H_5HgBr	C_6H_5	58
$p\text{-}FC_6H_4HgBr$	$p\text{-}FC_6H_4$	57
$p\text{-}H_2NC_6H_4HgCl$	$p\text{-}H_2NC_6H_4$	26
$p\text{-}ClC_6H_4HgBr$**	$p\text{-}ClC_6H_4$	54
$\alpha\text{-}C_{10}H_7HgBr$**	$\alpha\text{-}C_{10}H_7$	11
		14
		51
$CH_3OCH_2CH_2HgCl$	$CH_3OCH_2CH_2$	32
$(n\text{-}C_5H_{11})_2Hg$	$n\text{-}C_5H_{11}$	32

---

* Reactions were carried out under an atmosphere of carbon monoxide unless otherwise specified.

** Reaction carried out under an atmosphere of dry nitrogen.

$$(RCHI)_2Hg + HCCo_3(CO)_9 \xrightarrow{\text{benzene}} RCH_2CCo_3(CO)_9$$

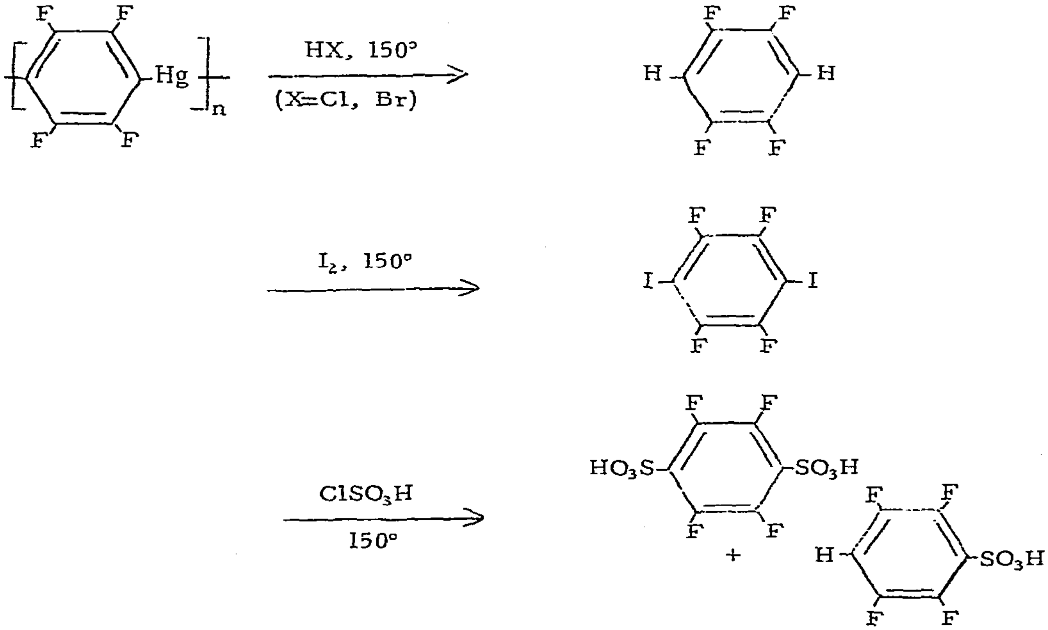
(R = H, 77% product yield; R = Me, 88% product yield)

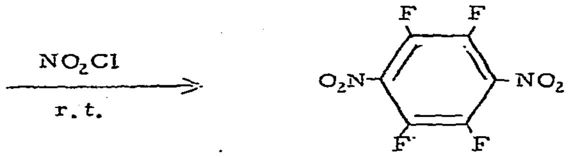
Nothing is known at the present time about the mechanism of these reactions.

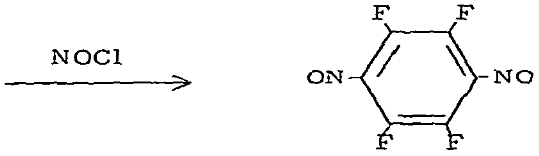
B. Organic Synthesis

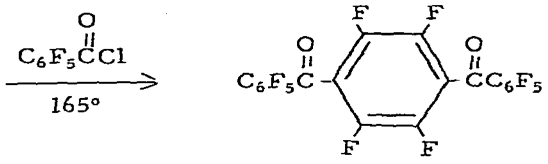
Electrophilic cleavage of the mercury-carbon bond has been used often as a route to various organic compounds, mostly organic halides. Some new examples have been published.

The tetrafluorophenylenemercury polymer was a source of 1,4-disubstituted tetrafluorobenzenes (28a):

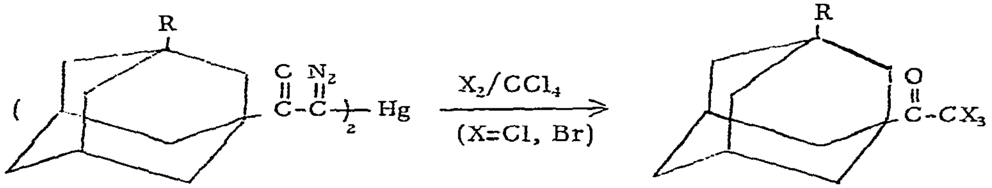






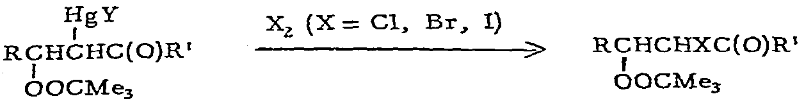


Trihalomethyl ketones were obtained by halogenation of mercurated diazoketones (61):



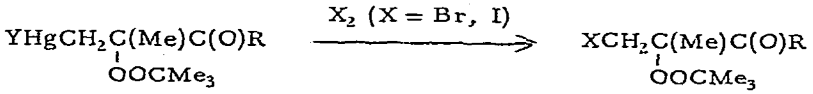
(R=H, Cl, Br)

The previously unknown classes of β- and α-carbonyl-β-halo-peroxides were made accessible by halogenolysis of β- and α-carbonyl-β-mercuri-peroxides (62):



$$\underset{\text{OOCMe}_3}{\text{RCH}}\overset{\text{HgY}}{\text{CH}}\text{C(O)R'} \xrightarrow{X_2\ (X = \text{Cl, Br, I})} \underset{\text{OOCMe}_3}{\text{RCH}}\text{CHXC(O)R'}$$

(R = Ph, OMe)

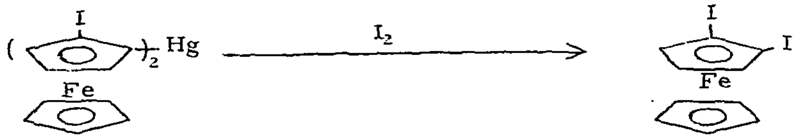


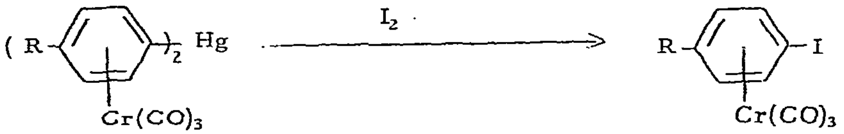
$$\underset{\text{OOCMe}_3}{\text{YHgCH}_2\text{C(Me)C(O)R}} \xrightarrow{X_2\ (X = Br,\ I)} \underset{\text{OOCMe}_3}{\text{XCH}_2\text{C(Me)C(O)R}}$$

(R = Me, OMe)

These mercurials were available via oxymercuration of appropriate α,β-unsaturated ketones and esters.

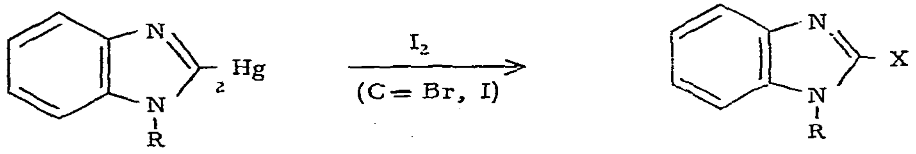
Useful C-Hg cleavage reactions have been described in ferrocene chemistry (48) and in benzenechromium tricarbonyl chemistry (63):



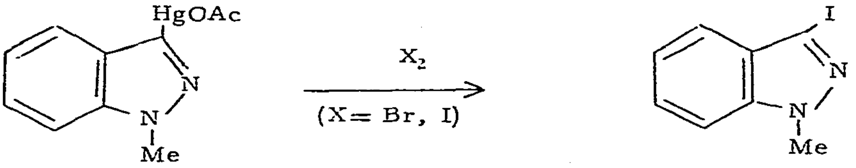


(R = Me_2N, MeO, Me, H)

and for indazole and benzimidazole systems (29):



(R = Me, Ph)



Organomercury intermediates also are involved in new ester syntheses. A reaction sequence of olefin ($RCH{=}CH_2$) hydroboration, alkyl transfer from the trialkylborane to a mercuric carboxylate, $Hg(O_2CR')_2$, and iodinolysis gave high yields of esters, $RCH_2CH_2O_2CR'$ (Table 3), presumably by the mechanism shown below (64). The last two steps of this sequence were confirmed when it was shown that IHgOAc reacts with n-butyl iodide in the presence of 10% boron triacetate to give n-butyl

$$3RCH{=}CH_2 + BH_3 \longrightarrow (RCH_2CH_2)_3B$$

$$(RCH_2CH_2)_3B + 3Hg(O_2CR')_2 \longrightarrow$$
$$RCH_2CH_2HgO_2CR' + B(O_2CR')_3$$

$$RCH_2CH_2HgO_2CR' + I_2 \longrightarrow RCH_2CH_2I + IHgO_2CR'$$

$$IHgO_2CR' + B(O_2CR')_3 \longrightarrow IHgB(O_2CR')_4$$

$$IHgB(O_2CR')_4 + RCH_2CH_2I \longrightarrow$$
$$RCH_2CH_2O_2CR' + HgI_2 + B(O_2CR')_3$$

acetate in 88% yield. Highly substituted olefins cannot be used in this synthesis. This organic halide-based ester synthesis has been studied in detail (65). Carboxylic acids or their esters also can be prepared by the transition metal-catalyzed carbonylation of organomercurials in the presence of water or an alcohol, e.g. (66):

TABLE 3. The Anti-Markovnikov Esterification of Olefins (from R. C. Larock, J. Org. Chem., 39 (1974) 834).

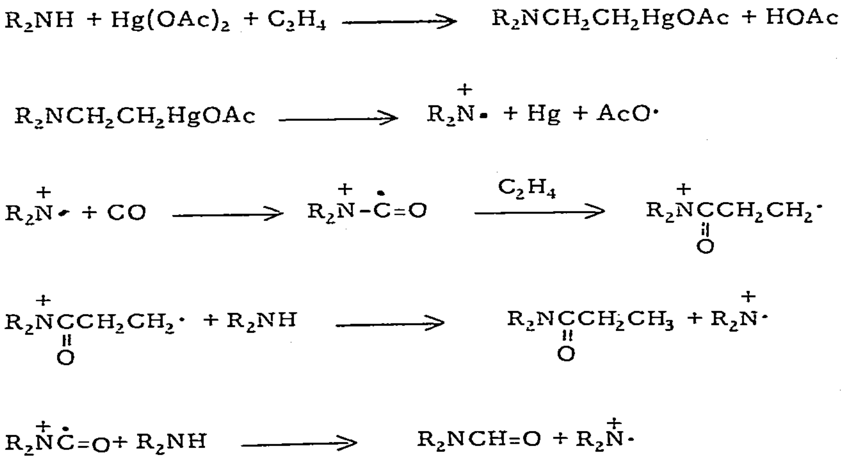
$$RCH{=}CH_2 \xrightarrow{{}^1/_3BH_3} \xrightarrow{Hg(O_2R')_2} \xrightarrow{I_2} RCH_2CH_2O_2CR'$$

Alkene	Mercuric carboxylate	Ester	Yield, %
Ethylene	Mercuric acetate	Ethyl acetate	92
	Mercuric trifluoroacetate	Ethyl trifluoroacetate	17
	Mercuric butyrate	Ethyl butyrate	97
	Mercuric benzoate	Ethyl benzoate	86
1-Butene	Mercuric acetate	*n*-Butyl acetate	93
	Mercuric butyrate	n-Butyl butyrate	84
Isobutylene	Mercuric acetate	Isobutyl acetate	30
3-Methyl-1-butene	Mercuric acetate	Isoamyl acetate	88
3,3-Dimethyl-1-butene	Mercuric acetate	3,3-Dimethyl-1-butyl acetate	73
1-Decene	Mercuric acetate	n-Decyl acetate	89

$$EtHgOAc \xrightarrow{CO/MeOH,\ (Ph_3P)_3RhCl\ catalyst} EtCO_2Me\ \ (66\%)$$

Bis(triphenylphosphine)palladium dichloride also catalyzed these reactions.

Nefedov, Sergeeva and Eidus have continued their series of papers on the carbonylation of organic compounds in the presence of mercuric acetate. The $Hg(OAc)_2$-catalyzed carbonylation of amines had been reported previously (67). Dialkylamines gave N,N-dialkyl formamides and the substituted urea, while aniline gave N,N'-diphenylurea. In further studies (68), the carbonylation of preformed mercuric acetate-amine complexes was examined in order to shed more light on the $R_2NH/CO/Hg(OAc)_2$ reaction. The mercuric acetate/piperidine complex in piperidine reacted with carbon monoxide (95 atm) to give $C_5H_{10}NC(O)OC(O)CH_3$. The mechanistic discussion is rather speculative, considering its meager experimental support. The propionic acid amide and small amounts of the corresponding formamide were formed when carbonylation of β-aminoethylmercuric acetates was attempted (69). The following reaction course was suggested:



$$R_2NH + Hg(OAc)_2 + C_2H_4 \longrightarrow R_2NCH_2CH_2HgOAc + HOAc$$

$$R_2NCH_2CH_2HgOAc \longrightarrow R_2\overset{+}{N}\cdot + Hg + AcO\cdot$$

$$R_2\overset{+}{N}\cdot + CO \longrightarrow R_2\overset{+}{N}-\overset{\bullet}{C}=O \xrightarrow{C_2H_4} R_2\overset{+}{N}\underset{\underset{O}{\|}}{C}CH_2CH_2\cdot$$

$$R_2\overset{+}{N}\underset{\underset{O}{\|}}{C}CH_2CH_2\cdot + R_2NH \longrightarrow R_2N\underset{\underset{O}{\|}}{C}CH_2CH_3 + R_2\overset{+}{N}\cdot$$

$$R_2\overset{+}{N}\overset{\bullet}{C}=O + R_2NH \longrightarrow R_2NCH=O + R_2\overset{+}{N}\cdot$$

The yields of propionamides (from diethylamine, piperidine and aniline) were high. The reactions could be carried out in a two-step manner ($R_2NH + C_2H_4 + Hg(OAc)_2$ at 25°, 30 atm, then reaction with CO at 190°, 60-100 atm) or in a one-step mode.

It has been pointed out to your reviewer that much of the work on the carbonylation of organic compounds in the presence of mercuric acetate reported in 1972-1973 by this Russian group (see previous surveys for summaries: J. Organometal. Chem., 62 (1973) 53; 75 (1974) 30) had been published previously by D. M. Fenton in the period 1966-1969 in the form of United States patents assigned to the Union Oil Company of California (70). The content of these patents is summarized briefly below:

U.S. patent 3,277,061 (Oct. 4, 1966): preparation of substituted ureas.

$$RR'NH + CO + Hg(OAc)_2 \xrightarrow{400\text{ psig, }200^\circ} (RR'N)_2CO \quad (+\text{ some } RR'NC(O)Me)$$

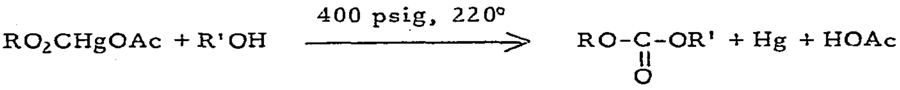
With diamines, polymeric ureas were obtained.

U.S. patent 3,227,740 (Jan. 4, 1966): preparation of symmetrical dialkyl carbonates.

$$2\ ROH + CO + Hg(OAc)_2 \xrightarrow{400\text{ psig, }110\text{-}220^\circ} (RO)_2C{=}O + Hg + 2\ HOAc$$

Polycarbonates were obtained in this manner from diols.

U.S. patent 3,227,741 (Jan. 4, 1966): preparation of unsymmetrical carbonates.



$$RO_2CHgOAc + R'OH \xrightarrow{400\text{ psig, }220^\circ} RO-\underset{\underset{\displaystyle O}{\|}}{C}-OR' + Hg + HOAc$$

U.S. patent 3,654,337 (Apr. 4, 1972): preparation of dialkyl carbonates by another mercury-based route.

$$2\ \mathrm{ROH} + \mathrm{CHX_3} + \mathrm{HgO} \longrightarrow \mathrm{(RO)_2C{=}O} + \mathrm{Hg} + 3\ \mathrm{HX}$$

$(X = Cl, Br)$

U.S. patent 3,316,290 (Apr. 25, 1967): preparation of β-alkoxypropionate esters.

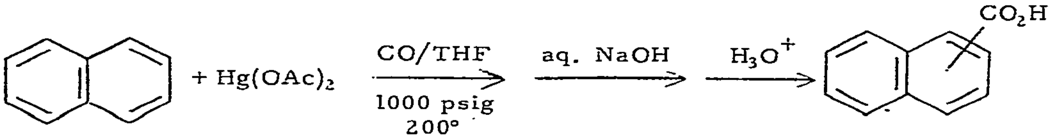
$$2\ \mathrm{ROH} + \mathrm{C_2H_4} + \mathrm{CO} + \mathrm{Hg(OAc)_2} \xrightarrow{800\ \mathrm{psig},\ 200^\circ} \mathrm{ROCH_2CH_2CO_2R} + \mathrm{Hg} + 2\ \mathrm{HOAc}$$

(Also reactions in which propene and cyclohexene were the olefins used).

U.S. patent 3,337,436 (Aug. 22, 1967): preparation of bis(β-alkoxyalkyl) ketones.

$$\mathrm{ROH} + \mathrm{C_2H_4} + \mathrm{CO} + \mathrm{Hg(OAc)_2} + \mathrm{HgO} \xrightarrow[600\ \mathrm{psig},\ 200^\circ]{\mathrm{(Me_3COOCMe_3)}} \mathrm{(ROCH_2CH_2)_2C{=}O}$$

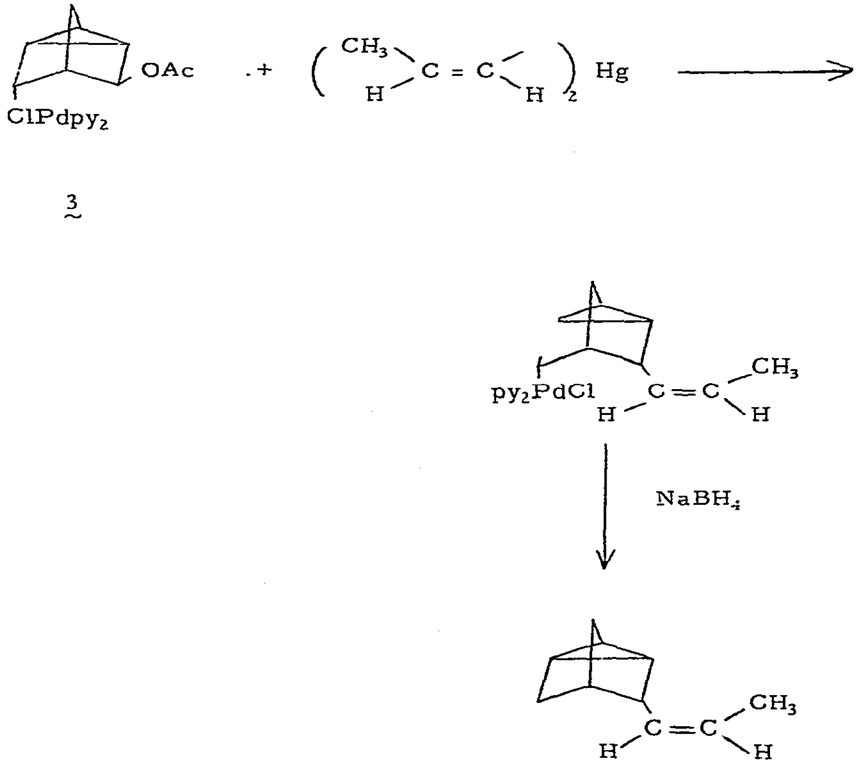
U.S. patent 3,480,669 (Nov. 25, 1969): oxidative carbonylation of aromatics.



(isomer mixture)

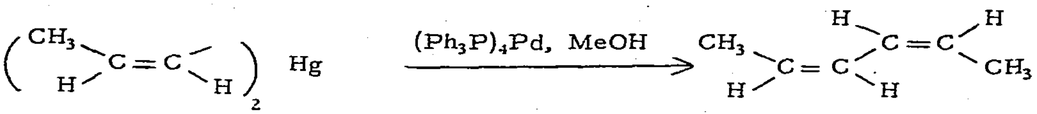
The reactions of organomercurials with dicobalt octacarbonyl and nickel tetracarbonyl are known to give ketones. A more "exotic" metal carbonyl derivative, $(OC)_5CrC(OMe)Ph$, has now been shown to react with phenylmercuric bromide to give benzophenone and metallic mercury (71).

Vinylmercurials have found new application in organic synthesis. Reaction of di-*cis*-propenylmercury with the palladium complex **3** resulted in a coupled product (72):

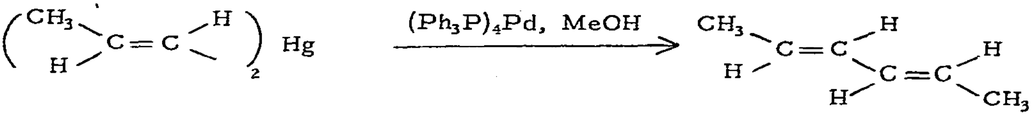


3

Of interest was the observation that some palladium derivatives, e.g., $Cl_2Pd(CH_3CN)_2$, reacted with bis-*cis*-propenylmercury to give a 78:17:5 mixture (15-20% yield) of *cis*,*cis*-, *cis*,*trans*- and *trans*,*trans*-2,4-hexadiene. A much more efficient coupling was induced catalytically by $(Ph_3P)_4Pd$ with high stereoselectivity (73):



(92% isomeric purity)

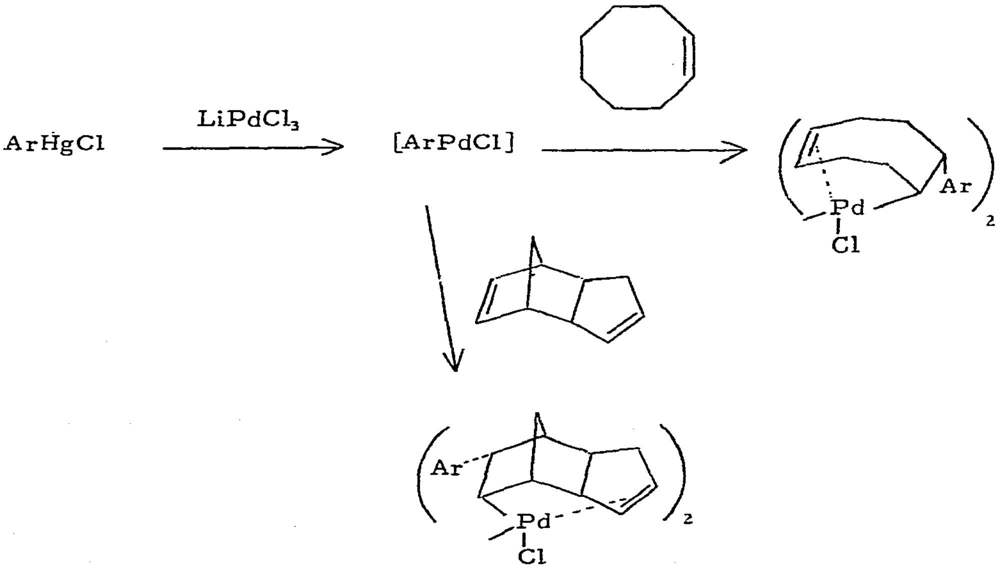


(96% isomeric purity)

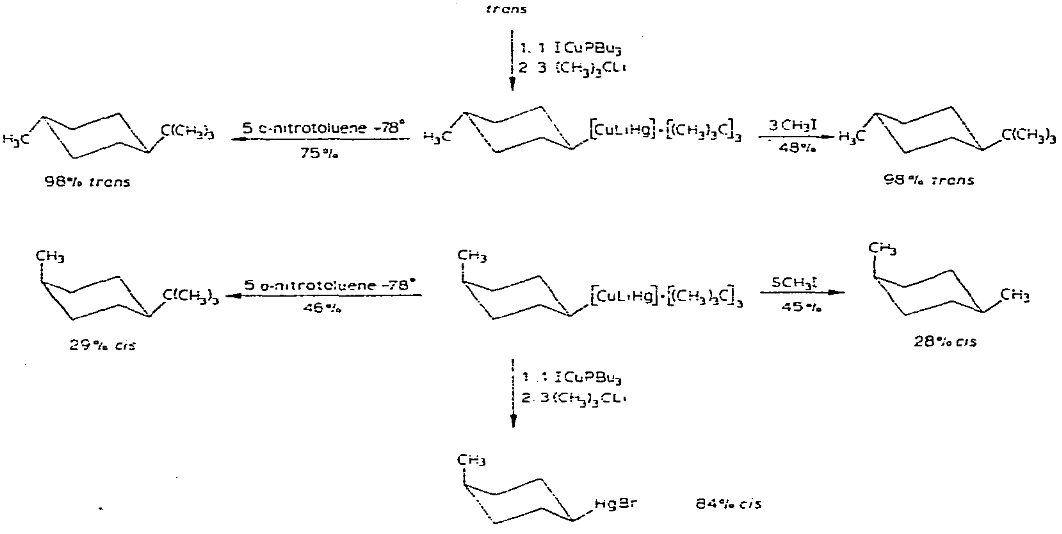
Such coupling also can be effected photochemically in some instances, e.g. (35):

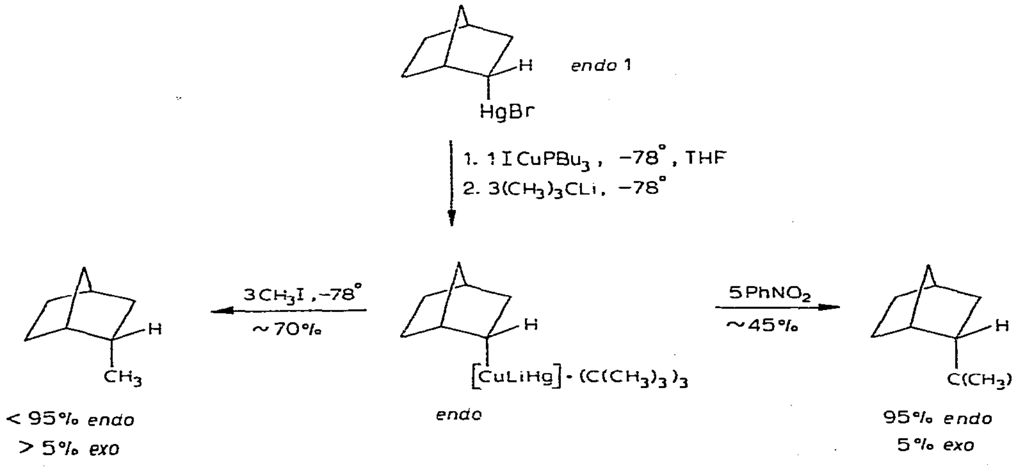
$$Hg(CH_2CN)_2 \xrightarrow{h\nu} Hg + NC(CH_2)_2CN$$

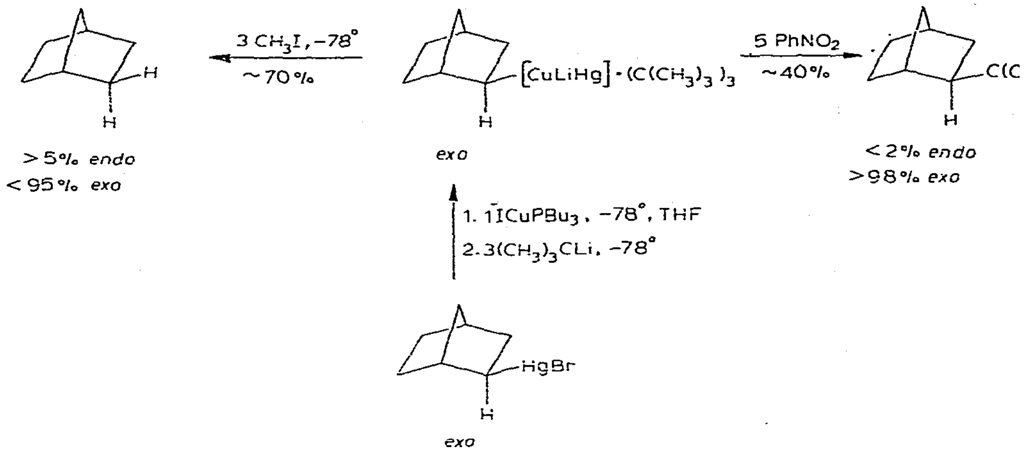
Another example of the use of arylmercuric halides to generate reactive arylpalladium intermediates has been reported (74):



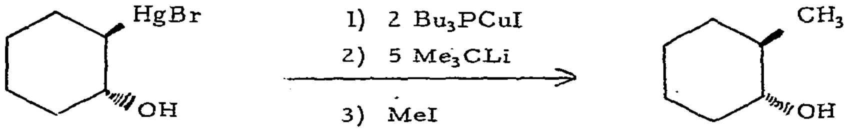
A witches' brew containing an alkylmercuric halide, three molar equivalents of tert-butyllithium and one of n-Bu_3PCuI in THF at -78° resulted in the formation of a reactive reagent believed to incorporate all three metals which approximates $LiCuR_2$ reagents but which does not undergo conjugate addition to α, β -unsaturated ketones (75). Some of the alkyl transfer reactions of this "reagent" were shown to proceed with *retention of configuration* of the carbon atom originally bound to mercury. Some typical reactions are shown in the schemes below.







Also, some oxymercuration products of olefins can be used in this reaction, but this does not appear to be a generally useful variation.

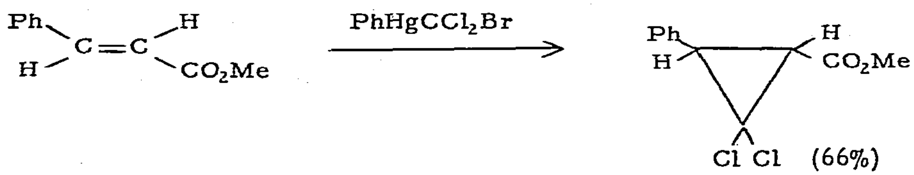


41% Yield
(98+ % trans)

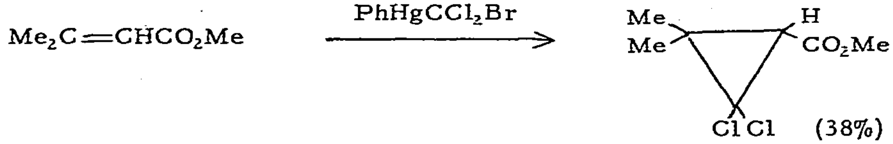
C. Halomethyl-Mercury Compounds

Since their initial development as dihalocarbene sources in 1962, the phenyl(trihalomethyl)mercury reagents have enjoyed a clear superiority in application over the haloform/metal alkoxide system of Doering and Hoffmann, which generally is used in hydrocarbon medium. Many olefins which the latter system was not able to cyclopropanate were readily converted to dihalocyclopropanes, usually in high yield, by the $PhHgCX_3$ reagents (1, 76). The recently developed (Makosza; Starks) phase transfer catalysis variation of the Doering-Hoffmann procedure, the $R_4N^+X^-$-catalyzed haloform/50% aqueous NaOH/olefin reaction, has been shown to be successful in many cases where the conventional Doering-Hoffmann reaction fails (77), and thus some of the unique advantages of the phenyl(trihalomethyl)mercury compounds have been lost. Nevertheless, the $PhHgCX_3$ compounds still have some unique applicability. For instance, some of the more electrophilic olefins, such as acrylonitrile, intercept the CX_3^- intermediate when the phase transfer procedure for CX_2 generation is attempted in their presence; this is not a problem with the thermal generation of CX_2 from $PhHgCX_3$ since the trihalomethyl anion is not an intermediate. Also, some olefins (e.g., polychloroethylenes) are unreactive toward phase transfer-generated CCl_2 but react readily with $PhHgCX_3$. The phenyl(trihalomethyl)-mercurials are clearly superior as reagents for inserting CX_2 into C-H bonds, and some of their other CX_2 transfer reactions to poor carbenophiles may not be available via the HCX_3/50% NaOH/$R_4N^+X^-$ system. Carbenes of type CF_3CCl and CF_3CF, which are readily generated by the organomercury procedure, will not be accessible by the phase transfer catalysis route since the anionic intermediates undergo halide elimination to form an olefin faster than they form the carbene.

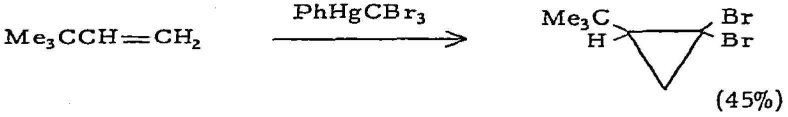
Among the cyclopropanation reactions of the phenyl(trihalomethyl)-mercury reagents reported during the past year are the following:



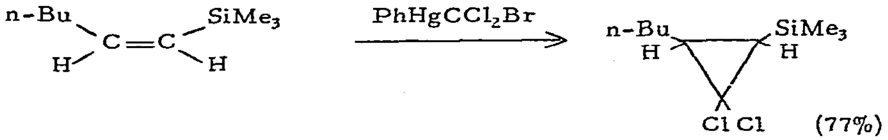
(ref. 78)



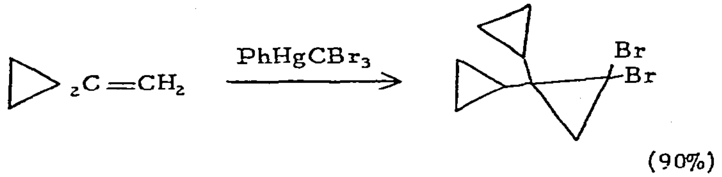
(ref. 78)



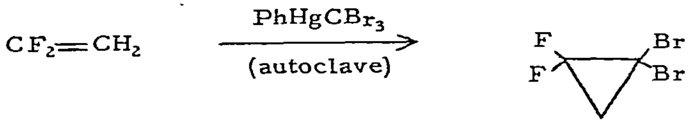
(ref. 79)



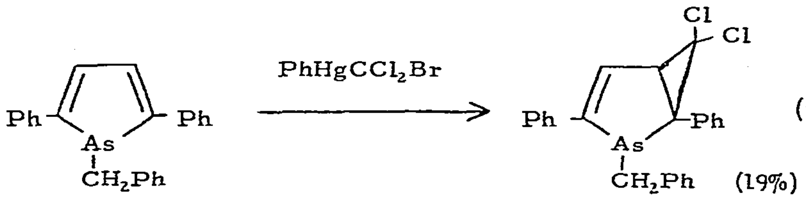
(ref. 50)



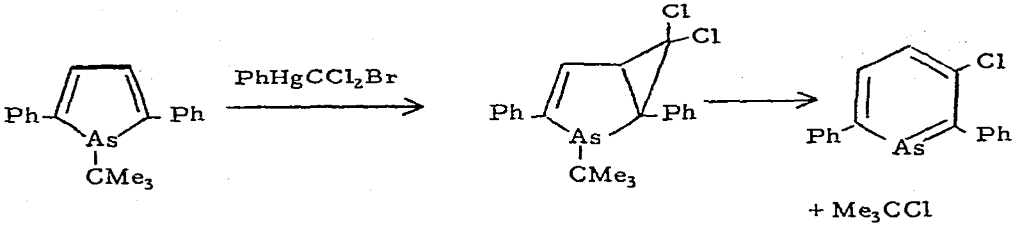
(ref. 81)



(ref. 82)



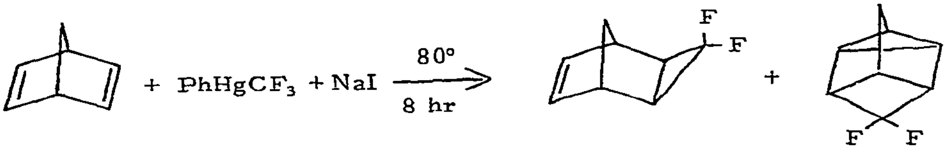
(ref. 83)



(ref. 83)

A study of the effect of the solvent on the relative rate constant value k(cyclohexene)/k (1-heptene) for reaction of these olefins with $PhHgCCl_2Br$-derived dichlorocarbene at 80° is summarized in Table 4 (84). The lack of a solvent effect which was observed confirms earlier work at M.I.T.

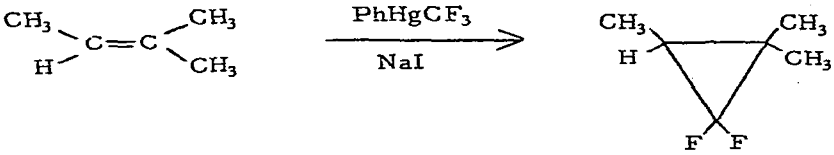
The $PhHgCF_3$/NaI reagent has been used to effect interesting CF_2 additions:



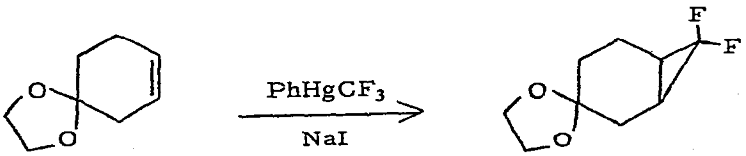
0.85 : 1.0 ratio

(92% yield)

(ref. 85)



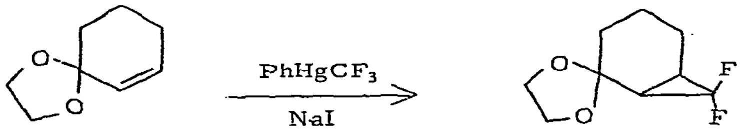
(ref. 86)



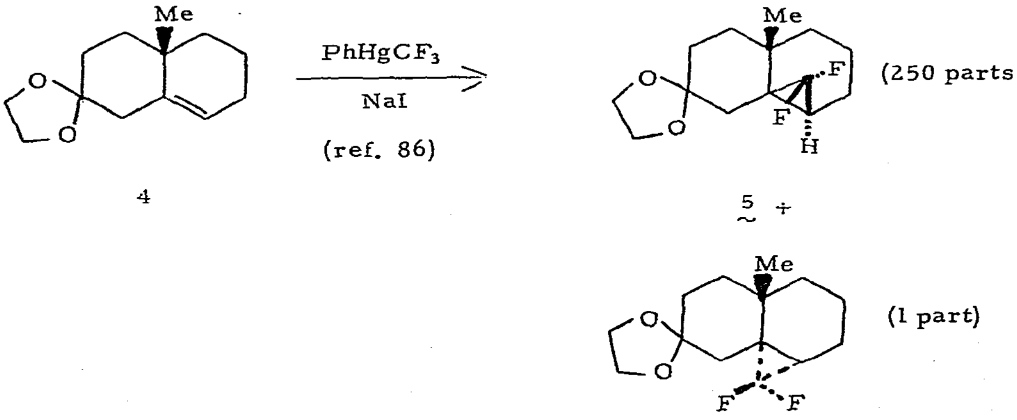
(ref. 86)

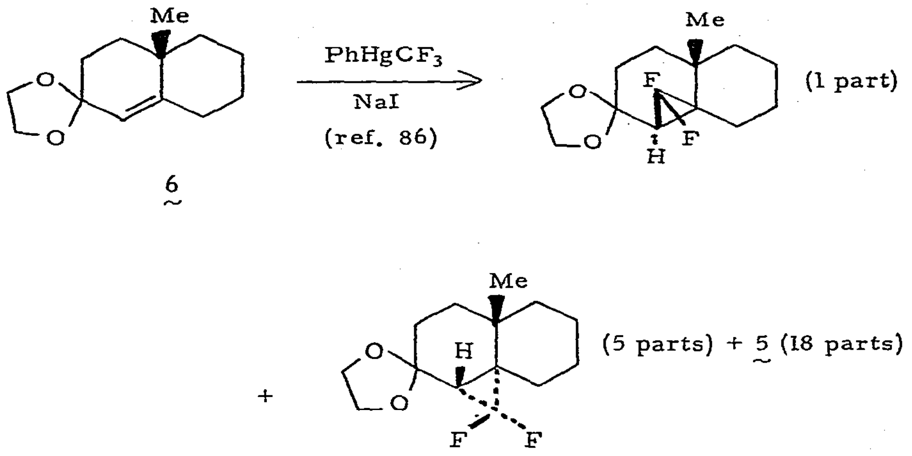
TABLE 4. The effect of solvent of the relative reactivity of phenyl(bromodichloromethyl)mercury toward olefins (84).

Solvent	k(cyclohexene)/k(1-heptene)
n-heptane	4.55
benzene	4.37
toluene	4.66
p-xylene	4.75
di-n-propyl ether	4.69
diisopropyl ether	4.60
di-n-butyl ether	4.76
tetrahydrofuran	4.81



(ref. 86)





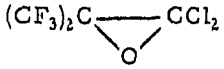
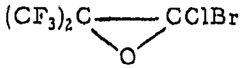
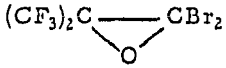
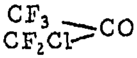
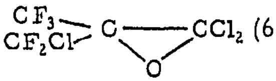
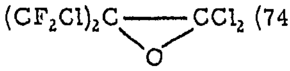
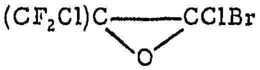
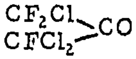
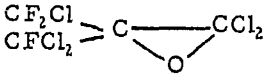
In the last reaction, 5 was formed as a result of the isomerization of 6 to 4 under the reaction conditions. The product yields in these reactions were around 75%. The relative reactivities of these olefins (and cyclohexene) toward the $PhHgCF_3/NaI$ reagent were determined by means of competition reactions (86).

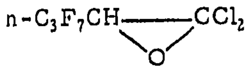
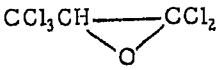
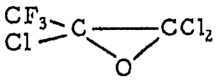
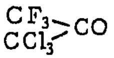
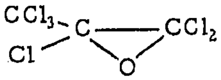
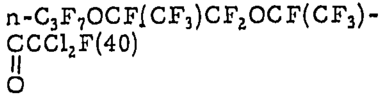
The following reaction has been reported for the $PhHgCCl_3/NaI$ reagent (87):

$$PhHgCCl_3 + NaI + CCl_4 \xrightarrow[52^\circ]{\text{benzene/DME}} Cl_3C\text{-}CCl_3 \quad (16\%)$$

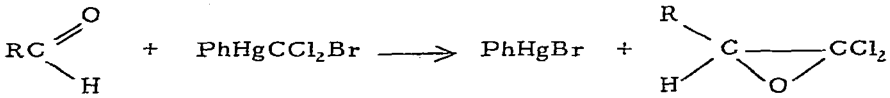
Other products were not isolated. It was claimed that the hexachloroethane obtained was formed by insertion of CCl_2 into the C-Cl bond of carbon tetrachloride. However, such a reaction has not been observed in the case of thermally generated CCl_2. Furthermore, the hexachloroethane very likely could have been formed by a radical process of the type which occurs readily when dialkyl- and diarylmercurials react with carbon tetrachloride in the presence of a radical initiator (Nesmeyanov et al., 1960-62; Jensen, 1968).

TABLE 5. Reactions of Phenyl(trihalomethyl)mercury Compounds with Carbonyl Compounds (88)

Mercurial	Carbenophile	Reaction Conditions	Products (% Yield)
$PhHgCCl_2Br$	$(CF_3)_2CO$	72 h at 60°, sealed tube	 (36)
$PhHgCClBr_2$	$(CF_3)_2CO$	72 h at 60°, sealed tube	 (18)
$PhHgCBr_3$	$(CF_3)_2CO$	12 h at 80°, sealed tube	 (26)
$PhHgCCl_2Br$	 $\begin{matrix}CF_3\\CF_2Cl\end{matrix}\!>CO$	18 h at 60°, sealed tube	 (66)
$PhHgCCl_2Br$	$(CF_2Cl)_2CO$	72 h at 60°	 (74)
$PhHgCClBr_2$	$(CF_2Cl)_2CO$	72 h at 60°	 (48)
$PhHgCCl_2Br$	 $\begin{matrix}CF_2Cl\\CFCl_2\end{matrix}\!>CO$	20 h at 60°	 (33)

$PhHgCCl_2Br$	$n\text{-}C_3F_7CHO$	1.5 h at 90° sealed tube	 (43)
$PhHgCCl_2Br$	CCl_3CHO	20 h at 70°	 (46)
$PhHgCCl_2Br$	CF_3COCl	18 h at 60-65°, sealed tube	 (8)
			 $\substack{CF_3\\CCl_3}{>}CO$ (26)
$PhHgCCl_2Br$	CCl_3COCl	18 h at 70°	 (17)
			$(CCl_3)_2CO$ (33)
$PhHgCCl_2Br$	$n\text{-}C_3F_7OCF(CF_3)\text{-}$ $CF_2OCF(CF_3)COF$	3 h at 80°^{g}	 $n\text{-}C_3F_7OCF(CF_3)CF_2OCF(CF_3)\text{-}C(=O)CCl_2F$ (40)
$PhHgCCl_2Br$	C_6F_5COF	4.5 h at 80°	C_6F_5COF (98), C_2Cl_4 (36), cyclo-C_3Cl_6

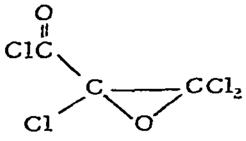
Full details have been provided concerning the reactions of phenyl(trihalomethyl)mercurials with highly fluorinated carbonyl compounds (88). In most cases, stable oxiranes were produced (Table 5).



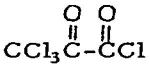
(R = n-C_3F_7, 43%; CCl_3, 46%)

(X= F, 8%; Cl, 17%) (X= F, 26%; Cl, 33%

In the case of hexachloroacetone and n-$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$, ketones were obtained instead. Reaction of $PhHgCCl_2Br$ with oxalyl chloride produced a mixture of products:

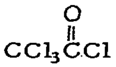


(19%)



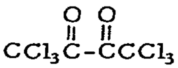
$CCl_3C(O)C(O)Cl$

(40%)



$CCl_3C(O)Cl$

(7%)

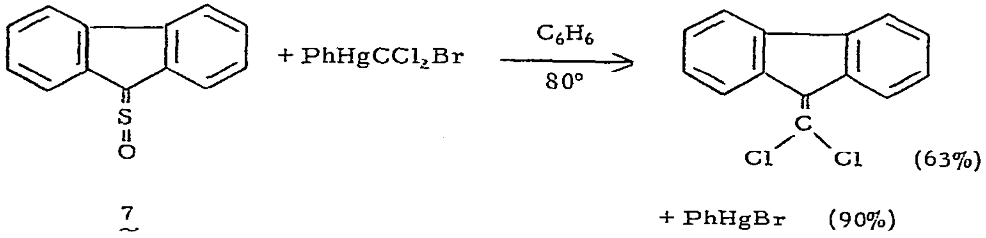


$CCl_3C(O)C(O)CCl_3$

(5%)

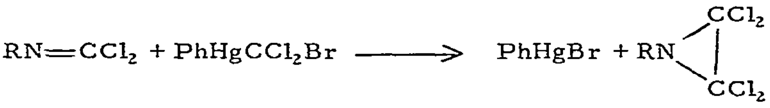
and its reaction with benzil, PhC(O)C(O)Ph, gave PhC(O)CCl(Ph)C(O)Cl, most likely by rearrangement of the initially formed oxirane.

The reaction of phenyl(bromodichloromethyl)mercury with the sulfine 7 led to replacement of the S=O function by CCl_2 in a process which may not have involved free CCl_2 (89):

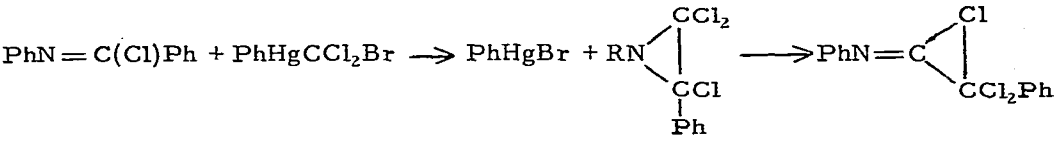


7

The results of an extensive study of the reactions of phenyl(trihalomethyl)mercurials with compounds containing C=N or N=N bonds have been reported. Phenyl(bromodichloromethyl)mercury reacts readily with alkyl- and arylcarbonimidoyl dichlorides to give aziridines (Table 6) (90):

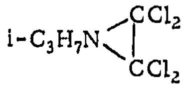
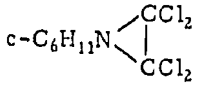
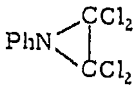
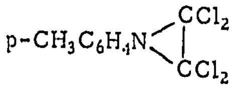
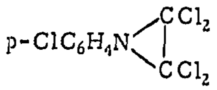


also:

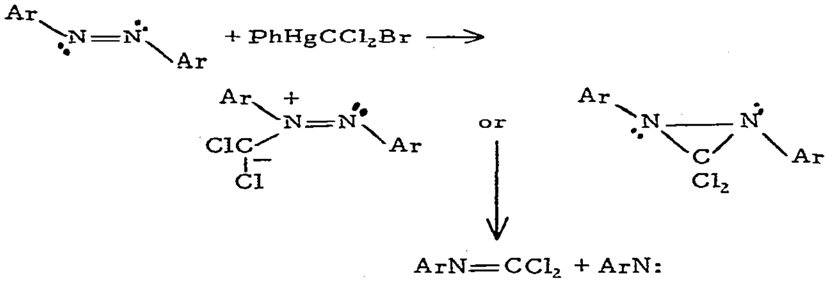


Depending on the reactant stoichiometry, the major product of the reactions of $PhHgCCl_2Br$ with azoarenes is either the arylcarbonimidoyl dichloride (azoarene in excess) or the C-tetrachloroaziridine (mercurial

TABLE 6. Reactions of Carbonimidoyl Dichlorides with Phenyl(bromodichloromethyl)mercury (90)

$RN{=}CCl_2$ (mmol)	$PhHgCCl_2Br$, mmol	Reaction Conditions	Product (% yield)	PhHgBr, %
$i\text{-}C_3H_7N{=}CCl_2$ (50)	50	3 hr, 80°	 (43)	80
$c\text{-}C_6H_{11}N{=}CCl_2$ (30)	30	12 hr, 60°	 (29)	84
$PhN{=}CCl_2$ (40)	30	12 hr, 60°	 (53)	84
$p\text{-}CH_3C_6H_4N{=}CCl_2$ (16)	10	3 hr, 80°	 (78)	90
$p\text{-}ClC_6H_4N{=}CCl_2$ (12)	10	3 hr, 80°	 (54)	99

in excess). Such reactions are accompanied by complications and the product yields did not exceed 40-50% and often were lower. The formation of the initial product, the carbonimidoyl dichloride, may be pictured as occurring via an open or a cyclic intermediate which then decomposes to give the observed $ArN{=}CCl_2$ and an arylnitrene (90):

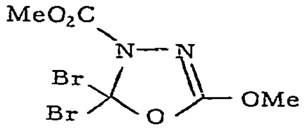

(7)

The reaction of $PhHgCCl_2Br$ with one molar equivalent of azoxybenzene in benzene solution at 80° gave three products: azobenzene (6% yield), phenylcarbonimidoyl dichloride (3% yield) and 1-phenyl-2,2,3,3-tetrachloroaziridine (12% yield). The use of an excess of the mercurial in such a reaction increased the yield of the aziridine to 35%, and in such reactions no $PhN{=}CCl_2$ was obtained. The course of this reaction is the same as those of the azobenzenes after an initial deoxygenation of the azoxyarene by the mercurial to give the corresponding azoarene.

The reactions of azodicarboxylate esters with phenyl(trihalomethyl)-mercury compounds provide rare examples of 1,4-addition of a dihalocarbene to a conjugated system (91). The products isolated were hydrazonodihalomethanes:

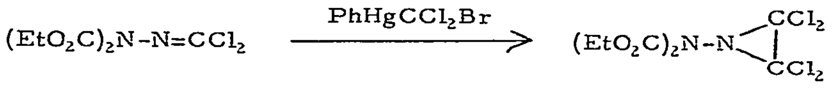
$$PhHgCX_3 + RO_2CN{=}NCO_2R \longrightarrow PhHgX + (RO_2C)_2NN{=}CX_2$$

However, these reactions proceed by way of an intermediate which usually is unstable but detectable by spectroscopy. In the case of the $PhHgCBr_3/MeO_2CN{=}NCO_2Me$ reaction at room temperature, this intermediate was isolated and assigned structure 8 on the basis of spectroscopic data. The reactions carried out are summarized in



8

Table 7. Hydrazonodihalomethanes react with $PhHgCCl_2Br$:



The mechanism of these $PhHgCX_3/RO_2CN{=}NCO_2R$ reactions is believed to be:

$$PhHgCCX_2Br \rightleftharpoons PhHgBr + :CX_2 \qquad (X{=}Cl \text{ or } Br)$$

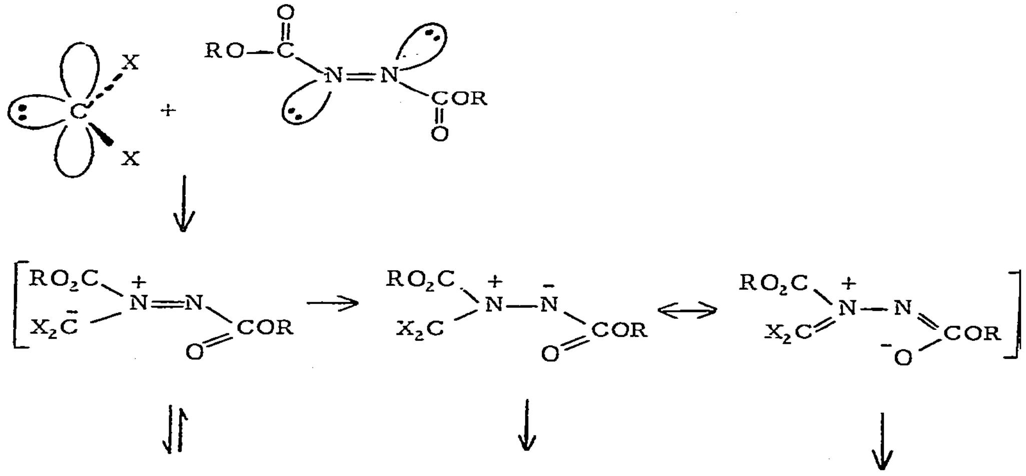
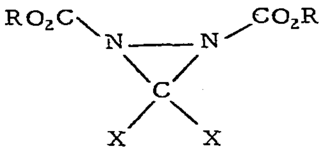
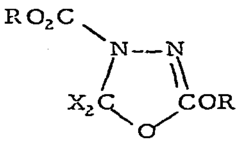


TABLE 7. Reactions of $PhHgCX_3$ with $RO_2CN{=}NCO_2R$ in Benzene at Reflux

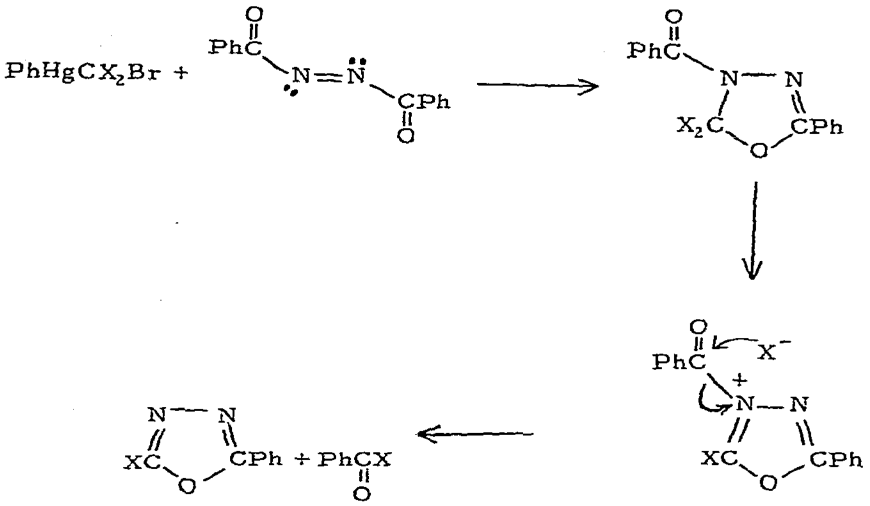
$RO_2CN{=}NCO_2R$	Product (yield, %)
$PhHgCCl_2Br$	
$MeO_2CN{=}NCO_2Me$	$(MeO_2C)_2NN{=}CCl_2$ (61)
$EtO_2CN{=}NCO_2Et$	$(EtO_2C)_2NN{=}CCl_2$ (87)
$Me_3CO_2CN{=}NCO_2CMe_3$	$(Me_3CO_2C)_2NN{=}CCl_2$ (38)
$PhCH_2O_2CN{=}NCO_2CH_2Ph$	$(PhCH_2O_2C)_2NN{=}CCl_2$ (53)
$PhO_2CN{=}NCO_2Ph$	$(PhO_2C)_2NN{=}CCl_2$ (34)
$PhHgCBr_3$	
$MeO_2CN{=}NCO_2Me$	$(MeO_2C)_2NN{=}CBr_2$ (47)
$EtO_2CN{=}NCO_2Et$	$(EtO_2C)_2NN{=}CBr_2$ (59)
$Me_3CO_2CN{=}NCO_2CMe_3$	$(Me_3CO_2C)_2NN{=}CBr_2$ (30)
$PhCH_2O_2CN{=}NCO_2CH_2Ph$	$(PhCH_2O_2C)_2NN{=}CBr_2$ (65)
$PhO_2CN{=}NCO_2Ph$	$(PhO_2C)_2NN{=}CBr_2$ (41)
$PhHgCBr_2Cl$	
$EtO_2CN{=}NCO_2Et$	$(EtO_2C)_2NN{=}CBrCl$ (55)
$Me_3CO_2CN{=}NCO_2CMe_3$	$(Me_3CO_2C)_2NN{=}CBrCl$ (15)



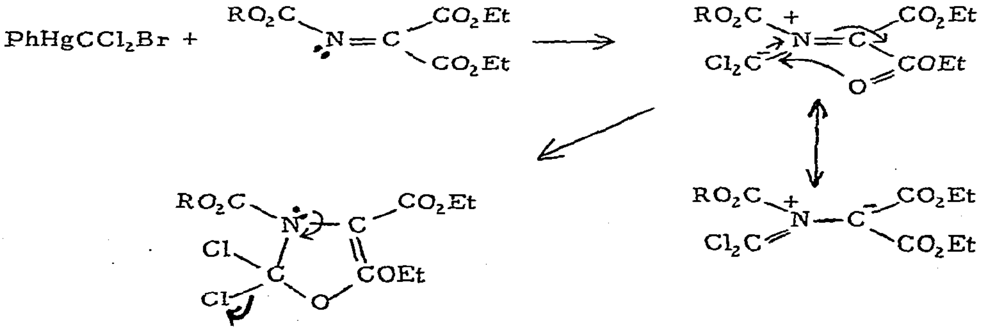
$(RO_2C)_2NN{=}CX_2$

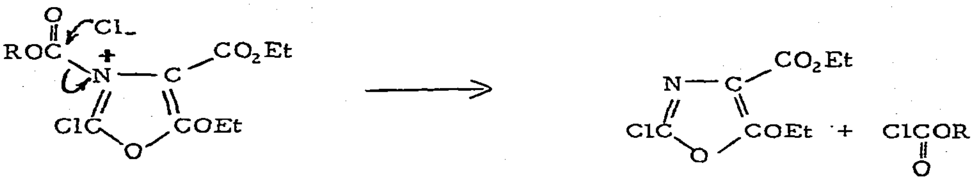


Phenyl(bromodichloromethyl)mercury reacted with azodibenzoyl at room temperature to give two organic products, benzoyl chloride and 2-chloro-5-phenyl-1,3,4-oxadiazole (54%). A similar reaction of $PhHgCBr_3$ gave 2-bromo-5-phenyl-1,3,4-oxadiazole (80%). The following mechanism was suggested (92):



A similar 1,4-addition took place in the reaction of $PhHgCCl_2Br$ with $RO_2CN{=}C(CO_2Et)_2$ (R = Me, Et). The products were the alkyl chloroformate and 2-chloro-4-carboethoxy-5-ethoxy-1,3-oxazole (92). A similar mechanism was proposed to account for the formation of these products:



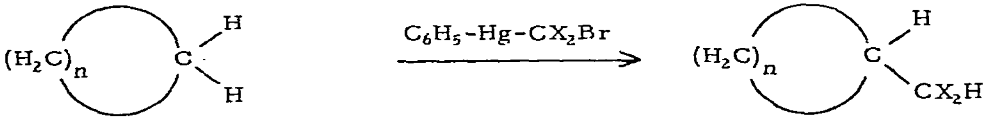


The 1:1 reaction of phenyl(trichloromethyl)mercury with a transition metal-carbene complex in benzene at 80° was studied by De Renzi and Fischer (71). Twenty percent of the carbene complex was consumed by the process shown in the equation below. However, much of the carbene complex was diverted by reaction with PhHgCl to give benzophenone and some methyl benzoate. A reaction with $PhHgCCl_2Br$ gave the

$$PhHgCCl_3 + (OC)_5CrC(OMe)Ph \longrightarrow PhHgCl + (MeO)(Ph)C{=}CCl_2$$

vinyl ether in somewhat lower yield. The mechanism of vinyl ether formation remains unknown, but a direct encounter between two carbenes, CCl_2 and C(OMe)Ph, seems unlikely.

Some insertion reactions of $PhHgCX_3$-derived dihalocarbenes have been described. Insertions into C-H bonds of cycloalkanes is a preparatively useful reaction (Table 8) (93):



Insertions into metal-bromine bonds of Group IV tetrabromides have been accomplished (94):

TABLE 8. Preparation of (Dihalomethyl)cycloalkanes using Phenyl(trihalomethyl)mercurials.

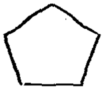
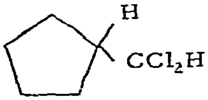
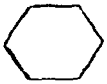
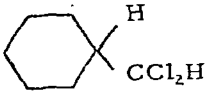
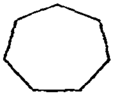
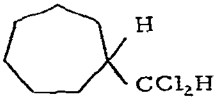
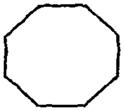
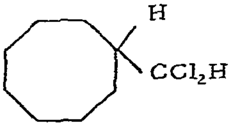
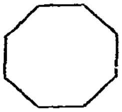
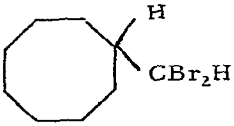
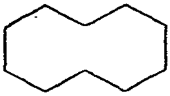
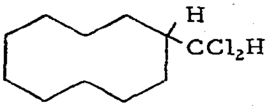
Cycloalkane (ml)	Mercurial (mmol)	(Dihalomethyl)-cycloalkane (% Yield)
 [a] (75)	C_6H_5-Hg-CCl_2Br (44)	 (57)
 (275)	C_6H_5-Hg-CCl_2Br (200)	 (32)
 (50)	C_6H_5-Hg-CCl_2Br (33.3)	 (48)
 (75)	C_6H_5-Hg-CCl_2Br (43.8)	 (83)
 (35)	C_6H_5-Hg-CBr_3 (22)	 (58)

TABLE 8. - continued

 (15)	C_6H_5-Hg-CCl_2Br (10)	 (64)

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[a] Reaction carried out in a sealed tube.

$$PhHgCCl_3 + NaI + SiBr_4 \xrightarrow{120^\circ} PhHgX + Br_3SiCCl_2Br \quad (30\%)$$

$$PhHgCCl_3 + NaI + GeBr_4 \longrightarrow PhHgX + Br_3GeCCl_2Br$$

$$PhHgCCl_3 + NaI + SnBr_4 \longrightarrow PhHgX + Br_3SnCClBr_2$$

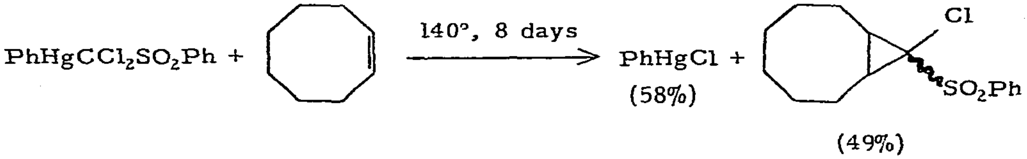
The unexpected product formed in the tin tetrabromide reaction was rationalized in terms of a second carbene transfer from the initially formed product:

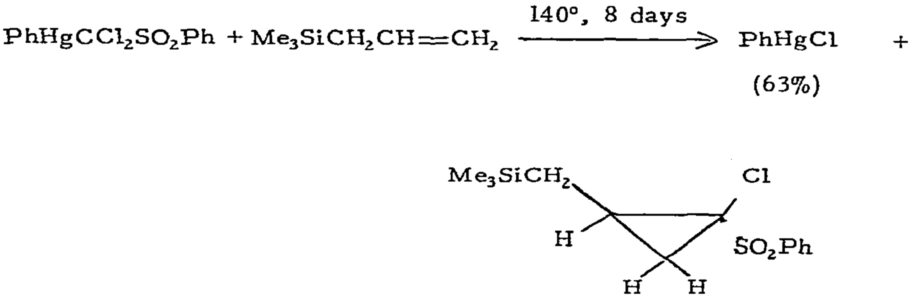
$$Br_3SnCCl_2Br + SnBr_4 \longrightarrow Br_3SnCClBr_2 + SnBr_3Cl$$

Some new functional halomethyl-mercury compounds have been reported. Phenyl(phenylsulfonyldihalomethyl)mercurials have been prepared and examined as reagents for the transfer of phenylsulfonylhalocarbene (95):

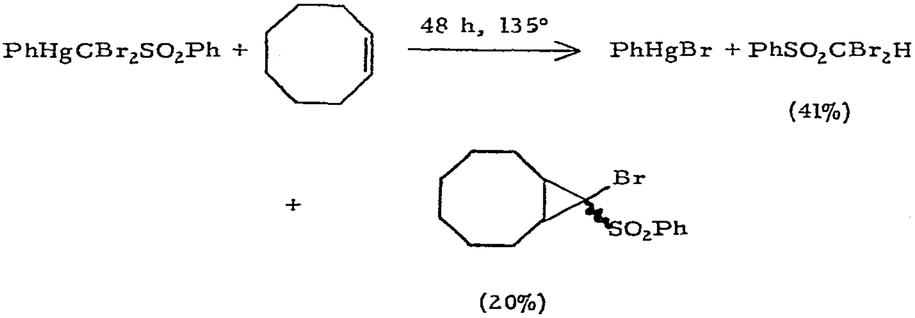
$$PhSO_2CX_2H + Me_3COK + PhHgCl \xrightarrow{THF,\ -60^\circ} PhHgCX_2SO_2Ph + Me_3COH + KX$$

$(X = Cl,\ Br)$





(47%; 1/1 isomer ratio)



High temperatures and long reaction times in sealed tubes were required to effect such reactions. However, decomposition of PhHg-CCl_2SO_2Ph via α-elimination was not the only process which occurred. The formation of substantial yields of $PhSO_2CX_2H$, metallic mercury and diphenylmercury indicated that a competing homolytic decomposition must be taking place as well:

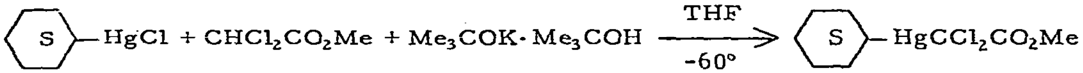
$$PhHgCCl_2SO_2Ph \longrightarrow PhHg^\bullet + {}^\bullet CCl_2SO_2Ph$$

$$2\ PhHg^\bullet \longrightarrow Ph_2Hg + Hg$$

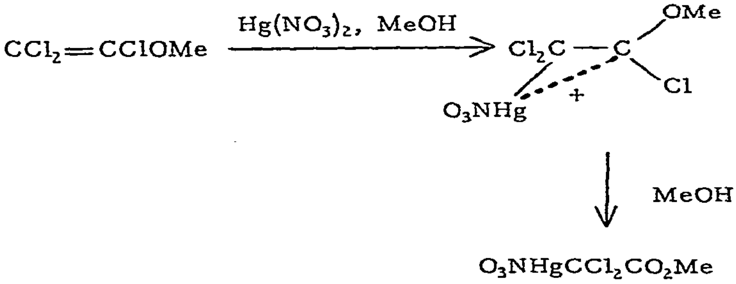
$$PhSO_2CCl_2^\bullet + R\text{-}H \longrightarrow PhSO_2CCl_2H + R^\bullet$$

New (dihalocarbomethoxymethyl)mercury compounds also were prepared in the hope of obtaining more useful reagents than the previously prepared $PhHgCXYCO_2Me$ compounds (95):

$$PhHgCl + CHClICO_2Me + Me_3COK\cdot Me_3COH \xrightarrow[-60^\circ]{THF} PhHgCClICO_2Me$$

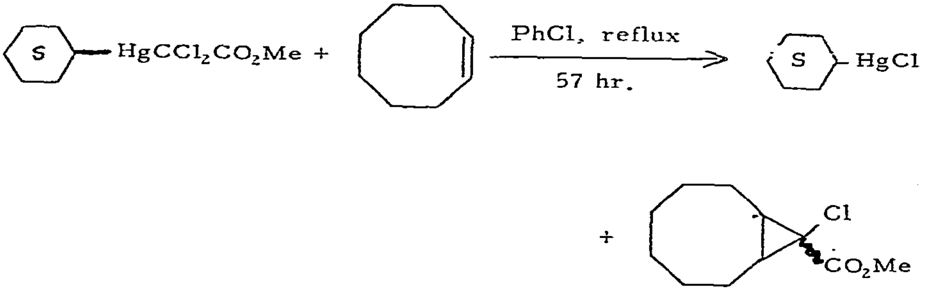


and



$$\begin{tikzcd}
O_3NHgCCl_2CO_2Me \arrow[r, "NaCl/H_2O"] & Hg(CCl_2CO_2Me)_2 + HgCl_2 \arrow[d, "(PhCH_2CH_2)_2Hg"'] \\
 & PhCH_2CH_2HgCCl_2CO_2Me
\end{tikzcd}$$

Of these, only the cyclohexyl derivative was a satisfactory $ClCCO_2Me$ transfer agent:

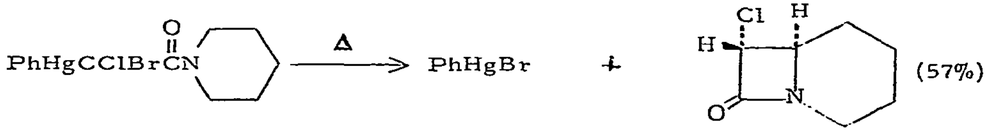


(78%)

$PhHgCHClCO_2Et$, prepared as shown below, was not effective as a $HCCO_2Et$ source. After it had been heated in cyclooctene at 155-160° for 3 days, it had decomposed only to the extent of 20%, and only a low yield of the two 9-carboethoxybicyclo[6.1.0]nonane isomers was obtained (95).

$$\begin{tikzcd}
CHCl{=}CClOEt \arrow[r, "Hg(OAc)_2/EtOH"] & AcOHgCHClCO_2Et \arrow[d, "NaCl/H_2O"] \\
 & ClHgCHClCO_2Et \arrow[dl, bend right] \\
 \arrow[r, "Ph_2Hg"] & PhHgCHClCO_2Et + PhHgCl
\end{tikzcd}$$

Amide-substituted halomethyl-mercury compounds also have been studied. $PhHgCCl_2C(O)NMe_2$, prepared by reaction of N,N-dimethyl dichloroacetamide with potassium tert-butoxide in the presence of phenylmercuric chloride in THF at -60°, gave little or none of the expected cycloaddition product when it was heated in cyclooctene at 148° (95). The amide 9, however, underwent phenylmercuric bromide elimination on being heated in bromobenzene at reflux, and an intramolecular C-H insertion of the carbene which was formed followed (96):



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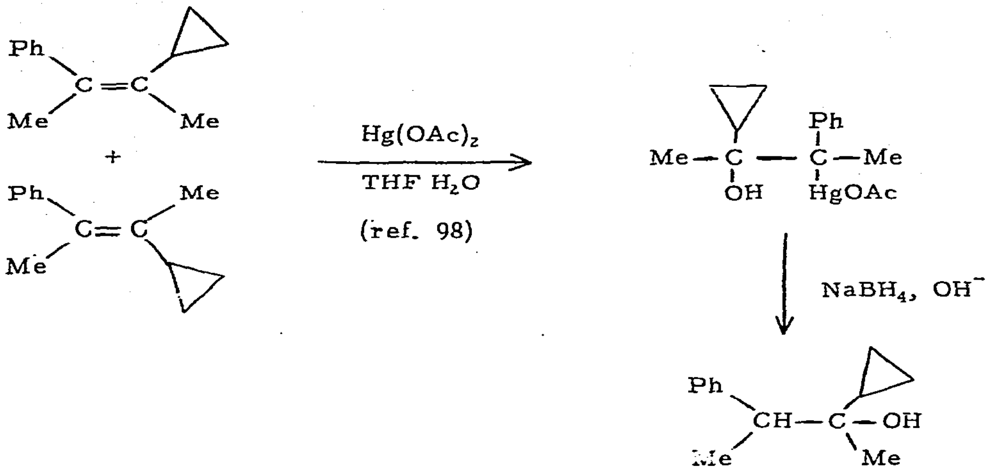
(Similar decomposition of the corresponding dichloro and dibromo mercurials had been reported previously: cf. J. Organometal. Chem., 75 (1974) 40).

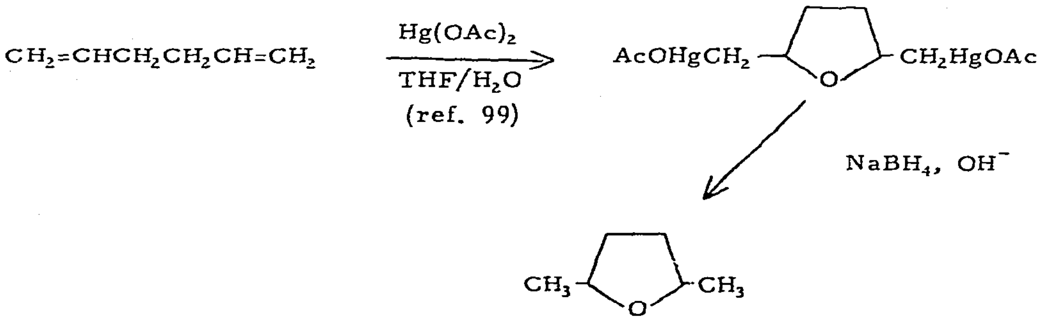
4. MERCURATION OF UNSATURATED COMPOUNDS

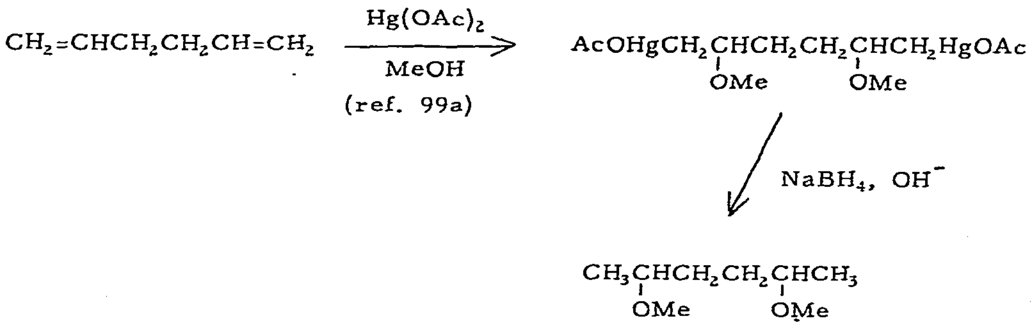
A. Olefins

The solvomercuration of olefins and the solvomercuration-demercuration synthesis of functional alkanes from olefins continue to be important aspects of organomercury chemistry.

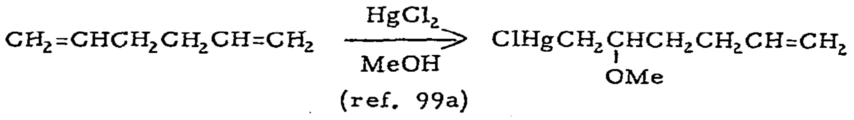
The preparation of 1-methylcyclohexanol, based on the oxymercuration-demercuration of cyclohexene, has been described in detail in a "Organic Syntheses" preparation (97). Other examples from the literature since last year's survey include the following:



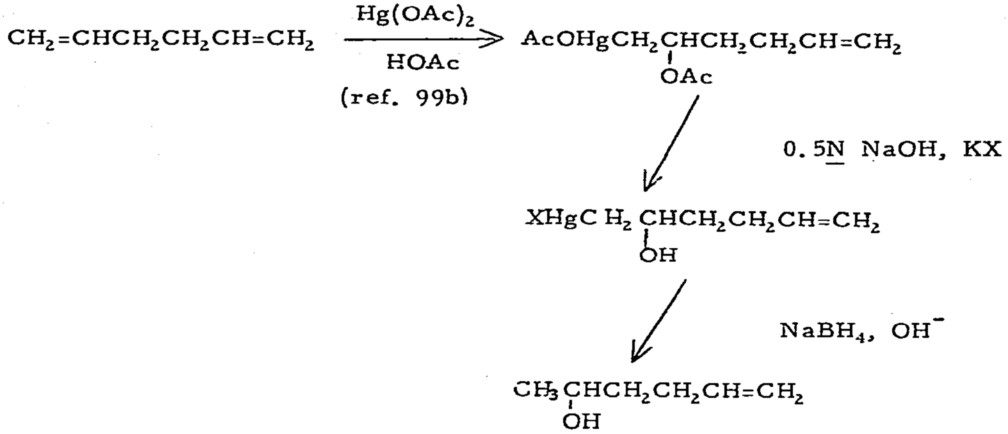


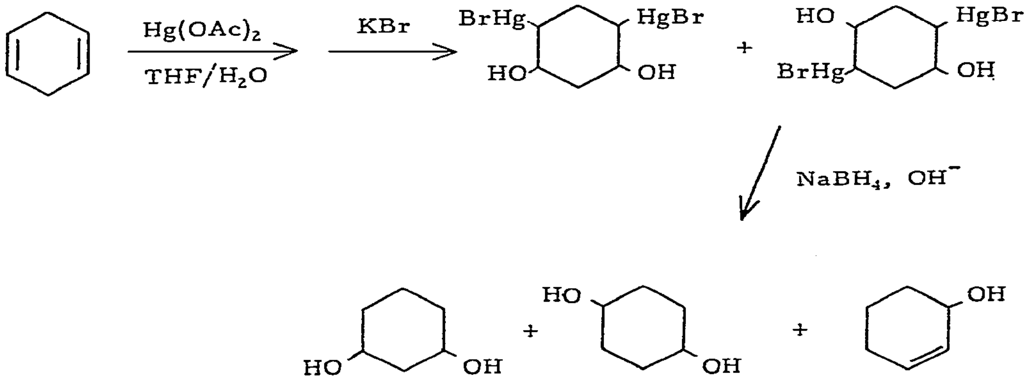


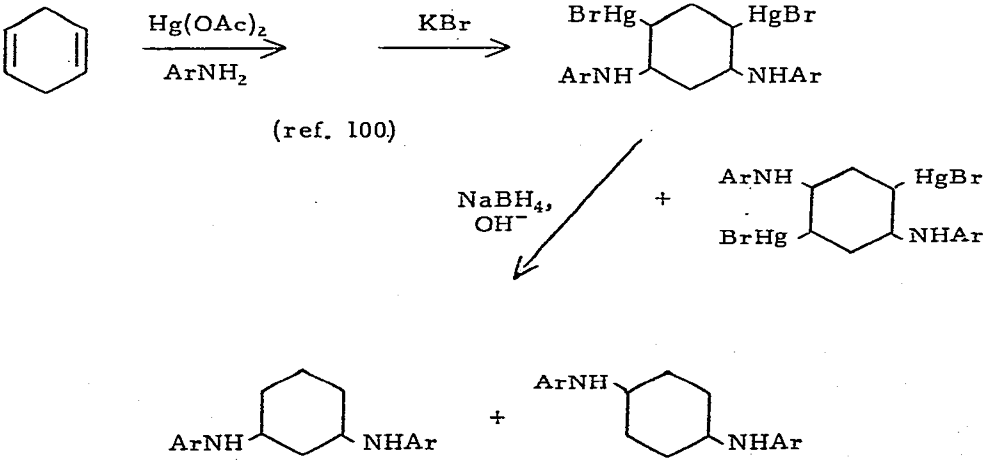
$$CH_2{=}CHCH_2CH_2CH{=}CH_2 \xrightarrow[\text{MeOH (ref. 99a)}]{Hg(OAc)_2} AcOHgCH_2\underset{|\atop OMe}{C}HCH_2CH_2\underset{|\atop OMe}{C}HCH_2HgOAc \xrightarrow{NaBH_4,\ OH^-} CH_3\underset{|\atop OMe}{C}HCH_2CH_2\underset{|\atop OMe}{C}HCH_3$$

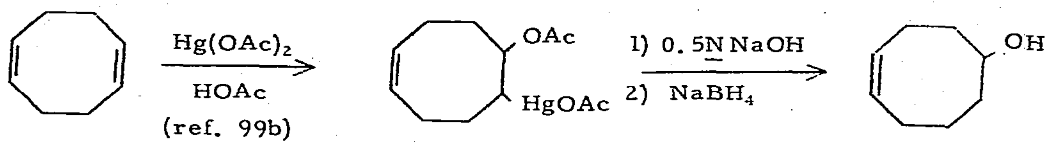


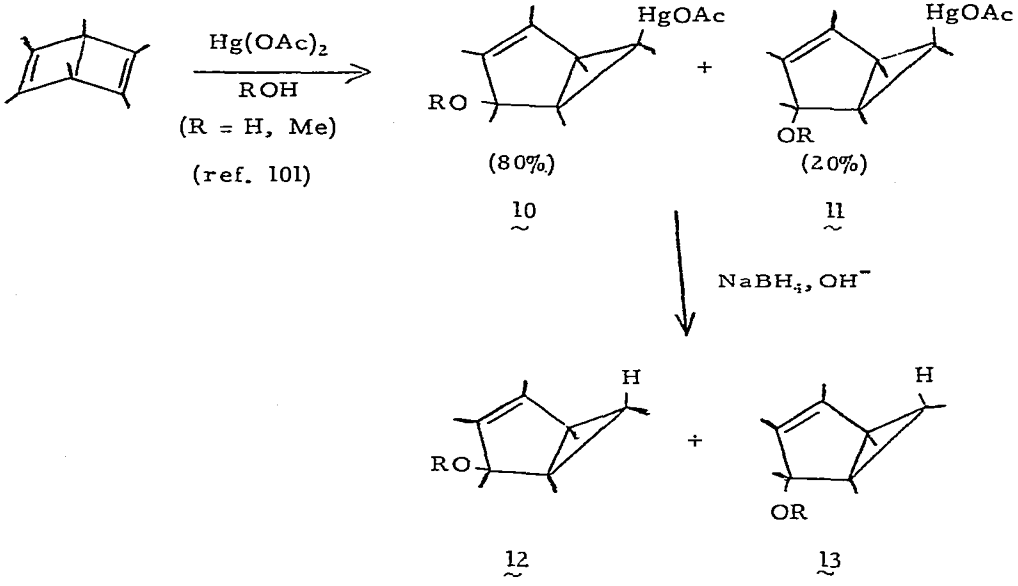
$$CH_2{=}CHCH_2CH_2CH{=}CH_2 \xrightarrow[\text{MeOH (ref. 99a)}]{HgCl_2} ClHgCH_2\underset{|\atop OMe}{C}HCH_2CH_2CH{=}CH_2$$


CH₂=CHCH₂CH₂CH=CH₂
Hg(OAc)₂
HOAc
(ref. 99b)
AcOHgCH₂CHCH₂CH₂CH=CH₂
OAc
0.5N NaOH, KX
XHgCH₂CHCH₂CH₂CH=CH₂
OH
NaBH₄, OH⁻
CH₃CHCH₂CH₂CH=CH₂
OH

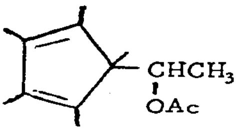

Hg(OAc)₂
THF/H₂O
KBr
BrHg
HgBr
HO
OH
+
HO
HgBr
BrHg
OH
NaBH₄, OH⁻
HO
OH
+
HO
OH
+
OH

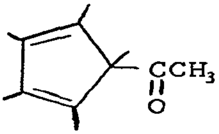

Hg(OAc)₂
ArNH₂
(ref. 100)
KBr
BrHg
HgBr
ArNH
NHAr
NaBH₄,
OH⁻
+
ArNH
HgBr
BrHg
NHAr
ArNH
NHAr
+
ArNH
NHAr

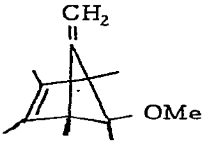




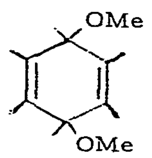
The mercury adducts must be reduced immediately after their preparation since they undergo decomposition with loss of elemental mercury in methanol or water solution. Thus, when the 10/11 mixture was kept in methanol at room temperature for times of minutes to hours, subsequent treatment with $NaBH_4$ gave not only 12 and 13, but also the following compounds:



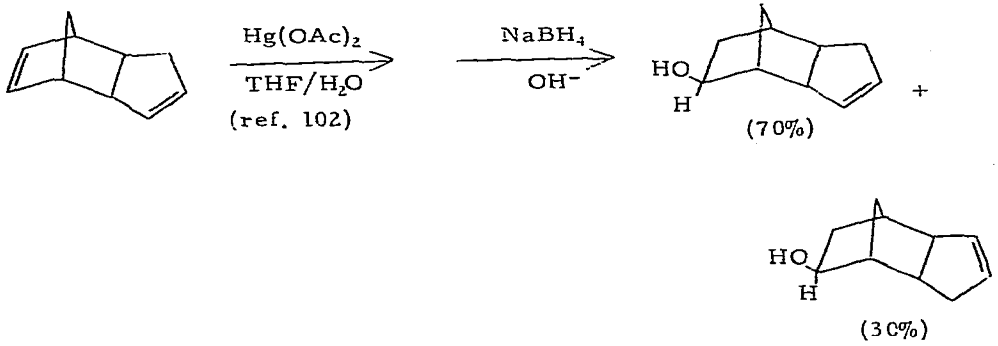


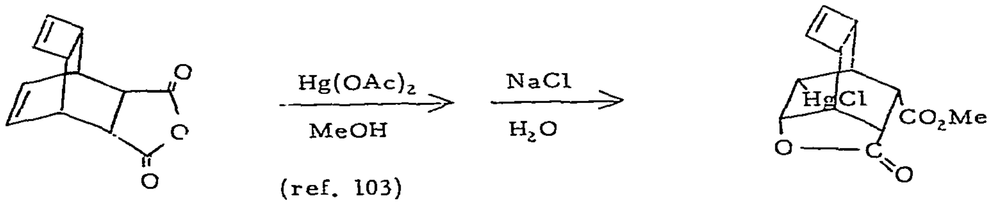


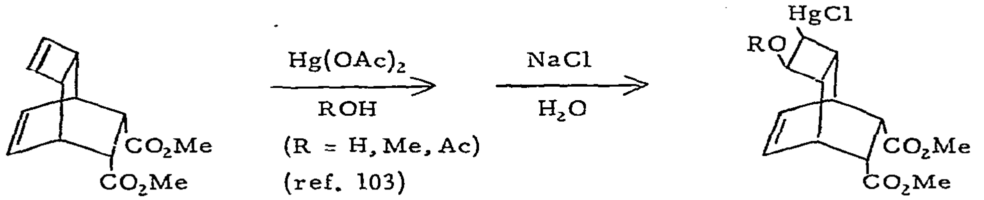
and

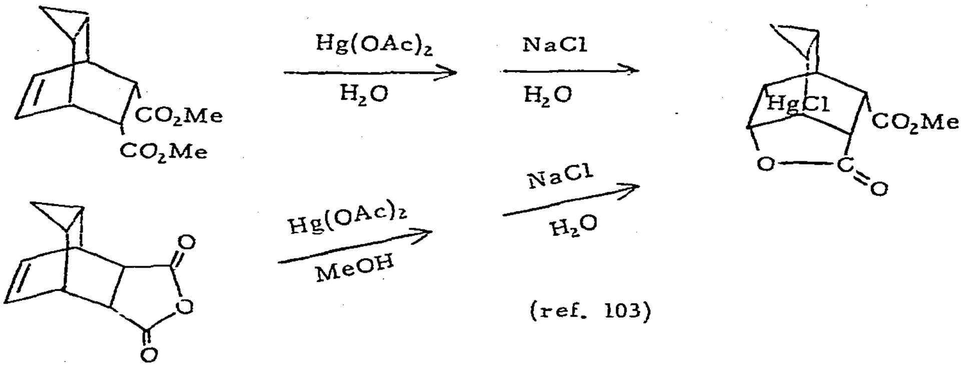


The possible mechanisms of these transformations were discussed.

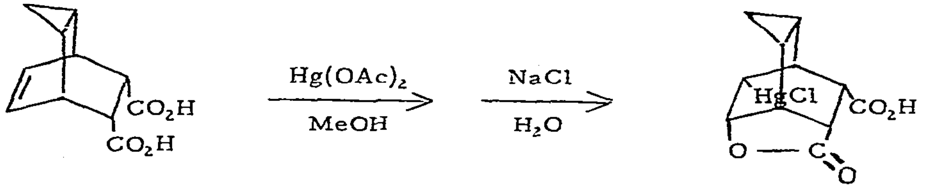




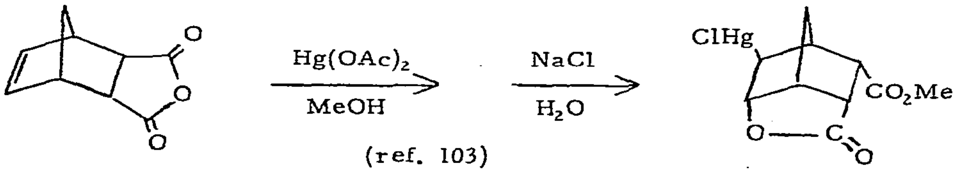




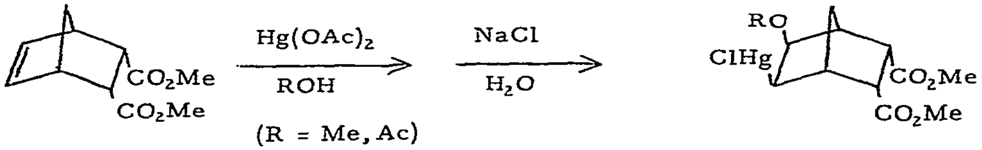
(ref. 103)



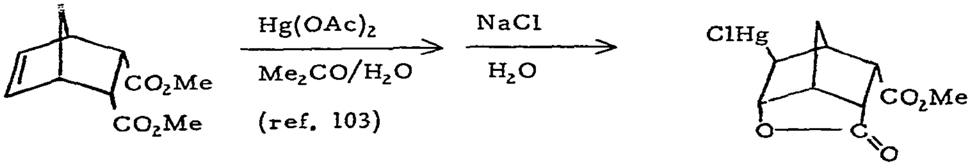
(ref. 103)



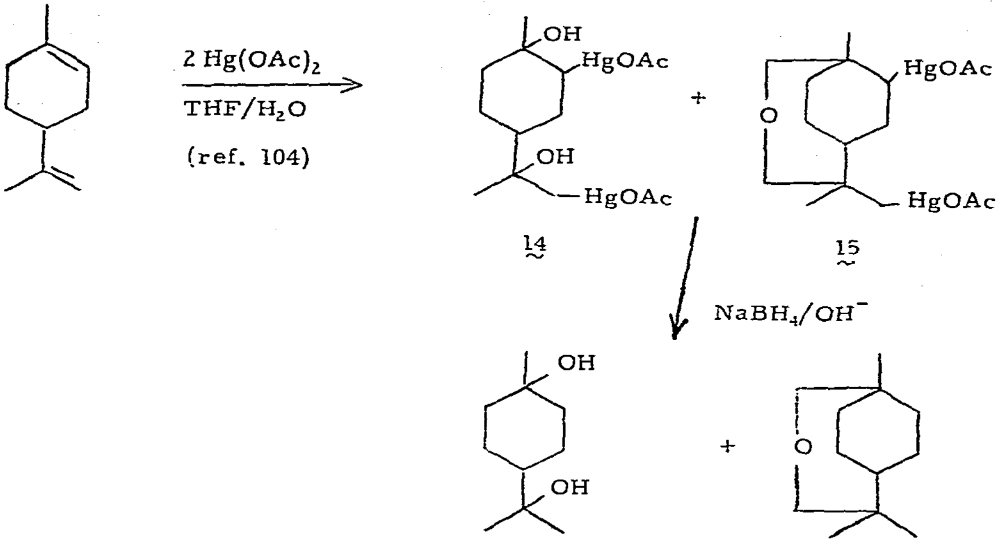
(ref. 103)

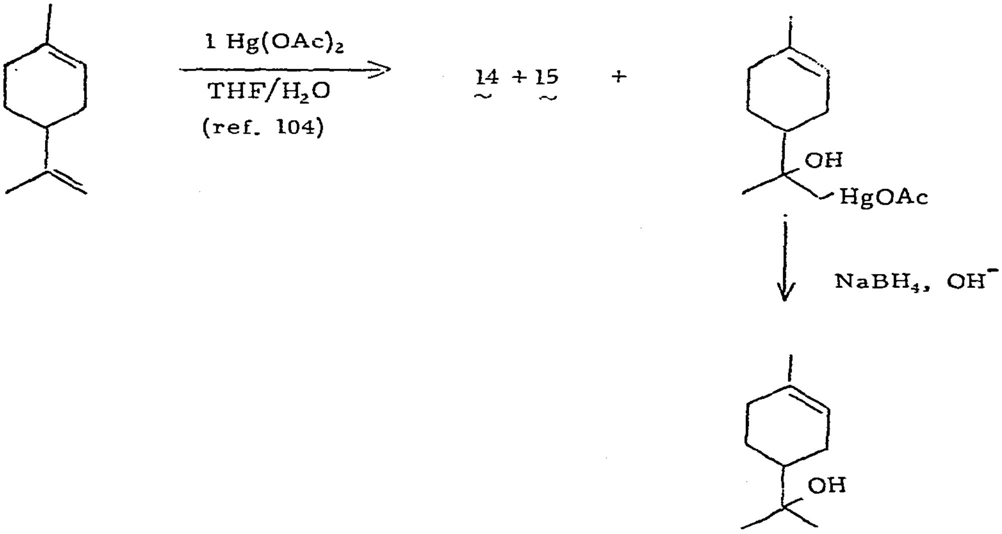


(ref. 103)

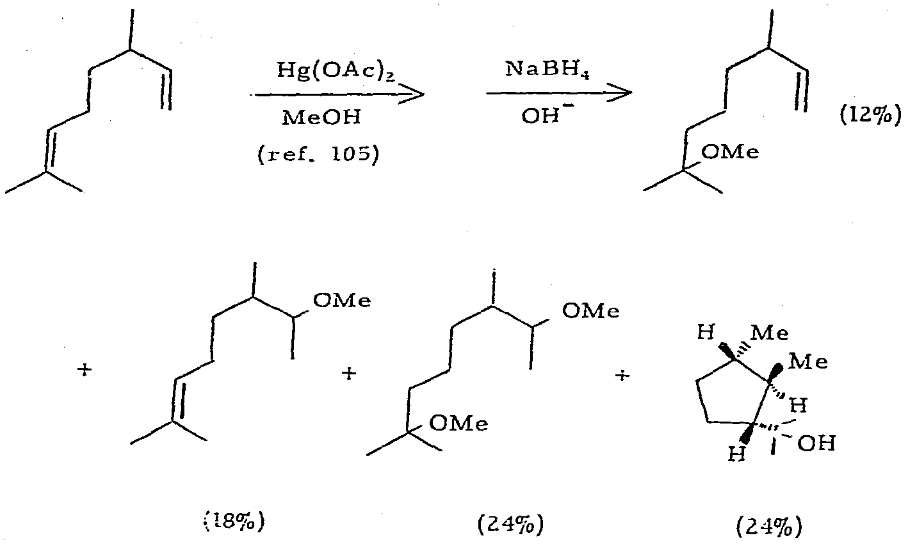


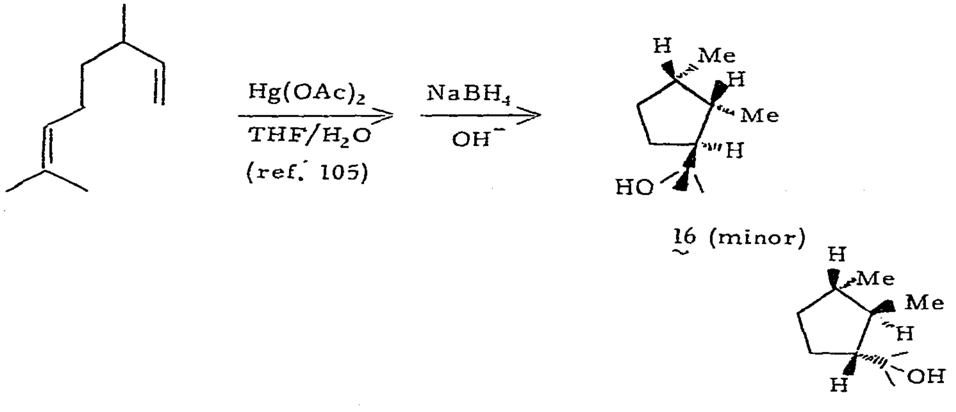
(ref. 103)





(It was shown that the first OH group introduced via oxymercuration of the side chain double bond enhances the reactivity of the internal double bond).

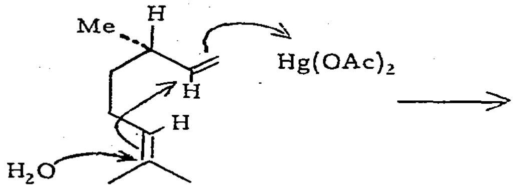




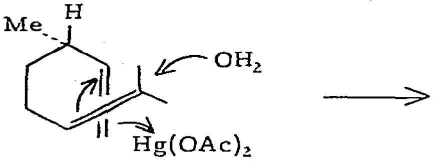
16 (minor)

17 (major)

It was stated that cyclization in the above cases predominates in the water system (vs. the reaction in methanol) because a water/THF interaction retards the reaction of water as a nucleophile (105):

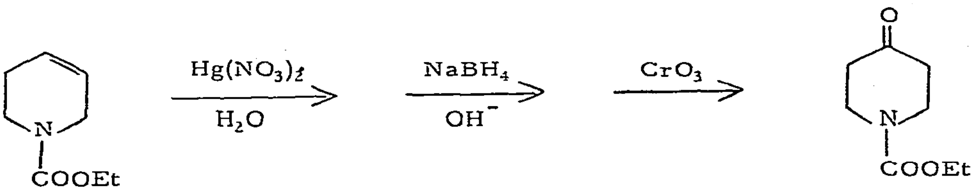


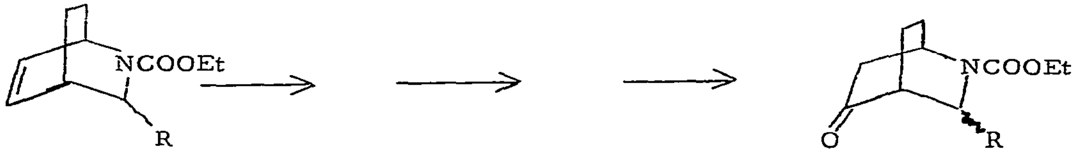
17



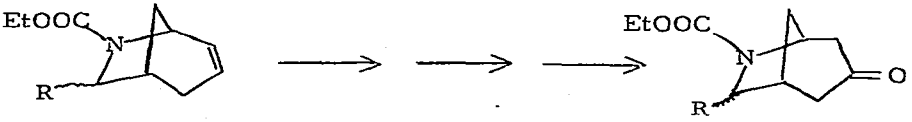
16

Proximate urethane functions have been shown to have a specific directing effect on the regioselectivity of oxymercuration, as shown by Krow and Fan (106) in their study of "ketofunctionalization" of olefins. Among the reactions described are the following:

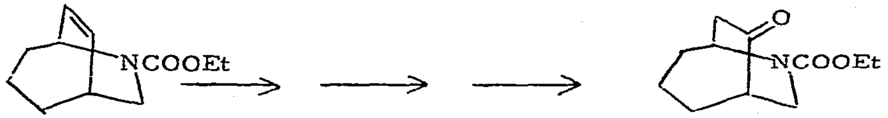


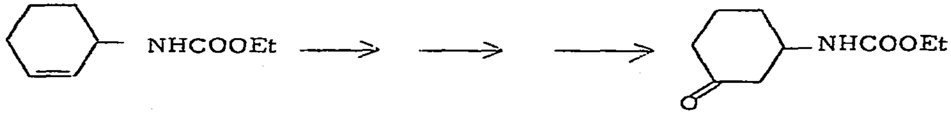


(R = H, Ph)

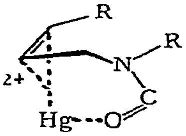


(R = H, Ph, CCl_3)

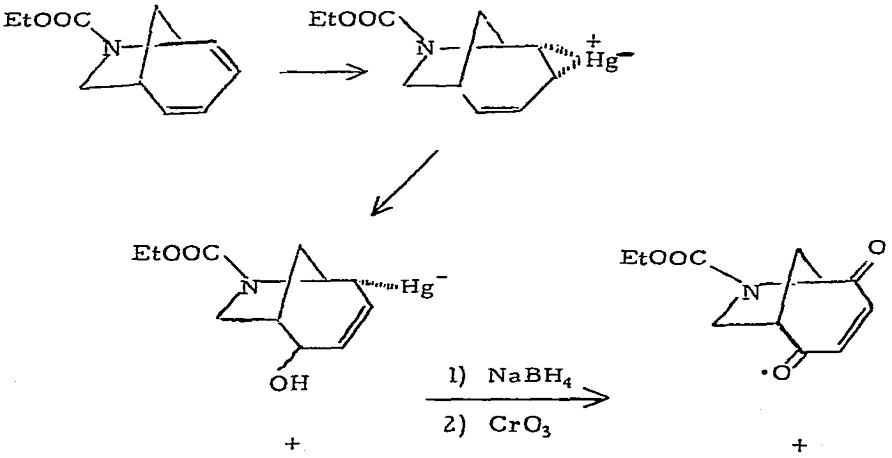


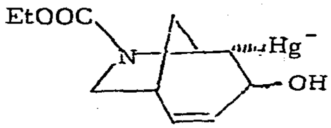


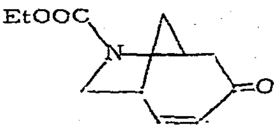
Coordination of the urethane carbonyl at the mercuric ion of the reagent was believed responsible for this useful regioselectivity:



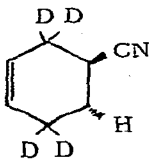
With a bicyclic dienic urethane, the reaction course was more complicated:



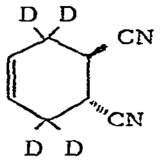




In contrast, the results obtained with the oxymercuration of the nitriles 18 and 19 in CD OD suggested that prior coordination at the nitrile groups did not occur (107).

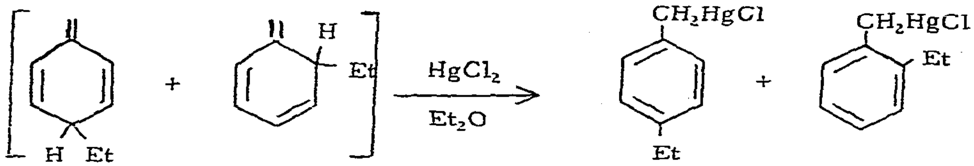


18



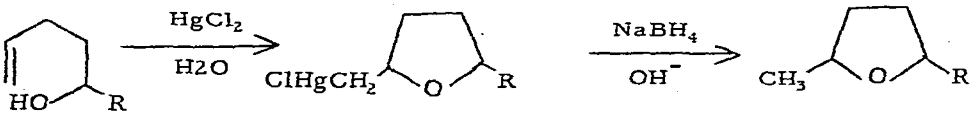
19

An interesting aromatization reaction involving mercuric chloride attack on the triene mixture 20 has been reported by Reutov and his coworkers (108):

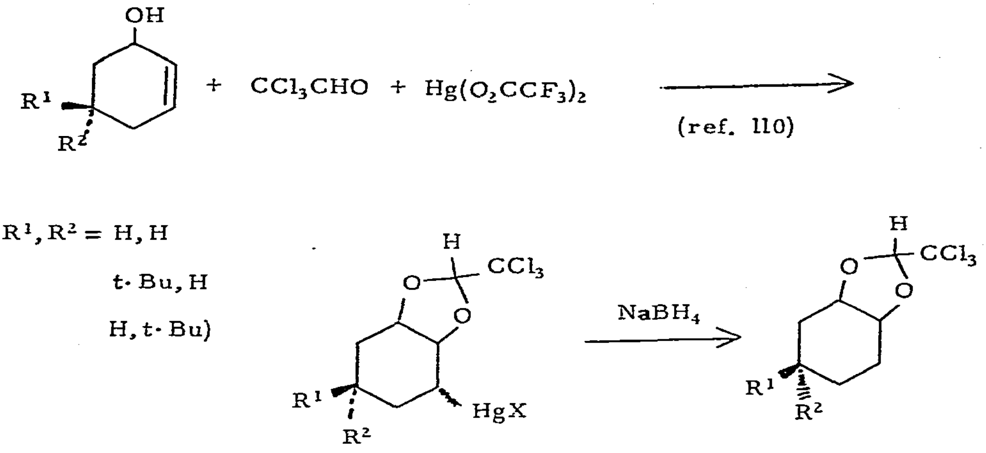


20

More examples of olefin mercurations have been reported in which cyclization occurred:

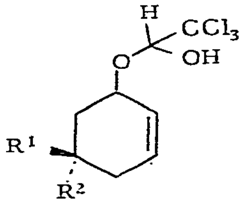


(R = Me, Me_3C, Ph) (ref. 109)



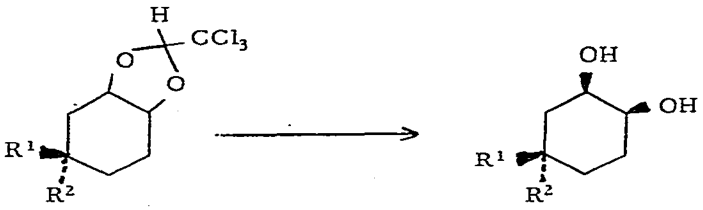
(R^1,R^2 = H,H
t-Bu,H
H,t-Bu)

The intermediate which is mercurated in these reactions is 21. This

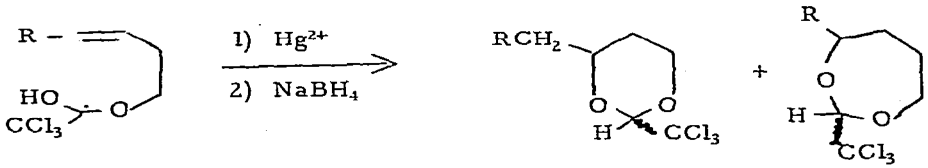


21

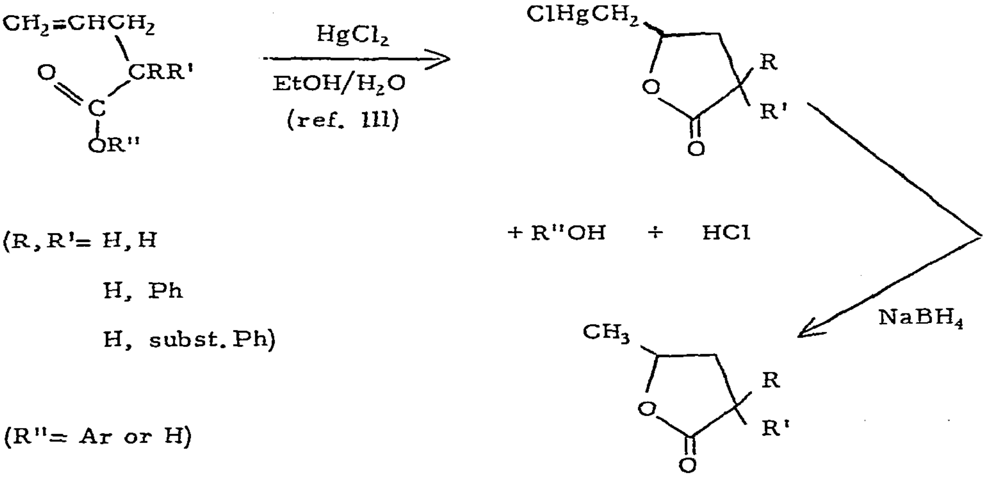
reaction is a useful route to diols since the acetals produced can be reductively cleaved by sodium in ether or zinc in acetic acid:



Further examples were provided (110):



(R = Et, n-Pr)



(R,R'= H,H

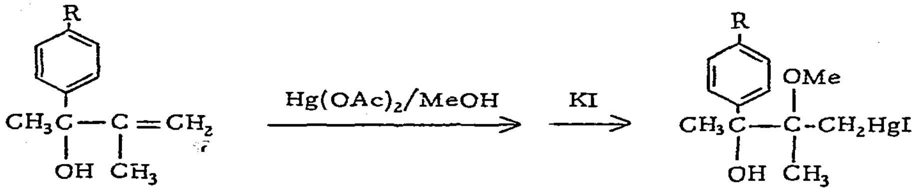
H, Ph

H, subst. Ph)

(R''= Ar or H)

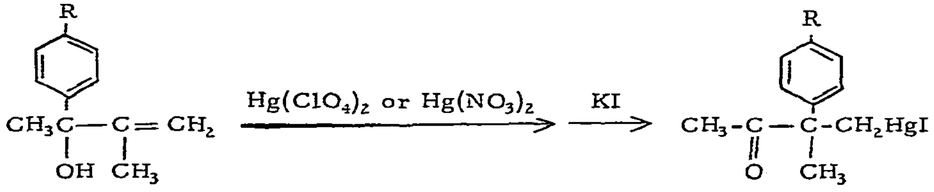
The kinetics of these reactions were studied. The rate law R = k_2(ester)($HgCl_2$) was followed.

Skeletal rearrangements in oxymercuration reactions are very rare, but some do occur. Russian workers have shown that the more ionic the inorganic mercury reagent used, the more likely are such rearrangements (112):

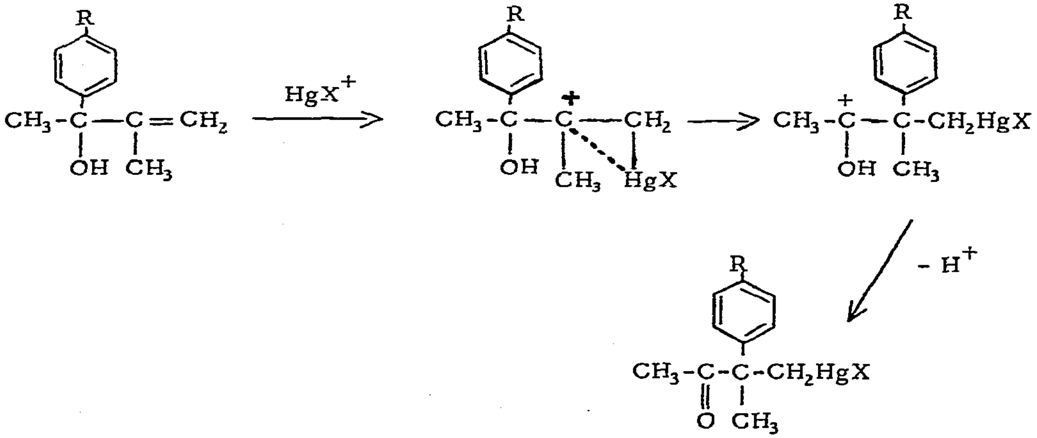


(R = Me, OMe)

but:



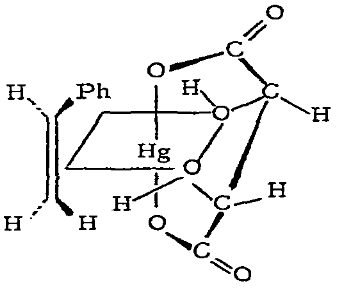
The ketone was formed by way of a 1,2-phenyl shift:



Asymmetric synthesis in solvomercuration reactions is possible when optically active mercuric carboxylates are used (113):

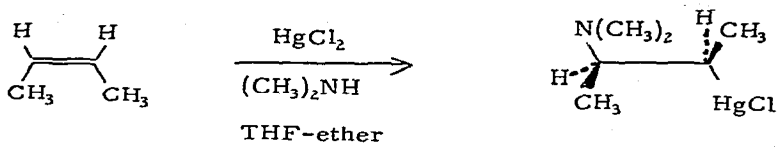
$$\mathrm{PhCH{=}CH_2} \xrightarrow[\mathrm{THF/H_2O}]{\mathrm{Hg(O_2CR^*)_2}} \xrightarrow[\mathrm{OH^-}]{\mathrm{NaBH_4}} \mathrm{Ph\text{-}}\overset{*}{\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{C}}}\mathrm{HCH_3}$$

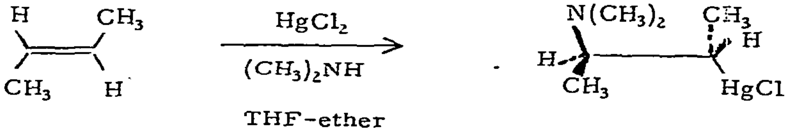
Of the optically active mercury(II) carboxylates examined, mercuric tartrate was the only one which gave relatively high (25-30%) optical yields. An intermediate of the type 22 was suggested for this reaction.



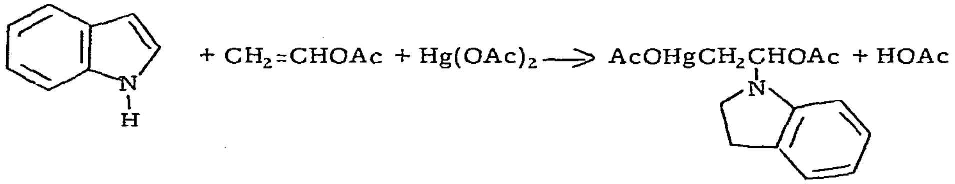
22

De Brule and Hess (114) have reported that when aminomercurations of gaseous olefins are carried out at higher pressures (350 psig), the reactions proceed much more rapidly and give higher product yields. Moreover, in contrast to the reactions carried out at atmospheric pressure, the products are obtained as nicely crystalline materials. Examples provided included the synthesis of the aminomercuration products $C_5H_{10}NCH_2CH_2HgCl$, $Et_2NCH_2CH_2HgCl$ and $Me_2NCHMeCHMeHgCl$. The stereochemistry of the aminomercuration of the isomeric 2-butenes has been studied (115). Trans-addition with complete stereospecificity was found:





Heterocyclic amines such as indole and carbazole also are capable of participating in olefin aminomercuration (116):

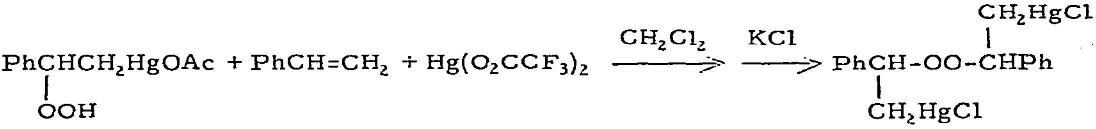


(β -Acetoxymercuriindole, the aromatic mercuration product, was a by-product in the absence of water). Carbazole was much less reactive than indole.

Peroxymercuration of olefins (without the acyloxymercuration which usually accompanies this reaction when mercuric acetate is used) can be effected in high yield when mercuric trifluoroacetate is used (117):

$$\mathrm{RCH{=}CHR' + Hg(O_2CCF_3)_2 + Me_3COOH \xrightarrow{CH_2Cl_2} CF_3CO_2H + RCH(OOCMe_3)CH(R')HgO_2CCF_3}$$

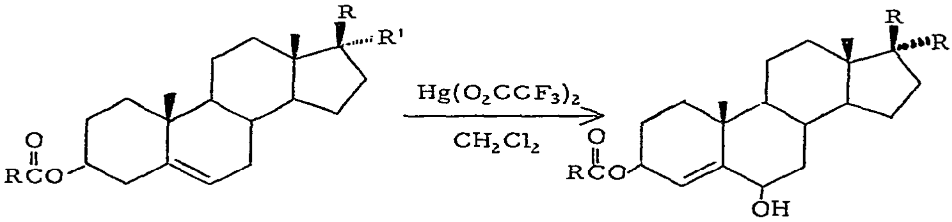
The fact that $Hg(O_2CCF_3)_2$ is soluble in dichloromethane has obvious advantages, including new possibilities of reactions with poorly soluble substrates, e.g.:

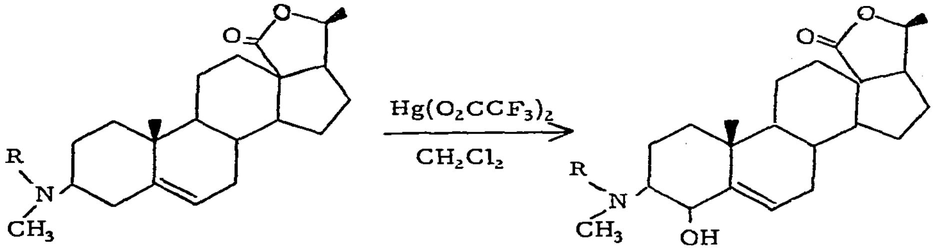


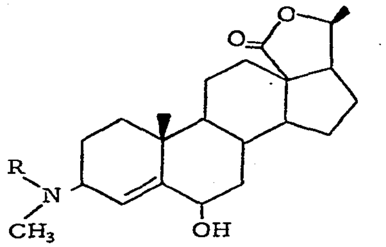
$$\underset{OOH}{PhCHCH_2HgOAc} + PhCH{=}CH_2 + Hg(O_2CCF_3)_2 \xrightarrow{CH_2Cl_2} \xrightarrow{KCl} Ph\underset{CH_2HgCl}{CH}\text{-}OO\text{-}\overset{CH_2HgCl}{CH}Ph$$

Calculations on the electronic structure of the Hg(II)-ethylene complex have been carried out using the CNDO-MO method (118). Also the subject of such calculations has been the attack of hydroxide ion on such a complex to give the β-hydroxyethylmercurial.

Oxidation of olefins by mercury(II) salts involves oxymercuration products, and, in some cases, allylic mercurials, as intermediates. In new examples, allylic oxidations of some steroidal olefins by mercuric trifluoroacetate have been described (119):

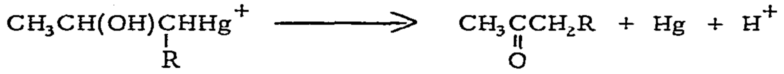






Oxidation of olefins to alcohol, aldehyde and ketone products also can be carried out catalytically using mercury(II) salts supported on active charcoal (which has been pretreated with nitric acid) in the presence of oxygen and steam (Tables 9 and 10) (120). A mechanism similar to that of the homogeneous process was indicated.

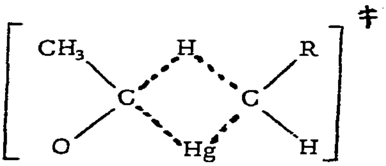
Kinetic deuterium isotope effects on the redox demercuration of olefin oxymercuration products in aqueous solution have been studied by ^1H NMR spectroscopy (121):



$$CH_3CH(OH)\underset{R}{\underset{|}{C}}HHg^+ \longrightarrow CH_3\underset{O}{\underset{\|}{C}}CH_2R + Hg + H^+$$

$(R = H,\ CH_3)$

Mercurials deuterated either on the β -carbon atom (e.g., $CH_3CD(OH)$-CH_2Hg^+) or on the α -carbon atom (e.g., $CH_3CH(OH)CHDHg^+$) showed primary and secondary deuterium isotope effects of 1.35-1.40 and 1.17-1.19, respectively. On the basis of these results, a transition state of type 23 was suggested.



23

TABLE 9. Oxidation of Olefins Over Mercuric Chloride-Charcoal Catalyst (ref. 120).

Olefin	Conversion[a] (%)	Product distribution (%)							
		Methyl vinyl ketone	Methyl vinyl carbinol	Unsaturated aldehyde	Unsaturated alcohol	Saturated ketone	Saturated alcohol	Acetaldehyde	Carbon dioxide
Ethylene	0.049	0	0	0	0	0	0	0	100.0
Propylene	0.64	0	0	59.2[b]	3.2[c]	2.4[d]	12.9[e]	2.6	19.7
1-Butene	2.39	64.5	15.7	5.6[f]	4.4[g]	0.8[h]	0	0.3	4.1
cis-2-Butene	0.70	39.9	4.7	4.3[f]	3.6[g]	4.7[h]	24.7[i]	4.7	7.4
trans-2-Butene	0.49	36.9	4.7	10.0[f]	3.0[g]	3.9[h]	18.9[i]	4.7	14.0
Isobutene	21.3	0	0	78.9[j]	1.9[k]	0	7.8[l]	0.1	2.1

Experimental conditions: temp, 140°C; W/F = 18-19 g-cat hr/mol; reaction feed ratio, olefin:oxygen: water = 1.0:1.0:10.0; total pressure, 1 atm; catalyst, 5.0 wt%.

[a] Olefin basis.

[b] Acrolein.

[c] Allyl alcohol.

[d] Acetone.

[e] Isopropyl alcohol.

[f] Croton aldehyde.

[g] Crotonyl alcohol.

[h] Methylethylketone.

[i] sec-butyl alcohol.

[j] Methacrolein.

[k] Methallyl alcohol.

[l] tert-butyl alcohol.

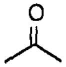
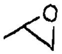
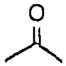
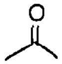
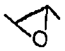
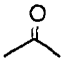
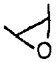
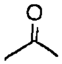
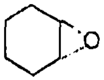
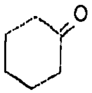
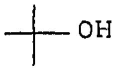
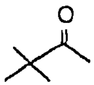
TABLE 10. Oxidation of Propylene Over Mercuric Salt-Charcoal Catalysts (ref. 120).

Salt[a]	Propylene Conversion (%)	Product distribution (%)						
		Acrolein	Allyl alcohol	Acetone	i-Propyl alcohol	Acetal-dehyde	Carbon dioxide	Others
$HgCl_2$	3.5	77.6	4.6	0.9	3.2	1.4	10.3	2.0
$Hg(CH_3COO)_2$	4.1	80.8	4.3	1.0	0.4	1.4	10.2	1.9
$Hg(CF_3COO)_2$	2.5	46.8	2.5	0.2	1.2	0.7	14.3	34.8
$HgBr_2$	2.1	78.1	7.5	0.8	1.5	1.4	5.5	5.2
$HgSO_4$	3.6	41.0	2.7	6.3	36.9	0.6	6.9	5.6
HgI_2	2.8	61.5	4.2	0.1	0.4	6.3	21.1	6.5

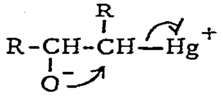
Experimental conditions: 160°C; total pressure, 1 atm; mole ratio, propylene:oxygen:water = 1.0:1.0:10.0; W/F = 14-15 g-cat hr/mol.

[a] Mercuric salts supported are 5.0 wt% as metallic mercury.

TABLE II. Oxidation of Olefins with Mercuric Salts at pH 13 (ref. 122)

Substrate	Salt	Products (%)				Total yield, %
Propene	$HgSO_4$		(6)		(94)	51
Propene	$Hg(OAc)_2$		(4)		(96)	43
1-Butene	$HgSO_4$		(7)		(93)	30
2-Butene (trans)	$HgSO_4$		(64)		(36)	72
2-Butene (cis)	$HgSO_4$		(44)		(56)	62
Cyclohexene	$HgSO_4$		(84)		(16)	48
Isobutene	$HgSO_4$		(32)		(68)	63
2, 3-Dimethyl-2-butene	$HgSO_4$		(100)			

The decomposition of such β-oxyalkylmercurials in basic aqueous medium, on the other hand, gave a mixture of saturated ketone and epoxide (Table 11) (122). A *trans*-intramolecular attack to give the epoxide was believed to be involved in a path parallel to that of ketone formation:



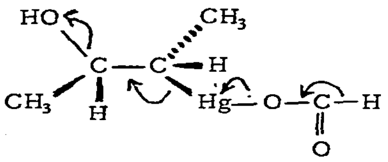
$$\mathrm{R{-}\underset{O^-}{CH}{-}\overset{R}{CH}{-}Hg^+}$$

Such oxidative decomposition also could be effected in basic alcoholic medium. Thus such a reaction of $CH_3CH(OH)CH_2HgCl$ in sec-butyl alcohol in the presence of sec-BuOK at 82° gave an 83% yield of a product mixture containing 87% propylene oxide, 11% acetone and 2% isopropanol.

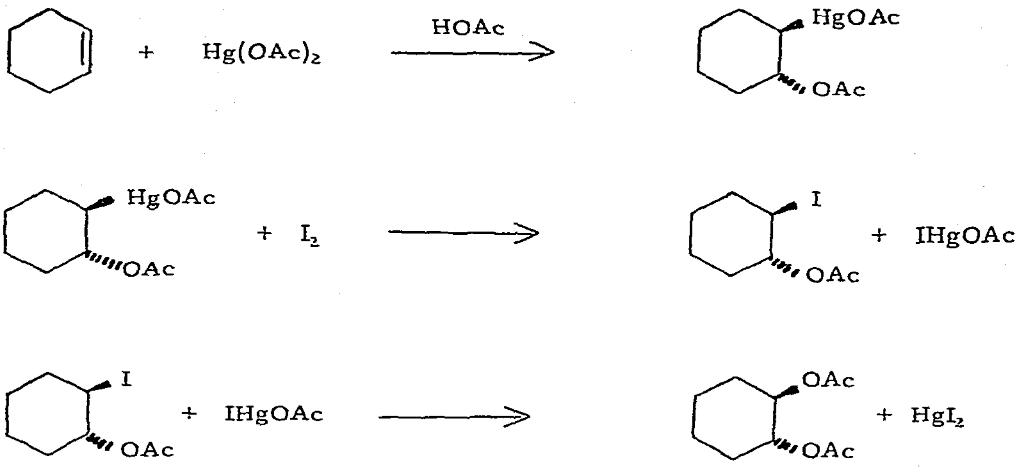
A redox-type reaction also was found to occur when $CH_3CH(OH)CH_2$-$HgClO_4$ was treated with sodium formate in aqueous solution (123):

$$CH_3CH(OH)CH_2Hg^+ + HCO_2^-Na^+ \longrightarrow CH_3CH{=}CH_2 + Hg + CO_2 + H_2O + Na^+$$

A mechanistic study (by NMR techniques) indicated that the reaction involves a unimolecular redox decomposition of a formato-mercurial intermediate, with an *anti*-elimination of the olefin:



The diacetyloxylation or dihydroxylation of olefins by the $Hg(OAc)_2/I_2/HOAc$ system was shown to proceed by way of an intermediate oxymercuration product (124):



B. Cyclopropanes

A study of the stereochemistry of the ring-opening methoxymercuration of some cyclopropanes (various stereoisomers of 1,2,3-trimethyl-1-phenyl-, 2,3-dimethyl-1-phenyl-, and 2,3-dimethyl-1-methoxy-cyclopropane) with mercuric trifluoroacetate suggested that a corner-mercurated cyclopropane is formed in the rate-determining step. This then is opened by nucleophilic attack by the solvent (125). In general, the $HgO_2CCF_3^+$ species reacts at the least substituted ring bond and ring opening occurs in the direction of the more stable carbonium ion. Both steps ($HgO_2CCF_3^+$ attack and nucleophilic ring opening) can occur with retention or inversion of configuration. The stereochemical results are summarized in Table 12. In the case of cis-1,2,3-trimethylcyclopropane, these processes would be:

TABLE 12. Cyclopropane Ring Opening by Mercuric Acetates in Methanol: Stereochemical Results (ref. 125).

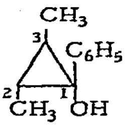
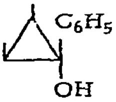
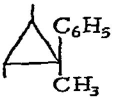
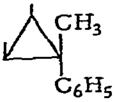
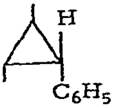
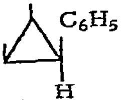
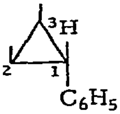
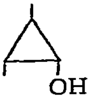
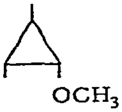
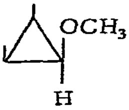
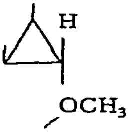
Cyclopropane	Hg^{2+} ret:inv		CH_3OH ret:inv	
	0	100		
	0	100		
	0	100	0	100
	0	100	0	100
	0	100	0	100
	88	12	10	90[b]
	18	82	9	91

TABLE 12 - continued

	28	72	25	75
	95	5		
	90	10		
	60	40		
	5	95		
	38	62	0	100

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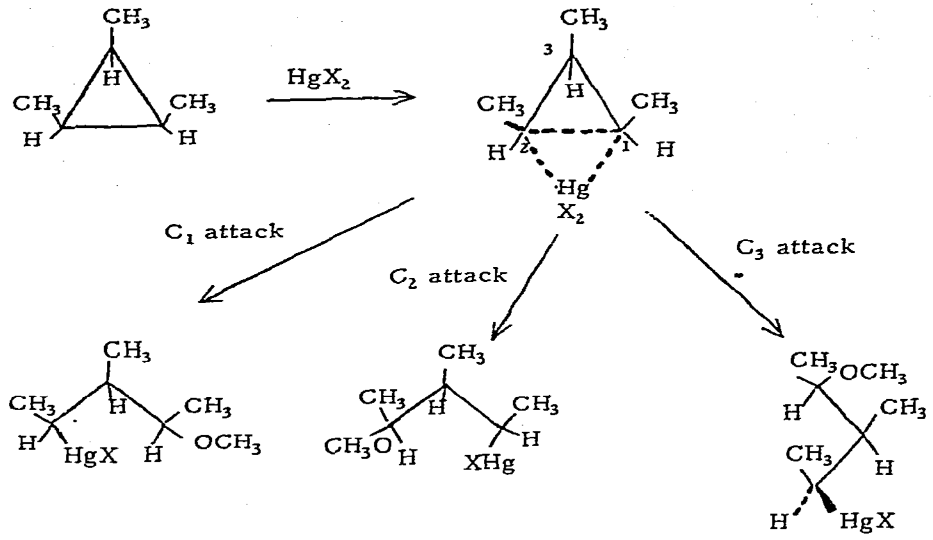
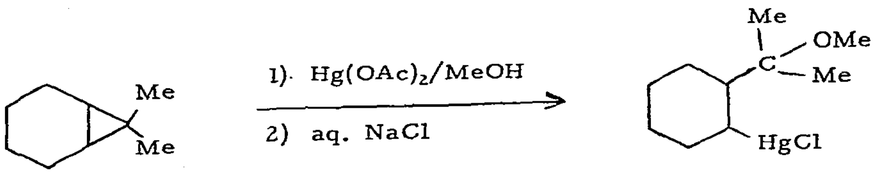
[b] Only C_1-C_2 cleavage is assumed.

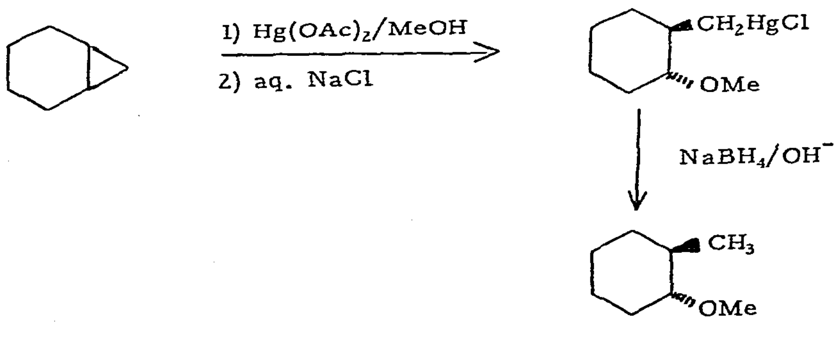


Jensen and his coworkers (126) have investigated the stereochemistry of similar reactions of 7,7-dimethylnorcarane and of norcarane:

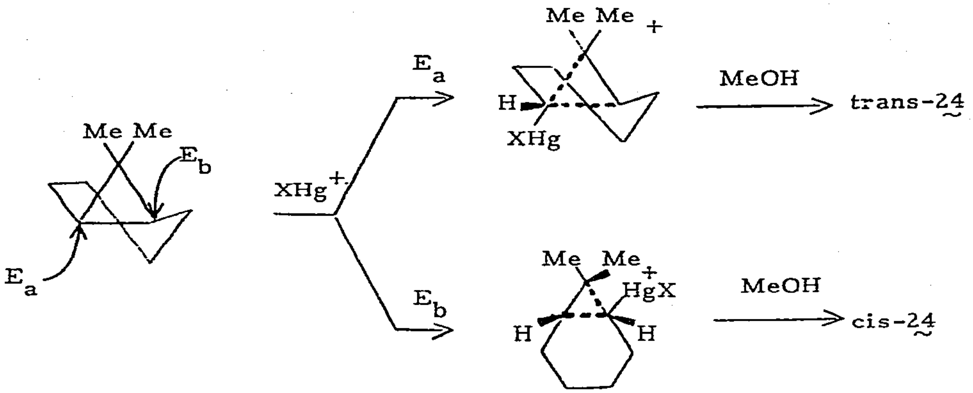


24

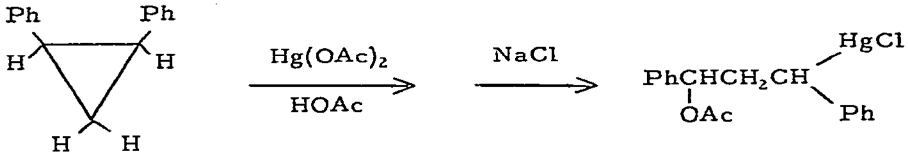
(83% trans, 17% cis)



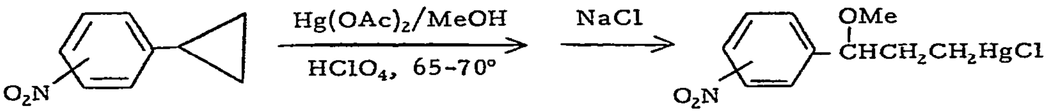
A corner-mercurated intermediate was suggested:

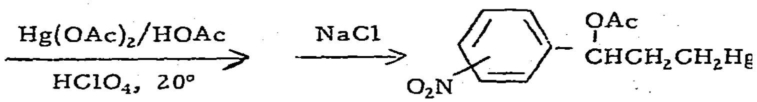


The methoxymercuration of cis-1,2-diphenylcyclopropane could not be effected under conditions which served well with the trans isomer. However, acetoxymercuration of this compound in acetic acid at 75-80° did occur (127):

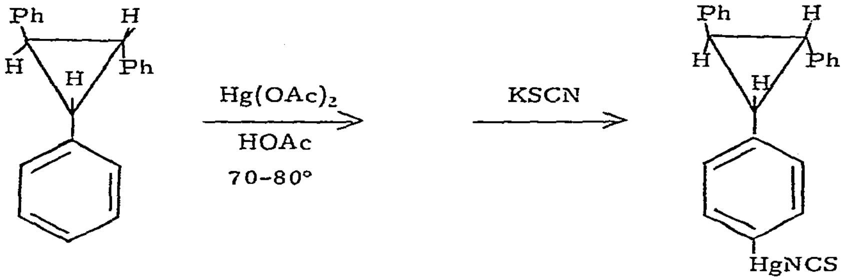


o- and p-Nitrophenylcyclopropane were resistant to even these forcing conditions, but ring opening did take place in the presence of perchloric acid (128):

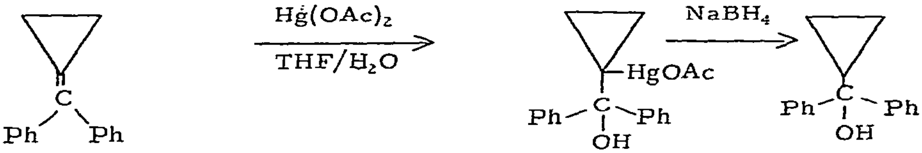




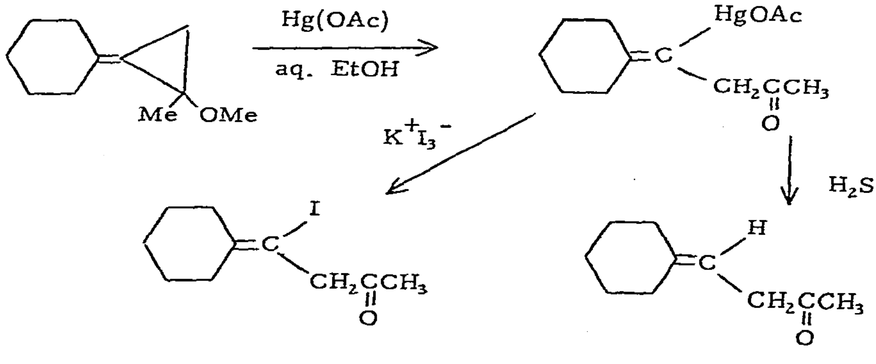
<u>trans</u>-1,2,3-Triphenylcyclopropane proved to be resistant to ring opening and was mercurated at a phenyl ring instead (129):

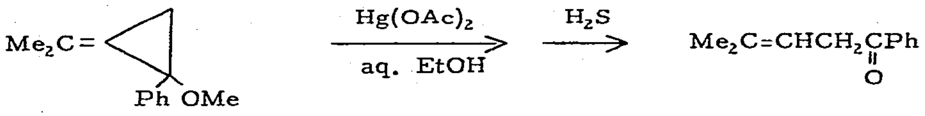


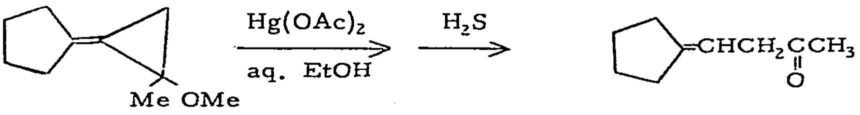
The action of mercuric acetate on diphenylmethylenecyclopropane did not cause ring cleavage (130):



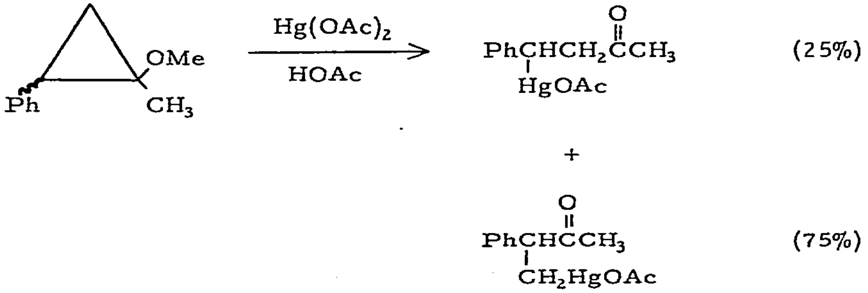
Some other alkylidenecyclopropanes, however, were attacked at the cyclopropane ring (131):

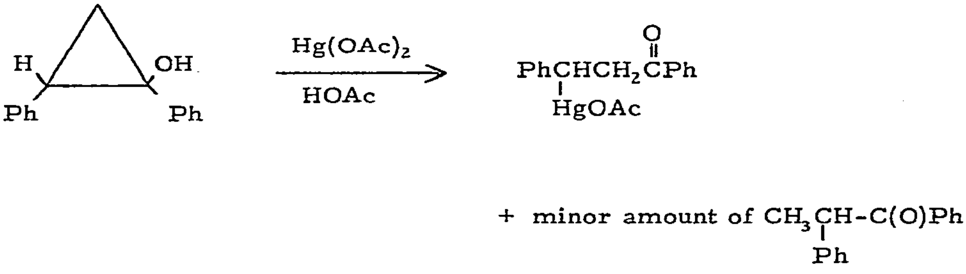


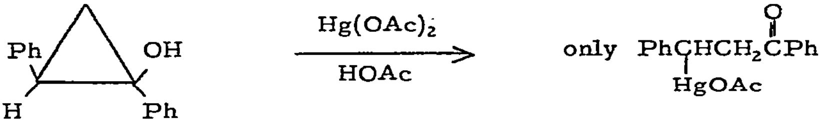




The oxymercuration of some substituted cyclopropanols and their methyl ethers has been studied (32):







C. Aromatic Compounds

Of special interest is the report by Deacon and Farquharson (133) that fusion of mercuric trifluoroacetate with a number of benzene derivatives results in permercurated products:

$$C_6H_5CO_2Na + 5\ HgX_2 \longrightarrow C_6(HgX)_5CO_2Na \qquad (X = O_2CCF_3)$$

$$C_6H_5NO_2 + 5\ HgX_2 \longrightarrow C_6(HgX)_5NO_2$$

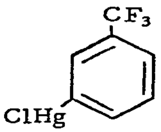
$$C_6H_5CONH_2 + 5\ HgX_2 \longrightarrow C_6(HgX)_5CONH_2$$

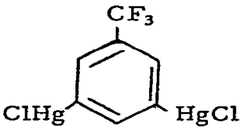
$$C_6H_5HgCl + 6\ HgX_2 \longrightarrow C_6(HgX)_6$$

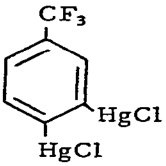
$$p\text{-}MeOC_6H_4CO_2H + 5\ HgX_2 \longrightarrow C_6(HgX)_5OMe$$

All products were cleaved with bromine to give the expected polybrominated, mercury-free arenes, and other synthetically useful mercury replacement reactions may be envisioned.

The mercuration of benzotrifluoride with mercuric oxide in perchloric acid medium gave, after treatment of the product mixture with aqueous sodium chloride, the following products (134):

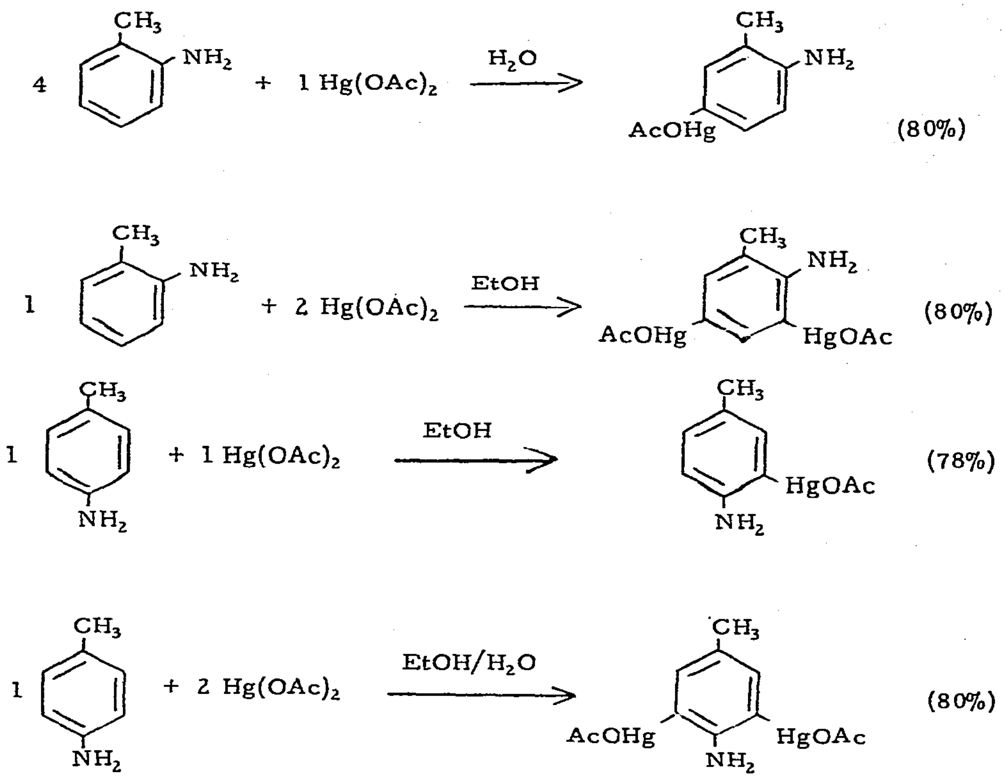




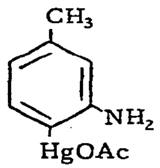


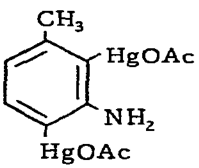
Surprisingly, the dimercurated products predominated even at a HgO:$C_6H_5CF_3$ ratio of 1:3.

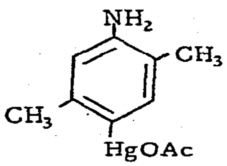
A number of aromatic amines has been mercurated (135). The products find application in the preparation of special dyes. It was found that the solvent medium used (water or ethanol) and the reactant ratios both are important in determining which of the possible products is formed. The following examples are illustrative.

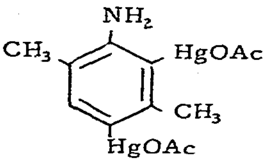


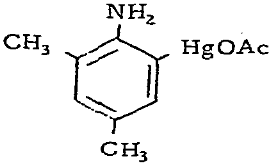
The selective, high-yield preparation of the following also was described:

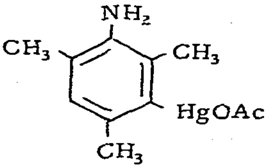


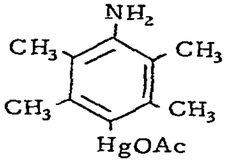






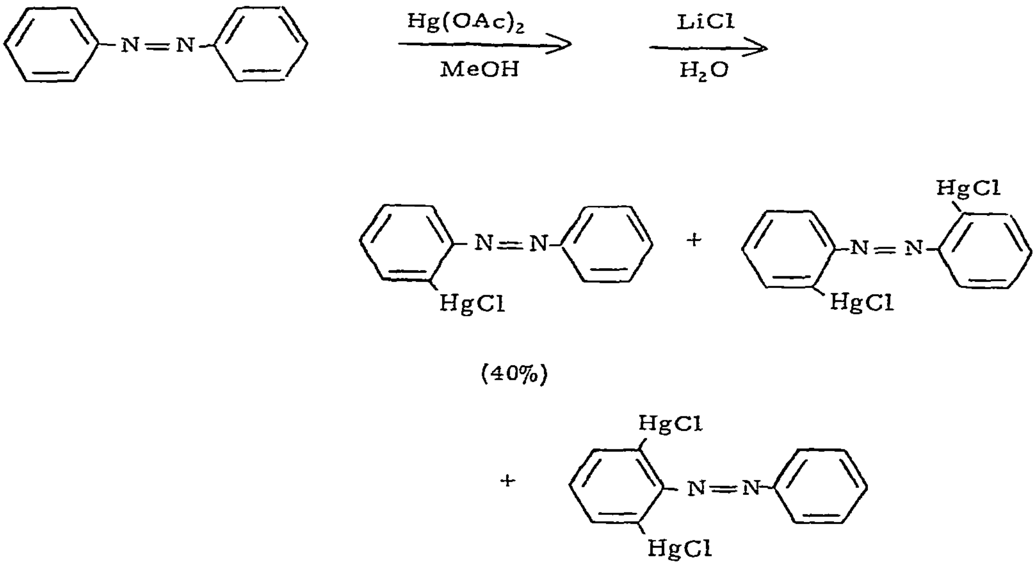




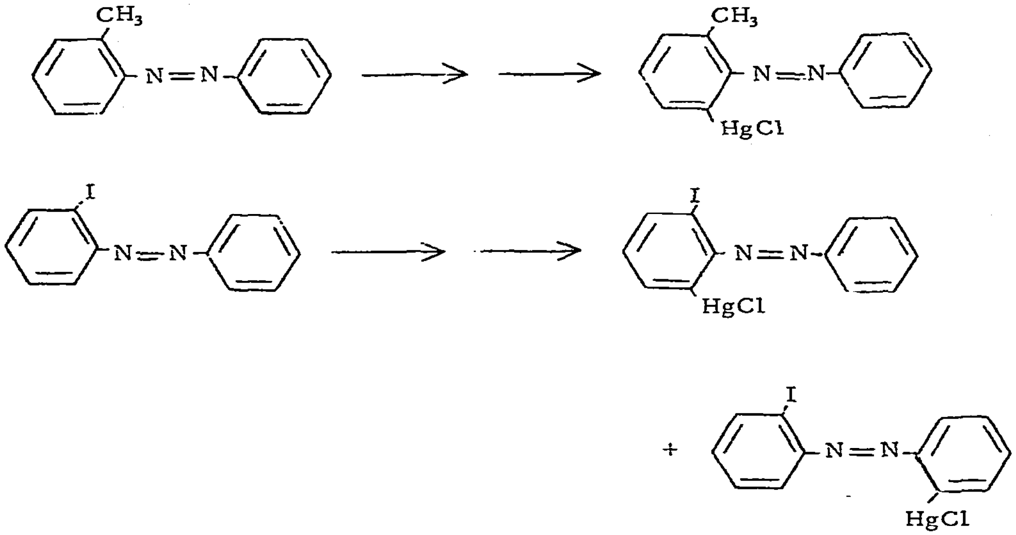


In the case of 2,4,6-trimethylaniline, the intermediate N→Hg bonded 1:1 adduct with mercuric acetate was isolated (135).

Azobenzene reacts with mercuric acetate in refluxing methanol to give mono- and dimercurated products (136):

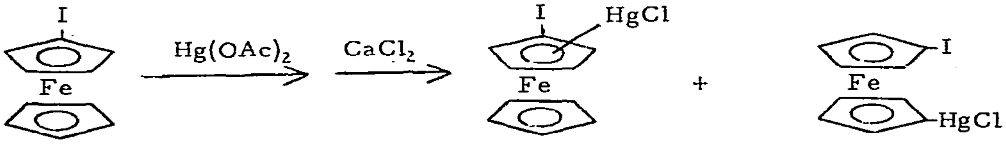


Also:



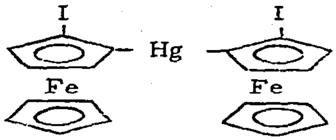
It was suggested that the azo nitrogen function directs the mercury substituent into the ortho position by a coordination process.

More examples of the direct mercuration of transition metal complexes containing aromatic ligands have been described:



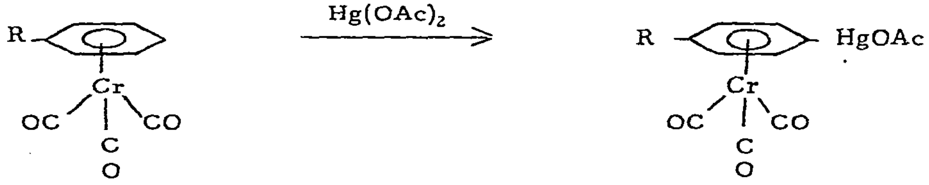
(1,2 and 1,3 isomers)

When this mercuration product mixture was passed through a column of alumina, symmetrization occurred. Only 25 was isolated as a pure compound (48). This work corrects earlier work of Nefedov (1966) that this procedure gives 3-chloromercuriiodoferrocene.



25

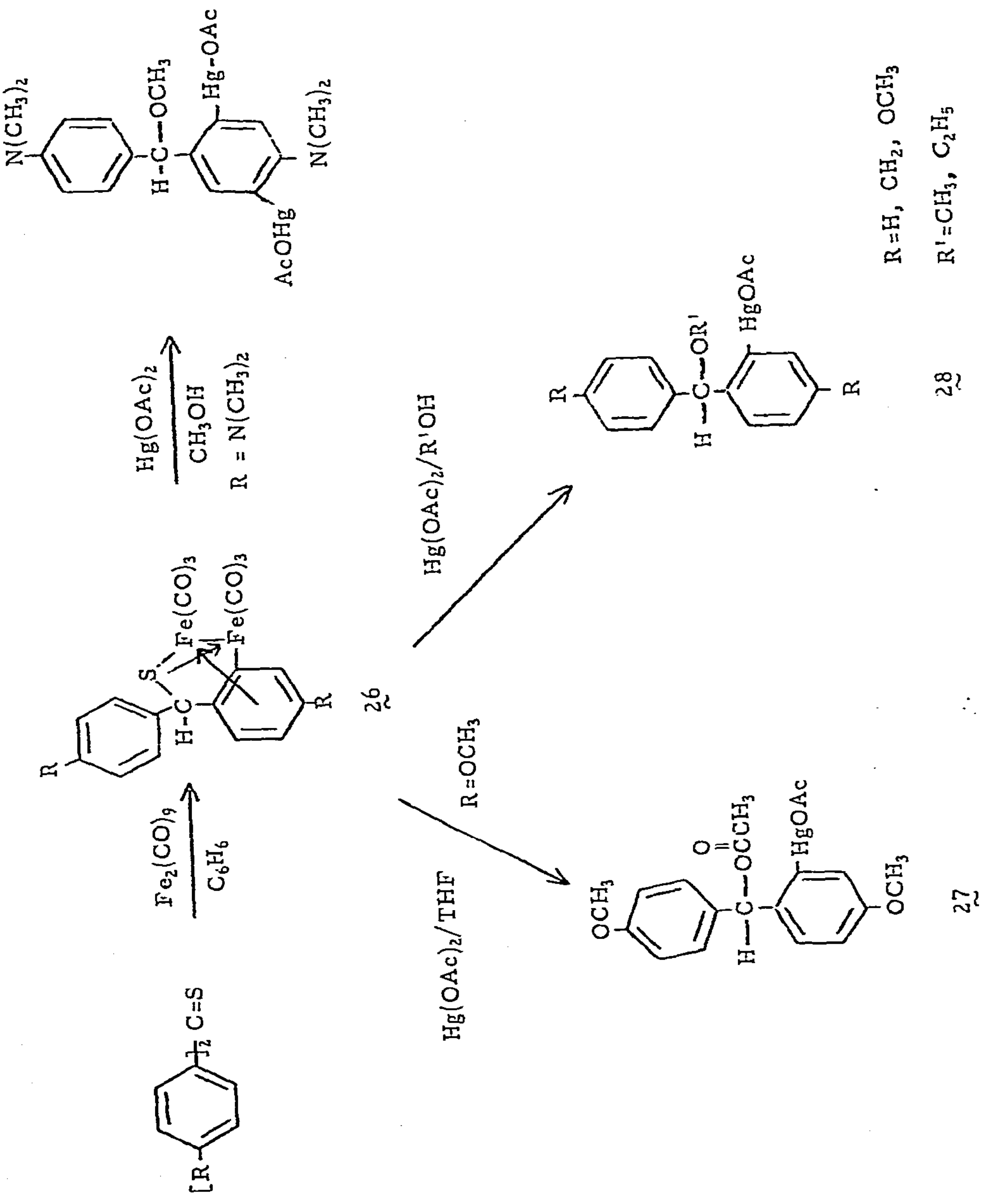
The mercuration of arenechromium tricarbonyl complexes has been described (137):



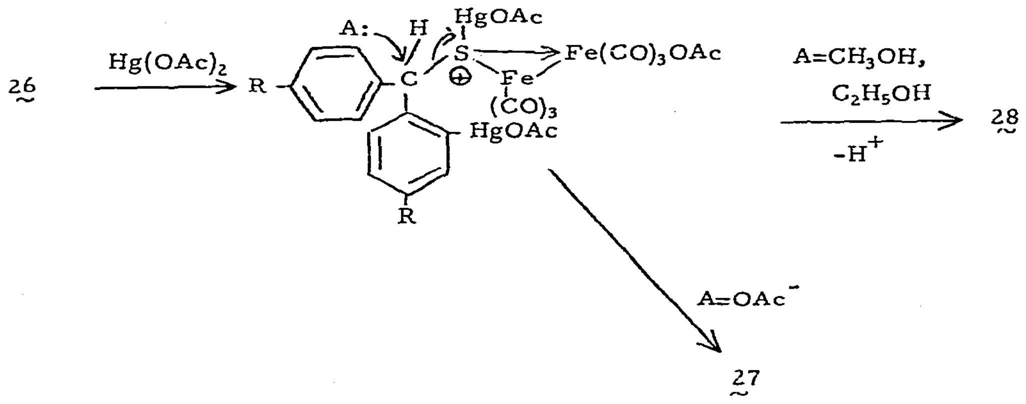
(R = H, Et_3Si)

(R = H, 22%
R = Et_3Si, 29%)

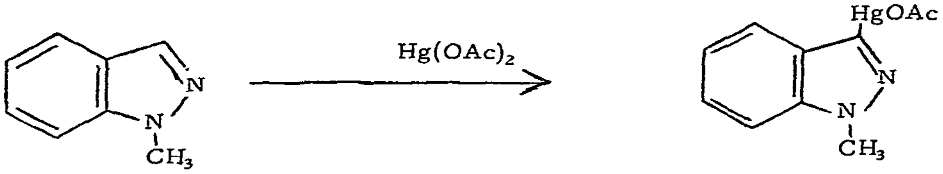
In contrast, the action of mercuric acetate on the iron carbonyl complexes 26 resulted in loss of the iron moiety to give novel arylmercurials (138):


[R-C6H4]2 C=S
Fe2(CO)9
C6H6
R
H-C
S
Fe(CO)3
Fe(CO)3
R
26
Hg(OAc)2
CH3OH
R = N(CH3)2
N(CH3)2
H-C-OCH3
Hg-OAc
AcOHg
N(CH3)2
Hg(OAc)2/R'OH
R
H—C—OR'
HgOAc
R
28
R=H, CH2, OCH3
R'=CH3, C2H5
R=OCH3
Hg(OAc)2/THF
OCH3
O
H—C—OCCH3
HgOAc
OCH3
27

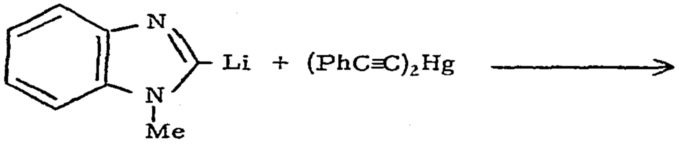
The following mechanism was suggested:

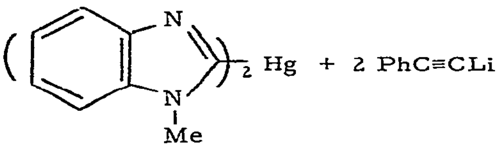


The mercuration of 1-methylindazole has been described (29):



Attempted mercuration of 1-methylbenzimidazole was unsuccessful, but the desired product could be prepared by decarboxylation of the appropriate carboxylic acid or by transmetalation:





5. ORGANOFUNCTIONAL ORGANOMERCURY COMPOUNDS

A. Highly Halogenated Organomercurials

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

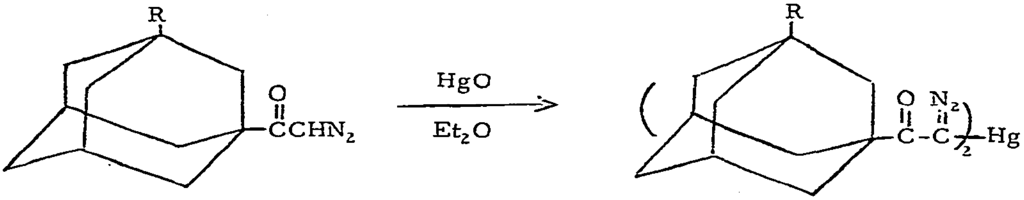
polyfluoroarylmercurials (13, 28a, 28b, 134)

polyfluoroalkylmercurials (9, 14, 22, 36, 85, 86)

halomethylmercurials (Section 3C)

B. Mercurated Diazoalkanes, Carbenes and Ylides

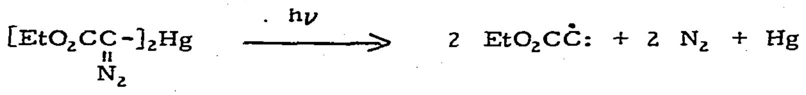
The mercury derivatives of three diazoacetyladamantanes have been prepared (61):



(R = H, Cl, Br)

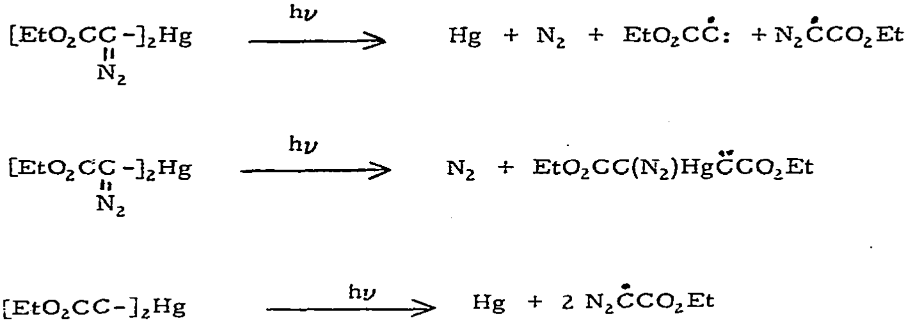
Their halogenation gave the respective adamant-1-yl tribromomethyl and trichloromethyl ketones.

Short wave length photolysis of mercurated ethyl diazoacetate produced a carbyne (139):



$$[EtO_2C\underset{\underset{N_2}{\|}}{C}-]_2Hg \xrightarrow{h\nu} 2\ EtO_2C\dot{C}: + 2\ N_2 + Hg$$

The reactions of the carbyne with olefins were studied. In addition to the process shown in the equation above, other fragmentations produced carbene and radical species:

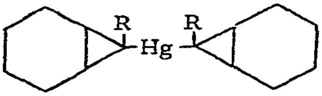


$$[EtO_2C\underset{\underset{N_2}{\|}}{C}-]_2Hg \xrightarrow{h\nu} Hg + N_2 + EtO_2C\dot{C}: + N_2\dot{C}CO_2Et$$

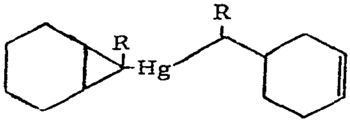
$$[EtO_2C\underset{\underset{N_2}{\|}}{C}-]_2Hg \xrightarrow{h\nu} N_2 + EtO_2CC(N_2)Hg\ddot{C}CO_2Et$$

$$[EtO_2CC-]_2Hg \xrightarrow{h\nu} Hg + 2\ N_2\dot{C}CO_2Et$$

Thus the photolysis of $Hg[C(N_2)CO_2Et]_2$ in cyclohexene gave some organomercury products, 29, 30 and 31, in addition to wholly organic products.

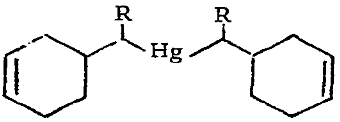


29



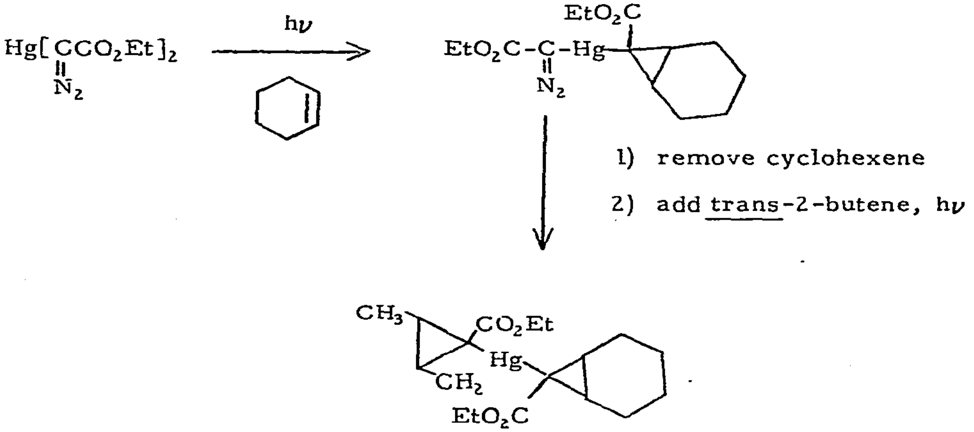
30

(R = CO_2Et)

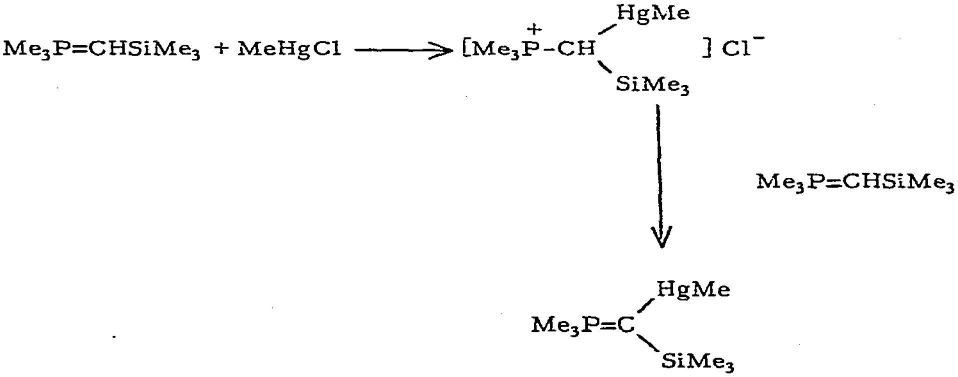


31

One experiment proved the intermediacy of the mercury-containing carbene:

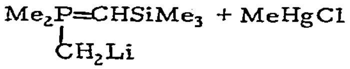


A new mercurated ylide containing an organosilicon substituent has been prepared (140):



$$\mathrm{Me_3P{=}CHSiMe_3 + MeHgCl \longrightarrow [Me_3\overset{+}{P}\text{-}CH(HgMe)(SiMe_3)]\,Cl^- \xrightarrow{Me_3P=CHSiMe_3} Me_3P{=}C(HgMe)(SiMe_3)}$$

or:

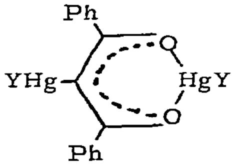


$$\begin{array}{l} Me_2P{=}CHSiMe_3 + MeHgCl \\ \quad\; | \\ \quad CH_2Li \end{array}$$

This compound, a distillable liquid, was not very thermally stable and was very sensitive toward atmospheric oxidation and hydrolysis. Simpler mercurated ylides could not be prepared. Thus the action of base (BuLi or $Me_3P{=}CH_2$) on $[Me_3\overset{+}{P}CH_2HgMe]Cl^-$ or $[Me_3\overset{+}{P}CH_2HgCH_2\overset{+}{P}Me_3]$ $2Cl^-$ did not cause deprotonation to give the expected ylides, $Me_3P{=}CHHgMe$ and $Me_3P{=}CH{-}Hg{-}CH{=}PMe_3$. It would seem that an organomercury substituent does not enhance the acidity of α-protons on attached alkyl groups.

C. Mercurated β-Diketones

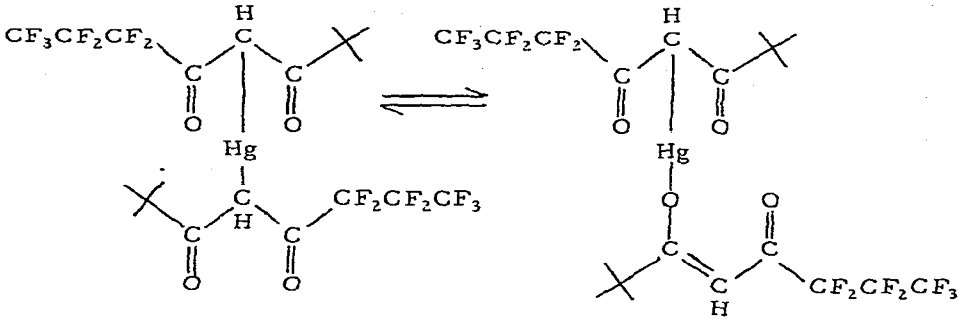
Mercuric acetate reacts with dibenzoylmethane and arylmercuric halides with its monosodium salt to give dimercurated products which have the structure 32 (by IR) (141). For the Y = Ph compound the



32

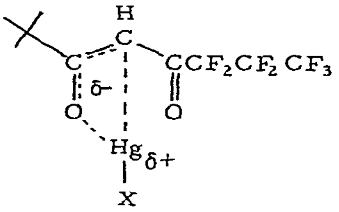
(Y = OAc, Ph, C_6F_5, p-HC_6F_4)

structure $(PhCO)_2C(HgPh)_2$ had been assumed previously (Nesmeyanov and Kravtsov, 1962). The mercuration of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione with mercuric acetate gave the bis-C-bonded product 33. This compound was found (by dynamic NMR) to undergo stereospecific keto-enol tautomerization in acetone-d_6 (142):



33

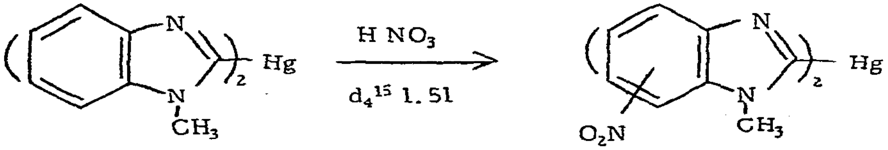
An intramolecular process, 34, is indicated. The free energy of activation for this tautomerization is 10.35±0.4 Kcal/mol at 25°C.



34

D. Miscellaneous Organofunctionals

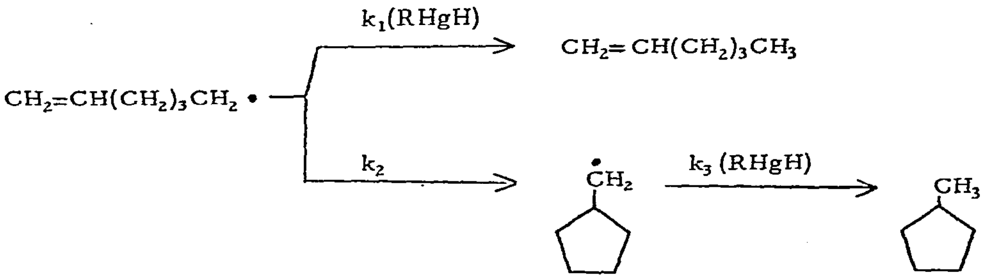
The nitration of bis(benzimidazolyl)mercury was effected with 98% nitric acid containing oxides of nitrogen in glacial acetic acid at 70-80° (29). More dilute (49%) nitric acid merely gave the dinitrate salt of the starting material.



6. C-Hg BOND REACTIONS OF ORGANOMERCURIALS

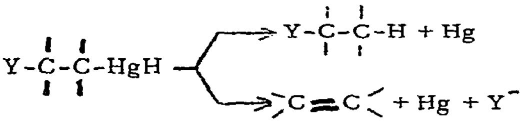
The reduction of organomercurials to the hydrocarbon ($R_2Hg \longrightarrow 2\,R$ Hg or $RHgX \longrightarrow RH + Hg + 2X^-$) is an important reaction, particularly in the olefin solvomercuration-demercuration sequence which is of preparative significance. Alkaline sodium borohydride is the most commonly used reducing agent for this purpose. As a result, much work has been done to elucidate the mechanism of such reduction processes. In the case of $NaBH_4/RHgX$ reactions, the formation of a transient organomercury hydride, RHgH, and a subsequent radical chain process was the mechanism indicated (cf. J. Organometal. Chem., 62 (1973) 121). Isotope effect studies of the reduction of $CH_2{=}CHCH_2CH_2CH_2CH_2HgBr$ by $NaBH_4$ vs. $NaBD_4$ and $LiAlH_4$ vs. $LiAlD_4$ have provided good confirmation of this, and moreover, support the view that metal hydride reductions of alkylmercuric halides, in general, proceed by a common mechanistic pathway involving hydrogen atom transfer from RHgH to alkyl radicals (143). The ratio of methylcyclopentane to 1-hexene produced in these reactions was the experimental variable of interest in these studies:

$$CH_2{=}CH(CH_2)_4HgBr \xrightarrow{NaBH_4} CH_2{=}CH(CH_2)_4HgH \longrightarrow CH_2{=}CH(CH_2)_3CH_2\bullet$$

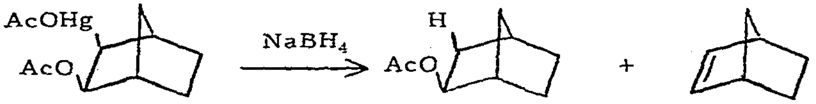


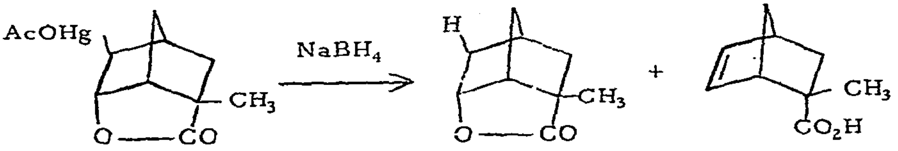
It is noteworthy that the previous finding of a nonradical mechanism for sodium amalgam reduction of organomercuric halides was confirmed by the observation that Na/Hg reduction of $CH_2{=}CH(CH_2)_4HgBr$ in D_2O medium gave only $CH_2{=}CH(CH_2)_3CH_2D$.

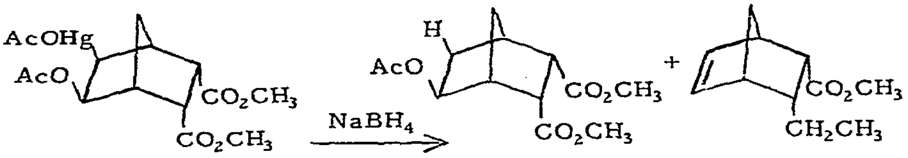
Olefin formation can interfere with the radical chain reaction in some $RHgX/NaBH_4$ reactions (144):



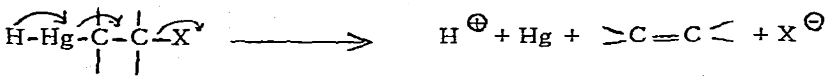
The following examples illustrate this:





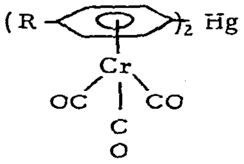


Evidence in favor of a nonradical pathway for olefin formation was presented:



$$H{-}Hg{-}C{-}C{-}X \longrightarrow H^{\oplus} + Hg + {>}C{=}C{<} + X^{\ominus}$$

Reduction of 35 with lithium aluminum hydride gave the corresponding arenechromium tricarbonyl complexes (63).



(R = Me_2N, MeO, Me, H)

35

The formation of an alcohol rather than an alkane when the RHgX/$NaBH_4$ reaction is carried out in the presence of oxygen was reported by Quirk in 1962. When the $CH_2{=}CH(CH_2)_4HgBr/NaBH_4$ reaction mentioned above was carried out under an oxygen atmosphere, the major product was $CH_2{=}CH(CH_2)_4OH$ (55%), but the reduced products, 1-hexene (16%) and methylcyclopentane (8%) also were formed (143). The mechanism of the RHgX/$NaBH_4/O_2$ reaction has been studied by Hill and Whitesides (145). Several lines of evidence suggested that free, non-caged radicals are intermediates:

$$RHgBr \xrightarrow{\text{"BH"}} RHgH$$

$$RHgH \longrightarrow R\bullet$$

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

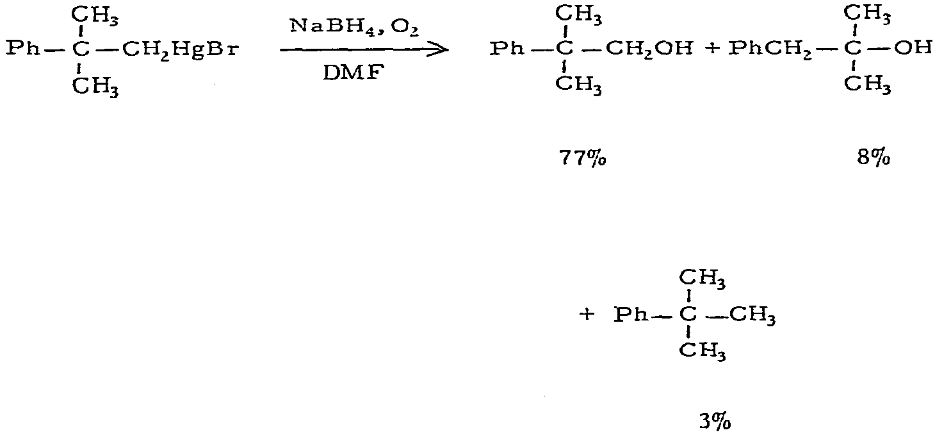
$$ROO\bullet + RHgH \longrightarrow ROOH + R\bullet + Hg(O)$$

$$ROO^\bullet \xrightarrow{\text{"BH"}} ROOH$$

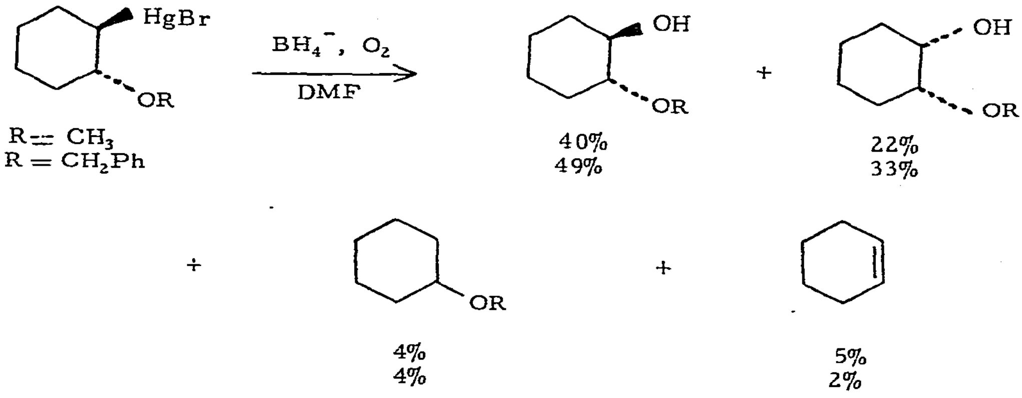
$$ROO^\bullet \xrightarrow{SH} ROOH$$

$$ROOH \xrightarrow{\text{"BH"}} ROH$$

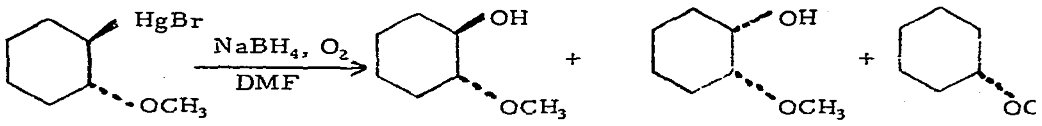
Among the systems studied were the following"

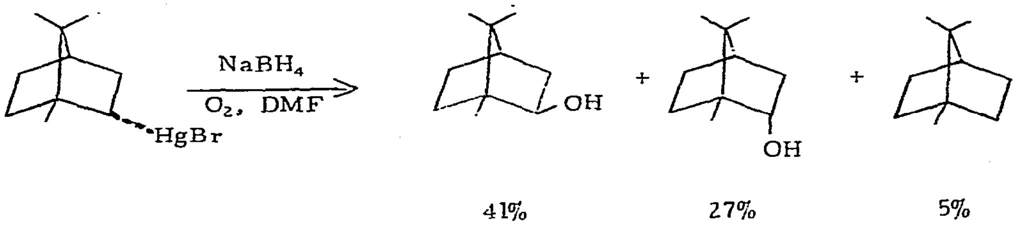


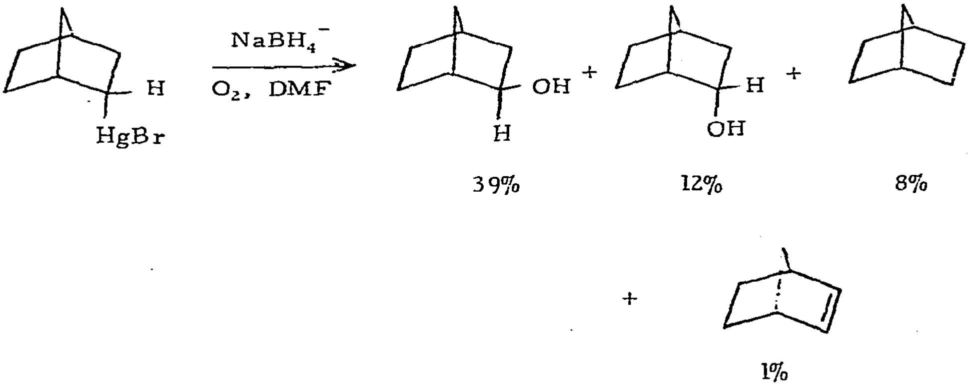
$$Ph-C(CH_3)_2-CH_2HgBr \xrightarrow[\text{DMF}]{NaBH_4,\,O_2} \underset{77\%}{Ph-C(CH_3)_2-CH_2OH} + \underset{8\%}{PhCH_2-C(CH_3)_2-OH} + \underset{3\%}{Ph-C(CH_3)_2-CH_3}$$



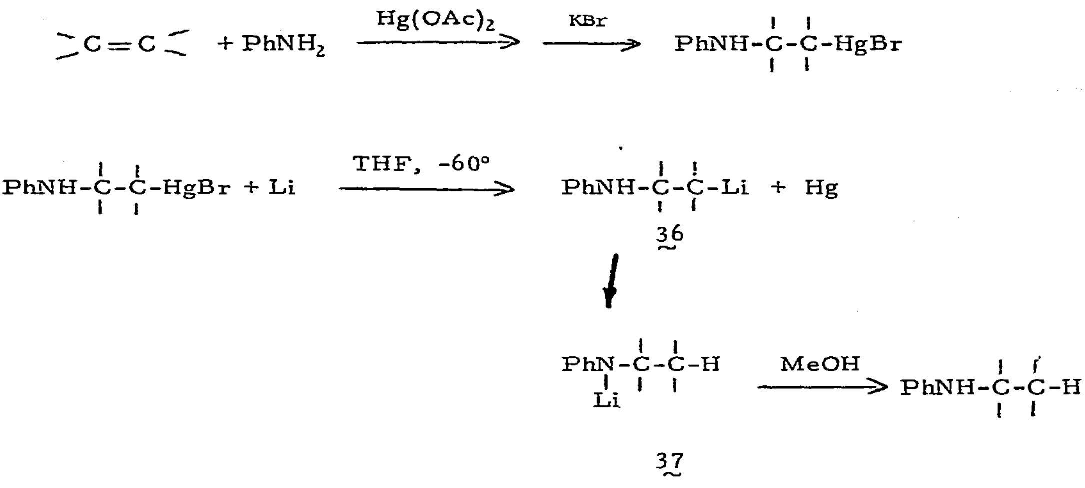
R = CH$_3$: 40%, 22%, 4%, 5%
R = CH$_2$Ph: 49%, 33%, 4%, 2%







An alternate method of reducing organomercuric halides involves treating them with lithium in THF (146). This reaction has been applied to the reduction of olefin aminomercuration products. It involves initial transmetalation to form a lithium intermediate:



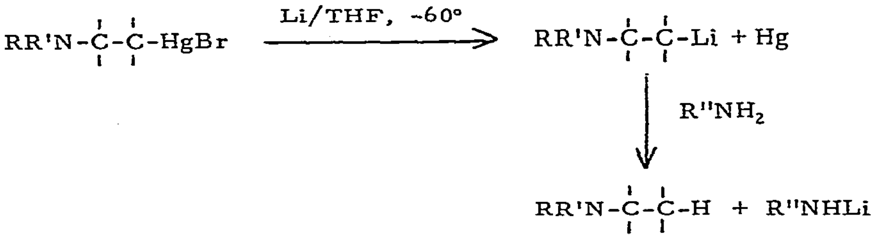
$$\gt C=C\lt + PhNH_2 \xrightarrow{Hg(OAc)_2} \xrightarrow{KBr} PhNH-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-HgBr$$

$$PhNH-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-HgBr + Li \xrightarrow{THF,\ -60^\circ} \underset{36}{PhNH-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Li} + Hg$$

$$\downarrow$$

$$\underset{37}{Ph\underset{Li}{\underset{|}{N}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H} \xrightarrow{MeOH} PhNH-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H$$

Aminomercuration products of ethylene, propene, cyclohexene and 1,5-cyclooctadiene were reduced in 70-85% yield by this method. This procedure was not applicable to the reduction of aminomercuration products of secondary amines since the intermediate lithium reagents underwent β -elimination, giving the lithium amide and olefin. In the case of primary amine-derived products, the conversion of 36 to stable 37 apparently is faster than the β -elimination reaction. A simple (and successful) solution to this difficulty was to carry out the lithium displacement reaction with secondary aminomercuration products in the presence of a primary amine (147):



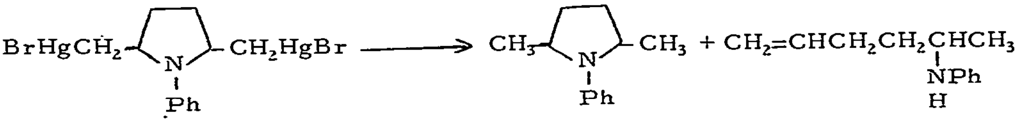
$$RR'N-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-HgBr \xrightarrow{Li/THF,\ -60^\circ} RR'N-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Li + Hg$$

$$\downarrow R''NH_2$$

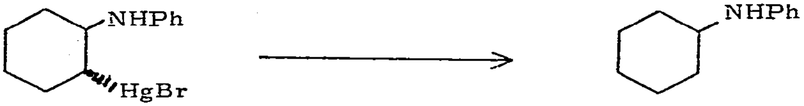
$$RR'N-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H + R''NHLi$$

The intermediate aminomercuration product need not be isolated, but can be reduced in the solution in which it was formed. Examples of such reductions include:

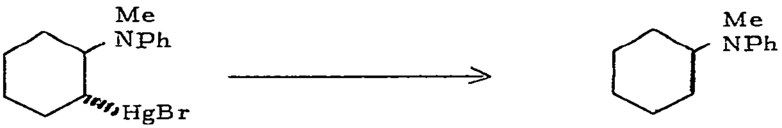
$$PhNHCH_2CH_2HgBr \longrightarrow PhNHC_2H_5 \quad (75\%)$$



(31%) (47%)



(87%)



(58%)

The reduction of dibenzylmercury to the benzyl anion by electron pulse radiolysis in THF has been studied by Bockrath and Dorfman (148) using an electron linear accelerator delivering 3-4MeV electrons:

$$(PhCH_2)_2Hg + e^-_{sol} \xrightarrow{k = 2.7\times10^{10}\ M^{-1}\ sec^{-1}} PhCH_2^- + PhCH_2Hg\bullet$$

The $PhCH_2Hg\bullet$ radical was detected and found to be stable toward dissociation to $PhCH_2\bullet$ and Hg over a time of at least 10 microseconds.

In contrast, the dissociation of dibenzylmercury upon one-electron oxidation in 1,2-dichloroethane in related pulse experiments gave the benzyl radical and the benzyl cation (149).

$$e^- + RCl \longrightarrow \overset{+}{RCl}\bullet + 2e^-$$

$$\overset{+}{RCl}\bullet + (PhCH_2)_2Hg \longrightarrow RCl + PhCH_2^+ + PhCH_2\bullet + Hg$$

Organomercury radicals also have been generated by exposure of various alkylmercuric halides to ^{60}Co γ rays at 77°K and characterized by their ESR spectra (150). Both (a) carbon- and (b) mercury-centered radicals were observed:

(a) $\bullet CH_2HgBr$
$\bullet CH_2HgI$
$\bullet CH_2HgCH_3$
$Me_2\dot{C}HgCl$

(b) $EtHg\bullet$
$ClHg\bullet$
$(Me_2Hg)^{\overline{\bullet}}$ (tentative assignment)

Class (a) radicals were characterized by only small hyperfine interaction with magnetic mercury isotopes, class (b) types by very large hyperfine coupling to mercury.

A single electron reduction mechanism giving $PhHg\bullet$ and the phenyl anion was proposed for the reaction of diphenylmercury with lithium naphthalenide (151). When this reaction was carried out in THF at -30° in the presence of trimethylchlorosilane, the phenyl anion was trapped to give phenyltrimethylsilane. Similar experiments were carried out with dibenzylmercury and bis(2-phenylcarboran-1-yl)-mercury.

Oxidation with copper(II) bromide is a useful procedure for converting organomercurials to organic bromides. Reutov and his coworkers (152) have studied this reaction in some detail. Good yields of organic bromide can be obtained when this reaction is carried out at room temperature in the absence of oxygen in DMF solution:

$(PhCH_2)_2Hg \longrightarrow PhCH_2Br$ (90%)

$PhCH_2HgBr \longrightarrow PhCH_2Br$ (97%)

$(C_6F_5CH_2)_2Hg \longrightarrow C_6F_5CH_2Br$ (94%)

$C_6F_5CH_2HgBr \longrightarrow C_6F_5CH_2Br$ (99%)

$Ph_2Hg \longrightarrow PhBr$ (quant.)

$PhHgBr \longrightarrow PhBr$ (quant.)

$(C_6F_5)_2Hg \longrightarrow C_6F_5Br$ (quant.)

$C_6F_5HgBr \longrightarrow C_6F_5Br$ (quant.)

$(n\text{-}C_4H_9)_2Hg \longrightarrow n\text{-}C_4H_9Br$ (99%)

$(CCl_3)_2Hg \longrightarrow CCl_3Br$ (95-97%)

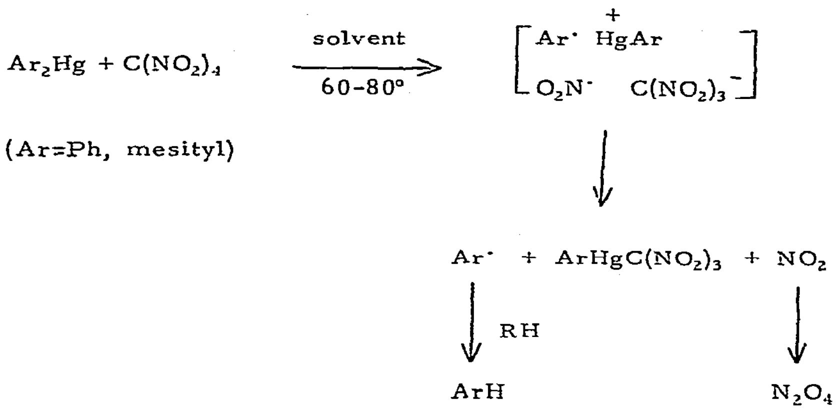
$[(CF_3)_2CH]_2Hg \longrightarrow (CF_3)_2CHBr$ (80-83%)

$[PhC(O)CH_2]_2Hg \longrightarrow PhC(O)CH_2Br$ (78%)

$PhCH(HgBr)CO_2Et \longrightarrow PhCHBrCO_2Et$ (99%)

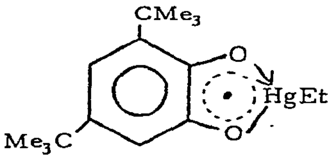
When these reactions were carried out in the presence of oxygen, organic bromide yields dropped precipitously in the case of benzyl- and alkylmercurials and oxygenated products (alcohols, aldehydes) were formed as well. The formation of benzyl formate as a by-product was observed on longer reaction times and was attributed to a solvent reaction. Possible mechanisms were discussed for the $R_2Hg/CuBr_2$ reactions; in any case, radical intermediates must be involved.

A radical mechanism also is indicated for the reaction of diarylmercurials with tetranitromethane and trinitrocarbinyl halides (153,154):



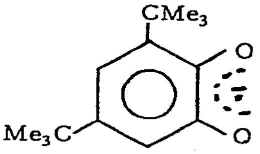
The solvents used were acetonitrile, sulfolane and chloroform. No nitration to give nitroarenes was observed. The trinitrocarbinyl halides (X= F, Cl, Br) reacted similarly, forming benzene in the case of diphenylmercury (together with bromobenzene in the reaction with $(O_2N)_3CBr$).

A one-electron transfer process was involved in the reaction of diethylmercury with 3,5-di-tert-butyl-1,2-benzoquinone in toluene at 40-50° (155). The radical <u>38</u> was shown (by ESR) to be an intermediate.



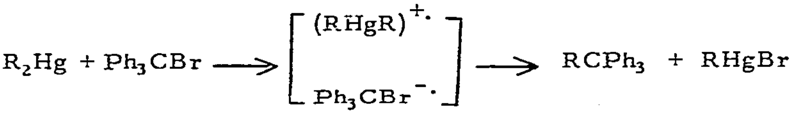
38

This radical, which forms a green solution in toluene and is stable at room temperature in the absence of oxygen and moisture, can also be prepared by reaction of <u>39</u> with ethylmercuric chloride.



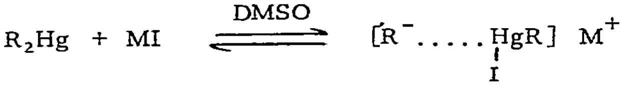
39

A CIDNP effect was observed for the methylene protons of Ph_3CCH_2Ar compounds produced in the reaction of benzylmercuric bromides with trityl bromide (156). This is in line with the electron transfer mechanism believed to be operative:



$$R_2Hg + Ph_3CBr \longrightarrow \begin{bmatrix} (RHgR)^{+\cdot} \\ \\ Ph_3CBr^{-\cdot} \end{bmatrix} \longrightarrow RCPh_3 + RHgBr$$

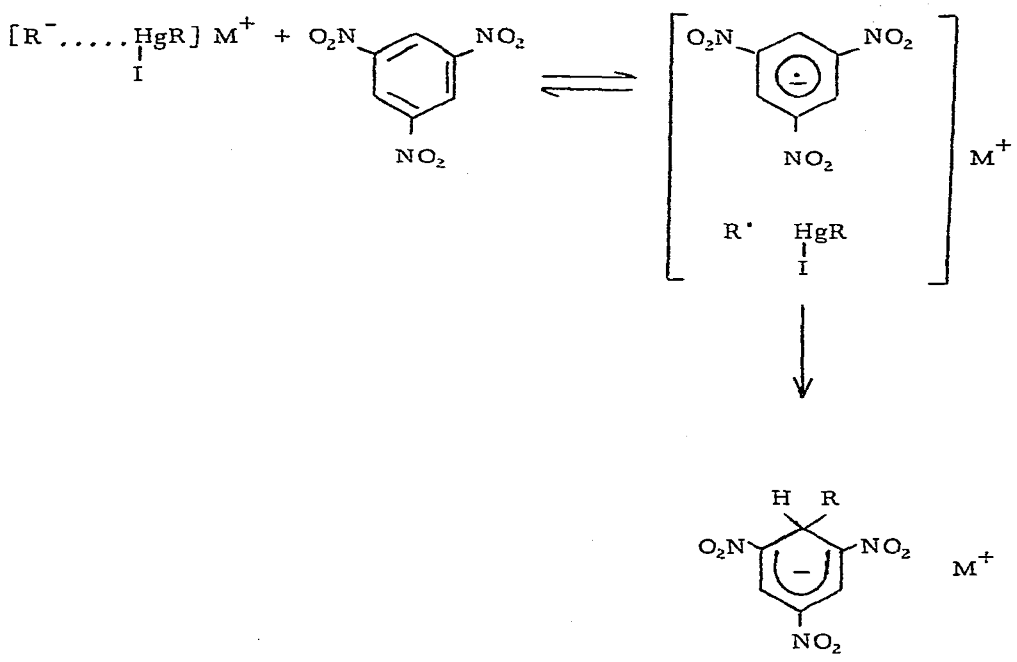
A CIDNP signal also was detected in the Meisenheimer complex 40, which suggests the following reaction course for its formation in the previously reported reaction of certain diorganomercurials with trinitrobenzene in the presence of an alkali metal iodide in DMSO (156):



$$R_2Hg + MI \overset{DMSO}{\rightleftharpoons} [R^{-}.....\underset{I}{\overset{|}{Hg}}R]\ M^{+}$$

$(R = C_6F_5$ or

$CH_3C(O)CH_2)$



40

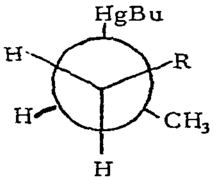
Such Meisenheimer complexes have been formed from the following organomercury compounds: $(CH_3COCH_2)_2Hg$, CH_3COCH_2HgBr, $PhCH(HgBr)CO_2Et$, $(CCl_3)_2Hg$, $(C_6F_5)_2Hg$, $[(CF_3)_2CH]_2Hg$, $Hg(CN)_2$ and bis(*o*-carboranyl)mercury (157).

Carbonium ions were suggested to be involved in the reactions of the pyridine complex of bromine nitrate with benzylmercuric and cyclohexylmercuric halides and acetates in chloroform solution (158). In addition to the expected bromides, which were formed in only moderate yields in the case of $PhCH_2HgX$ compounds and in high yield in the case of the cyclohexylmercury compounds, benzyl and cyclohexyl nitrates also were formed, as were small quantities of aldehydes and alcohols.

The β hydride abstraction reaction from di-sec-butylmercury by Ph_3C^+ has received further study (159). The composition of the olefin

$$Hg(CH(CH_3)CH_2CH_3)_2 + 2\ Ph_3C^+X^- \longrightarrow 2C_4H_8 + 2\ Ph_3CX + HgX_2$$

was $CH_3CH{=}CH_2$, 22%; cis-$CH_3CH{=}CHCH_3$, 71%; trans-$CH_3CH{=}CHCH_3$, 7%. An anti-elimination reaction was assumed, with conformer 41 being the precursor of cis-2-butene. The preferential formation of this isomer was attributed to steric factors associated with the bulky Ph_3C^+ cation.



41 .

The well-studied redistribution reaction

$$R_2Hg + HgX_2 \rightleftharpoons 2\ RHgX$$

has received further attention. For a series of R_2Hg compounds, reactions with mercuric chloride in methanol at 20° decreased in rate as R was varied in the order Et > n-Pr > Me ~ iso-Pr, and for corresponding reactions of diethylmercury in methanol with various mercury (II) compounds, the rates decreased in the order $Hg(OAc)_2 \gg HgCl_2 > HgBr_2 > HgI_2$. Solvent effects on these reactions were not straightforward and had no obvious connection with known parameters of solvent polarity (160). Symmetrization is the opposite of redistribution ($RHgX \longrightarrow R_2Hg + HgX_2$), and to effect it efficiently, in most cases the HgX_2 must be removed from the equilibrium by reduction or complexation. Electrochemical reduction is very effective in this application (35), as the following new example shows:

$$2\ \mathrm{ClHgCH_2CN} \xrightarrow[\mathrm{(NaOAc)}]{\mathrm{DMF/H_2O}} \underset{(92\%)}{\mathrm{Hg(CH_2CN)_2}} + \mathrm{Hg} + 2\ \mathrm{Cl^-}$$

Detailed investigations have been devoted to the reaction of diorganomercurials with metallic mercury (161, 162). The adsorption layers formed on the surface of a mercury electrode were studied by a galvanostatic method for the following processes: (a) adsorption of $EtHgC_6F_5$ from 9:1 water/methanol; (b) coadsorption of Et_2Hg and $(C_6F_5)_2Hg$; (c) reduction of EtHgCl on mercury covered by a layer of $(C_6F_5)_2Hg$; (d) simultaneous one-electron reduction of EtHgCl and C_6F_5HgBr. The conclusion reached from the results obtained was that a mercury(I) intermediate, RHgHgR, is formed in the reaction of R_2Hg with metallic mercury and that mercury exchange between metallic mercury and R_2Hg proceeds *via* this intermediate:

$$\mathrm{R_2Hg} + \mathrm{Hg} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RHgHgR}$$

A rate study of the forward and back reactions was carried out. A mercury(I) intermediate, EtHgHgEt, also is formed on the mercury surface in the reaction of diethylthallium chloride with metallic mercury, very likely by way of an initially formed cation, $\mathrm{EtHgTl^{+}Et}$ (163).

Anionic cleavage of the mercury-carbon bond is rather rare, being observed only in the case of rather electronegative substituents. A recent example is the displacement of $C_6F_5^-$ from mercury by halide ions (13):

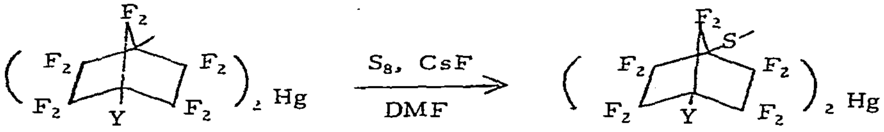
$$(C_6F_5)_2Hg + 4X^- + 2\,H_2O \text{ (or } 2ROH) \longrightarrow HgX_4^{2-} + 2\,C_6F_5H + 2\,OH^-$$

$(X = I, Br)$

$$PhHgC_6F_5 + I^- + H_2O \xrightarrow{\text{acetone}} PhHgI + C_6F_5H + OH^-$$

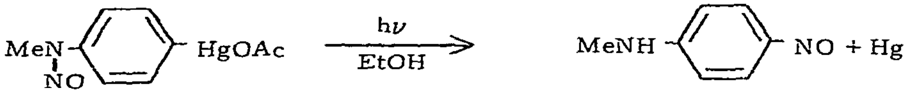
Miscellaneous Hg-C bond reactions worth noting are the following:

A sulfur insertion reaction (9):



(Y = F, H)

Rearrangement during a photochemical demercuration (164):



A study of the thermal decomposition of <u>cis</u>- and <u>trans</u>-$ClCH{=}CHHgX$ ($X =$ Cl, Br, I) (165).

7. MERCURY-FUNCTIONAL MERCURIALS

Reactions of trifluoromethylmercuric iodide with appropriate silver salts gave CF_3HgNCO, CF_3HgN_3, CF_3HgSCF_3, $CF_3HgO_2CCO_2HgCF_3$, and $(CF_3Hg)_2O$; on reaction with Tl_2CS_3, the sulfide, $(CF_3Hg)_2S$, was formed (166).

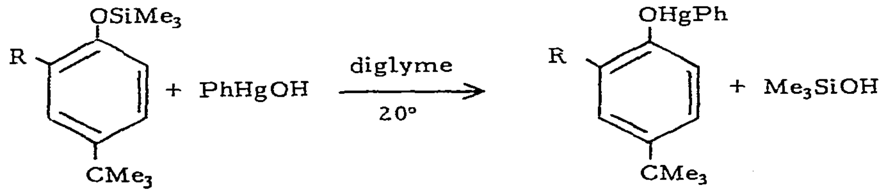
Equilibrium constants have been determined for two reactions of the $MeHg^+$ ion in aqueous solution (167):

$$MeHg^+(aq) + H_2O \rightleftharpoons MeHgOH(aq) + H^+ ;\ \log[K\pm3\sigma(K)] = -4.40\pm0.07$$

$$MeHg^+(aq) + H_2PO_4^- \rightleftharpoons MeHgHPO_4^-(aq) + H^+ ;\ \log[K\pm3\sigma(K)] = -1.74\pm0.03$$

Radiometric and spectrophotometric titration methods were used.

Organomercury phenoxides have been prepared from phenol trimethylsilyl ethers (19):



(R = H, CMe_3)

The formation of isopropylmercuric percaprate, $CH_3(CH_2)_8C(O)OO$-$HgCHMe_2$, by reaction of percaproic acid with $(i\text{-}PrHg)_2O$ has been studied (168), as have the preparation and thermolysis of $(PhCMe_2OO)_2Hg$ (169).

Organomercury thiophenoxides have been the subject of several studies. They may be prepared by organotin or organolead routes (170):

$$Bu_3SnSC_6H_4Me\text{-}p + PhHgCl \longrightarrow Bu_3SnCl + PhHgSC_6H_4Me\text{-}p$$

$$Ph_3PbSC_6H_4Me\text{-}p + PhHgCl \longrightarrow Ph_3PbCl + PhHgSC_6H_4Me\text{-}p$$

NMR studies of the exchange reactions:

$$PhHgSAr + Ar'SH \rightleftharpoons ArSH + PhHgSAr'$$

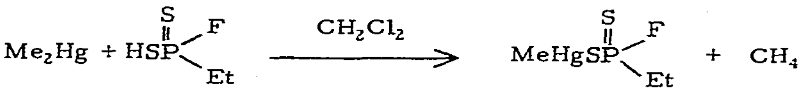
$$PhHgSAr + Ph_3MSAr' \rightleftharpoons PhHgSAr' + Ph_3MSAr$$

(M = Sn, Pb)

$$PhHgSAr + Ph_2SbSAr' \rightleftharpoons PhHgSAr' + Ph_2SbSAr$$

provided equilibrium constants as well as data on kinetic and substituent effects (171, 172). A four-center, cyclic transition state was favored for such processes.

Methylmercuric ethylfluorodithiophosphonate has been prepared (173):



$$Me_2Hg + HS\overset{\overset{S}{\|}}{P}(F)(Et) \xrightarrow{CH_2Cl_2} MeHgS\overset{\overset{S}{\|}}{P}(F)(Et) + CH_4$$

Compounds containing Se-Hg, Te-Hg and As-Hg linkages have been reported (174, 175):

$$2\ MeHgBr + H_2Se \xrightarrow{MeOH} (MeHg)_2Se$$

$$2\ MeHgBr + H_2Te \xrightarrow{MeOH} (MeHg)_2Te$$

$$3\ MeHgNO_3 + H_2Se \xrightarrow{Et_2O} [(MeHg)_3Se]NO_3$$

$$MeHgX + 3\ MeHgOCMe_3 + AsH_3 \xrightarrow{i\text{-}PrOH} [(MeHg)_4As]X + 3\ Me_3COH$$

$(X = NO_3,\ BF_4,\ PF_6)$

$$MeHgOCMe_3 + AsH_3 \xrightarrow{i\text{-}PrOH} (MeHg)_3As$$

The vibrational spectra of these compounds were of assistance in their structural characterization. Similar compounds of antimony could not be prepared.

Various compounds containing Hg-N bonds also have been described.

$$MeHgN(SiMe_3)_2 + HN{=}P(NME_2)_2 \xrightarrow{(ref.\ 176)} MeHgN{=}P(NMe_2)_3 + (Me_3Si)_2NH$$

$$PhHgOAc + S_7NH \xrightarrow{MeOH} PhHgNS_7 + HOAc$$

Reactions of heptasulfur N-phenylmercuriimide with covalent halides (Me_3SnCl, BCl_3, etc.) were used to prepare a number of new heptasulfur imide derivatives (177). The compound $Hg(NSF_2)_2$ was found to react with bis(trifluoromethyl)diazomethane to give $(CF_3)_2C{=}NSF$, nitrogen and mercuric fluoride (178).

Exchange reactions of N-phenylmercurisulfonamides have been studied by NMR techniques (179). These second order reactions were suggested to proceed by way of a four-center cyclic transition state.

$$PhHgNSO_2Ar + PhSO_2NHAr' \rightleftharpoons PhHgNSO_2Ar' + PhSO_2NHAr$$

Raman difference spectroscopy was used to good advantage in a detailed study of N-bonded methylmercuri derivatives of purine and pyrimidine nucleotides and nucleosides in solution (180, 181).

8. MERCURY-GROUP IV COMPOUNDS

Mitchell has prepared compounds of type $RHgMR'_3$ ($M = Si, Ge, Sn$) (182):

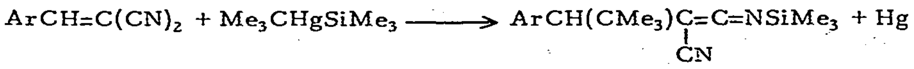
$$\begin{tikzcd}
(Me_3M)_2Hg + RHgX \arrow[r, "-40^\circ"] & RHgMMe_3 + & Me_3MHgX \arrow[d] \\
 & & Me_3MX + Hg
\end{tikzcd}$$

($M = Si, Ge; R = Me, Et,$
n-Pr, i-Pr, t-Bu)

$$RHgSiMe_3 + R'_3SnOMe \xrightarrow{r.t.} RHgSnR'_3 + Me_3SiOMe$$

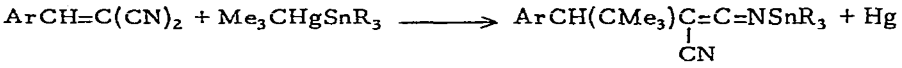
The second reaction was used to prepare $EtHgSnEt_3$, $PrHgSnEt_3$, $BuHgSnEt_3$, $Me_3CHgSnMe_3$, $Me_3CHgSnEt_3$, $Me_3CHgSnBu_3$ and $Me_3CHgSnBu\text{-}i_3$, none of which could be distilled because of their thermal lability. They were, however, more stable than simple $(R_3Sn)_2Hg$ compounds. The compounds $MeHgSnMe_3$ and $EtHgSnMe_3$ could not be detected. The compound $MeHgSn(CH_2SiMe_3)_3$ also was not stable since the reaction of $(Me_3SiCH_2)_3SnLi$ with methylmercuric chloride gave $MeSn(CH_2SiMe_3)_3$ (183).

The thermolysis and photolysis of these Group IV-mercury compounds were studied (182). Reactions of such compounds with some organic substrates also were examined (184):

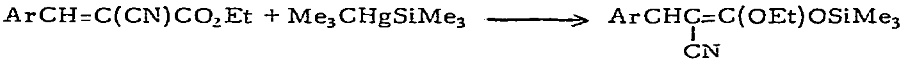


$$\mathrm{ArCH{=}C(CN)_2 + Me_3CHgSiMe_3 \longrightarrow ArCH(CMe_3)\underset{CN}{C}{=}C{=}NSiMe_3 + Hg}$$

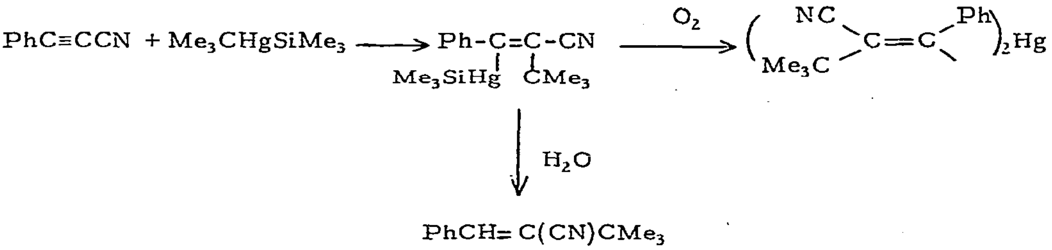
(but no reaction with other $\mathrm{RHgSiMe_3}$)



$$\mathrm{ArCH{=}C(CN)_2 + Me_3CHgSnR_3 \longrightarrow ArCH(CMe_3)\underset{CN}{C}{=}C{=}NSnR_3 + Hg}$$



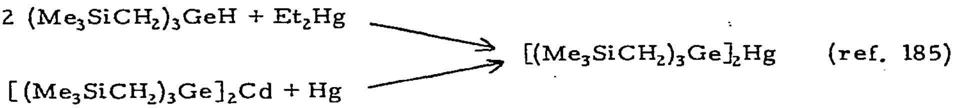
$$\mathrm{ArCH{=}C(CN)CO_2Et + Me_3CHgSiMe_3 \longrightarrow ArCH\underset{CN}{C}{=}C(OEt)OSiMe_3}$$



$$\mathrm{PhC{\equiv}CCN + Me_3CHgSiMe_3 \longrightarrow Ph\text{-}\underset{Me_3SiHg}{C}{=}\underset{CMe_3}{C}\text{-}CN \xrightarrow{O_2} \left((NC)(Me_3C)C{=}C(Ph)\right)_2Hg}$$

$$\mathrm{Ph\text{-}\underset{Me_3SiHg}{C}{=}\underset{CMe_3}{C}\text{-}CN \xrightarrow{H_2O} PhCH{=}C(CN)CMe_3}$$

Other Group IV-mercury compounds have been prepared by various procedures by Vyazankin and his coworkers:



$$\mathrm{2\ (Me_3SiCH_2)_3GeH + Et_2Hg \longrightarrow [(Me_3SiCH_2)_3Ge]_2Hg} \quad \text{(ref. 185)}$$

$$\mathrm{[(Me_3SiCH_2)_3Ge]_2Cd + Hg \longrightarrow [(Me_3SiCH_2)_3Ge]_2Hg} \quad \text{(ref. 185)}$$

$$\mathrm{[(C_6F_5)_3Ge]_2Zn + Hg \longrightarrow [(C_6F_5)_3Ge]_2Hg + Zn} \qquad \text{(ref. 186)}$$

The intermediate Ge-Hg-Ge compound in the following reaction was not stable and underwent demercuration (186):

$$\begin{tikzcd}[column sep=large]
2\ (C_6F_5)_2GeHBr + Et_2Hg \arrow[r, "100^\circ"] & {[(C_6F_5)_2BrGeHgGeBr(C_6F_5)_2] + 2\ C_2H_6} \arrow[d] \\
 & Hg + (C_6F_5)_2BrGeGeBr(C_6F_5)_2
\end{tikzcd}$$

$$[(Me_3SiCH_2)_3Sn]_2Cd \xrightarrow{Hg\ or\ Hg(CH_2CO_2Me)_2} [(Me_3SiCH_2)_3Sn]_2Hg \quad \text{(ref. 185)}$$

$$2\ (Me_3CCH_2)_3SnH + Et_2Hg \longrightarrow [(Me_3CCH_2)_3Sn]_2Hg + 2\ C_2H_6 \quad \text{(ref. 187)}$$

$$(Et_3Ge)_2Hg + 2\ (C_6F_5)_3SnBr \xrightarrow{h\nu} [(C_6F_5)_3Sn]_2Hg + 2\ Et_3GeBr \quad \text{(ref. 188)}$$

$$\begin{aligned} Et_3GeHgGe(C_6F_5)_3 + (C_6F_5)_3SnBr \xrightarrow{h\nu} & (C_6F_5)_3GeHgSn(C_6F_5)_3 \\ & + Et_3GeBr \quad \text{(ref. 188)} \end{aligned}$$

The high stability of such Group IV-mercury compounds in which the Group IV atom is substituted with three Me_3SiCH_2, Me_3CCH_2 or C_6F_5 groups is noteworthy.

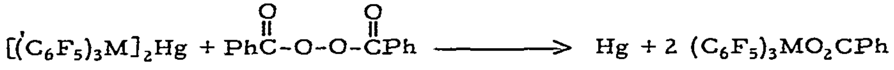
Diverse reactions of Group IV-mercury compounds have been studied.

$$\begin{tikzcd}[column sep=large]
{[(Me_3SiCH_2)_3Sn]_2Hg + I_2} \arrow[r, "-60^\circ\ to\ -10^\circ", "\text{(ref. 185)}"'] & (Me_3SiCH_2)_3SnI \\
 & {+\ [(Me_3SiCH_2)_3SnHgI]} \arrow[d] \\
 & (Me_3SiCH_2)_3SnI + Hg
\end{tikzcd}$$

$$[(Me_3SiCH_2)_3Sn]_2Hg + 2\ I_2 \xrightarrow[\text{(ref. 185)}]{-20^\circ} HgI_2 + 2\ (Me_3SiCH_2)_3SnI$$

$$\begin{tikzcd}[(Me_3CCH_2)_3Sn]_2Hg + I_2 \arrow[r, "20^\circ", "\text{(ref. 187)}"'] & {[(Me_3CCH_2)_3SnHgI]} \arrow[d] + (Me_3CCH_2)_3SnI \\ & (Me_3CCH_2)_3SnI + Hg\end{tikzcd}$$

$$\begin{tikzcd}[(Me_3CCH_2)_3Sn]_2Hg + HgY_2 \arrow[r, "\text{THF, }20^\circ", "\text{(ref. 187)}"'] & 2\ [(Me_3CCH_2)_3SnHgY] \arrow[d] \\ (Y = Cl,\ CH_2CO_2Me) & 2\ (Me_3CCH_2)_3SnY + 2\ Hg\end{tikzcd}$$



$$[(C_6F_5)_3M]_2Hg + PhC(=O)\text{-}O\text{-}O\text{-}C(=O)Ph \longrightarrow Hg + 2\ (C_6F_5)_3MO_2CPh$$

(M = Ge, Sn) (ref. 188)

$$[(C_6F_5)_3M]_2Hg + HgX_2 \longrightarrow 2\ Hg + 2\ (C_6F_5)_3MX$$ (ref. 188)

(M = Ge, X = OAc)

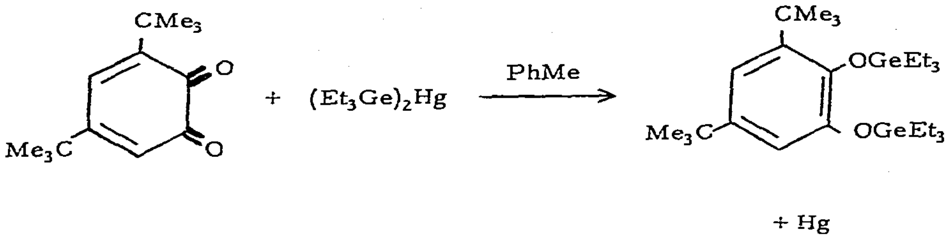
(M = Sn, X = Cl)

$$[(C_6F_5)_3Ge]_2Hg + S_8 \xrightarrow{\text{THF, }50^\circ} (C_6F_5)_3GeHgSGe(C_6F_5)_3$$ (ref. 189)

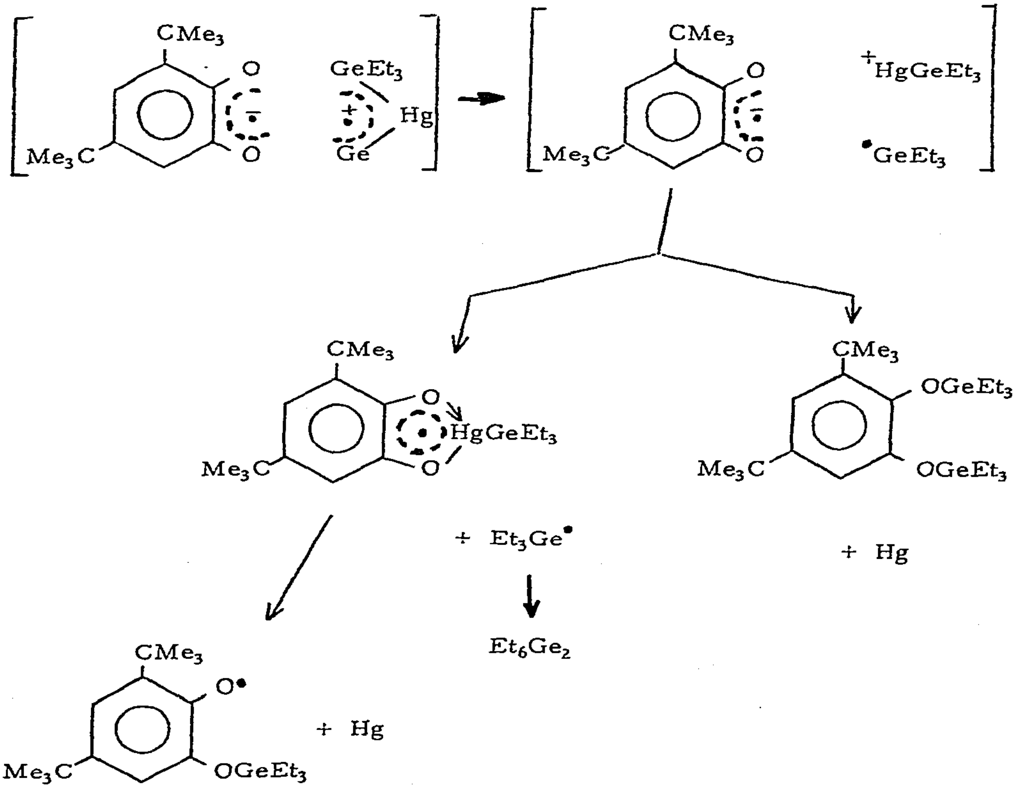
(A similar compound was prepared by another route (189):

$$(C_6F_5)_3GeSH + Et_2Hg \longrightarrow (C_6F_5)_3GeSHgEt + C_2H_6)$$

Bis(triethylgermyl)mercury underwent some novel electron-transfer chemistry (155):

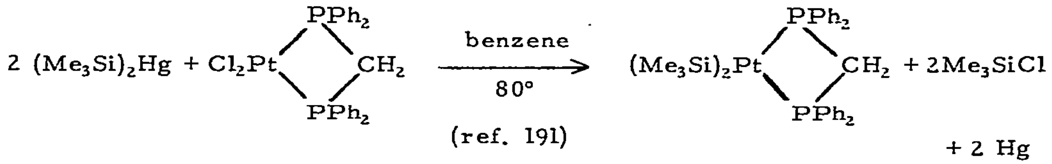


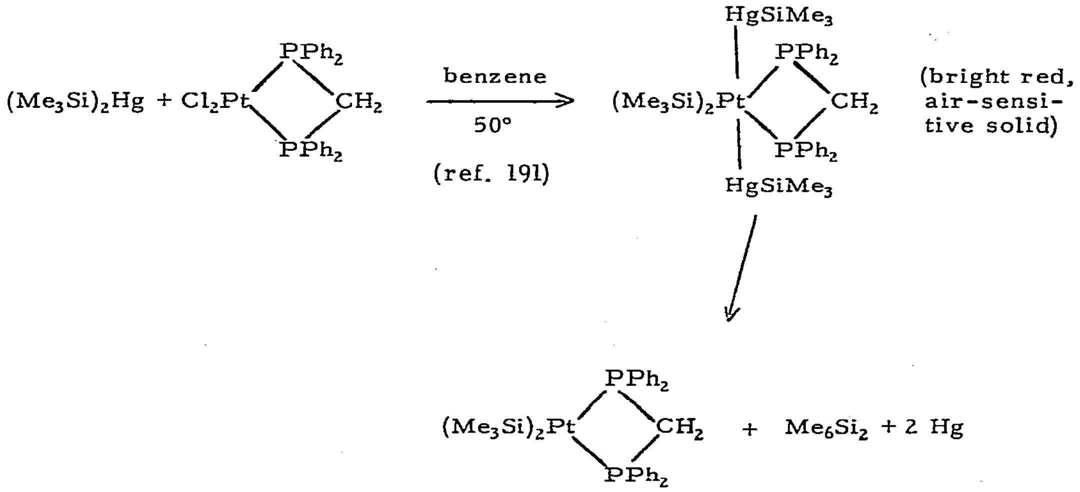
A green intermediate was involved in this reaction. An ESR signal could be observed when the reactants were mixed at -80°, and on the basis of the ESR results, the process shown below was suggested:



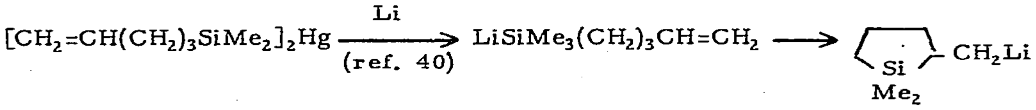
Reactions of Group IV-mercury compounds with transition metal compounds have been described:

$$(Me_3Si)_2Hg + Fe(CO)_5 \xrightarrow[\text{(ref. 190)}]{h\nu} cis\text{-}(OC)_4Fe(SiMe_3)_2 + Hg[cis\text{-}(OC)_4FeSiMe_3]_2$$





Especially useful is the application of Group IV-mercury compounds in the preparation of Group IV-alkali metal reagents:



$(Et_3Ge)_2Hg + M \longrightarrow Et_3GeM$ (M = Li, Na, K, Rb, Cs) (ref. 192)

$[(Me_3SiCH_2)_3Sn]_2Hg \xrightarrow[\text{or benzene}]{\text{Li, hexane}} (Me_3SiCH_2)_3SnLi$ (ref. 183)

9. COMPLEXES OF ORGANOMERCURIALS

Thermodynamic data for $(C_6F_5)_2Hg \cdot L$ complexes (L = py, bipy) were reported in last year's survey (J. Organometal. Chem., 75 (1974) 105). New work by others has added new thermodynamic data for 1:1 complexes of bis(pentafluorophenyl)mercury with eight nitrogen bases (Table 13) (193). Noteworthy is the high stability of the 1,10-phenanthroline adduct in which the ligand is believed to be bidentate. The calorimetric approach used in this study failed to detect complex formation in solution between bis(pentafluorophenyl)mercury and tri-n-butylamine, tri-n-butylphosphine, $Ph_2PCH_2CH_2PPh_2$ or tetrahydrofuran, or between diphenylmercury and 1,10-phenanthroline. NMR techniques were used to show that weak 1:1 and 1:2 complexes were formed when $(PhCH_2)_2Hg$ and $PhCH_2HgCF_3$ were dissolved in donor solvents such as acetone, pyridine, DMF and DMSO (194, 195). The 1:2 complexes existed only at low temperatures. Trifluoromethylmercury compounds, CF_3HgX with X = Cl, I, O_2CCF_3, were shown to form similar complexes (1:2 stoichiometry in DMSO, DMF, THF and acetone; a 1:1 and 1:2 mixture in pyridine) (196). In nondonor solvents such as dichloromethane and benzene CF_3HgI appears to exist in the form of the iodine-bridged dimer.

Various complexes of the CH_3Hg^+ ion have been reported. Methylmercuric cyanide can function as ligand (197):

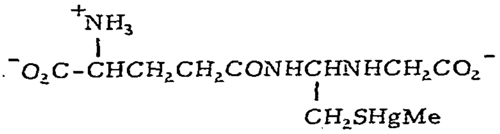
TABLE 13. Thermodynamic data for the reactions $(C_6F_5)_2Hg + L \rightleftharpoons (C_6F_5)_2Hg\cdot L$ at 30° (ref. 193).

L	K (l/mole)	$-\Delta G^0$ (kJ/mole)	$-\Delta H^0$ (kJ/mole)	$-\Delta S^0$ (J/K/mole)
Pyridine	2,1 ± 0,2	1,8 ± 0,3	11,8 ±1,8	33 ± 5
4-Methylpyridine	4,7 ±0,9	3,8 ±0,5	12,6 ±0,3	29 ± 3
2,2'-Bipyridine	14,0 ± 0,8	6,7 ±0,2	17,2 ± 0,1	36 ± 2
1,10-Phenanthroline	2,3 ± 0,6 x 10^3	19,4 ±0,7	47,4 ±0,8	93 ± 4
$(CH_3)_2N(CH_2)_2N(CH_3)_2$	23,5 ±1,8	7,9 ±0,3	29,5 ±3,0	71 ±6
$(CH_3)_2N(CH_2)_3N(CH_3)_2$	4,2 ±0,1	3,6 ±0,1	34,8 ±1,2	102 ± 5
$(CH_3)_2N(CH_2)_4N(CH_3)_2$	13,1 ± 1,8	6,4 ±0,4	28,8 ±0,8	74 ± 2
$H_2N(CH_2)_2NH_2$	386 ± 14	15,0 ±0,1	43,5 ±0,3	94 ±2

$$2\ \mathrm{MeHgBr} + \mathrm{AgCN} + \mathrm{AgNO_3} \xrightarrow{\mathrm{Et_2O}} [\mathrm{MeHgC{\equiv}N \rightarrow HgMe}]^+\ \mathrm{NO_3}^-$$

The cation in this complex has a linear structure (by IR and Raman spectroscopy). In a donor solvent (D), dissociation to MeHgCN and $[\mathrm{MeHgD}]^+$ occurs.

Chelate complexes of Hg^{2+}, CH_3Hg^+, and $PhHg^+$ with a number of substituted quinolines, 2,2'-bipyridines and 1,10-phenanthrolines have been investigated in water and in aqueous dioxane by pH and pHg methods (198). Stability constants were determined; the phenylmercury complexes were found to be more stable than the methylmercury species. The formation of chelate complexes was suggested. Proton NMR spectroscopy was used to determine formation constants of complexes of CH_3Hg^+ with a series of amines and amino acids in aqueous solution (199). The complexes with amines formed only at intermediate pH since at low pH the amine was protonated and at high pH the complex dissociated to form MeHgOH. With amino acids, the site of CH_3Hg^+ complexation was found to be pH-dependent. At low pH CH_3Hg^+ was bound to the carboxylate group, at higher pH to the amino group. Formation constants for CH_3Hg^+ binding at the two different sites in some amino acids are given in Table 14. Methylmercury(II) formed a 1:1 complex with glutathione (200):



$${}^-\mathrm{O_2C\text{-}}\overset{{}^+\mathrm{NH_3}}{\mathrm{C}}\mathrm{HCH_2CH_2CONH}\underset{\mathrm{CH_2SHgMe}}{\mathrm{C}}\mathrm{HNHCH_2CO_2}^-$$

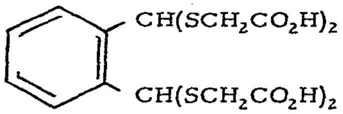
(The complexes formed between glutathione and $Hg(OAc)_2$ and $HgCl_2$ also were studied (200), and other reports of Hg(II)-amino acid (ester) complexes may be cited (201-203)).

TABLE 14. Formation Constants of Methylmercury Complexes of Amino Acids at 25°. Log $K_{f,O}$ for oxygen-binding; Log $K_{f,N}$ for nitrogen binding (D. L. Rabenstein et al., J. Coord. Chem., 3 (1974) 263).

Amino Acid	log $K_{f,O}$	log $K_{f,N}$
Glycine		7.88 ± 0.05
β-Alanine	2.52 ± 0.10	7.56 ± 0.07
4-Aminobutyric Acid	2.74 ± 0.13	7.54 ± 0.03
5-Aminovaleric Acid	2.98 ± 0.10	7.75 ± 0.05
6-Aminohexanoic Acid	3.10 ± 0.01	7.83 ± 0.02
8-Aminooctanoic Acid	3.15 ± 0.09	7.60 ± 0.04
Valine	2.7 ± 0.02	7.41 ± 0.01
Phenylalanine	--	8.29 ± 0.05

X-ray crystal structures of methyl-L-cysteinatomercury(II) and methyl-DL-methioninemercury II) have been determined (204). It was found that the CH_3Hg moiety is bound via a deprotonated sulfhydryl group in the former and via an amino group in the latter (Fig. 2).

Also of interest is the new chelating agent, phthalyltetrathioacetic acid, 42. Its mercury (II) complex has a stability constant greater than those of its other complexes with divalent ions (Ca, Zn, Co, Pb, Ni, Cd) by a factor of at least 10^{10}. This high selectivity for Hg(II) is due to the presence of the closely spaced group of sulfur atoms and a rather wide separation of the carboxylic acid groups (205).



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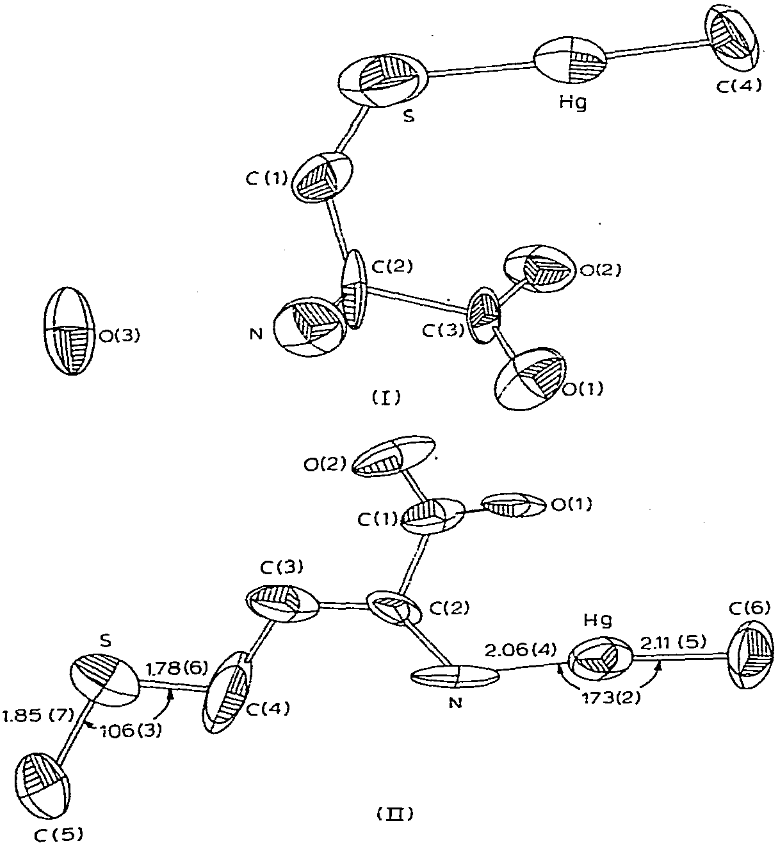
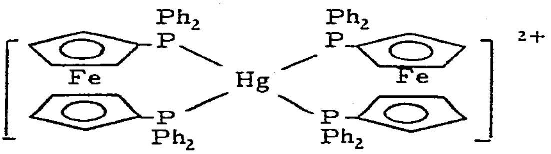


Figure 2. The molecular structures of $MeHgSCH_2CH(\overset{+}{N}H_3)CO_2^-.H_2O$ (I) and $MeSCH_2CH_2CH_2CH(\overset{+}{N}H_2HgMe)CO_2^-$ (II). In (I) 0(3) is the oxygen atom of the solvent water molecule of crystallization (Y. S. Wong, N.J. Taylor, P.C. Chieh and A.J. Carty, J. Chem. Soc., Chem. Commun. (1974) 625).

The chelate complex 43, although not strictly an organomercury species, merits mention (206).



43

Mercuric halides form poorly stable solid molecular complexes with aromatic hydrocarbons (207). In dichloromethane solution 1:1 complexes are formed. Among the solid complexes which were isolated were the following: $2HgX_2\cdot$toluene ($X = Br, I$); $2HgBr_2\cdot EtPh$; $3HgI_2\cdot 2EtPh$; $HgBr_2\cdot$acenaphthene; $HgI_2\cdot$pyrene; $HgI_2\cdot 2$anthracene. Mercuric chloride complexes were too unstable to isolate.

10. STRUCTURAL, SPECTROSCOPIC AND PHYSICAL STUDIES

A. Structural Studies

Several X-ray diffraction studies of organomercurials and of some inorganic mercury compounds which might be of interest to organometallic chemists have been published.

Methylmercuric azide (Fig. 3). An essentially linear C-Hg-N grouping is present, and in the crystal the $MeHgN_3$ molecules are associated in layers bearing the methyl groups on the outer side (208).

Phenylmercuric 2,6-dimethylthiophenolate (Fig. 4) (209). It is not known whether the relatively short intermolecular S...Hg distance of 3.18Å represents S→Hg coordination or is due to packing effects.

Benzylmercuric triphenylmethylmercaptide (Fig. 5) (210). A weak intra-

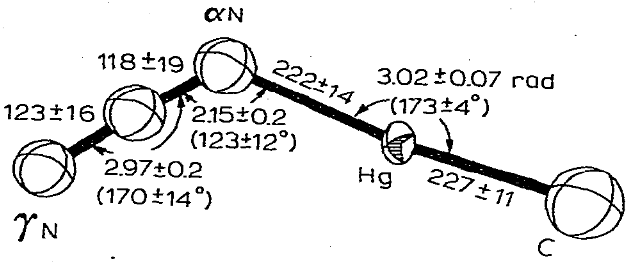


Figure 3. Structure of Methylmercuric Azide (distances in pm) (U. Müller, Z. Naturf., 28b (1973) 426).

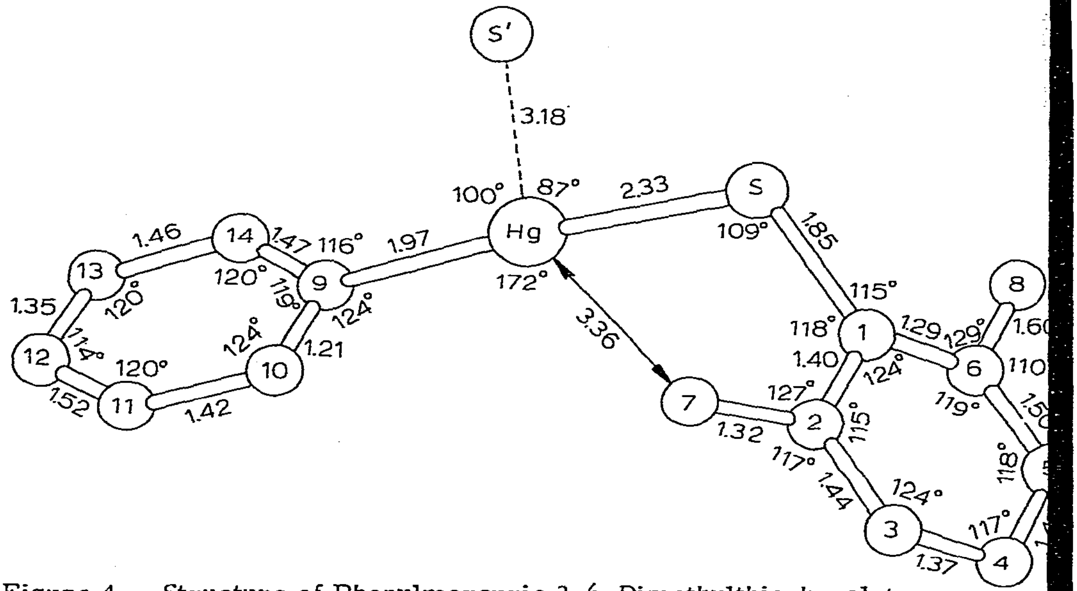


Figure 4. Structure of Phenylmercuric 2,6-Dimethylthiophenolate (distances in Å) (L.G. Kuz'mina et al., Zh. Strukt. Khim., 15 (1974) 491).

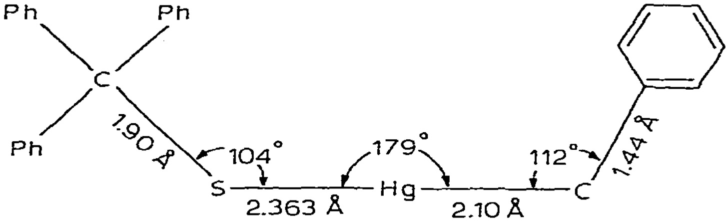


Figure 5. Structure of Benzylmercury Triphenylmethylmercaptide (R. D. Bach, A. T. Weibel, W. Schmonsees and M. D. Glick, J. Chem. Soc., Chem. Commun. (1974) 961).

molecular interaction between one of the aromatic rings of the Ph_3CS group and the mercury atom may be present.

Phenylmercuric salicylalmethylimidate (Fig. 6) (211). The mercury is covalently bonded to the nitrogen atom, but a strong Hg-O interaction also exists, as indicated by the short Hg-O distance and the deviation of the C-Hg-N angle from linearity.

Mercury(I) trifluoroacetate (212). The crystal contains discrete molecules of C_2 symmetry connected by 2.64Å intermolecular Hg... O bonds to form puckered ribbons extending along the c direction. The Hg-Hg bond distance is 2.505 ± 0.003A and the Hg-Hg-O angle is 166.6°.

Cesium tricyanomercurate(II) (Fig. 7) and cesium trithiocyanatomercurate(II) (Fig. 8) (213).

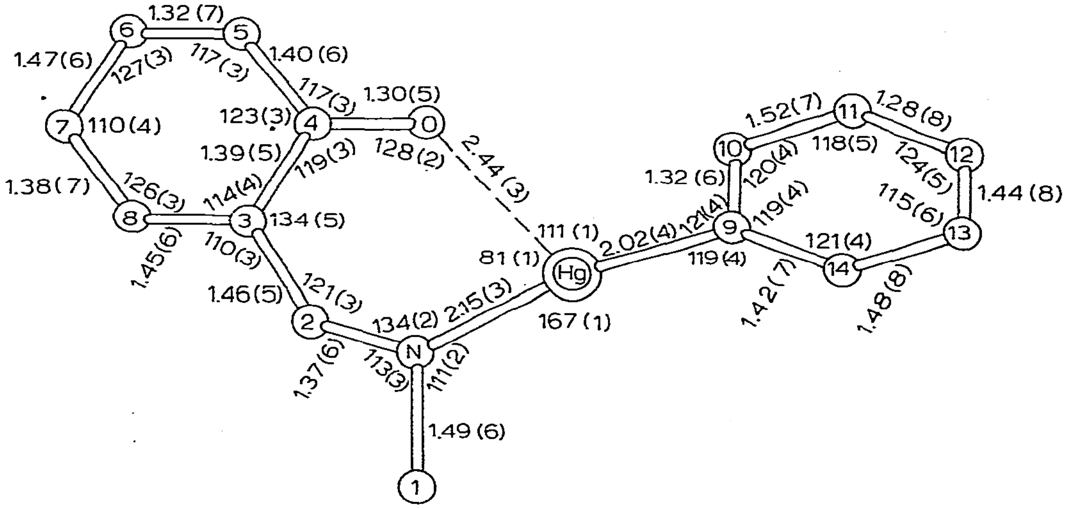


Figure 6. Structure of Phenylmercuric Salicylalmethylimidate (distances in Å) (L.G. Kuz'mina et al., Zh. Strukt. Khim., 15 (1974) 659).

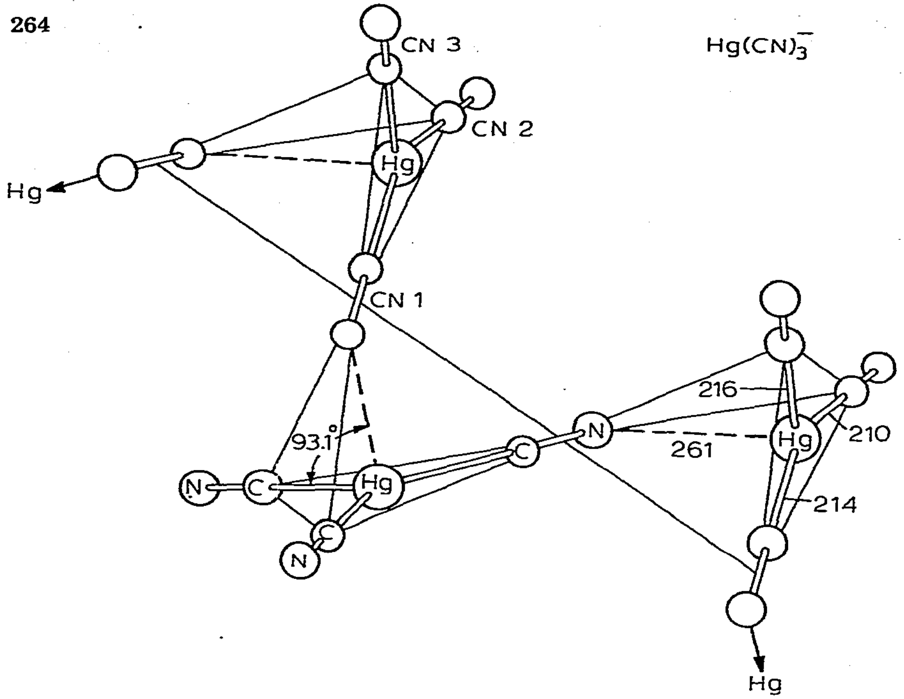


Figure 7. The Structure of Cesium Tricyanomercurate(II) (G. Thiele, R. Bauer and D. Messer, Naturwiss., 61 (1974) 215).

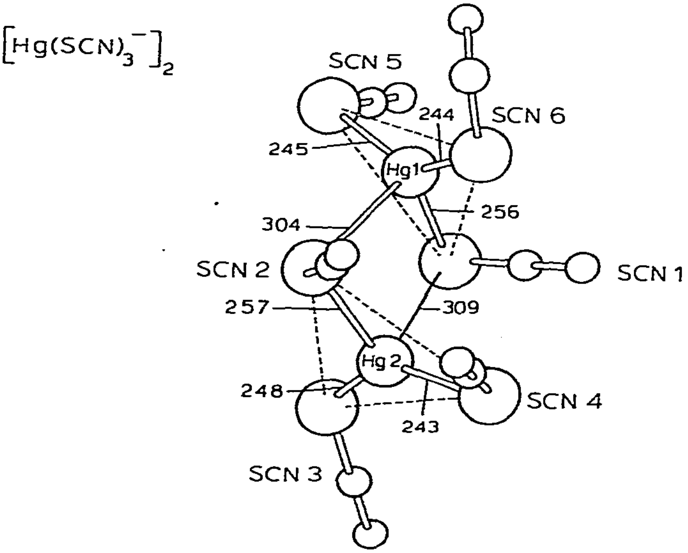


Figure 8. The Structure of Cesium Trithiocyanatomercurate(II) (G. Thiele, R. Bauer and D. Messer, Naturwiss., 61 (1974) 215).

B. Spectroscopic Studies

i. Vibrational Spectroscopy

Publications have dealt with the vibrational spectra and force constants of solid CH_3HgI and CD_3HgI (214) and of $(CH_3)_2Hg$ and $(CD_3)_2Hg$ (215), with the vibrational spectra of a number of diarylmercurials and arylmercuric acetates (216), of $(CH_3S)_2Hg$ (217) and other $(RS)_2Hg$ compounds (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *t*-Bu) (218), with the infrared spectra of cyanomethylmercurials (35) and ferrocenylmercuric chloride (219).

A study of the IR spectra and the polarographic behavior of the mercurials **44** suggested that $\sigma-\pi$ conjugation of the C-Hg bond with the C = O bond does not occur (220). An investigation of $ClCH_2HgNO_3$ in aqueous solution by Raman spectroscopy showed it to be 83 ± 7% dissociated into $ClCH_2Hg^+$ and NO_3^- ions (221).

ii. Electronic Spectroscopy

The ultraviolet spectrum of $(CH_2{=}CHCH_2CH_2)_2Hg$ in the vapor showed maxima at 208, 210, 213 and 216 nm, in isopentane solution at 187 and 210(br) nm. Presumably $\pi \rightarrow \pi^*$ transitions are involved (38). The ultraviolet spectrum of dimethylmercury was studied (Fig. 9) and the extiction coefficients determined (222). The results are given in Table 15. At the photochemically important wavelength of 253.7 nm the extinction coefficient is 2.1 cm^{-1} atm^{-1}.

iii. Nuclear Magnetic Resonance Spectroscopy

The magnetic shielding anisotropy, $\sigma_{\parallel}-\sigma_{\perp}$, of ^{199}Hg in methylmercuric bromide dissolved in the nematic phase of 4,4'-dihexyloxyazoxybenzene has been determined to be 5345 ± 25 ppm (nuclear magnetic double resonance) (223).

Proton NMR data have been recorded for CH_3Hg^+ complexes of some amines and amino acids (Table 16). It can be seen that the value

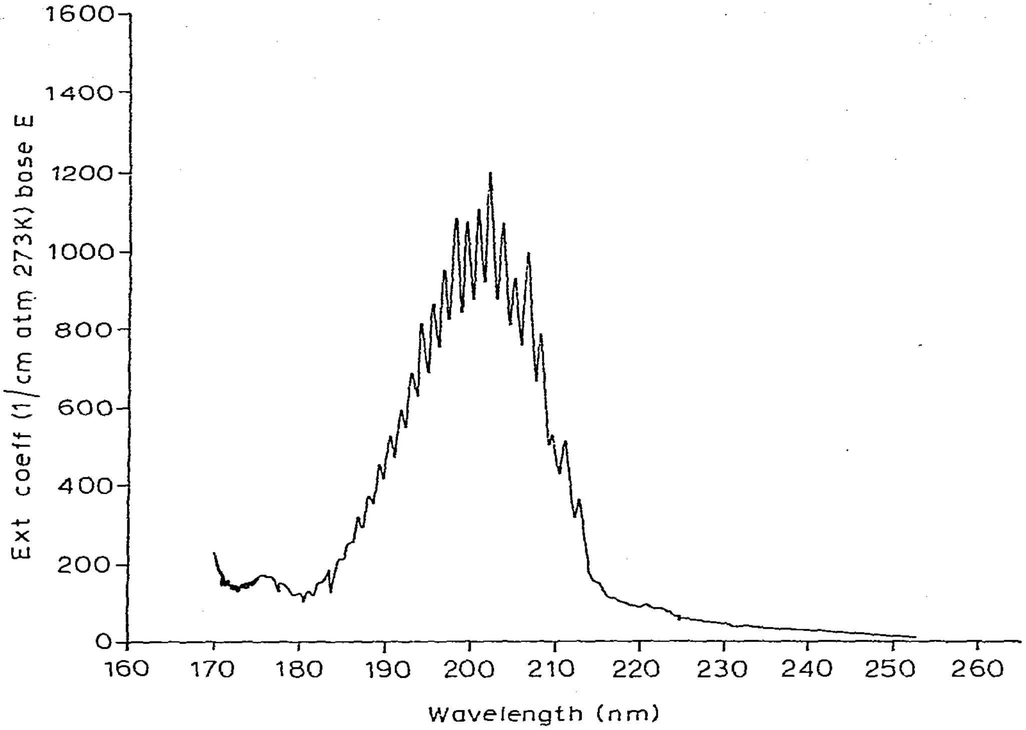
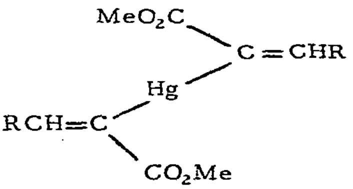


Figure 9. The Ultraviolet Spectrum of Dimethylmercury (A.M. Bass and A.H. Laufer, J. Photochem., 2 (1974) 465).

of $J(^{199}Hg-^{1}H)$ is diagnostic for the binding site (oxygen or nitrogen) of CH_3Hg^+ (199).

Reutov and his coworkers have extended Scheffold's pK_{Hg} scale which is based on $J(^{199}Hg-^{1}H)$ values of CH_3HgY compounds to include some wholly organic mercurials, CH_3HgR ($R = Me$, Et, $CH_2=CH$, CF_3, $HC\equiv C$, CN) (224). It was found that there is a linear correlation between



44

R = *trans*-Me,
trans- or *cis*-Ph,
trans-p-BrC_6H_4
trans-p-$MeOC_6H_4$

the pK_{Hg} values determined for these CH_3HgR compounds and the pK_a values for the corresponding RH compounds, thus providing a simple method for estimating carbon acid acidities.

Proton, ^{13}C and ^{199}Hg NMR spectra of a number of $MeOCMe_2CH_2HgX$ compounds (X = OAc, Cl, Br, I, SCN, CN) have been studied in chloroform solution with the intention of obtaining information concerning the nature of the Hg-X bond (225). Effects were observed when X = CN and SCN which suggested that π -bonding was occurring.

Proton and ^{13}C NMR spectroscopy also has been used in the conformational analysis of organomercurials. The HgX substituents of cyclohexylmercuric chloride and acetate showed negative A values ($\Delta G°$ in Kcal/mol for the equatorial-to-axial conformational change) as determined by high field (59Kgauss) proton and ^{13}C NMR spectroscopy (226). Hence, in contrast to previous work (Jensen, 1959, 1969), the cyclohexylmercury compounds must exist preferentially in the axial form. The long C-Hg bond and the polarizable nature of the large mercury atom are consistent with these small negative A values. Conformational analysis of β -methoxyalkylmercuric chlorides by proton NMR spectroscopy and extended Hückel calculations also has been carried out (227). It was found that the more polar was the solvent used, the greater was the preference for the conformation with the HgCl group trans to the methoxy function.

The ^{13}C NMR spectra of dibenzylmercury and benzylmercuric chloride (228) and of β -methoxyalkylmercuric chlorides (229) have been reported.

The ^{19}F NMR spectra of m- and p-fluorophenylmercurials, FC_6H_4HgX (R = F, CF_3, O_2CCF_3, SCF_3 and $OSOCF_3$) were used to determine σ_i and σ_c constants of these HgX substituents (Table 17) (230). The electronic effect of the HgX substituents appears to be mainly inductive

TABLE 15. Absorption Maxima in the Ultraviolet Spectrum of Dimethylmercury

λ (nm)	ϵ(cm^{-1}atm^{-1})	ν(cm^{-1})	$\Delta\nu$(cm^{-1})
184.56	218.4	54,183	
			327
185.68	258.5	53,856	
			346
186.88	316.3	53,510	
			319
188.00	372.5	53,191	
			315
189.12	449.5	52,876	
			355
190.40	522.5	52,521	
			307
191.52	592.3	52,214	
			347
192.80	683.9	51,867	
			342
194.08	815.2	51,525	
			337
195.36	859.2	51,188	
			334
196.64	949.6	50,854	
			369
198.08	1083.7	50,485	
			325
199.36	1079.2	50,160	
			359
200.80	1108.9	49,801	
			335
202.16	1198.6	49,466	
			350
203.60	1074.4	49,116	
			336

TABLE 15. - continued

205.04	933.8	48,780	
			368
206.56	998.1	48,412	
			354
208.08	790.9	48,058	
			312
209.44	517.2	47,746	
			380
211.12	508.2	47,366	
			374
212.80	367.3	46,992	
			437
214.80	153.5	46,555	

in nature, the σ_c values of ~0.0 indicating that π -bonding involving the π -electrons of the phenyl ring and the vacant mercury 6p orbitals is negligble. The ^{19}F NMR spectra of other CF_3HgY compounds ($Y = NCO, N_3, SCF_3, (O_2C)_{\frac{1}{2}}, O_{\frac{1}{2}}, S_{\frac{1}{2}}$) (166), Cl, I, O_2CCF_3 (196) and CH_2Ph (195)) have been reported, with emphasis on solvent effects in the latter two publications.

Measurement of ^{79}Br NMR relaxation times was used to study the fast bromine exchange between aqueous KBr and methylmercuric bromide, bromomercuribenzoic acid, bromomercuricinammic acid and bromomercuri-N-acetyl-L-phenylalanine (231).

iv. Nuclear Quadrupole Resonance Spectroscopy

Halogen NQR spectra (^{35}Cl, ^{79}Br, ^{81}Br, ^{127}I) of organomercuric halides at liquid nitrogen temperature have been measured by Russian workers (Table 18) (232). It was suggested that intermolecular Hg...Y coordination was of greater importance in determining the behavior of the quadrupole constants than through-bond electronic effects.

TABLE 16. Chemical Shifts and Coupling Constants for CH_3Hg Complexes of Amines and Amino Acids (Ref. 199).

Species	δ_{CH_3}[a]	$J(^1H - ^{199}Hg)$[b]
CH_3Hg^+	2.072	260.0
$(CH_3Hg)_2OH^+$	2.188	232.5
CH_3HgOH	2.345	203.0
$CH_3HgNH_3{}^+$	2.285	214.1
$CH_3HgNH_2CH_3{}^+$	2.279	211.5
$CH_3HgNH_2CH_2CH_3{}^+$	2.263	211.0
$CH_3HgNH_2CH(CH_3)_2{}^+$	2.244	209.0
$CH_3HgNH_2C(CH_3)_3{}^+$	2.226	210.2
$CH_3HgNH(CH_3)_2{}^+$	2.250	216.6
$CH_3Hg\overset{+}{N}H_2CH_2CO_2{}^-$	2.294	216.0
$CH_3Hg\overset{+}{N}H_2(CH_2)_2CO_2{}^-$	2.287	213.9
$CH_3Hg\overset{+}{N}H_2(CH_2)_3CO_2{}^-$	2.264	211.9
$CH_3Hg\overset{+}{N}H_2(CH_2)_4CO_2{}^-$	2.264	211.2
$CH_3Hg\overset{+}{N}H_2(CH_2)_5CO_2{}^-$	2.268	211.8
$CH_3Hg\overset{+}{N}H_2CH(CH_2C_6H_5)CO_2{}^-$	2.800	
$CH_3HgO_2C(CH_2)_2\overset{+}{N}H_3$	2.167	230.5
$CH_3HgO_2C(CH_2)_3\overset{+}{N}H_3$	2.175	230.0
$CH_3HgO_2C(CH_2)_4\overset{+}{N}H_3$	2.179	230.2
$CH_3HgO_2C(CH_2)_5\overset{+}{N}H_3$	2.177	230.4

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[a] In units of ppm relative to the central resonance of TMA.

[b] In units of Hz; the sign of the coupling constant is negative.

v. Photoelectron Spectroscopy

Evidence for the occurence of $d_{\pi} - \pi^*$ back-donation in the Hg-CN bond of CH_3HgCN and $Hg(CN)_2$ was provided by the He-I PE spectra of these compounds when compared with that of dimethylmercury (ionization of the mercury inner 5d electrons) (233).

vi. Mass Spectroscopy

The mass spectra of diphenyl- and dibenzylmercury (234), of some alkynylmercurials, $(RC{\equiv}C)_2Hg$ (R = Cl, Br, Me, Et, n-Pr, t-Bu, Ph, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$) (235) and of $(C_6F_5S)_2Hg$ (236) have been obtained and the fragmentation processes discussed.

11. ANALYTICAL ASPECTS OF ORGANOMERCURY CHEMISTRY

The environmental mercury problems, which involve organomercurials as well as inorganic mercury compounds and elemental mercury, have made necessary the development of new analytical methods. In one study, a method was devised for the detection and determination of particulate mercury, CH_3HgX compounds, HgX_2 compounds, elemental mercury and dimethylmercury in air samples using sequential, selective absorption tubes for separation (Table 19) and a dc discharge spectral emission type detector (237). This system was used to analyze for mercury and its compounds in air in buildings and in air above a lake exhibiting methylation of heavy metals. In a separately published study (238), this method was used for the determination of atmospheric mercury species near ground.

Gas-liquid chromatography has been applied to the detection and analysis of inorganic mercury. The application of this procedure requires the prior conversion of Hg^{2+} to a volatile organomercurial. Methylpentacyanocobaltate(III) (239) and sodium 2,2'-dimethyl-2-silapentane-5-sulfonate (240) were effective reagents for the methylation of Hg^{2+} in ppm

TABLE 17. (A) Chemical Shifts ($\delta^{19}F$) of meta- and para-Substituted Fluorobenzenes, RC_6H_4F

(B) σ-Constants of Substituents Containing a Mercury Atom (Ref. 230)

(A) R	δ_m			δ_p		
	$CHCl_3$	DCE[a]	THF	$CHCl_3$	DCE[a]	THF
HgF	--	-1,83	-0,65	--	-1,56	-0,43
HgCl	--	--	-0,58	--	--	-0,62
HgBr	--	--	-0,59	--	--	-0,72
HgI	--	--	-0,62	--	--	-0,85
$HgCF_3$	-1,3	-0,54	0,18	-2,7	-1,41	-0,27
$HgSCF_3$	-2,04	-1,68	-0,65	-3,5	-2,7	-1,1
$HgOCOCF_3$	-2,83	-2,0	-1,0	-3,9	-2.75	-1,1
$HgOSOCF_3$	-2,95	-2,4	-1,25	-3,85	-3,12	-1,93

(B) R	σ_i			σ_c		
	$CHCl_3$	DCE[a]	THF	$CHCl_3$	DCE[a]	THF
HgF	--	0,34	0,18	--	-0,01	-0,01
HgCl	0,31	--	0,17	0,04	--	0,01
HgBr	0,44	--	0,18	0,00	--	0,00
HgI	0,24	--	0,20	0,04	--	0,00
$HgCF_3$	0,27	0,16	0,06	0,05	0,03	0,01
HgCN	0,23	--	0,07	0,11	--	0,02
$HgSCF_3$	0,37	0,32	0,18	0,05	0,04	0,02
HgSCN	--	--	0,20	--	--	0,00
$HgOCOCH_3$	0,38	--	0,16	0,02	--	0,00
$HgOCOCF_3$	0,48	0,37	0,22	0,04	0,03	0,00
$HgOSOCF_3$	0,50	0,42	0,26	0,03	0,02	0,02

[a] DCE = dichloroethane.

TABLE 18. Halogen Nuclear Quadrupole Resonance Spectra of Some Organomercuric Halides at 77°K (Ref. 232)

Compound	Isotope	Frequency of NQR transition, MHz*		e^2Qq_{zz}, MHz	η, %
		$(\pm 1/2 \leftrightarrow \pm 1/2)$	$(\pm 3/2 \leftrightarrow \pm 5/2)$		
CH_3HgI	^{127}I	127,42	254,85	849,5±0,3	0±1,8
$2CH_3HgI \cdot CH_3HgCl^a$	^{127}I	127,4			
CH_3HgCl	^{35}Cl	14,75			
n-C_4H_9HgI	^{127}I	124,17			
trans-$ClCH{=}CHHgI$	^{127}I	131,27	262,60	875,2±0,3	0±1,8
	^{35}Cl	33,77			
cis-$ClCH{=}CHHgI$	^{127}I	135,82	271,60	905,4±0,5	1±1
	^{35}Cl	32,948			
cis-$ClCH{=}CHHgBr$	^{35}Cl	33,08			
	^{81}Br	109,10			
	^{79}Br	130,50			
cis-$ClCH{=}CHHgC_5H_6$	^{35}Cl	32,35			
$CH_2{=}CHHgI$	^{127}I	126,00			

$(O_2N)_3CCH_2CH_2HgBr$	^{81}Br	114,02			
	^{79}Br	136,50			
$BrHgCH_2CHO$	^{79}Br	139,72			
	^{81}Br	116,54			
$ClHgCH_2CHO$	^{35}Cl	17,65			
C_6H_5HgI	^{127}I	120,18	240,57	801,7±0,3	0±1,7
Cl_3CHgI	^{127}I	155,7			
p-$CH_3OC_6H_4HgI$	^{127}I	119,52	238,89	796,4±0,3	2,2±1
p-ClC_6H_4HgI	^{127}I	122,59	245,44	817,7±0,3	0±1,8
p-$(CH_3)_2NC_6H_4HgI$	^{127}I	119,65	239,13	797,2±0,5	2,3±1
2,4,6-$(CH_3)_3C_6H_2HgI$	^{127}I	145,17	290,09	967,1±0,5	2,5±1

[a] The compound is not a molecular complex, but instead is a solid solution, since the ^{127}I frequency coincides with the frequency of CH_3HgI, while the width of the line increases exceedingly ($\Delta\nu \sim 3$ MHz).

concentration in aqueous solution to CH_3Hg^+. Sodium tetraphenylborate served in the conversion of aqueous Hg^{2+} to phenylmercury species (239). Extraction of these organomercury species into an organic solvent was followed by their gas chromatographic determination.

TABLE 19. Specific Absorption Tubes for Mercury in Air (ref. 237)

Tube order no.	Composition	Function
1	Glass wool filter, preheated to blank	Removes some particulate, passes other mercury forms
2	Chromosorb-W, 45-60 mesh, 3% SE-30	Removes $HgCl_2$, particulate which passes the filter; passes CH_3HgCl, $(CH_3)_2Hg$, and elemental Hg
3	Chromosorb-W, 45-60 mesh treated with 0.05M NaOH	Removes CH_3HgCl; passes elemental Hg and $(CH_3)_2Hg$
4a	Silvered glass beads	Removes elemental Hg; passes $(CH_3)_2Hg$
4b	Gold-coated glass beads	Removes $(CH_3)_2Hg$

Organomercuric halides (alkyl and aryl) can be analyzed by a rapid titrimetric method in which the mercury-bound halogen is first displaced as halide ion by a thiol, separated by aqueous extraction and determined by Volhard titration (241). This procedure gave uniformly excellent results.

Neutron activation analysis can be used for the selective determination of mercury in various mercury compounds and for the determination of methylmercury(II) in fish tissue (242).

High-speed liquid chromatographic separations of organomercurials (MeHgCl, EtHgCl, PhHgCl, PhHgOAc) on Corasil I (hexane eluent) have been reported (243).

12. MISCELLANEOUS

A few miscellaneous items remain.

Although they are not strictly organomercury compounds, the novel mercurated porphyrins prepared by Hudson and Smith (244-246), e.g., types 44, 45 and 46, merit inclusion in this survey.

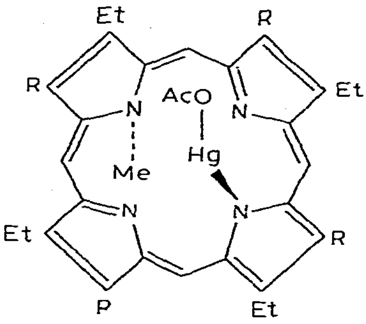
Other items of interest include:

The use of a modified cellulose absorbent containing vicinal thiol groups in scavenging Hg^{2+} and CH_3Hg^+ from aqueous solutions (247).

The preparation of the following ^{197}Hg-labelled mercurials: PhHgCl; $2\text{-}HO_2CC_6H_4HgCl$, $4\text{-}HO_2CC_6H_4HgCl$, $4\text{-}HOSO_2C_6H_4HgCl$ (248).

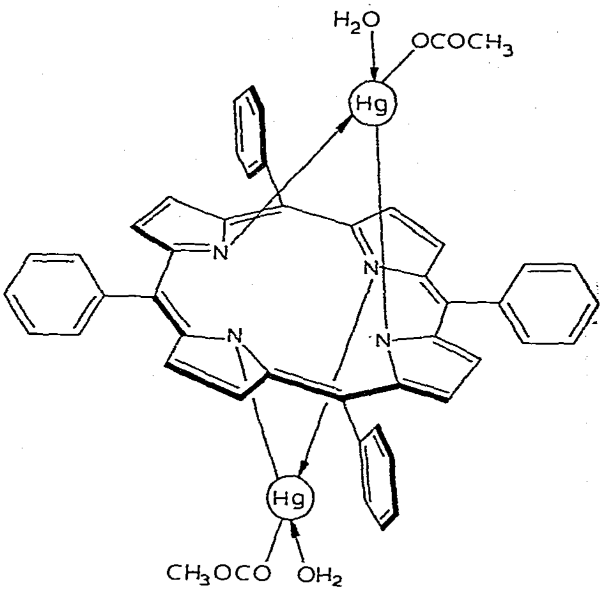
The determination (column chromatography, analysis, degradation, NMR) that commercial "2,7-dibromo-4-hydroxymercurifluorescein" contains three components (4,5-dibromofluorescein, 4,5-dibromo-2,7-bis(acetoxymercuri)fluorescein and 4,5-dibromo-2-acetoxymercurifluorescein), but none of the material it was purported to be ! (249).

An organomercury experiment for an undergraduate laboratory course involving mercuration of benzene with $Hg(OAc)_2$, conversion of the PhHgOAc obtained to PhHgCl and PhHgBr, their thin layer chromatography (dithizone detection) and preparation of their 1,10-phenanthroline complexes (250).

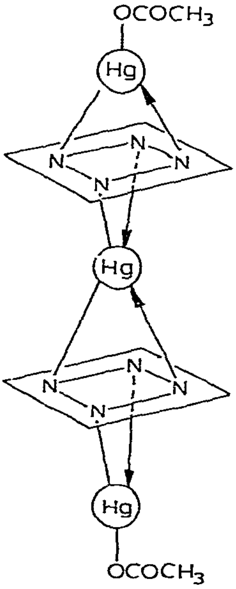


a; R = Et
b; R = Me

44

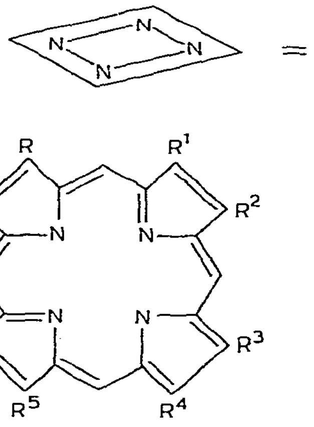


45



46

where



$R = Et$ $\quad$ $R = CH_2 \cdot CH_2 \cdot CO_2Me$

a; $R^1 = R^3 = R^5 = Me; R^2 = R^4 = R^6 = R$

b; $R^1 = R^4 = R^5 = R; R^2 = R^3 = R^6 = Me$

c; $R^1 = R^3 = R^6 = Me; R^2 = R^4 = R^5 = R$

d; $R^1 = R^3 = R^6 = R; R^2 = R^4 = R^5 = Me$

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